

Interactions of Rocks with Supercritical CO₂ and Water in Enhanced Geothermal Systems and Beyond

M. Petro, A. Tuganov, A. Bell, L. Song

Palo Alto Research Center (PARC, A Xerox Company)
3333 Coyote Hill Road, Palo Alto, CA 94304, mpetro@parc.com

ABSTRACT

There is an abundance of heat but lack of fluids underground. Current drilling and fracturing technologies can provide necessary access to the hot rocks, creating Enhanced Geothermal Systems (EGS). Despite the 100-fold increase in the geothermal energy potential that EGS could yield, the reservoir development costs are very high, and adding water in sufficient quantity is not always economically viable.

As an alternative fluid, supercritical CO₂ has been considered for its potential to yield up to 50% more electricity than water, mainly due its lower viscosity and greater ability to permeate the reservoir. Nevertheless, there are substantial risks associated with reactions triggered by introduction of a new fluid like CO₂.

PARC has developed a multichannel system for purpose of studying geothermal rock-water-CO₂ interactions under harsh underground conditions, but could be used as a generic tool in many other areas that can benefit from better understanding solid-fluid interactions.

Keywords: geothermal, natural gas, drilling, fracturing, energy, supercritical CO₂

1 INTRODUCTION

The 2006 MIT report on the U.S. geothermal potential [1] revealed, that new fluids are necessary to unlock the geothermal potential of hot dry rocks underground. This has revitalized an older idea of using supercritical CO₂, and triggered an avalanche of interest in related issues.

While advanced modeling software [2,3] is useful to simulate use of CO₂ as a geothermal working fluid, there are an increasing number of reports on significant challenges associated with introduction of CO₂ into reservoirs containing at least some traces of water [4-8], requiring experimentation to understand mineral alteration, fluid chemistry, and permeability evolution [9-10]. During the water-to-CO₂ transition, there would be three distinct zones present – a core region dominated by a supercritical CO₂ fluid phase, a surrounding intermediate zone, and peripheral region containing an aqueous phase with dissolved CO₂ [11-15].

To mitigate some of the risks associated with transition of an EGS reservoir from water to supercritical CO₂, PARC

has developed a multi-reactor batch and flow-through capability for solid-fluid interactions, operating at high-pressure and high-temperature conditions to mimic an underground setting and geothermal-like situations. Each reactor is coupled to an on-line analytical system to monitor the chemical/physical processes inside and at the real time, including complex composition of dissolved minerals. Additional geothermal applications include understanding the role of naturally dissolved gasses and minerals on development of underground water pathways, predicting the effect of injected waste water purity on native rock solubility, assessment of risks and benefits associated with precipitation-redissolution processes during reservoir stimulation, and many others.

In addition to studying behavior of diverse rocks in a wide range of water-CO₂ fluid combinations to predict the flow of underground fluids and truly assess both risks and benefits of CO₂-EGS operation, this unique capability can address challenges well beyond geothermal use. The additional application areas span from topics of interest for traditional industries such as oil & gas exploration (well cementing, rocks fracturing, brine water reuse, flow-path clogging, etc), up to addressing new challenges in green buildings technologies (heat pumps, solar-thermal, cooling fluids, and construction materials).

2 EXPERIMENTAL

PARC's multichannel reactor system, capable to heat up to 200 °C and a set of pumps that can push up to 20 MPa of fluid pressure into 50 mL reactors. In addition to generating underground conditions, the system has a unique sampling ability that preserves the fluid composition under the reaction conditions, with subsequent complex analysis to monitor chemical composition changes in real time. A flow-through circulation channel is currently being added to the system, sharing the fluid feed as well as the measurement parts of the system. Figure 1 shows the whole system as well as its individual components, with a suite of five high-pressure / high-temperature reactors inside the oven, connected to the feed and sampling components via complex electrical and fluidic pathways, with a control center outside of the oven. To extend the experimental temperature range, we have equipped reactors with additional heaters, which will allow us to perform certain experiments well above the oven temperature.

