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Transforming Silica into Silicate – Pilot Scale Removal of Problematic Silica from Geothermal Brine

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ABSTRACT

The condensation of dissolved silica species to form a hard silica scale is a major issue in the generation of electrical energy and heat recovery from geothermal hot water and wet steam resources. In previous publications we have shown that nano-structured calcium silicate hydrate (NCaSilH) forms readily from dissolved silica species in the separated geothermal brine and, therefore, provides an attractive solution to the world wide problem of the formation of silica scale. NCaSilH is placed into context with silica species and other calcium silicate hydrates to demonstrate why the controlled formation and uses of this material are of interest in geothermal resource operation and management and in various end user applications. The formation and removal of this novel precipitated silicate from the brine is discussed in the lead up to pilot scale trials. Pilot scale test rigs for such trials are being constructed that directly compare our NCaSilH approach to removing the problematic supersaturated dissolved silica species from a geothermal brine to that of an untreated brine from which silica will precipitate uncontrollably. This will demonstrate that the technology offers a novel disruptive approach to facilitate the reduction in silica scale-forming species by removing most or all of the problematic dissolved silica species from such geothermal brines, along with calcium carbonate and some other species.

1. Introduction - Geothermal Energy and the Formation of Silica Scale

Geothermal energy is an attractive natural renewable energy resource, as it can produce large quantities of heat and electrical energy continuously and also on demand. The potential for harvesting geothermal energy is present, when underground water reservoirs a few hundred meters to several kilometers below the surface, are located close to geothermal heat sources (e.g. magma). Water reservoirs can be natural or artificially generated. The hot geothermal water is piped to the surface and flashed to produce a wet steam which is used to drive a turbine and produce electricity. The flashing simultaneously produces a separated geothermal water or brine flow, which is usually supersaturated in dissolved silica species, for further binary cycle electricity generation, heat recovery uses, discharge or re-injection. Re-injecting the separated brine and the condensed water from the steam turbines into a geothermal reservoir increases the life time of this underground reservoir, prevents subsidence and places this method of energy generation firmly into the realm of both benign and renewable energy resources.

Due to microbial and chemical processes, the sub surface rock containing and surrounding geothermal water reservoirs is partially dissolved, resulting in a cocktail of species (cations and anions) and suspended particles within the sub surface hot geothermal water. During utilization of this hot geothermal water resource, these dissolved species, notably silica and carbonate entities, can precipitate out to form an intractable scale, which blocks pipes, valves, heat exchangers and other process equipment. They can also be carried over with wet steam to damage turbines. Therefore, wet steam is scrubbed and treated to reduce the amount of carry-over, which leads to a loss of energy. Issues surrounding dissolved and suspended species become further problematic in the separated brine, as the species are concentrated up due to the flashing of about 30 % of the water flow into steam and downstream extraction of further heat energy resulting in a lowering of the brine temperature, hence increasing the silica deposition. This is a major problem in the recovery of heat energy in the heat exchangers in a binary cycle electricity producing plant.

The composition of the separated brine is somewhat production well and process specific, and various levels of toxic species, such as arsenic or selenium, valuable species, such as lithium, zinc, boron or gold, and environmentally harmless but problematic species, such as dissolved silica and calcium carbonate, are invariably present at different levels. The dissolved supersaturated silica species in the separated brine are therefore particularly problematic as they can precipitate out and form a hard amorphous silica scale that needs to be removed using considerable mechanical force and effort, or by the use of corrosive hydrogen fluoride or both. These dissolved silica species become concentrated to super-saturation levels after the generation of steam in the flashing process and/or after reduction in the brine temperature in a binary plant. For example, sub surface geothermal water at 260 °C can contain up to 600 mg/kg of dissolved silica (Iler, 1979). Upon flashing 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. The temperature of the brine correspondingly decreases to about 120 - 160 °C as heat energy is removed with the steam. At 120 °C only approximately 350 mg/kg of silica are soluble in water. The separated brine therefore becomes supersaturated with dissolved silica, which can condense (polymerize) and precipitate to form a hard amorphous silica scale blocking pipes, heat exchangers and re-injection wells.

