REMOVING SILICA FROM GEOTHERMAL WATER - YEAR ONE OF PILOT PLANT OPERATION WITH A FOCUS ON CARBONATE AND SILICA ANALYSIS

Thomas Borrmann[1], Michael Schweig[1], Mathew J. Cairns[1], James H. Johnston[1] and Alexander K. Gray[1]

[1] School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, 6140 Wellington, New Zealand

thomas.borrmann@vuw.ac.nz

Keywords: *Scale formation, silica scale, calcium silicate hydrate, nano-structured calcium silicate hydrate, geothermal energy, calcite, calcium carbonate*

ABSTRACT

Amorphous silica and carbonate depositions as intractable sinters on the surface of pipework, valves and heat exchangers and in reinjection wells are major worldwide problems in geothermal energy utilisation. The formation of the sinters from supersaturated geothermal brine limits the amount of energy that can be generated and leads to down times and considerable clean-up and remediation costs. Current approaches to alleviate the problem are only partially successful, particularly for high enthalpy resources. The dissolved silica also represents a potentially useful material resource.

Our technology which transforms unwanted silica into novel nanostructured calcium silicate hydrate turns the issue of silica formation into an opportunity through controlled formation of a competing material from geothermal brine that prevents sinter formation. Carbonate can be captured in the silicate and is removed along with it. A pilot plant was built on site at MB Century, New Zealand, sourcing geothermal brine from the Wairakei resource. The plant was commissioned in August/September 2017 and has been in operation since.

We present data from the operation of the pilot plant focussing on the analysis of the incoming brine and the products recovered from it. Various methods for analysing and tracking carbonate throughout the treatment procedure will be illustrated and compared. Titration is the primary tool for analysing the brine for carbonate content. While titration can also be used to analyse the carbonate content in the solids recovered from the brine, it is a comparatively expensive and work intensive method. X-ray diffraction patterns can provide similar information. However, as the silicate and silica components are amorphous or polycrystalline, evaluation of relative amounts in the sample is difficult. Thermogravimetric analysis is shown to allow the analysis of several samples in parallel delivering satisfactory accuracy reducing the amount of work required per sample.

1. INTRODUCTION

1.1 Geothermal Energy and the Formation of Silica Scale

A geothermal heat source such as magma located a few hundred meters to several kilometers below the surface can heat a natural or artificially created underground water reservoir. Piping water from the reservoir to the surface allows the extraction of large quantities of heat and/or electrical energy continuously and also on demand. High enthalpy sources are usually used in flash plants, while low enthalpy resources are exploited in direct use and binary cycle heat exchangers. All three methods can be combined to increase the efficiency of plants and amount of energy extracted. Microbial and chemical processes dissolve the subsurface rock containing and surrounding geothermal water reservoirs. This means that the geothermal water pumped to the surface contains a cocktail of species (cations and anions) and suspended particles. Silica and carbonate are two problematic, scale-forming species contained in geothermal waters.

During flashing processes part of the geothermal waters is turned into steam to drive turbines and produce electricity. The residual fluid is termed geothermal or flashed brine. Some of the silica and carbonate in the fluid is carried over in water droplets in the steam and can deposit and damage turbines. Consequently the steam is scrubbed, which lowers the energy that can be extracted from it. The majority of the scale forming species remains in the brine and is concentrated to supersaturation. To remedy this, part of the steam is re-condensed and combined with the spent brine. Direct use and binary cycle applications extract heat energy. While the amount of fluid is not reduced using these processes, the temperature of the fluid decreases, which in turn lowers the solubility of silica and, hence, can also lead to supersaturation and scale formation. For example, subsurface geothermal water at 260 ºC can contain up to 600 mg of dissolved silica per kg of brine (Iler, 1979). Upon flashing to 1.7 bar at the surface about 30% of this water is transformed into steam and the concentration of dissolved silica in the residual separated brine representing about 70 % of the mass flow increases to approximately 800-900 mg/kg brine. The temperature of the brine correspondingly decreases to about 150 to 160 ºC as heat energy is removed with the phase change. The brine is further cooled to 130 ºC to prevent boiling in the pipes (White, 1998). At this temperature only approximately 350 mg/kg of silica are soluble in water. Part of the brine is channelled towards binary cycle power plant, which lowers the temperature further to 90 ºC (Montague, 2013).

