

Assessing silica precipitation using calcium hydroxide addition on Dieng's geothermal brine

A D P Putera^{1,2,*}, A Wiranda², S Mergiana², I Perdana² and M Olvianas²

¹Department of Engineering Science, The University of Auckland, Private Bag 92019, Auckland, New Zealand

²Department of Chemical Engineering, Universitas Gadjah Mada, Grafika 2, Bulaksumur, Yogyakarta 55281, Indonesia

*Corresponding author: Email: aput932@aucklanduni.ac.nz

Abstract. Geothermal is one of the most reliable energy sources in Indonesia. The utilization of geothermal energy in the electricity generation provides green energy, as it can slow down the global warming and help control the climate change. However, the development of its capacity is still considerably slow. One of the most common problems encountered in geothermal power plants is silica scaling. This limits energy production by inhibiting the mass flow of the geothermal fluid and also adding resistance to the heat transfer. This study focuses on the silica precipitation of geothermal fluid using the addition of calcium hydroxide ($\text{Ca}(\text{OH})_2$) in a continuous reactor. The experiment was conducted by varying the reaction times of 5.00 and 8.33 minutes; reaction temperatures of 30 and 70°C; and pH levels of 7 and 9. The silica concentration of the initial and processed fluids was analyzed using UV-Vis Spectrophotometry. The observed silica concentration of the initial fluid was 600 ppm, with the best concentration at 150 ppm (25%) under 5 minutes reaction time, 70°C of reaction temperature, and pH of 9. Significance analysis showed that the silica concentration in the fluid is decreased when pH is increased, but with a shorter time of reaction. In addition, pH has a significant effect on the silica precipitation, while temperature and reaction time are much less significant.

1. Introduction

Geothermal is one of the most reliable energy sources in Indonesia. With around 28,000 MW of predicted potential, Indonesia possesses about 40% of the total geothermal energy resource in the world [1]. The geothermal energy has the least gas pollution emitted from its power plant compared to coal, oil, and gas energy sources. Geothermal power plants only emit about 27.2 kg of CO_2 per MWh and almost zero SO_2 and NO_x while normally coal-fired power plants emit about 994, 4.71, and 1.955 kg/MWh of CO_2 , SO_2 , and NO_x respectively [2]. Albeit slow, the growth capacity of geothermal utilization in Indonesia is steady. In 2014, Indonesia generated 1,385.1 MW of electricity from the geothermal source [2], while in May 2018, the installed capacity of a geothermal power plant in Indonesia reached 1,924.5 MW [3].



However, there are still hurdles to be faced in increasing the capacity of geothermal power plants in Indonesia. Among the many obstacles, operation and maintenance costs cannot be ignored as they will consume about 1.79C kW^{-1} [4]. The O&M costs include the renovation of the apparatuses, such as the piping and heat exchanger. There are two main causes of piping problems in a geothermal power plant: (1) corrosion and (2) silica scaling.

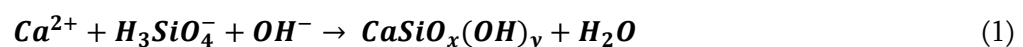
Silica scaling usually occurs when the concentration of amorphous silica exceeds its solubility. Several operational problems and even clogging in the heat exchanger, piping, and injection drill holes can occur because of silica deposits in the geothermal fluid. A great deal of research has been carried out to study the prevention of silica scaling. Gunnarsson and Arnórsson (2005) found that the rate of silica scale formation can be significantly decreased by changing the monomeric form of the silica into a polymeric form [5]. Pambudi et al. (2015) found that acidification of the geothermal brine can reduce the silica precipitation rate [6]. Santiago and Pajarito (2016) also studied the silica precipitation of geothermal brine using NaOH at different temperatures and reaction times in a batch reaction. The study shows that the concentration of NaOH significantly affects the yield of silica precipitated [7].

However, there is still a lack of research that discusses the treatment of geothermal brine in a continuous cooling pond. Therefore, this research focuses its attention on the potential of calcium hydroxide ($\text{Ca}(\text{OH})_2$) as a reactant in forming calcium silicate (Ca_2SiO_4) from Dieng's geothermal brine in various pH, temperature, and reaction time in a continuous model.

