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A Combination of Nano-structured Calcium Silicate Hydrate (CaSil) and Calcium Inhibitor Technologies Eliminates Calcite, Silica, Stibnite and Aluminate Scales

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ABSTRACT

The development of high enthalpy geothermal resources is held back by the formation of a variety of mineral scales formed from minerals dissolved in geothermal reservoirs. Calcite scaling can occur just before the wellhead, while silica, stibnite, orpiment, and aluminate scales form in heat exchangers, pipes, valves and reinjection wells.

Calcite scale inhibitors (CIS) can be injected down well to control calcite scale formation. For other mineral scales, current remediation techniques only act as delay tactics and do not solve the issue. Removal of scales using costly processes necessitate significant plant downtimes. Reinjection wells block up and need to be treated regularly or even abandoned and new ones drilled.

We have demonstrated on fully automated pilot plant scale operation an alternative and transformational silica treatment technology, the CaSil technology, which reliably eliminates the silica scale problem. The CaSil technology works by transforming silica into a calcium silicate hydrate material (CaSil), which does not form a scale or stick to tubes, pipes and heat exchangers. This is a very fast chemical transformation that removes silica from the brine and is distinctly different from the use of sequestering agents or acid dosing approaches that are currently used by the industry. The technology also eliminates stibnite, orpiment and aluminium and and other metal silicate related scales due to the resulting increase in pH of the treated brine preventing the formation of the first two and aluminium and other metal ions being trapped in the CaSil product.

Combining the CaSil technology with calcite inhibitors enables more heat to be extracted and electricity to be generated from the geothermal brine. Direct heat applications now become possible that cannot be unlocked otherwise. We present laboratory findings and results from our fully automated pilot plant scale work to demonstrate the opportunities that are opened by the combined use of the CaSil technology and calcite inhibitors.

INTRODUCTION

1.1 Silica Scales

Silica scaling is the most pressing hindrance to efficient and full utilization of the heat energy contained in geothermal brines from high enthalpy, liquid dominated geothermal resources. In geothermal reservoirs, rocks dissolve according to the temperature and pH dependent solubility of quartz (Iler 1979, Brown 2011, Zarrouk 2014). The resulting brine in the geothermal reservoir can reach saturation in silica and other minerals. When geothermal brine is brought to the surface, e. g. via a production well, the pressure of the silica containing water is reduced to transform part of it into steam that drives turbines to generate electricity. This production of steam necessarily lowers the temperature of the brine. Temperature/heat can additionally or alternatively be extracted via heat exchangers or direct use applications. The loss of water as steam and the lowering of the brine temperature mean that silica can become supersaturated; the solubility of silica follows amorphous silica behaviour (Iler 1979, Brown 2011). If silica becomes supersaturated, it can start to polymerise forming sol particles that aggregate to form silica scale (Borrmann 2009, Brown 2011). Scale formation is temperature and pH dependent and usually expressed via the silica saturation index (SSI), which is the fraction of silica in the brine divided by the fraction of soluble silica. As more silica is soluble at higher temperatures, keeping the exit temperature of a geothermal plant helps to reducesilica scaling, but this comes overall of utilisation of the geothermal resource. at the cost of energy/electricity extracted and efficiency (Iler 1979, Borrmann 2009, Brown 2011, Zarrouk 2014).

Additives, e.g. acids that lower the pH and slow doen the silica polymerisation process on;y act as delay tactics for the silica scale formation. If scale is formed, it blocks heat exchangers, pipework, valves and reinjection wells, requiring laborious and expensive treatments that involve extended plant downtime. Calcium, magnesium, aluminium, and other metals, such as iron, can promote silica scale formation and lead to formation of especially tough scales (Gunnarsson and Arnórsson 2005, Dubin 1984).

