

PRELIMINARY KINETIC STUDY ON ROCK-FLUID INTERACTION OF THE ENHANCED GEOTHERMAL SYSTEMS IN COOPER BASIN, SOUTH AUSTRALIA

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Keywords: *Kinetic study, granite dissolution, rock-fluid interaction, enhanced geothermal system.*

ABSTRACT

Kinetic studies on the interactions between rock and circulating fluid are essential for determination of the chemical changes and mineral alteration in geothermal systems. Preliminary mineralogical investigation and geothermal experiments have been performed to investigate the dissolution of granites from Habanero 3 well (Cooper Basin, South Australia). Samples of drill cutting from a borehole 5 km deep were reacted with pure water in autoclaves (no mixing) at 120°C, 140°C, 160°C, 170°C, 200°C, and 220°C for 56 days. Drill cuttings were also used for rock-water interaction experiments in a titanium flow through geothermal cell at 250°C at saturated vapor pressure (35 bar). Fluid and rock samples were analyzed prior to and after circulating the water through the crushed sample of the rock (diameter: 100-200 μ m) for 1, 3, 5, 10, 17 and 28 days. Water analyses were undertaken using ICP-MS to determine the cation concentrations, silicomolybdate method using HACH spectrophotometer to determine the reactive silica or silicic acid (H_4SiO_4) concentrations, and ICP-OES to determine the total dissolved silica (SiO_2) concentration. Experimental results showed that the silica concentration is 320ppm after 28 days interaction in the flow-through cell, which is quite low, compared to the literature. However, this deviation may be due to the increasing of other dissolved species which reduce the solubility of the silica over time. Another variable investigated was the dissolution rate constant. The dissolution rate constant obtained was lower than the literature since this study was performed in the absence of mixing.

1. INTRODUCTION

1.1 Overview

Geothermal energy (heat mining) is seen as a potential alternative energy resource by the Australian government. This is due to the vast amount of high temperature thermal area (>250°C) discovered in Australia. Figure 1 shows Australia's geological temperature at various depths. This study focuses on the geothermal system in Copper Basin which is located in the northern part of South Australia.

The geothermal system mentioned above is an enhanced geothermal system (EGS) or hot fractured rock (HFR) system, where the heat exchange occurs in the reservoir at great depth (approx. 5km) and the thermal energy source is radioactive decay rather than volcanism (Geodynamics, 2009).

Existing reservoir granites are currently in equilibrium with the surrounding ground water, and injection and reinjection

of fresh water to extract the thermal energy will alter this fluid-rock natural equilibrium.

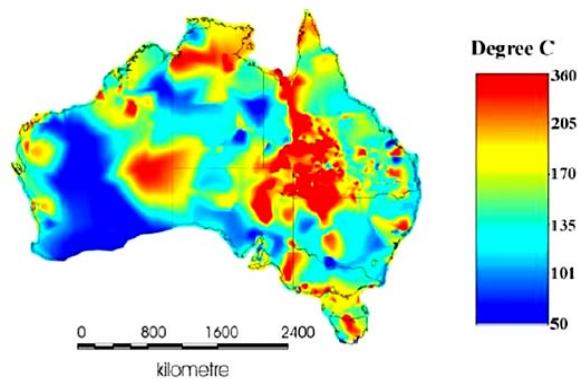


Figure 1: Australia's geological temperature at various depths (Chopra and Holgate, 2005).

This alteration may cause partial chemical dissolution which may potentially lead to the increase of dissolved solids such as silica and other metals in the water. These dissolution products of the components have different equilibria, which is highly dependent on temperature and pressure. Thus, precipitation or scaling of pipes and closures of fractures in the granite body are possible. The saturation of metals in fluid is volume-dependent, where very small volumes of fluid may require slight under-cooling before precipitation occurs. Therefore, characterization of fluid geochemistry is crucial in evaluating the performance of geothermal systems (Grigsby et al., 1989). Furthermore, understanding the chemical interactions due to fluid injections into hot granite is critical for problems concerning precipitation that leads to clogging, and heat loss caused by dissolution (Azaroual and Fouillac, 1997).

