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**Two Dynamic Hydrothermal Systems and Fluid Samplers
for Studying Rock-Fluid Interactions**

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TWO DYNAMIC HYDROTHERMAL SYSTEMS AND FLUID SAMPLERS FOR STUDYING ROCK-FLUID INTERACTIONS

by

R. W. Charles, G. K. Bayhurst, and R. J. Vidale

ABSTRACT

Two circulation systems have been designed, built and tested over the last three years. These systems greatly aid in the study of rock-fluid interactions under flow conditions. A solution sampler has also been developed for fluid extraction under the pressure and temperature conditions of the experiment, eliminating fractionation on sampling.

I. INTRODUCTION

Circulation systems are an important tool in the study of rock-fluid interactions for many natural systems. Any system in which chemical leaching results in mass transport underground at the ambient pressure and temperature requires a circulation system at that temperature and pressure for experimental modeling. One is interested in the kinetics of reaction as the rock and fluid attempt to come to equilibrium as well as the final equilibrium assemblage.

Several areas of application for circulation systems are particularly important to current DOE interests. The successful function of a geothermal well requires definition of the reactions as fluid is circulated at depth. Proposed radioactive waste forms can be tested in such systems for leachability under various proposed pressures and temperatures much more readily than in the field. Determination of the feasibility of chemical extraction of elements of economic value from underground deposits is another use for such systems. In all of these cases dynamic testing of rock samples is much more relevant than tests in static or merely agitated hydrothermal systems.

Two dynamic (circulatory) systems are outlined here in detail. Both have been extensively tested and used in experiments of up to nine months' duration.

II. CIRCULATION SYSTEM WITH THE REACTION VESSEL AT A FIXED TEMPERATURE

A. Introduction

Figure 1 and plate 1 show the "fixed temperature" circulation system. Flow is counterclockwise. The name, fixed temperature, indicates that all rock samples placed in the reaction vessel are at the same run temperature. The entire circulating system could be maintained at up to 200°C, but this would offer no advantage over a stirred reaction vessel. Consequently, the temperature is allowed to drop to ambient outside the reaction vessel while pressure is maintained at run condition.

B. Maximum conditions

Run durations are indefinite at 0.33 kbar P_{tot} and 300°C. The longest thus far has been nine months. The system was tested successfully with circulation at $P_{\text{tot}}=0.55$ kbar for one week.

C. Hardware

Polished rock disks are placed on a tantalum pedestal inside the vertically mounted 500 ml Autoclave Engineers pressure vessel. An Ohio Thermal tube furnace (model Q7C) controlled by a Love Instruments controller (model 72) maintains the desired temperature. All valves and tubing are 0.64 cm (1/4") high pressure hardware with cone in cone fittings of 316 ss. Two solution samplers are placed at the points indicated. These will be explained in detail in a later section. Temperature is maintained at run temperature from the vessel to the hot sampler by means of heat tapes. A line filter with a 5 micron element catches any particulate matter and serves as a surface for scale accretion. A Bourden tube gauge is used to measure pressure. It is protected from the circulation fluid by a one-to-one piston gauge protector.

Circulation is achieved by means of a Scientific Systems C-239 variable speed, electrically driven, circulation pump. The pump was modified by designing new pistons because those supplied by the manufacturer failed to operate satisfactorily at 0.33 kbar. Pistons of 440C stainless, hardened to Rockwell 32C were found to be corrosion and abrasion resistant for initially distilled water experiments up to 0.55 kbar under continuous use. Pistons of A-286 stainless (Rockwell 22C) were more corrosion resistant but less abrasion resistant and have

been used for 0.1M sodium chloride up to 0.33 kbar P_{tot} . The pistons are sealed with graphite impregnated teflon packings.

After a few days operation, the seals begin to leak slowly (less than 50 cc/d). This fluid is captured and returned to the system by an air-driven Haskell piston pump through a manifold valve. Back leaks into the piston pump are prevented by means of a ball check valve.

Temperature is monitored with cromel-alumel thermocouples inserted in the vessel well and in the system flow. These readings are recorded intermediately on a Honeywell 24 channel recorder.

While the system is being heated, pressure is prevented from rising above the desired level by a dripper type safety valve. This valve also releases any excess pressure after run pressure has been attained.

Volume of the system is about 560 ml. More volume may be included by the use of ballast tanks.

D. Comments

Typical run durations are 4 to 8 months at 0.33 kbar and temperatures up to 300°C. Granodiorite and basalt have been reacted with distilled water and solutions of sodium chloride. Results of the granodiorite reactions with distilled water are reported in LA-7334-MS (Charles, 1978) and LA-7735-MS (Charles, 1979).

In most cases, scaling deposits were common but did not constrict flow with one exception. Columbia River Basalt containing a fine grained groundmass of alkali feldspar and quartz was quite reactive. After 4 months, the 0.64 cm (1/4") tubing underneath the heat tapes was completely sealed with feldspar of the structural variety sanidine. Capillary tubing connects some of the hardware. This tubing, at room temperature, did not clog with material under any of the run conditions.

The temperature calibration curve for the pressure vessel is shown in figure 2. This was prepared under flow conditions at a nominal temperature of 300°C and 0.33 kbar P_{tot} . A gradient of a few degrees over the samples can be expected for a given run. Thermocouples placed inside the pressure vessel did not indicate temperature instability caused by convective flow.