1.2 CaSil Prevents Silica Scaling

Over the past few years, we have developed and demonstrated our proprietary CaSil technology, where silica is transformed into nano-structured calcium silicate hydrate (CaSil), which does not stick to metal surfaces, and hence does not form silica scales in pipes, heat exchangers, valves of reinjection wells, thereby enabling the full utilization of a geothermal resource. The transformation to CaSil is a chemical reaction using up reactive silica. As such it is very fast (completed within seconds) and removes this reactive silica. As silica is removed, CaSil captures aluminium, iron, magnesium and other silicates based on bivalent or trivalent cations as well. These are trapped in the particles of CaSil (Borrmann 2011). The CaSil technology is distinctly different to sequestering agents and other silica polymerization delaying tactics like acid dosing in that it uses elimination of active silica. The CaSil treatment can be modified to allow power plant exit temperatures of 80 ºC or lower. More heat energy can be extracted from the CaSil treated brine and more electricity generated accordingly. Plant downtime is minimized. This means a significant efficiency gain for geothermal resource utilisation, electricity generation and overal resource utilisation. The CaSil product is separated continuously from the treated geothermal brine, and can be used in environmentally bebeficial applications (Johnston et al 2006, Johnston and Borrmann, Schweig et al 2023, Schweig et al 2024, and Johnston 2025).

The CaSil technology has been successfully developed in the laboratory and demonstrated at automated pilot scale operation using geothermal brines at the Wairakei, Kawerau, Mokai and Tauhara geothermal resources ocated in the Taupo Volcanic Zone (TVZ), New Zealand (Johnston et al 2006, Johnston and Borrmann 2017, Schweig et al 2023, Schweig et al 2024, and Johnston 2025).

1.3 Calcite Scales

Calcite scales commonly form in brines from geothermal reservoirs at temperatures between 140 and 240 ºC. Flashing or pressure changes cause carbon dioxide to be stripped from the brine leading to the formation of calcite according to the following equilibrium (01):

$$Ca^{2+} + 2HCO_3^- \underset{\leftarrow}{\rightarrow} CaCO_3 \downarrow + CO_2 + H_2O \quad (01)$$

A certain amount of supersaturation is required for the calcite scaling to start. Calcite solubility is retrograde meaning it diminishes with increasing temperature. As a consequence, calcite scaling occurs typically before wellheads or flashing stages. Careful control of pressure can keep calcite scale from forming or dictate the depth at which the scale forms, so it can be targeted with cacite inhibitors (Wanner 2017, Cosmo 2022, Brown 2011, Gunnlaugsson 2014).

Calcite scaling can also occur along with silica scaling. A treatment of one of these scales also affects the other. Calcite scaling was present at all the above fields, where the CaSil technology was demonstrated at pilot plant scale operation. At the Tauhara field a calcite inhibitor was already in use by the operator.

1.4 Calcite Inhibitors

Two types of calcite inhibitors (CIS) can be used that have slightly different modes of action. Compounds such as ethylene diamine tetraacetate (EDTA) chelate calcium ions and, hence prevent calcium carbonate formation. EDTA decomposes at temperatures exceeding 150 ºC, making it unsuitable for many geothermal applications, particularly for treatment down hole in high temperature production wells. The second type of inhibitor prevents calcite and aragonite seeds from agglomerating to form a scale, by wrapping around them. phosphonic, acrylic, and maleic acid derivatives have been employed as these types of inhibitors. To increase their temperature resistance these inhibitors are usually used in a polymeric form. Temperature resistance is important, as it allows inhibitors to be employed down hole in production wells. Together with the aforementioned pressure control, this CIS technology proves effective in preventing calcite scaling (Wanner 2017, Cosmo 2022, Brown 1985, Gunnlaugsson 2014). Typical levels of CIS dosing depend on the amount of calcium carbonate present but are on the order of 0.5 to 3 ppm.

1.5 Antimony and Arsenic Scales

Under certain pH and redox conditions (neutral/slightly reducing), sulfides of arsenic (e. g. orpiment) and antimony (e. g. stibnite – Figure 1) are formed (Gill et al, 2013). These scales are very hard and toxic. Their handling and removal require special care. Orpiment and stibnite scaling were observed in the geothermal plant equipment at the Kawerau site. The yellow orpiment interferred the colorimetric molybdate analysis for silica (Borrmann et al 2023). In the typical silica analysis, molybdate forms a series of yellow complexes with silica. The molybdenum blue method was used iunstead (Webster 1990, Krupp 1988, Wilson 2007).