2. Experiment

2.1. Literature Review and Theory

Silica in an amorphous form is the main cause of silica scaling and is more reactive than that of its crystalline form. A lower bonding energy between the amorphous silica molecule and a larger specific surface are the main reason for this characteristic [8]. As the first step of the scaling process, the geothermal brine will reach a supersaturated condition of amorphous silica in the solution. The precipitation process begins. However, silica scaling can be avoided by a new method which converts soluble silica into calcium silicate. This technology was later known as Nano-Structured Calcium Silicate or NCS. The synthesis reaction of the NCS is shown in the equation (1) below [9].



Furthermore, Johnston et al. (2007) stated that when mixing the reactants, the NCS precipitates quickly. Therefore, the NCS synthesis can be applied in the cooling pond as it will quicken the precipitation rate.

2.2. Procedures

2.2.1. Standard calibration curve for spectrophotometry analysis. As much as 1000 mg of amorphous silica powder was dissolved in 1 L of aquadest (1000 ppm). The solution was then diluted with water to create 900, 800, 700, 600, 500, 400, 300, 200, 100, 75, 50, and 25 ppm amorphous silica solutions. In this work, the silica concentration was analyzed using a UV Vis Spectrophotometer. However, the silica cannot be detected directly from the solution using the spectrophotometer. The

solution needs to be acidified until the pH reaches 2 or below, and yellow molybdate is used as the reagent [10]. In this study, H₂SO₄ 96% is used to acidify the solution.

As much as 1 mL samples were diluted in 100 mL of water along with 100 ppm of 205 μ L reagent. The H₂SO₄ was added gradually until the target pH was obtained. After 5 minutes, the samples were put into a cuvette and were analyzed using the UV-Vis Spectrophotometer at a wavelength of 407 nm [11]. A Vernier SpectroVis Plus Spectrophotometer (SVIS-PL) was used in this work. This instrument is connected to a personal computer with LoggerPro® software installed in it. The result is provided in Figure 1. below.

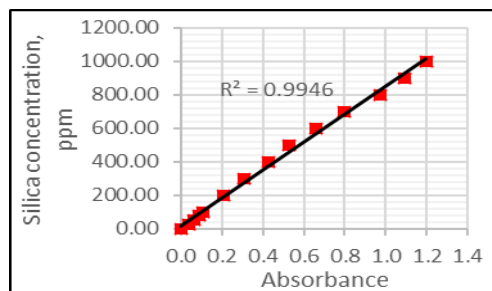


Figure 1. A standard curve of absorbance versus silica concentration.

Using the linear trendline, provided by Microsoft Excel, the equation for the standard curve is:

$$S = 834.75A + 16.595 \quad (2)$$

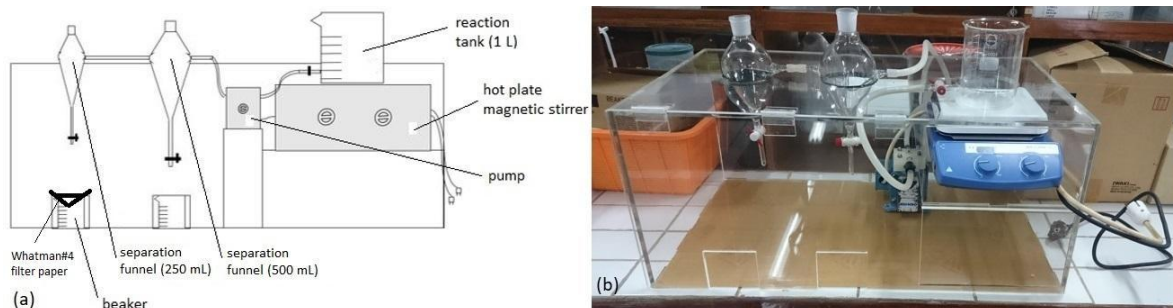
Where S is the amorphous silica concentration in ppm and A is the absorbance result of the liquid.

