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EXPERIMENTAL STUDY OF ROCK–FLUID INTERACTIONS USING AUTOMATED MULTI-CHANNEL SYSTEM OPERATED UNDER CONDITIONS OF CO2-BASED GEOTHERMAL SYSTEMS

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ABSTRACT

Rock–water–CO_2 interactions play a significant role in various hydrothermal systems that often produce carbonated waters, at CO_2 sequestration in aquifers, during CO_2 enhanced oil recovery and, finally, when considering an enhanced geothermal system with CO_2 replacing water as the working fluid.

To mimic these processes and accurately quantify the corresponding rock-fluid interaction, PARC has built a multichannel experimental system equipped with several batch reactors confined in a large oven and each connected on-line to a sophisticated analytical system that monitors dissolution profiles of individual minerals. The system has been recently upgraded by adding a flow-through circulation channel that allows us to simulate the reservoir injection-production loop and study additional factors related to the complex interaction kinetics.

Synchronized high-throughput operation in both batch and flow-through modes provides numerous data on thermodynamic and kinetic parameters of the interaction for modeling and additional studies at LBNL. In addition to mapping out mineral solubilities under high pressure and high temperature conditions in supercritical CO_2 – water environments, we have studied in more detail the dynamic effects of surface area and changes in other parameters during the course of the interaction. Along with better understanding of generic issues with hot rock-water-CO_2 interactions, we obtained samples from relevant fields, such as from the Southeast Regional Carbon Sequestration Partnership test site in Cranfield, Mississippi. Our goal is to evaluate potential impact of rock-fluid interactions on large scale underground processes triggered by the injection of CO_2.

INTRODUCTION

As reported previously (Petro et al., 2012), PARC's multichannel rock-fluid interactions system can produce a wide range of mineral solubility and dissolution data on diverse minerals under the conditions relevant to geothermal underground processes, mostly in support of the modeling activity using TOUGHREACT at LBNL (Jung et al, 2013).

The multi-channel experimental system has been used to map-out behavior of diverse minerals in a variety of CO_2/water environments and under a range of pressures and temperatures. The resulting findings are complementary to the efforts focusing on certain aspects of the rock-fluid interactions in specific geological settings. The recent studies address a wide range of relevant topics, from the role of supercritical CO_2 in a granite-based geothermal system (Ré et al, 2012), through an acidizing effect of dissolved CO_2 on evolution of a volcanic hydrothermal system (Rina, 2012), or a long-term reaction of injected CO_2 with a caprock (Rochelle, 2011), up to a CO_2-assisted mineral re-precipitation and fluid immiscibilities in several active geothermal reservoirs (McLin, 2012).

Several other experimental systems were built in the last decade to study various aspects of high-temperature/pressure rock-fluid interactions (Ueda, 2005; Rosenbauer, 2005; Magliocco, 2011; Bai, 2012), with at least one of the reports revealing a significant effect of CO_2 on dissolution kinetics of carbonates at various pressures and temperatures (Pokrovsky et al, 2009). In order to better understand

the complexity of dynamic rock-fluid interaction, applicable for a diverse set of samples and under the whole range of possible conditions, we have integrated a highly sensitive ion analysis into our automated multi-channel reactor system, and recently added a new flow-through channel that allows us to circulate any gaseous, liquid, or supercritical fluid mixture through a column packed by a solid sample, and monitor complex dissolution/precipitation processes. The experimental results obtained using brine-CO_2 mixtures under relevant conditions can be directly linked to several important aspects of the CO_2-EGS reservoir development and operation, such as prediction of seal formation, rock-fluid contact area, rock formation permeability, overall assessment of the reservoir volume and changes over its lifetime.

In this paper, we report on recent enhancements in the experimental capabilities as well as on some results of expanded rock-fluid interaction studies. Also, the focus of our study has shifted from thermodynamics to kinetics of the interactions, taking into account a dynamic effect of changing surface area, and from pure minerals to more complex real rock components. In that respect, a set of samples was recently obtained from a CO_2 injection well at the carbon sequestration site in Cranfield, MS, described elsewhere (Lu et al, 2012, 2013). Some of the experimental data served as entries for the LBNL modeling activity using TOUGHREACT modules, as presented separately (Jung et al, 2013).

