

Water Resources Research

RESEARCH ARTICLE

10.1002/2015WR017547

Key Points:

- Supercritical CO₂ has a lower residual saturation than air and CO₂
- The nonwetting phase is preferentially trapped in the larger pores
- NMR is a valuable tool for studying capillary trapping

Correspondence to:

S. L. Codd,
scodd@montana.edu

Citation:

Prather, C. A., J. M. Bray, J. D. Seymour, and S. L. Codd (2016), NMR study comparing capillary trapping in Berea sandstone of air, carbon dioxide, and supercritical carbon dioxide after imbibition of water, *Water Resour. Res.*, 52, 713–724, doi:10.1002/2015WR017547.

Received 12 MAY 2015

Accepted 13 JAN 2016

Accepted article online 18 JAN 2016

Published online 5 FEB 2016

NMR study comparing capillary trapping in Berea sandstone of air, carbon dioxide, and supercritical carbon dioxide after imbibition of water

Cody A. Prather¹, Joshua M. Bray^{1,2}, Joseph D. Seymour³, and Sarah L. Codd⁴

¹Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, Montana, USA, ²Now at School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK, ³Department of Chemical and Biological Engineering, Center for Biofilm Engineering, Montana State University, Bozeman, Montana, USA, ⁴Center for Biofilm Engineering, Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, Montana, USA

Abstract Nuclear magnetic resonance (NMR) techniques were used to study the capillary trapping mechanisms relevant to carbon sequestration. Capillary trapping is an important mechanism in the initial trapping of supercritical CO₂ in the pore structures of deep underground rock formations during the sequestration process. Capillary trapping is considered the most promising trapping option for carbon sequestration. NMR techniques noninvasively monitor the drainage and imbibition of air, CO₂, and supercritical CO₂ with DI H₂O at low capillary numbers in a Berea sandstone rock core under conditions representative of a deep underground saline aquifer. Supercritical CO₂ was found to have a lower residual nonwetting (NW) phase saturation than that of air and CO₂. Supercritical CO₂ behaves differently than gas phase air or CO₂ and leads to a reduction in capillary trapping. NMR relaxometry data suggest that the NW phase, i.e., air, CO₂, or supercritical CO₂, is preferentially trapped in larger pores. This is consistent with snap-off conditions being more favorable in macroscale pores, as NW fluids minimize their contact area with the solid and hence prefer larger pores.

1. Introduction

Anthropogenic CO₂ emissions are becoming increasingly prevalent in our society and the increase in atmospheric concentrations of this greenhouse gas is believed to contribute to the observed global warming [Bachu, 2008]. A currently investigated viable means of reducing anthropogenic CO₂ emissions is through a method called carbon capture and storage (CCS) [Klusman, 2003]. CCS is the process by which CO₂ is captured and securely stored in deep underground saline aquifers or in depleted oil and gas fields. When CO₂ is injected into these deep underground reservoirs, it is stored in a supercritical state, that is, at temperatures and pressures above the critical point of CO₂. Supercritical fluids exhibit both properties of gases and liquids with transport properties comparable to gases and densities similar to liquids [Carles, 2010; Rassi et al., 2012]. Thus, CO₂ in its supercritical state will have a larger storage capacity than in its gaseous state while at the same time enhancing mass transfer of the CO₂ into brine and is therefore ideal for geologic sequestration.

There are four dominant trapping mechanisms that contribute to the long-term storage of CO₂: structural trapping (stratigraphic trapping), capillary trapping (residual trapping), solubility trapping, and mineral trapping. Structural trapping is where the buoyant CO₂ plume becomes immobilized underneath an impermeable cap rock, essentially stopping the upward migration of the CO₂ plume from reaching the surface [Benson and Cole, 2008]. Capillary trapping is the mechanism that traps ganglia (tiny droplets of CO₂) within the pores of the rock. This happens primarily after injection stops at which point water begins to imbibe back into the CO₂ plume, immobilizing a fraction of the trailing end of the CO₂ plume [Andrew et al., 2014; Benson and Cole, 2008; Herring et al., 2013; Iglaier et al., 2011; Krevor et al., 2015; Pentland et al., 2011; Tanino and Blunt, 2012; Wildenschild et al., 2011]. Capillary trapping is considered as the most promising option for carbon sequestration [Krevor et al., 2015]. Modeling efforts that take into account the known properties of reservoirs in the USA [Halland et al., 2011; Juanes et al., 2010] and in the North Sea [Gammer et al., 2011] estimate that between 65% and 95% of the capacity for CO₂ storage is in the form of capillary trapping of the

CO₂. Indeed methods that enhance the degree of capillary trapping are being developed which coinject CO₂ and brine, or inject chase brine after the CO₂ injection [Juanes *et al.*, 2010]. The injected water helps move the CO₂ through the entire formation and traps the CO₂ in the pore ganglia. Solubility trapping is the dissolution of the trapped CO₂ into the surrounding brine, a process that takes considerable time but lessens the amount of CO₂ that could migrate upward due to buoyant forces [Benson and Cole, 2008; Neufeld *et al.*, 2010]. Lastly, mineral trapping happens when the dissolved CO₂ reacts with the minerals in the rock creating solid carbonate minerals that precipitate into the pores. This process has the longest time scale of all the trapping mechanisms [Benson and Cole, 2008].

