A REVIEW OF CURRENT EXPERIMENT FULID-ROCK INTERACTION IN EGS RESERVOIRS

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ABSTRACT

Laboratory based experimentation is a cost effect method for exploring and testing developments in enhanced geothermal systems. Flow-through experiments are a powerful tool in such investigations. A wide range of concepts are presently being investigated using flow-through systems. These vary from the testing of new flow fluids, water – rock interactions at critical and super-critical temperature of water, and the development of new de-scaling methods. At the University of Adelaide and the division of mineralogy of the South Australian Museum, a wide range of water rock interactions are under study. Fundamental studies include coupled dissolution-re-precipitation and mineral replacement, with a focus on changes in porosity. Important applied studies are in progress on materials from exploratory wells at potential EGS sites. A flow-through system is used to investigate water- rock interactions at temperatures and pressures found at the site being explored.

1. LABORATORY BASED EXPERIMENTS IN FLUID-ROCK INTERACTION, USING FLOW-THROUGH TECHNIQUES, RELEVANT TO ENHANCED GEOTHERMAL SYSTEMS (EGS) RESERVOIRS

The defining feature of an enhanced geothermal system (EGS) is that the heat reservoir is without sufficient water for circulation to enable heat exchange and thus the exploitation for generation of energy. Typically such systems have granitic rocks at significant depth as host, with an overlaying insulating layer of geological cover. In order to harness the energy from such a system, a fluid source must be identified and a fluid permeable path created in the heat reservoir (by fracture stimulation). Present rate of development of EGS is accelerating with heightened awareness of the need to find new energy sources that emit less CO_2. Other factors create significant local incentives to pursue EGS energy generation. The close proximity of uranium and copper mining sites, and the increasing power needs of these expanding ventures, are key driver s of the establishment of power sourced from EGS generation in the Cooper Basin, South Australia. In Japan, heightened concerns of the risk of nuclear energy are a significant factor. A summary of such systems is available on the world wide web, including a Wikipedia site[1].

Work in this area involves a high level of international collaboration. A major EGS European Union initiative is at Soultz – sous –Fôrets in Alsace France[2] and is a leader in geothermal research. Japanese researchers are actively involved in research based in Europe, as well as North America and Australia. Japanese involvement with Australian EGS research includes collaboration with School of Chemical Engineering at The University of Adelaide[3], and focuses on the processes of establishing operational enhanced geothermal systems for the commercial production of power. Companies involved in such projects include Petratherm[4] and Geodynamics[5]. A major focus of attention is the Cooper Basin in South Australia, where the heat reservoir incorporates horizontal fracture zones, making the development particularly attractive. The Pilbra region in Western Australia is another potential area for EGS development in Australia.

New EGS sites for research and development in the USA are under development in Nevada and Arizona. Research continues with issues arising from water based systems. In addition to such studies, a new research initiative is the use of carbon dioxide as the heat transmission fluid.[6]For such systems, laboratory based research has centered on batch reactor tests and computer simulation techniques. Fluid-rock interactions are a central issue of concern for such a system, and include the complication of interaction with even minor amounts of water within the host rock and this has significant implications for the porosity and permeability of any such system. An EGS research site at Ogachi Japan[7] is part of an international collaboration on this project.

The role of fluid-rock interactions influences the functioning of power generation utilising an EGS on multiple levels, from the establishment of the system, the continued functioning of the system and the exchange of heat from the system. Laboratory based experiments provide a cost effective way to guide the development of on-site systems. The characterising of the solid and fluid components of a system is a vital first step, to understanding a system and guiding the selection of the rock zone for the fissure pathway and the nature of the fluid to be used. The identification of potential problems is a key aspect of such studies. An early example of this was at Fenton Hill where the presence of a concentrated in-situ pore fluid was identified. The displacement of this in-situ fluid and the mixing with meteoric make-up water was responsible for the composition of the circulating water, rather than thermodynamic equilibrium[8]. The Fenton Hill experimental site operated from 1983 to 1996. The project included an operational plant utilizing energy from the hot dry rock (HDR) heat source. [9, 10] The work of researchers such as C. Grigsby, J. Tester, P. Trujillo, L. Blatts, D. Counce, R. Charles, C. Holley (to name a few) has formed an invaluable base for the present surge of interest in utilising EGS for energy production.

