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A NEWLY DEVELOPED FLOW-REACTOR, WITH pH MEASUREMENT SYSTEM, FOR LABORATORY SIMULATION OF WATER-ROCK INTERACTION PROCESSES.

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ABSTRACT

A tube-type flow-reactor, with a pH measurement system, has been developed to simulate fluid-rock interaction processes over a wide range of temperatures and pressures. Our reactor system has an application in studying dissolution-deposition processes in natural flow systems, as well as fracture formation, for HDR (Hot Dry Rock) geothermal energy extraction.

The flow system can accommodate the mixing of two pre-heated (hydrothermal) fluids, of differing input temperature and chemistry, to flow through a column of rock (either chip or fractured core) with a pre-set thermal gradient.

Modifications to the flow reactor allow experiments are to be conducted at temperatures up to 500°C and pressures of 10-50MPa.

The pH of reacted hydrothermal fluid (i.e. fluid having undergone chemical water-rock interaction) in the flow system may be measured '*in-situ*' (under reaction conditions) or at room temperature. The pH of the hydrothermal fluid at 'reservoir' conditions was assessed using SOLVEQ92, based on; (i) the ΔE (potential difference) between an external pressure equilibrated, Ag/AgCl (0.1M KCl) reference electrode and a Pt-hydrogen electrode, for fluid which had interacted with granite at 20MPa and 100°C, 150°C, 200°C and 250°C, (ii) pH and ΔE of standard buffer solutions under the same experimental conditions; and (iii) major element chemistry of the reacted solutions.

HDR experiments were undertaken at standard operating conditions of 20MPa and thermal gradient up to 425°C. We found that host rock characteristics, fluid chemistry, flow rate, temperature and temperature gradient are important factors that dictate the mechanisms of mineral dissolution and/or precipitation, and the condition of induced and natural fracture-pathways.

1. INTRODUCTION

Fluid-rock reactions in deep geothermal reservoirs may be regarded as being in chemical equilibrium, since the duration of their interactions can be regarded as sufficiently long. Hot fluids, however, obtained by downhole sampling or discharge of a deep well, have undergone steam separation, gas loss and/or mixing, and no longer reflect the (chemical) character of the geothermal reservoir.

Numerous workers have attempted to model geothermal reservoir conditions (Reed, 1982; Reed and Spycher, 1984; Mok *et al.*, 1995; to name only a few), whilst others have attempted laboratory simulation of fluid-rock interactions at a range of pressures and temperatures, using a variety of apparatus (e.g., Savage *et al*, 1986, 1992; Kojima, 1994; and Chigira and Watanabe, 1994; Watanabe *et al.*, 1995).

A major consideration, for the management of 'conventional' geothermal development projects, and the understanding of deep fluid-rock interaction processes, is the 'in-situ' analysis of reservoir chemistry, particularly pH. Since direct measurement of reservoir pH is often impractical, methods have been developed to determine pH values, based on the chemical analysis of reservoir fluids discharged via deep geothermal wells, or surface features.

A variety of electrodes have been developed to measure fluid pH at high temperature, and these have found applications for the laboratory study of multicomponent aqueous systems. Reliable and accurate high temperature pH measurements have been made using hydrogen concentration cell (Mesmer and Base, 1974), palladium hybrid electrodes (Macdonald *et al.*, 1980; Tsuruta and Macdonald, 1981) and ceramic membrane electrodes (Hettiarachchi *et al.*, 1985; 1990). Fewer studies, however, have attempted to develop pH-measuring systems for multicomponent homogeneous chemical equilibria at high temperature and high pressures.

This paper describes an innovative flow-through reactor, with pH-measuring system (Figure 1). We use the reactor to simulate chemical interaction processes in a hypothetical hydrothermal system operating at temperatures and pressure of up to 400°C and 40MPa respectively, (see Bignall *et al.*, 2000, these proceedings) with recent modifications allowing experiments to now be undertaken to 500°C and up to 50MPa.

2. APPARATUS - METHODOLOGY

The main features of the flow reactor system are two pressure pumps (for two fluids, with respective flow rates of up to 10ml/min), a central 1 metre-long tubular, stainless steel autoclave (for modeling the geothermal reservoir, and containing either chip or block rock samples) with five external heaters, a pre-heat autoclave, pH measurement apparatus and sample collection system.

The five separate heaters, placed around the central tubular autoclave, can be controlled to establish any temperature gradient. Calibration tests were performed, with five thermocouples located inside the length of the reactor tube, as shown in Figure 2. The reactor tube has an internal volume of $500cm^3$, with a cross-sectional area of $5cm^2$. Porosity in the tube is about 35%.

