TURNING THE PRESSURE ON FOR THE NANO-STRUCTURED CALCIUM SILICATE HYDRATE (CASIL) SOLUTION TO SILICA SCALING

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ABSTRACT

The nano-structured calcium silicate hydrate (CaSil) technology has been shown to prevent the formation of hard intractable silica scale. Such scale forms due to the supersaturation and precipitation of silica from geothermal water during energy production. Using the CaSil technology suspended silica is converted and precipitated as calcium silicate hydrate, which does not stick to surfaces and can be recovered via solid-liquid separation to yield useful products. Additionally, CaSil can capture and trap calcium carbonate species formed in parallel. So far, this technology has been employed after flashing processes with the recovery happening at atmospheric pressure and below boiling temperatures.

Feedback from the geothermal industry suggested that it would be very interesting to capture and transform the silica prior or during the flashing process. Doing so would offer a significant advantage. Currently during flashing silica can be carried over with the steam and damage sensitive equipment. Transformation of the silica into a non-volatile and particulate silicate hydrate reduces the carry-over. Furthermore, applying the CaSil technology under pressure would allow to retain elevated pressure at the end of the process, which aids in the transport of liquids over distances and reinjection.

In this article we present preliminary findings regarding employing the technology at elevated pressures. We have investigated and answered several research questions. The CaSil process does not significantly change the vapour pressure or lower the temperature of the geothermal water. It significantly reduces the carry-over of silica into the vapour phase depending on the extent of treatment. Lastly, the lamellar separation process can be carried out at elevated pressure. Elevated temperature has a larger impact on the efficiency of a lamella separator than pressure.

1. INTRODUCTION

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. Hot geothermal water is sourced from an underground reservoir to the surface and can be flashed to produce saturated steam to drive a turbine and generate electricity. Alternatively, or in addition the hot brine can be used for binary cycle electricity generation or direct heating. All methods of energy extraction lower the temperature of the geothermal water used leading to the supersaturation of species dissolved underground at the reservoir conditions (e.g. temperature, pressure, chemistry and extremophiles). Flashing also removes material in the form of steam creating a separated geothermal water or brine flow, which is usually even more supersaturated in dissolved species such as silica. The supersaturation is somewhat mitigated by the addition of condensed steam to the brine. Re-injecting the spend geothermal water and condensed steam into a geothermal reservoir replenishes the reservoir and subsequently increases its life time of the geothermal resource, prevents subsidence and places this method of energy generation firmly into the realm of both benign and renewable energy resources (Dubin 1984, Gunnarsson and Arnórsson 2005).

1.1 Silica Scale

Due to microbial and chemical processes subsurface 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, amongst them 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 saturated steam during the flashing process to scale and damage turbine blades. Therefore, saturated 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 separated brine. The dissolved and suspended minerals are concentrated due to the flashing, which converts about 30 % of the water flow into steam. Not only production equipment is affected by scaling; reinjection wells can become clogged due to silica scale requiring costly chemical treatments or drilling of new reinjection wells. This is a major problem in the recovery of heat energy in the heat exchangers in a binary cycle electricity producing plant as well as for the general operation (Dubin 1984, Gunnarsson and Arnórsson 2005).

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 particularly problematic as they are the main source of hard, amorphous scale that needs to be removed using considerable mechanical force and effort, or by the use of corrosive hydrogen fluoride or both. Several methods have been investigated to address the issue of silica scale formation. Examples of these are the addition of acid to partially delay the condensation of the dissolved silica species (Dubin 1984, Gunnarsson and Arnórsson 2005), the addition of silica seeds to capture such dissolved silica onto a pre-existing silica material (Sugita et al. 1999, Sugita et al. 2003), the addition of aluminium species, EDTA and other compounds to form silica and silicate species that do not precipitate (Sugita et al. 1999, Gallup 1999). Gill (1998) presents a good overview regarding the problematic issue of silica scale formation and the effect of pH and other ionic species on it. In a parallel development, we and a group from Japan realized that the use of calcium ions (dissolved lime) allowed removal of silica from geothermal brine (Sugita et al. 1999, Sugita et al. 2003, Harper et al. 1992). 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. (1999) 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.

1.2 The CaSil Technology

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, CaSil, 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 CaSil which forms readily, does not polymerize further and does not bind to metal surfaces. Instead the CaSil 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 the essentially zero, depending on the amount of calcium ions used in relation to the dissolved silica species in the water (Borrmann 2009).

