A Preliminary Study on Na-Cl-H_2O-Rock Interactions of the Hot Fractured Rock Geothermal System in Cooper Basin, South Australia

Gideon B. Kuncoro[1], Yung Ngothai[1*], Brian O'Neill[1], Allan Pring[2], Joël Brugger[2]
[1] The University of Adelaide, School of Chemical Engineering, North Terrace, Adelaide, SA, 5000
[2] South Australian Museum, North Terrace, Adelaide, SA, 5000
*Corresponding author: yung.ngothai@adelaide.edu.au

A preliminary study was undertaken to observe the fluid-rock interaction in Na-Cl-H_2O system. Samples of drill cuttings from a borehole 5 km deep from Habanero 3 well were contacted with 250 ppm sodium chloride solution in a thermosyphon induced loop reactor at 250°C and 40-50 bar. The experiments were carried out in a Titanium flow through cell for 1, 7, and 28 days at 250°C and 40 bars). The fluid was replaced every 24 hours in order to accelerate the dilution rate to observe which minerals are reactive (soluble) and to mimic a condition which uses fresh water or treated water from a precipitation tank that is reinjected to the fracture. Fluid and rock samples were analysed prior to, and after circulation to observe the dissolved minerals and mineralogy.
Water analysis was performed using ICP-MS, and rock analyses were conducted using an optical microscope, SEM and XRD. The experimental results indicated that mineral dissolution was more rapid in the early stages of the experiment. This may be a consequence of the dissolution of finer rock particles. SEM observations showed evidence of etching of the mineral surfaces consistent with partial dissolution. XRD results indicated that the feldspars ($NaAlSi_3O_8$ and $KAlSi_3O_8$) in the rock had completely dissolved and small amount of quartz remained. ICP-MS analysis on the water sample confirmed that some mineral dissolution has occurred. The concentrations of the elements increased with time.
Experiment running for 14 days is currently being undertaken and the results will be used to complement this study. Future work will involve reaction path modelling to predict mineral precipitation.

Keywords: hot fractured rock, fluid-rock interaction, Na-Cl-H_2O system, geothermal, Cooper Basin, Habanero, thermosyphon

Introduction

A study of the interactions between rock and circulating fluid is essential to determine the chemical changes and mineral alteration of a geothermal system. This study was undertaken to observe mineral dissolution due to the interaction with Na-Cl-H_2O system. Existing reservoir granites are currently in equilibrium with the surrounding ground water. The injection of fresh water to extract thermal energy from the host rock will alter the ground water chemistry and thus the fluid-rock equilibrium. While recirculating the brine, partial chemical dissolution or mineral species alteration may occur. This may potentially increase the dissolved solids such as silica and other metals in the water. These dissolution products of the components have different equilibria, which will be a function of temperature and pressure, thus precipitation or scaling of pipe work and closure 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. Clearly, characterization of fluid geochemistry is important in the evaluation of the performance of geothermal systems (Grigsby et al., 1989). Moreover, understanding the chemical interactions due to the injection of fluid into hot granite is crucial for problems concerning clogging by precipitation and heat loss caused by dissolution (Azaroual and Fouillac, 1997).

The study of fluid-rock interaction will allow determination of mineral alteration and dissolution of minerals due to the circulating water. To date, there are a number of geochemical modelling codes therefore thermodynamic data bases are available and improved to predict equilibrium conditions and dissolution-precipitation rates (such as EQ3/6, TOUGH-REACT, SOLVEQ-CHILLER, SOLMINEQ, GWB, etc). However, fundamental processes associated with mineral dissolution and precipitation, pressure-temperature gradient remain poorly understood (Marks et al., 2010). Unfortunately, it is impossible to generalize the actual field experience of mineral deposition in geothermal systems into one consistent theory due to the vast chemical and operational variation between field sites (Robinson, 1982). Therefore, although there have been a number of studies on fluid-rock interactions for different geothermal sites (Rimstidt and Barnes, 1980; Robinson, 1982; Posey-Dowty et al,. 1986; Savage et al., 1987; Grigsby et al., 1989; Savage et al., 1992; Azaroual and Fouillac, 1997; Yangisawa et al., 2005; Tarcan et al., 2005; Castro et al., 2006; Marks et al., 2010), and studies of rock-chloride solutions (Ellis, 1968; Dove and Crerar, 1990; Icenhower and Dowe, 2000) these are probably not directly applicable to the hot granite-based geothermal systems in the Cooper Basin.