The initial (unreacted) solution is saturated with H_2 before being pumped into the reactor system, at a flow rate of 1.0ml/min and 200kgf/cm^2 (about 20MPa), with the fluid-rock (cleaned granite chips) simulation experiments typically running for about 100 hours.

Fluids in the upper, middle and lower parts of the main tube reactor can be extracted via capillary tubes to the pH measuring cell, or allowed to outlet at the base of the reactor tube, and then pass to the output solution tank. The pH measuring cell holds a platinum-hydrogen electrode in a reservoir tank with an external Ag/AgCl (0.1M KCl) pressure-balanced reference electrode (Figure 3). Using this cell, the pH of the reacted solutions can be measured at the same temperature, pressure and saturated solubility conditions as in the main reactor tube. The Ag/AgCl reference electrode is maintained at room temperature, and is not in direct contact with the high temperature sample fluid.

pH values were calculated using calibration curves, produced using the standard solutions (Table 1; Hettiarachchi *et al*., 1986; Yuvaraju *et al*., 1994). Electric potential are measured for each sample solution, corresponding to fluid-rock interactions at a variety of operating temperatures. Major element concentrations of the resulting fluids may be analyzed by ICP-AES and AAS.

The results of laboratory experiments, comprising the continuous alteration of Iidate Granite at temperatures and pressures up to and exceeding supercritical conditions, are discussed by Bignall *et al*. (2000). Our experiments indicate that hydrothermal fluid-rock interactions are affected by a variety of experimental conditions, including flow rate, pH and chemistry of the hydrothermal solutions, temperature and temperature gradient, mineral composition, and the characteristics of the natural and induced fracture pathways.

3. RESULTS

3.1 Measurement of pH

The pH of output hydrothermal ('reservoir') fluid was measured during operation of the flow-reactor using the pH measuring system, and additionally at room temperature. The software, SOLVEQ92 was used to calculate the pH of fluid that had interacted with the ('reservoir') granite chips (Wang *et al.* 1999), based on the potential difference (ΔE), major element chemistry and pH of the reacted (hydrothermal) solution, analyzed at room temperature.

The potential difference between the external pressure equilibrated Ag/AgCl reference electrode and the Pt-hydrogen electrode was measured, for hydrothermal fluids that had interacted with granite at 100°C, 150°C, 200°C and 250°C respectively (Table 2). The pH of 'reservoir' fluid, extracted directly from the main reactor tube can be approximated, based on a plot of potential (ΔE) values, versus pH of standard buffer solutions, measured at 100°C, 150°C, 200°C and 250°C, and pressure of about 20MPa.

Major element chemistry, and pH, of reaction solutions measured at room temperature, are shown in Table 3. These data were used to calculate 'reservoir' pH, using SOLVEQ92, with the relationship between the reaction temperature, and calculated and measured (*in-situ* and at room temperature) pH values, shown in Figure 4.

The pH of the reaction solution is temperature dependent, and it is not possible to simply interchange the *in-situ* (reservoir) pH values with those measured at (low) room temperature, to make an assessment of 'reservoir' pH. Never the less, there is a close agreement between the *in-situ* pH values and those calculated by SOLVEQ92. The latter is clearly an effective method of assessing the pH of fluid in a geothermal reservoir.

3.2 Laboratory simulation of HDR system

We used Iidate Granite, for a series of HDR experiments in the tube-reactor, at typical operating conditions of 20MPa and a thermal gradient up to 425°C. Modifications to the flow reactor system are proposed that will allow operative conditions as high as 500°C and 50MPa.

The chemical composition of output solutions is monitored, and analysed for Si, Ca, Mg, Al and Fe using ICP-AES, and for Na and K using AAS. The weight change of granite samples from the (maximum temperature) 350°C, 400°C and 425°C experiments are shown in Bignall *et al.* (2000).

As a result of the dissociation capacity of hot water, ion product under saturated vapour pressures, and density changes, Iidate Granite readily dissolves below 330°C. Above 330°C, the ion product is not high, and deposition of secondary minerals (predominantly sericite, and a subordinate calc-silicate phase) results from saturated solutions carrying material dissolved from reactions at 250-330°C.

Figure 5 shows major element chemistry, versus time, of output solutions from the 400°C experiment. After about 12 hours there is little variation in the major element chemistry. The system may be regarded as having reached some 'apparent' equilibrium condition at this time.

Granite samples, in the upper part of the flow reactor (i.e. where temperatures are typically between 250 and 340°C) are characterised by quartz and feldspar crystals that have a pitted appearance (Figure 6).

