Moving the Calcium Silicate (CaSil) Pilot Plant to Kawerau

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ABSTRACT

Silica scale formation due to supersaturation in geothermal brine results in the formation of intractable silica scale deposits in pipes, heat exchangers and reinjection wells. This is a major problem in liquid dominated geothermal fields worldwide. Heat energy extraction and hence electricity generation are adversely affected, and blockages of process equipment and reinjection wells necessitate costly maintenance and plant downtime. We have developed a proprietary technology that definitively prevents the scale formation and enables full utilisation of geothermal resources for electricity generation and direct-heat applications.

Our technology addresses the problem by producing a nanostructured calcium silicate (CaSil), which is formed in and recovered from geothermal brine in an automated pilot scale operation. The process lowers the silica saturation index (SSI) substantially below 1 within seconds. Laboratory work and batch field worked showed that the technology is applicable to a range of brine compositions, temperature, and pressure conditions. The CaSil material does not stick to metal surfaces because of its unique surface chemistry, significantly reducing maintenance costs for process equipment and reinjection wells as well as plant downtime.

From commissioning of an initial proof-of-concept plant in 2017, through the construction (November 2019) and operation of our pilot plant (2019 to 2021) we were located on the Wairakei geothermal field. Mid 2021 we were invited to relocate the pilot plant to the Kawerau geothermal field. The new field and chemicals in the Kawerau brine posed some challenges and surprises regarding the on-site silica analysis of samples (molybdenum blue and yellow tests) but reconfirmed that our overall process is very robust and can cope with very different brine compositions. We successfully operated the pilot plant for several weeks in 2021 and 2022 and present insights from the operation.

1. INTRODUCTION AND BACKGROUND

Heading into a carbon-neutral future, geothermal energy is an essential natural and renewable energy resource, as it can produce large quantities of heat and electrical energy continuously and on demand. One major factor holding back geothermal developments is the formation of scale and sinter deposits, such as intractable silica scale formed due to the supersaturation of silica in used geothermal water. The silica together with other species originates from underground reservoirs, where conditions (e.g., temperature, pressure, chemistry, and extremophiles) promote the saturation of geothermal water with chemicals (mainly soluble salts, but also silica, carbonates, arsenic, antimony, sulphides, and others). When hot geothermal water is sourced from an underground reservoir, it can be flashed to produce saturated steam to drive a turbine and produce electricity. Alternatively, or in addition, the hot water can be used for binary cycle electricity generation or direct-heat applications. All methods of energy extraction lower the temperature of the geothermal water used and can produce steam. Especially, flashing converts about 30 % of the superheated water to steam, creating a separated geothermal water or brine flow, rich in dissolved and suspended species. Thereby, usage of geothermal resources leads to the supersaturation of species in geothermal fluids. The supersaturation can be somewhat mitigated by the addition of condensed steam, fresh or wastewater to the brine, diluting the chemical species. Re-injecting the spent geothermal water, condensed steam and added waters into a geothermal reservoir replenishes the reservoir and subsequently increases the lifetime of the geothermal resource, prevents subsidence, and places this method of energy generation firmly into the realm of both benign and renewable energy resources (Dubin 1984, Gunnarsson and Arnórsson 2005).

1.1 Silica Scale Formation

During utilization of hot geothermal water resources, dissolved species, amongst them silica and carbonate entities, can precipitate to form an intractable scale, which blocks pipes, valves, heat exchangers, and other process equipment. They can also be carried over with saturated steam during the flashing process to scale and damage turbine blades. Calcite forms close to the well head and in conjunction with silica deposits there. Hydrogen sulphide can be oxidized by contact with air to form sulphur deposits (in the condensate) or can form antimony and arsenic sulphides due to cooling. Silica deposits typically form after flashing and in binary cycle heat exchangers (**Figure 1**). During flashing about 30 % of water is converted into steam; dissolved and suspended minerals are concentrated to the degree that scale forms. Heat extraction promotes the formation of silica scale in heat exchangers.

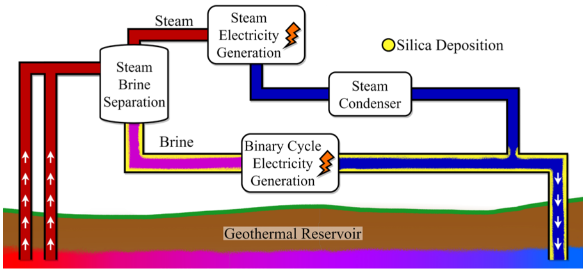

Figure 1: Silica scale formation in a geothermal power plant.