The role of laboratory-based experimentation does not end with the establishment of a system. New ways of testing pathways for problem solving can be developed. Laboratory based studies involving water, or aqueous based solutions, flowing through a mineral assemblages or a single mineral at high temperature and pressure, are carried out by a limited number of groups, distributed throughout the world. Significant research in this area can be found in; Iceland, USA, China, Japan, Switzerland, Australia, New Zealand.

Single mineral studies at high temperature and pressure which describe the use of a flow-through include studies of albite (using a one pass flow through)[11]; boehmite[12]; gibbsite (column experiment)[13] and wollastonite. [14] Work studying the dissolution of quartz is extensive and the techniques used include rocking autoclave and spinning basket experiments[15] as well as pump-driven flow-through studies.[16, 17]

The Energy and Geoscience Institute at the University of Utah, under the leadership of Peter Rose is an important centre for the development of tracers for the geothermal industry and for work in the area of identifying and testing possible reagents to dissolve unwanted precipitates within a system.[18]A flow-through system, with temperatures in the range 150 – 300 ^{0}C, was used in the recent development of a method for the simultaneous removal of silicate and calcium carbonate scale, using a combination of high pH and chelating agents.[19]

The Chinese Academy of Geological Sciences, Institute of Mineral Resources (located in Bejing) has a specialized ‘Laboratory of Geothermal Kinetics’. A group led by Ronghua Zhang has a particular interest in rock-water reactions in the temperature range 300 – 450 ^{0}C (the region of critical and super critical water). The group has a series of studies over a 20 year period, Zhang et al. (1990 – 2011).[20,21, 22, 23.] In the temperature region studied, large variations in the properties of water are observed. The maximum release of Si from minerals was found to occur in this temperature range and this can lead to the collapse of rock structures.

Kochi University, Japan hosts the ‘Research Laboratory of Hydrothermal Chemistry’. Granite – fluid interaction has been studied using a flow through, tube type, autoclave developed for temperatures up to 425^{0}C.[24] Studies included dissolution – deposition reactions over a range of temperatures. The *in-situ* production of hydrothermal synthetic materials is another area of study. The experimental system allows studies at sub- critical to super – critical temperatures.

An example of the expansion of the concept of laboratory-based experiments is the development and use of a portable test rig in New Zealand. The purpose of the rig is the study of scaling and scaling mitigation methods, on site at geothermal installations (Brown and Rock 2010)[25]

2. WORK BY THE GROUP IN THE SCHOOL OF CHEMICAL ENGINEERING AT THE UNIVERSITY OF ADELAIDE AND THE DEPARTMENT OF MINERALOGY AT THE MUSEUM OF SOUTH AUSTRALIA

A group within the School of Chemical Engineering at the University of Adelaide, jointly with members of the Department of Mineralogy at the South Australian Museum, have developed a closed-loop flow through cell (see Figure 1). Rather than using a pump, fluid is circulated by the thermo-siphon principle, resulting from a temperature differential within the system[26,]. This system can operate at low to moderate hydrothermal conditions (up to 300 ^{0}C at vapour pressure) Techniques used by the group also include pump driven systems which can operate up to 450 ^{0}C and 700 bars. These systems have also been adapted to enable in situ monitor of replacement reactions using powder neutron diffraction methods. Use is also made of static Teflon lined autoclave vessels and titanium autoclaves.