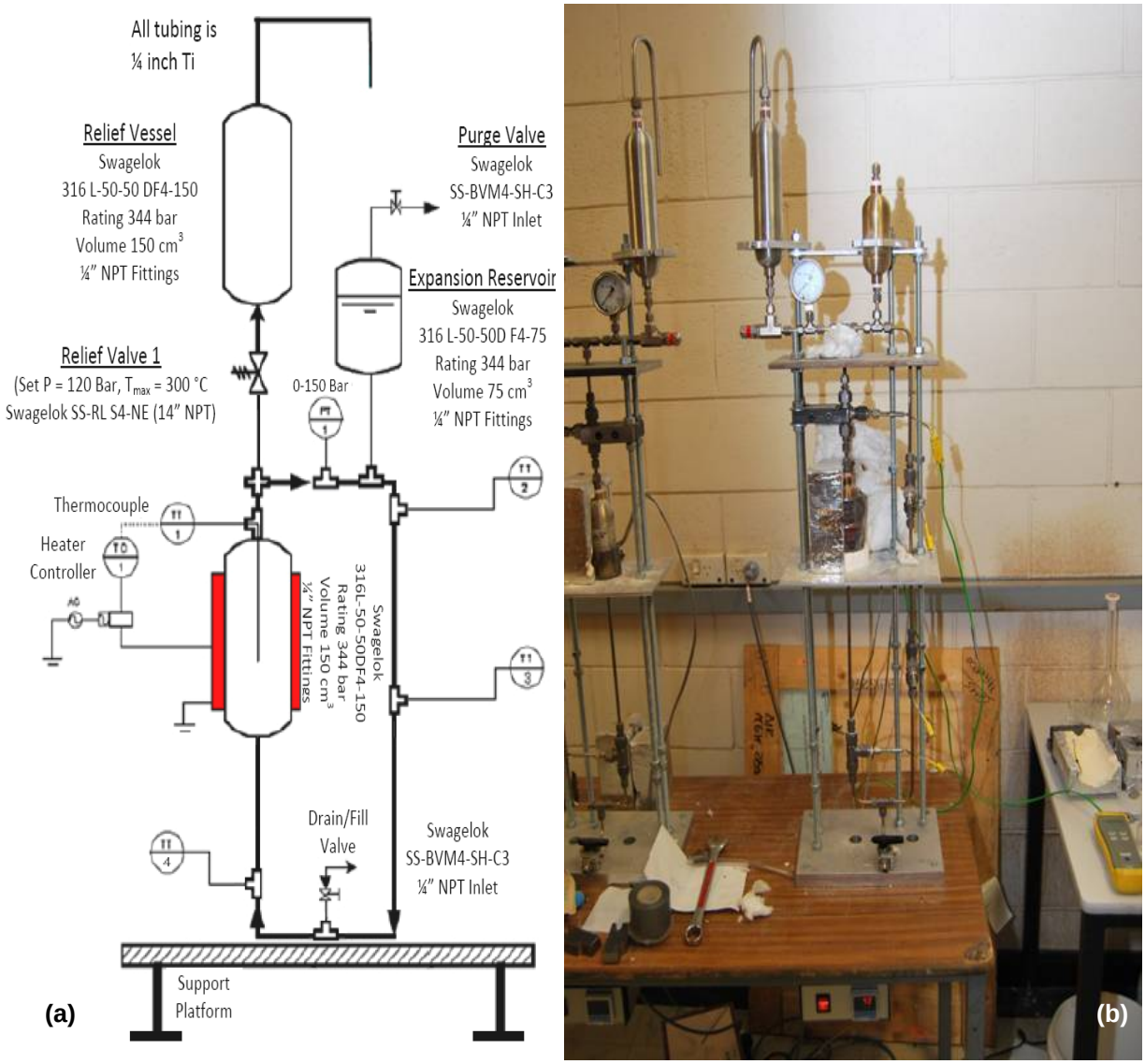


Figure 1: (a) Diagram of the flow through cell (b) Photograph of the geothermal flow through cell