Not only production equipment is affected by scaling; reinjection wells can become clogged due to silica scale requiring costly and environmentally undesirable chemical treatments or drilling of new reinjection wells. Additionally, surface coverage by silica scale impedes the transfer of heat energy, increases the pressure loss and hence reduces the efficiency of binary cycle heat exchangers (Dubin 1984, Gunnarsson and Arnórsson 2005).

The chemical composition of the separated brine is production well and process specific. Toxic species (arsenic, mercury or selenium), valuable elements (lithium, zinc, boron, or gold), and environmentally harmless but problematic species (dissolved silica and calcium carbonate) are invariably present at different levels. The issue of silica and carbonate scale formation affects geothermal energy production on a global scale. Traditionally, removal of deposited silica scale requires considerable mechanical force and effort, sometimes even necessitating the replacement of plant equipment, or use of corrosive hydrogen fluoride or a combination thereof. Recently, promising advances have been made in the chemical removal of silica scale using alternate washing with acids and bases (Muller et al. 2021). However, all efforts occur after scale has already formed, degraded equipment and heat transfer and negatively affected plant operations. Therefore, several methods have been investigated to prevent the formation of silica scale rather than dealing with the consequences. Examples of these are the addition of acid to partially delay the condensation and polymerisation of the dissolved silica species (Dubin 1984, Gunnarsson and Arnórsson 2005), the addition of silica seeds to capture such dissolved silica onto a pre-existing silica material (Sugita et al. 1999, Sugita et al. 2003), or the addition of aluminium species, EDTA and other compounds to form silica and silicate species that do not precipitate (Sugita et al. 1999, Gallup 1999). Gill (1998) presents a good overview regarding the problematic issue of silica scale formation and the effect of pH and other ionic species on it. We were the first to realise that the use of calcium ions (dissolved lime) allowed removal of silica from geothermal brine and demonstrated this at the Kawerau and Wairakei resources (Harper et al. 1992). Johnston was the first to capture the problematic dissolved silica as a nano-structured calcium silicate material, which was followed with extensive work by Johnston and Borrmann over the following years (Johnston 1993, 2002). Starting from a focus on the production of fine chemicals, we built pilot plants to precipitate a silica product for use as a filler to enhance the optical and print quality of paper (together with Tasman Pulp and Paper) and to use as a filler in paint (together with Sherwin-Williams).

1.1 The CaSil Technology

Through research work on the nature of nano-structured calcium silicate hydrate, CaSil, we came to realise that this calcium silicate offers a disruptive and attractive potential solution to preventing the occurrence of silica scale. The technology works by transforming reactive silica species present at supersaturated levels in separated geothermal brine into CaSil. The CaSil forms readily and does not adhere to metal surfaces. Instead, the CaSil particles remain suspended in the geothermal brine flow and can be separated as a useful product. The level of residual dissolved silica species can be controlled by the process chemistry from below the silica solubility index at the brine temperature down to the essentially zero (Borrmann 2009). CaSil is distinct from other forms of precipitated silica in that it forms an open framework similar to "desert rose", where the calcium ions are accommodated on the surface of the particles (**Figure 2**). This gives CaSil a slightly positive surface charge (depending on the Ca^{2+} content) and hence the ability to bind other silica, calcite (calcium carbonate) or particulate and ionic species to its surfaces. The positive surface charge also means that CaSil does not form scale on metal surfaces in contrast to silica and calcite trapped in CaSil particles.

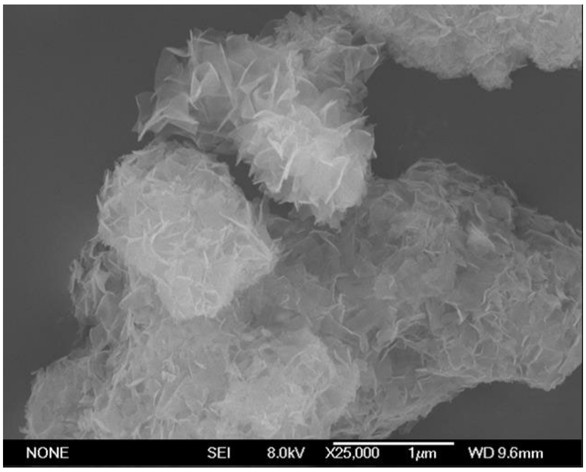

Figure 2: Scanning electron microscope image of nano-structured calcium silicate hydrate (CaSil).