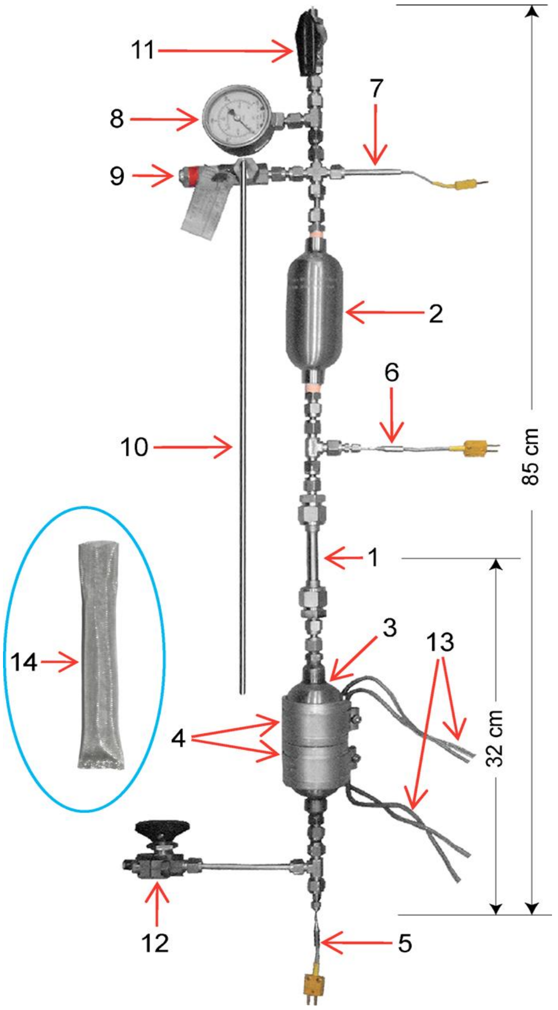


Figure 1: Design of the geothermal cell and the sample holder:

(1) Ti–Zr alloy sample compartment;
(2) 150 ml expansion vessel;
(3) 150 ml fluid reservoir;
(4) two tabular heaters;
(5 – 7) K-type thermocouples, measuring the temperatures at (5) the centre of the fluid reservoir, (6) the top of the sample compartment, and (7) near the pressure relief valve;
(8) pressure gauge;
(9) pressure relief valve;
(10) condensation tube ;
(11) top ball valve;
(12) bottom fill/drain ball valve ;
(13) power leads of the heaters, connecting to a temperature controller;
(14) enlarged view of the sample tube constructed from 316-type stainless steel mesh .

Table 1: ICP-MS results for sample (A)

Sample A	**1 -10 ppb**	**10 - 10^2 ppb**	**10^2 – 10^3 ppb**	**10^3 -10^4 ppb**	**10^4 – 10^5 ppb**	**>10^5 ppb**
After leaching 28 days	V; Mn; **Sb**	Mg; Fe; Cu; Zn; **As;** Sr; Mo; Ba	Al	K;Ca	Na	
After the wash cycle	V; Cr; **Sb**	Li; Mn; Cu; **As;** Cd	Mg ; Fe; Zn; Sr; Mo; Ba	Na	K; Al; Ca	

A focus of research continues to be coupled mineral replacement reactions, using a combination of static and flow through techniques. In all cases the re-precipitated material is micro porous, facilitating solution access to the reaction interface. Studies include pseudomorphic replacement, as in the case of replacement of leucite ($KAlSi_2O_6$) by analcime ($NaAlSi_2O_6$)[27] and in the transformation of pentlandite to volarite.[28, 29]Studies have also been made of the transformation of pyrrhotite to pyrite and magnetite[30] and the reverse process, magnetite to pyrite.[31] In some cases, but not all, the crystallographic orientation was preserved during mineral replacement reactions. The nature and stability of the porosity of the product minerals resulting from mineral replacement reactions[32] are of significant interest. Experiments are in progress using a flow through system which can monitor changes in permeability of a rock during reactive fluid rock interaction.

A second major focus of research in the group is the use of the thermosiphon flow-through cell to investigate the fluid-rock interaction of samples extracted from possible enhanced geothermal energy sites, at temperatures typically found in the potential heat reservoir. In addition, studies concerning the dissolution of quartz and precipitation of silica are in progress. In examining the fluid-rock interaction of material sourced from geothermal areas, solution analysis to monitor dissolved species as a function of time is essential, as is the measurement of pH. Solid samples have been examined using XRD and SEM. Data obtained has been be used to; identify cations which may have implications for scaling, correlate changes in silica behaviour with solution pH, and monitor dissolution and re-precipitation reactions.

