Eliminating the Problematic Deposition of Silica from Separated Geothermal Brine and Enhancing Geothermal Energy Utilisation Through a Novel Nanostructured Calcium Silicate Technology: An Overview

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ABSTRACT
The polymerisation and precipitation of silica from separated geothermal brine supersaturated in dissolved silica resulting in the formation of intractable silica sinter deposits in pipes, heat exchangers and reinjection wells is a major problem in geothermal resource utilisation worldwide. This sinter compromises the heat energy recoverable for binary cycle electricity generation, blocks reinjection wells and increases maintenance costs. Current approaches attempt to address the problem by using higher steam/water separation temperatures to reduce silica saturation, acid dosing and additives to retard silica polymerisation. However, these are not wholly satisfactory, silica still precipitates and the problem remains.

We have developed a new technology and are demonstrating it at pilot scale operation, whereby we rapidly react the supersaturated dissolved silica entities in the brine with calcium ions under controlled conditions to form a novel nanostructured calcium silicate hydrate (CaSil) material, before the silica entities can polymerise and deposit the problematic sinter scale. The technology is applicable to any brine temperature and pressure conditions, and the residual level of dissolved silica entities in the brine is controlled by the relevant chemistry rather than by temperature dependent solubility. Hence, sufficient dissolved silica can be removed to just prevent silica sinter formation, or essentially all of it can be removed to facilitate the recovery of other dissolved mineral species such as lithium and base metals by selective membrane or adsorbent methodologies.

A key feature is that the CaSil particle surface morphology and chemistry are distinctly different from those of problematic silica particles and as such the CaSil particles do not accrete or deposit on metal surfaces or reinjection wells, thereby eliminating silica sinter formation. This attribute enables lower steam/water separation temperatures and lower exit temperatures in binary plant heat exchangers to be used. In turn more heat energy can be extracted from a geothermal resource. There is no further propensity for silica to deposit in pipework, heat exchangers, or in reinjection wells. The CaSil particles are recovered continuously as a useful product that has a range of industrial and environmental remediation applications.

The CaSil material has a unique 3D framework structure, providing it with high liquid absorbent and surface area properties. By careful control of the calcium silicate chemistry and hence the properties of the material, the technology generates CaSil products which have high volume use applications in the building, paper, paint, polymer, absorbent, mining and environmental remediation industries.

The CaSil technology therefore provides the attractive opportunities to potentially:
- eliminate the current worldwide problem of silica deposition from geothermal brine and sinter formation in geothermal resource utilisation;
- enhance the utilisable heat energy and hence electricity generated;
- enable reinjection of the geothermal brine from which silica precipitation cannot occur;
- reduce maintenance costs;
- provide useful CaSil products and generate additional revenue.

This paper presents an overview of the technology, the different components, its implementation at pilot scale operation and the nature and uses of the CaSil products. New business opportunities are also presented and discussed.

1. INTRODUCTION
Geothermal energy is an important renewable base-load resource for electricity generation in countries which have such resources that can be utilised. With the worldwide move away from fossil-fuelled thermal electricity generation to increased generation from sustainable and renewable resources, there is a significant driving force and interest in the exploration and development of new geothermal resources for electricity generation. Geothermal energy resources are very diverse and complex in nature, with essentially each having its own unique characteristics that need to be accommodated for successful utilisation of heat recovery and electricity generation. These characteristics include the enthalpy and chemistry of the steam and separated geothermal brine (water) phases, which are used for electricity generation through steam turbine and binary cycle technologies respectively.

In water dominated geothermal systems, which occur most commonly in nature, the hot water (brine) contained in the subsurface geothermal reservoir is typically heated to about 200 – 300 °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, forming a brine. The dissolution of silica occurs essentially according to the quartz/water temperature solubility relationship, to provide dissolved silica at saturation levels at the respective reservoir brine temperature. Here, the dissolved silica is present largely
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as the $\text{H}_3\text{SiO}_4^-$ ion and some $\text{H}_4\text{SiO}_5$ species (Borrmann et al. 2009; Gunnarsson and Arnórsson 2003; Chan 1989). $\text{Na}^+$, $\text{Ct}^+$, $\text{HCO}_3^-$, $\text{SO}_4^{2-}$ ions, together with much lower concentrations of other alkali, alkaline earth, transition metal, 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 °C depending on the pressure at which the flash process is operated. 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 polymerise to progressively form colloidal size silica particles which aggregate and precipitate out as an intractable amorphous silica sinter deposit on metal and other surfaces, according to the simplified reaction below. 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 polymerisation process begins to occur (Chan 1989, Borrmann et. al. 2010). Reducing the pH increases the induction time but an acid environment results in corrosion of pipework.

$$\text{H}_3\text{SiO}_4^- \rightarrow \text{SiO}_2 + \text{OH}^- + \text{H}_2\text{O}$$

This progressive polymerisation 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 utilisation worldwide. The problem has not been satisfactorily addressed.