Dissolution trapping and mineral trapping occur on long time scales and are dependent on the security and the amount of CO₂ trapped during the capillary trapping stage, it is therefore important to understand this mechanism and determine the residual saturation of CO₂ trapped within the pores in order to optimize CO₂ injection and trapping security. CO₂ becomes trapped when the capillary forces are greater than the pressure gradient and buoyant forces. This occurs at low capillary numbers (Ca), where the capillary number is a dimensionless quantity that describes the ratio of viscous forces to the surface tension between the two fluids. It is defined as $Ca = \mu V / \gamma$, where μ is the dynamic viscosity, V is the pore velocity, and γ is the surface tension. In the case where CO₂ is the nonwetting (NW) phase in a deep sandstone saline aquifer, CO₂ ganglia are produced via snap-off at which point it becomes residually trapped [Deng *et al.*, 2014]. Snap-off is an important phenomena in geologic sequestration because it prevents the separated CO₂ ganglia from continuing to migrate upward with the rest of the plume, reducing the risk of leakage. NW fluids minimize their contact area with the solid and hence prefer larger pores leading to snap-off conditions in the larger pores. Snap-off occurs in the pore throats, a constriction in the pathway between larger pore bodies. Essentially, when the capillary pressure in the pore throat is greater than the capillary pressure across the NW phase front in the pore body, snap-off occurs and the NW phase becomes trapped within the pore body [Deng *et al.*, 2014; Roof, 1970; Rossen, 2000]. This process occurs naturally via the slow flow of brine through the storage rock, but may also be elicited intentionally by the use of chase water [Krevor *et al.*, 2015].

The bulk description of capillary trapping (at the macroscopic scale) is done in terms of the fractional saturation of the pore volume by the NW phase. One approach is to compare the residual saturation (S_R) with the initial saturation prior to imbibition (S_i) to determine the trapping efficiency, S_R/S_i [Andrew *et al.*, 2014; Herring *et al.*, 2013]. While this is a commonly quoted metric, it neglects the dependence of the residual saturation on the specific initial saturation state, and the more general trapping behavior for a given rock is described by an initial-residual (IR) constitutive relationship. The Land model [Land, 1968] is a simple, one-parameter empirical equation that has been shown to have broad application for describing trapping in rocks

$$S_R = \frac{S_i}{1 + CS_i} \quad (1)$$

The essential characteristic is that the amount of trapped NW phase is a monotonically increasing function with decreasing marginal saturation. Certain sandstones with mixed wettability characteristics [Krevor *et al.*, 2015] and unconsolidated media with analogue oil-water system. Pentland *et al.* [2010] show nonmonotonic or discontinuous saturation behavior, but in general, water-wet Berea cores are well described by the Land model under a wide range of conditions [Krevor *et al.*, 2015; Niu *et al.*, 2015]. The IR characteristics are specific to the rock and are reflected in the Land constant, C , where $C = 0$ represents perfect trapping of all initial NW phase ($S_R = S_i$) and increasing C represents less and less efficient trapping at higher initial saturations.

Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) are noninvasive techniques that can monitor the protons in the water trapped within porous media. The amount of water, spatial distribution of the water, and the local environment (pore size) of the water are all accessible with NMR measurements. Previous work has used MRI to look at rate of displacement of the front associated with supercritical CO₂ displacement processes in a model glass bead pack [Liu *et al.*, 2011]. An earlier study looked at the transport properties of atmospheric carbonated brine as it flowed through a sandstone rock core [Hussain *et al.*, 2011]. This study extends these applications by looking at the water when supercritical CO₂ is flowing in a water saturated sandstone rock core. In this study, nuclear magnetic resonance (NMR) techniques are used to noninvasively monitor the drainage/imbibition of air, CO₂, and scCO₂ with DI H₂O in a Berea

