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EGS rock reactions with supercritical CO_2 saturated with water and water saturated with supercritical CO_2

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ABSTRACT

EGS using CO_2 as a working fluid will likely involve hydro-shearing low-permeability hot rock reservoirs with a water solution. After that process, the fractures will be flushed with CO_2 that is maintained under supercritical conditions (> 70 bars). Much of the injected water in the main fracture will be flushed out with the initial CO_2 injection; however side fractures, micro fractures, and the lower portion of the fracture will contain connate water that will interact with the rock and the injected CO_2. Dissolution/precipitation reactions in the resulting $scCO_2$/brine/rock systems have the potential to significantly alter reservoir permeability, so it is important to understand where these precipitates form and how are they related to the evolving 'free' connate water in the system. To examine dissolution / precipitation behavior in such systems over time, we have conducted non-stirred batch experiments in the laboratory with pure minerals, sandstone, and basalt coupons with brine solution spiked with $MnCl_2$ and $scCO_2$. The coupons are exposed to liquid water saturated with $scCO_2$ and extend above the water surface allowing the upper portion of the coupons to be exposed to $scCO_2$ saturated with water. The coupons were subsequently analyzed using SEM to determine the location of reactions in both in and out of the liquid water. Results of these will be summarized with regard to significance for EGS with CO_2 as a working fluid.

INTRODUCTION

There is a growing interest to use supercritical carbon dioxide ($scCO_2$) as a working fluid in engineered geothermal reservoirs (EGS). Recent numerical modeling results have suggested that the use of $scCO_2$ may have advantages as an EGS working fluid for better heat recovery and reduced geochemical reactions. Although dry $scCO_2$ is relatively non-reactive with most suggested EGS reservoirs, $scCO_2$ introduced into a system with residual injected or reservoir connate water can cause digenetic reactions to occur in the reservoir rocks (Schaef and McGrail 2012). These digenetic reactions and secondary mineralization could reduce permeability and potentially block fluid pathways resulting in a reduction in the efficiency of heat extraction from the system.

Many systems considered useful for EGS have low natural permeability. It is likely that many of these reservoirs will be hydraulically fractured with water (hydrosheared) to increase their permeability. Hydraulic fracturing of rock requires the injection of a fluid at a pressure that is greater than the minimum principal stress and the tensile strength of the reservoir rock. As the reservoir rock begins to fracture additional pressure is needed to continue to propagate the fracture from the well. The final applied pressure during fracturing is much higher than either the initial reservoir pressure or the anticipated system operating pressure.

Based on experience in hydrofracturing shales for natural gas and oil, one can expect that a fracturing operation can may require a hundred thousand to several million liters of fluid to fracture a formation about a single well. A portion of the injected fluid occupies the newly created hydraulic fracture while another portion is lost from the fracture to the surrounding reservoir (leakoff). The amount of leakoff is dependent on the injection pressure and the overall permeability of the reservoir. For reservoirs with a permeable matrix (1 to 10 mD) this fluid is invades the surrounding reservoir matrix for some distance from the fracture. In naturally fissured reservoirs, the injected fluid can often use these natural fractures as permeable conducts, diverting fluid from the hydraulic fracture.

At the end of pumping, the pressure in the hydraulic fracture is lowered (either through the well head or by continued imbibition of the fluid into the reservoir) allowing the hydraulic fracture to close to its final aperture. During the development stage, the injected fluid is recovered at the surface, however, not all the fluid injected for the fracture is returned to the surface. For unconventional fossil energy reservoirs, estimates of recovered fluids range from 80 to as low as 15% of the injected volume (EPA, 2013). The remaining water will be trapped in the hydraulic fracture, in the surrounding matrix, and in associated natural fractures. This water can later react with the $scCO_2$ working fluid and the reservoir minerals resulting in lower permeability and reduced efficiency of heat extraction

We have conducted a series of laboratory batch experiments to examine potential mineral reactions at the residual water- $scCO_2$ interface in an EGS system. In this paper, we focus on improving our understanding of the distribution of these reactions about that interface.

