ELIMINATION OF THE PROBLEMATIC DEPOSITION OF SILICA FROM SEPARATED GEOTHERMAL BRINE

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ABSTRACT

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

We are turning this problem into an attractive operational and business opportunity though the development and demonstration of a new technology that captures the dissolved silica species as a novel nanostructured calcium silicate material, thereby reducing the silica level below that from which silica can precipitate and the sinter forms.

The nanostructured calcium silicate material has a unique 3D framework structure, providing it with high liquid absorbent and surface area properties. The particle surface is different from that of silica and desirably the calcium silicate particles do not deposit on metal surfaces, thus eliminating silica sinter formation. It has the potential to enable lower steam/water separation temperatures and lower exit temperatures in binary plant heat exchangers to be used, thereby enabling more heat energy to be recovered from a geothermal resource. There is no further propensity for silica to deposit in process equipment or in reinjection wells.

We control the calcium silicate chemistry and composition, and hence its properties, to provide products which have multiple potential applications in the building, paper, paint, polymer, absorbent, mining and environmental remediation industries. We have progressed the development to pilot scale operation at a New Zealand geothermal field and are evaluating commercial opportunities for the calcium silicate products. An overview of the technology and product applications is presented here.

1. THE SILICA DEPOSITION PROBLEM

Geothermal energy offers an attractive renewable resource for base-load electricity generation. It is not dependent on sunshine hours or wind velocity as are solar and wind renewable electricity generation systems.

The water in the subsurface geothermal reservoir is typically heated to about 200-330 °C and is generally maintained in the single liquid phase due to the pressure of the overlying several kilometres of rock. This superheated water is essentially a slightly alkaline dilute brine. It contains dissolved silica from partial dissolution of the reservoir rocks up to the silica saturation level at the particular elevated temperature, according to the temperature dependent quartz solubility diagram, This silica is present mainly as the $H_3SiO_4^-$ ion but some fully associated H_4SiO_4 is also present. (Borrmann et al. 2009, Gunnarsson and Arnórsson 2003, Chan 1989). Following cooling in the steam/water flashing stage there is a further increase in the dissolved silica concentration due to removing about one third of the mass flow as the steam phase. The temperature of this separated geothermal water stream is typically about 120-130 °C depending on the flash pressure, and represents a significant source of lower grade thermal energy. Some of this heat energy is captured in the heat exchangers of the downstream binary cycle plants and converted to electrical energy by this technology. The binary cycle heat exchange exit temperatures are about 100 °C. However at these cooler temperatures the silica which is now present at supersaturation levels in the separated water, polymerizes and precipitates out according to the temperature dependent solubility of amorphous silica, as an intractable silica sinter deposit. A separated water flow can typically contain supersaturated levels of dissolved silica of about 500-900 mg kg^{-1} SiO_2. At a separated water temperature of about 120-130 °C following the steam/water flash, the silica saturation solubility level is much less at about 350-500 mg kg^{-1} SiO_2. Hence this supersaturated silica content in the water necessarily polymerises and forms colloidal size silica particles which aggregate and precipitate out according to the simplified reaction below. Depending upon the separated geothermal water temperature, pH and dissolved silica concentration, there can be a short induction period of up to a few minutes before the silica polymerisation process begins (Chan 1989, Borrmann et al. 2010).

$$H_3SiO_4^- \rightarrow SiO_2 + OH^- + H_2O$$

This silica precipitation progressively builds up on the surface of pipes, valves, heat exchangers, drains and reinjection wells as a hard intractable silica sinter deposit. It is a major problem in geothermal resource utilisation that limits energy recovery and generates high maintenance and operating costs (Gunnarsson and Arnórsson 2003).

Current approaches to address this silica deposition problem include operating the steam/water flash at a higher temperature than ideally desired in order to keep a high separated brine temperature of 130 °C or greater, thereby reducing the extent of silica supersaturation and the propensity for initiating and continuing silica deposition. Unfortunately this also reduces the amount of steam produced in the flash and hence the amount of electricity generated from the steam phase. Another approach is to retard the 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, which is a precursor to silica polymerisation and deposition. However the low pH can cause corrosion of the steel pipework. Furthermore, the subsequent reduction in temperature of the separated water across the binary cycle heat exchanger, readily facilitates additional silica deposition inside the heat exchanger tubes. This compromises the efficiency of heat transfer across the heat exchange surfaces and reduces the amount of heat energy that can be exchanged to the binary cycle working fluid, hence the amount of electricity generated by the binary cycle technology. This necessitates regular shut downs and cleaning of the intractable silica deposits from the heat exchanger surfaces. The silica also progressively precipitates in reinjection wells and the local geologic substructure, which over time compromises the reinjection process and can lead to the need to ream out the well, or to drill a new well.