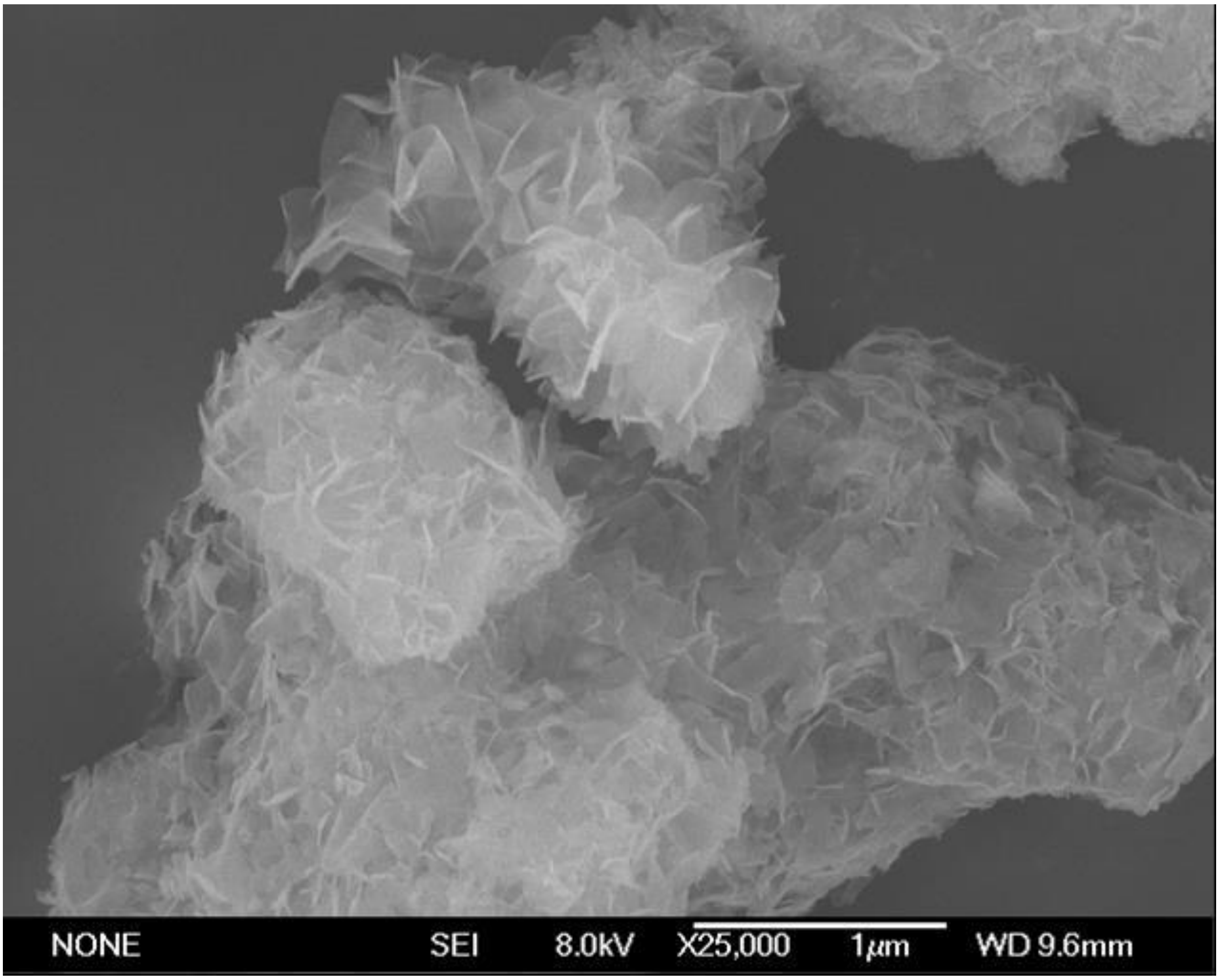

Figure 1: Scanning electron microscope image of nano-structured calcium silicate hydrate (CaSil).

CaSil is distinct from other forms of precipitated silica in that the base unit present is related to the calcium silicate wollastonite CaSiO3 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, CaSil it is not crystalline or has the long-range order prevalent in these other structures. Fundamental silicate units do, however, link together to form the backbone of the CaSil structure and provide an open framework similar to "desert rose", where the calcium ions are accommodated on the surface of the particles (Figure 1). This gives CaSil a slightly positive surface charge and hence the ability to bind other silica, calcite (calcium carbonate) or particulate and ionic species to its surfaces. The positive surface charge also means that CaSil does not form scale on metal surfaces in contrast to silica and calcite trapped in CaSil particles. The particles observable in scanning electron microscope images (Figure 1) are about 1 to 15 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 to millimetres in diameter. This is partially verified by volume weighted particle size measurements, where particles with a diameter of 10 to 50 micron, being agglomerates of about one thousand particles are observable (Borrmann 2009). Although it is possible that the individual 1 to 15 micron CaSil particles could likely be reinjected with the cooled brine, the larger particle agglomerates would probably block pores in the rock formation of an underground geothermal reservoir. Hence, the CaSil 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 calcite are removed from the brine at the same time along with CaSil.