Above about 340°C, but <400°C there is a strong weight gain, reflecting the precipitation of quartz and secondary K-feldspar (adularia), and lesser amounts of sericite which deposits into fractures (Figure 7). The slow rate of mineral dissolution (mainly feldspar) in the >400°C zone corresponds to lower Kw values, whilst the preference for few mineral species to deposit, at these physical and chemical conditions, has significant implications for maintaining fluid pathways.

4. SUMMARY

A flow-reactor system, with pH measurement apparatus, has been developed to study the character of hydrothermal solutions and the chemistry of fluid-rock interactions under various pressure-temperature conditions. The system consists of a main reaction tube, and pH measuring cell, containing an external pressure-balanced reference electrode (Ag/AgCl; 0.1M KCl) and a platinum electrode.

We investigated the fluid-rock interaction processes, under a variety of conditions, and demonstrate direct measurement of pH in our flow-reactor system closely approximates pH values calculated using SOLVEQ92, for chemical reactions occurring at 150-250^{o}C, 20MPa, and flow rate of 1.0ml/min.

Fluid-rock interactions in a laboratory-simulated hydrothermal system are affected by several factors, including temperature (and thermal gradients), pressure, composition of the reactive fluid and the type of reservoir rocks - as well as flow rate, and shape and width of fracture surface/permeable channels. Such factors have a large influence on dissolution-deposition processes in a HDR hydrothermal system, maintenance of fluid pathways, and their exploitation as an energy resource.

In a developed HDR system, the nature of any induced fracture surface will be constantly changed in shape and form by the interaction of the (heated) injected fluid, which is mixed with hydrothermal fluids, and the host rocks; and these are important considerations for controlling heat extraction.

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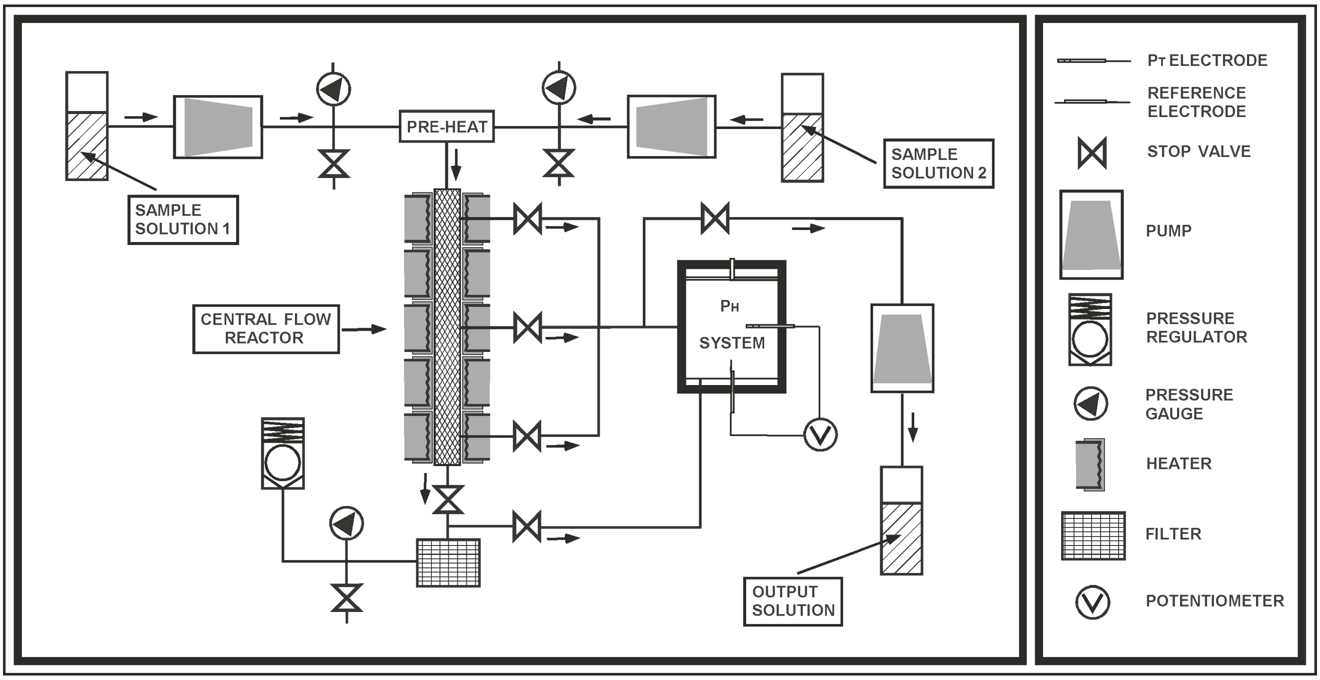

Figure 1: Schematic representation of the flow-reactor system, with pH measuring apparatus (after Wang *et al*, 1999).