2. REMOVAL OF DISSOLVED SUPERSATURATED SILICA BY RAPID PRECIPITATION OF CALCIUM SILICATE

We have innovatively turned this problem into an opportunity for both the geothermal industry and at the same time providing a useful product to industrial companies concerned with paper, plastics, building and environmental remediation activities. We achieve this by capturing the dissolved silica species as a nanostructured calcium silicate material in a controlled reaction between added Ca^{2+} and the $H_3SiO_4^-$ species under particular alkaline conditions (Johnston et al 2006, Borrmann et al 2009, 2017), before silica polymerisation and precipitation can take place. The reaction is very rapid and the nanostructured calcium silicate forms essentially immediately, hence the problem of silica deposition is removed. The nanostructured calcium silicate particles remain in suspension and do not form an intractable sinter deposit as silica itself does. The simplified chemical reaction is:

$$H_3SiO_4^- + Ca^{2+} + OH^- \rightarrow CaSiO_{3-x}(OH)_{2x} . H_2O$$

Following formation, the fine particles of the nanostructured calcium silicate flow cleanly through the downstream pipes and heat exchangers carrying the geothermal water. No silica formation or deposition takes place. This enables a larger temperature differential to be maintained across the binary plant heat exchangers and hence more heat energy can be recovered and more electricity generated from the separated water flow.

After the particles flow through the binary cycle heat exchangers they are separated continuously as a concentrated slurry, using a lamellar separator that we are developing (Borrmann et al. 2017).

It is also worth noting that as we can control the extent of silica removal (Borrmann et al 2009), it is possible to remove only the amount of dissolved silica down to or marginally above the silica saturation level at the particular temperature concerned, in order to prevent silica deposition and sinter formation and leave the residual dissolved silica below supersaturation level in the water. This would be the case if the objective was to only prevent silica deposition.

However, if there is interest in recovering other components from the separated water, notably lithium or base metals etc., silica deposition can interfere with the respective recovery processes. For this we are able to adjust the chemistry to essentially remove all the dissolved silica species down to a level of a few mg kg^{-1} SiO_2 (Borrmann et al. 2009, Borrmann et al 2010, Johnston et al 2006).

3. CHARACTERISTICS OF THE NANOSTRUCTURED CALCIUM SILICATE

The nanostructured calcium silicate material comprises nanosize platelets stacked together in a unique 3D open framework structure forming discrete particles of about 1-5 µm in size (Figure 1). The material has a surface area of up to about 100-300 m^2 g^{-1} depending on the precipitation conditions. The unique stacking arrangement also gives it a high pore volume and hence a high liquid absorbency of up to about 200-300 g oil 100 g^{-1} silicate, which means it can absorb some 2-3 times its weight of a liquid whilst remaining as a solid.

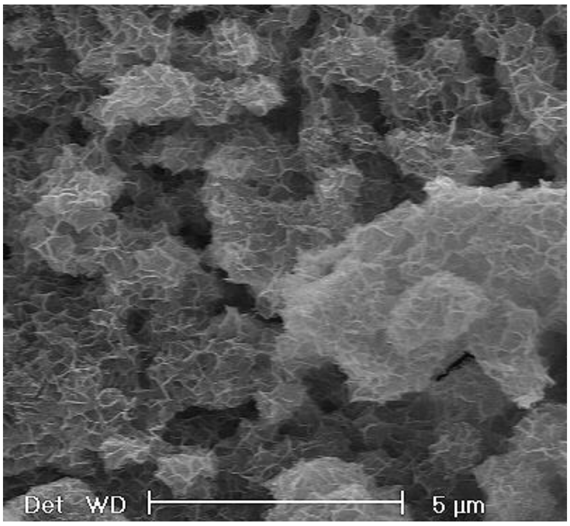

Figure 1: A scanning electronmicroscope image of a typical nanostructured calcium silicate material showing the open framework of randomly stacked nanosize platelets.

The material has a good whiteness as long as the levels of other dissolved species in the geothermal water such as iron, are low. The negative surface charge on the particles means the material can consequently attract positively charged metal cations. This enables the material to be used to recover base metals e.g. Cu^{2+} and Zn^{2+} etc. from waste mining and industrial streams. Also the Ca^{2+} ions on the surface of the platelets can readily react with phosphate anions to form a calcium phosphate species within the framework structure. We have utilised this reaction and property to recover phosphate from surface waters in environmental remediation applications.

When dried and depending upon the precipitation conditions, the nanostructured calcium silicate solid can have a bulk density as low as about 0.2 g cm^{-3} which makes it useful for insulation applications. It also has inherent fire retardant properties due to the hydroxyl groups and water of hydration in the structure. These properties are particularly relevant for the building industry.