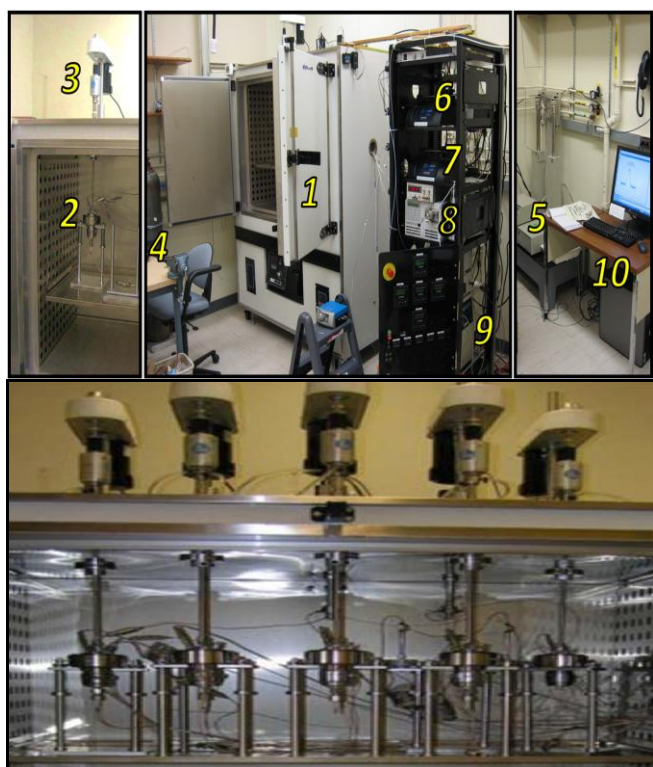


Figure 1 – PARC Solid-Fluid Interaction System.

Individual components include: Oven (1), Reactor cell assembly (2), Stirring assembly (3), Gas source (4), Supercritical fluid feed pump (5), Liquid feed pump (6), Sample withdrawal pump (7), Sample analysis pump (8), Chemical analytics (9), System control & Data acquisition station (10), and Multi-channel reactors view (bottom).

For the batch rock-fluid interaction experiments, after placing specific amounts of crushed and sieved rock samples into individual reactors, the water and supercritical CO₂ feeds are delivered to the reactor vessels using syringe pumps. Then, the rock particles are mixed with water and supercritical CO₂ into slurry, optionally stirred by a high-torque stirrer. Since dissolution may start immediately upon contact of rock sample with fluids, therefore, the system is brought up to the operating temperature and pressure conditions as quickly as possible. The interaction conditions are monitored by thermocouples and pressure transducers at several points, and optionally by a conductivity or pH sensor built inside a larger reactor that could be connected for a special study. Once the reaction conditions are reached, small aliquots of the reaction mixture (typically 200 μL) are sampled and analyzed through the synchronized action of the sampling pump, selection valve, sampling valve, sample analysis pump, ion separation column, and mineral concentration detector. While the small fluid sample travels to the on-line connected ion-exchange High-Performance Liquid Chromatography (HPLC) system for detailed ion analysis,

it is filtered and diluted in a strong solvent environment to insure that the dissolved components stay in solution.

Control over the individual components of the whole system is provided by custom-made PARC software. The instrument control modules are combined with data-acquisition software that collects mineral concentration traces during the course of the experiment. Then, the experimental inputs, with actual pressure and temperature stamps at the sampling points, are linked to the mineral concentration traces and, after a calibration of our mineral ion detector, turned into the final solubility data at the specific interaction conditions.

3 RESULTS & DISCUSSION

After a thorough engineering validation, the system achieved an excellent stability of the interaction conditions, monitored by the pressure and temperature consistency throughout the experiments, and sufficient sampling precision and ion analysis accuracy. Experiment-to-experiment repeatability of the final concentration response is the ultimate measure of both precision and accuracy, covering the whole process from sample preparation to data processing, and currently is within a relatively narrow error margin of 20% in most cases, as exemplified in Figure 2.

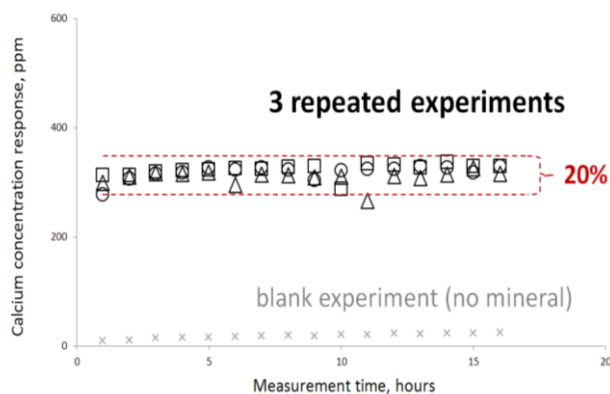


Figure 2 – Experiment-to-experiment repeatability.