Experimental

Samples of drill cuttings from the Habanero 3 well were provided by Geodynamics. The samples were ultrasonically cleaned and analysed using,the scanning electron microscope (SEM) at the Adelaide Microscopy Centre to observe both surface and cross-sectional area. Powder X-ray diffraction (XRD) analysis was carried out by AMDEL to observe the mineralogy. A preliminary set of experiments to observe the fluid-rock interaction were performed in batch mode. The drill cutting was used as the rock sample. The rock sample was crushed and sieved to give 100 – 200 µm size fraction and approximately 0.7 grams of rock were used in each batch. The sample was enclosed in a pre-weighed wire basket (approx. 50 µm mesh size) made from stainless steel and placed in the sample holder of the cell. The cell was filled through a valve in the base of the cell with 250 ppm sodium chloride solution and 90 ml was drained from the cell to allow for fluid expansion upon heating. The velocity of the thermosyphon circulating fluid is estimated to be approximately 0.1 m/s. The fluid-rock interaction periods were 1, 7, and 21 days. At conclusion of this interaction period, the rock sample was dried (105°C for 48 hours), cooled in a desiccator, and weighed to determine any weight loss.

The rock samples were analysed using SEM and XRD, and the water samples were stored and preserved with 4% w/w of 1M nitric acid until analysis by ICP-MS to identify the dissolved metals. The silica content was quantified using heteropoly blue method (HACH, 2009). Unfortunately, the anions were unable to be analysed since the concentrations of HCO_3^- and $SO4^{2-}$ in the sample are lower than the detection limit of the current analysis.

Results and Discussion

Preliminary results from the geothermal cell experiment illustrate that the dissolution of the

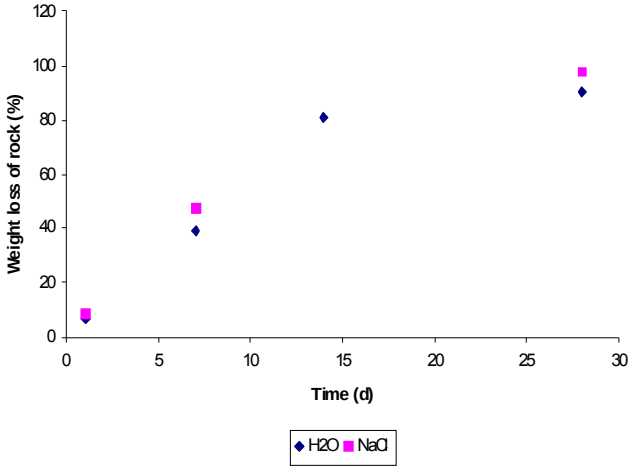


Figure 2: Change in weight loss of rock (% w/w) versus time

rock (% w/w) increases with time (Figure 2). It shows that the dissolution appears more rapid in the early stages of the experiment. This is probably due to the dissolution of the more reactive minerals (feldspars). It is seen that more minerals dissolved in the Na-Cl-H_2O system compared to pure water (reverse osmosis treated water). The presence of higher electrolyte concentration (e.g., Cl^-) in Na-Cl-H_2O system increases the dissolution rate of some minerals such as quartz (Dove and Crerar, 1990). The latter stage of the experiment approached an equilibrium state. However the fluid is not necessarily saturated with minerals (feldspar), but due to the exhaustion of the soluble phase(s) and slower dissolution rate of the remaining phase(s). Note that the circulating fluid is replaced every 24 hours.