4. PILOT SCALE DEVELOPMENT OF THE NANOSTRUCTURED CALCIUM SILICATE TECHNOLOGY

We have successfully developed and demonstrated our nanostructured calcium silicate technology on a laboratory scale in both a batch and a continuous process using sodium silicate as a model source of the dissolved silica, and also using geothermal water from the Kawerau, Ohaaki and Wairakei geothermal fields.

Following this, we have designed, constructed, commissioned and are operating a pilot plant facility which is located at a MB Century Ltd site in Wairakei, New Zealand. The purpose of the pilot plant is to optimise and demonstrate the technology in a continuous manner, on a meaningful scale. The plant is operating successfully as designed. It is also being used to produce sufficiently large quantities of the nanostructured calcium silicate material under different operating conditions, with different properties for larger scale testing in various applications. The robustness of the technology in regard to it being able to accommodate the variations in the temperature, flow rate and composition of the geothermal water feed stream is being evaluated. So far we are very pleased with it. The plant is portable and will be relocated to other geothermal sites for a similar testing and evaluation regime in due course. The overall information we are collecting and analyzing will be used to inform and develop the design for a world first commercial scale plant..

5. INDUSTRIAL APPLICATIONS OF NANOSTRUCTURED CALCIUM SILICATE

The industrial applications we are pursuing for the nanostructured calcium silicate product take advantage of the unique structural, chemical and physical properties of the material, with a view to providing the end user with a competitive advantage in their particular product by incorporating the silicate into it. The applications we have identified and are progressing include:

- The use as a functional filler in cement and concrete to produce a lightweight cement-based building product.
- The use as a filler in paper to reduce print through and enhance print quality. This takes advantage of the high liquid absorbency of the nanostructured calcium silicate material when it is added as a filler to paper to absorb and prevent the spread (wicking) of printing ink (Johnston et al. 2004, Mesic and Johnston, 2017). Also it can be added as a component to a coating formulation to provide a sharper image and localize the ink thereby enhancing ink holdout and colour definition. These attributes are desirable in high quality printing and communication papers.
- The recovery of base and heavy metals from waste mining and metallurgical industrial processing streams. In a laboratory study we have shown that Cu^{2+}, $Fe^{2+/3+}$ and Zn^{2+} can be readily removed and lesser amounts of Ni^{2+} and Mn^{2+} can be similarly removed from a simulated mining waste stream (Cairns et al 2006). In the case of Cu^{2+} in an oxidised sulfur or sulfate environment common in copper processing, the mineral brochantite $Cu_4(OH)_6SO_4$ is formed.
- The uptake of phosphate from solution. Here the nanostructured calcium silicate readily takes up PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ species from solution depending upon the pH, to form calcium phosphate in the brushite phase within the silicate particles. (Southam et al 2004. Cairns et al 2013). The accumulation of phosphate in rivers and lakes due to run off from farm land where calcium phosphate is used as a fertilizer, is becoming an increasing problem in agriculturally based countries. Recent work by us has shown that nanostructured calcium silicate can be used to recover such dissolved phosphate from lakes and reduce the phosphate content from the ambient problematic level of 0.35 mg kg^{-1} down to 0.05 mg kg^{-1} (Cairns et al 2013). The resulting calcium phosphate loaded silicate can then be recovered and re-used as a fertilizer.
- Passive moisture control. The high water absorbency property of nanostructured calcium silicate 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.
- Fire retardancy. The non-flammability of the nanostructured calcium silicate as well as its OH^- and absorbed water content, make it useful as a fire retardant filler when incorporated into building materials. The silicate undergoes about a 30 % weight loss on heating as a result of water release which makes the it potentially useful for this application.
- As a filler in rubber tyres to potentially reduce rolling resistance.

Overall these applications are diverse and wide ranging. Currently we are pursuing those that are most suited to the particular characteristics of the nanostructured calcium silicate material that we are able to produce from NZ geothermal separated water streams.

6. NEW OPPORTUNITIES

This novel nanostructured calcium silicate technology which addresses and obviates the world-wide problem of silica deposition from the separated water in the utilisation of a geothermal resource for electricity generation, offers distinct advantages and new business opportunities in both the energy and materials sectors. In order for the technology to be implemented successfully on a commercial scale both these sectors must be addressed concurrently and the respective operations fully integrated. For the energy sector the opportunities and advantages are:

- 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, the replacement of equipment and the cleaning out or re-drilling new reinjection wells.
- The opportunity to reduce the steam/water separation temperature to provide a greater quantity of steam to the turbine and hence 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 much below that currently used, hence enabling the generation of additional electricity.

For the industry sector the potential applications and associated opportunities for the nanostructured calcium silicate products are detailed above.

In conclusion, our novel nanostructured calcium silicate technology provides a new approach to preventing silica deposition from separated geothermal water in the utilisation of the resource for electricity production. At the same time it provides a useful material for a range of industrial applications. Collectively they open up new business opportunities. Interest and investment is currently being sought.

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