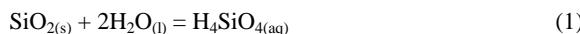
The study of fluid-rock interaction will enable the determination of mineral alteration and dissolution of minerals. There have been a number of fluid-rock interaction studies carried out (Ellis, 1968; Rimstidt and Barnes, 1980; Robinson, 1982; Posey-Dowty et al., 1986; Savage et al., 1987; Grigsby et al., 1989; Dove and Crerar, 1990; Savage et al., 1992; Azaroual and Fouillac, 1997; Durst and Vuatas, 2000; Icenhower and Dove, 2000; Gianelli and Grassi, 2001; Burton, et al., 2004; Yanagisawa et al., 2005; Tarcan et al., 2005; Castro et al., 2006; Pfingsten, W. et al., 2006; Nami et al., 2008; Marks et al., 2010), although these may not be directly applicable to the hot granite-based geothermal system in the Cooper Basin. To date, there are a number of geochemical modeling codes and

thermodynamics data bases available and being improved to predict equilibrium conditions and dissolution-precipitation rates (TOUGH-REACT, EQ3/6, SOLVEQ-CHILLER, SOLMINEQ, Geochemist Workbench, etc).

1.2 Kinetics of silica dissolution in water

Since silicate minerals are found abundantly in most of geothermal reservoirs, the study of dissolution of silica in water is important in characterizing geothermal systems. The kinetics of quartz dissolution has been studied by many researchers (Van Lier et al., 1960; Morey et al., 1962; Fournier and Rowe, 1977; Rimstidt and Barnes, 1980; Robinson, 1982; Worley, 1994; Schott and Oelkers, 1994; Rimstidt, 1997; Brantley et al., 2008; and many more).

The silica-water reaction is a simple surface reaction to form silicic acid monomer, for quartz:



The above reaction (1) is temperature dependent. The equilibrium concentration of quartz at a particular temperature obeys the following equation, valid for 0-250°C at saturated vapor pressure (Brown, 2011):

$$\log C = -1309/T + 5.19 \quad (2)$$

where C is the silica concentration in mg/kg and T is the absolute temperature in Kelvin.

According to Robinson (1982), the rate of dissolution follows the following reaction:

$$\frac{dc}{dt} = ka^*(C^\infty - C) \quad (3)$$

where C is the concentration of silicic acid (mg/kg), t is time (s), k is the kinetic rate constant for dissolution, $a^* = S/V$ = ratio of quartz surface area to fluid volume (m^{-1}), and C^∞ is the equilibrium concentration of dissolved silica (mg/kg). Figure 2 shows a generic profile of dissolution concentration versus time response.

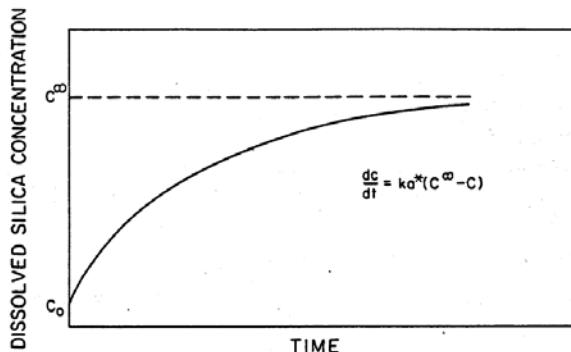


Figure 2: Quartz dissolution concentration versus time response (Robinson, 1982).

For a constant temperature and volume experiment, the integration of equation (3) is:

$$\ln\phi = -ka^*t \quad (4)$$

where $\phi = \frac{C^\infty - C}{C^\infty - C_0}$, and C_0 is the initial concentration of silica (mg/kg)

Plotting $\ln\phi$ versus t of equation (4) will give a straight line with slope $-ka^*$ where the rate constant may be evaluated, as can be seen in Figure 3.