EXPERIMENTAL

Detailed description of the multi-channel high-temperature/pressure batch reactor system with an on-line ion-analysis, together with the associated sample preparation and characterization workflow, has already been provided earlier (Petro, 2012). In this report, we limit our description only to new features added to the experimental capabilities through a major system upgrade, resulting in several improvements described as follows:

1) Circulation / flow-through (CF) channel.

The CF channel consists of several parts as shown in Figure 1, designed to mimic a fluid flow from an injection to a production well across a reservoir rock formation. The fluid flow-path typically follows the numbering in the Figure 1, with several optional arrangements such as the single-pass flow, or gradient of fluid composition.
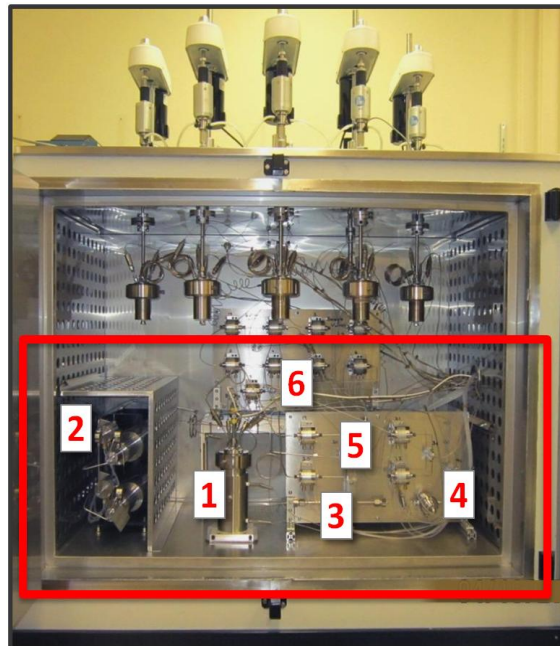

Fig. 1 - Solid-Fluid Interaction System: CF upgrade.

The new CF channel components are placed under the original five batch reactors (red box): Fluid Reservoir / Mixer (1), High-Performance Circulation Pump (2), Flow-Through Column (3), Back-Pressure Regulator (4), Circulation Valve Assembly (5), and Effluent Sampling Valve Assembly (6).

Any gas, liquid, or supercritical fluid can serve as a source, automatically pre-mixed at the beginning of each experiment in the 600 mL fluid reservoir start. In a typical experiment, 125, 250 or 500 mL of DI water was dispensed into the reservoir, pressurized to a controlled partial pressure of CO_2 and/or helium, and brought to targeted conditions of 1200 or 1500 psi and 120, 150 or 180 $^{\circ}$C. High CO_2 content under these conditions is expected to create a separate supercritical phase on top of the aqueous phase. The mixture is then pumped at 3 mL/min flow-rate through a 20 mL column of a high aspect ratio packed by a grinded rock sample. There is a choice of feeding the pump from different phase-separated zones, but usually we pump the heavier aqueous phase from the bottom of the reservoir only. The pressure drop across the column depends on the rock sample permeability, but the upstream-downstream pressure difference can be maintained constant using the back-pressure regulator. The effluent from the column is typically returned to the mixing reservoir, diluted with its content and re-circulated again through the column. In an optional arrangement, the effluent can also be re-directed for a single-pass

experiment. The whole flow-path is managed by the pneumatically-driven circulation valve assembly. Small aliquots of the reservoir fluid are periodically withdrawn and injected into the on-line connected analytical system based on High-Performance Liquid Chromatography coupled with Evaporative Light-Scattering Detector (HPLC-ELSD), with its function and ion-analysis performance described in the previous report (Petro et al., 2012). The sampling path is interconnected with the rest of the multi-channel system via the sampling valve assembly, and shares its ion analysis part with the five original batch reactors. Therefore, the operation of the whole system requires a very high level of automation, capable of perfect synchronization of all of the channels and multi-step operation of the whole complex experiment. A typical dissolution experiment lasts between two days and two weeks, depending on complexity of the process to be mimicked and kinetics of the dissolution of the slowest-dissolving mineral in the system.

2) Semi-automated wet-sieving process.