Calcite equilibrated in CO₂-saturated water at 150 °C and 8.3 MPa pressure.

PARC's solid-fluid interaction system represents a high-throughput experimental setup that allows us to screen rapidly for changes in solubility or degradation of solids as a result of changing conditions or fluid environment. We can perform experiments using the whole spectrum of fluid compositions. Additionally the stirrer may serve as a rheometer to sense thickening of a slurry of solid particles dispersed in fluids. Figure 3 shows an example of resulting data streams from such an experiment, with a single mineral sample reaching equilibrium solubility in water over time in one reactor vessel, while in the other vessels is interacting with water-CO₂ mixtures of different compositions.

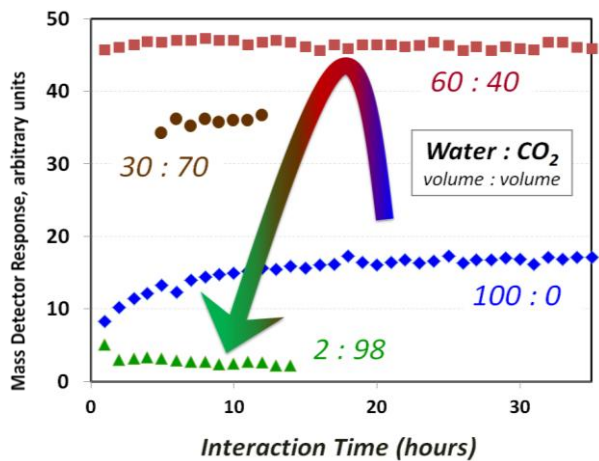


Figure 3 – Screening for mineral solubility changes across a wide range of fluid compositions.

Mineral sample: Barite; Particle sizes: 25-150 μm ;
Temperature: 100 $^{\circ}\text{C}$; Pressure: 8.3 MPa.

It is apparent that its low initial aqueous solubility rapidly increases with increased amounts of dissolved CO_2 , and then slowly decreases in solubility when separate fluid phases are created until becoming negligible in fairly dry supercritical CO_2 phase. This behavior is quite typical for many other minerals studied, but the magnitude of the response and the range of sensitive fluid compositions differ significantly. For example, calcite responds very promptly even to traces of CO_2 , which makes it difficult to quantify as even perfectly deionized water absorbs some CO_2 immediately upon exposure to air. The importance of such a CO_2 -responsiveness test is in the rapid determination of potential risk factors associated with large differences in rock and mineral solubilities across the whole range of water- CO_2 compositions, which may result in sealing-off a geothermal reservoir at the interface of those two fluids.

As opposed to screening a single mineral in whole range of fluid environments and/or under different conditions, we can also devote each vessel to individual minerals and screen such a mineral diversity against a fixed set of conditions. In the case when solubility is expected to change very little when going from one set of conditions to another, we can speed up the screening process by reusing the mineral sample already exposed to the previous set of conditions with a step change in conditions after reaching equilibrium solubility at the previous set of conditions. Figure 4 shows an example of such an experiment with diverse minerals in individual vessels and two sets of conditions applied in steps, one at the time. It appears that the increase in pressure results in somewhat lower solubilities of calcite and dolomite, higher solubility of anorthite, while quartz appears to be insensitive to pressure change. A slight increase of the background as measured for the blank fluid environment with no mineral present suggests that the observed changes might be within experimental error.

