Magnetic Resonance Measurements of Flow-Path Enhancement During Supercritical CO₂
Injection in Sandstone and Carbonate Rock Cores

Sarah J. Vogt^{1,+}, Colin A. Shaw², James E. Maneval³, Timothy I. Brox^{4,++}, Mark L. Skidmore²,
Sarah L. Codd⁵, Joseph D. Seymour^{1*}

1. Department of Chemical and Biological Engineering, Montana State University, Bozeman, MT, United States

2. Department of Earth Sciences, Montana State University, Bozeman, MT, United States

3. Department of Chemical Engineering, Bucknell University, Lewisburg, PA, United States

4. Department of Physics, Montana State University, Bozeman, MT, United States

5. Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, MT, United States

* Corresponding Author

P.O. Box 173920

Bozeman, MT 59717

United States

jseymour@coe.montana.edu,

phone: 01-406-994-6853

fax: 01-406-994-5308

+Current Address: School of Mechanical and Chemical Engineering, University of Western
Australia, Crawley, WA, Australia

++Current Address: MacDiarmid Institute for Advanced Materials and Nanotechnology, School
of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

Abstract

Sandstone and carbonate core samples were challenged with a two phase supercritical CO₂ and brine mixture to investigate the effects of chemical processes on the physical properties of these rocks during injection of CO₂. Experiments were monitored in real-time for pressure, temperature, and volumetric rate discharge. Pore geometry and connectivity were characterized before and after each experimental challenge using Magnetic Resonance (MR) imaging and two dimensional MR relaxation correlations. Quartz arenite sandstone cores were largely unaffected by the challenge with no measurable change in effective permeability at moderate and high temperatures (~50°C, ~95°C) or brine concentrations (~1g/L, ~10g/L). In contrast, a carbonate core sample showed evidence of significant dissolution leading to a six-fold increase in effective permeability. MR images and relaxation measurements revealed a marked increase in the volume and connectivity of pre-existing pore networks in the carbonate core. We infer that the increase in permeability in the carbonate core was enhanced by focused dissolution in existing pore and fracture networks that enhanced fast-flow paths through the core.

Keywords: Carbon sequestration, Berea sandstone, Madison limestone, magnetic resonance imaging, permeability, supercritical CO₂

1. Introduction

Enhanced oil recovery (EOR) has long utilized CO₂ injection and recently carbon capture and geological storage (CCGS) is emerging as a viable climate mitigation technology for isolating anthropogenic CO₂ from the atmosphere by redirecting emissions from large point sources into deep subsurface reservoirs (Jenkins et al., 2012). CCGS leverages existing technologies and can be combined with EOR operations to offset CO₂ emissions from the combustion of the recovered petroleum (Anderson and Newell, 2004; Lackner, 2003). This makes it an attractive option for mitigating the climate impact of CO₂ emissions during a transition to more sustainable non-fossil-fuel-based energy sources (Celia, 2008; Nordbotten et al., 2005). Pilot studies and large scale demonstration projects are underway to investigate the efficacy of carbon storage in a variety of geologic contexts including deep saline aquifers, depleted hydrocarbon reservoirs, unminable coal beds and mafic to ultramafic igneous bodies (Anderson and Newell, 2004). Experimental studies of the interaction of reservoir rocks with supercritical CO₂ and displaced pore fluids provide information that is necessary to predict changes in the physical properties of potential reservoirs resulting from CO₂ injection. Such changes have important consequences for engineering efficient injection strategies and for ensuring the integrity and longevity of CCGS reservoirs (Kharaka et al., 2006).

Recent laboratory studies have used medical computer tomography (CT) with CsCl doped brines (Ott et al., 2013) to determine wormhole density and size and X-ray computed microtomography (Smith et al., 2013) to evaluate porosity and permeability changes in limestone cores in response to brine plus supercritical CO₂ challenges. However, Magnetic Resonance (MR) imaging and analytical techniques have received less attention for such experimental work. This research presents experimental results on the change in pore volume, pore connectivity, and

effective permeability resulting from injection of supercritical CO₂ + CO₂-saturated brine into mineralogically simple limestone and quartz-sandstone rock cores. Continuous monitoring of flow rate and pressure allowed us to assess permeability at the start and end of the CO₂ challenge. Magnetic Resonance (MR) imaging and relaxation measurements were obtained pre- and post-challenge and were used to visualize and assess physical changes in the pore structure.

