RECOVERY OF NANO-STRUCTURED CALCIUM SILICATE HYDRATE FROM GEOTHERMAL BRINE USING A LAMELLA SEPARATOR

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ABSTRACT

The formation of silica scale from supersaturated geothermal brine is one of the major challenges of geothermal energy utilization for heat recovery and electricity generation. The scale blocks pipes, valves, heat exchangers and other equipment and reinjection wells. Most current remediation approaches only delay the formation of scale and are not wholly successful. Also, they can lead to advanced corrosion issues.

The competitive transformation of dissolved silica into nano-structured calcium silicate hydrate (NCaSilH) particulate material in the silica supersaturated brine stream prevents the formation of silica scale. The NCaSilH silicate forms rapidly, reducing the amount of available dissolved silica down to safe levels where the dissolved silica species cannot polymerize and precipitate as the problematic silica scale. The NCaSilH particles do not stick to metal, are slightly passivating and can trap other scale forming species like calcium carbonates. However, the silicate hydrate particles are comparatively large and would likely block porous rock media like geothermal reservoirs. This means that NCaSilH needs to be removed from the spent brine prior to reinjection of the brine.

In laboratory tests, the solid liquid separation of NCaSilH particles was investigated in sedimentation and other experiments, which have led to the choice of lamella separation as a promising technology for the recovery of the silicate. Laboratory models were constructed, tested and up-scaled. A pilot-scale separator was build, which will be used in two pilot scale test rigs. Present here is the design of the lamella separator and preliminary results from its use.

1. INTRODUCTION AND PRIOR RESEARCH

1.1 Geothermal Energy and the Formation of Silica Scale

Geothermal energy is an important, natural, renewable energy resource, as it can produce large quantities of heat and electrical energy on demand and also continuously. Geothermal energy can be harvested, 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. 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 and other mineral species. This brine could be used for further binary cycle electricity generation, heat recovery uses, discharge or re-injection. Re-injecting the separated brine combined with condensed water from the steam turbines into a geothermal reservoir increases the life time of the underground reservoir, prevents subsidence and places this method of energy generation firmly into the realm of both economical and renewable energy resources.

Sub surface rock containing and surrounding geothermal water reservoirs is partially dissolved due to microbial and chemical processes resulting in a cocktail of ionic species (cations and anions), non-ionic species (such as silicic acid) and suspended particles within the sub surface hot geothermal water. During utilization of a hot geothermal water resource, these dissolved species, notably silica and carbonate entities, can precipitate out to form intractable scale, which blocks pipes, valves, heat exchangers and other process equipment. The silica and carbonate 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 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 further heat energy, such as in binary cycle electricity producing plants.

The composition of the separated brine is to a large degree specific for each production well and process. 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. Dissolved silica species reach supersaturation 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 ºC 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 ºC as heat energy is removed with the steam. At 120 ºC 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. The removal of hard amorphous silica scale requires considerable mechanical force and effort, the use of corrosive hydrogen fluoride or both.

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 utilization. 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) and Lichti (2013) present good overviews regarding the problematic issue of silica scale formation and the effect of pH and other ionic species on it.

1.2 Nano-structured Calcium Silicate Hydrate

In a parallel development, Harper and Johnston in New Zealand (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. Harper and Johnston 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. However, Sugita et al. appeared not to have realized the nature and potential of the silica and silicate species generated.

In 2008, Johnston and Borrmann shifted their focus away from the production of fine chemicals towards the geothermal energy sector as they realized that one of the materials produced, notably nano-structured calcium silicate hydrate, NCaSilH, offers an 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 from below the equilibrium solubility level at the brine temperature down to essentially zero, depending on the amount of calcium ions used in relation to the dissolved silica species in the water.

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 (Johnston et al., 2006). It appears that other researchers have also used lime in a similar way, but have been less successful (Sugita et al., 2002). Harper and Johnston's 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 1a**). 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). Studies of the reaction of sodium silicate solution and also geothermal brine with different quantities of lime under controlled pH conditions showed that using a calcium to silicon ratio of 0.8, a novel nano-structured calcium silicate hydrate, NCaSilH, material (**Figure 1b**) is produced very rapidly from either synthetic or natural sources of dissolved silica (Johnston et al., 2006).