Current approaches to address the silica deposition problem include operating the steam/water flash process at a higher temperature than ideally desired in order to maintain a high separated brine temperature of about 130 °C (or possibly greater), in an effort to approach the silica saturation index and hence reduce the extent of silica supersaturation and the propensity for further initiating and continuing silica deposition. Unfortunately, this also reduces the amount of steam produced in the flash process and the amount of electricity generated from the steam phase is reduced accordingly. Furthermore, any subsequent reduction in temperature of the separated brine such as necessarily occurs across a binary cycle heat exchanger, readily facilitates additional silica deposition inside the heat exchanger tubes. This build up of silica scale compromises the efficiency of heat transfer across the heat exchange surfaces, impedes brine flow and consequently reduces the amount of heat energy that can be exchanged to the binary cycle working fluid accordingly. The amount of electricity generated by the binary cycle technology is consequently reduced. This necessitates regular shut downs and cleaning of the intractable silica deposits from the heat exchanger surfaces. It involves mechanical cleaning and chemical cleaning using hydrofluoric acid, with ensuing environmental and corrosion issues. The silica also progressively precipitates in reinjection wells and the local geologic substructure, which over time, compromises the brine reinjection process and can lead to the need to ream out the well, or drill a new well. Another approach is to retard the silica polymerization process by reducing the pH of the water to about pH=6 or lower, to increase the length of time for the induction period that precedes silica polymerisation and deposition. The purpose here is try and delay the silica precipitation or at least reduce the extent of it, during the time that the brine takes to travel through the pipework, heat exchangers and down the reinjection well. In practice this does not work effectively. Also, the low pH causes corrosion of the steel pipework which is problematic. Collectively the unwanted silica deposition impacts negatively on the operational efficiency and cost of the geothermal heat energy recovery and electricity production processes, together with compromising the amount of heat energy that can be recovered and hence electricity produced.

2. PREVENTING SILICA SCALING BY THE NANOSTRUCTURED CALCIUM SILICATE HYDRATE TECHNOLOGY (CASIL)

We have approached this silica deposition problem differently. Rather than trying to slow down the silica precipitation or keep the dissolved silica species in solution at these thermodynamically unfavourable supersaturation levels, we capture the dissolved silica species as a proprietary nanostructured calcium silicate hydrate (CaSil) material by the controlled reaction between added $\text{Ca}^{2+}$ and the $\text{H}_3\text{SiO}_4^-$ species under alkaline conditions (Johnston et. al. 2004, 2006, Borrmann et. al. 2009, 2017), before silica polymerisation and precipitation can take place. The reaction between the $\text{Ca}^{2+}$ and $\text{H}_3\text{SiO}_4^-$ species is very rapid and the nanostructured calcium silicate hydrate forms much faster than the polymerization of silica can occur. The simplified chemical reaction is:

$$\text{H}_3\text{SiO}_4^- + \text{Ca}^{2+} + \text{OH}^- \rightarrow \text{CaSiO}_3\cdot(\text{OH})_2\cdot\text{yH}_2\text{O}$$

This rapid reaction to form CaSil particles effectively prevents unwanted silica polymerisation from taking place. 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 aggregate or form an intractable deposit as silica does.

The chemical nature of the surface of the CaSil particles means they do not polymerise further, but desirably remain as fine particles suspended in the brine. They move freely with the brine flow through the pipework and heat exchangers without adhering to or depositing on the surfaces of the pipework. 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 then flocculated and separated continuously as a concentrated slurry (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). In the form of CaSil there is no propensity for silica to polymerise and precipitate from the residual brine, which can now be reinjected into the subsurface strata without causing blocking of the reinjection wells or compromising subsurface strata permeability, as silica deposition does. The separation process for removing the CaSil particles continuously from the brine flow is currently being addressed by us (Borrmann et. al. 2017, 2018, 2019; Schweig et. al. 2018). 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 that can be readily dispersed later into an aqueous medium or product formulation, or dried to produce a friable filter cake or powder.

Co-formation of calcium carbonate (calcite) can be an issue if the $\text{HCO}_3^-$ 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. Consequently the CaSil and calcite particles form together and can be separated continuously as a 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.

The CaSil technology provides the attractive opportunity whereby the residual level of dissolved silica in the brine can be reduced to just below the silica saturation index to prevent silica precipitation and sinter formation, or down to much lower levels to facilitate effective removal of all the dissolved silica in the treated brine. The extent of silica removal and the residual level of dissolved silica in the brine is controlled by the Ca:Si ratio and the reaction conditions. As well as providing the opportunity to recover more heat energy from the brine, this latter feature 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 utilise membranes or ultrafiltration, which would otherwise be compromised by silica deposition and membrane fouling.