2.2.2. NCS Synthesis and Precipitation. As much as 25 liters of geothermal brine sample was collected from PT. Geo Dipa Energi, Dieng, Jawa Tengah Indonesia, using plastic drum containers. As much as 700 mL of geothermal brine is inserted into the reaction tank. The magnetic stirrer is set at 300 rpm and the certain temperature as mentioned in table 1 is set. The addition of Ca(OH)₂ powder began when the target temperature is reached. After the desired pH of the solution is reached, the addition of Ca(OH)₂ is stopped and the pump is turned on. The pH target, temperature, and reaction time of this experiment are provided in Table 1.

The calcium silicate will precipitate in the first separation funnel, and the clear solution from the second separation funnel is collected. The fluid is also filtered using Whatman #41 filter paper to ensure that there are no solids in the clear solution. The silica concentration from this liquid will be analyzed using the same method in point 2.2.1 to calculate the silica concentration of the liquid from each run.

Table 1. 2³ full factorial design for geothermal silica precipitation.

Run Label	Time, minutes	Temperature, °C	pH
ABC	8.33	70	9
AB	8.33	70	7
AC	8.33	30	9
A	8.33	30	7
BC	5.00	70	9
B	5.00	70	7
C	5.00	30	9
I	5.00	30	7

**Figure 2.** (a) Schematics of the experimental apparatus and (b) photograph of the apparatus

3. Results and Discussion

3.1. Silica concentration

The initial condition of the mother liquor emits an absorbance point of 0.7. Therefore, the initial silica concentration is 600 ppm. On the other hand, with the same calculation method, the silica concentration of the processed samples is presented in Figure 3. The lowest silica concentration obtained was by run BC (5.00 minutes, 70°C, pH 9) while the highest obtained was by run AB (8.33 minutes, 70°C, pH 7). A lower silica concentration in the fluid represents a good result because there was more silica precipitated from the initial liquid.

Figure 4. presents the main effect of each factor on the silica concentration of the processed geothermal brine. The results show that pH has the most significant effect on the precipitation of the silica in the geothermal brine. In addition, at higher pH condition, there is more silica precipitated from the geothermal brine. This result is in agreement with the study of Santiago and Pajarito [7]. On the other hand, temperature has almost no effect on the observed result. However, longer reaction time yields higher silica concentration in the fluid.

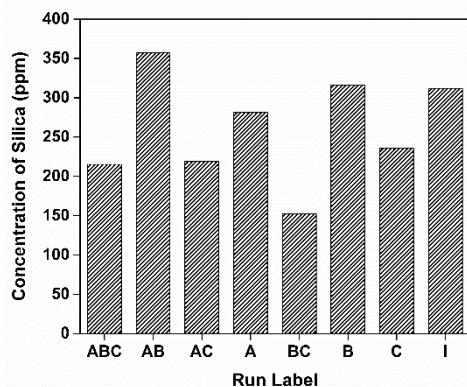


Figure 3. Silica concentration of processed geothermal brine for each run.

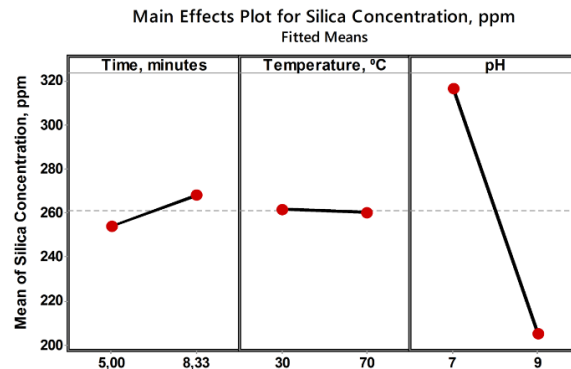


Figure 4. Main effects of factors on the silica concentration of the processed geothermal brine.

4. Conclusions

In this research, a full two-level factorial design is proven to be effective and valid in determining the most significant variable affecting the precipitation of calcium silicate from a geothermal brine using $\text{Ca}(\text{OH})_2$. The pH of the solution greatly affects the precipitation. At a higher pH condition, there is more silica precipitated from the geothermal brine. Temperature shows almost no significant effect on the observed result. On the other hand, longer reaction times yield higher silica concentration in the processed fluid. With the effort to make geothermal energy becomes a more efficient power source, it is expected that geothermal energy, as a pioneer of the green energy industry in Indonesia, has a better prospect in the future.

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