INTEGRATION OF THE CALCIUM SILICATE (CASIL) TECHNOLOGY INTO GEOTHERMAL POWER GENERATION TO PREVENT SILICA DEPOSITION

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ABSTRACT

Silica supersaturation in geothermal brine results in the formation of intractable silica scale deposits in pipes, heat exchangers and reinjection wells. This scale prevents the full effective utilisation of geothermal resources for electricity generation and heat recovery applications. It is a major problem worldwide. Also, process equipment and reinjection wells can be blocked, which necessitate costly maintenance and plant downtime. Current approaches attempt to address the problem by using higher steam/water separation temperatures to reduce silica saturation, acid dosing or additives to retard silica polymerisation. However, the use of these is not wholly satisfactory; silica still precipitates and electricity generation and heat recovery remain compromised.

We have developed our proprietary new nanostructured calcium silicate, CaSil, technology to address the problem and are demonstrating it in an automated pilot scale operation at Wairakei. We remove the problematic dissolved silica as a novel CaSil material. This lowers the silica saturation index (SSI) substantially below 1. The technology is applicable to a range of brine compositions, temperature and pressure conditions. The technology opens up opportunities for further mineral extraction (e.g. lithium, base metals). Additionally, more heat energy can be safely extracted from the brine without causing silica scaling during electricity generation or industrial direct use applications. Because of its unique surface chemistry the CaSil material does not stick to metal pipes, significantly reducing maintenance costs for process equipment and reinjection wells, and plant downtime.

The CaSil material is a useful product that has a range of industrial and environmental remediation applications. These applications utilise the unique 3D framework structure of CaSil, which provide it with high liquid absorbent and surface area properties. By careful control of the calcium silicate chemistry and some post-separation treatment, new CaSil materials are generated with properties suitable for high volume applications in the building, paper, paint, absorbent, mining and environmental remediation industries.

1. BACKGROUND

Geothermal energy is an attractive natural, renewable energy resource, as it can provide large quantities of heat and base load electrical energy continuously and also on demand. Hot geothermal water is piped 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 before being discharged or re-injected back to the geothermal reservoir. All methods of energy extraction lower the temperature of the geothermal brine leading to the supersaturation of silica which are dissolved in the subsurface hot geothermal waters as a result of rock-water interactions. Flashing at the surface removes a portion of the fluid in the form of steam, thereby further concentrating the supersaturated dissolved silica species in the brine. The supersaturation can be somewhat mitigated by the addition of condensed steam to the brine from the steam turbine. Re-injecting the spent geothermal water and condensed steam into a geothermal reservoir replenishes the reservoir and subsequently increases the lifetime of the geothermal resource, prevents subsidence and positions geothermal energy as a benign and renewable energy resource (Dubin 1984, Gunnarsson and Arnórsson 2005).

1.1 Silica Scale Formation

In liquid dominated geothermal systems, which occur most commonly in nature, the water (brine) sourced from the subsurface geothermal reservoir is typically heated to about 200 – 300 ^{o}C and largely maintained in the liquid phase due to the overlying hydrostatic pressure. This superheated brine dissolves the rock forming silicate minerals and other species in the reservoir formations, contributing them to the brine. Here, the dissolved silica is present largely as the $H_3SiO_4^-$ ion and some H_4SiO_4 species (Borrmann et. al. 2009; Gunnarsson and Arnórsson 2003; Chan 1989). Na^+, Cl^-, HCO_3^-, SO_4^{2-} ions, together with much lower concentrations of other alkali, alkaline earth, transition metals, arsenic, boron, halides and ammonia species can be present in the superheated brine. Following the piping of this geothermal brine through production wells to the surface, the brine undergoes a steam/water flash process where the pressure is lowered to slightly above atmospheric. The brine necessarily cools to about 120-130 $^{\circ}$C depending on the pressure at which the flash process is operated which is typically about 2-3 bar. This rapid reduction in brine temperature and the consequent further concentration of dissolved species in the brine due to the production of steam in the flash process, means the concentrations of dissolved silica species are now significantly above their equilibrium temperature-dependent solubility concentrations. These species polymerize to progressively form colloidal size silica particles which aggregate and precipitate out forming an intractable amorphous silica sinter deposit on metal and other surfaces (Equation 1). Depending upon the temperature, pH and dissolved silica concentration of the separated geothermal brine, there can be a short induction period of up to a few minutes before the silica polymerization process begins to any extent (Chan 1989, Borrmann et. al. 2010). Reducing the pH increases the induction time, but the low pH required to facilitate a significant increase in the induction time can cause severe corrosion of pipework.

