A CASE STUDY OF ROCK-FLUID INTERACTION IN THE ENHANCED GEOTHERMAL SYSTEM IN COOPER BASIN, SOUTH AUSTRALIA

Gideon Kuncoro[1]*, Yung Ngothai[1], Brian O'Neill[1], Allan Pring[2,3], Joël Brugger[2,3]

[1]School of Chemical Engineering, The University of Adelaide, North Terrace Campus, Adelaide, SA, 5005
[2]School of Earth and Environmental Sciences, The University of Adelaide, North Terrace Campus, Adelaide, SA, 5005
[3]South Australian Museum, North Terrace, 5000
*Email:gideon.kuncoro@adelaide.edu.au

ABSTRACT

This study was undertaken to observe mineral dissolution by replacing the circulating fluid (fresh water) every 24 hours. This was an attempt to accelerate the dissolution rate and to mimic the condition of the Cooper Basin geothermal site when fresh water or treated water from a precipitation tank is reinjected to the fracture. The experiments were carried out in a Titanium flow through cell for 1, 7, 14 and 28 days at 250°C and 40 bars (reaction cell id. 0.25 inch and cell volume 250 ml). Water analysis was performed and rock analyses were conducted. A comparison of the dissolution reaction was made between the 1, 7, 14 and 28 days circulation period. The experimental results revealed a linear correlation of mineral (element) dissolution at the early stages of the experiment. However at later stages, the mineral dissolution proceeds at a slower rate. This may have been caused by the exhaustion of the more soluble mineral phase in the sample. The rapid dissolution may enlarge the pore size in the fracture path. SEM observations showed evidence of etching of the mineral surfaces consistent with partial dissolution. SEM backscattered images reveals that mostly quartz phase (SiO_2) remains after 28 days of circulation. XRD results complement these finding, that after 28 days albite-feldspar ($NaAlSi_3O_8$) and microcline ($KAlSi_3O_8$) in the rock had dissolved completely and a small amount of quartz still remain. As well, high SiO_2, Na, K, Al concentration were observed in the liquid phase. XRF study was used to generate an elemental mass balance. Determination of the dissolution kinetics of the various minerals phase is being undertaken.

INTRODUCTION

While the energy demand in Australia is increasing, reserves of coal, oil, and natural gas are depleting. Therefore, many alternative energy sources are currently being developed. One example is geothermal energy. The geothermal energy in Australia is an enhanced geothermal system/hot fractured rocks (HFR) which occurs at much greater depth than natural geothermal system, up to five kilometres, and the heat source is radioactive decay rather than volcanism (Geodynamics, 2009). Australia has a vast amount of high temperature thermal area (250°C) at 5 km depth (refer to Chopra and Holgate, 2005). Therefore, the HFR has great potential to supply electricity by harnessing stored thermal energy from high temperature granitic rocks without producing greenhouse gas emissions or long-lasting nuclear wastes, at cost competitive with those for energy generated from fossil fuels.

Thermal Energy Extraction from Hot Fractured Rocks

The basic technique for extracting energy from hot dry rock was established in the early 1970s at the Los Alamos National Laboratory, New Mexico (Wyborn et al., 2005). Refer to SEN (2010) for illustration of HFR thermal extraction process. The first step in the technique is the construction of a well with sufficient depth in to the hot rock. Wells drilled for HFR projects are similar to those for hydrothermal/volcanic sites apart from the depth, which is deeper for HFR applications. After the first well has been completed, a segment of the bottom portion is isolated using a packer, which provides pressure and flow isolation. Hydraulic fracturing fluids are then pumped with increased pressure through the packer and forced in the surrounding rock body to form a permeable reservoir consisting of interconnecting fractures. The shape and orientation of the reservoir are influenced by the natural stress features of the host rock (Mink, 2004). To complete the subsurface system, a second well is required to be drilled into the permeable zone sufficiently separated from the first well. It is expected that when water is pumped through the permeable fractures on a tortuous path, returns to the surface at a higher temperature through the production well. On the surface, thermal energy is extracted from the outlet geothermal fluid using a binary or a kalina cycle. After the thermal energy has been removed, the fluid is reinjected into the permeable reservoir through the injection well.