Our laboratory and field results present a further strong argument as to why the CaSil material should be removed from the brine. The surface chemistry of CaSil 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 CaSil 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 CaSil 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 CaSil acts to capture the reactive silica species and hence prevent the formation of the unwanted hard silica scale, if the CaSil 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 CaSil material in the system before removal, is very short. In contrast to several other treatment technologies, CaSil can be removed from the brine thereby irreversibly lowering the risk of silica scale formation.

Through laboratory scale and field trials, we have successfully developed the CaSil geothermal technology and have since constructed a small-scale pilot plant test rig. We have carried out 18 months of field testing on our pilot plant, which is currently being upgraded and automated. In parallel we have carried out laboratory research to further develop our technology and elucidate underlying mechanisms and respond to research questions arising during pilot plant operation, such as the efficient removal of CaSil from geothermal brine. The removal of nano-structured calcium silicate hydrate (CaSil) from geothermal brine is a solid-liquid separation, which is non-trivial due to the high surface area and pore volume of CaSil, low difference in the respective bulk densities of CaSil (1.6 g.cm-3) and water (0.998 g.cm-3), hindered settling behaviour, and the low mass concentration of CaSil in geothermal brine, about 0.1 %wt. This is aggravated by the comparatively high brine flow rates found in geothermal power plants. In our pilot plant test rig we employ a lamella separator to achieve a CaSil removal efficiency above 90 %. Currently the lamella separator is being revised to introduce a new model with an even higher removal efficiency.

Based on previous presentations and publications we have received several questions from researchers, engineers and geothermal power plant operators regarding the following:

- Can our CaSil technology, which has been successfully demonstrated on laboratory, field, and small pilot plant scale, be operated at elevated pressure?
- How does the presence of CaSil influence the chemical composition of steam? Is the carry-over of silica and other species into the steam phase affected? Are there any new species introduced that will affect the steam composition?

2. RESULTS AND DISCUSSION

To start an investigation into the use of our CaSil technology under pressure and to answer the research questions we progressed in three steps. First, we built a model of a lamella separator and operated it under pressures equivalent to those found during pilot plant operations. Then we used autoclave experiments and numerical models to predict the effect of the presence of CaSil on the amount of steam that can be extracted in its presence. Lastly, we studied the chemical composition of steam and the carry-over of species in the absence and presence of CaSil.

2.1 Lamella Separator under Pressure

The pilot plant test rig based on the CaSil technology is located at Wairakei, Taupo, New Zealand, on the site of MB Century and sourcing spent geothermal brine from the Wairakei power plant. The brine stream arriving at the plant is split off from the stream prior to entering the binary plant. It travels about 500 m uphill to a heat exchanger associated with a paint drying shop. Our line is taking part of the brine travelling towards the heat exchanger. As such the incoming brine at our plant has a temperature between 105 and 110 °C and a low pressure of about 0.25 bar (3 to 4 psi) above atmospheric pressure due to being open at one end. Coincidentally the low pressure in the pilot plant matched the range of pressure employed in this laboratory study. We built a model lamella separator out of transparent acrylic plastic, which allowed us to study the flows and turbulences inside the separator using dyes and CaSil particles but limited the pressure to 0.25 to 0.5 bar above atmospheric. Further, acrylic plastic cannot stand elevated temperatures beyond 80 °C. In prior laboratory studies we had already established a temperature related increase in turbulence and thermal currents (Schweig 2018).

A model lamella separator was fitted with needle valves at the slurry outlet (bottom) and the supernatant outlet (top). It was pressurized by pumping liquid/slurry into it from the top left using a peristaltic pump. A pressure release valve and manometer at the top allowed control of a constant pressure throughout the experiments. The separator was operated continuously at an inflow of about

500 to 2000 mL a minute (comparable flow to pilot plant operation based on volume of the separator) for 30 minutes. Samples of the slurry and supernatant were collected at 5-minute intervals and the flows through the separator monitored. No significant differences between the flows under pressure or in the open were noticed. The flows observed matched those already reported (Borrmann 2018). The bottom slurry release valve could be left slightly open allowing a continuous removal of precipitated material without impacting the operational pressure. By comparison the supernatant outlet valve located at the top had a significant impact on the pressure. It could be used to regulate the operational pressure very effectively. Overall a continuous operation was easy to establish and the separator removed CaSil efficiently, achieving comparable removals under pressurized and open conditions. By comparison changes in temperature had a significant impact on separation efficiency lowering them from above 99.4 % at room temperature to about 98.2 % at 90 °C (pilot plant operational temperature).