BACKGROUND

Previous experiments

$scCO_2$ rock interaction experiments have been carried out at various institutes using high pressure cells to examine geochemical reactions that could occur at in geologic formations if used for geologic sequestration of carbon. Most of these experiments have used batch reactors where rock minerals are mixed with a solution of either carbon dioxide (CO_2) saturated water brines, or mixtures of brines and $scCO_2$ (e.g. Rosenbauer et al., 2005, Kaszuba et al., 2005, McLing et al., 2012, etc). Kaszuba et al. (2005) ran experiments for 45 days with $scCO_2$ and brine with Arkose and shale at 200°C and 20 MPa in gold-titanium reaction cells. Under these conditions, the $scCO_2$ is largely an immiscible fluid but not totally insoluble in the brine. These experiments had excess water with ratio a brine:solid of 11:1 during the experiment at initiation of $scCO_2$. Magnetite (Fe_3O_4) and siderite ($FeCO_3$) crystals formed during the experiment due to the reaction with $scCO_2$.

Experiments with limited water have also been conducted using ground up rocks in the form of saturated pastes. Sugama (et al., 2010) conducted 5 rock mineral carbonation experiments at 250°C, 17.23 MPa for 3 days. These experiments used powders of 0.2 mm (less than a 70 mesh sieve) with approximately 20% water by weight to make a paste that was then exposed to $scCO_2$. For the granite anorthoclase-type albite was reacted to form amorphous sodium and potassium carbonates with clay-like by-products where as the reaction with the quartz was minimal. The location of the secondary minerals was not specified.

Halite precipitation in brine saturated sandstone cores have been studied by Ott (et al., 2010). These studies saturated the sandstone with a NaCl brine (~20%) then flowed scCO2 through the sandstone core at 50 C and ~1200 psi decreasing the permeability by a factor of 4. They found a zone near where the $scCO_2$ enters the core becomes dry and precipitates halite in concentrations that suggest a capillary backflow of brine towards the injection point. MicroCT scans by Ott, suggest that the salt precipitates in the vicinity of the $scCO_2$ pathways but leave the pathways unobstructed. Wigand (et al., 2009) conducted experiments examining a fractured wellbore cement cores under conditions of (19.9 MPa, 54 C) for 99 days in a Hassler core holder. These experiments were designed to examine geochemical reactions and mass transfer processes along the fractured cement core with scCO2 flow. They concluded that the wet scCO2 infiltrated the cement core from the fracture with initial carbonation (the orange zone) followed by precipitation SiO_2 in a thin transition zone (with possible decreased permeability thus limiting the reaction front).

From these studies it is clear that dissolution/precipitation reaction occur in $scCO_2$/brine/rock systems. What is less clear is where these precipitates form and how are they related to the amount of 'free' brine in the system. In Ott's system there was sufficient brine and permeability to allow capillary drive water movement to the halite precipitation front. Sugama system was excess saturated to make a paste and no attempt was made to determine the ending water saturation. Wigand conclude that SiO_2 precipitation reduced the permeability to an extent that the reaction front stopped, however, a similar situation would have occurred if all the brine was depleted from the cement core. Kaszuba and others conducted their experiments with excess brine and did not have a brine limited situation.

Modeling

Modeling studies of EGS systems have mostly focused on heat removal from the reservoir and assume no flow boundaries along the fracture walls. Water remaining in the hydraulic fracture is quickly removed by immiscible displacement by $scCO_2$ followed but a slower evaporation of residual water in the hydraulic fracture by the dry $scCO_2$ (e.g. Wan et al., 2011, Xu, 2012, Pan et al., 2012).