$$H_3SiO_4^- \rightarrow SiO_2 + OH^- + H_2O \qquad (1)$$

This progressive polymerization and precipitation of dissolved silica as an intractable silica sinter in the brine leads to the major silica deposition problem, which manifests itself in geothermal resource utilization worldwide. The problem has not been satisfactorily addressed.

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 initial stage of polymerisation of the dissolved silica species (Brown and McDowell 1983, 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) to form larger particulates, the addition of aluminium species, EDTA and other compounds to form silica and silicate species that do not precipitate as readily (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). In our earlier work, Harper et al. (1992) focused on precipitating the dissolved silica as a random network structure of colloidal size silica particles for use as a filler in newsprint to enhance print and optical properties. This was developed and implemented at pilot scale silica product production stage at the Kawerau geothermal field with full scale newsprint manufacturing trials at Tasman Pulp and Paper Co Ltd, Kawerau. 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 Preventing Silica Scaling by the CaSil Technology

In our new approach, rather than trying to slow down the silica precipitation or keep the dissolved silica species in solution, we capture the dissolved silica species as a proprietary nanostructured calcium silicate (CaSil) material by the controlled reaction between added Ca^{2+} and the $H_3SiO_4^-$ species (Johnston et. al. 2004, 2006, Borrmann et. al. 2009, 2017), before silica polymerization and precipitation can take place. The reaction between the Ca^{2+} and $H_3SiO_4^-$ species and the nanostructured calcium silicate hydrate forms faster than the polymerization of silica. The simplified chemical reaction is:

$$H_3SiO_4^- + Ca^{2+} + OH^- \rightarrow CaSiO_{3-x}(OH)_{2x} \bullet yH_2O \qquad (2)$$

The CaSil formation reaction is controlled chemically to produce fine CaSil particles of about 1 – 5 µm in size (Figure 1), that remain in suspension and do not form an intractable sinter deposit as silica does. Some agglomeration of the particles to yield clusters of 10 to 100 µm in size is encouraged and used to facilitate their recovery from the brine.

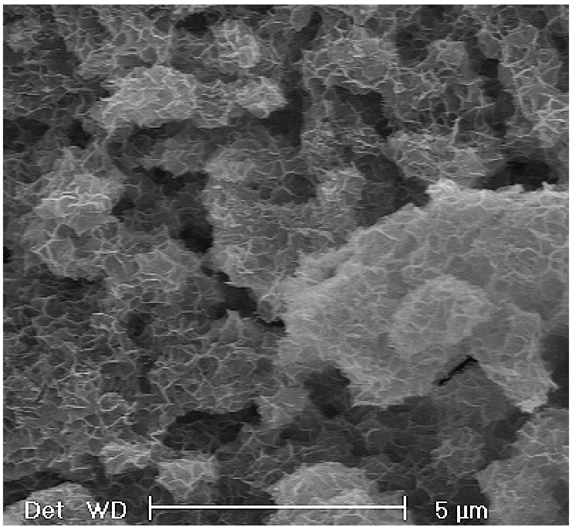

Figure 1: Scanning electron microscope image of nano-structured calcium silicate (CaSil).

The particles move freely with the brine flow through the pipework and heat exchangers without adhering to or depositing on the surfaces of the pipework. Importantly as discussed below, this enables lower binary cycle heat exchanger exit temperatures to be used, thereby, enabling more electricity to be generated. The CaSil particles are separated continuously as a concentrated slurry (Johnston et. al. 2014, 2017, Schweig et. al. 2018) to provide useful products that have a range of industrial applications (Johnston et. al. 2004, 2006, 2017, 2018; Borrmann et. al. 2009, 2010, 2017; Cairns et. al. 2006, 2013, 2018).