Preparation of the flow-through column required setting up a new protocol for better rock grinding and purification, as well as column-packing. In addition to the attritor and other parts of the sample preparation workflow described earlier (Petro et al, 2012), a wet-sieving system has been recently incorporated into the process. The new sample workflow, with semi-automated separation of grinded mineral sample into several particle-size bins, is shown in Figure 2.

Figure 2 – CF sample preparation workflow.
Grinding (a), wet-sieving (b) and column-packing (c).

The surface areas for most of the minerals studied, also before and after an experiment, were obtained using the BET method at LBNL. In addition, the particle size distribution profiles have been collected using Horiba Analyzer LA-950 at PARC

RESULTS & DISCUSSION

The results are discussed in two parts, one devoted to the effect of inherent properties of minerals on dissolution kinetics, another one devoted to the effect of fluid conditions on dissolution of mineral components of the specific real rock samples of our interest.

1) Effect of surface area on dissolution profiles.

Some discrepancies between the experimental and modeled data indicated that there might be an effect of the surface area that is wetable by the fluid environment and accessible for ions to freely diffuse in and out of the mineral surface. Therefore, we have started to identify and sort out the minerals by their particle size, total surface areas, particle shape, surface morphology or even by their eventual nano-porosity differences. The most descriptive results for a specific mineral sample that relate to its dissolution behavior are the particle size distribution profiles and associated surface areas, as exampled in Figure 3.
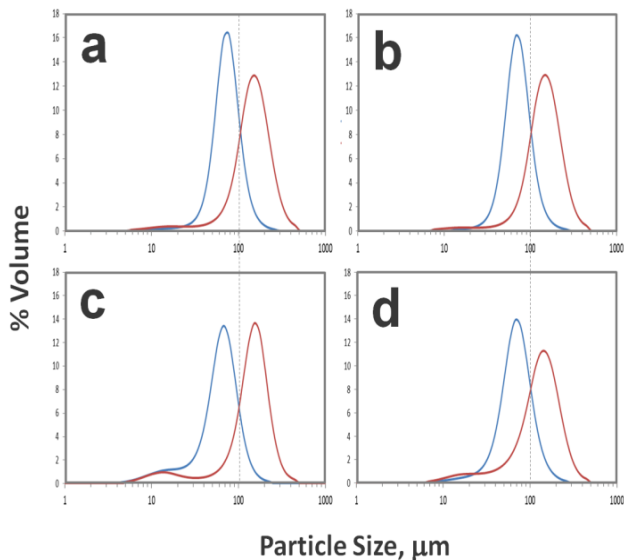

Figure 3 – Particle size distribution profiles.
Obtained by multi-angle light scattering after wet-sieving to different particle size bins. Minerals: a) dolomite, b) labradorite, c) illite, d) chlorite. Particle size bins: 25-63 μm (blue), 63-150 μm (red).

The sub-micron fines were completely removed by sedimentation during the sample preparation process, but a bimodal particle size distribution was still observed for most of the mineral samples. As shown

in Figure 4, the bimodality is more pronounced after a fluid exposure, probably due to breaking up some large agglomerates into smaller particles, but changes occurred on both ends of the size distribution.
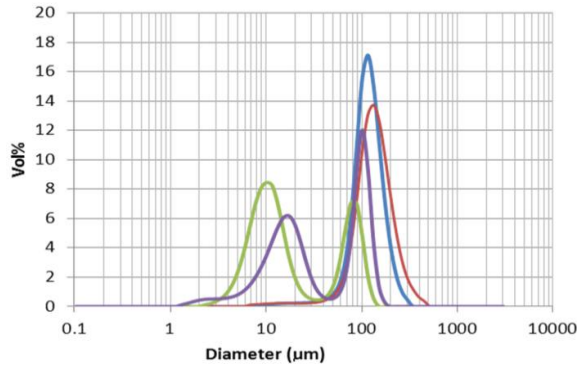

Figure 4 – Particle size distribution changes caused by the interaction with fluids.

Mineral: dolomite. Particle sizes: 63-150 μm. Fluid exposure: unreacted (blue); after 60-hr contact with 150 °C water (red); after a 60-hr interaction with 150 °C CO₂-saturated water (purple); and after a 60-hr contact with 120 °C CO₂-saturated water (green).