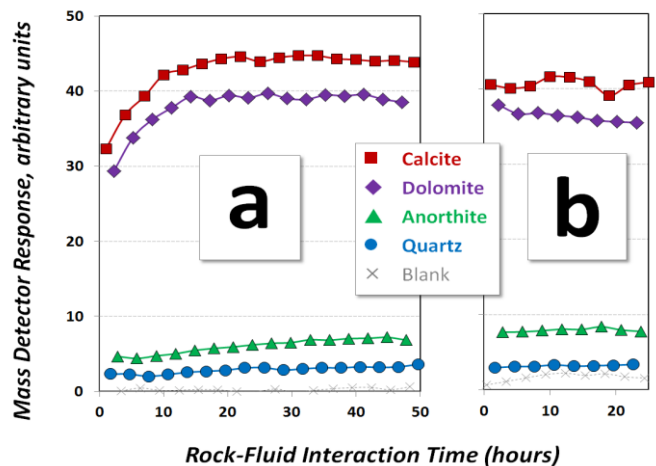


Figure 4 – Screening for diverse mineral solubilities at step-changed conditions.

Mineral samples: Calcite, Dolomite, Anorthite, Quartz, and no mineral (Blank); Particle sizes: 63-150 microns; Temperature: 120 $^{\circ}\text{C}$;
Pressure: 8.3 MPa (a) changed to 10.4 MPa (b).

The data on individual ion concentrations at different mineral-fluid interaction times represent the dissolution profile of each mineral at the specific set of experimental conditions, and can be combined into the overall mineral solubilities, or correlated with other parameters, including those important for modeling processes at a specific geothermal site. The complex dataset on the equilibrium solubilities and dissolution profiles of numerous diverse minerals in the whole range of water- CO_2 environments and under a variety of underground pressures and temperature conditions is serving as a base for development of a new, more accurate, model of a CO_2 -EGS reservoir. Figure 5 depicts such a reservoir, with all three zones and a target sign showing the primary focus of our study – the seal formation.

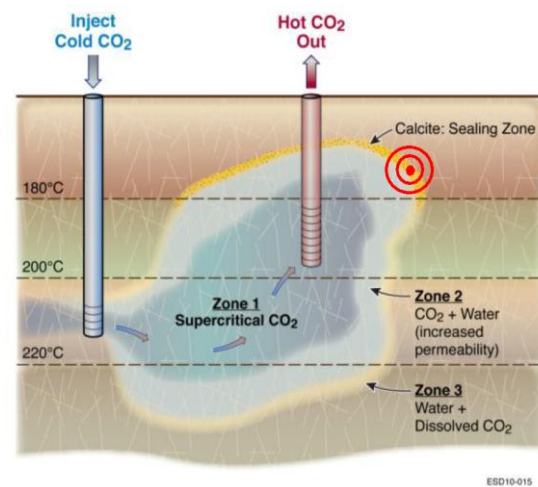


Figure 5 – Schematics of a CO_2 -EGS reservoir. Modified after Xu, 2012 [16].

4 SUMMARY AND CONCLUSIONS

PARC's multichannel Rock-Fluid Interactions System is fully operational, capable of simulating various underground conditions relevant to geothermal processes, and producing mineral solubility and dissolution data that can provide valuable knowledge on the behavior of well-known or unusual minerals in yet untested environments and/or under conditions not previously explored in the laboratory. While continuing to generate more batch solubility data, including investigation of untested territories, we are expecting to upgrade the system by installing a flow-through capability with a water-CO₂ circulation through a column packed with several rock samples, which may allow us to see the effect of one dissolved mineral on dissolution/precipitation of others, together with many other effects that are relevant to the CO₂-EGS reservoir development and operation.

In our future work, we intend to utilize this unique capability to address solid-fluid interaction challenges in other application areas, directed towards various pressing clean energy issues. For example, we could lower the environmental impact of oil and gas exploration activities through better well cementing materials, cleaner rocks fracturing processes, brine water reuse. Or, on another side of clean technologies spectrum, we could address new challenges in green buildings technologies, including development of new heat pump techniques, cooling fluids, construction materials, or combined solar-thermal and geothermal systems.

Acknowledgement

This work was supported by the U.S. Department of Energy, Energy Efficiency and Renewable Energy Office, Geothermal Technologies, Award No. DE-EE0002765.

We also thank Patrick Dobson and Tianfu Xu from the Lawrence Berkeley National Laboratory for collaborating with us on the rock characterization and modeling issues, and UC Berkeley Earth and Planetary Sciences Department for facilitating the rock sample characterization.