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 (Dubin, 1984; Gunnarsson and Arnórsson, 2005) to partially delay the condensation of the dissolved silica species, the addition of silica seeds (Sugita et al., 1999; Sugita et al, 2003) to capture such dissolved silica onto a pre-existing silica material, and the addition of aluminum 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.

In 2008, we shifted our focus away from the production of fine chemicals towards the geothermal energy sector as we realized that one of the materials we produced, notably nano-structured calcium silicate hydrate, NCaSilH, offers a disruptive and attractive potential solution to preventing the occurrence of silica scale. The technology works by transforming the reactive silica species which is present at supersaturated levels in separated geothermal brine, into NCaSilH which forms readily, does not polymerize further and does not bind to metal surfaces. Instead the NCaSilH particles remain suspended in the geothermal brine flow and can be separated out as a useful product. The level of dissolved silica species remaining in the brine can be controlled to 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 are now constructing two small-scale pilot plant test rigs to address the following research questions, process chemistry issues and product characteristics as we progress the technology towards commercial scale development and demonstration:

1. Confirmation that our NCaSilH technology, which has been successfully demonstrated in laboratory and field scale work, is indeed able to prevent silica scale formation in an operational geothermal field.

2. What are the preferred process chemistry and operating conditions to effectively prevent scale formation in an operational geothermal environment? Here, a comparison will be made with an untreated system.

3. As individual geothermal wells essentially have a slightly different brine composition in terms of its ionic and particulate content, which of these dissolved and particulate species are captured along with NCaSilH material in its formation?

4 Are there a particular set of process chemistry conditions to form the NCaSilH material that can be identified to provide a small enough particle size for the NCaSilH to be reinjected directly along with the cooled brine, or does the NCaSilH need to be recovered as a useful product prior to reinjection?

5. If the NCaSilH product needs to be recovered from the cooled brine prior to reinjection, which will likely be the situation, what is the best process chemistry technology available for this and how will it be interfaced and implemented? The important issue here is

dealing with the high flow rates of the brine stream which contains the suspended NCaSilH particulates.

6. Further investigate and confirm the possible uses for the recovered NCaSilH product and how can the particular characteristics of the material be controlled to meet the requirements for these uses? This will build upon our current knowledge and interactions with potential end user companies.

There are likely further issues to be addressed which will become apparent during the program, which we will investigate in future studies.

In this paper, we describe, the design and operation of our two pilot scale test rigs and the type of information we are seeking to obtain from them in relation to the above research, process development and product characterization and end use questions.

2. Pilot Scale Test Rigs

In early 2016 we entered into a collaborative research and development effort with the Heavy Engineering Research Association (HERA), located in Auckland, New Zealand, for incorporating some specific requirements we desired into the pilot plant they were designing and constructing. Their purpose here is to carry out a variety of different tests relating to steel and coating coupon testing under a range of treatment regimens to address the nature and composition of the steel surface in relation to corrosion issues and silica scale formation.