The experimental conditions of the CO₂ challenge approximated realistic chemical and physical conditions in a sedimentary reservoir containing aqueous brine pore fluids at a depth of near 1000 m. In addition to lithology experimental variables included temperature (~50°C and ~95°C) and brine strength (0.99 g/L and 9.9 g/L). These preliminary experiments provide a simplified view of processes that may affect real reservoir rocks to different degrees depending on rock composition, temperature, and pore-fluid chemistry. Results are most relevant to short-timescale changes in reservoir properties due to two-phase flow near the dynamic supercritical CO₂/brine interface during the injection phase of CCGS. The effects of long-term residence of CO₂ and of relatively slow volumetric transport processes such as capillary drainage (Bachu and Bennion, 2008; Iglaue et al., 2011) are not explicitly addressed by these experiments.

MR imaging has been used to study rocks since the development of the technique 30 years ago (Rothwell and Vinegar, 1985) and MR images commonly have been applied to spatially map and calculate porosity (Borgia et al., 1996; Marica et al., 2006; Merrill, 1993), permeability (Romanenko and Balcom, 2013) and imbibition (Fernø et al., 2013) as well as other properties and dynamic phenomena. MR observations of supercritical fluids in porous media have been conducted on pure fluids such as pentane (Dvoyashkin et al., 2007), on fluorinated gases (Rassi et al., 2012), on rocks in the presence of hydrate formation (Hirai et al., 2000) and on rocks challenged by supercritical fluids (Zhao et al., 2011). However, due to sample size

limitations and magnetic field inhomogeneities caused by magnetic susceptibility differences and high magnetic fields, signal-to-noise ratio challenges are significant using laboratory magnets. In recent years, two-dimensional relaxation and displacement correlation experiments have become a useful tool for studying a variety of porous systems including rocks (Callaghan, 2011; McDonald et al., 2007; Mitchell et al., 2010; Song, 2009; Van Landeghem et al., 2010; Washburn and Callaghan, 2006). Spin-spin relaxation T_2 - T_2 experiments such as those presented in this research obtain information about pore geometry by probing molecular surface interactions on the time scale of milliseconds. The application of two dimensional MR relaxation correlation to characterize the pore evolution in CO₂ challenged rock cores extends the long established use of MR relaxation distribution data to characterize rock pore size distributions for petroleum recovery applications (Talabi et al., 2009).

2. Materials & Methods

2.1. Samples

Samples representing unreactive and reactive lithologies were tested to establish end-member models for the response of reservoir rocks to supercritical CO₂ flooding. Quartz arenite (>95% quartz) from the Mississippian Berea formation from Cleveland Quarries, Ohio was chosen to represent relatively inert quartz-rich clastic lithologies. Dolomitic limestone from the Mississippian-age Madison formation collected in the Black Hills, South Dakota, was used to represent more reactive carbonate lithologies. Most target reservoir rocks for CCGS are likely to have chemical reactivities somewhere between these bracketing end-members (e.g. carbonate cemented sandstone, impure limestone and marl).

2.1.1. Berea Formation Sandstone

Four samples of Berea formation sandstone (Table 1) were uniform massive to finely-bedded fine-grained quartz arenite (>95% quartz) with accessory phases including feldspar (<5%), muscovite (<1%) and miscellaneous silicates and oxides (<1%) and dispersed calcite and/or dolomite infillings (~1%). Quartz grains were sub-angular to sub-rounded and moderately- to well-sorted with typical grain sizes ranging from <0.1 mm to >0.2 mm. Intragranular pore space was evenly distributed at grain triple junctions. The nominal permeability of the block from which samples were drilled was 250 mD (Cleveland Quarries, written communication).