REFERENCES

- [1] Tester, J.W., Anderson, B., Batchelor, A., Blackwell, D., DiPippo, R., Drake, E., Garnish, J., Livesay, B., Moore, M.C., Nichols, K., Petty, S., Toksoz, N., Veatch, R., Augustine, C., Baria, R., Murphy, E., Negru, P. and Richards, M., (2006), "The future of geothermal energy: Impact of enhanced geothermal systems (EGS) on the United States in the 21st century," *Massachusetts Inst. Technology, Final Report for the DOE Contract DE-AC07-05ID14517*.
- [2] Xu, T., Sonnenthal, E.L., Spycher, N., and Pruess, K. (2006), "TOUGHREACT: A Simulation Program for Non-isothermal Multiphase Reactive Geochemical Transport in Variably Saturated Geologic Media," *Computers & Geosciences*, 32, 145-165.
- [3] Pruess, K. (2006), "Enhanced geothermal systems (EGS) using CO₂ as working fluid – a novel approach for generating renewable energy with simultaneous sequestration of carbon," *Geothermics*, 35, 351-367.
- [4] Garcia, J. (2001), "Density of Aqueous Solution of CO₂," *Lawrence Berkeley National Laboratory Report*, LBNL-49023, Berkeley, CA.
- [5] Kneafsey, T. and Pruess, K. (2010), "Laboratory Flow Experiments for Visualizing Carbon-Dioxide-Induced, Density-Driven Brine Convection," *Transp. Porous Med*, 82, 123-139.
- [6] McGrail, B.P., Schaefer, H.T., Glezakou, V.A., Dang, L.X. and Owen, A.T. (2009), "Water Reactivity in the Liquid and Supercritical CO₂ Phase: Has Half the Story Been Neglected?," *Energy Procedia*, 1, 3415–3419.
- [7] Pruess, K. and Azaroual, M. (2006), "On the Feasibility of using Supercritical CO₂ as Heat Transmission Fluid in an Engineered Hot Dry Rock Geothermal System," *31st Workshop on Geothermal Reservoir Engineering, Stanford University*, 386–393.
- [8] Regnault, O., Lagneau, V., Catalette, H., Schneider, H. (2005), "Étude Expérimentale de la Réactivité du CO₂ Supercritique vis-à-vis de Phases Minérales pures, Implications pour la Séquestration Géologique de CO₂," *C. R. Geoscience*, 337, 1331–1339.
- [9] Morrow, C.A., Moore, D.E. and Lockner, D.A. (2001), "Permeability Reduction in Granite under Hydrothermal Conditions," *J. Geophys. Res.*, 106, 30551-30560.
- [10] Xu, T., Apps, J.A. and Pruess, K. (2004), "Numerical Simulation of CO₂ Disposal by Mineral Trapping in Deep Aquifers," *Appl. Geochem.*, 19, 917–936.
- [11] Liu, L., Suto, Y., Bignall, G., Yamasaki, N. and Hashida, T. (2003), "CO₂ injection to granite and sandstone in experimental rock/hot water systems," *Energy Conversion & Management*, 44, 1399-1410.
- [12] Fouillac, C., Sanjuan, B., Gentier, S. and Czernichowski-Lauriol, I. (2004), "Could Sequestration of CO₂ be Combined with the Development of Enhanced Geothermal Systems?," *3rd Annual Conference on Carbon Capture and Sequestration*, Alexandria, VA.
- [13] Ueda, A., Kato, K., Ohsumi, T., Yajima, T., Ito, H., Kaieda, H., Meycalf, R. and Takase, H. (2005), "Experimental Studies of CO₂-Rock Interaction at Elevated Temperatures under Hydrothermal Conditions," *Geochem. J.*, 39, 417–425.
- [14] Pruess, K. (2008), "On Production Behavior of Enhanced Geothermal Systems with CO₂ as Working Fluid," *Energy Conversion and Management*, 49, 1446–1454.
- [15] Wan, Y., Xu, T. and Pruess, K. (2011), "Impact Of Fluid-Rock Interactions on Enhanced Geothermal Systems with CO₂ as Heat Transmission Fluid," *36th Workshop on Geothermal Reservoir Engineering, Stanford University*, 792-801.
- [16] Xu, T. (2012), "Mineral Carbonation in a CO₂-EGS Geothermal Reservoir," *37th Workshop on Geothermal Reservoir Engineering, Stanford University*.