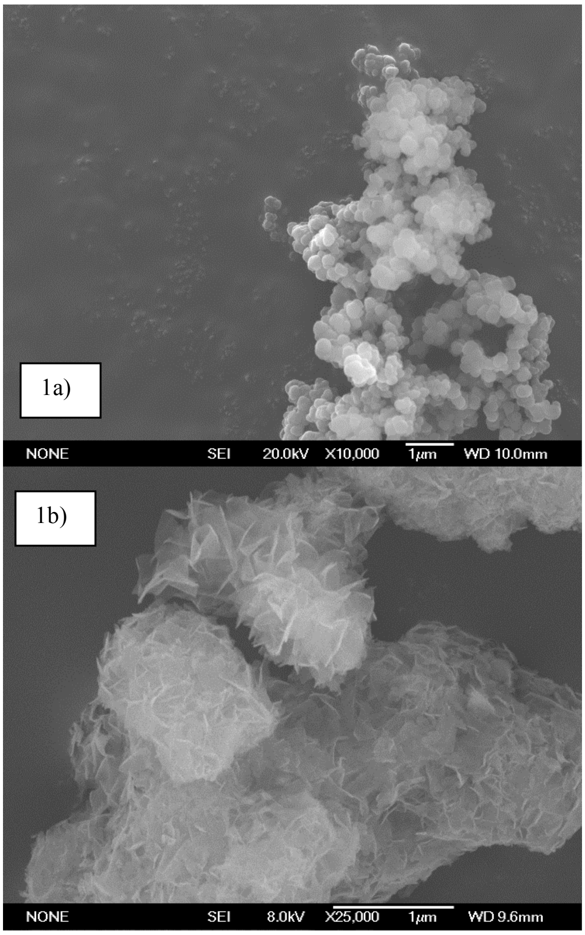

Figure 1: Scanning electron microscope images. A silica with a type III network structure (a) and nano-structured calcium silicate (b).

NCaSilH is distinct from other forms of precipitated silica in that the base unit present is related to the calcium silicate wollastonite, $CaSiO_3$, as shown in studies of the material using ion bombardment (Borrmann et al., 2006), nuclear magnetic resonance, X-ray diffraction and X-ray photoelectron spectroscopy (Borrmann et al., 2008). In contrast to other C-S-H phases and silicates, NCaSilH is either not crystalline or 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 2a**), 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 2b**.

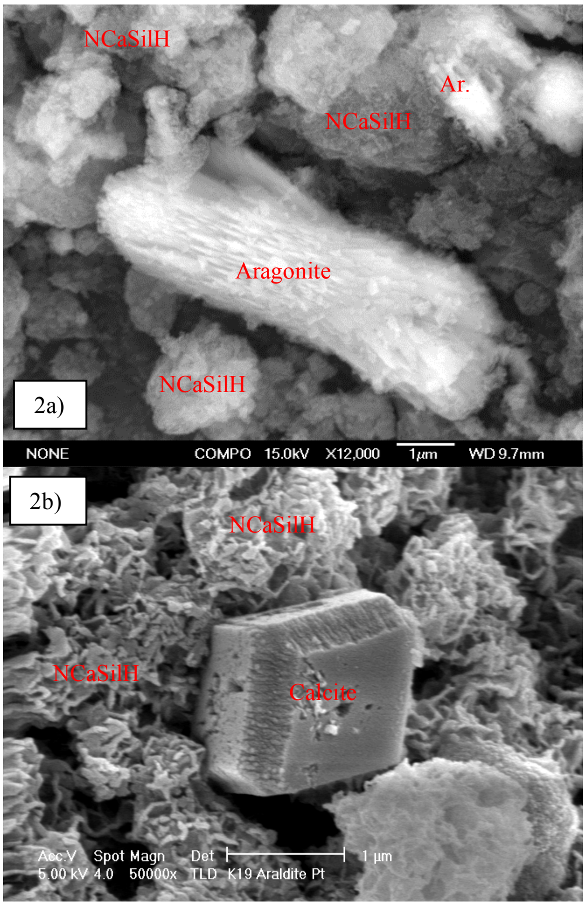

Figure 2: Scanning electron microscope images. Calcium carbonate trapped in NCaSilH; aragonite (a), calcite (b).