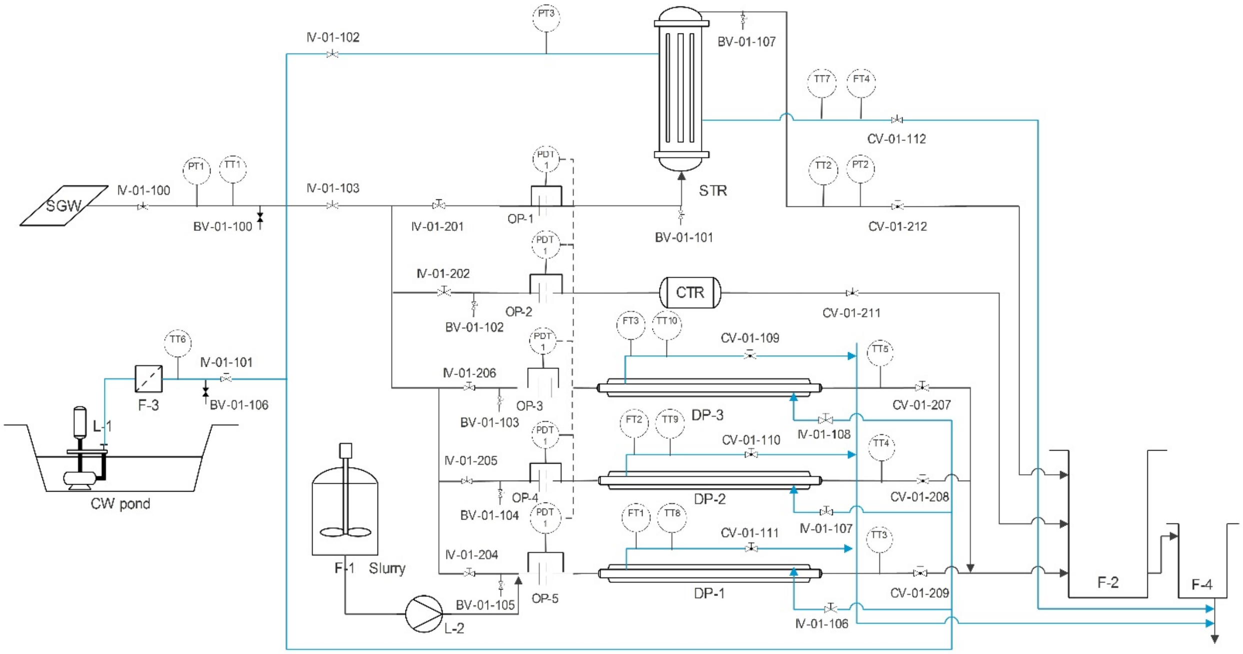

Figure 1: Sketch of the test rig developed in collaboration with HERA.

Geothermal brine enters this plant wherein the flow is split and distributed into four different streams thereby allowing parallel testing of various technologies, materials and assemblies. The flow rate and amount of brine in each of the streams is controlled over the various orifice plates, and related operational parameters such as flow, pressure and temperature are monitored constantly. Sampling ports are distributed over the whole setup, which will allow us to monitor changes in the brine composition as it travels through the test rig. Two of the streams are intended for use in coupon and materials testing. We have access to two other streams that are flowing through short heat exchangers before being delivered to a silencer and then discharged into a nearby water stream, to test our NCaSilH technology and product formation.

One of these two streams will be used as a control, which means we will not modify it in any way but at regular intervals take samples from it to establish the chemical composition of the flowing brine. Through an early sampling port in the other stream, we will inject our NCaSilH treatment agents. By comparing the outputs of the control and treated streams, we will establish the effect of various chemical and physical process parameters and treatment regimens and the effectiveness of our NCaSilH technology on preventing silica deposition and producing a useful NCaSilH product accordingly. We will also establish the optimum operating conditions that reduce the amount of reactive dissolved silica species below levels where scale formation occurs.

The test rig is built on a short container base and as such can be uplifted and moved to different sites and sources of geothermal brine. This way we can collect data and determine the optimal treatment conditions based on a variety of brines from different geothermal wells and resources, and hence on the characteristics of the NCaSilH material obtained and the nature of species captured along with its formation. This will entail the production and collection of a range of samples of NCaSilH under different process chemistry operating conditions for ensuing analyses and characterization. It will provide insights into the properties, chemical composition and potential uses of NCaSilH and the other species captured during the NCaSilH formation. Our laboratory work has already provided useful information on the various NCaSilH materials we expect to form and other species we expect to capture, and how the properties and characteristics of these materials are influenced by the different species in the brine stream and the process chemistry conditions used. The respective control samples can be directly compared and used to show how such different conditions control our NCaSilH material formation and process chemical technology accordingly.