Scale formation is problematic, as scale deposits on pipes, in valves, equipment and heat exchangers, lowering the functionality and efficiency of the affected equipment. The removal of scale is laborious and requires hard work and the occasionally the use of acids (HF), which can damage production equipment and reduce generation. The problem of scale formation is exacerbated as most of the spent fluid is usually reinjected underground. Reinjection replenishes and increases the life time of geothermal reservoirs, prevents subsidence and pollution, and places this method of energy generation firmly into the realm of both benign and renewable energy resources. Costs associated with the re-drilling of re-injection wells and cleaning of pipes and equipment are significant and present one of the major challenges and impediments facing geothermal energy generation. Several methods have been investigated to address the issue of silica scale formation. Examples of these are the addition of acid (Brown 1983, Dubin, 1984; Gunnarsson and Arnórsson, 2005) to partially delay the condensation of the dissolved silica species, the addition of silica seeds (Featherstone et al, 1979, Sugita et al., 1999; Sugita et al., 2003) to capture such dissolved silica onto a pre-existing silica material, and the addition of aluminium species, EDTA and other compounds to form silica and silicate species that do not precipitate (Gallup, 1999; Sugita et al., 1999). Gill (1998), presents a good overview regarding this problematic issue of silica scale formation and the effect of pH and other ionic species on it. In a parallel development, we (Harper et al., 1992) and a group from Japan (Sugita et al., 1999 and 2003) realized that the use of calcium ions (dissolved lime) allowed removal of silica from geothermal brine. We focused on the silica-derived products building a pilot plant to precipitate a silica product with a network structure from geothermal brine for use as a filler to enhance the optical and print quality of paper. Meanwhile, Sugita et al. (1992), carried out successful trials in the reduction of dissolved silica species in geothermal systems in New Zealand (Mokai) and Japan but they appeared not to have realized the nature and potential of the silica and silicate species they generated.

Our approach is different: The reactive silica species present at supersaturated levels in separated geothermal brine is transformed into nano-structured calcium silicate hydrate, NCaSilH, which forms readily, does not polymerize further and does not bind to metal surfaces (Borrmann et al., 2017). The NCaSilH particles remain suspended in the geothermal brine and can be separated out as a useful product. The level of dissolved silica species remaining in the brine can be controlled from a level just below the equilibrium solubility level at the brine temperature down to the essentially zero, depending on the amount of calcium ions used in relation to the dissolved silica species in the water. Through laboratory scale and field trials, we have successfully developed the NCaSilH geothermal technology and have constructed a pilot plant test rig sourcing spent brine from the Wairakei Power Plant, New Zealand, to test our technology in a continuous process and demonstrate its viability. In laboratory and field trials we found that formation of NCaSilH also allowed to capture and trap low levels of carbonate species and remove this scale forming species from geothermal brine (Borrmann et al., 2017). Operating the test rig we found that the brine from Wairakei contained comparatively low levels of silica and high levels of dissolved carbonate (Borrmann et al., 2017). This means that the brine is outside the target composition for our technology but presents a very valuable stress testing ground. Instead of dealing with NCaSilH containing minor impurities, we are likely encountering a range of different species posing the following research questions:

(1) If carbonate is captured by the use of our technology, what is the nature of the carbonate particles, and which method is fast and reliable enough to analyse the products captured?
(2) Can the separator remove particles and solids with varying chemical nature from the brine?
(3) What is the separation efficiency for our technology in light of the changing products?