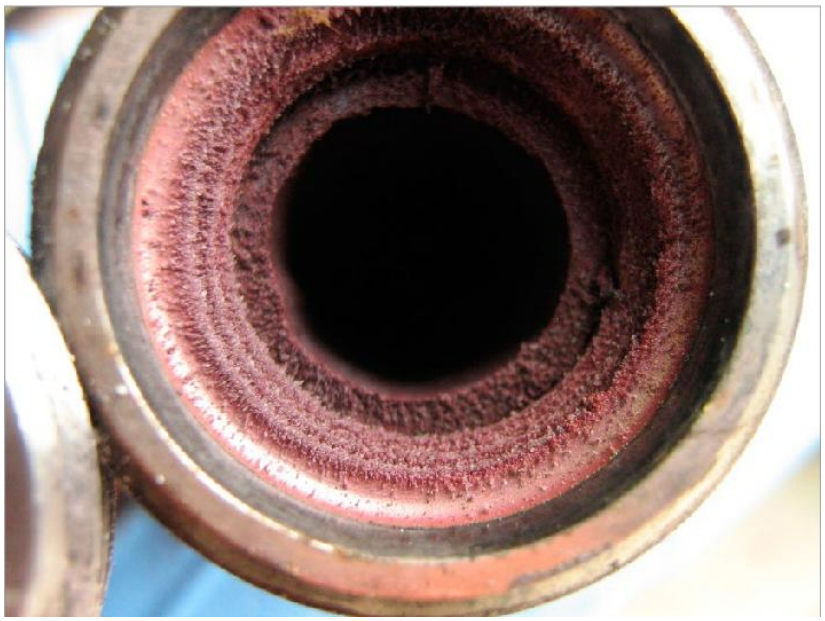


Figure 1: End coupling of a heat exchanger reproduced with permission from Gill et al, 2013.