2.1.2. Madison Formation Limestone

One sample of Madison formation dolomitic limestone (Black Hills, South Dakota) was challenged at high-temperature (~95°C) and low-salinity (0.99 g/L) experimental conditions to achieve maximum reactivity (Table 1). The composition of the sample comprised approximately 70% calcite and 30% dolomite as determined in thin section by Alzarín Red-S staining. Few pores were observed between the interlocking crystalline grains in thin sections of the pristine rock. Rather, pore space was concentrated in void spaces ranging from < 0.1 mm to > 2 mm. Some voids were partially filled with sparry calcite crystals. Although no through-going fractures were observed at the thin section scale, interconnected vuggy calcite-filled veins and fractures were evident in the sample block and in the core prior to CO₂ challenge.

2.1.3. Fluids

Two end-member brines with dissolved solid concentrations of 0.99 g/L and 9.9 g/L, respectively, were prepared using Type-1 ultrapure de-ionized water (Millipore Milli-Q) and

laboratory-grade chemicals. The brine recipe was designed to approximate natural brines reported from the Powder River basin, Wyoming (Busby et al., 1995) with 0.033 M/L NaCl and CaCl₂, 0.035 M/L MgSO₄ and 0.001 M/L MgCO₃. Brines were pH balanced to 6.5 ± 0.2 units using HCl and NaOH.

2.2. Experimental Apparatus and Procedure

Cylindrical 25mm x 100 mm rock cores were drilled from cut blocks using a one-inch diamond core bit then dried at 120°C for 24 hours and weighed. Prior to the experimental challenge cores were saturated with brine under vacuum for 24 hours, removed from the brine solution, blotted dry to remove surface wetness, weighed and transferred to a sealed PEEK tube for pre-challenge MR experiments. The cores were then transferred to the pre-heated core reactor for the CO₂ challenge. Rock cores were challenged in a flow-through core reactor equipped with in-situ influent and effluent pressure transducers to monitor the pressure drop across the core in real-time (Hanson, 2009), as shown in Figure 1. The entire fluid pathway except for pump and accumulator was enclosed in a heated, insulated incubator capable of maintaining stable temperatures up to about 95°C. Fluid flow through the system was driven by a 500 ml Teledyne-ISCO[®] syringe pump with a heated glycol-filled jacket to pre-heat the fluids. Internal system pressure was controlled by nitrogen backpressure on a 3.8 L piston accumulator with a target pressure of 10 MPa. The system is capable of maintaining CO₂ as a supercritical fluid (>31°C, >7.38 MPa) throughout the flow path. The sample rock core was held in a Hasler-type pressure cylinder with a Viton[®] sleeve compressed at 16-18 MPa hydraulic confining pressure. Experimental conditions broadly bracket realistic subsurface conditions at depths of about 1000 m assuming hydrostatic pore pressure and a geothermal gradient of >30°C/km.

During the experimental runs core samples were initially flooded with 500 ml of brine followed by three recharges of brine + supercritical CO₂. Recharges were prepared by filling the pump cylinder with 400 ml of brine and ~100 ml of CO₂ at tank pressure (approximately 1.4 MPa). The two phase mixture was pressurized to 12 MPa to achieve supercritical conditions for CO₂. For each recharge, final fluid volume after pressurization was about 405 ml including 400 ml brine and approximately 5 ml supercritical CO₂. A measured decrease of approximately 2 units in the pH of the brine indicates that CO₂ dissolved into the brine although it is unlikely that the brine was completely saturated during the relatively short residence time of the CO₂ phase in the pump cylinder (~20min). The total fluid volume for each core flood was approximately 1700 mL – equivalent to about 35 core volumes.