External sources from surface water (Darby's Bore and Lance's Bore) are used as make up water to the recirculating water (Wyborn, 2010). The composition of the groundwater may differ significantly from the fresh water injected through the granite to extract energy. Due to the injection of fresh water to the reservoir, the equilibrium with the surrounding groundwater may be altered. The flow of large volumes of water injected may cause partial chemical dissolution or alteration of some granites, which could potentially increase the dissolved solids such as silica, and other metals in the circulating fluid. Therefore, the study of fluid-rock interaction is crucial. Unfortunately, fundamental processes associated with mineral dissolution and precipitation, and pressure-temperature gradient remain poorly understood (Marks et al., 2010). To date, literature demonstrates that different geothermal reservoirs generate wide variations in the geochemical composition in the circulating water. Furthermore, 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). 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; Tarcan et al,, 2005; Yangisawa et al., 2005; Castro et al., 2006; Marks et al., 2009), these are probably not directly applicable to the hot granite-based geothermal systems in the Cooper Basin.

METHODS

A hydrothermal flow through cell has been developed to investigate the fluid-rock interaction. The flow inside the hydrothermal cell circulates in such manner as a thermosyphon. A diagram and a photograph of the flow through cell are provided in Figure 1. The total cell volume is approximately 345 ml. The safe operating working volume is approximately 255 ml to allow for fluid expansion. All tubing is made from ¼ inch titanium with standard Swagelok titanium fittings. The reservoirs used are made in stainless steel (SS316). Four thermocouples are installed to monitor the temperature changes throughout the cell. A pressure transducer is installed to monitor the pressure. Temperature is controlled by a simple relay controller and two heaters were used and

arranged in parallel. The heaters are intact with the main reservoir and insulated with ceramic bricks. The operating temperature and pressure are 250°C and approximately 40 - 50 bar, respectively.

Experimental

Drill cuttings from the Habanero 3 well were provided by Geodynamics. The drill cuttings were then prepared to 100-200 μm particle size. The samples were ultrasonically cleaned to remove fine particles. The samples were analysed using field emission scanning electron microscope (FESEM) at the Adelaide Microscopy Centre. The secondary electron of the FESEM was used to observe the surface particles. The backscattered electron detector of the FESEM equipped with an energy dispersive x-ray (EDAX) were used to identify and semi-quantify the mineral content. Mineralogical analysis of the sample was carried out using x-ray diffraction (XRD) by AMDEL and x-ray fluorescence (XRF) analysis by The School of Earth and Environmental Sciences, The University of Adelaide.
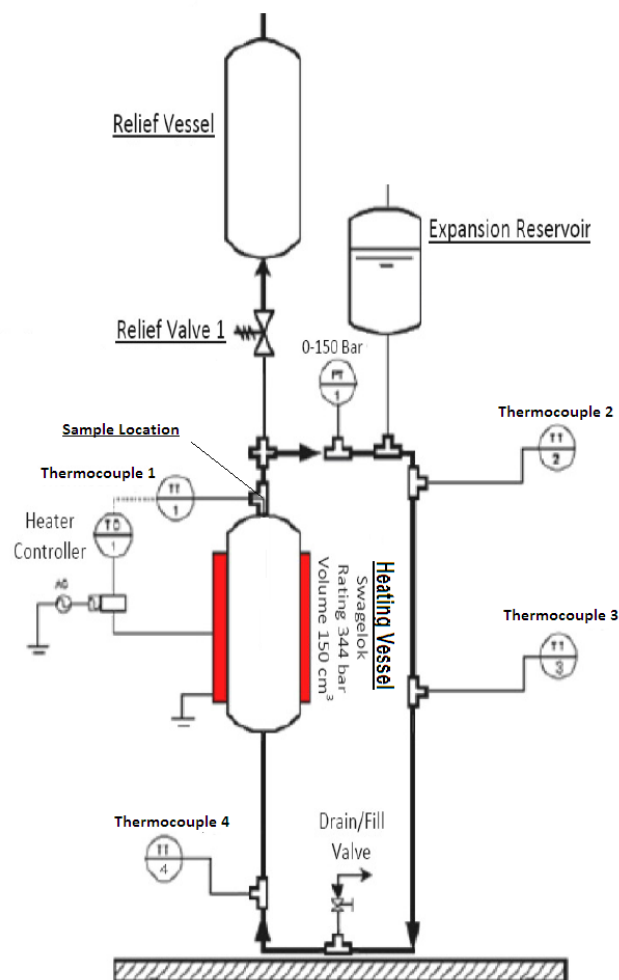