2 CASIL TECHNOLOGY AND ITS EFFECT ON PH, AND SSI, STIBNITE AND ORPIMENT SCALING

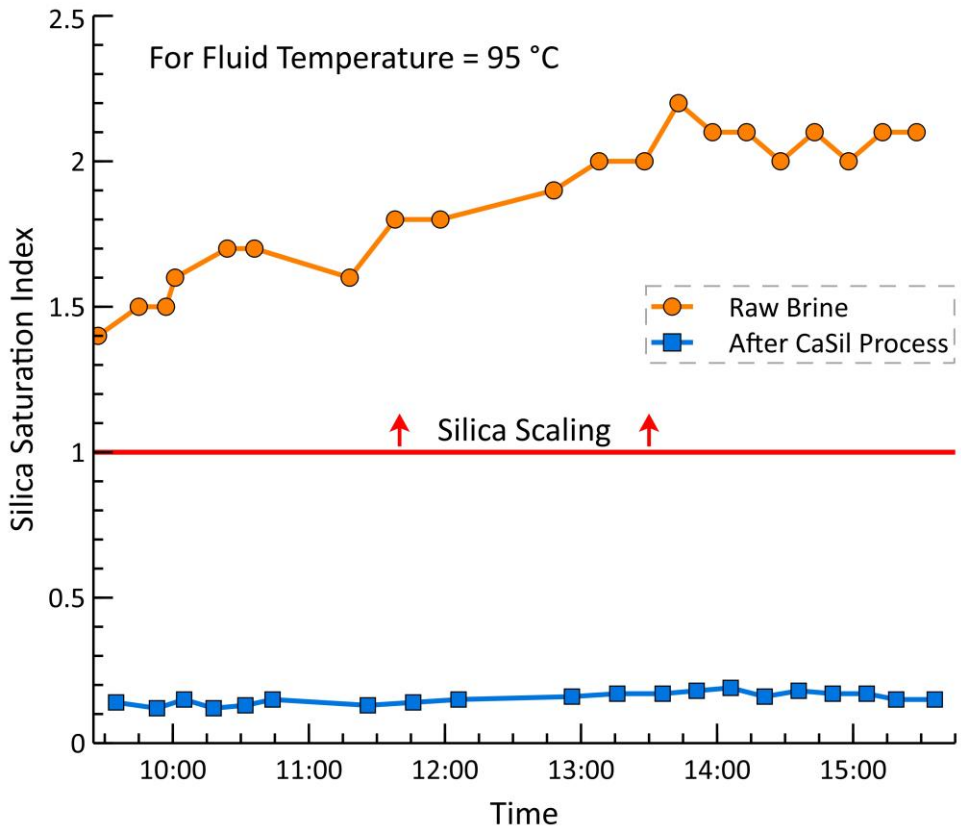


Figure 2: SSI of untreated raw brine and CaSil treated fluid over the course of a day at the Tauhara site.

As detailed above, the CaSil technology eliminates silica scaling through the transformation of dissolved silica species in the geothermal brine to a calcium silicate hydrate material thjat is separated as a useful product. The process provides a treated brine that is undersaturated in silica. The Silica Saturation Index, SSI, is reduced significantly from values much greater than 1 to values less than 1. A consequence of the process is that the pH of the treated brine is increased to pH values between 8.3 and 10.7. Figure 2 (Schweig et al 2023) shows the SSI of the untreated brine and the CaSil technology treated brine for the pilot plant operation at the Tauhara geothermal site over a 7 hour timeframe. The data show also that although the silica content and SSI of the untreated brine varied over the course of these measurements, the SSI value of the brine treated by the CaSil technology was reduced to a SSI=0.15-0.25 by the CaSil technology and was essentially constant. This demonstrates the chemical robustness of the technology.

This increas in pH of the treated brine also affects the solubility of orpiment and stibnite in the brine in an advantageous way.

Orpiment and stibnite form in neutral and acidic environments in the presence of hydrogen sulfide (02, 93)

$$2\ H_3\mathrm{AsO}_3 + 3\ H_2S \underset{\leftarrow}{\rightarrow} As_2S_3 + 6\ H_2O \quad (02)$$

$$2\ H_3\mathrm{SbO}_3 + 3\ H_2S \underset{\leftarrow}{\rightarrow} Sb_2S_3 + 6\ H_2O \quad (03)$$

For Orpiment a complex system of equilibria (04 to 07) with various thioarsenites depending on sulfur levels and pH is present:

$$As_2S_3 + 3\ OH^- + H_2O \underset{\leftarrow}{\rightarrow} 2\ As(OH)_2S^- + HS^- \quad (04)$$

$$As_2S_3 + SH^- + 3\ OH^- \underset{\leftarrow}{\rightarrow} 2\ As(OH)S_2^{2-} + H_2O \quad (05)$$

$$As_2S_3 + 3\ SH^- + OH^- \underset{\leftarrow}{\rightarrow} 2\ HAsS_3^{2-} + H_2O \quad (06)$$

$$As_2S_3 + 5\ SH^- + 3\ H_2O \underset{\leftarrow}{\rightarrow} 2\ As(SH)_4^- + 3\ OH^- \quad (07)$$

The common representation of these equilibria involves the release of protons. However, in the increase on pH in the CaSil technology treated brine to 8.5 and 10 provides considerably more hydroxide ions compared to protons in the treated brine. Accordingly, the equations based on work by Webster (1990) have been modified to represent this alkaline environment. If oxygen is present, dissolved hydrogen sulfide ions (sulfur), are partially or fully oxidised to sulfhate and arsenic exists as arsenite or arsenate species depending on the redox environment. Orpiment (As_2S_3) has a low solubility (K_{SP} about 10^{-25}) under neutral and slightly acidic conditions (meaning that up to pH 6.45 only 1 to 3 ppm of As are soluble). More arsenic is soluble at elevated temperatures. Orpiment scales occur in the cooler sections of power plants, after flash steps, in heat exchangers and pipes. At a pH of 7 the solubility increases significntly to 41 ppm As in the absence of sulfur due to the formation of arsenite. In the presence of sulfide, As solubility can be up to 1400 ppm under alkaline conditions.