Selected examples of the results obtained are presented and the following points of methodology should be noted. Samples were taken from within granitic rock and from boundary layers. Experiments were done using the continuous flow, thermo-siphon system with the sample holder heated to 180±5^{0}C. Each experiment included a wash cycle. After draining the system and removing the rock sample, fresh water was circulated for 24h at 180 ^{0}C and the solution collected and analysed. At the end of each run the system was allowed to cool to below 40 ^{0}C before the fluid was drained, and then divided for pH measurement and determination of solution species. Measurement of reactive silica (monomeric and oligomeric silica) was made using a colourmetric molybdate method.

A survey of cations released to the circulating solution and (after sample removal) from the wash can be used to identify precipitates possible sources of scaling. Cation concentration was measured on acidified solutions using ICP-MS. Table 1 Shows the results for a selected sample (A), measured using acidified samples. The presence of As and Sb are both a source of problematic scaling and to obtain a more accurate measurements, alkaline solution samples were used (because of the particular chemistry of these elements).

Data for another rock sample (X) is presented in Figures 2(a,b) and 3. The release of silica and cations as a function of leach time is shown in Figure 2(a,b). and the dominance of silica can be seen. Evidence for the precipitation of Ca, Al and Fe species can be clearly seenin Figure 2(b). A comparison of cations recovered from the wash and the circulating leach solution is shown in Figure 3 and the high percentage of Ca, Al and Fe as well as K and Mg and silica confirms the formation of precipitates of these species.

The pH of recovered circulating solution and wash solution is shown for 3 samples (including sample X) in Figure 4. The high pH of the circulating solutions is consistent with the precipitation of hydroxyl species. The alkaline nature of the wash is consistent with the dissolution of precipitated hydroxyl species.

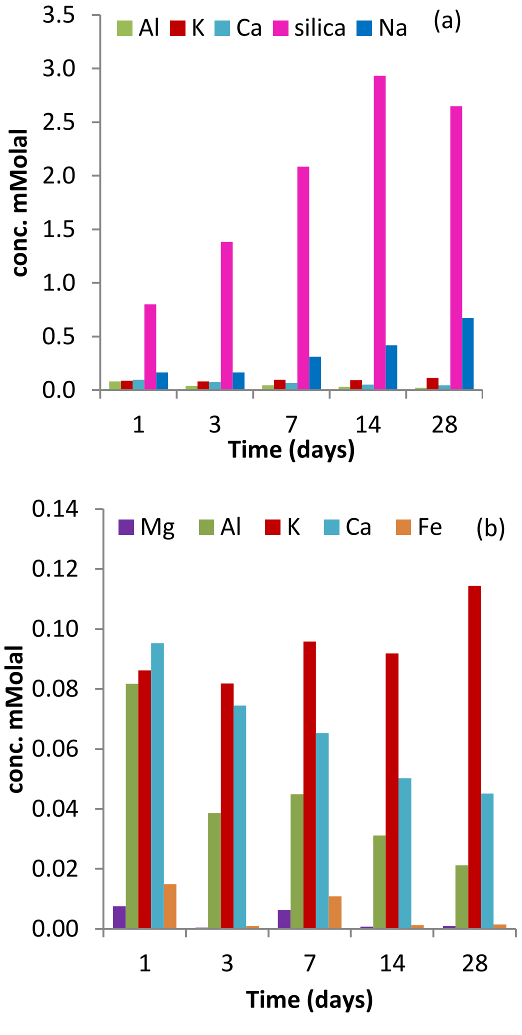


Figure 2 (a, b): Silica and cation release for sample X.

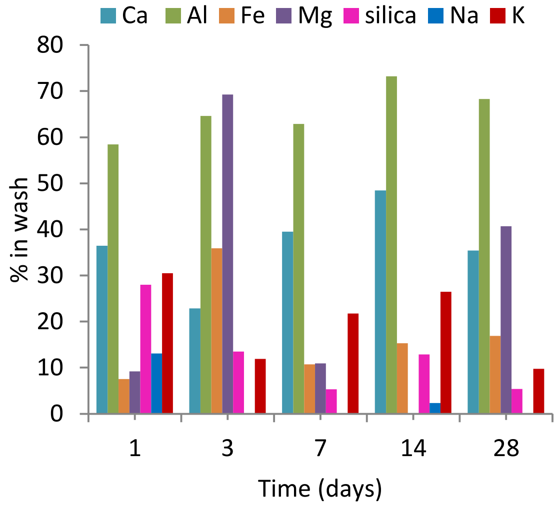
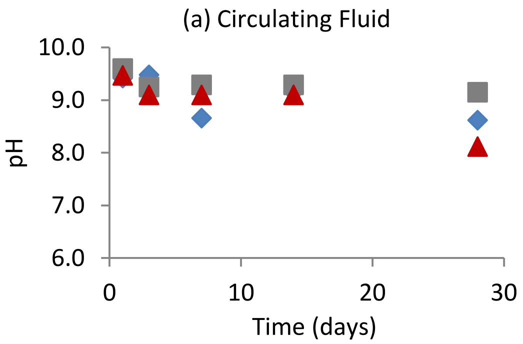