The particles observable in the scanning electron microscope images (**Figure 2**) 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, verified by volume weighted particle size measurements - average somewhere between 20 and 30 microns (**Figure 3**). It should be noted that particles with a diameter of 10 micron are agglomerates of about one thousand 1 micron particles (Borrmann, 2011). Although it is possible that the individual 1 micron NCaSilH particles could likely be reinjected with the cooled brine, the larger 30 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 the NCaSilH technology. In current geothermal resource field operation and management calcium carbonate scale tends to be soft and brittle, while silica scale is hard and intractable. However, the occurrence of carbonate is still problematic and the consequent need for its removal also entails operational down times and expenditures, as does the silica scale removal.

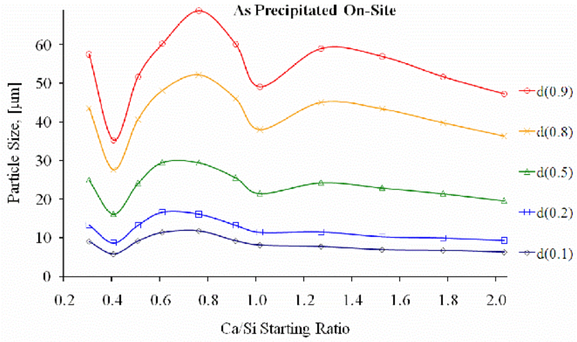

Figure 3: Particle size distribution of NCaSilH formed in field trials at different calcium to silicon starting ratios.

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 concluded 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), the 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 filtered, the comparatively small particle size and the thixotropic and hydrophilic nature of the NCaSilH (Johnston et al 2006). Presented in this article are findings in relation to separating NCaSilH from geothermal brine and the reasons for deciding on trialing a lamella separator in a test rig, which will commence operation in August 2017.

2. FROM SETTLING TANKS TO LAMELLA SEPARATORS

The removal of nano-structured calcium silicate hydrate (NCaSilH) from geothermal brine is a solid liquid separation, which is non-trivial due to the high surface area and pore volume of NCaSilH, low difference in the respective densities of NCaSilH (1.6 g.cm^{-3}) and water (0.998 g.cm^{-3}), and the low mass concentration of NCaSilH in geothermal brine, about 0.1 %wt. This is aggravated by the comparatively high brine flow rates found in geothermal plants.

2.1 Settling Behavior

Despite the aggregation of particles and formation of larger (10 to 60 micrometer) agglomerates, the sedimentation of NCaSilH was slow (4 to 6 minutes to compression point). The aggregates of NCaSilH were very porous. BET surface area measurements delivered results in the range of 100 to 500 m^2.g^{-1} of material. Oil absorption measurements showed that a typical sample of NCaSilH could absorb up to 1 to 7 times its weight in oil (or water), which indicated that the pores were quite accessible. The openness of the structure in combination with the mass concentration lead to zone settling behavior. Therefore, the settling rate of the particles had to be determined empirically. Most of the sedimentation was completed after approximately 4 minutes, at which point a very slow compression of particles occurred. This means that the settling process could be terminated after about 4 minutes, as further sedimentation is inefficient after the compression point. Prior to the compression point settling velocities were constant (linear region in between minutes 1 and 3 in **Figure 4**). It should be noted that the results presented here are based on using a slightly conical vessel with a 3 L volume, 190 mm height and a diameter between 155 (top) and 130 mm (bottom). A differently shaped and larger or smaller vessel will yield different results due to wall effects and the compression point being dependent on the vessel height. For the samples shown in **Figure 4**, collected at the Ohaaki Kiln, Broadlands, New Zealand (named Ohaaki) and at a well-head of the Ohaaki power plant prior to flashing (Broadlands) the samples settled from 3000 mL down to about 750 mL within 4 minutes. All NCaSilH samples studied displayed zone settling behavior.

