NANO-STRUCTURED CALCIUM SILICATE – A SOLUTION TO THE FORMATION OF SILICA SCALE IN GEOTHERMAL WATER AND A USEFUL PRODUCT

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SUMMARY - The condensation of silica to form hard scale is a major issue in the generation of energy from geothermal resources. Presented here is nano-structured calcium silicate (NCS) as a solution to this issue. NCS prevents the unwanted silica deposition by formation of a competing product, which is highly porous and interesting for various applications in materials science. While the suppression of the formation of silica scale is the main benefit of applying NCS technology to geothermal water, spill-over benefits from the production of NCS are significant. NCS can be used as a filler to partially replace TiO_2 pigments and act as a flattening agent in paints. NCS can be coated on paper to improve ink-jet print quality and be incorporated in the paper sheet to reduce print-through. NCS can be used as an ingredient of ceramics and concrete, a photoactive material, a catalyst carrier and to treat environmental hazards by the sorption of ionic species and gases.

1 GEOTHERMAL ENERGY AND THE FORMATION OF SILICA SCALE

The growing demand for energy and increasing concerns regarding the environmental impact of burning oil and gas resources have placed renewable and environmentally benign energy resources into the spotlight. Geothermal energy is one of these energy sources and has gained a lot of interest over the past 10 years. The potential for geothermal energy is present, when underground (a few hundred meters to several kilometres below the surface) water reservoirs are located close to geothermal heat sources (e. g. magma). The water is pressurised due to the layers of rock above it and superheated, if it has no means of release. The geothermal water can be piped to the surface and flashed to produce steam to drive a turbine, and a separated brine flow for discharge or re-injection. Re-injecting the separated water into a geothermal field increases the life time of the reservoir and places this method of energy generation into the realm of both benign and renewable energy resources. Unfortunately due to microbial and chemical processes rock surrounding geothermal water reservoirs is dissolved, resulting in a cocktail of ionic species which can mainly be found in the separated brine after steam production giving rise to a number of issues. The composition of the geothermal brine is different from well to well, and toxic species containing arsenic or uranium, valuable species like gold, silver or uranium and harmless but problematic species like dissolved silica occur in various amounts. The dissolved silica species become concentrated after the generation of steam by the flashing process (reduction in liquid volume by approximately 30% due to generation of steam). Geothermal water at 260 °C contains about 600 $mg.kg^{-1}$ dissolved silica (Iler, 1979). Upon flashing of about 30% of this water into steam the concentration of dissolved silica in the residual separated brine rises to approximately 800-900 $mg.kg^{-1}$. After flashing off steam, the temperature of the brine decreases to about 120 °C, depending upon the operating

pressure of the flashing process. At this temperature only approximately 350 $mg.kg^{-1}$ of silica are soluble in water. The separated brine is therefore supersaturated with dissolved silica, which can condense and precipitate to form a hard amorphous silica scale blocking pipes, re-injection wells and heat exchangers. The costs associated with the re-drilling of re-injection wells and cleaning of pipes and equipment are significant and present one of the major challenges facing geothermal energy generation. The microbes responsible to some degree for the ionic content of the brine can get encapsulated in the scale, bringing with them unwanted species like arsenate and arsenite (Mroczek et al, 2000; McKenzie et al, 2001; Garcia et al, 2004). Several methods have been developed to address the issue of scale formation. The most notable of these are the addition of acid (Dubin, 1984; Gunnarsson & Arnórsson, 2005) to delay the condensation of silica, the addition of silica seeds (Sugita et al, 1999; Sugita et al, 2003) to attract dissolved silica, and the addition of aluminium species (and EDTA and other compounds) (Gallup, 1999; Sugita et al, 1999) to form silica and silicate species that do not form precipitates. Gill (1998) presents a good overview regarding the issue of silica scale formation and the effect of pH and other ionic species.

2 NANO-STRUCTURED CALCIUM SILICATE – AN OPPORTUNITY

Presented here is nano-structured calcium silicate (NCS) as an alternative technology to prevent the formation of unwanted silica scale from geothermal water. Proprietary NCS has been developed as a highly porous material for use in materials science applications (Johnston et al, 2006). In the laboratory it is generated by the addition of calcium ions to dissolved silica under controlled conditions.

Rapid Precipitation

The formation of NCS is very rapid, it is completed within milliseconds of the various components coming into contact with each other. After this initial step the NCS particles, a few micrometers in diameter, ripen to form a highly porous and amorphous nano-structured material as shown in Figure 1 (Borrmann et al, 2008; Johnston et al, 2006; Borrmann et al, 2006). Because the formation of NCS is very fast, the problematic dissolved silica is removed as NCS thereby preventing the polymerisation and deposition of amorphous silica. The precipitation of NCS is so efficient that all the dissolved silica down to (under optimal conditions even below) the solubility limit (residual silica levels are below 25 $mg.kg^{-1}$ at room temperature) can be removed from solution.

