NANOSTRUCTURED CALCIUM SILICATE HYDRATE – A POTENTIAL SOLUTION TO PROBLEMATIC SILICA DEPOSITION FROM GEOTHERMAL BRINE AND A USEFUL PRODUCT

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ABSTRACT

The deposition of amorphous silica as an intractable sinter on the surfaces of pipework, valves and heat exchangers and in reinjection wells, from separated geothermal brine supersaturated in dissolved silica, is a major problem in geothermal energy utilisation. It limits the amount of energy that can be recovered from the steam and especially the brine. Current approaches to alleviate the problem are not fully successful. The dissolved silica also represents a potentially useful material resource.

We have turned this problem into an opportunity through the controlled formation of a novel nanostructured calcium silicate hydrate material from geothermal brine. We utilise the rapid reaction of the dissolved silica species with calcium cations under particular conditions to precipitate the nanostructured calcium silicate hydrate. Our technology allows the silica solubility to be controlled by the chemistry and not by the temperature as silica precipitation is. There is no further propensity for silica to precipitate and form the intractable sinter deposits. The nanostructured calcium silicate hydrate is separated from the brine leaving a low silica-containing water which is amenable for reinjection. Lower steam-water flash temperatures and lower binary plant heat exchanger exit temperatures can be used, enabling more heat and electrical energy to be recovered.

Nanostructured calcium silicate hydrate has excellent whiteness, chemical reactivity, adsorbent and absorbent properties. Potential large volume applications are being explored. They include its use as a functional filler in tyres, plastics, paper, concrete, thermal insulation and fire retardancy; in the recovery of dissolved phosphate from waterways and lakes, and base metals from mine waters; and as a general absorbent and soil conditioning agent.

We are developing the technology at a pilot scale operation in New Zealand geothermal fields, and are optimising the product characteristics for these uses. We are seeking expressions of interest as we move the technology to commercialisation.

1. GEOTHERMAL BRINE AND PROBLEMATIC SILICA PRECIPITATION

Geothermal energy is an important resource of renewable energy. These are typically located at plate boundaries where the hot magma is nearer the surface. The water in the subsurface geothermal reservoir is typicaly heated to about 200-300 °C, and is maintained largely in the liquid phase due to the pressure of the overlying several kilometres of rock. In high enthalpy resources the water temperature can be up to about 350 °C. This superheated water is generally present as a slightly alkaline dilute brine due to the dissolved sea salts, mainly sodium chloride, that are carried down the subduction zone with the plate movement. The water also contains a cocktail of other dissolved species, most notably silica. At these elevated reservoir temperatures the silicate minerals in the reservoir rock dissolve in the superheated water approximating the quartz-water solubility curve, to the respective silica saturation level. Here the dissolved silica is present in the superheated brine mainly as the $H_3SiO_4^-$ ion due to the alkaline pH (Borrmann et al. 2009, Gunnarsson and Arnórsson 2003, Chan 1989). In geothermal energy utilisation this silica-saturated sub-surface superheated geothermal brine is piped to the surface and the pressure is reduced to about 1.4-2.7 kPa, whereby about 30% of the mass flow is flashed into steam which drives a turbine to generate electricity. The remaining 70% of the brine containing the dissolved silica, consequently cools to about 110-130 °C under this slightly elevated pressure. The level of dissolved silica in the brine increases further due to this concentration effect and is now supersaturated. It then flows through the heat exchangers of a binary cycle turbine to extract further heat energy and generate additional electricity. The cooler water is then usually reinjected back into the reservoir to recharge it.

This separated water typically contains levels of dissolved silica of about 600-900 mg kg^{-1} SiO_2. However at about 120-130 °C the silica saturation level is only about 350-500 mg kg^{-1} SiO_2 and hence on cooling, this water becomes further supersaturated in silica, which polymerises and precipitates out as an amorphous silica deposit 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, heat exchangers, drains and reinjection wells as a hard intractable silica sinter deposit. It is a major problem in geothermal resource utilisation, which limits energy recovery and generates high maintenance and operating costs (Gunnarsson and Arnórsson 2003). If this elevated temperature geothermal water is flashed at atmospheric pressure and whereby the temperature of the separated water is 100 °C, the silica supersaturation level is higher and the rate and extent of silica precipitation is greater. Similarly, if further heat energy is recovered from the separated geothermal water following the flash process for binary cycle electricity generation, the water is cooled further to about 80 °C whereupon unwanted silica precipitation takes place in the tubes of the shell and tube heat exchangers used in this process. This steadilly compromises the heat transfer and water flow to such an extent that frequent shutdowns and cleaning are required. Again, this is an undesired maintenance cost.