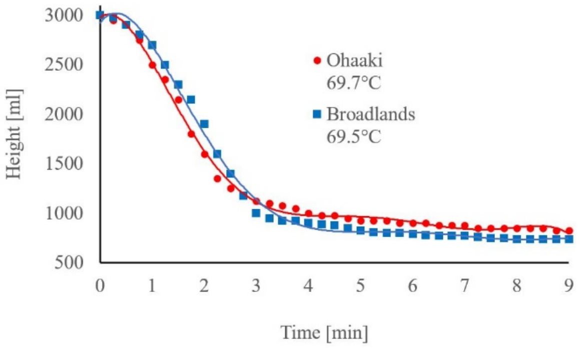

Figure 4: Settling height vs time for two samples of NCaSilH produced from geothermal brine collected from the Ohaaki kiln (Ohaaki) and a wellhead of the Ohaaki power station (Broadlands).

The rate of the settling process was determined to be about 5 cm.Min^{-1} Based on this settling rate the minimal theoretical size of a settling tank could be calculated (**Figure 5**). The flow rates quoted in **Figure 5** are examples for brine flow before a potential flashing stage. It needs to be noted that no safety factor was included in the calculation; for a real life example a safety factor of about 22 % of the theoretical minimal diameter would have to be included. This is equal to a 50 % increase of the surface area of the settling tank. Furthermore, the settling rate is strongly dependent on the salt content of the brine. Increasing the salt content of the brine reduces the solubility and miscibility of silica and related species. Impurities, like silica, zinc or iron, can bind to NCaSilH raising its density and hence lead to an increased settling rate. Additionally, at higher temperatures, the viscosity of the fluid is lower and consequently the settling rate is elevated.

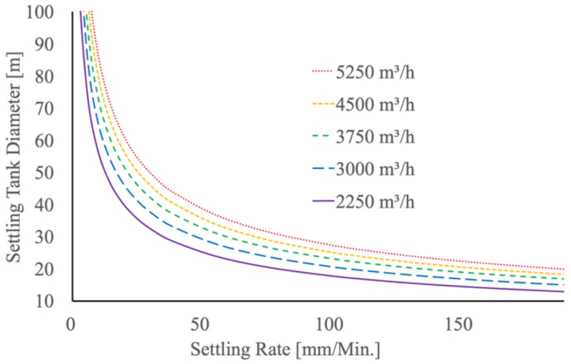

Figure 5: Minimum settling tank diameter vs settling rate for selected flow rates at 80 ºC.

Taking into account the settling rate for the Broadlands and Ohaaki samples investigated here a tank diameter of 30 m for a flow rate of 3000 m^3.h^{-1} (see **Figure 5**) would be necessary; if a safety factor is included that diameter would need to be about 37 m, which is comparatively large. Experiments showed that a flocculent can increase the settling rate but not by a significant amount. Furthermore, dosing the flocculent into the brine would lead to potential impurities remaining in the brine or the silicate product and incur costs for dosing equipment and flocculent.

2.2 Lamella Separator

Several solid liquid separation technologies were considered in the approach for separating NCaSilH from geothermal brine. While rotary drum filters, band filters, continuous centrifuges and filter presses could deal with the challenges presented by NCaSilH, they all have moving parts, require electricity and are comparatively expensive. At the volume and flow rates and low concentrations of NCaSilH particles present they were considered uneconomical.

Hydrocyclones are very efficient at solid liquid separations and have a comparatively low footprint. Additionally, their principle use is familiar to the geothermal industry in the form of cyclone separators used in flash plants to separate steam from brine. Due to a lack of expertise no attempt was undertaken to construct a hydrocyclone at this stage in the project.

Filter cartridges and membranes were tested successfully in the separation of NCaSilH and geothermal brine but experienced fouling. The pressures and temperatures prevalent in geothermal energy producing environments put considerable stress on the filters and membranes, which implied that their service life might be prohibitively short.

On advice from Edgar Schicker we started to investigate lamella separators. Lamella separators are also referred to as lamella clarifiers or inclined plate settlers. These separators are characterized by an array of inclined parallel plates providing a large settling surface. Because the plates are stacked a lamella separator has a comparatively small footprint (20 to 35 % of the size of a comparable settling tank). A schematic showing the main flows and settling along the plates is shown in **Figure 6**.