A neglected process in these models includes the flowback of injected water into the fracture and the flow of connate water into the EGS fracture due to the lower operating conditions. These processes could provide a continual source of water to the EGS system if the EGS system has sufficient permeability and is operated below the fluid reservoir pressures over time scale necessary for mineralization reactions to occur. Current models suggest (e.g. Wan et al., 2011, Pan et al., 2012) operating the EGS where at least part of the EGS fracture pressure is below the initial reservoir fluid pressure. In EGS systems operating with $scCO_2$, the static pressure profile of the $scCO_2$ fill hydraulic fracture and that of the water filled reservoir will also enhance the egress of water into the hydraulic fracture (Figure 1).

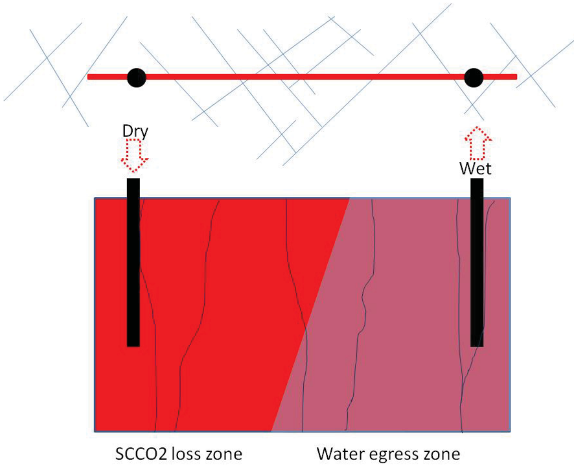

Figure 1. More complex conceptual model of $scCO_2$ fracture flow in a reservoir with naturally occurring fractures.

APPROACH

Non-stirred 1 liter batch reactor experiments were conducted at the Idaho National Laboratory (INL) and the Center of Advance Energy Studies (CAES) and used to evaluate the intensity of chemical reactions as a function of the water content. The experiment were carried out using mineral/rock slabs that were placed in the reactor such that they were only semi-submerged in the aqueous phase. The aqueous phase was composed of two salts. Potassium chloride (100 mmol) was added to mimic the high TDS found in most hydraulic fracturing fluids and connate water whereas manganese chloride (23.8 mmol) was added to use as an indicator of where “leakoff” water reacts with the $scCO_2$. Since Mn has no vapor pressure we expect the location of the Mn precipitates will delineate the zone where free water (and the soluble minerals in that water) reacts with the $scCO_2$ on the coupons. The manganese was expected to react with the CO_2 to produce manganese carbonate (rhodochrosite). Rhodochrosite in its pure form is a rose-red color but impurities will often result in a pink color. We will use color as an indicator of the formation of rhodochrosite. In addition, the surface of the rock coupons can be vertically scanned with a scanning electron microscope (SEM) to examine the vertical extent of the Mn. A SEM equipped with a Chroma cathodoluminescence (CL) detector was used to examine the luminescence of the MnCO3 precipitation. Rhodochrosite crystals should appear a dull to black object in the image.

Laboratory non-stirred batch experiments were conducted in INL’s titanium reaction vessels (~15 cm deep x 9.5 cm diameter). Due to the oxidation treatment on the Ti (Ulmer and Barnes, 1987), these experiments can be conducted at EGS temperatures (200°C) with no anticipated corrosion of the vessel or cups. Whole rock and mineral coupon experiments were conducted using individual Ti cups to control the water level at approximately mid-way on the coupon. Excess DI water was added to the vessel at the base of the Ti cups. The reactors were purged several times with CO_2 gas to remove oxygen. Liquid CO_2 was added to the head space above the water to a pressure that would produce a super critical fluid at the final temperature (200°C) and pressure (~110 bars). The pressure vessel was then heated over a period of several hours to 200°C and held at this temperature for 5 days. After cooling, the pressure was slowly bled from the vessel over a period of approximately 1 hour. Samples were then removed and allowed to air dry before photographing.

Mineral Coupon Samples

A simulated granite granular media composed of pure albite (a mineral in granite that is known to react with $scCO_2$ (Sugama et al.) was used as a test material with little to no permeability. Alibite samples were obtained from Ward’s Natural Sciences (Bancroft, Ontario, Canada). Hand specimen crystals were cut on a tile saw to form rectangular coupons of approximate dimension of 1 cm wide, ½ cm thick, by 4 cm in length. The mineral coupons were rinsed to remove residual cuttings and oven dried at 105°C over night to remove free moisture.

