A Novel Composite Nanostructured Calcium Silicate - Calcium Carbonate Material Produced from Geothermal Water and its Environmental Remediation and Industry Applications

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ABSTRACT

We have developed a novel nanostructured calcium silicate – calcium carbonate composite material with good whiteness, chemical reactivity and physical absorbent properties, from the problematic dissolved silica contained in separated geothermal water.

Potential applications of this naturally-sourced composite material which we are developing include its use as a functional filler in paper, tyres, fire retardancy, moisture control and photochemical degradation applications; in the recovery of dissolved phosphate from rivers and lakes, and base metals from mine waters; and as a general absorbent and soil conditioning agent.

The removal of the dissolved silica in this way also provides a new opportunity to increase the amount of heat energy recovered and hence electricity generated from a geothermal resource.

Keywords: calcium silicate, nanostructured, silica, geothermal, energy, filler.

1 AN UNWANTED SILICA DEPOSITION PROBLEM TURNED INTO A NEW MATERIAL'S OPPORTUNITY

We have developed a proprietary new chemical process technology to precipitate a novel nanostructured calcium silicate – calcium carbonate composite material with excellent whiteness, chemical reactivity and physical absorbent properties, from the problematic dissolved silica present at supersaturation levels in separated geothermal water [1].

The propensity for silica to precipitate from such geothermal waters as a result of the water being cooled in the flash separation process to produce steam to drive a turbine and generate electricity, or by the passage of the water through the heat exchangers of a binary cycle plant to generate electricity, is a major problem in geothermal resource utilisation for electricity generation worldwide [2].

We have turned this problem into an opportunity, whereby we innovatively utilise this sustainable resource of dissolved silica to produce novel calcium silicate products for a range of industrial applications. These are environmentally attractive products produced from a natural resource with a very low manufacturing energy footprint.

Also, this removal of the problematic silica from the geothermal water desirably enables more heat energy to be recovered from a geothermal resource, and hence more electricity generated, thus increasing the overall resource utilisation efficiency.

2 GEOTHERMAL RESOURCE AND SILICA PRECIPITATION

Geothermal energy represents a significant renewable energy resource worldwide. In the subsurface geothermal reservoir, the superheated water typically at 250-350 °C, is maintained in the liquid phase due to the pressure of the overlying 2-3 km of rock. This geothermal water is saturated in dissolved silica, mainly as the H₃SiO₄⁻ ion, at the elevated reservoir temperature, due to some dissolution of the silicate minerals in the surrounding reservoir rock formations [3]. In geothermal energy utilisation this silicasaturated sub-surface superheated geothermal water is piped to the surface where the pressure is reduced and some 30 % of the water is flashed into steam which drives a turbine to generate electricity. Simultaneously, the remaining 70 % of water containing the dissolved silica, cools to about 110-130 °C under slightly elevated pressure and flows through the heat exchangers of a binary cycle turbine to extract further heat energy and generate additional electricity. The cooler water in 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. However at about 120-130 °C the silica saturation level is only about 350-500 mg kg⁻¹ and hence on cooling this water becomes 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 [3,4].

 $H_3SiO_4 \rightarrow SiO_2 + OH + H_2O$

This silica precipitation progressively builds up on the surface of pipes, heat exchangers, drains and reinjection wells as a hard intractable silica sinter deposit (Figure 2). It is a major problem in geothermal resource utilisation, which limits energy recovery and generates high maintenance and operating costs.



Figure 1: Precipitated amorphous silica sinter deposits on the surfaces of a drain, flow valve and pipe.

The current industry approach to address this silica precipitation problem is to maintain the temperature of the water in the flash plant separators at a suitably high level, typically 120-130 °C (depending on the field enthalpy), rather than at 100 °C and atmospheric pressure, whereby the induction period that precedes silica precipitation is hopefully just long enough for the water to flow through the separators, pipework and reinjection wells before there is any appreciable silica precipitation. A consequence of the higher separation temperature is that the amount of steam available for electricity production is reduced thereby lowering the overall energy recovery efficiency of the resource. In a binary cycle plant the temperature of the water exiting the heat exchangers must be similarly high and the temperature gradient across the exchangers is reduced accordingly in order to minimize silica deposition in the heat exchangers, pipework and reinjection wells. A parallel approach which is often used to increase the induction time and hence reduce the amount of silica precipitation, is to reduce the pH of the water by acid dosing. This has an associated acid cost as well as increasing the corrosion of the steel pipework.

Even with these two approaches, silica deposition still occurs and hence a paradigm shift in addressing the problem is required.

3 NANOSTRUCTURED CALCIUM SILICATE – CARBONATE

We have turned this silica deposition problem into an opportunity by producing a useful nanostructured calcium silicate material. This involves the reaction between added Ca²⁺ and the H₃SiO₄⁻ species in the geothermal water under alkaline conditions [5]. The reaction is very rapid and the nanostructured calcium silicate forms immediately. However, as geothermal water typically contains some dissolved CO₂ as the HCO₃⁻ ion, this material usually contains a low level of calcium carbonate and is therefore strictly a nanostructured calcium silicate - carbonate

composite, although we generally refer to it as nanostructured calcium silicate. The simplified chemical reaction is:

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

Under the mildly alkaline conditions present in geothemal water, the solubility of nanostructured calcium silicate is very low and the dissolved silica level in the geothermal water can be removed down to a level of a few mg kg^{-1} SiO₂. This completely obviates any silica deposition and the associated unwanted consequences.