Fig. 1: Diagram of the hydrothermal flow through cell

A preliminary set of experiments were conducted in batch with replacing the circulating fluid every 24 hours. The fluid velocity of the thermosiphon was estimated to be approximately 0.1 m/s. The drill cuttings were used as the rock sample and pure water (reverse osmosis treated water) were used as the circulating fluid. Approximately 0.7 grams of rocks was used for each batch. The fluid-rock interaction durations were 1, 7,

14 and 28 days. The experiments were conducted at 250°C and 45 bars. At the end of every 24 hour period, the liquid is drained and preserved with acid and stored at 5°C in a refrigerator until it is ready to be analysed. After a fresh 255 ml water is reinjected, the experiment proceeds until the end of the interaction period. At termination of each interaction period, the rock samples were dried (110°C for 48 hours) in an oven, cooled in a dessicator, and weighed to determine any weight loss. The rock samples were then analysed using FESEM, XRD and XRF, and the water samples were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to identify the dissolved metals (cation). The silica content was quantified using the heteropoly blue method (HACH, 2009).

RESULTS AND DISCUSSION

Preliminary results of the fluid-rock interactions reveal dissolution reaction. The amount of rock (%) lost to the solution increases with time (Figure 2). The dissolution of fine particles would be expected in the initial stage of the experiment. Moreover, due to the replacement of the recirculating fluid with fresh water every 24 hours, dissolution reaction would be very apparent. This can be seen after 7 days of experiment, 40% of the rock has dissolved to the liquid phase. The introduction of fresh water resulted in particles breaking down to finer particles. Since the amount of fine particles increases, dissolution reaction becomes more rapid. This may explain that the dissolution curve is slightly steeper for 7 days to 14 days experiment compared to the initial stage. After 14 days of fluid-rock interaction, the dissolution rate becomes slower dur to the exhaustion of the more soluble minerals and the little amount of rock sample remaining.

Rock Analysis

Petrographic analysis was performed on the drill cuttings from Habanero 3. The rock is a feldspar syenite containing albite and microcline with carbonate alteration, which has been subjected to hydrothermal alterations (Pring, pers. comm., 2009). The specific surface area, 0.54 m^2/g for 100 – 200 µm size fractions, was measured using the N_2-BET method carried out by RMIT University.
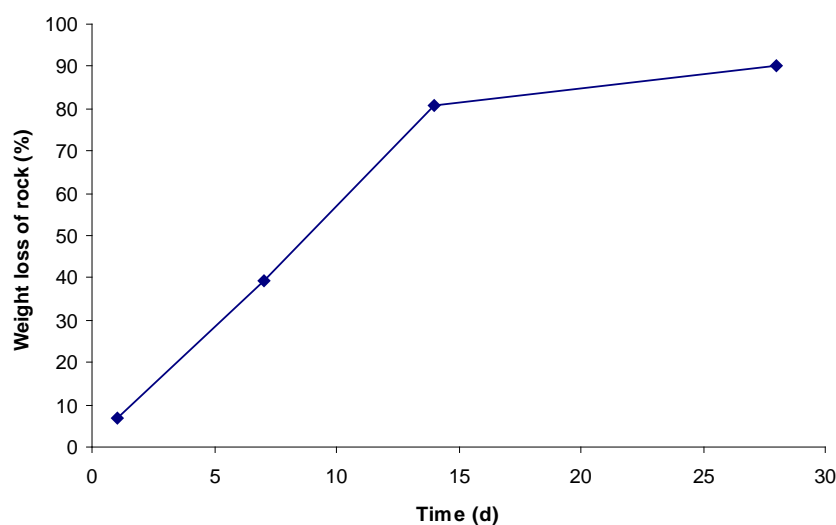

