MECHANISM AND KINETICS OF CASIL PRECIPITATION

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ABSTRACT

Silica formation is a problem in geothermal power generation from wet steam resources, especially in binary plants. Our proprietary method has been successfully proven in removing silica by forming nano-structured calcium silicate hydrate (CaSil) at pilot plant scale. CaSil particles do not adhere to pipes and can be removed prior to re-injection to provide a useful product.

The CaSil process has shown to be effective in our pilot plant located at the MB Century site and sourcing brine from the Wairakei binary cycle power plant, Taupo, New Zealand. If this process is to be applied widely, the kinetics and mechanism of the CaSil precipitation need to be fully understood to optimise the process for different brine compositions and recovery procedures.

The precipitation reaction of our proprietary CaSil is facile and difficult to monitor, as there is no consistent accompanying pH or colour change. Using batch methods and filtration, combined with AAS, UV-Vis spectrophotometry and SEM, we investigated the Ca to Si ratio in the filter cake product and residual filtrate generated from reaction mixtures using different SiO_2 and Ca concentrations, different Ca to Si ratios and being produced at different temperatures.

Our results so far showed that the CaSil forming reaction is robust and leads to useful and recoverable products under a variety of different synthesis parameters. CaSil precipitation is preferred over SiO_2 formation in most typical plant operating ranges therefore it provides a proprietary way of capturing dissolved silica species before a problematic silica deposition can take place.

1. INTRODUCTION

The formation of intractable silica scale in the pipework, equipment and reinjection well of geothermal plants utilizing wet steam resources can decrease power output and increase maintenance cost of geothermal power generation (Thorhallsson, 2011). Several methods of managing silica scaling have been trialed but all of them have major drawbacks. Acid and chemical dosing usually only delay scale formation and tend to increase corrosion issues (Gunnarsson and Arnórsson, 2005). Higher exit temperature in heat exchangers of binary plants reduce the amount of heat energy that can be utilized.

The proprietary approach developed by our group avoid these problems (Borrmann et al., 2018). In general, a calcium-containing slurry is added in-situ to geothermal brine. Our research has shown that the CaSil particles do not aggregate or adhere to metal surfaces as silica particles do. (Johnston et. al., 2018, 2019; Borrmann et. al, 2018, Schweig et. al., 2018). This proprietary approach was developed on a laboratory scale using synthetic and natural geothermal brine. Following this, a pilot plant was designed, constructed, commissioned and operated using the brine from the Wairakei power plant in Taupo, New Zealand. Detailed information on the pilot plant and its operation will be presented in two papers by Schweig et. al. (2019) and Borrmann et. al. (2019). In two other papers, Johnston et. al. (2019) will provide an overview of the project, the CaSil technology and CaSil uses, while Cairns et. al. (2019) will discuss some of the application of our CaSil products.

Our research and operational experience have shown that as expected, the nature of the reaction to form the CaSil material is complex and an overview of our research in this area is presented here. Most of the information is proprietary so only a general approach can be provided. The CaSil formation reaction is relatively rapid and measuring its kinetics is a challenge. The reaction process is hard to follow by a change of color, pH, or temperature, so using an in-line detection method to determine the extent of the reaction is not feasible. We utilized a careful batch process approach under different conditions, analyzing both the filter cake and filtrate produced at different times as the reaction proceeded to provide the information we need.

2. METHODS

In a typical batch reaction, calcium containing slurries were added quickly in a plastic beaker containing a sodium silicate solution as a model geothermal water. The pH was adjusted to the required value, and temperatures of 50°C and 70°C and dissolved silica concentrations of 600 and 1200 ppm SiO_2 were used. The Ca to Si mol ratios were maintained at 0.6 or 0.8 (ref Borrmann and Johnston paper). The reaction was stopped at different time intervals (10 s, 20 s, 1 minute and 5 minutes) and the CaSil product separated by vacuum filtration. The filter cake was washed prior to being dried in an oven at 120°C overnight. The filtrate was acidified to stop any further reaction. The amount of Ca and Si in the filtrate was analyzed using atomic absorption spectroscopy (AAS) and UV-Vis spectroscopy (molybdate method). The filter cake was characterized by field emission scanning electron microscopy (SEM, JEOL SEM-6500F) and the Ca and Si contents determined by energy dispersion spectroscopy (EDS).