1.2 Pilot Scale Test Rig Commissioned September 2017

In August 2017 we started to assemble a test rig designed by us, separator (author MS), pipework, dosing and silencers (author TB), and built in the workshop of Victoria University. Early September the plant was commissioned and started operation. The test rig is operated 6 to 8 hours per day for about 1 week per month. A schematic layout and photo of the test rig is presented in **Figure 1**. The test rig is connected to a pipe from the Wairakei Power Plant via gate and non-return valves and ¾-inch pipe. The maximum brine flow possible through the pipe is about 14 L/min. Entering the test rig the brine passes a set of sensors (pressure and temperature) and a brine sampling port before being split into a control and treatment stream. The split was set to provide a flow of 10.5 L/min towards the treatment side and the rest towards the control. Due to a reduction in source pressure the split had to be removed. Now all brine passes through the treatment side of the test rig. On the treatment side a slurry of lime is added to the brine continuously via a dosing pump. Then the treated and control sides pass through about 10 m of pipework before entering a silencer and discharging into a local waterway. On the treatment side two different silencers can be chosen. One silencer is attached to a lamella separator used for recovery of NCaSilH and any other solids contained in the brine. The use of lamella separators for our application was suggested by Professor Edgar Schicker. Lamella separators were chosen over other technologies, such as cyclone separators, as NCaSilH forms weak aggregates that can be broken up easily by turbulences or shear forces.

Figure 1: Digital render and photo of test rig.

A lamella separator is a type of advanced settling tank, where angled settling surfaces assist the separation of brine and solids. This reduces the footprint of the separator to less than a quarter of the surface area of a comparable conventional settling tank, while potentially increasing its separation efficiency. Commercially available lamella separators usually achieve separation efficiencies around 70 %. We modeled several different designs of lamella separator in the laboratory out of Perspex, tested them and observed the flows through them. Based on our observations a laboratory separator was designed with a nominal separation efficiency of over 99%. The design of this separator was up-scaled for the test rig and the separator was built by AE Tilley, Wellington, New Zealand, in August 2017.

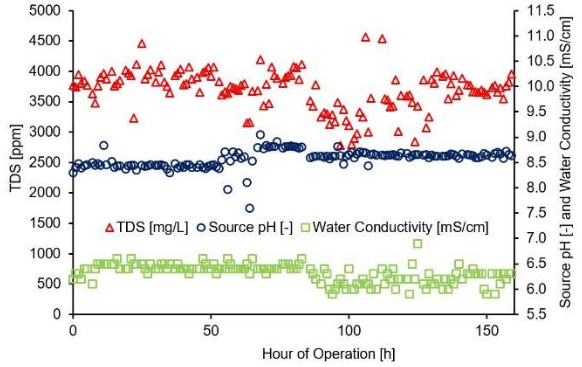

Figure 2: pH, ionic strength, and TDS during test rig operation over time.

The plant is located on site at MB Century in Wairakei, New Zealand, and has access to geothermal brine from the Wairakei Power Plant located about 3 km away. By the time the brine enters the test rig it has passed through a flash plant, several kilometers of pipework, and a binary plant. Samples of the brine entering the test rig were collected at regular intervals and tested for their content in silica (molybdate method and atomic absorption), carbonate (titration), total dissolved solid content (TDS, gravimetric), flow (volume over time), pH, and water conductivity (electrochemical measurements). The values for the pH, ionic strength and TDS remained relative constant during the 177 hours of operation (**Figure 2**). The amount of dissolved carbon dioxide and suspended silica and the brine flow changed significantly over time (**Figure 3**). Especially large changes were noticeable when production wells were brought online or old ones turned off at the power station. Some of these changes were noticeable due to the appearance and disappearance of plumes of steam. This also affected the flow of brine available and eventually required that we disconnected the control side of the test rig to provide a sufficient brine flow. At the start of each day of operation the flow was set over the opening of gate valves. The gate valves remained in the same position over the course of the day without further adjustments. The lime dosing level was also set at this time. However, as the flow and composition of the brine changed over the course of a day, the compositions of solids produced also changed **(Figure 3**).