Pressure (P , MPa) and discharge (Q , mL/minute) were monitored at 60 s intervals during the experiments using three transducers: the first integrated into the pump, the second in-line (just down-stream from the core) and the last in the nitrogen backpressure system on the dry-side of the piston accumulator. The difference between the pump pressure and the in-line pressure was taken as the pressure drop or differential pressure (ΔP) responsible for driving flow through the core. Effective permeability is defined from Darcy's Law written as a linear relationship between discharge Q and the pressure drop across the core ($\Delta P = P_{\text{pump}} - P_{\text{effluent}}$):

$$(1) \quad Q = -k_{\text{eff}} \cdot \Delta P \quad \text{where} \quad k_{\text{eff}} = \frac{k}{\mu} \cdot \frac{A}{L}$$

The effective permeability k_{eff} is a function of k = true permeability, μ = dynamic viscosity, and a geometric constant A/L = Area/Length. In a plot of discharge vs. differential pressure the slope ($Q/\Delta P$) represents the effective permeability assuming that the cross sectional area of flow and the length of the flow path are constant. Continuous in-line measurement of pre- and post-core

pressure and volumetric discharge allowed us to assess change in effective permeability during the experiment. Values of effective permeability calculated from the experiments include unknown contributions arising from viscous drag on the walls of tubing, possible restriction of the effective cross-sectional area of the flow path within the core holder, fluid viscosity and other factors.

Behavior of the carbonate core was quite different from the sandstone. Initial permeability of the sample was so low that the standard constant discharge of 0.5 mL/min could not be achieved within the pressure limits of the apparatus (~16 MPa). Thus, at $t = 744$ min the pump was switched to constant pressure mode at ~14 MPa with minimal backpressure to maximize the differential pressure across the core. Under these conditions flow slowly increased to ~0.2 mL/min, stabilized and then started a rapid rise at $t \sim 2400$ min. With flow rates accelerating at experimental time $t = 2577$ the pump was switched back to constant discharge (0.5 mL/min). For the remainder of the experiment differential pressure dropped continuously as discharge remained constant. The effective permeability ($Q/\Delta P$) increased continuously during all phases of the experiment.

After the CO₂ challenge cores were stored in brine to maintain saturation for post-challenge MR experiments. Immediately before imaging the cores were blotted dry, transferred to the PEEK sample holder and immediately re-imaged in the same orientation as the pre-challenge image.

2.3. Magnetic Resonance (MR) Methods

Physical changes in pore volume and structure due to CO₂ and brine challenge were assessed by comparing two and three dimensional Magnetic Resonance (MR) images and T_2 - T_2 relaxation measurements of the cores taken before and after the experimental CO₂ challenge. These experiments used a novel 300 MHz super-wide-bore 7 T magnet (Bruker) with a radio frequency (r.f.) coil of 37 mm diameter networked to an AVANCE III spectrometer. This enabled the imaging of 25 mm in diameter by 100 mm in length core samples, which also allowed the CO₂ challenge experiments to be obtained over a large core sample length.

2.3.1. MR Imaging

Two types of imaging experiments were conducted: multi-slice spin echo and 3-D spin echo images (Blumich, 2000; Callaghan, 1991). Multi-slice experiments utilized a slice-selective r.f. pulse to excite a slice thickness of 1.5 mm in the axial direction and had an in-plane resolution of 0.27 mm x 0.27 mm. 12 slices with a gap of 2.5 mm between each slice were obtained for each experiment, for a total field of view (FOV) in the axial direction of 45.5 mm. Two experiments were performed with interleaving slices to ensure imaging coverage of the entire rock core. 3-D spin echo images begin with an r.f pulse which excites the whole sample and then utilize two phase-encoding gradients and a read gradient, leading to 3-D images with no gaps between slices. 3-D experiments had a resolution of 0.47 mm x 0.55 mm x 0.55mm and a FOV of 50 mm x 35 mm x 35 mm. The total experimental time for the set of experiments was about 30 hours. The bottom half of each rock core was imaged first and then was repositioned to image the top half. The cores were then challenged with CO₂ and the experiments were repeated in the same order with the cores in the same positions. Images were normalized with total signal intensity from the middle part of the core, avoiding the background noise around the core. High image signal intensity correlates to high density of fluid-filled pore space. MR images of the

same rock cores repositioned in the same orientation within the magnet were obtained before and after the CO₂ challenge without any additional sample processing to facilitate direct comparison of images. Difference images were constructed by subtracting intensity values of corresponding pixels in the before and after images.