3. RESULTS

3.1 The effect of time and temperature on the residual SiO_2 content of the model geothermal water

An important feature of the CaSil treatment is the consequent reduction in the dissolved (unreacted) SiO_2 level in the model geothermal water and the lowering of the silica saturation index. This prevents unwanted silica precipitation and the formation of intractable silica sinter deposits. We monitored the silica concentration in the water and extent of CaSil formation at four different time intervals as the CaSil formation reaction proceeded: 10 s, 20s, 1 minutes and 5 minutes. These intervals were chosen as they represent particular residence times at various key stages in our pilot plant operation. Figure 1 shows that overall, the concentration of problematic unreacted dissolved SiO_2 in the water decreased over time by an appreciable amount. A comparison of the data presented in Figure 1 shows that as more dissolved SiO_2 is removed, the unreacted silica concentration is reduced from the water, resulting to a higher Ca to Si ratio and formation of more CaSil particles.

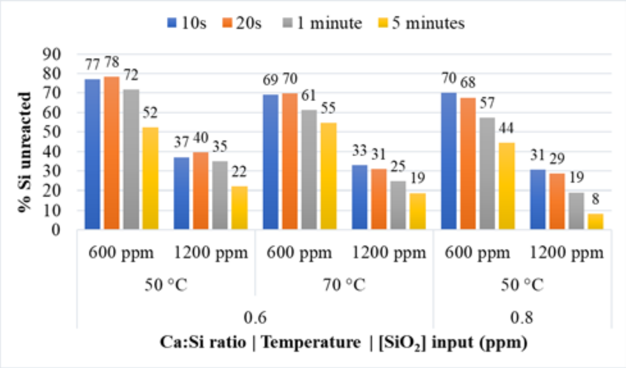

Figure 1. Percentage of unreacted SiO_2 in the model geothermal water after different time intervals.

Figure 1 also shows that the effect of temperature on the CaSil reaction. At 600 ppm SiO_2 for a 0.6 Ca to Si ratio, more of the dissolved silica reacts to form CaSil when the temperature is increased from 50 °C to 70 °C. Essentially a 10% reduction in unreacted silica at higher temperature of 70°C compared to 50 °C. At the higher Ca to Si ratio of 0.8 the data at 50 °C shows more dissolved SiO_2 is removed as CaSil for both 600 ppm and 1200 ppm SiO_2 containing waters. Hence as expected, the ratio of Ca to Si determines the amount of unreacted SiO_2 remaining in the treated water. Higher Ca to Si ratios resulted in lower unreacted SiO_2 concentrations (Borrmann et al, 2009).

Figure 2 shows the average concentration of unreacted SiO_2 at 5 minutes for 600 ppm and 1200 ppm concentrations of SiO_2 for 0.6, 0.8 and 1.2 Ca to Si ratios at 50 °C and 0.6 ratio at 70 °C. This data confirms a greater amount of dissolved SiO_2 is removed with increased temperature, higher Ca to Si ratio, and higher dissolved SiO_2 concentration. This can be attributed to the agglomeration behavior of CaSil (Schweig et al, 2018).

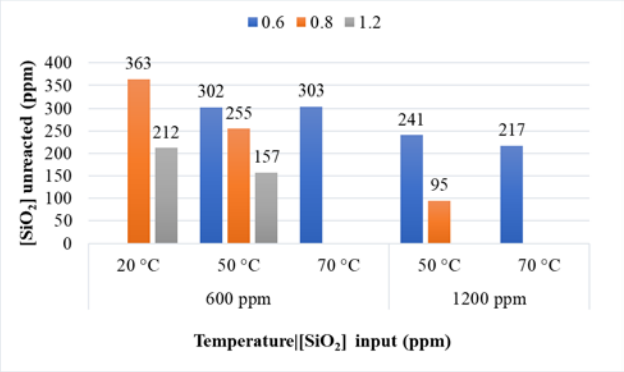

Figure 2. Unreacted SiO_2 based on different SiO_2 source concentrations, temperature and Ca to Si ratios after 5 minutes reaction time

A set of reactions involving low concentrations of SiO_2 were conducted at 70 °C (Figure 3). These experiments showed that at lower concentrations, only a small amount of silica is being removed even after 10 minutes. This suggests that CaSil technology requires a certain concentration of silica in the brine to work.