2.2 Steam

The carry-over of species into steam presents a challenge to geothermal power plant operators and turbine manufacturers. Silica carried along with water droplets in steam can damage turbine blades and therefore a technology minimising the presence of such a species in steam would be interesting to the geothermal industry. The CaSil technology reduces the amount of reactive silica in geothermal brine; maybe the CaSil treatment could be implemented prior to steam production. In the following two chapters preliminary research into the impact of CaSil on the vapour pressure and the chemical composition of steam are presented.

2.2.1 Vapour Pressure

Solutions containing silica at various levels were placed in an autoclave and the vapour pressure measured at increasing temperatures. Similarly, the CaSil treatment was applied to these solutions and the vapour pressures recorded. Due to the small amounts of silica (250 to 1500 ppm) and corresponding levels of CaSil no significant changes in vapour pressure were observed (Figure 2). This is not unexpected as numerical models show that the maximum change in relative vapour pressure expected would be about 0.2 % based on the mol fraction of impurities added (Formula 1).

$$P = (1 - x)P_0$$

where P is the measured pressure, x the mol fraction of impurities, and P_0 the pressure of pure water vapour.

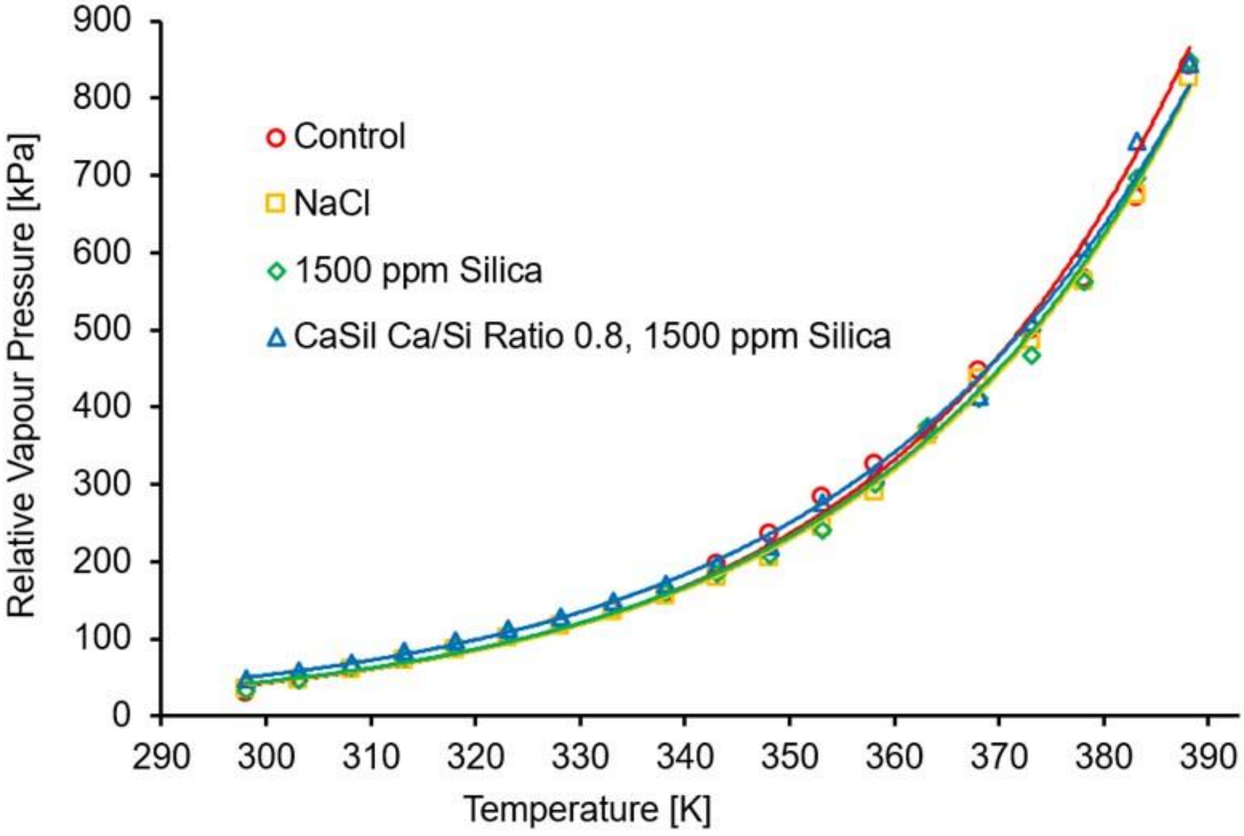

Figure 2: Vapour pressure of distilled water (red), brine containing 4000 ppm NaCl (yellow), brine containing 4000 ppm NaCl and 1500 ppm silica (green), and the silica from the 'green' solution transformed into CaSil (blue).