While the particle size distribution represents the important properties of a mineral sample, and sensitively reflects significant changes in the sample properties upon exposure to a reactive fluid, the measured BET surface areas are generally very low due to non-porous character of the material and more sensitive to the amount of residual fines than to any other changes. For example, the freshly sieved and dried dolomite possessed only 0.188 m^2/g for the 25-63 μm, and 0.137 m^2/g for the 63-150 μm fractions. The surface areas usually dropped upon exposure to a reactive fluid, despite the more pronounced bimodality. As a result, the original surface area of dolomite (>63μm) went from 0.137 m^2/g down to 0.116 m^2/g after 60-hr exposure to 150 °C water, and then to 0.060 m^2/g after a 60-hr reaction with 120 °C water-CO_2 mixture. This indicates that most of the surface area is in the very fine particles, which dissolve completely before the larger particles can significantly be eroded. Since the BET method is based on isothermal adsorption of an inert gas in vacuum and optimized for highly porous amorphous media, it doesn't necessarily reflect the relevant area and subsequent changes. Even if it is difficult to quantify the relevant surface area that is engaged in the interaction with reactive fluids, it surely affects the dissolution kinetics and complicates the understanding of the whole process. Generally, the dissolution of smaller particles goes faster and reaches a thermodynamic equilibrium in a shorter time, thus appearing to be higher than more slowly dissolving large particles that haven't reached

equilibrium yet. Figure 5 demonstrates that effect, by comparing the dissolution profiles for several minerals, each sieved into two different particle sizes.
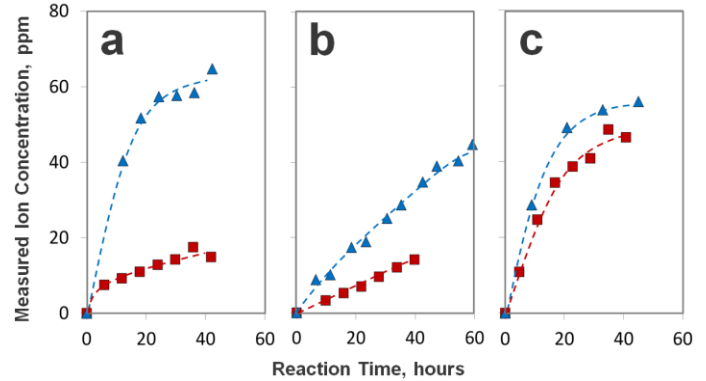

Figure 5 – Dissolution profiles for minerals of different particle sizes.

Minerals and ions: a) labradorite Ca^{2+}, b) illite Mg^{2+}, c) chlorite Mg^{2+}. Particle sizes: 63-150 μm (red squares); 25-63 μm, overlay of 3 runs (blue triangles). Fluid: CO₂-saturated water (all). Conditions: Temperature 150 °C (all); Pressure 1,200 psi (all).

2) Dissolution of presumably insoluble rock sample.

The Cranfield rock formations are composed mostly of kaolinite, illite, and chlorite, balanced by different ratio of quartz versus carbonates (Lu et al, 2012, 2013). Before evaluating the real rock samples obtained in scarce quantities, we have focused our effort on dissolution behavior of their individual components. Typically, carbonates show significant increase in solubility in CO_2-saturated waters that decreases with increasing temperature above 100 °C (Pokrovsky et al, 2009; Petro et al, 2012). Quartz, in contrast, possesses only limited solubility in those environments. While these components are quite well understood, not much is known about the behavior of the remaining minerals. Kaolinite disperses upon contact in aqueous fluids quickly to very fine particles, with the process slowing down when reaching ca. 100 nm particle size. Such fine particulates stay dispersed for a very long time and pass through any filter in our system, thus skewing the solubility data into a measure of originally dispersed mineral and undistinguishable from the ions truly dissolved. Therefore, most of our experimentation was devoted to understanding the dissolution behavior of illite and chlorite under the relevant reservoir conditions of a potential CO_2-EGS project. Originally, both illite and chlorite were presumed to be fairly insoluble in a wide range of conditions; however, very little appears to be known what happens to those minerals when exposed to various blends of water with supercritical CO_2 at temperatures above 120 °C.

