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Magnetic resonance measurements of flow-path enhancement during supercritical CO_2 injection in sandstone and carbonate rock cores

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ABSTRACT

Sandstone and carbonate core samples were challenged with a two-phase supercritical CO_2 and brine mixture to investigate the effects of chemical processes on the physical properties of these rocks during injection of CO_2. The 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 ($\sim$50 °C and $\sim$95 °C) or brine concentrations ($\sim$1 g/L and $\sim$10 g/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 the existing pore and fracture networks that enhanced fast-flow paths through the core.

1. Introduction

Enhanced oil recovery (EOR) has long utilized CO_2 injection, and recently carbon capture and geological storage (CCGS) is emerging as a viable climate mitigation technology for isolating anthropogenic CO_2 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 CO_2 emissions from the combustion of the recovered petroleum (Lackner, 2003; Anderson and Newell, 2004). This makes it an attractive option for mitigating the climate impact of CO_2 emissions during a transition to more sustainable non-fossil-fuel-based energy sources (Nordbotten et al., 2005; Celia, 2008). Pilot studies and large scale demonstration projects are underway to investigate the efficacy of carbon storage in a variety of geological 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 CO_2 and displaced pore fluids provide information that is necessary to predict changes in the physical properties of potential reservoirs resulting from CO_2 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 CO_2 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 $CO_2 + CO_2-$saturated brine into mineralogically simple limestone and quartz–sandstone rock cores. Continuous monitoring of

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flow rate and pressure allowed us to assess permeability at the start and end of the CO_2 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 CO_2 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 CO_2/brine interface during the injection phase of CCGS. The effects of long-term residence of CO_2 and of relatively slow volumetric transport processes such as capillary drainage (Bachu and Bennion, 2008; Iglauer 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 have commonly been applied to spatially map and calculate porosity (Merrill, 1993; Borgia et al., 1996; Marica et al., 2006), 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 (Washburn and Callaghan, 2006; McDonald et al., 2007; Song, 2009; Mitchell et al., 2010; Van Landeghem et al., 2010; Callaghan, 2011). 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 CO_2 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 CO_2 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).

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

Sample	*Time range (min)*	*Brine strength (g/L)*	*Target temp. (°C)*	*Target discharge (Q)*	*Target pressure (P)*
BER.04	0–2917	9.90	50	0.5 mL/min	–
BER.05	0–2885	9.90	95	0.5 mL/min	–
BER.07	0–3640	0.99	50	0.5 mL/min	–
BER.08	0–2555	0.99	95	0.5 mL/min	–
MAD.01	const. *P*: 0–744	0.99	95	–	14 MPa
	const. *Q*: 744–5000			0.5 mL/min	–

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 Alzarin 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 the CO_2 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 $CaCl_2$, 0.035 M/L $MgSO_4$ and 0.001 M/L $MgCO_3$. Brines were pH balanced to 6.5 ± 0.2 units using HCl and NaOH.

2.2. Experimental apparatus and procedure

Cylindrical 25 mm × 100 mm rock cores were drilled from cut blocks using a 1-in. diamond core bit, then dried at 120 °C for 24 h and weighed. Prior to the experimental challenge, cores were saturated with brine under vacuum for 24 h, 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 CO_2 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 Fig. 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