III. CIRCULATION SYSTEM WITH A CONTROLLED TEMPERATURE GRADIENT IN THE REACTION VESSEL

A. Introduction

Figure 3 and plate 2 show the controlled temperature gradient circulation system. Flow is clockwise. A temperature gradient is maintained across a 102cm pressure vessel. Fluid temperature at the hot end is maintained until the fluid passes the hot fluid sampler after which it is allowed to drop to ambient temperature. The system models the water-rock interaction as an initially cool fluid enters and flows through a rock fracture at depth, for example, in the LASL hot dry rock geothermal system.

B. Maximum Conditions

Run durations up to 2 months at 0.33 kbar and a temperature range of 40 to 320°C are typical. The vessel was proof tested to 0.67 kbar. All fittings are rated to 2 kbar.

C. Hardware

Rock prisms (6) are placed along the axis of the pressure vessel and attached to a tantalum rod with tantalum wire. The reaction vessel was fashioned from a piece of A-286 stainless 102 cm long and 3.8 cm in diameter. A deep hole of 1.3 cm diameter was drilled and honed centered on the long axis of the vessel. Seals are cone in cone with cones of A-286 and caps and thrust rings of heat treatable 4340E. Caps are hardened to Rockwell 35C and washers to Rockwell 50C.

The high temperature end of the vessel is heated by a standard 30.5 cm (12") Lindberg Hevi-Duty clamshell furnace, model 55031A. Temperature control is established with a Love Instruments model 71 controller.

A coolant system must be added to the opposite end of the vessel to produce the desired gradient. Copper coils are wrapped around about 35 cm of the vessel. The coolant is circulated by a Forma Scientific (model 2095) refrigeration unit and pump.

The remainder of the system is similar to that of the fixed temperature circulation system. Total volume with one 500 ml ballast tank is 700 ml.

D. Comments

Typical run durations are about 2 months at 0.33 kbar and a gradient of 280°C. Both granodiorite and basalt have been reacted with distilled water. Scaling did not cause constrictions. The system can react sodium carbonate and sodium chloride solutions as well. Results are currently being interpreted. One

important observation is that the cooler rock samples gained weight while those in relatively high temperature portions of the vessel lost weight (see figure 4).

The reaction vessel was calibrated under run conditions (P, T, and flow). A thermocouple was placed at the cool end of the vessel and then withdrawn in 9 cm increments. The calibration is shown in figure 5. The tantalum holder and rock samples were in place during calibration so that flow conditions would be similar to run conditions.

IV. FLUID SAMPLERS

In initial experiments fractionation of solution during sampling was a serious problem - especially for the hot solutions. A pressure and temperature quench during sampling always produced fractionation. In order to avoid this problem a constant temperature and pressure sampler was developed.

Figure 6 shows a schematic diagram of the sampling system. The system is mounted vertically (the right side is up). Valves and fittings are standard 0.64 cm (1/4") high pressure tubing with cone in cone seals. Valves A and B are modified with an extended valve stem and graphite asbestos packings when they are used to sample hot solution. C is the sample chamber made of 316ss 2.54 cm O.D. X 9 cm long. The volume is about 35 cm³. H is a Haskell gas pump.

Initially the sampler is pumped up to run pressure with argon gas and heated up to run temperature by heat tapes with valves A, E and J closed. Valve A is opened. Valve E is opened. Valve J, a micrometer valve, is opened and argon is bled off through the water trap. Argon and H₂O were found to be immiscible when A is opened over a period of as long as 48 h. When H₂O appears in the trap, the sampler is full. Then valves A, B and D are closed and the sampler is allowed to cool. The sample is contained at this point in C, except for a small amount in the 0.64 cm tubing which is of negligible volume. One merely has to open the sampler and analyze. No precipitates have been found thus far in the sampler.

Solutions taken show a systematic difference between hot and cold samples. Hot samples, as one might expect, have a higher element concentration. Figure 7 gives data for a 2 month experiment in which 9519 biotite granodiorite was reacted in the controlled temperature gradient circulation system with a temperature gradient of 270°C. Obviously, scale is being precipitated in the system.

These samplers have been in use for over a year and have eliminated the solution fractionation problem.

V. CONCLUSION

Two new circulation systems with fluid samplers developed here have been built and tested over a period of three years. They show wide application in studies of material-flowing fluid interactions at pressures relevant to the upper few kilometers of the earth's crust and temperatures up to 350°C.

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Figure 1. Fixed temperature circulation system.

Figure 2. Temperature calibration of the pressure vessel in the fixed temperature system. Bottom of the vessel is at left. Nominal temperature is 300°C. Temperature was measured during flow conditions at $P_{\text{tot}} = 0.33$ kbar.

Figure 3. Controlled temperature gradient circulation system.

Figure 4. Sample weight loss vs temperature for samples run in the controlled gradient circulation system. This example reacts 9519 biotite granodiorite with initially distilled water at a gradient of 40 - 310°C, $P_{\text{tot}} = 0.33$ kbar for 2 months.

Figure 5. Temperature calibration of the pressure vessel used in the controlled temperature gradient circulation system. Gradient was measured during flow conditions at $P_{\text{tot}} = 0.33$ kbar.

Figure 6. Fluid sampler. A, B, D, E, and G = high pressure valves. A and B have high temperature modification for use with hot fluid. C = sample chamber, F = pressure gauge, H = Haskell gas pump, I = argon reservoir, J = high pressure metering valve, and K = water trap.

Figure 7. Fluid sample results for SiO₂ from a temperature gradient experiment reacting 9519 biotite granodiorite with initially distilled water at $P_{\text{tot}} = 0.33$ kbar and a gradient of 40 - 310°C.

Plate 1. Fixed temperature circulation system.

Plate 2. Controlled temperature gradient circulation system.