More of an impact could be expected from the lowering of the geothermal water temperature due to the injection of the treatment agent to form CaSil. However, it could be calculated using Formula 2, that the expected lowering in the brine temperature is about 0.5 °:

$$T_{Final} = \frac{\dot{m}_1 \times c_{p1} \times T_1 + \dot{m}_2 \times c_{p2} \times T_2}{\dot{m}_1 \times c_{p1} + \dot{m}_2 \times c_{p2}}$$

where T are the temperatures, m are the masses, and cp are the heat capacities of the geothermal water (1), treatment agent (2) and combined slurry (Final) respectively.

2.2.2 Chemical Composition of Steam – Carry-Over

Solutions were prepared containing 4500 ppm sodium chloride and 4 ppm arsenic as sodium arsenite. Silica was added as sodium silicate at levels of 250, 500, 750, 1000, 1250 and 1500 ppm approximately. The pH value of the solutions was titrated to pH 7 using hydrochloric acid. The amount of sodium chloride was adjusted to accommodate for the amount of sodium contained in the sodium silicate stock and chloride from the acid used. For the 1000 ppm solution variations titrated solutions to a pH value of 5, 6, 8 and 9 were also produced to investigate the influence of pH on the carry-over. Half of each solution was placed in an autoclave and heated to 180 °C. Then a needle valve at the top of the autoclave was opened to release steam from the autoclave (flashing) until the temperature in the autoclave sank to 120 °C. The source solution and the condensed steam were analysed. The second half of the solutions was treated to form CaSil. Pharmaceutical grade calcium hydroxide was used as purchased from Panreac, Spain. The amount of calcium hydroxide depended on the amount of silica present; generally, calcium hydroxide was added to establish a calcium to silica molar ratio of 0.8. Ratios of 0.4 and 0.6 were also investigated. Part of the resulting slurries was again placed in an autoclave, heated, and flashed. The steam was again condensed and analysed along with the source.

The concentrations of sodium, chloride and arsenic in the starting solutions and slurries were all very similar within 20 ppm for chloride and sodium and within 0.1 ppm for arsenic of the expected values. Likewise, in the steam no significant differences between the various solutions with different silica levels and slurries with different amounts of CaSil present were observed. The errors for the measurements for the various elements contained in steam were comparatively large (up to 20 %) due to the low levels of contaminants present and levels being close to the detection limit of the atomic absorption spectrometer and ion selective electrode. Sodium was found at levels of about 2 ppm, chloride at 0.4 ppm, and arsenic at 4 ppb in all samples studied. Likewise, while the pH value of the starting solutions was set and the CaSil slurries had values of around pH 10 to 10.5, the condensed steam for all samples independent of origin was about pH 8.6 to 8.9. This was thought to be due to the ammonia used in the preparation of the arsenic additive. The additive was present at comparable levels in all samples.