2.3.2. T_2 - T_2 Relaxation Correlations

In a porous medium, magnetic spin-spin T_2 relaxation can be related to the pore size distribution via increased relaxation due to molecular interactions with magnetic impurities on the rock surfaces (Kleinberg, 1994; Talabi et al., 2009) and molecular diffusion through magnetic field gradients on the pore scale (Mitchell et al., 2010). In samples with a range of length scales and negligible magnetic field gradients, the measured T_2 relaxation distribution can be related to the surface to volume ratio and used to obtain a pore size distribution (Kleinberg, 1994):

$$(2) \quad T_2 = \frac{V}{\rho S}$$

where V is the pore volume, S is the active surface area, and ρ is the surface relaxivity of the rock. For a sample of a rock within a magnetic field, the magnetic susceptibility difference between the water within the pores and the rock walls will cause magnetic field gradients in the pore space, and the measurement of T_2 will be impacted by the dephasing of the magnetization caused by molecular diffusion through these gradients. The magnitude of the gradient will be dependent on the applied magnetic field amplitude used for the measurements and the magnetic characteristics of the geologic material surfaces at the liquid-solid interfaces. For example, at high magnetic fields sandstones have gradients as much as 3 orders of magnitude larger than for

limestones (Mitchell et al., 2010). The magnetic field gradients will be on the order of the pore size, so that this effect may also be used to relate the T_2 relaxation to pore size.

The T_2 - T_2 sequence consists of encoding for T_2 , waiting a mixing time τ_m , then measuring the T_2 . If molecules have the same T_2 before and after the mixing time, the distribution in the 2D spectrum will be along the diagonal, while if molecules have changed T_2 environments via diffusion through magnetic field gradients or surface interactions during the mixing time there will be off-diagonal peaks in the spectrum. The data will have the form:

$$(3) \quad M(t_{2,1}, t_{2,2}) = \iint M_0(T_{2,1}, T_{2,2}) \exp\left(\frac{-t_{2,1}}{T_{2,1}}\right) \exp\left(\frac{-t_{2,2}}{T_{2,2}}\right) dT_{2,1} dT_{2,2} + E(t_{2,1}, t_{2,2})$$

where $t_{2,1}$ and $t_{2,2}$ are time scales of the two T_2 encoding periods as defined and will define the range of T_2 values that are sampled, and $E(t_{2,1}, t_{2,2})$ is the noise of the measurement (Song, 2002). Inverse Laplace Transform (ILT) of the data converts the spin relaxation decays into 2D relaxation maps using 2D non-negative least squares (Callaghan et al., 2003; Song, 2002). T_2 - T_2 experiments were performed before and after CO₂ challenge on both the top and bottom halves of each rock. These experiments used a CPMG pulse sequence (Callaghan, 2011) with an echo spacing τ of 200 μ s, echo train of 512 points, indirect encoding for T_2 of 32 points and mixing times τ_m of 5 ms (results not shown) and 50 ms.

3. Results

3.1 Differential Pressure and Discharge

During each of the four sandstone experiments, pump pressure, post-core inline pressure and accumulator backpressure were nearly perfectly coupled so that differential pressure (ΔP)

was essentially constant except for transient instability following pump recharge. There is no substantial difference in the effective permeability ($Q/\Delta P$) of sandstone cores between experiments at different brine strength or temperature (Table 1). In contrast the rapid variation in effective permeability of the limestone sample, which required a modification of the core challenge process as discussed above in the methods section, was clearly evident.

3.2. MR Imaging – Pore Volume and Connectivity

The signal intensity of MR spin echo images of the cores indicates pore volume averaged fluid (brine) content over the sample volume represented by each pixel (1.5 x 0.27 x 0.27mm) for 2-D images or voxel (0.47 x 0.55 x 0.55 mm) for 3-D images. Both pre- and post-challenge images of Berea sandstone cores show a low-amplitude and apparently random distribution of normalized intensity (e.g. Figure 2a). This is interpreted to reflect a relatively even distribution of intergranular pore space consistent with the typical pore structure in well- to moderately-sorted sandstones such as the Berea. There is no evidence for large cracks or through-going fractures in the images. Post-challenge MR images of all sandstone cores (e.g. Figure 2b) are essentially identical to pre-challenge images suggesting that pore volume and structure was largely unaffected by the CO₂ challenge. Difference images calculated by subtracting pre-challenge intensity from post-challenge intensity show little evidence for changes in pore volume and do not reveal any significant pattern (e.g. Figure 2c). We interpret this to indicate that any change in pore volume during the challenge was below the resolution of the MR technique and more-or-less evenly distributed through the core. These results are consistent with MR relaxation results as discussed in the next section.