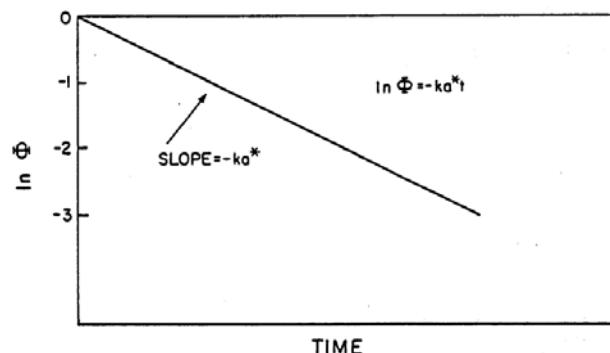


Figure 3: Quartz dissolution $\ln\phi$ versus time response (Robinson, 1982).

2. EXPERIMENTAL

The kinetic study consists of two segments. The first segment is to obtain the equilibrium concentration at various temperatures using the rock samples (drill cuttings) from Habanero 3 well. The drill cuttings were provided by Geodynamics. The samples were ultrasonically cleaned to remove fine particles and analyzed using the scanning electron microscope at the Adelaide Microscopy Centre (AMMRF). X-ray diffraction was also performed to obtain the composition of the rock sample. Surface area of the ultrasonically cleaned rock samples were measured using N₂-BET.

2.1 First segment. Equilibrium concentration determination

This first segment was done in Teflon tubes sealed in stainless steel autoclaves. The volume of the Teflon tubes is 18 ml. The rock samples were weighed (approx. 0.5 g) and placed to the Teflon tubes and reacted with 14 ml of pure water leaving 4 ml free space for expansion. Rock-fluid interaction experiments were performed at various temperatures (120°C, 140°C, 160°C, 170°C, 200°C, 220°C) for 56 days in an oven at saturated vapor pressure. At conclusion of the interaction, the autoclaves were quenched with cold water for 15 minutes, pH was measured and solutions were then preserved in 4% nitric acid. Solutions were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Na, K, Al, and Ca (data not shown). The HACH silicomolybdate method was used to measure the reactive silica (H_4SiO_4). Weighing of samples after the interaction will be carried out in the near future.

2.2 Second segment. Dissolution rate constant determination

The second segment is to obtain a dissolution rate constant using a flow-through cell at 250°C at saturated vapor pressure. A photograph of the flow-through cell is given in Figure 4.

The flow-through cell is designed to operate in a thermosiphon manner, where the flow of the fluid inside the cell is driven by temperature difference along the cell. The total cell volume is approximately 355 ml.



Figure 4: Flow-through cell used for rock-water interaction experiments.

The tubing is made from $\frac{1}{4}$ inch titanium and connected with standard Swagelok titanium fittings, with the reservoirs and sample cells in stainless steel (SS316). A safety relief valve and a relief vessel are employed for safety. A pressure regulator is also installed to monitor the pressure. An expansion reservoir is employed to allow fluid expansion and to allow pressure reduction for continuous flow. Thermocouples are installed to monitor the temperature changes throughout the cell and connected to a data logger. The temperature is controlled by a simple relay controller connected to two heaters that are arranged in parallel.

Using approximately 3 g of rock sample wrapped in stainless steel mesh and 250 ml pure water, water-rock interactions were performed for 1 day, 3 days, 5 days, 10 days, 17 days, and 28 days. At conclusion of the interaction, the cell was cooled for 2 hours and the water was then collected for pH measurements then preserved in 4% nitric acid. Solutions were analyzed using Inductively Coupled Plasma optical emission spectrometry (ICP-OES) for SiO_2 , Na, K, Al, and Ca. The HACH siliconmolybdate method (Hach, 2000) was used to measure the reactive silica (H_4SiO_4). The rock sample was collected, dried in an oven at 120°C for 48 hours and cooled in a desiccator for 24 hours and weighed to determine any weight loss. SEM analysis will be carried out in the near future.