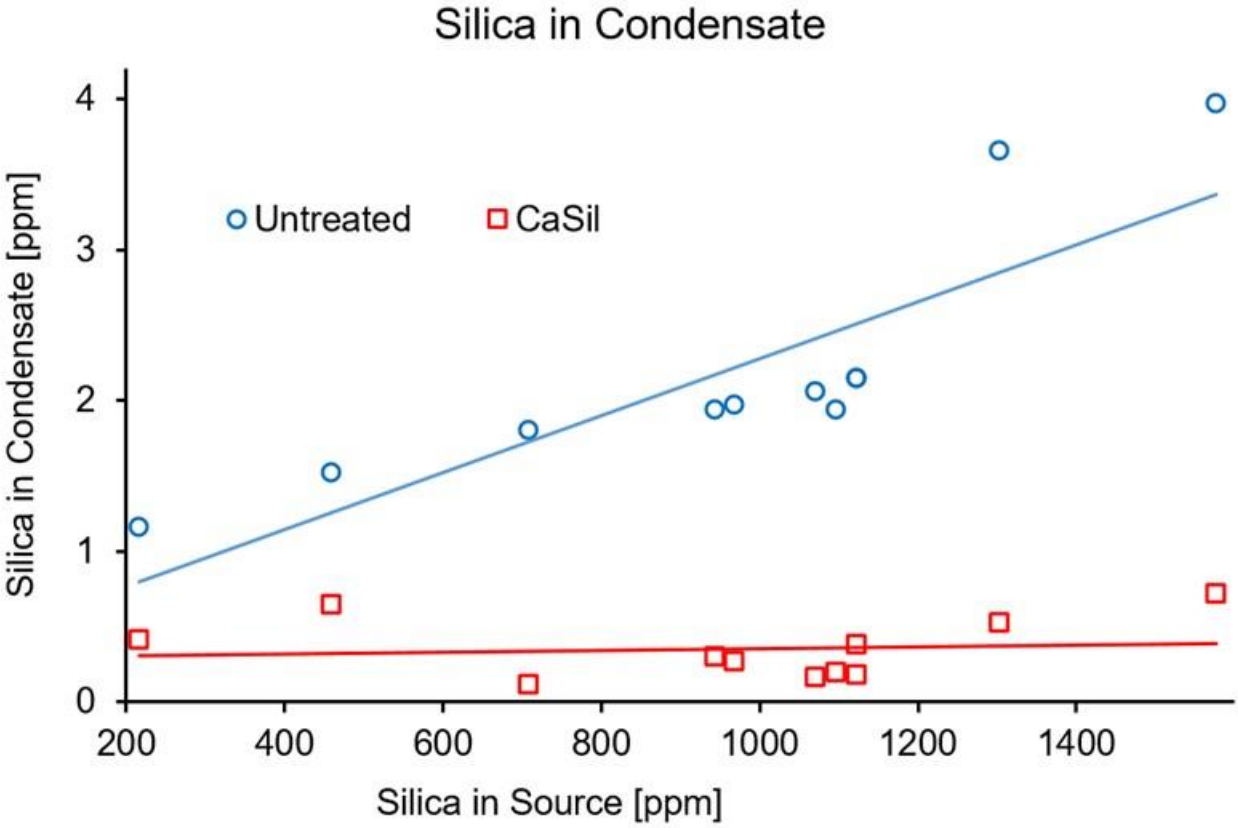

Figure 3: Silica in condensed steam depending on the initial level of silica.

In condensed steam generated from the untreated silica containing solutions the amount of silica carried over increased with the amount of silica present in the starting solution from about 1 ppm silica in condensate at a starting concentration of 216 ppm to 3 ppm silica in condensate at 1577 ppm silica in the starting solution (Figure3, blue circles). Conversely the concentration of silica in the condensate for CaSil appeared to be approximately the same for all samples (within the margin of error). It varied between 0.1 and 0.7 ppm silica in the condensed steam. Due to the very low levels of silica close to the detection limit of the atomic absorption spectrometer results were verified photospectrochemically using the molybdate method (Figure 3, red squares).

The silica concentration in the supernatant of the CaSil slurries was investigated. At 212 ppm silica no drop in the silica level between the untreated and CaSil treated solutions were observed. CaSil appeared to either not form at all or the particles formed were so small that they remained suspended in solution. As mentioned above, CaSil particles need to form agglomerates to precipitate and remove silica from solution. At the low concentration present it is unlikely that any agglomeration would occur and even if CaSil particles were formed they remained dispersed. Such dispersed micrometre sized particles could be injected in the AA or be readily dissolved by the sulphuric acid employed in the molybdate method. At higher concentrations of silica in the starting solutions the supernatants of the CaSil slurries contained about 300 ± 10 ppm of silica, which is below the solubility limit of silica at 120 °C. All CaSil slurries contained very comparable amounts of silica in the supernatant and the carry-over of silica into the condensate was consistently low for all slurries. This indicates that it is the amount of silica in the supernatant rather than the amount of CaSil present, which dictates the level of silica carry-over into the steam. It further indicates that CaSil particles are unlikely to be carried over into the steam. It was mentioned above that the difference in density between water and CaSil is comparatively small (about 1.0 compared to 1.6 g cm 3). This small difference might be enough to affect this steam water distribution. However, further investigations are required to ensure this is the case.

As described by Barassi (2013) CaSil releases calcium from its surface within minutes. A typical experiment took about 55 minutes from preparation of the solutions and slurries, heating, and steam collection. This is plenty of time for calcium to be released into solution. An investigation of the starting CaSil slurries found that up to 100 ppm of calcium was released with a clear trend observable that more calcium is released the more CaSil is present but also showing a plateau at higher levels (Figure 4). This plateau is likely due to the low solubility of calcium hydroxide and follows a trend similar to that observed in the pH values of the starting CaSil slurries.