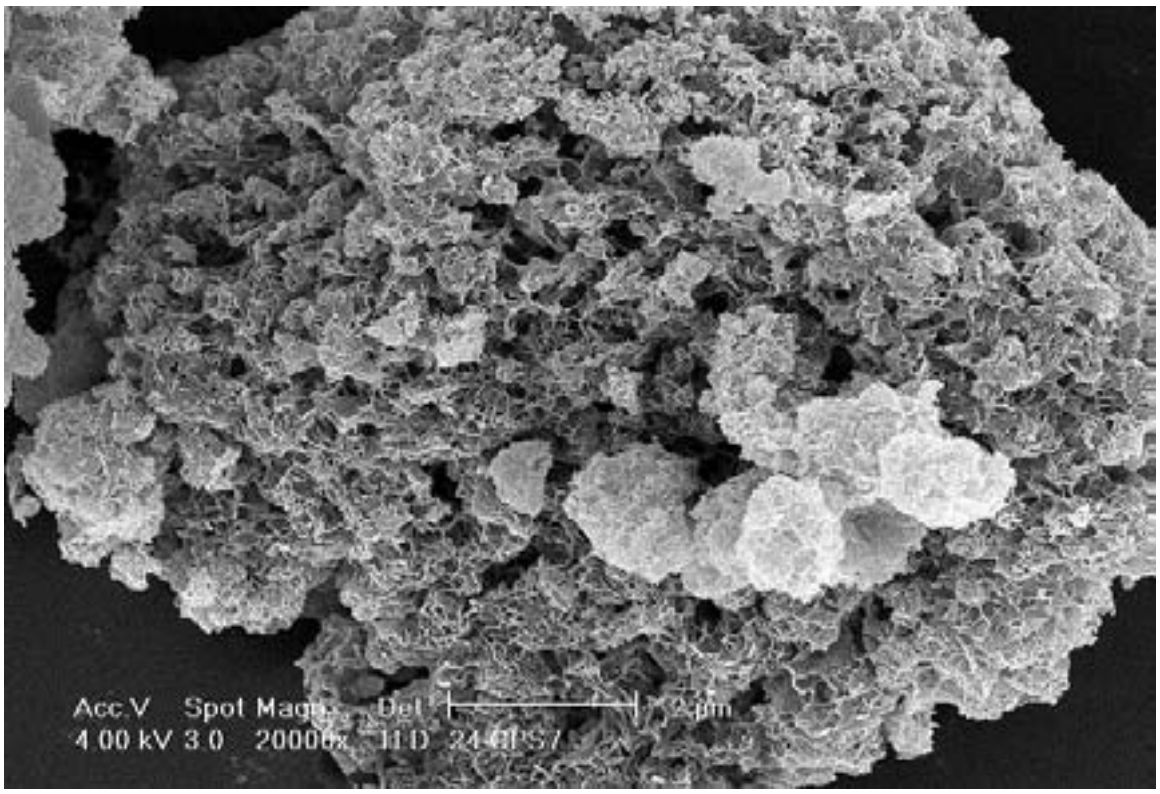

Figure 1: Scanning electron microscopy image of NCS.

The surface of the NCS particles comprises silanol groups and calcium species, which can react readily with any other silica species present (Borrmann et al, 2008; Johnston et al, 2006; Borrmann et al, 2006).

Opportunities for Geothermal Applications

The rapid precipitation of NCS makes the controlled formation of this material highly interesting for the prevention of fouling by the formation of amorphous silica scale. The NCS material remains an active scavenger of dissolved silica species, while travelling with the geothermal water through the pipes. If a temperature gradient was chosen so that the residual dissolved silica after NCS formation again reaches supersaturated levels, this dissolved silica can react with the NCS present. This means that the NCS approach to removing silica from geothermal water is adaptive to its environment, giving a large window of effectiveness.

This means that a lower steam-water flash temperature can be used to enable more steam production and, hence, more electrical energy generation in the steam turbines. Additionally a larger binary cycle heat exchanger temperature gradient can be chosen to enable more energy to be generated from a binary plant.

Further to this, the NCS process offers several spill-over benefits. NCS has been proven effective in sorbing transition metals from solution (e. g. copper, zinc, silver, gold). Should valuable species be contained in the brine during NCS formation, it is likely that they will be accommodated within the pore structure of the NCS. This scavenging and accumulation of valuable species alleviates one of the challenges facing the use of NCS. Looking at the average particle size of NCS, which is volume weighted about 10 micometre and number weighted about 1 micrometre, it is likely, that NCS needs to be removed from the geothermal brine prior to re-injection into the geothermal reservoir, by using a settling pond. The clarified “silica-free water” can then be reinjected.

A further challenge besides of its potential removal from the separated brine, is the question of how and for what purpose the recovered NCS is used. NCS has been identified as an additive for paper (reducing print-through and increasing opacity when used as a filler, and for enhancing the quality of ink-jet printed images, when used as a functional material in a coating on paper – Johnston, 2002), as a partial replacement for titanium dioxide and flattening agent in paint – Johnston, 2002), in ceramics (forms artificial wollastonite at comparatively low temperatures – Borrmann, 2006) and environmental treatments (sorption of phosphate and transition metals, Cairns, 2006; Borrmann, 2009), as a carrier material (Borrmann et al, 2004), soil conditioning, and moisture controlling agent (Johnston et al, 2006; Johnston et al, 2008). Impurities in the NCS from the geothermal brine will constrain and define the uses it can be put to. Preliminary tests have shown that arsenic species do not bind to NCS. However, the exact composition and presence of impurities in NCS will have to be assessed on a well by well, field by field basis.