Rock Coupon Samples

St Peters sandstone cores were obtained from INL core archives. These 2.5 cm sandstone cores were cut on a tile saw similar to that of the albite coupons. The sandstone has a significant porosity and exhibits a fairly sharp capillary rise of approximately 3 cm (Figure 2).

Figure 2. High temperature rock coupon test specimens in individual titanium cups.

Saturating Solution

The water solution in the titanium cups was composed of potassium chloride and manganese chloride. The concentration of KCl was 100 mmolal and should be fairly non-reactive with the minerals and $scCO_2$. The amount of $MnCl_2$ added (23.8 mmol) was based in part on calculations using The Geochemist's Workbench®. These calculations indicated minimum change in the overall total dissolved solids if the Mn^{2+} reacted with the CO_2. Further modeling suggests that a concentration of 23.8 mmol $MnCl_2$ (4716 g $MnCl_2 \cdot 4H_2O$) should precipitate approximately 1.75 g/kg $MnCO_3$ (Figure 3).

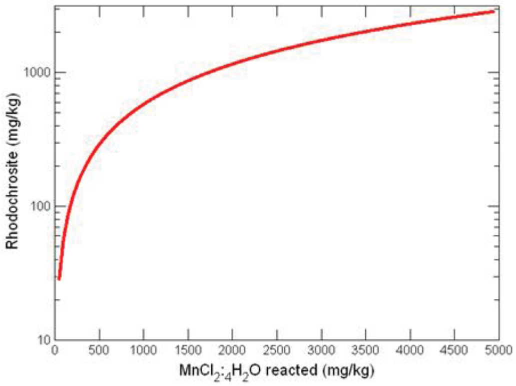

Figure 3. Precipitation modeling results of rhodochrosite for the experiments.

RESULTS

Three tests were conducted to examine $scCO_2$ reaction locations with soluble salts in the simulated leakoff water.

$H_2O/scCO_2$ Interface

The $H_20/scCO_2$ interface test examined the location of the Mn-precipitate as a function of the degree of capillarity of the coupon. Figure 4 illustrates the location of the Mn-precipitation on the exterior a sandstone and albite coupons. Sandstone is a porous material that allows capillary wicking of the $MnCl_2$ bearing solution from the titanium cup (Figure 2) where as the albite coupon exhibits little capillary wicking. In both cases, a strong reaction zone is noted at the $scCO_2$/water interface. In addition, the sandstone coupon also exhibits mineralization above the $scCO_2$/water interface suggesting that the reaction was due to $scCO_2$ interacting with water held by capillary forces in the sandstone pores.

The albite sample was also scanned by the SEM. Nine SEM images were taken across the orange color reaction zone using both the stand optical and cathodoluminescence detector.

Figure 4. Secondary mineralization on sandstone and albite coupons. Note higher staining at the $scCO_2$/water interface.