While this HERA test rig allows comparative studies and is mobile, which is useful, there are some shortcomings attached. The length of pipes and consequently the residence time of the geothermal brine in the test is short. Furthermore, the pipes have been welded together and all connections smoothed, which minimizes the propensity for silica deposition and scale formation in the pipework. We can adjust to these issues to some extent by carrying out experiments over longer durations. We will use this for initial experiments once it is commissioned, but at the same time we have designed and are building a second test rig with a much longer piping network, to enable us to better investigate the inherent characteristics of our NCaSilH technology to prevent silica polymerization and scale deposition (**Figure 2**).

This second test rig is designed in a modular way comprising a network of flanged tubes that are supported on a rack. The flanges and bends in the pipes provide effective potential deposition sites for silica scale. The overall path length through the pipes is approximately 10 m, which quintuples the residence time compared to the HERA test rig. Pressure, flow and temperatures will be similarly measured and recorded for the overall brine stream. As with the other test rig, the incoming brine stream is split into a control and a treated stream respectively. Short heat exchangers at the beginning of each stream are designed to cool down the incoming brine and increase the likelihood of scale formation by increasing dissolved silica super-saturation level. At the end of both streams (control and treated), sampling ports are located. The streams terminate in individual silencers to allow the treated stream to be collected and treated separately, and compared with the untreated control stream. It is intended that various technologies aimed at recovering NCaSilH from the brine will be tested. The test rig can be dissembled and the individual pipes can easily be visually investigated.