Laboratory Scale Tests – No Fouling, No Scale

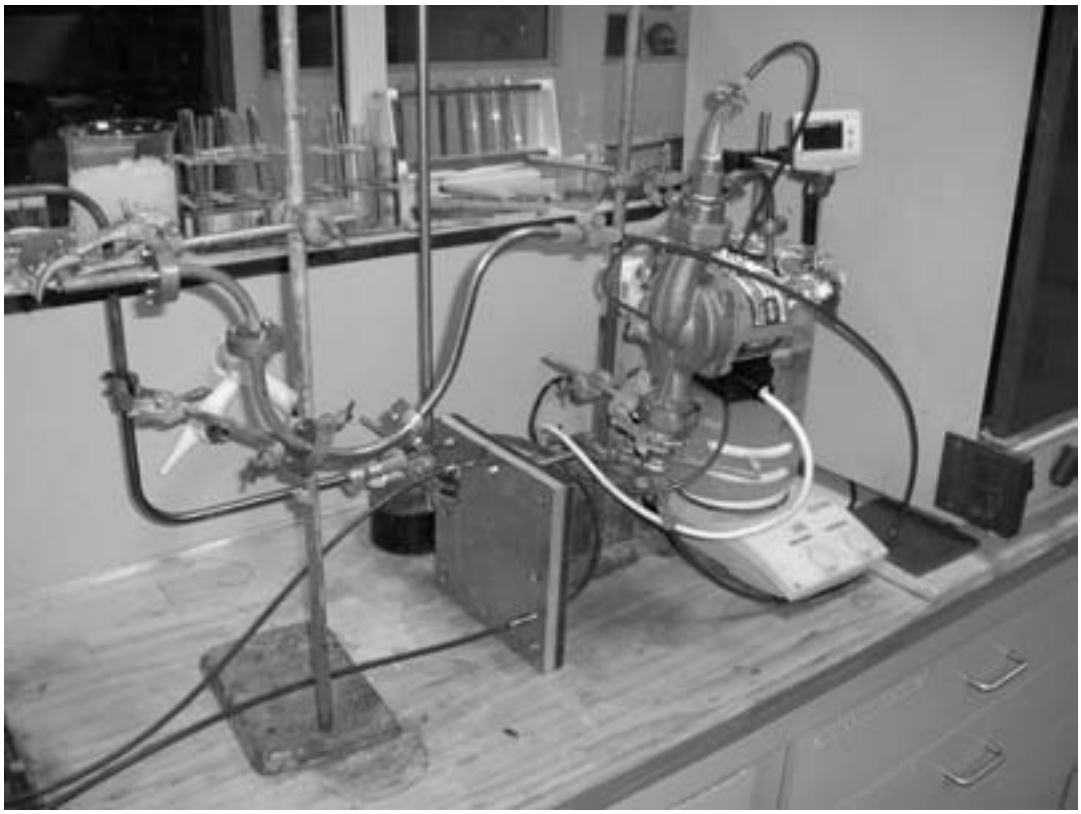

Figure 2: Simulation of a geothermal plant – circulation of NCS through pipes and a heat exchanger.

NCS generated from geothermal water and model geothermal water sources has been placed in a simulation of a geothermal plant. A pipe-system containing a variety of pipe shapes, bends and joints as well as a small heat exchanger has been constructed on a laboratory scale (Figure 2). A suspension of NCS in brine comparable to that obtained by precipitating NCS from separated geothermal water was placed into the system and circulated. The system was operated for times between one and six weeks and then disassembled and carefully studied. No formation of silica or NCS scale or any other form of fouling was observed. The results are very promising and based on them, a pilot scale plant at a geothermal site is under development.

3 CONCLUSIONS

The unwanted deposition of amorphous silica scale from separated geothermal water (brine) presents a major challenge to efficient energy recovery and the use of such water. The formation of this scale can be fully prevented by the formation of a nano-structured calcium silicate (NCS) to remove the dissolved silica. The formation of NCS is significantly faster than the polymerisation of silica and the formation of the silica scale, thereby completely inhibiting the silica deposition, as has been successfully demonstrated in laboratory scale tests. The NCS is adaptive to its environment, allowing the separated brine to be cooled to any desired temperature after NCS formation thereby facilitating enhanced energy recovery. As spill-over benefits, the conditions needed for NCS formation and NCS itself protect and self clean metal equipment, hence drastically reducing maintenance efforts and costs. A remaining challenge facing the implementation of NCS in geothermal energy generation is defining the actual process methodology required to recover NCS to avoid blockage of re-injection wells. This challenge is offset by the potential of recovering additional energy from the geothermal resource and well as potentially valuable species sorbed by NCS and a variety of useful applications for NCS.

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