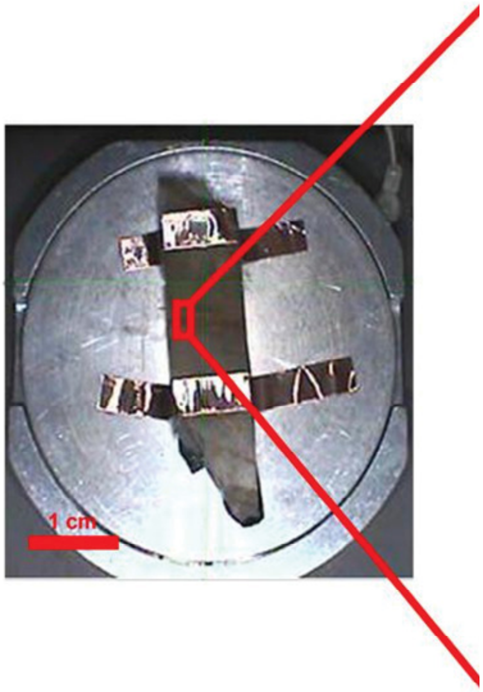

Figure 5 illustrates the albite coupon in the SEM and the location of the measurements on the sample. On the right hand side of this figure, SEM-CL images and standard SEM images have been stitched together to allow visual of the distribution of $MnCO_3$ across the $scCO_2$/water interface (at approximately 2500 um). The standard SEM image shows little change across the interface. The SEM-CL image shows a high density of dark crystals near the 2500 um level with some crystals above this point. . SEM-EDS analyses of these crystals indicate that they are a manganese carbonate, likely rhodochrosite. The highest density of these crystals is at the $scCO_2$/brine interface, possibly within the capillary meniscus along the face of the albite. The $MnCO_3$ crystals above the interface may be due to a slight amount of splashing in the vessel during placement in the heater. Very few $MnCO_3$ crystals are noted below the water interface.

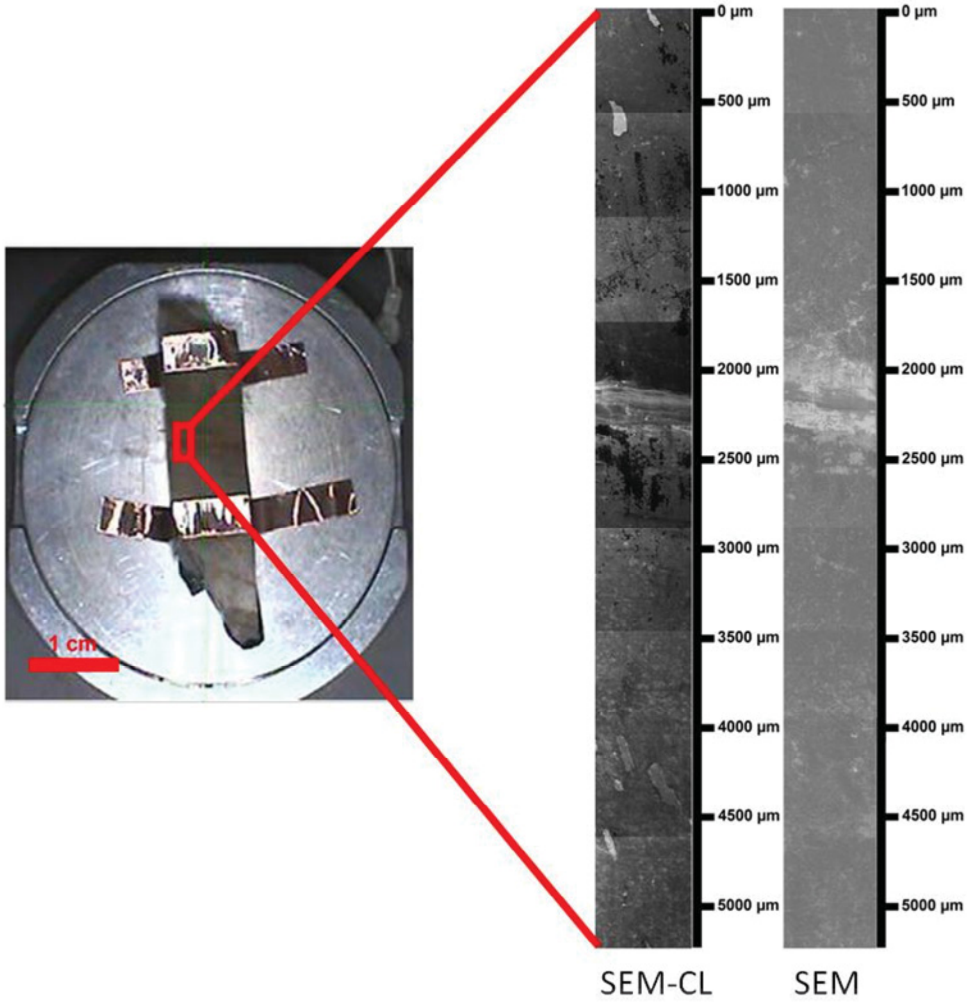

Figure 5. High temperature rock coupon test specimens in individual titanium cups.