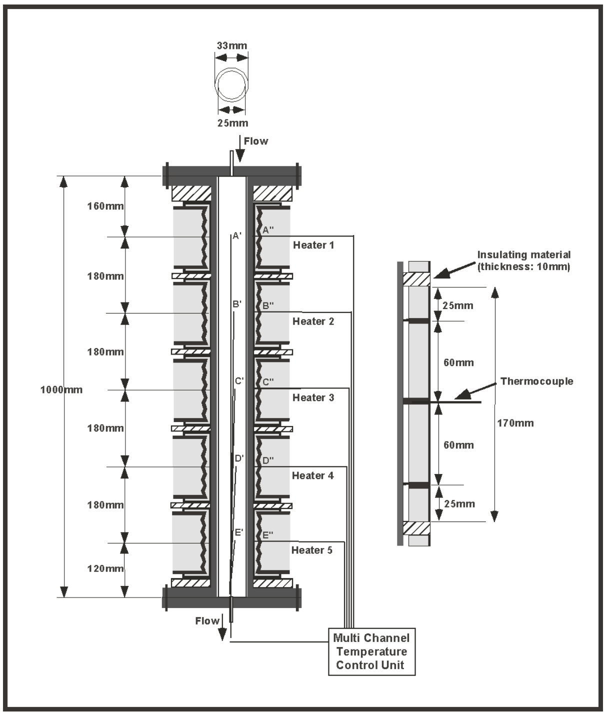

Figure 2: Schematic representation of the main/central flow reactor. A1, B1..... are thermocouple sites; A2, B2..... are control sites on the outside of the main reactor tube.

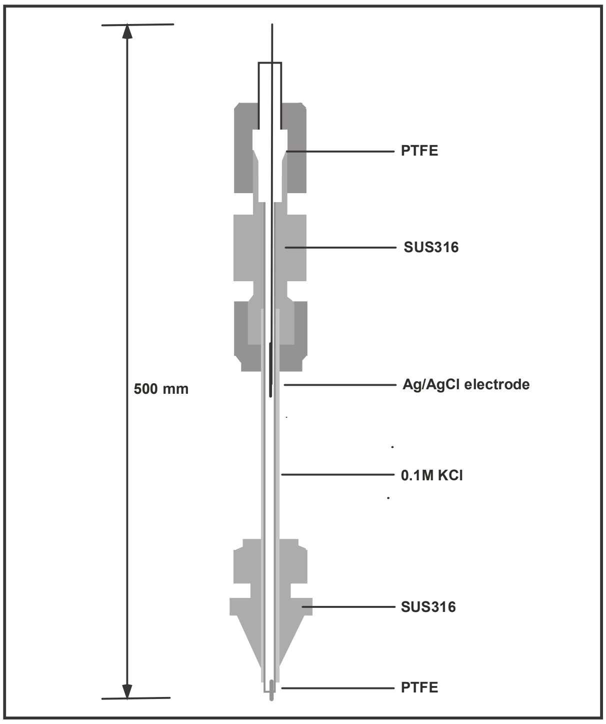

Figure 3: External pressure-balanced Ag/AgCl reference electrode.

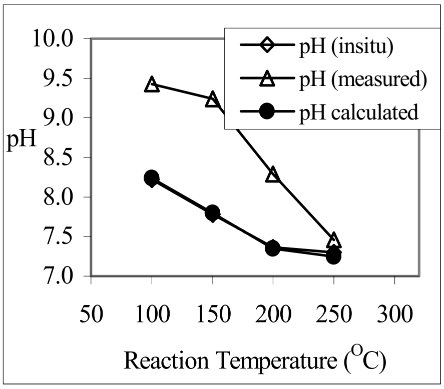

Figure 4: Plot of measured (in-situ and at room temperature), and calculated pH of (hydrothermal) reaction solutions after fluid-rock interactions at 100-250°C.