Current approaches to address this silica deposition problem include operating the steam/water flash process at a higher temperature than ideally desired in order to keep a high separated geothermal water temperature of 130 ^oC or greater, thereby reducing the extent of silica supersaturation and the propensity for initiating and continuing silica deposition. This undesirably reduces the amount of steam produced in the flash and hence the amount of eletricity generated. Another approach is to reduce the pH of the brine to about pH=6 or lower, to increase the length of time in the induction period which is a precursor to silica polymerisation and deposition. The low pH can adversely affect steel pipework. As mentioned above, further temperature drops across the binary cycle heat exchangers exacerbate the problem as they increase the silica supersaturation further and readily facilitate unwanted silica deposition. Overall, these approaches for controlling or reducing silica deposition are not wholly successful and it still remains as a major impediment to geothermal energy recovery and utilisation worldwide (Gunnarsson and Arnórsson 2003).

Overall the cooling of the supersaturated silica-containing separated water through the steam/water flash process or binary cycle heat exchanger is still problematic and a major issue in geothermal resource utilisation worldwide which has not been satisfactorily addressed. It still exists. A new paradigm approach is therefore needed to address it in a continuous and sustainable way. Here we provide such an approach through our proprietary nanostructured calcium silicate technology.

2. A NOVEL SOLUTION TO SILICA DEPOSITION THROUGH NANOSTRUCTURED CALCIUM SILICATE

An attractive opportunity exists to successfully address this silica deposition problem by removing the dissolved silica species as a potentially useful nanostructured calcium silicate hydrate material, by the controlled reaction between a flow of Ca^{2+} ions injected into the separated geothermal water stream which react with the $H_3SiO_4^-$ species under alkaline conditions (Johnston et al 2006). The reaction is very rapid and the nanostructured calcium silicate hydrate forms very quickly. The presence of the HCO_3^- ion in the brine can also co-precipitate calcium carbonate along with the silicate which uses up some of the added Ca^{2+}. As the HCO_3^- ions are in much lower concentrations than the $H_3SiO_4^-$ species, this may not present an issue of any real significance. A desirable outcome is that this nanostructured calcium silicate hydrate does not form an intractable sinter deposit as silica does, and can be recovered as a potentially useful product. The simplified chemical reaction is:

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

The extent of silica removal is now controlled chemically rather than thermally. If the main object is to prevent silica deposition then the level of $H_3SiO_4^-$ species in the supersaturated brine only needs to be reduced to that of saturation or slightly below, as the driving force for precipitation is dependent on the extent of supersaturation. If a larger amount of nanostructured calcium silicate hydrate is to be recovered for a particular end use, then a proportionally larger amount of the precipitating reagents can be used. It is also possible to remove the dissolved silica level in the geothermal brine down to a level of a few mg kg^{-1} SiO_2 to facilitate the subsequent recovery of other dissolved species such as lithium. In any event, this controlled deposition of the dissolved silica or $H_3SiO_4^-$ species as a nanostructured calcium silicate hydrate material, completely obviates any silica deposition and the associated unwanted consequences (Borrmann et al. 2009, Borrmann et al 2010, Johnston et al 2006).

The injection of the Ca^{2+} ions should take place after the steam-water flash separation process under conditions of effective mixing in order to remove the dissolved silica as nanostructured calcium silicate particles, before the resulting separated water flows through the geothermal pipework, binary cycle plant heat exchangers and to the reinjection wells.

The nanostructured calcium silicate hydrate material then needs to be separated from the geothermal water flow in an effective and continuous manner by a conventional settling process, followed by continuous filtration or centrifuging technologies, depending on the particular end use applications. This poses significant challenges due to the high total flow volumes of the brine from all the wells in an operational geothermal resource being used for electricity generation. Parallel banks of such separation equipment are likely to be needed. This separation challenge is currently being addressed by us (Borrmann et al. 2017). Depending on the dissolved silica content and the calcium / silica ratio used in the precipitation of nanostructured calcium silicate hydrate, a typical geothermal field can yield several thousand tonnes per year of nanostructured calcium silicate hydrate product. Hence it is necessary to find large scale applications and uses for the material.