Rock Analysis

Mineralogical analysis was performed on the drill cuttings from Habanero 3 well using x-ray fluorescence (XRF) and x-ray diffraction (XRD). The major elements and their host minerals of the rock are quartz (SiO_2), albite (Na,Ca)$AlSi_3O_8$, and microcline ($KAlSi_3O_8$) (Pring, pers. comm. 2009). The XRF analysis was carried out by the School of Earth and Environmental Sciences, Adelaide University (Table 1). The XRD analysis was performed by AMDEL (given in %wt) and converted to mg for better understanding. The results show clearly that rapid dissolution has occurred. Silicon internal standard was added to observe any possible amorphous, unfortunately the amorphous content were unable to be quantified by Amdel. Hematite, magnetite, anatase, chlorite and goethite may be accessory minerals due to corrosion of the stainless steel reservoirs and the stainless steel wire basket used in the experiment.

SEM images of the surface particles were obtained using the secondary electron detector (SE) of the XL30 in Adelaide Microscopy. The images are presented in Figure 3. The SEM images of the rock sample surfaces of feldspars before and after the experiments are shown in Figure 4. It can be seen that pitting has started to occur in 1 day circulation period. At the conclusion of 7 days circulation, the surface of feldspars experienced severe pitting and breakage. By the end of 28 days circulation, the feldspar has completely dissolved and some quartz and undissolved minerals remain.

Table 1 XRF analysis of the rock sample

Starting Sample	% Weight
SiO_2	77.27
Al_2O_3	10.62
Fe_2O_3	1.46
MnO	0.08
MgO	0.09
CaO	0.60
Na_2O	2.54
K_2O	4.45
TiO_2	0.07
P_2O_5	0.01
SO_3	0.15
LOI	2.10
Total	99.44

Table 2 XRD analysis of the rock sample

Mineral composition (mg)	Starting sample	After 1 day	After 7 days	After 28 days
Quartz SiO_2	273.5	252.2	119.6	7.6
Albite $(Na,K,Ca)Al_{(1-2)}Si_{(3-2)}O_8$	206.9	184.0	138.9	0.0
K-Feldspar $KAlSi_3O_8$	125.6	115.9	57.9	0.0
Muscovite $(Na,K,Ca)_2(Al,Fe,Mg)_{4-6}(Al,Si)_8O_{20}(OH,F)_4$	59.1	54.5	34.7	0.0
Pyroxene $XY(Si,Al)_2O_6$	14.8	13.6	0.0	0.0
Silicon* Si	44.3	47.7	27.0	1.4
Chalcopyrite and or Calcite $CuFe_2$ and or $CaCO_3$	7.4	6.8	3.9	0.0
Siderite $FeCO_3$	7.4	6.8	0.0	0.0
Hematite Fe_2O_3	0.0	0.0	0.0	3.7
Magnetite Fe3O4	0.0	0.0	0.0	1.0
Anatase TiO_2	0.0	0.0	0.0	0.4
Chlorite $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2.(Mg,Fe)_3(OH)_6$	0.0	0.0	0.0	2.3
Goethite FeO(OH)	0.0	0.0	3.9	0.6
Amorphous	0.0	0.0	0.0	2.5
Total sample	739.1	681.5	385.7	19.4

SEM analyses of the cross section of the rock samples were also conducted. Results are given

in Figure 4. These images were obtained using the backscattered electron detector (BSE) and analysed using the energy dispersive x-ray spectrometer (EDAX). The results suggest that albite feldspar is the most reactive (soluble) mineral, followed by microcline and quartz. The BSE image of the sample from 28 day circulation (Figure 4D) confirms that only quartz and other accessory minerals were observed, and no feldspars were present.