In contrast, the post-challenge image of carbonate sample MAD.01 shows a significant increase in normalized intensity in some pixels compared with pre-challenge images (Figure 3a, b). The difference image (Figure 3c) clearly shows that the most significant increases in intensity are concentrated near areas where signal intensity, and hence local fluid pore volume, was already high in the pre-challenge image (cf. Figure 3a). These areas likely represent cracks, voids and/or fractures observed in thin section where pore space was concentrated in the otherwise relatively low porosity limestone. The limited resolution of the MR images in the axial direction (~0.47 mm) restricts exact quantification of connectivity in three dimensions. However, the increase in connectivity can be visualized qualitatively in a 3-D isosurface reconstruction (Figure 4) that shows the surface enclosing 0.025% of total signal intensity. Thus, the isosurface represents the fraction of the sample volume with the highest probability of containing a significant volume of fluid-filled pore space. The amount of connected pore space increases after the CO₂ challenge. The timing for the imaging experiments was optimized to minimize the echo time and acquisition time in order to minimize the effects of relaxation and diffusion within internal magnetic field gradients. However, since these experiments were performed at a high magnetic field, the inhomogeneous broadening of the echo will impact the resolution of the images. This imaging effect will be the same before and after challenge, so by comparing the images to each other we normalize the relaxation effects and the conclusion that the larger pores got larger after dissolution is unaffected by the inhomogeneous broadening effect.

3.3. T_2 - T_2 Relaxation Correlations

T_2 - T_2 distributions for the two different rocks are shown in Figure 5. The limestone has a T_2 distribution along the diagonal centered around a higher T_2 than for the sandstone due to

larger pores, as also shown in the MR images. The use of a mixing time τ_m of 50 ms allows further quantification of the pore size distribution. Cross peaks are not present in the limestone indicating that molecules of water have not diffused throughout the entire pore during the mixing time, while the sandstone shows significant cross peaks indicating that water molecules have changed environments during the mixing time or relaxation has occurred due to surface relaxation. After the challenge, the T_2 of the limestone shifts to higher values along the diagonal while still exhibiting no cross-peaks, indicating that the pores are larger than before the challenge. The sandstone does not show any significant change due to the challenge in either the range of T_2 values or in the amount of cross-peaks.

4. Discussion

As expected, at the short timescales addressed by these experiments supercritical CO₂ and CO₂-saturated brine appear to have no significant effect on permeability of quartz sandstones. MR images from before and after the challenge were essentially unchanged for all experiments (Figure 2), and T_2 - T_2 relaxation distributions also showed no significant change (Figure 5). Minor mineral dissolution that occurred during the duration of the experiment was below the resolution of our images, relaxation tests, and effective permeability measurements. In contrast, MR images from the carbonate cores show evidence for substantial modification. This is not surprising as calcite and dolomite are highly reactive and susceptible to dissolution in the acidic environment of the CO₂-acidified brine. However, the imaging data shows that dissolution was focused along narrow conduits with limited surface area (Figure 3). Based on thin film and petrographic observations of the core and sample block we interpret these conduits to be pore networks that acted as fast-flow paths through the low-permeability limestone. With flow

concentrated in a small proportion of the total cross-sectional area of the core, dissolution of a relatively small volume of rock could substantially increase the effective cross-section of the flow path. This process would create a positive feed-back loop whereby dissolution of restrictions within fracture-controlled flow paths leads to enhanced flow of CO₂-acidified brine thereby further concentrating the chemical effects in the existing pore network (Hoefner and Fogler, 1988). The positive feedback between flow and dissolution generates changes in pore structure concentrated along preferred flow pathways and leads to enhanced connectivity of pore space accounting for the increase in effective permeability consistent with network models (Hoefner and Fogler, 1988). Comparison of the pre-challenge isosurface (Figure 4a) with the post-challenge isosurface (Figure 4b) shows both a significant increase in the total volume enclosed and an increase in the connectivity of the surface reflecting an increase in pore connectivity. We interpret this concentrated increase in interconnected pore space along pre-existing pore networks as the cause of the increase in effective permeability during the experiment.