Fig. 2: Weight loss of rock (%) versus time

SEM images of the rock sample were obtained using the XL30 microscope in Adelaide Microscopy. The surface images before and after experiments are given in Figure 3. It

can be observed in Figure 3 that after 7 days of interaction period, the surface of the rocks experienced etching. The etching develops as the interaction period continues. The rock particles become frail due to the dissolution reaction and eventually break into smaller or finer particles as shown in Figure 3d. The cross-section of the rock sample was analysed using the backscattered electron detector (BSE) combined with the energy dispersive spectrometer was used to identify the minerals in the sample. Figure 4 shows a comparison of the starting sample, 7 days, 14 days and 28 days of interaction period.
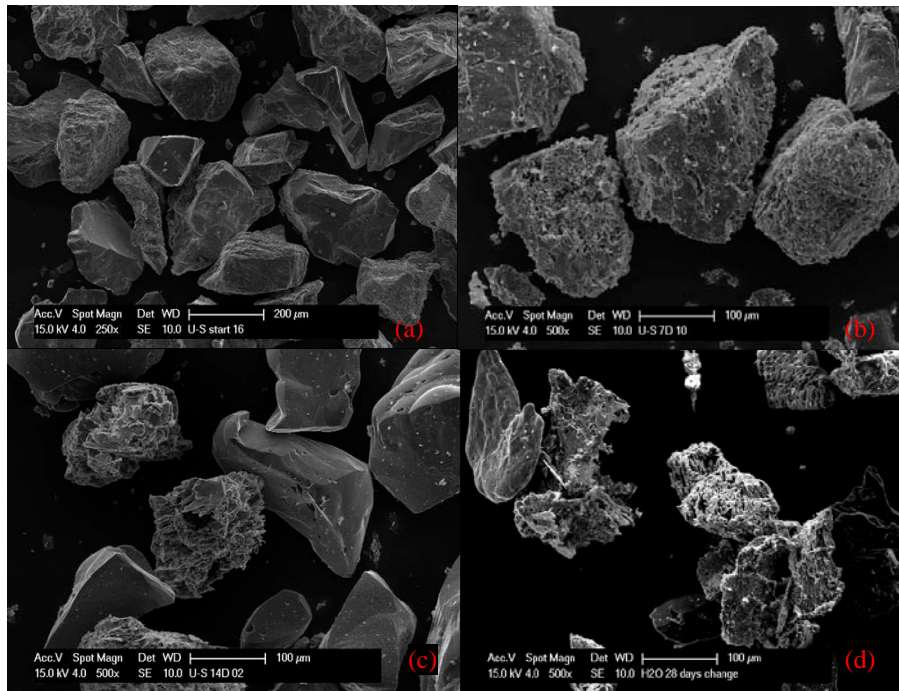