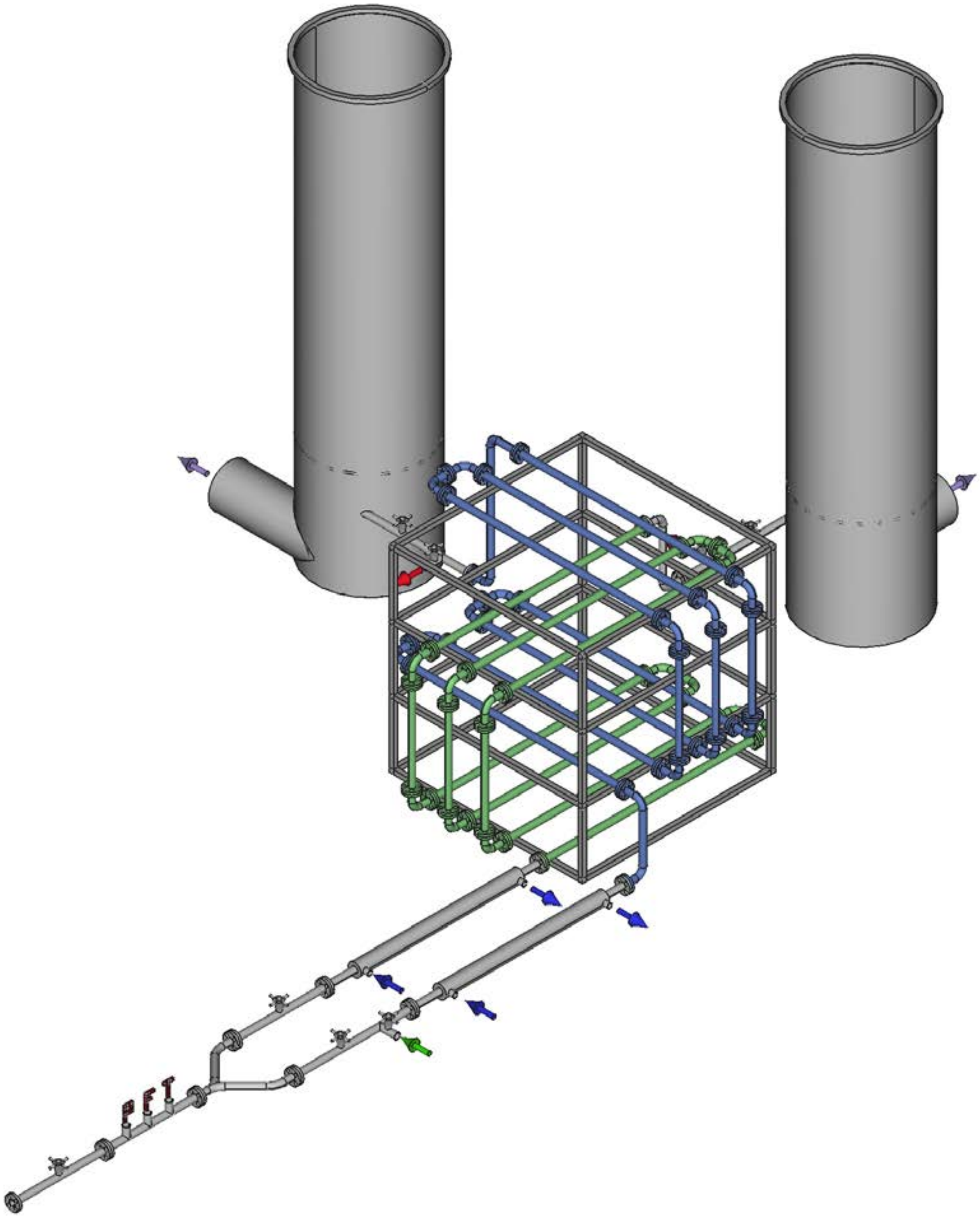

Figure 2: Sketch of the second test rig.

During operation the individual streams can be isolated, segments of the flanged tube can be removed, exchanged and examined. We are expecting that visual camera footage from inside the pipes will show scale formation inside the control stream, while hopefully the pipes from the treated stream will remain pristine. This will mimic and confirm our laboratory and field scale work and results accordingly. The test rig can also be readily transported to other sites and the same study carried out.

Both test rigs will be able to demonstrate the effectiveness of our NCaSilH technology in reducing silica scale formation. They will also facilitate optimization of the treatment conditions, as well as enhancing our understanding of the process chemistry, properties of the brine and effect of other dissolved entities in the brine on the NCaSilH formation. Both rigs are designed to allow collection of NCaSilH samples under different operating conditions. From the analyses of these samples, we will gain more information on both the potentially valuable and problematic species that may be captured in the NCaSilH precipitation process. This addresses the first four of our research questions above. We will also investigate different commercially available separation and drying technologies to recover the NCaSilH material from the treated brine stream, and to then characterize the properties of the NCaSilH material and determine and demonstrate potential applications for it. Also it will be necessary to determine and characterize any other species bound to and captured by NCaSilH.

3. Recovery of NCaSilH from Geothermal Brine

The production of NCaSilH with particular characteristics and properties from dissolved silica species in geothermal water and sodium silicate solutions by addition of lime under controlled conditions has been successfully demonstrated by us (Johnston et al., 2006). It appears that other workers have also used lime in a similar way, but have been less successful (Sugita et al., 2002). Our more detailed work has shown that if the dissolved silica is reacted with small doses of lime ($Ca/Si < 0.4$) a silica material with a type I network structure precipitates (Iler, 1979, Harper et al., 1992, Sugita et al., 2002, **Figure 3a**). The use of larger amounts of lime ($Ca/Si > 1.3$) results in the formation of calcium silicate hydrate species (C-S-H) like tobermorite and jennite (Richardson, 2008). In our detailed studies of the reaction of sodium silicate solution and also geothermal brine with different quantities of lime under controlled pH conditions, we found that using a calcium to silicon ratio of 0.8, a novel nano-structured calcium silicate hydrate, NCaSilH, material (**Figure 3b**) is produced very rapidly from either synthetic or natural sources of dissolved silica (Johnston et al., 2006).