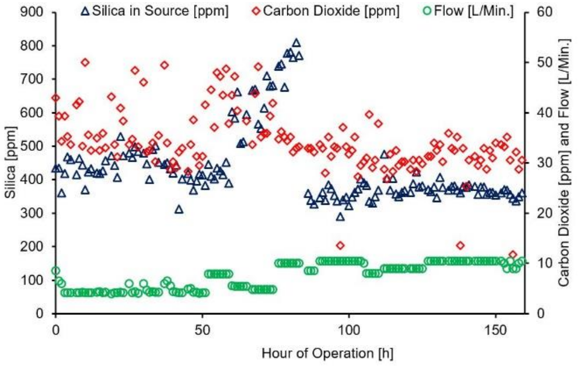

Figure 3: Silica and carbon dioxide concentrations in and flow of the brine provided to the test rig over time.

2. RECOVERY OF PARTICLES FROM GEOTHERMAL BRINE

While the brine composition and flow of incoming brine were variable, the dosing of lime was kept constant over the course of different treatment cycles. This meant that the products recovered from our process were quite diverse. Furthermore, at certain times the amount of calcium hydroxide added far exceeded the amount required to form NCaSilH, meaning that other products such as calcium carbonates could be formed. On a few occasions (pump failure, see below) the level of calcium hydroxide dosing fell very low meaning that type I and III silica instead of NCaSilH were produced. As these silica only require a small amount of calcium to form, any excess amount could react to produce calcium carbonates. Early observations showed that large amounts of carbonates formed could deposit on the surfaces of the test rig forming a soft scale.

Consequently a reliable method for assessing the amount of carbonates in the product needed to be found. Furthermore, due to the amount of samples the method applied needed to be fast and reproducible. The amount of carbonate in the brine could be easily determined via titrations. While this method could also be applied to solids, it was less practical. First, the samples produced were hygroscopic meaning that obtaining a defined sample weight was difficult. Secondly, the surface hydroxide and morphologically imposed (bottleneck pores) slow release of hydroxide by the silicate hydrate negatively impacted the titration. Lastly, the calcium hydroxide used contained a certain amount of calcium carbonate already due to reaction with atmospheric carbon dioxide over time. This last concern could be easily compensated for via a study of the calcium hydroxide used. An analysis of the calcium hydroxide showed that it contained about 10 % w/w calcium carbonate in the form of calcite. This could be confirmed by X-ray powder diffraction (XRD). The issues of attaining an accurate weighing and compensating for the slow release of hydroxide were harder to accommodate and led to significant errors for titration results.

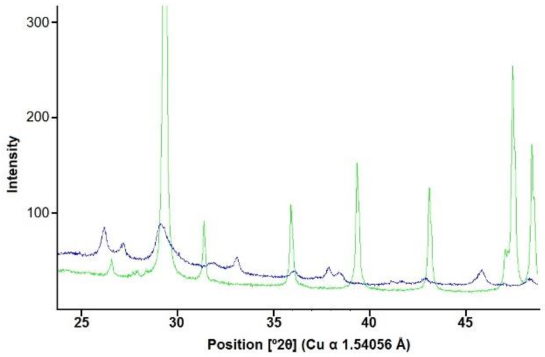

Figure 4: XRD patterns of model compounds; green line calcite, blue line NCaSilH.

The main components of the products recovered were polycrystalline NCaSilH, and crystalline calcium carbonate. This meant that XRD could be a useful analytical tool. First the nature of calcium carbonate in the products was analyzed. It was found that the majority of calcium carbonate species formed were calcites with few samples containing aragonite or vaterite. Model compounds of NCaSilH and calcite were studied. It was found that while the XRD patterns of these compounds overlapped on some reflections, others were very specific for the materials. Model compounds of calcite (pattern shown as green line) and NCaSilH (pattern shown as blue line) were produced and their pattern recorded (**Figure 4**). Characteristic reflections that did not overlap were identified and used to calculate the relative amounts of NCaSilH and calcite in model mixtures. An External Sample

Standard (ESS) approach was used to correlate the intensities measured to concentrations. Construction of an ESS calibration graph requires pure sample standards for standard addition, allowing for known concentrations to be correlated to respective intensity readings. The NCaSilH sample standard had amorphous SiO2 added for stabilization, which was accounted for in the results.