Figure 3: The percentage of each species recovered from the wash cycle solution for sample X



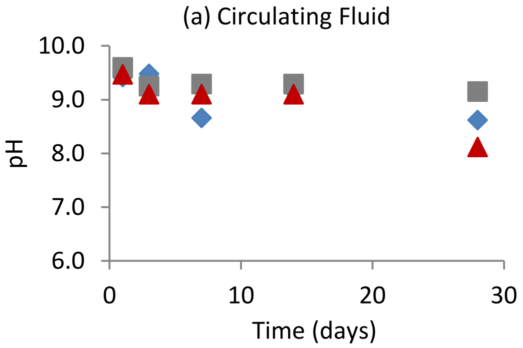


Figure 4(a, b): The pH of the solution recovered from 3 samples after continuous leaching and from the wash cycle.

When considering the reactive silica data it should be noted that the measurements were made within hours of the solution recovery. The variation of the behaviour of the two rock samples in Figure 5 is consistent with the widely different mineralogy of the samples as determined by XRD.

- Sample A: 52 % quartz; 7 % albite; 23 % muscovite; $KAl_2(AlSi_3O_{10})(OH)_2$
- Sample B: 7 % quartz; 29 % albite($NaAlSi_3O_8$); 27 % pyroxene ($Ca\ Mg_{0.74}\ Fe_{0.25})Si_2O_6$

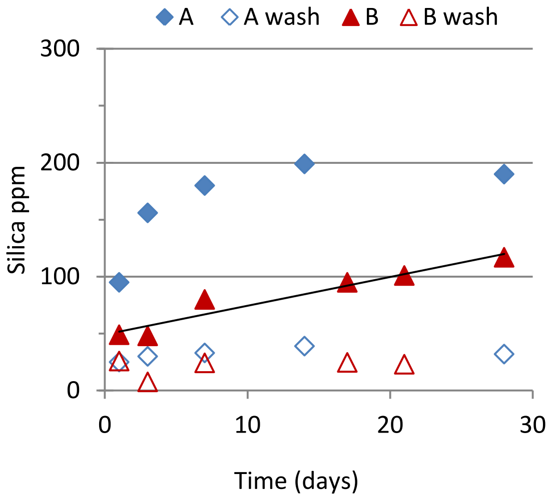


Figure 5: Comparison of silica recovery as a function of time for samples A and B

The silica data from sample A was used to confirm the temperature of the system, which had been monitored at 186 ^{0}C by the probe within the sample basket. Calculation using the equilibrium concentration of quartz (equation 1)[33] gives a temperature of 180^{0}C. The use of the total recovered silica (from the circulating solution and the wash) gives a value of 190±2^{0}C. The results would indicate that the measurement of the 'reactive silica' accounts for all the silica in solution (and that polymerisation had not occurred at the time of measurement). The results also indicated that the majority of the silica in the wash solution was generated by precipitation as the system was cooling.

$$\text{Log } C = -1309/T + 5.19 \qquad \{\text{Equation 1}\}$$

(where C= conc. Silica= mg/Kg; T = absolute temp. K)

In conclusion, the flow through system is a powerful, cost effective tool for studying rock water interaction.

Data obtained can be used to:

- identify cations which may have implications for scaling,
- correlate changes in silica behaviour with solution pH, and mineralogy
- monitor dissolution and re-precipitation reactions

In our work, future studies would be extended to the investigation of the interaction of specific solution compositions for a selected solid sample.

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