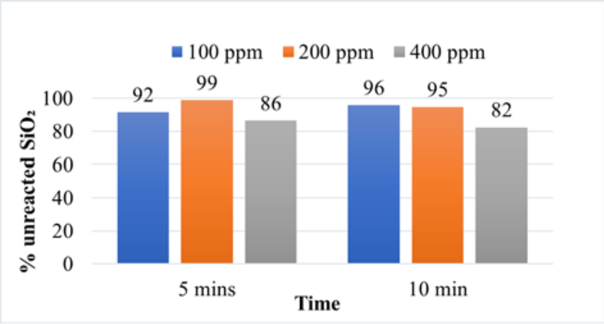

Figure 3. Percentage of unreacted SiO_2 in low SiO_2 input.

SEM images (Figure 4) from a series of batch reactions (1200 ppm SiO_2 input, 0.8 ratio, 50 °C) indicated that the formation of CaSil is immediate. The CaSil flocs could be seen forming immediately (a). At first CaSil occurs in cauliflower-like shapes and as time progressed, the open-framed desert rose could be observed (d). Two intermediate states showing the progression of the particle development are depicted in b) and c). The EDS ratio between Ca and Si on these four images are relatively constant at 0.71, suggesting that particles undergo surface transformation to a more open framework as the reaction progresses. This suggested a two-step process. The first one occurred faster than the first sample could be recovered (faster than 10 s). During the first step CaSil is formed, while the second step is more of a re-organization and gradual morphological change, as the ratio of Ca to Si stabilized.

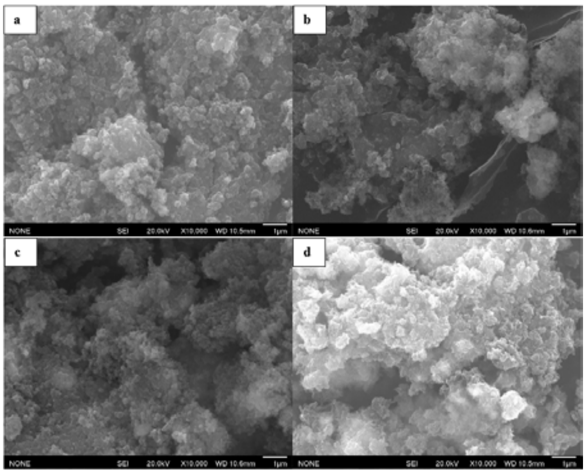

Figure 4. SEM images of a series of batch reaction over time: 1200 ppm input, 0.8 ratio, 50 °C. a: at 10 s, b: at 20s, c: at 1 minutes, and d: at 5 minutes. For all of these images the ratio of Ca to Si according to EDS is 0.71

4. CONCLUSIONS: IMPLICATION FOR SCALING ISSUES IN GEOTHERMAL POWER GENERATION

For water dominated geothermal power generation systems, one of the important parameters monitored to assess the silica scaling potential of geothermal brine is the silica saturation index (SSI). Saturation index values of less than 1.1 are considered manageable, but values lower than 1.0 would be ideal. The SSI is defined as the ratio between the dissolved silica concentration in brine and the solubility of amorphous silica at the relevant temperature and pH condition. The solubility of amorphous silica is determined from these two equations:

$$\log K_1 = -\frac{2549}{T} - 15.36\ \times 10^{-6} T^2$$

$$S = C \times \left[1 + \left(\frac{10^{pH} \times K_1}{\gamma_{(H_3SiO_4^-)}}\right)\right]$$

Where

S= solubility of amorphous silica in ppm
C= solubility of quartz in ppm
K_1= dissociation constant
T= temperature (K)
$\gamma(H_3SiO_4^-)$ = activity coefficient of $H_3SiO_4^-$.

Based on this formula, at 90°C and pH of 10 (the typical pH after CaSil formation) the SSI for a 400 ppm SiO_2 solution is 0.11. The temperature can be lowered to 70°C, with an increase in SSI to 0.21 indicating that the temperature can be lowered even further. The SSI shows that using our proprietary CaSil technology, the dissolved silica content will be low enough that silica scale formation will not be an issue. Furthermore, the energy that can be recovered by lowering the brine temperature means increased output for power generation (Johnston et. al., 2017, 2018)

It was noted that the pH of the slurries containing CaSil changed. The change did not allow monitoring of the CaSil formation reaction, as it appeared to be independent of the silica content and calcium to silicon ratio. However, it was further noted from the literature that the pH value has a significant effect on the SSI (see above, Brown, 2011). However, the effect of this change was not investigated as part of this study and will be highlighted in future research.

This study showed that the CaSil technology is robust, and the process is tolerant to fluctuation of SiO_2 content, Ca to Si ratio, and temperature. Although the precise mechanism and kinetics are still to be to be established, a general idea of how CaSil form and the facileness of the reaction can be established.

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