Quantitative phase analysis through basal reflection outputs is commonly achieved using net-peak intensity, or integrated net-peak area: the method chosen for interpreting intensity readings in this study implemented single-reflection intensity from a non-overlapping D3[Å/°2θ] peak of each major phase respectively. Peak intensities were calculated using the approach of Bougault et al. (1977). By gathering all comparable XRD data using identical program settings, within the same timeframe (to account for the X-ray output of the copper rod) the calculation could be simplified to the following quantitative formula **(1)** with C being the concentration, I the intensity, B a correlation coefficient and μ the mass absorption coefficient.

$$C_i = I_i \times B_i \times \mu_m \qquad \textbf{(1)}$$

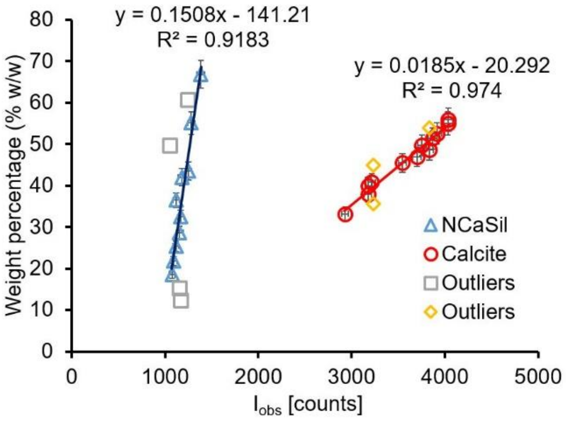

Figure 5: Correlation between concentration (weight percentage) and intensity of XRD reflections for calcite and NCaSilH.

Due to the impurities of silicon dioxide in the NCaSilH reference sample and its polycrystalline nature, the confidence value for NCaSilH was slightly lower than that for calcite (**Figure 5**). The relative concentrations (weight percentages) of both compounds in a mixture could be relatively accurately determined using X-ray diffraction. However, while the technique delivered a reliable method for analyses of products, it came with two issues. The XRD instrument was used extensively and access was limited. Furthermore, each measurement took about an hour and only one sample could be measured at a time, which limits sample throughput.

Prior studies of NCaSilH (MacFarlane, 2007) had shown that careful thermogravimetric analysis (TGA) allows determination of the amount of calcite impurities in NCaSilH accurately, and while carbonate is irreversibly lost upon heating, water and silanol groups present in NCaSilH can be recovered, if a sample is not heated above 700 ºC. A comparative study of thermogravimetric and XRD results revealed both to deliver very comparable data with acceptable errors. One significant advantage of TGA was that several samples could be quantified in parallel. Discrepancies were noticed for low amounts of samples (**Figure 6**). Through extensive review of the thermal decomposition trials the largest offset values were linked to sample sizes below 0.2g (such as samples 1, 2, 13, 14 and 15). This offset was in relation to the weighing balance sensitivity on the Sartorius® laboratory scales employed, which give units to the fourth decimal place. Hence, it was concluded that samples smaller than 0.15 g shouldn't be processed using the thermogravimetric method. A dedicated TGA instrument (Shimadzu TGA-50) could be used for these samples within reason.

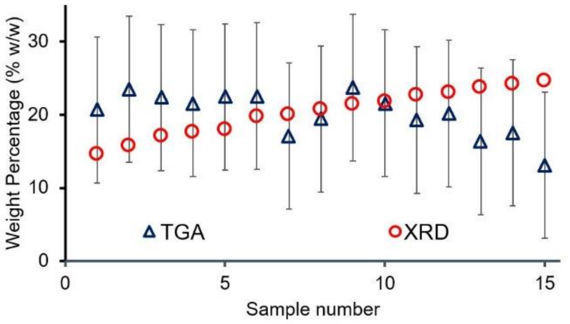

Figure 6: Comparison of concentrations (weight percentage) of calcite containing mixtures determined using XRD and TGA.