3. RESULTS AND DISCUSSION

SEM image after the rock samples have been ultrasonically cleaned is shown in Figure 5. As can be seen, most of the fines are removed from this treatment.

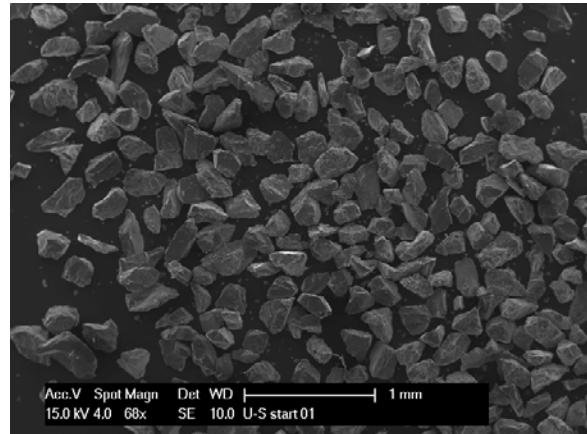


Figure 5: Rock samples after ultrasonically cleaned

The result for x-ray diffraction shows that the major constituents of the sample are quartz, albite, and microcline. The specific surface area of the rock sample using N_2 -BET is $0.5439 \text{ m}^2/\text{g}$.

3.1 Results for first segment

Preliminary results show that the equilibrium silica concentration increases with temperature. The pH of the starting water was about 7 and pH of the solutions increased to about 8.5 after 56 days interaction. Figure 6 shows the equilibrium silica concentration at various temperatures.

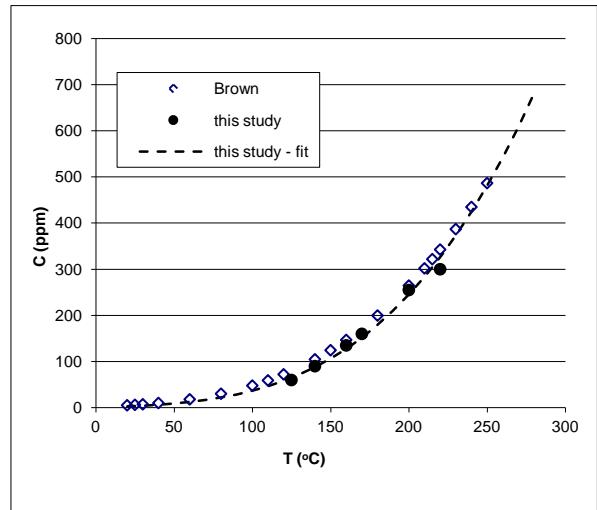


Figure 6: Equilibrium silica concentration at various temperatures.

The hollow diamonds data points were plotted using Equation (2). The solid circle data points were the experimental results from this study.

By plotting the results in terms of $\log C$ versus $1/T$ (K), and using a linear curve fitting, an equation was developed for the rock sample from Habanero 3 well:

$$\log C = -1448.6/T + 5.45 \quad (5)$$

However, it can be seen that the experimental results from this study is slightly lower, although fits quite reasonably well with the literature from Brown (2011). The slight lower equilibrium concentration value may be caused by:

- the kinetic equation used is for pure quartz. Since there rock sample is a mixture of several minerals, therefore, the presence of other dissolved elements may have an effect on the dissolution reaction
- polymerization of the dissolved monomeric silica (Brown, 2011) as a result of insufficient cooling rate of the quenching process

3.2 Results for second segment

Preliminary results show that both the dissolved total and reactive silica concentration increases with time as shown in Figure 7. The silica concentration shows the dissolved silica from all three silicate minerals (quartz, albite and microcline). The equilibrium concentration of the total silica would be approximately 480 ppm. The reactive silica concentration after 28 days of interaction is 320 ppm.