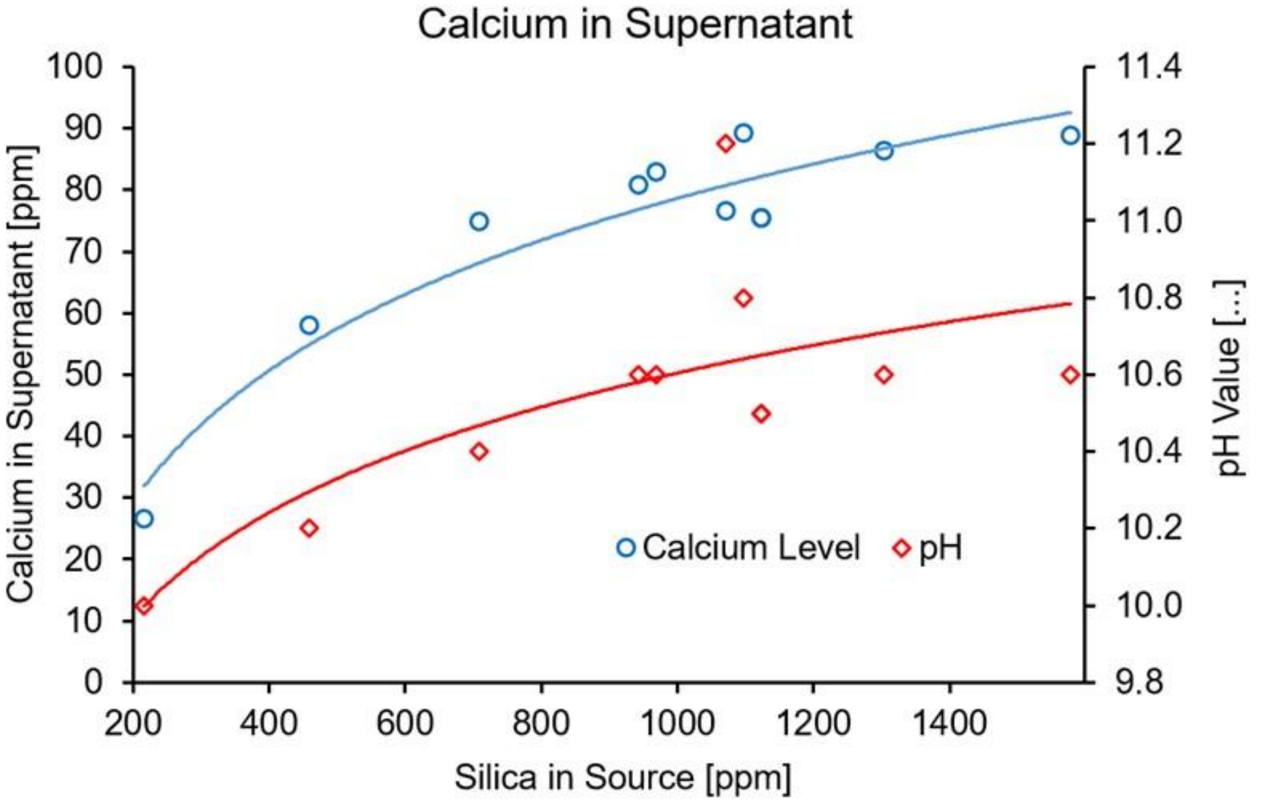

Figure 4: Calcium level and pH value of CaSil slurries at various silica concentrations in the source.

It is possible that some of the calcium present in the supernatant is in the form of calcium hydroxide. It is likely based on past studies (Barassi 2013) that the calcium independent of form is closely associated with the CaSil present and as such is localised. In favour of this theory is an investigation of the carry-over of calcium into the steam. It was found that the more CaSil was present the less calcium was carried over. The trend shown in Figure 5 is inverse to the trends for the pH and calcium levels in the starting CaSil slurries. Whether the lower amount of carry-over is due to association of the calcium with CaSil or due to the larger amount being present in the form of calcium hydroxide due to the slurry pH value will have to be established in future studies.

The presence of any calcium in the condensed steam raises a question towards its chemical nature and towards potential reactions with carbonate/carbon dioxide to form calcite. Experiments were carried out, where sodium carbonate was added to the starting solutions up to levels found at our pilot plant. However, no conclusions regarding the formation of calcite in the steam could be made due to the low levels of calcium carried over.