In order to find a triggering point for dissolution of those presumably insoluble minerals, a series of additional experiments have been performed using the CF channel, in which we have varied the partial pressures of CO_2 in contact with water and made several steps in temperature while keeping the overall pressure constant. Figure 6 shows such a series of conditions changes and solubility results for illite.
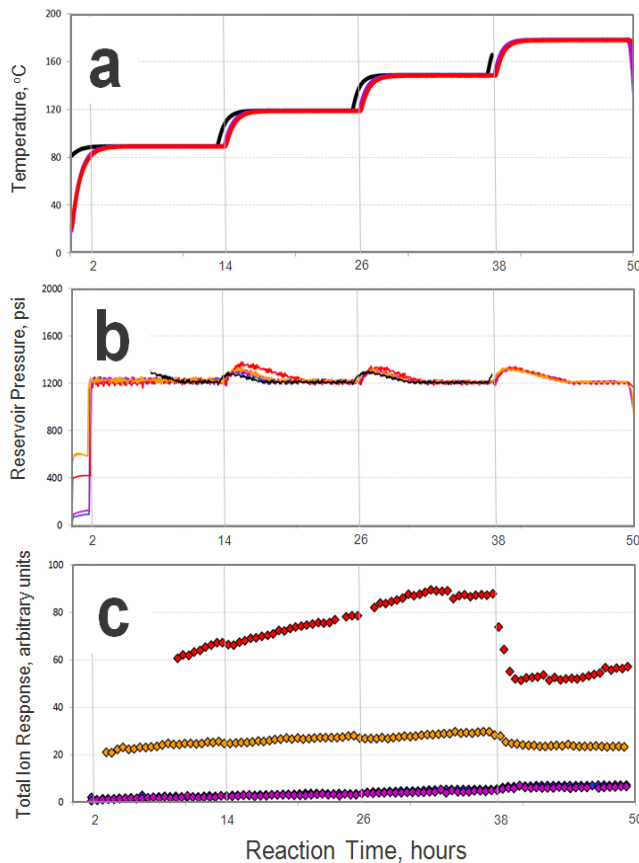

Figure 6 – Monitoring the dissolution of illite under various conditions of the CF channel.

Mineral: Illite, 63-150 μm, 28.39g in 20 mL CF column. Temperature profiles (a): The temperature of the whole circulation channel was programmed to change from 90, 120, 150 up to 180 ^oC in 12 hr. steps after an initial 2 hr. ramp-up from room temperature. Reservoir pressure profile (b): The pressure was set to be maintained at 1200 psi regardless the fluid composition. Total Ion Response monitored (c): Integrated peak are of all of the ions detected by the on-line ion chromatography system in 200 μL aliquots sampled from the bottom of the reservoir at 30 min intervals. Fluids (color coded): The 600 mL reservoir was pre-filled with 500 mL of DI water, primed by helium at 30 psi and pressurized further by helium only (black), or by CO_2 to 62 psi (blue), 88 psi (pink), 600 psi (orange), and 1200 psi (red), respectively, and topped in all cases by helium to maintain the total reaction pressure of 1200 psi.

As expected, the illite solubility in pure water, as well as in aqueous environments with fairly low partial pressures of CO_2, was rather negligible. However, when the CO_2 partial pressure reached the point of its phase transition to a liquid or supercritical fluid, the solubility started to increase dramatically. The most interesting changes in solubility behavior were observed when temperature reached 180 ^oC. Such a temperate increase in aqueous or slightly carbonated environments was followed by a slight increase in solubility, not surprising for the aluminosilicates. In contrast, the sudden rise in temperature of the water mixtures with liquid or supercritical CO_2 resulted in rather significant decrease in solubility. Also, the pressure drop across the column was rising as the solubility dropped (not shown) indicating re-precipitation and subsequent changes in permeability. Such a temperature response is more typical for carbonates, indicating that recirculation of CO_2-rich fluids may have resulted in re-mineralization of the illite. The post-experiment mineral characterization of the column content is expected to confirm that trend, but hasn't been performed yet to quantify its extend.

Further experimentation will be directed towards comparison of the real rock samples with the re-composed blends of the same, to assess what else could happen under an EGS conditions. One could expect that such a sudden solubility change may lead to an unexpected seal formation, redirecting flow-paths and defining the size of the whole reservoir and its permeability changes in time. The experimentation can not only reveal additional risk factors, but more importantly, provide a solution on how to get around the issues and therefore could significantly lower the risks involved.

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