This was observed during our work in Kawerau. Orpiment was only present in acidified samples, as seen via orpiment's distinctly yellow colouration.

Stibnite follows a very similar behaviour to orpiment, except that the hydroxothio compounds appear at lower pH values and can be part of stibnite deposits. Antimony sulfides also tend to form dimers and even polymers making stibnite scales difficult to remove. As with orpiment, sulfur plays an important role in the speciation of the antimony compounds. The equilibrium (08) between hydrogen sulfide and hydrosulfide is important:

$$H_2S + OH^- \underset{\leftarrow}{\rightarrow} HS^- + H_2O \quad pK_A = 6.88 \quad (08)$$

The pK_A of 6.88 (depending on the temperature shifted to 7 and above) means that at a pH value of about 10, greater amounts (>99.9%) of sulfur will be in the form of hydrosulfide. As this ionic species is incorporated in stibnites, they form soluble ionic forms. While dark grey stibnite deposits were observed at the site in Kawerau, there was no trace of stibnite observed in the CaSil process.

Overall, the elevated pH caused by the increase in alkalinity by the CaSil technology treatment, can likely eliminate orpiment and stibnite scale formation as well, along with the significant reduction in the SSI of the treated geothermal brine. As aluminate, iron and other metal silicates are captured in CaSil, the CaSil technology desirably addresses and reduces these five forms of scaling in one process.

3 CASIL TECHNOLOGY AND CALCIUM CARBONATE SCALING

Calcite scaling however typically occurs prior to the CaSil technology treatment. Once the CaSil product has formed, calcite and aragonite can be incorporasted onto the surface or within the CaSil particles and are recovered along with CaSil as an impurity in the product. Calcite scale inhibitors (CIS), described earlier, at usually injected into the high temperature and pressure 2-phase brine flow in the production well before the steam/water flashing process.

In a prior publication, we have studied the impact of a calcite inhibitor (CIS) on analysis methods and the CaSil treatment (Borrmenn et al 2025). We found that at typical dosing levels (≤1 ppm), CIS (in this case a polyacrylate) showed within the margin of error, that ther was no interference with the silica analysis using the UV-Visible spectroscopic colourimetric molybdate method. Only at totally unrealistically high concentrations (2000 ppm) did the CIS show any interference effects. For the atomic absorption spectroscopy (AAS), no significant effect of CIS on silica or calcium standard measurements was observed as CIS compound breaks down in the AAS flame.

As many geothermal field operations use calcite inhibitors, it was important to investigqte any effect of the CIS agent on the CaSil technology Further, we researched the impact of CIS on the CaSil technology process chemistry and the CaSil product. This work was carried out at pilot plane scale opersation at the Tauhara field. The results sowed that dosing the CIS agent up to levels of 9 ppm did not significantly impact the CaSil technology process chemistry (Figure 3). This dosing range considerably exceeds that typically used (1-3 ppm) in geothermal operations . Figure 3 shows that the addition of the CIS agent did not affect the silica content in the untresated brine. Also that the CaSil technology still worked very effectively at the the typical process chemistry treatment conditions by reducing the silica content of the treated brine to about 300 ppm. With the treastment the silica concentration was reduced to a level of about SSI=1.