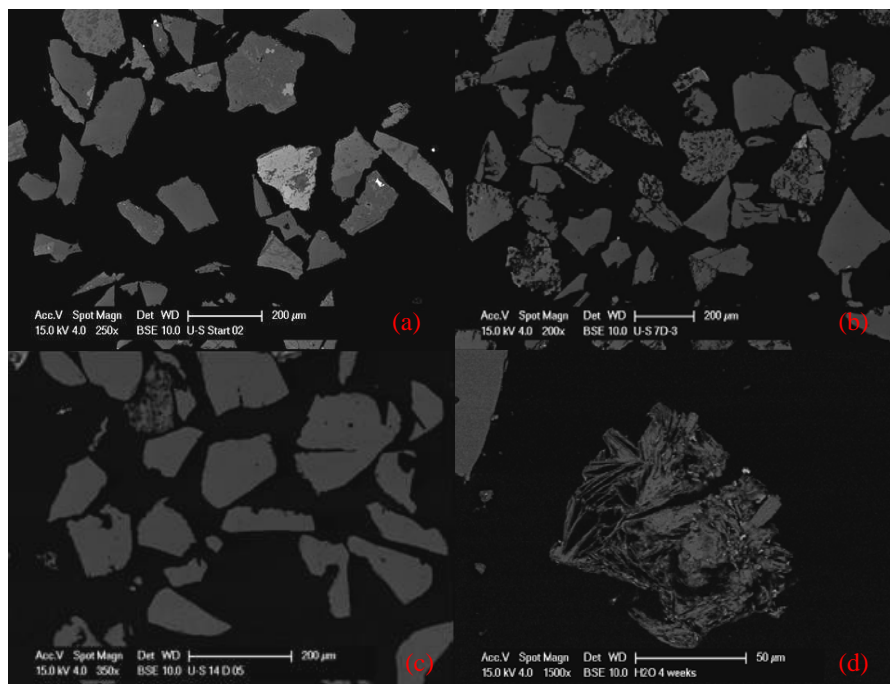Fig. 3: SEM images of surface (a) starting rock (b) 7 days (c) 14 days (d) 28 days

Fig. 4: BSE images of sample (a) starting rock (b) 7 days (c) 14 days (d) 28 days

The major minerals in the samples are quartz, albite feldspar, and K-feldspar. It is seen that at the end of 7 days interaction period, the feldspars experienced distinct etching or pitting, while quartz stays stable. At the end of 14 and 28 days interaction, mostly quartz was present and only a small number of feldspars were found. Figure 4d shows feldspar with very severe pitting after 28 days interaction. XRD results are presented in Table 1. Five percent of silicon standard was added to the sample to observe the quality of the analysis.

Tab.1: XRD result for different experimental periods in %wt.

Mineral	Chemical composition	Start	1 day	7 days	28 days
Quartz	SiO_2	39	35	49	65
Albite	$(Na,K,Ca)Al_{(1-2)}Si_{(3-2)}O_8$	30	25	12	0
K-Feldspar	$KAlSi_3O_8$	18	21	24	0
Muscovite	$(Na,K,Ca)_2(Al,Fe,Mg)_{4-6}(Al,Si)_8O_{20}(OH,F)_4$	9	9	7	8
Pyroxene	$XY(Si,Al)_2O_6$	2	1	0	0
Silicon	Si	6	7	7	7
Chalcopyrite	$CuFe_2$	1	1	1	0
Siderite	$FeCO_3$	1	1	0	0
Amorphous		0	0	0	20
Total		100	100	100	100

X: Ca,Na,Fe^{2+},Mg;   Y: $Cr,Al,Fe^{3+},Mg,Mn,Ti,Sc,V,Fe^{2+}$ (error $\pm$ 3% wt.)

Tab.2: XRF analysis of ultrasonically cleaned rock

Element	Sample
SiO_2 %	77.27
Al_2O_3 %	10.62
Fe_2O_3 %	1.46
MnO %	0.08
MgO %	0.09
CaO %	0.6
Na_2O %	2.54
K_2O %	4.45
TiO_2 %	0.07
P_2O_5 %	0.01
SO_3 %	0.15
LOI %	2.1
Total %	99.44

Unfortunately due to the apparatus limitations, every experiment requires a new starting material, which may increase the variability of the results. An effort to improve the homogeneity of the starting sample has been carried out. However, due to the small sample size (approximately 0.7 grams) it may not be completely homogenous for each experiment. Table 2 shows an XRF analysis on the rock sample after ultrasound cleaning. The results showed agreement with the XRD analysis, which confirms that the major components of the rock sample are quartz, albite feldspars and microcline.