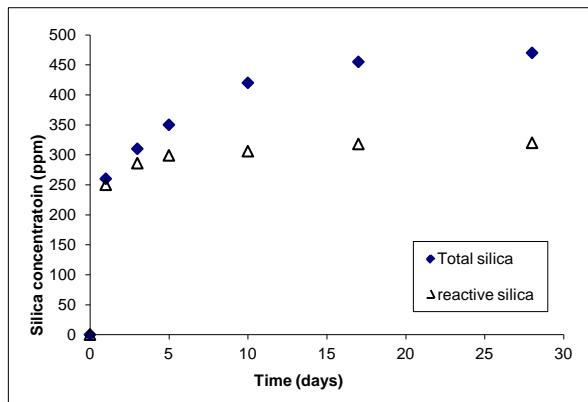


Figure 7: Silica concentration versus time response at 250°C.

The reactive silica concentrations were lower due to polymerization, since the solutions have pH about 7 in the earlier periods and increased to about pH 8-9 with increasing interaction time.

The dissolved cation concentrations are shown in Figure 8. Albite dissolution may be seen from the increasing sodium and aluminum concentration with time, and microcline dissolution may be seen from the increasing potassium and aluminum.

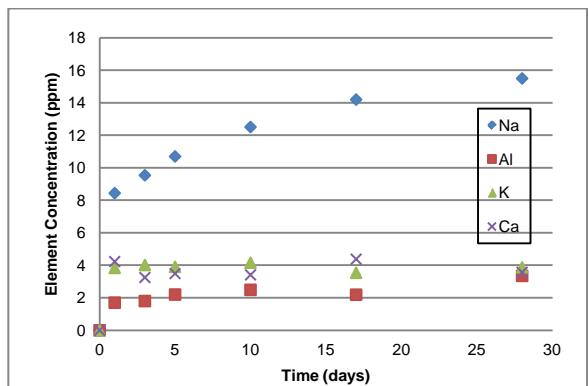


Figure 8: Cation concentrations versus time response at 250°C.

Equation 4 was used to obtain the dissolution rate constant. By plotting $\ln\emptyset$ versus time response versus time (s), a slope ($-ka^*$) of -2×10^{-6} was obtained, shown in Figure 9.

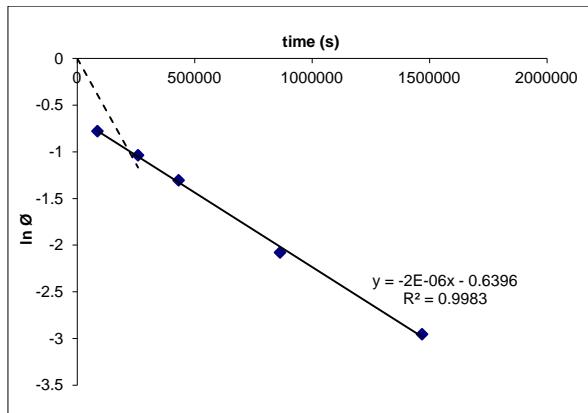


Figure 9: Quartz dissolution $\ln\emptyset$ versus time response at 250°C.