scCO$_2$ Diffusion into Sandstone

The effect scCO$_2$ diffusion into the sandstone was examined in a tall (~13 cm) sandstone (2.5 cm dia.) cylindrical core. Due to the size of the core, this experiment was conducted without the titanium cup in a stainless steel 1 liter reaction vessel. Excess MnCl$_2$-KCl salt solution was added to the bottom of the reaction vessel such that 4.5 cm of the sandstone core was immersed in water whereas approximate 8.5 cm of the sandstone core was above the scCO$_2$/water interface. Figure 6 shows the exterior of the core, a vertical cross section through the middle of the core and a numerical model of scCO$_2$ diffusion into the core after a 14 day treatment at 125°C. In this case some additional staining was noted below the scCO$_2$/water interface (Figure 6A). The core was cut lengthwise to examine the interior of the core (Figure 6B). In the lower few centimeters above the scCO$_2$/water interface, staining is noted along the exterior of the core with little staining within the interior of the core. In the top portion of the core, little staining was noted on the exterior of the core with significant staining on the interior of the core.

A numerical model (Hydrus 2D, Simunek et al., 1999) was used to examine the potential diffusion length of scCO$_2$ in a sandstone material as a function of height above a water table. The input parameters were estimated from look up tables for unconsolidated sand but are believe to be accurate enough to qualitatively evaluate relative scCO$_2$ diffusion lengths. Sand typically exhibits a uniform pore structure has therefore has a sharp capillary break above the interface at a few centimeters. Below the capillary break, the pores are filled with the in

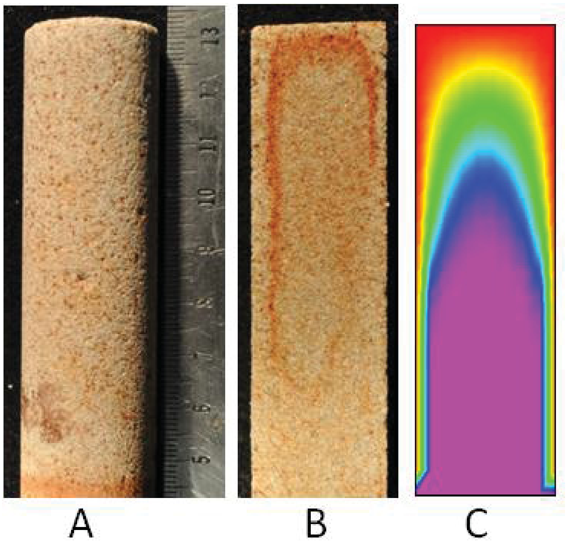

Figure 6. Sandstone core illustrating reaction staining A) exterior of the core, B) cross section of the core, and C) 2D model of $scCO_2$ diffusion into sandstone (red indicates $C_{scCO_2} = 1$, magenta indicates = $C_{scCO_2} = 0$).

invading solution. Above the capillary break, the sand stone pores are filled with both gas and liquid. For this simulation, we have assumed that the gas initially in the sandstone matrix is not $scCO_2$ but is composed of air.

$scCO_2$ can diffuse through both the liquid and the gas in the sandstone pores. The model assumes the Millington-Quirk function for tortuosity for both the gas and the water. We also assumed the diffusion of gas in air is approximately 10,000 times greater of that of diffusion through water (Jury and Horton, 2004).

The model results (Figure 6C) indicated that $scCO_2$ will diffuse into the sand stone to a much greater extent in the zones that are not completely saturated with a fluid. In this case, very little $scCO_2$ has penetrated the outer surface of the sandstone core near the interface whereas due to the decreasing fluid content as a function of height, $scCO_2$ has invaded the sandstone to some distance.