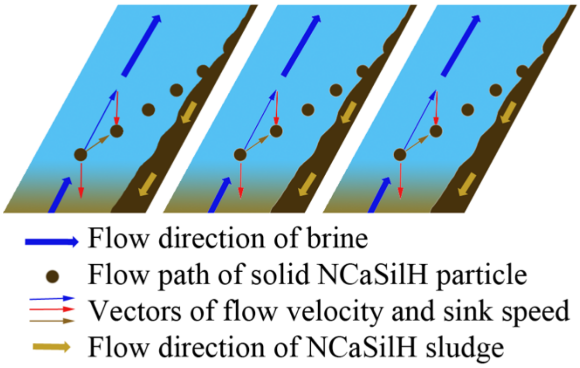

Figure 6: Schematic showing particle flows along the plates of a lamella separator.

A lamella separator can operate on the principle of a counter-current separator. Water rises up in the separator. Due to their higher density and related settling velocity particles progress at a slightly flatter angle than water and impact on the surface of the lamella, where they aggregate and slide down to a collection chamber and outlet at the bottom of the separator. Generally low flow velocities (and therefore low Reynolds numbers) mean that a lamella separator works very efficiently. Low flow velocities are desirable as it is less likely that turbulences occur, which disturb the settling process. Instead a laminar flow system is present. In the geothermal context, there is the possibility of the occurrence of temperature gradients, which introduce convection currents. Hence, steps need to be taken to avoid these, like insulating the surfaces of a lamella separator. The occurrence of convection currents was confirmed in laboratory tests.

The dimensions and arrangement of elements in each lamella separator is specific to the solid and liquid that require to be separated as well as to the ambient conditions present. Due to having no prior experience in the construction of a lamella separator an empirical approach was chosen for developing a suitable separator. First a laboratory model was constructed that allowed observation of the flows in the model and then refinement based on the observations. The refinement process took two steps until a model was constructed that had a separation efficiency above 99 percent (**Figure 7**). The first model developed an unwanted turbulence, where particles rapidly moved along the outside wall of the separator (**Figure 7**, top, yellow arrow), hence creating a circular current within the separator. This was thought to be due to the vertical entry of fluid and the wall angles within into the separator. Baffles added to the front of the separator intended to break the fast inflow resulted in some solid liquid separation (**Figure 7**, top, red arrow) but did not stop the circular current.

To prevent the occurrence of the circular current found in the first model, the entry into the second model was flattened to reduce fluid velocities. Tests showed that a laminar flow transported the fluid directly towards the first lamella (**Figure 7**, middle). Initially this was thought to be due to a thermal current but addition of insulation did not resolve this matter. Once past the first lamella a comparatively high current directed towards the outlet meant that only the first lamella was contacted by the fluid. Most of the fluid in the rest of the separator was still and did not participate in any settling process as shown in dye experiments.