The average T_2 of the limestone before challenge was 0.0672 s and after challenge was 0.146 s, representing a change of 134%. In contrast, the average T_2 before and after challenge for the sandstone was 0.0191 s and 0.0202 s respectively, representing a change of only 6%. In the following discussion, we define the “larger pores” as pores containing water with relaxation longer than 50 ms (to the right of the dashed line in Figure 5c). The amount of total signal in the larger pores of the limestone pre challenge was 23% with an average T_2 of 0.205 s, and post challenge the percentage of the total signal was 42% with an average T_2 of 0.320 s. The increase in average T_2 by 1/3 indicates a significant increase in the large pore structure size. In contrast, the average T_2 of the smaller pores (to the left of the dashed line) only changed from 0.0213 s to

0.0193 s pre and post challenge respectively. This indicates that the smaller percentage of brine in the small pores post challenge is in pores of essentially the same size as pre challenge, consistent with reaction induced pore morphology changes being focused in the larger preexisting pore structures as predicted by network models (Hoefner and Fogler, 1988) and observed in x-ray micro-CT studies (Ott et al., 2013; Smith et al., 2013). The projection of the 2D T_2 - T_2 distribution to 1D shown in Figure 5c clearly shows an increase in the longest T_2 components from < 1 s prior to challenge to > 1 s post challenge. This indicates prior to challenge brine in even the largest pores is interacting with the pore structure since the longest T_2 values are decreased relative to the free liquid or bulk value of approximately 2 s. Post challenge the increase in pore size is such that some brine is minimally interacting with the pore structure and has a T_2 approaching the bulk value. The values of the shortest T_2 components show no change, also consistent with dissolution occurring along pre-existing pore networks with little change to the smallest pore sizes. The entire distribution is homogenized by the dissolution process demonstrating that small pores in the walls of the preferential flow paths are increasing in size due to the reactive flow. Future experiments could exploit this relaxation effect more directly by varying the echo time of the imaging experiments to filter out the shorter relaxation components (smaller pores) and obtain images weighted to only show the largest pores in the structure (Young et al., 2004).

5. Conclusions

In this study MR imaging methods and T_2 - T_2 relaxation correlations have been applied to determine the nature of physical changes in the pore structure of quartz-rich and carbonate rock cores subjected to supercritical CO_2 + brine challenge at conditions relevant to EOR and carbon

sequestration in the subsurface. Quartz sandstone showed minimal reactivity and no measurable changes to permeability or pore volume/structure as expected. Carbonate rocks showed significant chemical dissolution that increased pore volume along pre-existing pore networks that enhanced connectivity between pores in fast-flow paths resulting in an increase of effective permeability. This process creates the positive feedback whereby increased flow increases the rate of dissolution along fast-flow paths which in turn promotes greater concentration of flow in these same paths. The coupling of MR imaging and two dimensional relaxation measurements enhances quantification of the evolution of pore size distribution during CO₂ challenge and can be used to interrogate a variety of rock types to assess the nature of pore alteration during such challenges. Future experiments will be performed using a high-pressure core flooding system optimized for use within the MRI apparatus so that the MRI and NMR experiments can be conducted during the supercritical CO₂ challenge. Additionally, imaging and relaxation NMR experiments performed at lower magnetic fields (~0.05 T vs. 7 T used in this study) are less impacted by inhomogeneous magnetic fields created by pore scale susceptibility gradients. High field NMR, as demonstrated here, allows for high spatial resolution imaging using strong magnetic field gradients. Hardware advances allowing strong magnetic field gradients for high spatial resolution in low applied field NMR systems will allow future studies to be performed at lower magnetic fields to yield additional information about pore connectivity and structure.