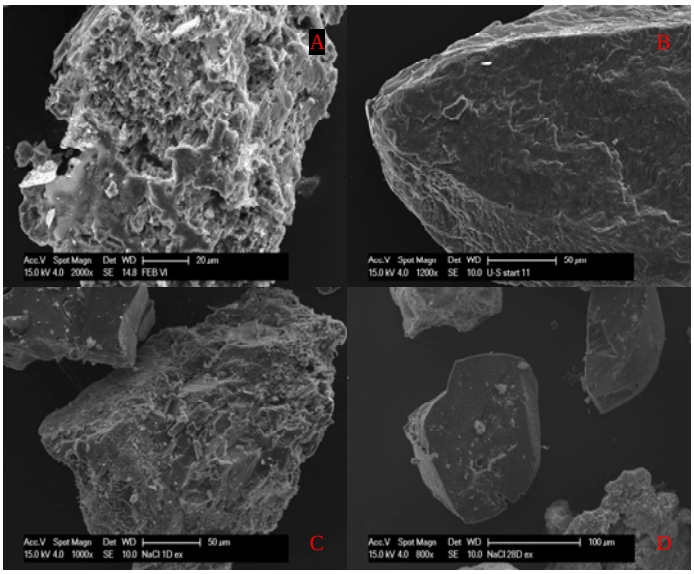
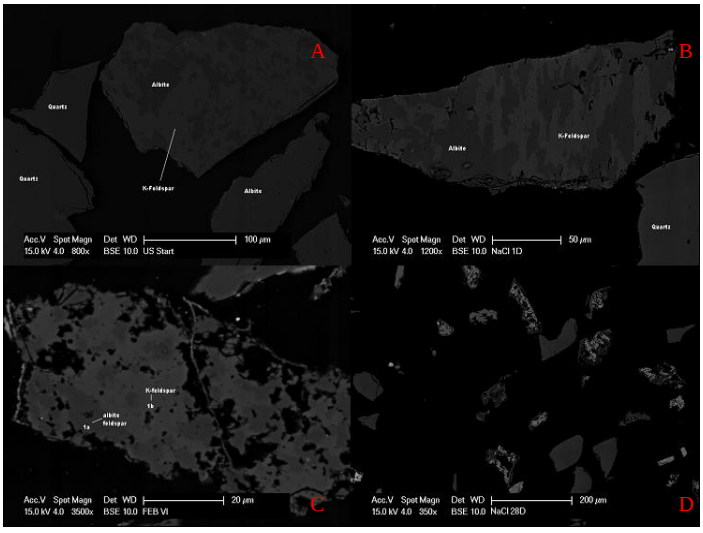


Figure 3: SEM images of the rock sample surface (a) starting rock (b) after 1 day experiment (c) after 7 days experiment (d) after 28 day experiment

Figure 4: BSE images of the rock cross sectional area (a) starting rock (b) after 1 day experiment (c) after 7 days experiment (d) after 28 day experiment



Water Analysis

The initial pH of the water was 5.5. This did not change significantly in all batch experiments. Figures 5 and 6 show the concentration of elements versus time from the ICP-MS analysis, and Figure 7 show the silica concentration on the circulating water after 1, 7, and 28 days of fluid-rock interactions.

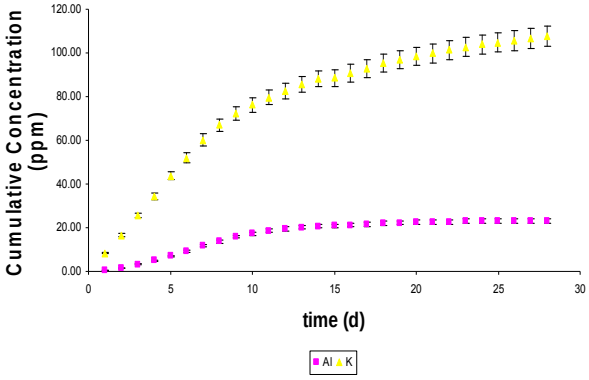


Figure 5: Concentration of Al and K in experimental liquid versus time

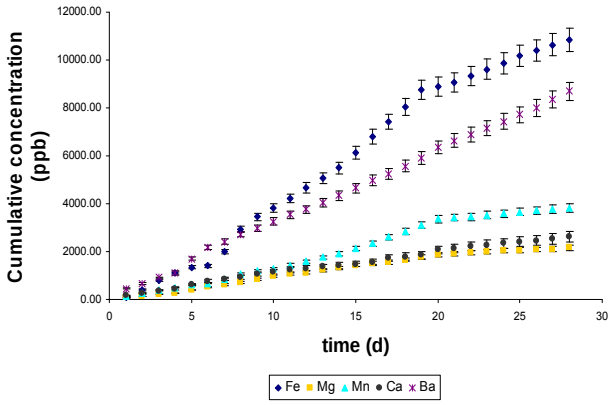


Figure 6: Concentration of Fe, Mg, Mn, Ca and Ba in experimental liquid versus time