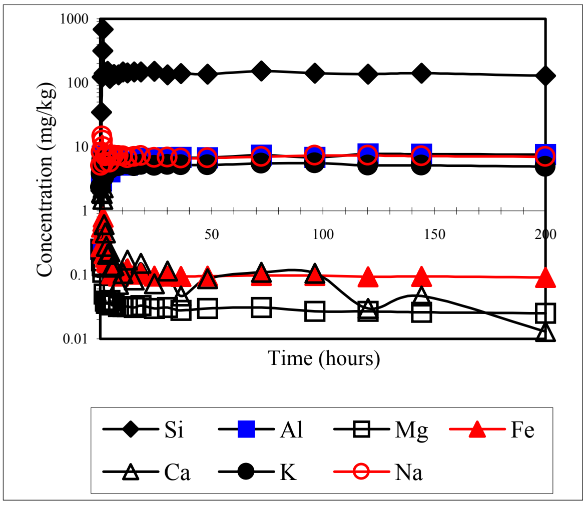

Figure 5: Major element chemistry (ppm) of output solution from 400°C, 20MPa flow reaction experiments, using H_2O as starting solution.

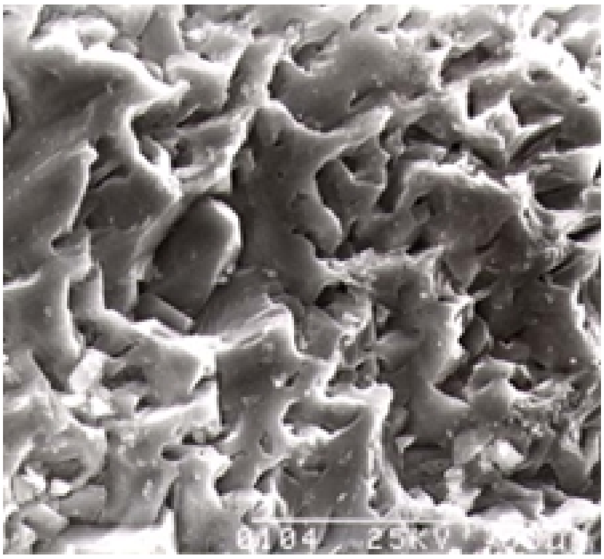

Figure 6: SEM micrograph of pitted quartz from the flow reactor experiment undertaken at 400°C, 20MPa. Starting solution was a NaCl solution (see Bignall *et al.*, 2000). Scale bar is 50µm.

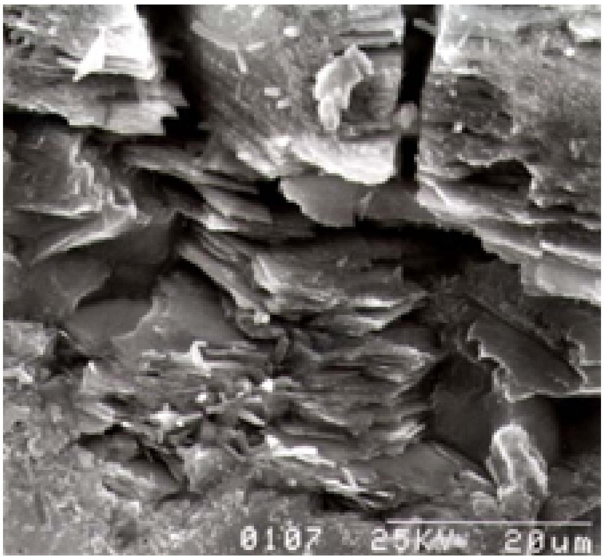

Figure 7: SEM micrograph of clay infilling a fracture in orthoclase, from the flow reactor experiment undertaken at 400°C, 20MPa. Starting Solution was H_2O. Scale bar is 20µm.

Table 1: Standard buffer solutions.

A	0.05M	Na_2SO_4	+ 0.01M	NaOH
B	0.05M	Na_2SO_4	+ 0.001M	NaOH
C	0.05M	Na_2SO_4		
D	0.05M	Na_2SO_4	+ 0.005M	H_2SO_4
E	0.01M	$B(OH)_3$	+ 0.01M	KOH
F	0.01M	$B(OH)_3$	+ 0.001M	KOH
G	0.01M	KOH		

Table 2: Potential values and measured pH of hydrothermal fluids after interaction with granite at high temperature.

Temperature (^{o}C)	ΔE (mV)	pH
100	803.2	8.22
150	777.9	7.78
200	752.1	7.36
250	745.5	7.30

Table 3: Major element chemistry (ppm) and pH of 100-250^{o}C fluids, collected and analysed at room temperature.

Temp. (^{o}C)	Si	Al	Fe	Mg	Ca	Na	K	pH
100	4.9	2.5	0.06	0.00	6.1	0.7	2.6	9.43
150	23.1	5.5	0.06	0.00	5.9	7.1	7.0	9.24
200	75.9	4.4	0.05	0.00	3.5	7.0	5.1	8.29
250	183.5	4.0	0.07	0.00	0.7	8.0	5.9	7.46