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Figure Captions

Figure 1: Schematic diagram showing flow-through reactor used in experiments. Confining pressures of 16-17 MPa were maintained within the TEMCO reactor cylinder (Black). Internal fluid pressures of approximately 10-12 MPa were controlled by a syringe pump and nitrogen back-pressure system (gray). A constant-temperature bath pre-heated fluids in the syringe pump and a modified incubator (heavy dashed rectangle) maintained all primary system components within 2-3°C of target temperatures for 50°C experiments and ~10°C for 95°C experiments. Internal pressures were continuously monitored at the pump, downstream of the core (in-line) and at the nitrogen back-pressure port of the accumulator cylinder (hexagon labeled 'P'). Temperatures were monitored at four points along the flow path (hexagon labeled 'T'). The pH of influent and pH and conductivity of effluent fluid was monitored continuously (gray boxes).

Figure 2: Examples of pre-challenge (a) and post-challenge (b) NMR spin echo images of selected axial slices near the middle of core sample BER.07. Each experiment consisted of 12 axial slices with thickness 1.5mm and in-plane resolution of 0.27mmx0.27mm. Slices were separated by 2.5mm. Timing parameters: $T_E = 4.636$ ms, $T_R = 2$ s, $T_{\text{read}} = 0.64$ ms (dwell time = 0.005 ms, 128 points acquired). (c) A pixel-by-pixel by comparison between the pre- and post-challenge images. The difference was quantified by subtracting the normalized intensities and squaring the difference for each pixel. The BER.07 sample showed very little difference between before and after challenge images.

Figure 3: Examples of pre-challenge (a) and post-challenge (b) MR spin echo images of selected axial slices near the middle of core sample MAD.01. Experimental protocol was the same as for Figure 2. (c) Difference comparison for MAD.01. The greatest pixel differences are shown to correspond with regions of high pixel intensity in the pre-challenge images. This indicates that supercritical CO₂ increases permeability by dissolution along preferential flow pathways.

Figure 4: Three dimensional isosurface images derived from normalized signal intensity of pre- and post-challenge 3-D spin echo image data from carbonate sample MAD.01. Resolution of images is 0.47mm x 0.55mm x 0.55mm. Timing parameters: $T_E = 1.984$ ms, $T_R = 1$ s, $T_{\text{read}} = 0.64$ ms (dwell time = 0.005 ms, 128 points acquired). The pre- and post-challenge images shown are each combinations of two separate 3-D images, one experiment for the top 50 mm of the rock core and another experiment for the bottom 50 mm of the core. The signal intensity was normalized to the total signal intensity for each experiment, and the same threshold of 0.025% of the total intensity was used for all four images. The isosurface is taken to represent areas of relatively high pore volume/rock volume ratio. The gray box regions are regions of low MR signal to noise near the ends of the r.f. coil.

Figure 5: (a) Pre-challenge T_2 - T_2 correlation results for a mixing time of 50 ms. (b) Post-challenge T_2 - T_2 correlation results for a mixing time of 50 ms. (c) Integration in the vertical direction onto the horizontal axis of plots in (a) and (b). The shift to longer T_2 times for the limestone post-challenge is clear in the growth of the peak about 1 second. In contrast, the sandstone distribution does not change significantly. The vertical dashed line is discussed in the text.

Tables

Table 1: Summary of samples, experimental conditions, and saturation conditions.

<i>Sample</i>	<i>Time Range (min.)</i>	<i>Brine Strength</i>	<i>Target Temp.</i>	<i>Target Discharge (Q)</i>	<i>Target Pressure (P)</i>
BER.04	0-2917	9.90 g/L	50°C	0.5 mL/min	--
BER.05	0-2885	9.90 g/L	95°C	0.5 mL/min	--
BER.07	0-3640	0.99 g/L	50°C	0.5 mL/min	--
BER.08	0-2555	0.99 g/L	95°C	0.5 mL/min	--
MAD.01	const. P: 0 - 744	0.99 g/L	95°C	--	14 MPa
	const. Q: 744 - 5000			0.5 mL/min	--

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