NCaSilH is distinct from other forms of precipitated silica in that the base unit present is related to the calcium silicate wollastonite $CaSiO_3$ structure, shown by Borrmann et al., (2006 and 2008), in a study of the material using nuclear magnetic resonance, ion bombardment and X-ray photoelectron spectroscopy. In contrast to other C-S-H phases and silicates, NCaSilH is not crystalline and does not have the long-range order prevalent in these other structures (Borrmann et al., 2006 and 2008). Fundamental silicate units do however link together to form the backbone of the NCaSilH structure and provide an open framework similar to “desert rose”, where the calcium ions are accommodated on the surface of the particles. This gives NCaSilH a slightly positive surface charge and hence the ability to bind other silica or ionic species to such surfaces (Johnston et al., 2006, Cairns et al., 2006, Borrmann et al., 2011). In the presence of anions such as carbonate or phosphate, the surface calcium ions can form insoluble calcium carbonate species (aragonite, **Figure 4a**), or calcium phosphate in the NCaSilH particle matrix. The large available surface area resulting from the open framework nature of the NCaSilH structure is important here. Also, cations react with surface silanol groups or exchange against calcium and bind to the silicate surface (Borrmann et al., 2011). Additionally, NCaSilH has a variety of pores from nano- to meso- in size, which allow it to act as a sponge and filter material and trap other solid particles on its surface (for example calcite crystals as shown in **Figure 4b**).

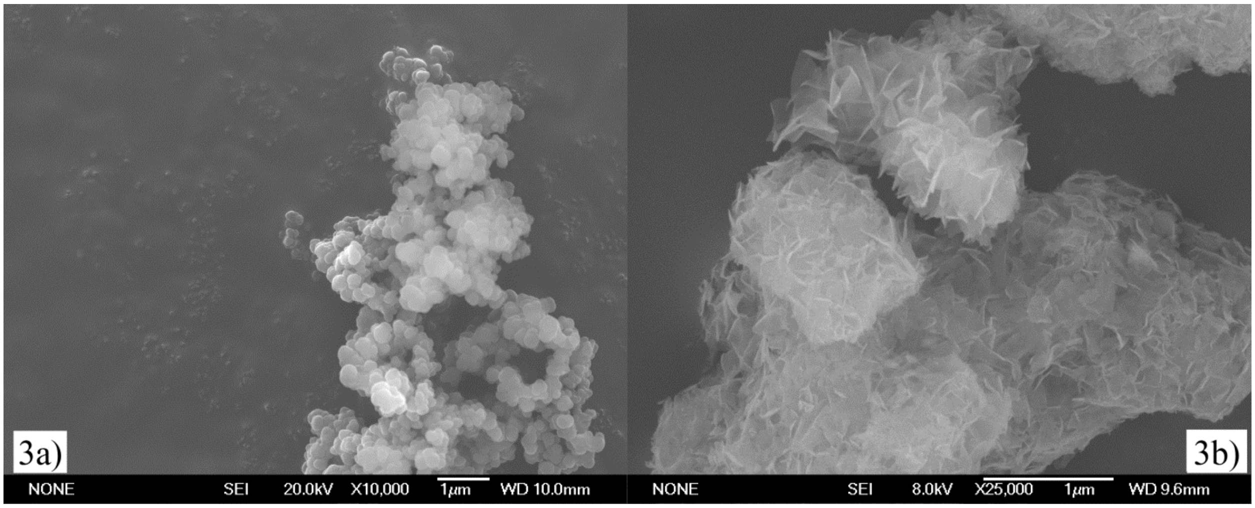

Figure 3: Scanning electron microscope images. A silica with a type III network structure (a) and nano-structured calcium silicate (b).