3. THE NATURE OF THE NANOSTRUCTURED CALCIUM SILICATE MATERIAL

The nanostructured calcium silicate hydrtae 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). The material typically has a surface area of up to about 100-300 m^2 g^{-1} depending on the precipitation conditions. The stacking arrangement also gives it a high pore volume and hence a high liquid absorbency of up to about 100-300 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 water are low enough not to adsorb on the surfaces of the platelets, or form hydroxides that could compromise this white colour. The negative surface charge on the particles means the material can consequently attract positively charged metal cations. Also the surface Ca^{2+} species can readily bond with phosphate anions. These physical and chemical attributes provide the basis for a number of industial uses of this novel material. When dried and depending upon the precipitation conditions, it can have a bulk density as low as about 0.2 g cm^{-3} and hence 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 an insulation material.

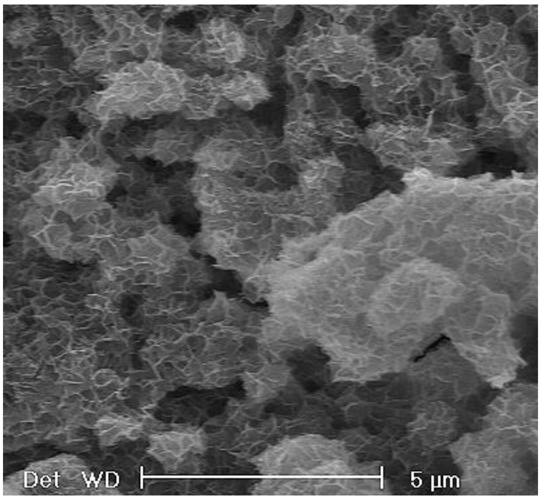

Figure 1: A scanning electronmicroscope image of a typical nanostructured calcium silicate material.

We have successfully developed the technology and nanostructured calcium silicate hydrate material on a laboratory scale using geothermal brine and a model synthetic sodium silicate brine as the sources of dissolved silica. We have constructed, installed, commissioned and are operating a pilot plant facility at a MB Century Ltd site in Wairakei, New Zealand, to optimise and demonstrate the technology on a meaningful scale, as well as producing sufficiently large quantities of the nanostructured calcium silicate hydrate material with different properties, for testing in various industrial applications.

4. APPLICATIONS OF NANOSTRUCTURED CALCIUM SILICATE

The nanostructured calcium silicate hydrate is an interesting material which offers a range of potential applications that take advantage of its particular properties notably; a large surface area, high liquid absorption, low buk density, fire retardancy, whiteness, surface adsorption of cations, reaction of surface Ca^{2+} ions with phosphate ions, and general absorbent properties. Some examples are provided here. As the successful adoption and implementation of the technology will produce large quantitiies of the nanostructured calcium silicate hydrate material, it is important to identify and pursue similarly large volume applications. The applications we have identified include:

Building industry – thermal insulation and fire retardancy: The low bulk density and low thermal conductivity make it ideally suitable for a light weight insulation material in the building industry. Also, 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 in building and similar materials. Thermogravimetric analysis has shown that the silicate undergoes about a 30 % weight loss on heating as a result of water release. This is very significant. Hence it is able to perform two important functions, thermal insulation and fire retardancy in building industry products.

The use as a functional filler in cement and concrete to enhance the performance properties of the concrete.

As a filler in paper to reduce print through and enhance print and optical qualities of the paper: When the material is added as a filler to paper, the high oil absorbency property is effective in absorbing and preventing the spread (wicking) of printing ink. Laboratory scale testing has shown that for 55 gsm newsprint, the addition of about 2.5 wt % of nanostructured calcium silicate to the paper sheet reduced print through by about 40 %. For 45 gsm newsprint the reduction was about 53 %. The material significantly out performed calcined clay, kaolin and calcium carbonate, which are typically used for this purpose (Johnston et al. 2004).