With suitable product analysis methods it was possible to analyze the samples of brine, supernatant and product collected and to establish the residual silica concentration, calcite amount in the product, and separation efficiency over time (**Figure 7**).

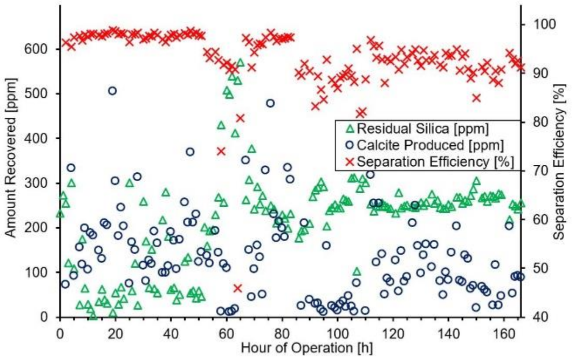

Figure 7: Residual silica concentration, calcite amount in the product, and separation efficiency over time.

For the first 56 hours of operation a comparatively high amount of calcium hydroxide was added to the brine. The products produced were mainly calcite and NCaSilH. The plant operated close to 98 % removal efficiency and depending on the dosing ratio, nearly all of the silica was removed from the brine. However, it was noticed that a significant part of the calcium hydroxide added reacted to form calcite. Some of the calcite concentrations were so high that calcite scale started to form on surfaces. Additionally it was thought that any calcium hydroxide used to produce calcite was in principle wasted.

Consequently, it was attempted to reduce the amount of calcium hydroxide added by changing the dosing pump. Unfortunately some of the pumps did not operate properly under the environmental conditions on site. From hour 57 to 87, we trialed various pumps before settling on a model that performed to our satisfaction. While there were 3 breakthrough events, when turbulence was induced in the separator, the overall removal efficiency for solids was above 90% for all types of solids encountered, which included silica, calcite, vaterite, aragonite and NCaSilH.

During hours 88 to 110 we attempted to dose the minimum possible of calcium hydroxide, thereby keeping the amount of calcite produced low. This proved to be very successful. However, as the amount of solids produced in the brine was very low, agglomeration of particles was difficult. This meant that the separation efficiency was also comparatively low.

From hour 111 to 177 we tried to keep the level of residual silica remaining after treatment constant. This proved to be very successful but meant that the separated products contained various amounts of carbonate and were inconsistent. Separation efficiencies were again dependent on the total amount of particles present at any point in time, and varied significantly, but stayed generally at the 90% mark.

3. CONCLUSION

A test rig for evaluation of our nano-structured calcium silicate hydrate NCaSilH) technology was designed, constructed, commissioned and operated on site at MB Century, sourcing brine from the Wairakei Power Plant, Taupo, New Zealand. The brine was found to contain comparatively low levels of silica but high levels of carbon dioxide. This means the brine provided a challenge and stress test for the method and associated technologies, such as lamella separators employed. In order to assess the viability of the plant, the nature of the products produced, especially carbonates, needed to be monitored. X-ray diffraction (XRD) and thermogravimetric analysis both allowed assessments of the level of carbonate in the product. XRD proved that the calcium carbonates produced were mainly calcite. The levels of calcite in the product varied greatly but could be reduced by minimizing the amount of calcium hydroxide dosed into the brine. In addition to calcite, NCaSilH and silica were the main products. Especially during a period of pump failures and equipment testing silica rather than NCaSilH was produced. However, the lamella separator employed could remove all particles independent of their nature from the brine with a separation efficiency between 90 and 98% at most times. Breakthroughs were rare and due to operational errors inducing turbulence into the separator. It was noted that when fewer particles were produced particles agglomeration was diminished and consequently separation efficiencies were also reduced. Overall the process and separation of solids from the brine proved to be very robust and reliable under unfavorable circumstances.