Water Analysis

The pH of the circulating water was approximately 5.5. The pH did not change significantly after each experiment. Figure 7 shows the cumulative concentration of dissolved elements versus time on the circulating water after 28 days period. Water analysis results revealed that there was an enhanced release of minerals to the liquid phase. This is due the use of pure water. As expected, replacing the circulating water every 24 hours exhaust the minerals showing linear curve. From the graphs in Figure 5, it is seen that basically there are two slopes. After 14 days, the dissolution rate seems to

decrease. This shows agreement with the rock analysis, where at the end of 14 days experiment, most of the feldspars have been dissolved (having greater dissolution rate). Data after 14 days indicate the dissolution of quartz.
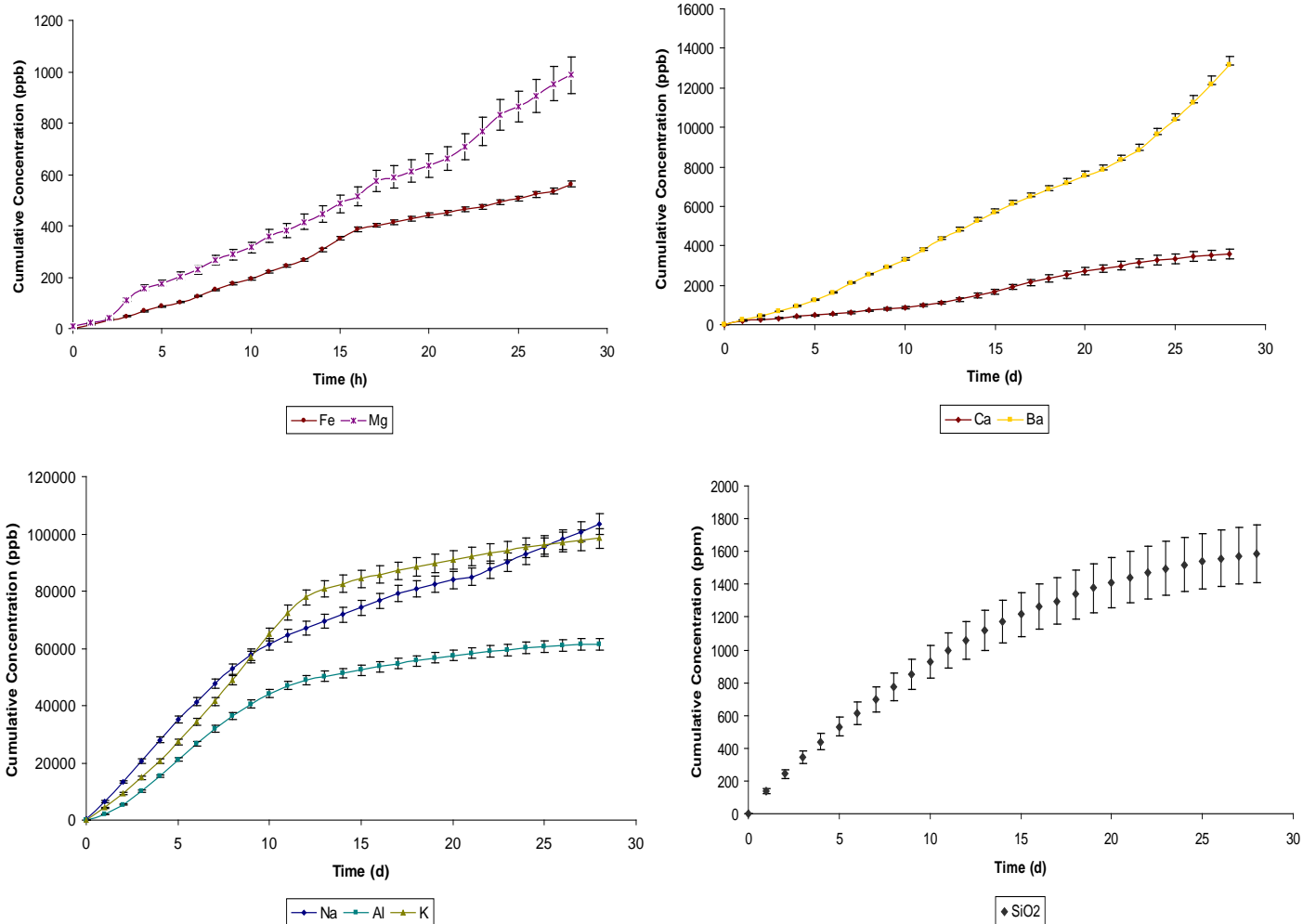