The individual particles observable in scanning electron microscope images (**Figure 2**) are about 1 to 15 microns in diameter and an open framework structure is observable. Number weighted particle size measurements using the dynamic light scattering measurement method, also show that about 99 % of the particles fall within this size range. However, our laboratory work has shown that the small particles tend to agglomerate and form clusters of several microns to millimetres in diameter. This is partially verified by volume weighted particle size measurements, where particles with a diameter of 10 to 50 micron, being agglomerates of up to about one thousand particles are observable (Borrmann 2009). Although it is possible that the individual 1 to 15 micron CaSil particles could likely be reinjected with the cooled brine, the larger particle agglomerates may bridge and block small pores in the rock formation of an underground geothermal reservoir. Hence, the CaSil material needs to be removed from the geothermal brine before reinjection. A positive side effect of these larger agglomerates is that two sources of scale forming species, silica and calcite are removed from the brine at the same time along with CaSil.

Through laboratory scale and field trials, we have successfully developed the CaSil geothermal technology and have since constructed a small-scale pilot plant test rig. We have carried out 18 months of field testing on our pilot plant. In parallel we have carried out laboratory research to further develop our technology and elucidate underlying mechanisms and respond to research questions arising during pilot plant operation, such as the efficient removal of CaSil from geothermal brine. The removal of nano-structured calcium silicate hydrate (CaSil) from geothermal brine is a solid-liquid separation process, which is non-trivial due to the high surface area and pore volume of CaSil, low density of CaSil particles, hindered settling behaviour, and the low mass concentration of CaSil in geothermal brine. This is aggravated by the high brine flow rates found in geothermal power plants.

First a proof-of-concept plant (August 2017 to October 2018) and then a fully automated pilot plant (**Figure 3a and 3b**) were operated using brine from the Wairakei geothermal field. The pilot plant was constructed and commissioned in October and November 2019. At that the time it was located on site at MB Century with brine being transported up through a pipe split off prior to the binary plant down the hill. The plant operated close to atmospheric pressure processing 30 L.min^{-1} of geothermal brine. All unit-operations required for a full scale plant were included in the pilot plant, which allowed us to test those units and gather valuable operational data. The pilot plant was operated at the MB Century site throughout 2020 and the beginning of 2021. In 2021 we relocated it to the Kawerau geothermal field to test and demonstrate the plant and technology on a different geothermal field and brine. We had carried out several earlier field tests in the Kawerau field between 1999 and 2009 and were confident that our technology could cope well with the brine chemistry present. This article reports on our experiences, surprises, and success.

Figure 3a: The fully automated CaSil pilot plant December 2019, Wairakei.

Figure 3b: The CaSil pilot plant May 2020, Wairakei.

2. CASIL IN KAWERAU

2.1 Moving and Recommissioning

After over 250 hours of operation on the Wairakei field we had collected a lot of operational data (example **Figure 4**) and experience that gave us confidence in the robustness of our technology. However, we intended to move the pilot plant to other sites and geothermal fields, to further prove our technology and gain additional insights into the process.

In 2021 the possibility of moving the pilot plant to the Kawerau geothermal field was raised. In July 2021 we carried out some preliminary studies on site using a batch approach. Some differences in the brine composition were noted compared to earlier work carried out between 1999 and 2009, namely a higher content of silica, carbonate, arsenic, and sulphide but a slightly lower presence of chloride. However, the CaSil process worked as expected with the different brine chemistry.

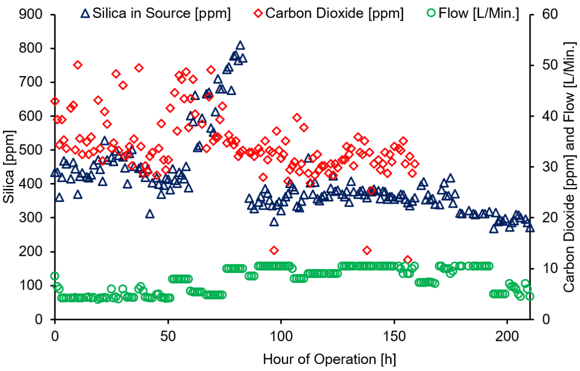

Figure 4: Data from the operation of the CaSil pilot plant on site at MB Century, Wairakei.

Our automated pilot plant was relocated to the Kawerau resource the following month (see **Figure 5**). Despite the plant not being skid-mounted, disassembly, reassembly and commissioning went smoothly and took less than 150 work hours to complete.

Figure 5: The CaSil pilot plant, August 2021, Kawerau.

2.2 Brine Analysis for Silica – the Molybdate Test Fails (Temporarily)

The only challenge to be overcome was presented by on site analysis of the silica content of the brine. We were using the conventional chemical molybdenum yellow method for measuring the content of silica in water via photo spectrometer at 410 nm (Strickland 1952, Iler 1977). This method relies on the formation of yellow coloured silicomolybdic acid complex from ammonium molybdate in oxidising acidic media. Phosphate, arsenic, and sulphide are known to interfere with this analysis method but require comparatively high levels of these species to be present. In our preliminary studies we noted the presence of hydrogen sulphide, which at high levels can interfere with this analysis technique. In some on site tests the analyte solutions turned green indicating that high enough levels of sulphur were present to interfere with the measurements. Following Berro et al (2014), samples were acidified, and air was bubbled through them to drive out hydrogen sulphide. This proved successful in eliminating sulphide as shown via titration with iodine, and sodium thiosulfate using a starch indicator. However, when samples tested in the field were analysed regarding their silica content by atomic absorption spectroscopy in the laboratory, the silica levels from the field results were up to twice what was measured in the laboratory.