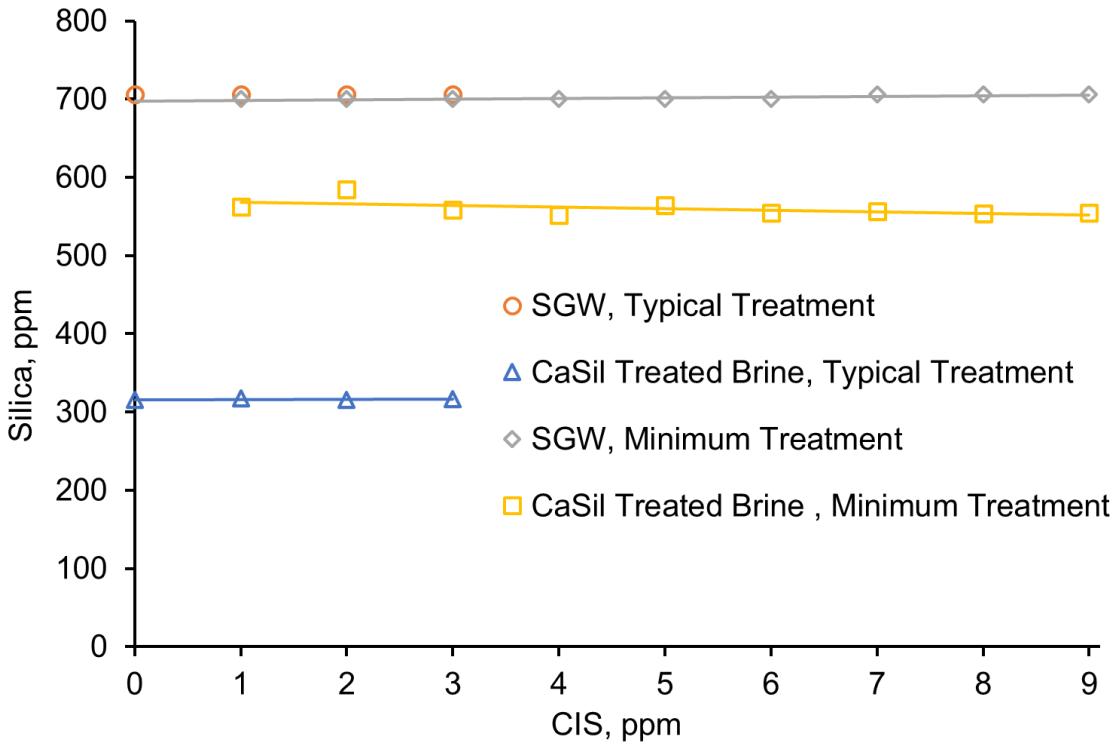


Figure 3: Silica levels in untreated brine aka SGW (separated geothermal water) and CaSil technology treated brine.

A slight decrease in silica levels was observed with higher CIS, but values remained within measurement errors.

The CaSil product recovered from the CaSil technology treated brine prior to reinjection was characterised by scanning electronmicroscopy (SEM) and X-ray powder diffraction (XRD) methods. The SEM images showed no morphological differences between the particles produced with 1 and 9 ppm CIS, the outer levels of CIS treatment used. The XRD patterns showed a small reduction in the amount of crystalline carbonate present in the CaSil product suggesting a potentially synergistic benefit of using the CIS.

CONCLUSIONS

The CaSil technology is based on a silica chemical reaction that captures and removes reactive silica species from the geothermal brine by rapidly transforming them into a calcium silicate hydrate (CaSil) product, thereby reliably preventing silica scaling. As such it can also remove iron, aluminium and other bivalent and trivalent ionic species by capturing them in the CaSil material, similarly preventing them from forming scale deposits. The CaSil technology process chamistry increases the pH of the treated brine, typically to a pH of 8.5 to 10. At these pH values, orpiment and stibnite scales do not form, as arsenic and antimony species are fully soluble in this pH region. The CaSil technology does not address calcite scaling but this can be effectively suppressed using calcite scale inhibitors (CIS).

CIS inhibitors and the CaSil technology can be used together without interference in silica analysis or treatment. CIS may even improve CaSil product purity by reducing the amount of calcium carbonate captured in the CaSil particles.. Their combined use of these two treatment processes offers enhanced prevention of silica scaling together with stibnite, orpiment, calcite scaling, thereby improving the overall heat energy extraction and electricity generation efficiency of geothermal resource utilisation.

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