The particles observable in the scanning electron microscope images (**Figure** 4) are about 1 to 5 microns in diameter. The open framework structure is observable. Number weighted particle size measurements using the dynamic light scattering measurement method, also show that about 99 % of the particles fall within this size range. However, our laboratory work has shown that the small particles have a tendency to agglomerate and form clusters of several microns in diameter. This is verified by volume weighted particle size measurements, where particles with a diameter of 10 micron, being agglomerates of about one thousand 1 micron particles are observable (Borrmann, 2009). Although it is possible that the individual 1 micron NCaSilH particles could likely be reinjected with the cooled brine, the larger 10 micron particle agglomerates would probably block the pores in an underground geothermal reservoir rock formations. Hence it is most likely that the NCaSilH material needs to be removed from the geothermal brine before reinjection. A positive side effect of these larger agglomerates is that two sources of scale forming species, silica and calcium carbonate are removed from the brine at the same time by our NCaSilH technology. In current geothermal resource field operation and management, while calcium carbonate scales tend to be soft and brittle as compares to the silica scale, the carbonate occurrence is still problematic and the consequent need for its removal also entails operational down times and expenditures, as does the silica scale removal.

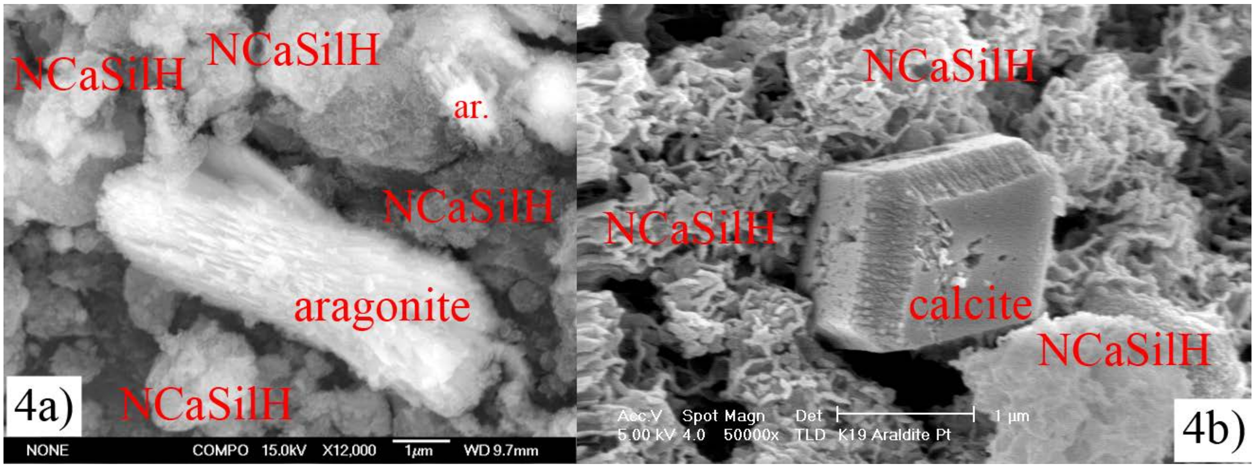

Figure 4: Scanning electron microscope images. Calcium carbonate trapped in NCaSilH; (a) aragonite, (b) calcite.

Our laboratory and field results present a further strong argument as to why the NCaSilH material should be removed from the brine. The surface chemistry of NCaSilH changes over time depending on the pH of the environment. As a result the calcium is very slowly leached from the platelet surfaces starting within minutes of the NCaSilH formation. This is particularly evident as the pH is lowered. The vacant sites then react with water to release hydroxide ions into solution. The calcium and hydroxide ions remain closely associated with the silicate particles and tend to facilitate reactions on the particle surface, so this is not an immediate issue. However, after several hours or days the NCaSilH does begin to dissolve noticeably releasing monomeric silica and silicate species back into solution, depending on the pH, ionic content and temperature (Barassi, 2013). This means that although NCaSilH acts to capture the reactive silica species and hence prevent the formation of the unwanted hard silica scale, if the NCaSilH material is not removed from the brine in a reasonable timeframe, this slow dissolution characteristic may result in silica precipitation. However, in reality this is not an issue as the water flow rates in geothermal pipework are fast and hence the residence time for a particular volume of brine and the associated precipitated NCaSilH material in the system before removal, is very short. In contrast to several other treatment technologies, NCaSilH can be removed from the brine thereby irreversibly lowering the risk of silica scale formation. Other researchers like Sugita et al., (2002), have also realized that removal of the solids offers this opportunity. While some other research groups have investigated the generation and removal of silica materials from geothermal brines (Bourcier et al., 2006 and 2014), our NCaSilH technology offers several opportunities and competitive advantages based on its process chemistry and the particulate structure and nature of the surface morphology of the material, which are not provided by such other approaches.