The maintenance costs in the utilisation of a geothermal resource for heat recovery and silica deposition are substantially reduced by the CaSil technology. Depending on the dissolved silica content and the Ca:Si ratio used in the precipitation of CaSil, a typical geothermal field can yield several thousand tons per year of CaSil products. Hence the requirement to find large volume applications and uses for the material, which is being progressed.

3. THE OPPORTUNITY TO RECOVER MORE HEAT ENERGY AND GENERATE MORE ELECTRICITY
The implementation of our nanostructured calcium silicate hydrate technology which facilitates the controlled removal of the problematic dissolved silica species and prevents silica polymerisation and deposition in pipework and heat exchangers, desirably removes the temperature constraints on the operation of a binary cycle plant heat exchanger. Current practice requires the temperature differential across the heat exchanger and the exit temperature to be maintained at values whereby the silica saturation index is not exceeded and the extent of silica precipitation and sinter formation is minimized. Even so, silica deposition still occurs and the extent of the heat recovered and electricity generated is compromised. In the CaSil technology, the residual level of dissolved silica species is controlled chemically by the Ca:Si ratio and not by temperature. The CaSil ratio can be chosen to effect the removal of dissolved silica to a much lower level than the silica saturation index. Therefore, with the CaSil technology it is now possible to increase the temperature differential across a binary cycle heat exchanger significantly and to lower the exit temperature much further e.g. down to 50 °C, or much closer to that of the secondary working fluid, which is largely determined by the thermodynamic efficiency of the binary cycle process.

The CaSil technology also provides the opportunity to reconsider the operating temperature for the steam/water flash process. It may be desirable to reduce this closer to 100 °C with the consequent flash pressure being closer to atmospheric. The actual choice of the most appropriate steam/water flash and separation temperature and hence the amount and temperature of steam supplying the steam turbines, together with the temperature of the brine flow to the binary cycle heat exchanger and the exchanger exit temperature can be controlled and optimized by the CaSil technology. Hence the amount of electricity generated from the resource, can be optimized through such modelling without the constraint of silica deposition and sinter formation. This opens up the opportunity to consider and model the complete geothermal steam and brine system to obtain the best overall thermodynamic efficiencies and the maximum electricity generated, without the constraint imposed by silica deposition.

4. THE NANOSTRUCTURED CALCIUM SILICATE HYDRATE MATERIAL
The nanostructured calcium silicate hydrate material comprises nano-size platelets stacked together in a unique open framework structure forming discrete particles of about 1-5 μm in size, which may also agglomerate to form larger flocs. (Figure 1). This agglomeration can be enhanced using chemical flocculants to effect separation of the CaSil particles from the treated brine flow.

Figure 1: Scanning electronmicroscope images of nanostructured calcium silicate hydrate material showing the nanosize (thick) platelets stacked together in an open framework structure.

The CaSil material typically has a surface area of up to about 100-300 m² g⁻¹ depending on the precipitation conditions. The stacking arrangement of the platelets gives it a high pore volume and hence a high liquid absorbency of up to about 100-300 g oil 100 g⁻¹. The CaSil currently being produced from the Wairakei geothermal field, New Zealand, has a surface area of about 200 m² g⁻¹ and an oil absorption of about 250 g oil 100 g⁻¹. The material has a good whiteness as long as the levels of other dissolved species such as iron in the geothermal brine are low enough not to absorb on the surfaces of the platelets, or form hydroxides that could compromise this

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white colour. The high whiteness and high liquid absorption capacity enables the CaSil material to be used in paper filling and paper coating to improve ink holdout and print quality of the paper (Johnston et. al 2004, 2006, Mesic 2013).

The negative surface charge on the CaSil particles means the material can consequently attract and bind positively charged metal cations. This enables it to be used to recover base metal ions e.g. Cu²⁺, Zn²⁺ etc. from industrial or mine waste streams.

Also, the surface Ca²⁺ species can readily bond with phosphate anions which facilitates its use in recovering dissolved phosphate entities from effluent streams and surface water run-off (Cairns et. al. 2006, 2013, 2018) to facilitate environmental remediation.

When dried and depending upon the precipitation conditions, the CaSil can have a bulk density as low as about 0.2 g cm⁻³ and a low thermal conductivity of about 0.03 W m⁻¹ K⁻¹ which is comparable to that of expanded polystyrene 0.03-0.04 W m⁻¹ K⁻¹. These properties make it useful as a naturally sourced, sustainable, non-flammable insulation material.