Fig. 5: Water analysis showing cumulative concentration of dissolved elements versus time after 28 days period

Mass Balance on the System

The mass balance is derived from the XRF data and dissolved minerals from the water analysis. A simple material balance equation is given:

$$m_i = m_o + d + error\ (loss) \tag{1}$$

where: mi = mass of element before experiment, mg
              mo = mass of element after experiment, mg
              d = mass of dissolved element, mg
              error or loss shows the mass that is lost in the system

Unfortunately, currently only the data for 7 days experiment is available to carry out the mass balance. Table 3 shows the results. More data are currently being analysed and will be reported in the future.

CONCLUSION

The fluid-rock interaction study is important for the prediction of dissolution and precipitation of minerals. The rock analysis showed that the major components of the rocks are albite, microcline and quartz. The result of this study showed that albite feldspar and microcline are more soluble compared to quartz.

Tab.3: Mass balance for 7 days experiment

Elements (mg)	Rock composition before	Rock composition after	Dissolved to water	Calculated loss
SiO$_2$	567.70	352.88	135.81	79.01
Al	41.30	23.78	6.470	11.04
Fe	7.49	3.16	0.056	4.28
Mn	0.44	0.17	0.066	0.21
Mg	0.41	0.00	0.060	0.35
Ca	3.13	0.90	0.203	2.03
Na	13.85	2.81	13.215	-2.17
K	27.12	16.65	8.786	1.69
Ti	0.43	0.25	Below trace	0.18
P	0.04	0.00	Not Analysed	0.04
S	0.45	0.01	Not Analysed	0.44

Water analysis showed that higher concentrations of sodium, potassium, aluminium and especially silica were present indicating dissolution of the primary feldspars, followed by quartz. The results would suggest silica scaling. With the injection of fresh water, it will introduce more dissolution, and improve permeability. However, since fresh water is not saturated with respect to silica, more silica would be dissolved and would eventually precipitate. The dissolution rate would also be underestimated as the presence of electrolyte (e.g. Cl$^-$) increases the dissolution rate of some minerals such as quartz (Dove, and Crerar, 1990). Future work will involve the modelling of the dissolution rate and precipitation rate of the minerals.

ACKNOWLEGMENTS

REFERENCES

Azaroual, M., and Fouillac, C., 1997, Experimental Study and Modelling of Granite-Distilled Water Interaction at 180°C and 14 Bars: Applied Geochemistry, V. 12, pp. 55-73.

Castro, M. R., Lopez, D. L., Reyes, J. A., Matus, A., Montalvo, F. E., Guerra, C. E., 2006, Expected Silica Scaling from Reinjection Waters After Installation of a Binary Cycle Power

Station at Berlin Geothermal Field, El Salvador, Central America, GRC Transcations, V. 30, pp. 487-492

Chopra, P., and Holgate, F., 2005, A GIS Analysis of Temperature in the Australian Crust, Proceedings of the World Geothermal Congress, Antalya, Turkey, 24-29 April 2005

Dove, P. M., and Crerar, D. A., 1990, Kinetics of Quartz Dissolution in Electrolyte Solutions using a Hydrothermal Mixed Flow Reactor: Geochimica et Cosmochimica Acta, V. 54, pp. 955-969

Geodynamics, 2009, Power from the Earth. Habanero 3, http://www.geodynamics.com.au/IRM/Company/ShowPage.aspx?CPID=1403, accessed 10 January 2009.