Sandstone Fracture Test

Two pieces of sandstone were mechanically fasten together (Figure 7A) to create a simulated fracture exposed to $scCO_2$. The two sandstone pieces were fasten together with silver wire to allow casting a (red) ceramic epoxy cap at one end of the two slabs. The sandstone pieces were of sufficient length to reach near the bottom of the titanium cup. The cup was filled with $MnCl_2$ solution and the test specimen was carefully placed in the cup allowing the epoxy pug to mostly seal the cup. The test cell was heated to 200C for 5 days as before.

Figure 7B are photographs before and after testing of the top surface of the sandstone fracture test. A slight uniform staining of the sandstone is noted over the top surface with a staining band near the simulated fracture. This would suggest some additional fluid transport through the fracture allowing excess $MnCl_2$ to be transported to the surface and precipitated in this area.

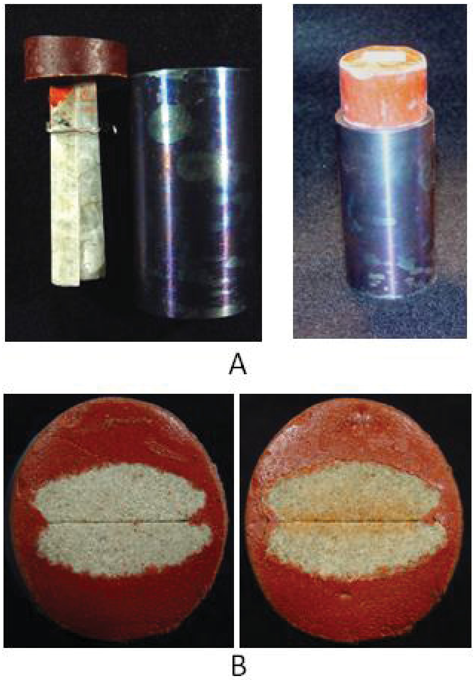

Figure 7. Reaction staining results from the fracture sandstone test.

SUMMARY

Hydraulic fracturing of EGS reservoirs to create permeable pathways for $scCO_2$ will likely result in water imbibition into the reservoir matrix and the reservoir natural fractures. Some of this injected water is expected to remain in the reservoir after initial fracture development. EGS operating pressures that minimize $scCO_2$ leakoff and will result in a long-term return flow of injected and connate waters. Solutes in these waters will react with the $scCO_2$ and could have implications on the overall permeability of the EGS system.

$scCO_2$-solute precipitation experiments were carried out using reservoir rock coupons to examine the location of potential reactions sites. $MnCl_2$ was used as a soluble solute to track locations of the $MnCO_3$ precipitation as indicated by staining of the reservoir rock and by SEM-CL.

Preliminary experimental results suggest limited $scCO_2$ diffusion into saturated porous reservoir rock (or limited imbibition of hydraulic fracturing fluid into low permeable reservoir rocks) will initially result in $scCO_2$ reactions at the liquid-supercritical fluid interface. These reactions tend to be located on the outer surface of the rocks in direct contact with the $scCO_2$.

For reservoir rocks that are not totally saturated with water, either due to capillary forces or through water loss due to partitioning into dry $scCO_2$, the reaction of the $scCO_2$ and solutes in the water will be spread more throughout the reservoir rock matrix. Depending on the net transport of this water, potential mineral precipitation bands may develop that could eventually reduce the permeability of the rock matrix.

Reservoirs with naturally occurring fractures that contain leakoff water from the fracture initiation process may be a source of long-term return flow to the EGS system. These experimental results suggest that precipitation of solutes reaction with the $scCO_2$ will occur at the intersection of the natural fracture and the EGS hydraulic fracture. Our experimental testing time was too short to hypothesize if these precipitates will affect the hydraulic fracture permeability or if they would begin to seal the natural fracture from the EGS system, suggesting that longer testing times are needed. Current models of EGS systems using $scCO_2$ as a working fluid have not accounted for such processes.

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