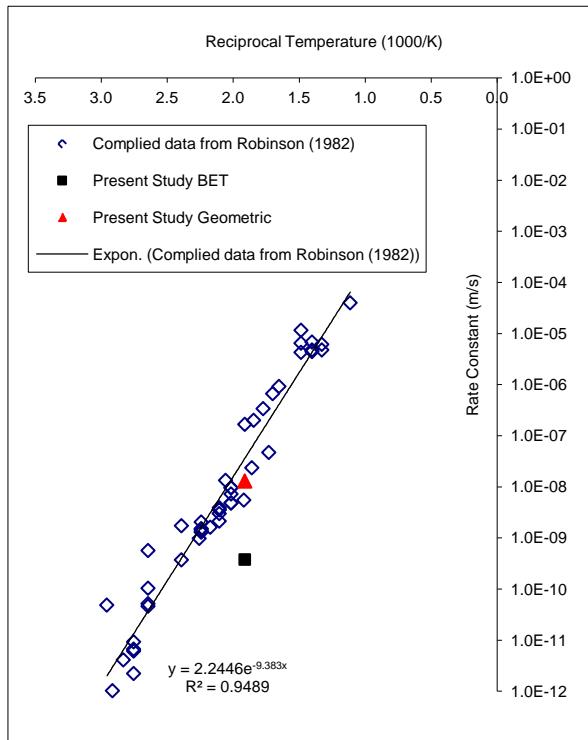


Figure 10: Arrhenius plot for quartz dissolution obtained from literature data (Robinson, 1982) represented by blue hollow diamond data points. Red triangle data point for present study using N_2 -BET and black square data point for present study using geometric surface area.

Combining this information with the N_2 -BET surface area and the volume of circulating fluid, the dissolution rate constant, $k = 3.797 \times 10^{-10} \text{ m/s}$. The dashed slope represents the rapid dissolution of fines that adhere to the rock sample particles.

The dissolution rate constant was also determined using the specific geometric surface area. The equation to determine the specific geometric surface area (Gautier et al., 2001) is:

$$A_s = \frac{6}{d_e \times \rho} \quad (6)$$

where d_e is the log mean diameter, and ρ is the average density of the rock sample. The specific geometric surface area calculated is $0.0158 \text{ m}^2/\text{g}$ giving the dissolution rate constant $k = 1.303 \times 10^{-8} \text{ m/s}$. The dissolution rate constants obtained in this study were then compared with the literature, shown in Figure 10.

It can be seen that the dissolution rate constant obtained from the geometric surface area fits reasonably well to that of N_2 -BET. This may be due to the over-estimation of the surface area obtained using N_2 -BET, since the area that is accessible to gas may not be accessible to liquid. In contrast, however, the technique of the geometric surface area estimation assuming spherical shape, where the diameter was determined from sieve tray is a crude approximation due to the surface roughness and shape irregularities (Robinson, 1982).

4. CONCLUSION

The fluid-rock interaction study is important for the prediction of dissolution and precipitation of minerals. The x-ray diffraction showed that the major components of the rock are quartz, albite and microcline. The experimental result for equilibrium concentration determination was found to fit reasonably well with the literature although the rock sample was not pure quartz.

The fluid-rock interaction experiment with the flow-through cell indicated that after 28 days the fluid is approaching equilibrium, where the total silica equilibrium concentration would be approximately 480 ppm. Due to the design of the flow-through cell, a rapid cooling is not possible; therefore a two hour cooling period was required. The long cooling period and high pH would then cause polymerization to occur which explains the low concentration of reactive silica, and the likelihood of silica scaling to be observed on the surface of the rock samples.

The dissolution rate constant was determined using N_2 -BET and geometric surface area. The result showed that the dissolution rate constant obtained using the geometric surface area fits better to the literature. According to Gautier et al. (2001), the dissolution reaction forms grain edge rounding and etch pits, where the dissolution predominantly deepened rather than widened the etch pits. Since similar etch pits development is common in natural systems, geometric surface area may provide a more accurate parameter for dissolution rate estimations.

ACKNOWLEDGEMENTS

This research has been supported by The Department of Primary Industries and Resources of South Australia (PIRSA) and Geodynamics. The authors would like to thank Geodynamics for providing the drill cuttings from Habanero 3 well. The authors would also like to thank the South Australian Museum for equipment access, Benjamin Wade and Aoife McFadden for their assistance in the Adelaide Microscopy, Kevin Li and Elita Santosaputri for their assistance in the laboratory, and also to Jason Peak, Michael Jung and Jeffrey Hiorns from the Chemical Engineering Workshop for their assistance in putting together the experimental apparatus, the equipments and maintenance.

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