5. PILOT SCALE DEVELOPMENT OF THE NANOSTRUCTURED CALCIUM SILICATE TECHNOLOGY

We are continuing to develop and demonstrate our nanostructured calcium silicate hydrate technology at pilot plant scale operation, which is located at a MB Century Ltd site, Wairakei geothermal field, New Zealand. The plant has enabled us to successfully scale up the technology and demonstrate it at a meaningful scale to the New Zealand geothermal industry. It has also enabled us to produce sufficiently large quantities of the CaSil material to facilitate our industry applications development work (Bormann et. al. 2017, 2018, 2019; Schweig et. al. 2018; Johnston et. al. 2017, 2018; Cairns et. al. 2006, 2013, 2018). The initially designed and commissioned pilot plant was manually operated. The geothermal brine feed was sourced from the pipeline supplying the Ormat binary plant and as such provided a suitable brine flow for us to demonstrate the technology in a meaningful way. However, during extended continuous operation it became obvious that the geothermal water supply varied in flow rate and chemical composition, depending upon the configuration of individual production wells and flash plants that made up the brine flow to the binary plant in order to provide a constant enthalpy feed. We had no influence or control over this. The manual operation of the pilot plant meant that it was not possible to continuously control the chemical conditions necessary to produce a particular CaSil product with a consistent composition and characteristics. Hence, we are now automating the operation and control of the pilot plant using a PLC system together with the appropriate sensing and measurement systems and control valves.

The overall intention is to make the pilot plant skid mounted and transportable to other neighbouring geothermal sites with different field enthalpies, geochemical features and water compositions, for a similar testing and evaluation regime in due course. The information we are collecting and analyzing will be used to inform and develop the design for a world first commercial scale plant.

6. APPLICATIONS OF GEOTHERMAL NANOSTRUCTURED CALCIUM SILICATE HYDRATE

Applications that utilise the properties of nanostructured calcium silicate hydrate detailed above, which we are progressing with various industries, include:

- “Green slow release phosphate fertilizers”. The CaSil material readily takes up and can accommodate up to about 17 wt% PO₄³⁻ within the silicate particle structure (Southam et. al. 2004; Cairns et. al. 2013, 2018), which amounts to some 28 wt% Ca(PO₄)₂ and compares favourably with fertilizer compositions sourced from natural rock phosphate resources. This facilitates the environmentally attractive opportunity to recover and recycle phosphate from farming and metropolitan effluent streams and treatment ponds as a regenerated “green phosphate fertilizer” for agriculture and horticulture applications.

- Environmental remediation of surface waters. In a similar way 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 Cu²⁺ and Fe²⁺⁺⁺⁺ and 97 % of Zn²⁺ could be readily removed by using CaSil. Lesser amounts of 37 % for Ni²⁺ and 20 % for Mn²⁺ could be similarly removed. (Cairns et. al. 2006).

- 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 absorptivity of the CaSil material to absorb and localize the printing ink. Significant reductions in print-through and improvements in print quality and image colour have been demonstrated by us in laboratory scale work (Johnston et. al. 2004, Mesic 2013). Pilot scale trials with a paper company are being carried out. The whiteness of the CaSil is important here.

- The use as a functional filler in cement and concrete to develop a lightweight cement-based building product. This utilises the open pore structure of the material. A similar effect is possible for gypsum based wall board.

- The passive moisture control in building environments. Here, the high water absorptivity property of CaSil due to its open pore structure, enables it to be used as a passive moisture control agent for moderating the humidity changes of a closed or semi-closed environment. This has the propensity to maintain the desired level of humidity and also to reduce mould growth in humid environments (Johnston et. al. 2006).

- 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.

7. SUMMARY OF OPPORTUNITIES OFFERED BY THE NANOSTRUCTURED CALCIUM SILICATE HYDRATE TECHNOLOGY AND PRODUCTS

Overall, our novel nanostructured calcium silicate hydrate technology has the potential to successfully address and obviate the worldwide 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. These are summarized below:
7.1 Energy Sector
- 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 additional electricity.

7.2 Materials Applications and Environmental Remediation Sectors
- The production of a nanostructured calcium silicate material which has unique structural, physical and chemical characteristics that facilitate its application in a range of industry and consumer products. These include:
  - The recovery and capture of environmentally problematic phosphate species from surface waters and effluent streams and ponds to provide a “green phosphate fertilizer” which recycles phosphate.
  - The recovery of base and heavy metals from waste mining, metallurgical processing and industrial processing streams.
  - The paper industry to enhance the print and optical properties of paper.
  - Lightweight cement-based materials.
  - Passive moisture control materials.
  - Fire-retardant materials.

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