ACKNOWLEDGEMENTS

Funding for the project was provided by the Ministry for Business, Innovation and Employment (MBIE), New Zealand. We would also like to thank MB Century, especially Richard Adams, for granting us access to their site and a line of brine from the Wairakei Power Plant and supporting the project. Further, we acknowledge Edgar Schicker for his input into lamella separators, Roy Mink, Duncan Foley and Fabian Sepulveda for insights into geothermal brine chemistry, geology and carbonates.

REFERENCES

Borrmann T., and Johnston J.H.: Transforming Silica into Silicate – Pilot Scale Removal of Problematic Silica from Geothermal Brine. *GRC Transactions* Vol. 41, pp. 1322-1333. (2017).

Bougault H., Cambon P., and Toulhoat H.: X-ray spectrometric analysis of trace elements in rocks. Correction for instrumental interferences. *X-Ray Spectrometry*, Vol. 6 (2), pp. 66-72. (1977).

Bourcier W.L., Mackenzie Johnson W.R., Bruton C., and Gutierrez P.: Silica Extraction at Mammoth Lakes, California. *Proceedings of the International Mineral Extraction from Geothermal Brines Conference. International Mineral Extraction from Geothermal Brines Conference* 09/04/2006; Tucson, Arizona: Geothermal Resources Council pp. 1-6. (2006).

Bourcier W.L., and Bruton C.J.: Silica extraction from geothermal water. *United States Patent* US8840859 B2. (2006).

Brown, K.L., and McDowell, G.D.: pH control of silica scaling. *Proc. of 5th New Zealand Geothermal Workshop* pp. 1157 – 1162. (1983).

Cairns M.J., Borrmann T., Johnston J.H., and Hoell W.: A Study of the Uptake of Copper Ions by Nano-structured Calcium Silicate. *Microporous Mesoporous Mater.* Vol. 95, pp. 126-134. (2006).

Dubin L.: Silica inhibition: prevention of silica deposition by boric acid/orthorborate ion. *United States Patent* 4584104. (1984).

Featherstone, J.L., Powell, D.R., AND VanNote R.H.: Stabilization of Highly Saline Geothermal Brines. *Geothemal Resources Council Transactions* Vol. 3, pp. 1-7. (1979).

Gallup D.L.: Inhibition of silicate scale formation. *United States Patent* 5858245. (1999).

Gill J.S.: Silica scale control. *Materials Performance* pp. 41–45. (1998).

Gunnarsson I. and Arnórsson S. “Treatment of Geothermal Waste Water to Prevent Silica Scaling.” *Proceedings World Geothermal Congress 2005*. Antalya, Turkey, 24-29 April 2005. International Geothermal Association. (2005).

Harper R.T., Thain I.A., and Johnston J.H.: Towards the Efficient Utilization of Geothermal Resources. *Geothermics* Vol. 21 (5/6), pp. 641-651. (1992).

Iler R.K.: *The chemistry of silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*. John Wiley and Sons. New York, (1979).

McFarlane A.J.: The synthesis and characterisation of nano-structured calcium silicate. *Ph.D. thesis, Victoria University*. (2007). http://researcharchive.vuw.ac.nz/handle/10063/312

Montague T., Christi W., and Legmann H.: The Wairakei Binary Power Plant: First Eight Years of Operation.

Geothemal Resources Council Transactions Vol. 37, pp. 47-50. (2013).

Richardson I.G.: The calcium silicate hydrates. *Cement and Concrete Research*, Vol. 38 (2), pp. 137-158. (2008).

Sugita H., Kato K., Ueda A., Matsunaga I., Sakurai Y., Yasuda K., Bando Y., and Nakamura M.: Field tests on silica removal from geothermal brines in Sumikawa and Onuma geothermal areas. *Journal of Chemical Engineering of Japan* Vol. 32 (5), pp. 696-700. (1999).

Sugita H., Matsunaga I., Yamaguchi T., Kato K., and Ueda A.: Silica removal performance of seed from geothermal fluids. *Geothermics* Vol. 32 (2), pp. 171-185. (2003).

White B.R., Morris G.L., and Taylor C.: Wairakei - a fresh look at rejected technologies. *Proceedings 20th NZ Geothermal Workshop* pp. 67-74. (1998).