The removal of the NCaSilH material from the geothermal brine is challenging due to the relatively high water flow rates and hence the volume of brine that needs to be treated, the comparatively small particle size and the thixotropic and hydrophilic nature of the NCaSilH (Johnston et al., 2006). Fortunately the NCaSilH agglomerates settle quickly and our field and early pilot scale work successfully demonstrated that a settling and sedimentation tank approach is viable. Such tanks are based on established technology and used widely in the treatment of sewage and waste, and in mineral separation and purification processes. Other options include continuous filtration systems as used in brewing waste and coal mining or electrocoagulation, which is also used successfully in municipal waste treatment systems. The different options will be researched and trialed as the work on the test rigs is progressed. It is likely that the elevated temperature and possibly the other species captured in the NCaSilH material will influence the separation characteristics. These will be explored and characterized accordingly. Our laboratory trials have been promising and these will be presented and discussed in future publications.

Leading on from the successful recovery of NCaSilH and any associated impurities from the brine, we will continue our applications and product development work on the potential uses of the NCaSilH material and in particular, progress our interactions and interactions with various interested filler, coatings, paper, plastics and cement companies. If valuable species are also captured, there is the potential for recovering them from NCaSilH in a later stage process step. Results will be presented in future discussions and publications accordingly, as we collect sufficient material to facilitate our extensive end user material testing and evaluation work.

4. Conclusions

Our novel and disruptive nano-structured calcium silicate hydrate (NCaSilH) technology allows the removal of the reactive, dissolved silica species present at supersaturated levels in geothermal brine by transforming such species into a competing non-scale forming calcium silicate hydrate material. Two test rigs are being developed that are aimed at testing the NCaSilH technology in comparison to an untreated control, at different operational geothermal sites around New Zealand. As the chemical composition of the brine at each site is invariably different, our work will provide valuable insights into the species trapped in the porous NCaSilH and develop and optimize treatment regimens for each site. Results from our laboratory experiments strongly suggest that NCaSilH needs to be recovered from the geothermal brine. While this has not been fully confirmed and the removal of a NCaSilH product is still considered to be a somewhat open research question, the particle size and chemical behavior of the calcium silicate hydrate imply that the NCaSilH material needs to be removed. Nonetheless it appears important to collect sufficient amounts of samples of NCaSilH for analysis and to provide material for end user testing and evaluation purposes.

Overall, the technology offers the opportunity to reduce the levels of not only the problematic dissolved silica species, but also calcium carbonate trapped in the silicate hydrate, to below levels were scale formation of either occurs. Furthermore, the removal of the dissolved silica species by our NCaSilH technology in turn allows either the simultaneous or subsequent recovery of valuable compounds from geothermal brine. This opens up possibilities for geothermal mining and access to new revenue streams. Future research projects will investigate this possibility more closely. On looking at some projects aimed at gaining access to supercritical geothermal resources, the need to solve the silica scale issue becomes even more pressing. Under supercritical conditions it is likely that the dissolution of the sub surface reservoir rock, the saturation of geothermal water and oversaturation of separated brines becomes a much more significant issue and problem to address. This is an interesting possibility in the medium and long term. However our current focus is on the successful implementation and demonstration of the NCaSilH technology and the removal of the NCaSilH on large scale, and also on establishing potential uses for the material. The possible issue of contamination of the NCaSilH material with a variety of other species will also be explored.

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