Formation of CaSil entails a change of the pH of the brine to more basic values. This together with the removal of dissolved silica reduces the silica saturation index (SSI) to much less than 1 (see below). As a result, following the recovery of the CaSil particles the residual brine can now be reinjected into the subsurface strata without causing blocking of the reinjection wells or compromising subsurface strata permeability. The separation process for removing the CaSil particles continuously from the brine flow is currently being developed and optimised by us (Borrmann et. al. 2017, 2018, 2019; Schweig et. al. 2018) in a pilot plant operated on site at MB Century using brine from the Wairakei field, Taupo Volcanic Zone, New Zealand. Depending upon the particular industry application being sought, the concentrated slurry of CaSil particles may be used directly without further processing, which is the simplest approach. If required, the separated slurry can be further processed into a moist filter cake or the filter cake can be dried to produce a friable cake or powder.

Co-formation of calcium carbonate (calcite) can be an issue if the HCO_3^- concentration of the brine is sufficiently high. We have encountered this on occasions. Very fine calcite particles can be precipitated along with and become incorporated into the CaSil particles (Borrmann et al. 2017). Consequently, the CaSil and calcite particles form together and can be separated continuously as the above concentrated slurry, leaving a particulate free water with no propensity to deposit silica or calcite which could block reinjection wells. This has the advantage of removing the fine calcite particles before they can aggregate and build up a calcite sinter deposit.

Overall, the maintenance costs in the utilization of a geothermal resource for heat recovery and silica deposition are substantially reduced by the CaSil technology.

A typical geothermal field can yield several thousand tons of CaSil products annually. To take advantage of this, large volume applications and uses for the CaSil material are being progressed.

As well as providing the opportunity to recover more heat energy from the brine, our technology opens up opportunities for other dissolved species, notably lithium, other metals and boron to be recovered from the brine flow by separation technologies, such as those that utilize membranes or ultrafiltration, which would otherwise be compromised by silica deposition and membrane fouling.

2. CaSil Proof-of-Concept and Pilot Plants and Looking at Applications of CaSil

To demonstrate the technology in a continuous process using hot, pressurized geothermal water, a proof-of-concept plant was planned, tested and commissioned in 2017 on site at MB Century, Taupo, New Zealand, sourcing geothermal water from the nearby Wairakei Geothermal Power Plant. The initial small-scale system featured most key unit-operations of this technology, only lacking a heat exchanger. This system had a nominal design flow rate of 10 L/min, but it was mostly operated between 10-15 L/min, which was made possible by large safety factors built into the process equipment. The comparatively low flow rate allowed easy handling of all components and represented the first proof of concept of the technology in a real-world geothermal environment, demonstrating the robustness and simplicity of the technology.

2.1 Silica Saturation Index

The chemical transformation of dissolved silica into colloidal calcium silicate decreases the silica saturation index (SSI) of the geothermal water. Enough dissolved silica is transformed in the reaction to lower the silica concentration well below the saturation level after flashing. This means that more heat energy can be extracted from the brine without risking silica precipitation and scaling. An example to illustrate and quantify this advantage, is the binary electricity generation of the Wairakei Power Plant in New Zealand. The brine flow through the binary plant is about 2800 t/h with an inlet temperature of 127 °C and discharge temperature of 87 °C, generating 14 MW electric power. The average silica concentration in the geothermal water is about 525 ppm. This means the SSI of the brine is about 1 on entering the heat exchangers (HEX) and 1.6 on exit from the heat exchangers. The HEX has to be cleaned approximately every six months due to silica deposition and drop in performance (Thain and Carey 2009, Zarrouk et al. 2014).

With the CaSil-technology, about 350 ppm of silica is left unreacted in the brine after treatment at a pH value of about 10 to 10.5. The reduction in silica concentration alone would result in an SSI of less than 0.7 once the brine enters the Wairakei binary HEX. However, the increased pH also increases the solubility of silica in the brine. Formulas to estimate the pH adjusted silica solubility were taken from Brown (2011). The values presented are based on a pH of 10. Due to the shift in pH the SSI of the incoming brine at 127 °C decreases from 0.7 to 0.04. If the same HEX exit temperature of 87 °C is chosen, an SSI of 0.1 at the exit would be the consequence. No silica depositions would form in the HEX and hence semi-annual cleaning can be avoided, saving maintenance cost and reducing system downtime. At exit temperatures as low as 60 °C, an SSI of only 0.3 would occur, enabling the binary plant to desirably generate 9.5 MW more electrical power, assuming a constant efficiency. This equals a 68 % increase in energy production from the binary plant without the need to change working fluids or the binary plant technology employed. In fact, a fluid temperature of 30 °C would have to be established in order to increase the SSI above 1 and thus initiate silica scaling. This makes the geothermal fluid very simple to handle and silica scaling virtually impossible – even at low temperatures.