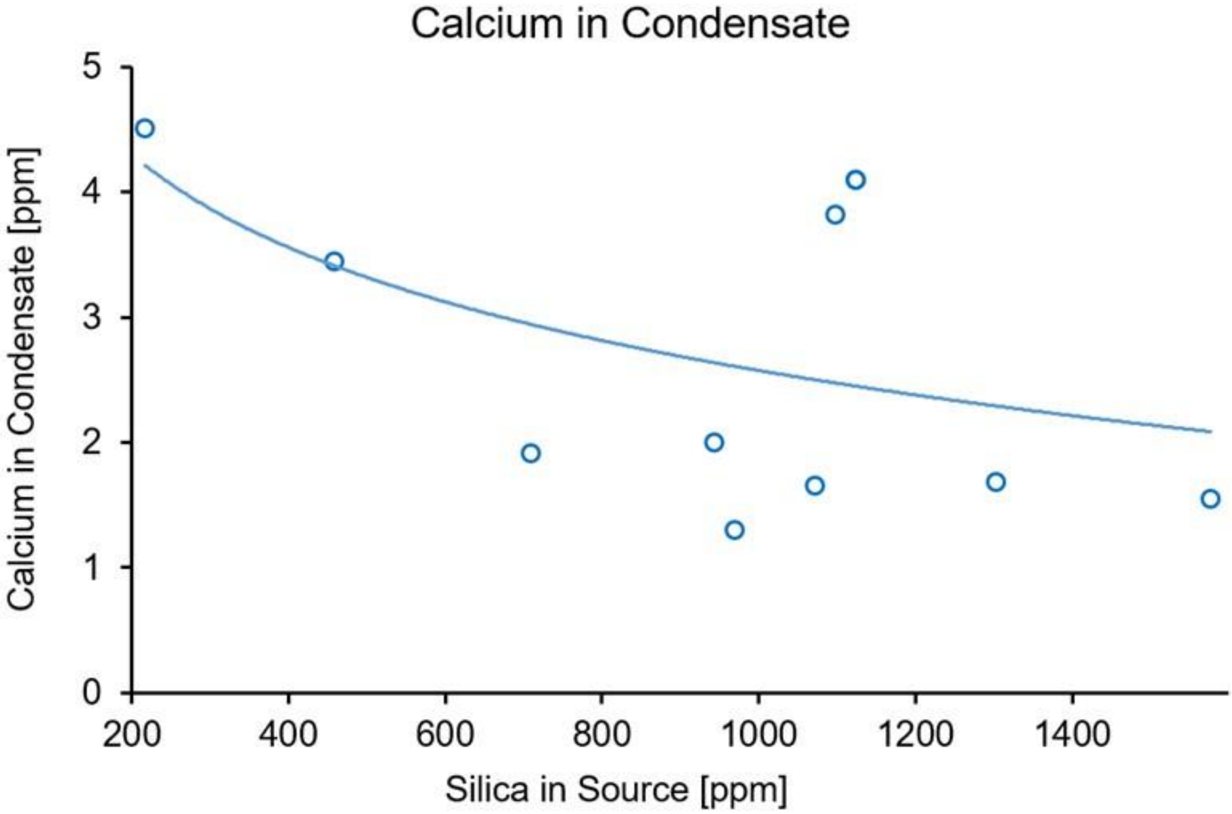

Figure 5: Calcium level in condensate.

3. CONCLUSIONS

The robust calcium silicate hydrate (CaSil) technology transforms silica into a CaSil product thereby preventing the formation of silica scale. Prior experiments had shown that CaSil forms at any temperature below 180 °C and that above 190 °C ceramic like materials were generated (Borrmann 2008). Further investigations were not carried out as part of this study but could be of interest to explore the temperature range at which the CaSil technology can be applied. This study focussed on the impact of pressure, especially on the impact of pressure on the recovery of the CaSil material formed and the flows inside the solid liquid separator. A pressurised solid liquid separator was built and no significant differences between the pressurised and unpressurised version were found in regards to flows and turbulences.

As expected, the CaSil technology had no significant impact on the vapour pressure of the treated silica containing solutions. We investigated the steam and its composition in regards to the elements carried over more closely. Most elements contained in the solution were carried over at comparative levels in the presence and absence of CaSil, namely sodium, chlorine, and arsenic. In case of sodium and chlorine this was expected as it was found in the past that sodium and chlorine do not interact with CaSil (Borrmann 2011). Arsenic is known to react with calcium to form calcium arsenate. However, the reaction is comparatively slow (minute scale) and the level of arsenic in the source solution was low (4 ppm). Consequently, we assume that calcium arsenate was not formed and hence no influence of CaSil on the arsenic carry-over was observed.

The CaSil technology drastically reduces the amount of reactive silica available in solution. As such it drastically reduced the carry-over of silica in the steam. This is good news for plant operators and turbine manufacturers, as silica carry-over can damage turbines due to the formation of hard scale. This is off-set by a new species introduced by the CaSil technology – calcium. Calcium carry-over was found for all samples, but it appeared to be inversely linked to the amount of CaSil present. This could indicate that most in solution calcium is closely associated and bound to CaSil. The more CaSil is present, the less calcium is free and can be carried over. This would have to be validated in further research, as the level of calcium was very close to the detection limit of the analysis method (atomic absorption) used. Furthermore, the question has to be posed, if the presence of carbonate would have an impact on the carry-over and the nature of species carried over. This will have to be investigated in further studies.

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