The addition of Ca^{2+} should take place immediately after the steam-water flash separation process 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.

An important observation is that these particles do not stick together as there is no propensity for them to polymerise further, which is the case for silica particles that ultimately form the intractable silica sinter. Similarly, they do not adhere to metal or other surfaces as silica particles do. Instead, they remain as a very dilute suspension of nanostructured calcium silicate particles in the geothermal water stream, somewhat like a suspension of clay particles in water. Their lack of agglomeration and adherence to surfaces means that as a suspension, they readily flow through steel pipework, valves and heat exchangers and do not block them, as does the silica sinter. This is a major advantage in geothermal resource utilisation as it provides a new approach to obviating silica deposition.

The nanostructured calcium silicate material then needs to be separated from the geothermal water flow in an effective and continuous manner by conventional settling or filtration technologies. Significant challenges exist here as the total flow from all the wells in an operational geothermal resource for electricity production can amount to some 3,000 tonnes per hour. Depending on the dissolved silica content and the calcium / silica ratio used in the precipitation of nanostructured calcium silicate, a typical geothermal field can yield some 10,000+ tonnes per year of nanostructured calcium silicate product. Hence it is necessary to find large scale applications and uses of the material [4,5].

The nanostructured calcium silicate material comprises nano-size platelets stacked together in a unique open framework structure forming discrete particles of about 1-5 μ m in size (Figure 2), giving it a high surface area of up to about 300 m² g⁻¹. The stacking arrangement also gives it a high pore volume and in turn gives a high liquid absorbency of up to about 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 oxygen atoms in the structure and particularly those on the surface of the platelets provide a negative surface charge to the particles, which can consequently attract positively charged metal cations. Also the surface Ca^{2+} species can readily bond with phosphate anions. These structural and chemical attributes provide the basis for a number of industial uses of this novel material. When dried, it has a bulk density of about 0.2 g cm⁻³ [5].



Figure 2: A scanning electronmicroscope image of nanostructured calcium silicate showing the Precipitated

4 APPLICATIONS OF NANOSTRUCTURED CALCIUM SILICATE

Our nanostructured calcium silicate applications development work has identified and explored opportunities that use the inherent characteristics and properties of the material as described above. These include the following.

The use of nanostructured calcium silicate as a filler in paper to reduce print through and enhance print quality: 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 which is typically used for this purpose [6].

The recovery of base and heavy metals from waste mining streams: This applications utilises the effective ability of nanostructured calcium silicate to capture metal cations on the negatively charged surface of the platelets. It 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 Cu²⁺ and Fe^{2+/3+} and 97 % of Zn²⁺ could be readily removed. Lesser amounts of 37 % for Ni²⁺ and 20 % for Mn²⁺ could be similarly removed [7]. Typically such a waste stream would flow through packed beds containing the nanostructured calcium silicate, or sacks of it immersed in the stream to facilitate the adsorption process. The resulting metal ion containing silicate material can then dissolved in a very small quantity of acid to provide a highly concentrated solutiion of these metal ions which can in turn be recycled back to the metal winning process.

The uptake of phosphate from solution: Here the nanostructured calcium silicate readily takes up PO_4^{3-} . HPO₄²⁻ and H₂PO⁴⁻ species from solution depending upon the pH, to form calcium phosphate in the brushite phase within the silicate particles. Up to 17 wt% PO4³⁻ can be accommodated within the silicate particle structure [8,9] which amounts to some 28 wt% Ca₃(PO₄)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 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 [9]. 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.

Passive moisture control: The high water absorbency property of nanostructured calcium phosphate 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 and release it as the soil dries out.

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 in particular materials. Thermogravimetric analysis has shown that the silicate undergoes about a 30 % weight loss on heating as a result of water release. This is a very significant amount and makes the silicate useful for this application.

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 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 [10].

5 INCREASED ENERGY RECOVERY

Under the mildly alkaline conditions usually present in geothermal water, the solubility of nanostructured calcium silicate is very low and hence the dissolved silica level in the geothermal water can be reduced down to a level of a few mg kg⁻¹. This completely removes the propensity for silica to polymerise and precipitate, and hence obviates any silica deposition and the associated unwanted silica sinter formation. As such, it is now possible in principle to operate the steam-water separation flash unit at lower pressures approaching atmospheric and hence lower temperatures, thereby providing an increased steam flow to the turbines to generate more electricity. Alternatively or as well as, the exit temperature of the heat exchangers in the binary cycle electricity generating plants which recover heat from the separated water streams, can in principle be lowered from the typical 100 °C temperature to a value closer to the boiling point of the secondary organic working fluid. This is usually n-pentane or iso-pentane and hence a heat exchanger exit temperature could likely be 50 °C. Either approach enables more heat energy to be recovered from the geothermal water and hence more electricity to be generated. A further advantage is a considerable reduction in maintenance costs as the silica sinter deposition problem in pipes, valves and heat exchangers is obviated, and reinjection wells do not block with deposited silca and hence do not need costly redrilling.

6 CONCLUSION

The production of a novel nanostructured calcium silicate material from separated geothermal water provides an attractive approach to obviating the world wide problem of silica deposition from separated geothermal water as an intractable sinter which blocks pipes, valves, heat exchangers and reinjection wells. The silicate material itself or in a composite with calcium carbonate, 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 very large.

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