No consistent trend was found between measurements in the laboratory and in the field.

Discussion with the field operators revealed that antimony species can precipitate from the Kawerau brine upon cooling. However, antimony sulphide is red, and the observed pigmentation was yellow in all field samples. This pigmentation intensified as samples cooled down but was present even in fresh, hot samples. The pigment was carefully recovered from brine samples and analysed via scanning electron microscopy and energy dispersive spectroscopy (EDS). The elements observed in EDS were arsenic (about 27 atom%), sulphur (about 42 atom%), silicon (9 atom%), oxygen (19 atom%), and small amounts of antimony (less than 2 atom%). Silica as impurity was not surprising due to its presence in the brine. Orpiment, arsenic trisulfide, As_2S_3, can occur in geothermal brines, if hydrogen sulphide levels are high. It is more soluble than its antimony counterparts and tends to precipitate only below 60 °C (Weres 2019). Orpiment is yellow in colour with the main peak in its absorption spectrum around 564 nm. As such, orpiment could interfere with molybdenum yellow method for silica analysis. It is also likely that the field operators were not aware of its presence, as it does not deposit and, hence, gets reinjected with the spent brine and does not pose an issue. During analysis in the field samples cooled down significantly (below 35 °C) as the silicomolybdic acid complex needs 15 minutes to develop. While being intensely coloured and having an impact, the pigment was only present at ppm levels and not enough material could be collected to prepare an X-ray diffraction sample. Hence, the presence of orpiment is only supposed, based on the colour of the pigment and the elemental composition from the EDS analysis. Final confirmation is outstanding, and it can't be ruled out that the pigment was a different material. We attempted to oxidise the sulphide to sulphate using sodium iodate, sulfuric acid, and hydrogen peroxide. However, use of these oxidants also bleached the silicomolybdic acid and did not lead to consistent results. Instead, the molybdenum blue method was employed (Brabson 1944, Zini et al 1985) which uses a wavelength of 828 nm thereby circumventing the presence of the pigment. This proved successful. However, the operating range for silica levels determined in this method is of on the order of 1 to 2 ppm, thereby requiring further dilution which causes a larger experimental error than observed for the molybdenum yellow method.

2.3 A Very Robust Process

An early concern was that the uncertainty in the silica level present would have a significant impact on the CaSil technology. We found that having an approximate measurement was already sufficient for the treatment to successfully prevent silica depositions, even at low brine temperatures. CaSil was formed as expected and was separated from the brine effectively. Despite the constant fluctuations in the chemical composition of the brine, the overall process proved to be very robust. CaSil product was formed and recovered independent of silica levels and impurities present. The pilot plant was designed to operate at 30 $L.min^{-1}$ but could readily cope with flows of up to 50 $L.min^{-1}$. The process on site was only limited by the discharge rate allowed by the drain.

3. CONCLUSION

The CaSil pilot plant was relocated from the Wairakei to the Kawerau geothermal field and was successfully recommissioned and operated. The chemistry of the brine at Kawerau posed a challenge, as pigment present in the brine interfered with the on-site determination of silica levels using the conventionally used molybdenum yellow method. This was overcome by acidifying samples and bubbling air through them, which removed sulphide from the brine. The use of the molybdenum blue method allowed measurement at a wavelength where any remaining pigment posed no problem but at a cost of higher uncertainty. While silica levels could be successfully determined in the field, measurements were only approximate, and results had to be reconfirmed in the laboratory later using atomic-absorption spectroscopy. Considering the flaws in the use of the molybdenum tests and the time delay in retrieving results from it, it would be beneficial, if a different, faster yet economically viable method for assessments of silica levels in brine can be found and implemented in our pilot plant. This is the subject of our present research.

Despite the issues facing the on-site analysis of silica, the overall CaSil process proved to be very robust, successfully lowering the SSI well below 1, thus preventing silica scaling. We were able to operate the process knowing only approximate silica levels due to the chemical interference in the testing method. This means that the recovered product has some chemical variation. However, our developed end-uses for the CaSil material can accommodate these natural variations. Added to this is the presence of impurities due to various calcium species captures along with CaSil. The management of these impurities and inconsistencies in regard to possible applications of the CaSil product is being progressed.

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