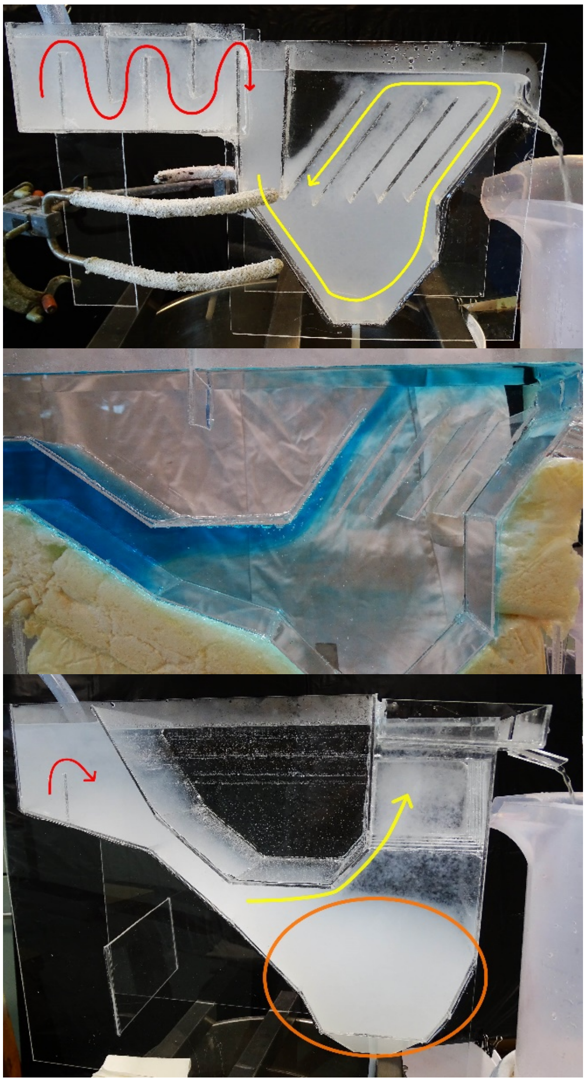

Figure 7: Perspex lamella separators tested in the laboratory. Top: Model 1. Middle: Model 2. Bottom: Model 3.

For the third model (**Figure** 7, bottom) the lamella were turned by 90 degrees to ensure that all lamellae were active, and the outflow area was widened to reduce flow velocities towards the outlet. A laminar flow was observed as in model 2 (yellow arrow). However, most particles settled directly into the compression area (orange circle). The rest of the particles entered the lamella area. Due to the turning of the lamella the flow went past every lamella, making use of their full surface area for settling. A flow breaker was added at the inlet (**Figure 7**, bottom, red arrow) to distribute the flow over the whole length of the inlet. A separation efficiency of 99.4 % was achieved. The residual NCaSilH particles that were transported into the supernatant were very small (not visible).

Based on the laboratory model a larger separator (for a flow rate of 8 L/Min.) to be used in a test rig was constructed. Results from the use of the larger scale separator in a pilot plant will be presented in future publications. To confirm our laboratory results, for this larger separator a computational fluid dynamics (CFD) model of the flows in the separator (**Figure 8**) was simulated by Haiam Abbas of the Heavy Engineering Research Association (HERA). Velocities and stream lines in the CFD simulation were the same as those observed for model 3 (**Figure 7**, bottom).

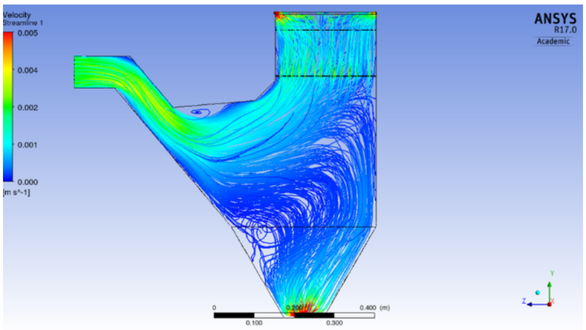

Figure 8: CFD model showing the flow rates in a large-scale lamella separator based on Perspex laboratory model 3.

The CFD simulation (**Figure 8**) was produced using ANSYS R17.0 software.

3. CONCLUSION

The formation of silica scale can be prevented by transforming the silica into nano-structured calcium silicate (NCaSilH). Due to its particle size and chemistry NCaSilH needs to be removed from geothermal brine to avoid the risk that it would block up reinjection wells and geothermal reservoirs. Lamella separation was successfully tested for the removal of NCaSilH from geothermal brine, reaching a solid liquid separation efficiency of 99.6 %. The residual supernatant is free of visible particles and silica levels in the supernatant are below saturation levels.

The shape and configuration of the lamella separator was determined empirically by building a model, observing the flows in it and designing the next model based on our findings. Overall 3 laboratory models were constructed. The validity of the third model was confirmed in a computational fluid dynamics simulation of a larger scale separator. The fluid velocities and Reynolds numbers in the model were the same as in laboratory model 3.

Lamella separators were chosen for the recovery of NCaSilH from brine due to their comparatively small footprint compared to settling tanks and as they don't contain any movable parts. Other solid liquid separation techniques were not explored at this stage in the project. NCaSilH is only going to be concentrated to a solid content of about 0.25 % in the lamella separator. Therefore, it is necessary that one of the other solid liquid separation techniques or further lamella separation cycles will be applied as a second stage processes. This along with uses for the recovered NCaSilH will be considered in future projects.

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