2.2 Pilot Plant

In order to incorporate a heat exchanger into the geothermal CaSil system at our pilot plant at Wairakei, we acquired a shell and tube heat exchanger. A thorough redesign process has enabled the maximum throughput of the system to be extended from 10 L/min to 30 L/min, as well as automating key unit operations and components in order to now realize a fully operational small-scale pilot plant. A pipework matrix with two 32 m long pipelines, one for the treated brine and one as an untreated control line has been added. The plant is using a programmable logic controller (PLC) for data collection and control of automated valves, pumps and motors. Figure 2 shows a photo of the pilot plant in operation. The performance of the heat exchanger is monitored in situ, via measurements of the pressure loss, transferred heat energy and rate of flow. Potential depositions in pipes, the plenum or on the tube sheets are being monitored and quantified periodically during downtimes. Current evidence shows that the HEX operates as intended.

As in the proof-of-concept plant, the pilot plant uses a proprietary design lamella separator to recover CaSil from the brine which is followed by gravity filtration. Large scale applications will use an automated filter system. Currently we produce a CaSil filter cake of about 20 to 25% solids, compared to 3% for the proof-of-concept plant.

Figure 2: New pilot plant in operation including shell and tube and one double pipe HEX.

We are operating the pilot plant for 8 hours a day, 6-10 days a month. CaSil filter cake that is produced is being used in our applications development.

2.3 Applications of CaSil

Applications that utilize the properties of CaSil, which we are progressing with various industries, include:

• Environmental remediation of surface waters. CaSil can be used to recover dissolved phosphate from polluted surface and lake water. A study by us has shown the phosphate content of an inland lake can be reduced from the ambient problematic level of 0.35 mg kg-1 down to 0.05 mg kg-1 (Cairns et. al. 2013).

• The recovery of base and heavy metals from waste mining and metallurgical industrial processing streams. We have demonstrated the removal of a range of dissolved metal ions from a simulated waste stream typical of those present in mining and ore processing operations. This showed that 100 % of Cu^{2+} and $Fe^{2+/3+}$ and 97 % of Zn^{2+} could be readily removed by using CaSil. Lesser amounts of 37 % for Ni^{2+} and 20 % for Mn^{2+} could be similarly removed. (Borrmann et al. 2011).

• The use of the material as a filler in paper to reduce print through and enhance print quality. This takes advantage of the high liquid absorbency of the CaSil material to absorb and localize the printing ink. Significant reductions in print-through and improvements in print quality and image color have been demonstrated by us in laboratory scale work (Johnston et. al. 2004, Mesic and Johnston 2013). Pilot scale trials with an international paper company are being carried out.

• As a functional filler in rubber.

• As a functional filler in cement and concrete to in cement-based building products.

• Fire retardancy. The non-flammability of the CaSil as well as its OH and absorbed water content, make it useful as a fire-retardant filler when incorporated into building materials. It can readily be incorporated into plastics.

3. Summary

Overall, our novel nanostructured calcium silicate technology has the potential to successfully address and obviate the world-wide problem of silica deposition from the separated brine in the utilisation of a geothermal resource for electricity generation. Collectively it offers distinct advantages and new business opportunities in both the energy and materials sectors. For the energy sector it these include:

• The removal of the propensity for problematic silica to precipitate and form an intractable sinter scale which blocks pipes, heat exchangers and reinjection wells.

• A consequent reduction in the operational and maintenance costs relating to the removal of the silica scale from pipes, valves and heat exchangers, the replacement of equipment and the cleaning out or drilling new reinjection wells.

• The opportunity to reduce the steam/water separation temperature to provide a greater quantity of steam to the turbine and enhance the amount of electricity generated here.

• The opportunity to increase the temperature differential across the binary plant heat exchanger by lowering the exit temperature to values significantly below those currently used, thereby enabling the generation of significantly more electricity.

The applications for the CaSil products which utilise the proprietary unique structural, physical and chemical properties and characteristics.

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