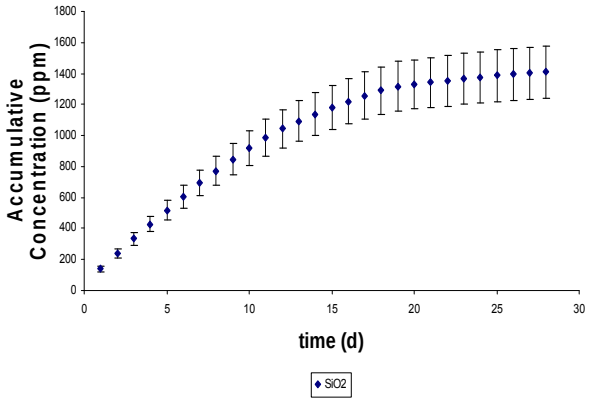


Figure 7: Concentration of SiO_2 in experimental liquid versus time

Water analysis results showed that there was enhanced leaching of the minerals, indicated by the increased element concentration in the liquid phase. The rapid reaction is probably the

consequence to the dissolution of more reactive (soluble) phases in the rock sample. It is seen that high concentration of silica, aluminium and potassium were dissolved in the liquid due to dissolution of albite, microcline and quartz.

Unfortunately the sodium concentration could not be analysed accurately due to the high initial concentration of sodium in the circulating fluid (250 ppm NaCl).

Mass Balance

A simple mass balance was undertaken to observe the sample loss to the circulating fluid. Since the sodium cannot be analysed accurately at this stage, it was assumed that the dissolved concentration would be similar to the dissolution of Albite Feldspars in pure water. Table 3 shows the system mass balance. A short circulating time would result in less sample loss. The sample loss may be due to the replacement of circulating fluid, since at the time of reinjection, the liquid must overflow through the sample and exiting the cell to remove excess air (any air bubble may disrupt the flow in the thermosyphon).

Table 3 System mass balance

time	Initial, mg	Remaining, mg	Dissolved (calc), mg	% wt.	Dissolved, (water analysis),mg	Loss, mg
1	745.2	681.5	63.7	8.55	41.30	22.40
7	734.4	385.7	348.7	47.48	271.00	77.70
28	737.7	19.4	718.3	97.37	427.95	290.35

Not including the concentration of the anions may also be another cause of the unclosed mass balance.

Conclusion

The mineralogical analysis showed that the major composition of the rock is quartz, albite and microcline. The fluid-rock interaction experiment showed that dissolution reactions occur predominantly in the early stages (to 7 days) of the experiment due to the dissolution of reactive minerals (feldspars). The dissolution reaction begins to decrease due to the exhaustion of the reactive mineral and proceeds with the dissolution of the less reactive phase. Results of XRD showed that feldspar experienced a clear reduction with time, followed by quartz.

Liquid analysis showed higher concentrations of Na, K, Si, and Al compared to other analysed elements. These results suggest that the dissolution reaction occurs primarily for the feldspars.

The dissolution of feldspar would suggest the improvement of the permeability (however, not necessarily improving the fracture where mineral deposits occur) and also suggest of potential silica scaling (if circulating fluid is near neutral pH). The concentration of silica 1400 ppm (from 0.7g rock sample) was released to the liquid phase throughout the experiment.

Future Work

An experiment is currently being conducted for 14 days period to obtain more understanding on the dissolution (Figure 2). Sodium concentration would need to be accurately analysed. The current work has used 250 ppm sodium chloride solution for the fluid-rock interaction and does not quite represent the actual interaction. Experiments with Increased amount of rock sample (increasing the rock/water ratio) are being carried out to observe any changes in equilibrium or saturated condition. A dissolution and precipitation model will be generated using the data from previous experiments (pure water) and the current study. The model will be used to predict the dissolution rate and precipitation rate of the actual fluid-rock interaction.

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