Grigsby, C. O., Tester, J. W., Trujillo JR., P. E., and Counce, D. A., 1989, Rock-Water Interactions in the Fenton Hill, New Mexico, Hot Dry Rock Geothermal Systems I, Fluid Mixing and Chemical Geothermometry: Geothermics, V. 18, pp. 629-656.

HACH, 2009, DR/2010 Portable Spectrophotometer Procedures Manual. http://www.hach.com/fmmimghach?/CODE%3A4930022286|1, p 767 – 772, accessed September 2009

Kuncoro, G. B., Ngothai, Y., O'Neill, B., Pring, A., Brugger, J., 2009, A Preliminary Study on Fluid-Rock Interactions of the Hot Fractured Rock Geothermal System in Cooper Basin, South Australia, Proceedings Australian Geothermal Energy Conference 2009, Brisbane, Australia 10-13 November 2009

Marks, N., Schiffman, P., Zierenber, R. A., Franzson, H., Fridleifsson, G. O., 2010, Hydrothermal Alteration in the Reykjanes Geothermal System: Insights from Iceland Deep Drilling Program Well RN-17, Journal of Volcanology and Geothermal Research: V. 189, pp. 172-190

Mink, R., 2004, Geothermal Energy, Kirk Othmer Encyclopedia of Chemical Technology, V. 12, pp 521-547

Posey-Dowty, J., Crerar, D., Hellerman, R., and Clarence, D. C., 1986, Kinetics of Mineral-Water Reactions: Theory, Design, and Application of Circulating Hydrothermal Equipment: American Mineralogist, V. 71, pp. 85-94.

Pring, A., 2009, personal communication.

Rimstidt, J. D., and Barnes, H. L., 1980, The Kinetics of Silica-Water Reactions: Geochimica et Cosmochimica Acta, V. 44, pp. 1683-1700.

Robinson, B. A., 1982, Quartz Dissolution and Silica Deposition in Hot Dry Rock Geothermal Systems, Thesis, Cambridge, Massachusetts Institute of Technology.

Savage, D., Cave, M. R., Milodowski, A. E., and George I., 1987, Hydrothermal Alteration of Granite by Meteoric Fluid: An Example from the Carnmenellis Granite, United Kingdom: Contributions to Mineralogy and Petrology, V. 96, pp. 391-405.

Savage, D., Bateman, K., and Richards, H. G., 1992, Granite-Water Interactions in a Flow-through Experimental System with Applications to the Hot Dry Rock Geothermal System at Rosemanowes, Cornwall, U.K.: Applied Geochemistry, V. 7, pp. 223-241.

SEN, 2010, Hot Dry Rocks – Geothermal, http://sen.asn.au/renewables/geothermal, accessed May 2010

Tarcan, G., 2005, Mineral Saturation and Scaling Tendencies of waters discharged from wells (>150oC) in geothermal areas of Turkey: Journal of Volcanology and Geothermal Research, V. 142, pp. 263-283.

Wyborn D., de Graaf, L., Davidson, S., Hann, S., 2005, Development of Australia's First Hot

Fractured Rock (HFR) Underground Heat Exchanger, Cooper Basin, South Australia: Proceedings World Geothermal Congress 2005, Antalya, Turkey, 24-29 April 2005

Wyborn, D., 2010, personal communication

Yanagisawa, N. Matsunaga, I., Sugita H., Sato, M., and Okabe T., 2005, Scale Precipitation During Circulation at the Hijiori HDR Test Field, Yamagata, Japan: Proceedings World Geothermal Congress 2005, Antalya, Turkey, 24-29 April 2005

BRIEF BIOGRAPHY OF PRESENTER

Gideon Kuncoro obtained his Bachelor degree in Chemical Engineering at The University of Adelaide (2004). He continued his study and obtained his Masters degree in Engineering at the same university (2008) in wastewater treatment area of the denitrification process at Glenelg Wastewater Treatment Plant with United Water. He then continued to do a PhD (2008) in alternative energy field specifically in geothermal energy.