The recovery of base and heavy metals from waste mining streams: This application utilises the effective ability of nanostructured calcium silicate to capture metal cations on the negatively charged surface of the platelets. This has been demonstrated in a study of 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. Lesser amounts of 37 % for Ni^{2+} and 20 % for Mn^{2+} could be similarly removed. Typically, such a waste stream would flow through packed beds containing the nanostructured calcium silicate hydrate, or sacks of it immersed in the stream to facilitate the adsorption process. The resulting metal ion containing silicate material can then be dissolved in a very small quantity of acid to provide a highly concentrated solution of these metal ions which can in turn be recycled back to the metal winning process (Cairns et al 2006). In the case of Cu^{2+} ions in an aqueous oxidised sulfur or sulfate environment common in copper ore processing, the mineral brochantite $Cu_4(OH)_6SO_4$ is formed.

The uptake of phosphate from solution: Here the nanostructured calcium silicate hydrate material 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. Up to 17 wt% PO_4^{3-} can be accommodated within the silicate particle structure (Southam et al 2004. Cairns et al 2013) which amounts to some 28 wt% $Ca_3(PO_4)_2$. This level of phosphate is only slightly below that of a phosphate fertilizer. 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 hydrate can be used to recover such dissolved phosphate from lakes and reduce the phosphate content from the ambient level of 0.35 mg kg^{-1} down to 0.05 mg kg^{-1} as shown in Figure 2 (Cairns et al 2013). The resulting calcium phosphate loaded silicate can then be recovered and re-used as a fertilizer. This recycling of phosphate provides an opportunity to reduce the undesirable environmental load of unwanted dissolved phosphate in rivers and lakes and at the same time to reduce the reliance on mined calcium phosphate ore as a fertilizer.

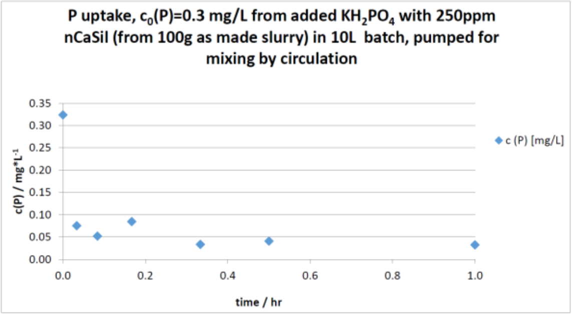

Figure 2: The uptake of problematic phosphate species by nanostructured calcium silicate from a polluted lake.

Passive moisture control: The high water absorbency property of nanostructured calcium silicate hydrate 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. At higher humidities the silicate absorbs water vapour from the air and releases it back into the air when the humidity decreases. Similarly, it can be used as a soil moisture control agent to enable the soil to hold more moisture in damp conditions and to release it to plants as the soil dries out. Here it is important to ensure the product does not contain any undesirable elements such as As and Sb from the geothermal water, to avoid contaminating the soil.

As a filler in rubber tyres: Preliminary work has shown that nanostructured calcium silicate can be added to a rubber mix used in tyres, whereby the resulting rubber shows evidence of reduced rolling resisitance.

Photoactive composites: Composites of nanostructured calcium silicate hydrate with photoactive titanium dioxide particles formed directly within the silicate particles, have been prepared and their use in the photochemical degradation of model organic compounds demonstrated accordingly (Johnston and Small, 2011).

These various applications are being pursued by us with the view to identifing those that are most suited to the particular characteristics of the nanostructured calcium silicate hydrate material that we are able to produce from NZ geothermal brine.

5. CONCLUSION

The production of a novel nanostructured calcium silicate hydrate material from separated geothermal water provides an atttractive approach to obviating the world wide problem of silica deposition from separated geothermal brine as an intractable sinter, which blocks pipes, valves, heat exchangers and reinjection wells. The silicate material does not agglomerate or adhere to metal surfaces and can be removed from the water stream as a potentially useful product which has a number of desirable properties for a range of industry applications. Furthermore, the removal of problematic dissolved silica from the separated geothermal water will enable more heat energy to be recovered and hence more electricity to be generated from the geothermal resource.

The technology is being implemented at a pilot scale operation and expressions of interest to provide investment in its further development and commercialisation are being sought. The New Zealand and international opportunities for implementing the technology are potentially significant.

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