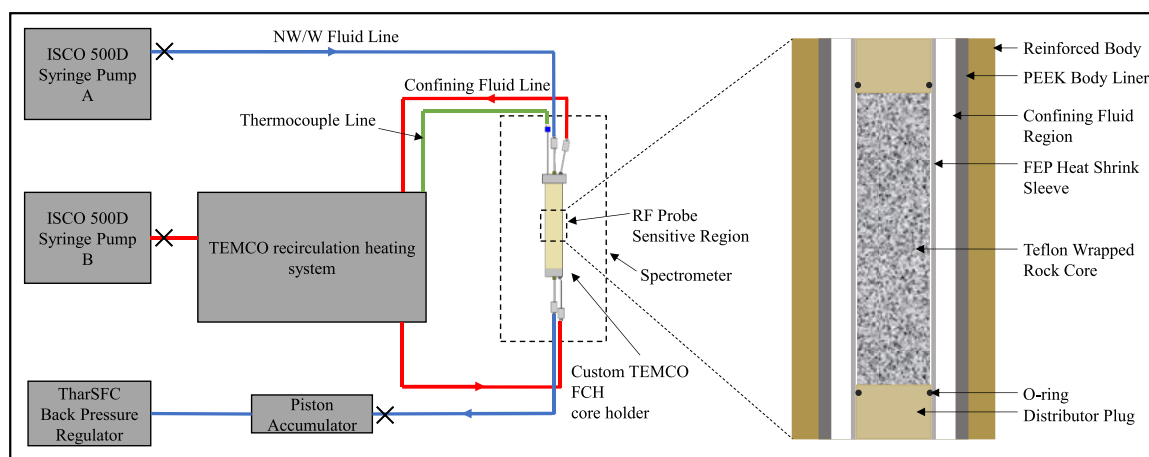


Figure 1. Schematic of the experimental setup with expanded view of a cross section of the core holder. Pump A controls the flow and pressure through the rock core while pump B maintains the confining pressure. The confining pressure is maintained at 9308 kPa (1724 kPa higher than the interior pressure in the rock core). Operating interior pressure was 7584 kPa. Heating was provided by the TEMCO recirculation heating system which allowed supercritical conditions to be reached, 35°C.

sandstone rock core under conditions representative of a deep underground saline aquifer. Understanding how the thermophysical properties of scCO_2 alter capillary trapping relative to air provides information to extend the use of data on air to model scCO_2 capillary trapping. This study will compare the capillary trapping of air with that of supercritical CO_2 , as well as subcritical CO_2 to supercritical CO_2 by measuring the distribution of the wetting (W) fluid in the pores via NMR imaging and relaxometry. The drainage/imbibition saturation through the pore structure is quantified as is the pore size distribution of the capillary trapping pores.

2. Experimental Methods

2.1. Experimental Setup

All experiments were performed using a Bruker AVANCE 300 MHz spectrometer with a 60 mm diameter Super-Wide Bore (SWB) radio frequency (RF) probe. The flow loop is shown in Figure 1. A custom TEMCO FCH core holder designed for high-field NMR housed the rock core and allowed flow through of the high-pressure fluids. The Viton sleeve that is provided with the core holder from TEMCO was not used for these studies. Instead, a Teflon taped rock core and a heat shrink sleeve separated the rock core from the confining liquid. There are two regions within the core holder, separated by an FEP heat shrink sleeve. The outer region contains the confining fluid, Fluorinert (Sigma-Aldrich), and the inner region contains the rock core and drainage/imbibition fluids. The confining fluid is maintained at a higher pressure than the drainage/imbibition fluids to securely pressurize the FEP sleeve around the Teflon wrapped rock core, restricting the drainage/imbibition fluids from flowing around the outside of the core. A partial cross section is shown in Figure 1. Two ISCO 500D syringe pumps were used to provide the desired pressures and flow rates. One pump maintained pressure, preheating, and flow of the saturation/imbibition fluids through the rock core while the other pump provided the pressure for the confining fluid. A TEMCO recirculation heating system provided the necessary circulation and heat for the confining fluid, this fluid maintained the temperature of the drainage/imbibition fluid going through the rock core, which was monitored via a thermocouple. This ensured supercritical temperatures for the entirety of the flow system when required. A piston accumulator attached to a back pressure regulator (TharSFC) allowed fluid to accumulate while maintaining the system at a constant pressure.

The rock cores used were a Berea sandstone with dimensions of roughly 26 mm in diameter and 97 mm long. They were both cored from a larger block of sandstone and thus are expected to have similar properties. The Berea sandstone was of the Dunham classification quartz arenite, of porosity 15% as determined by mercury porosimetry and permeability 150 mD. Before heat shrinking, the FEP sleeves around the rock core several layers of Teflon tape were wrapped around the rock core to help seal the rough rock exterior against the FEP helping to prevent flow around the core.

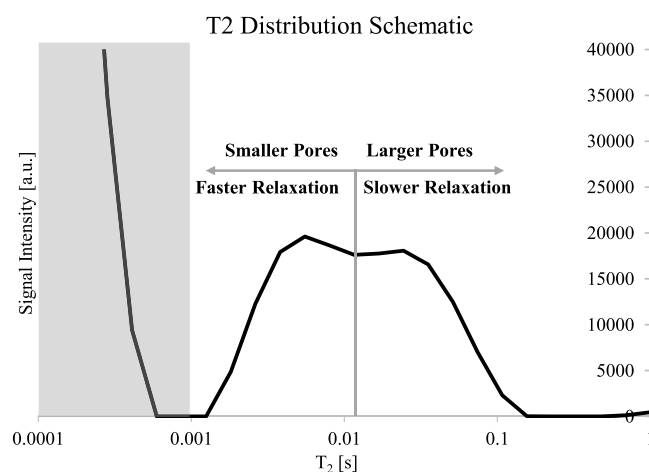


Figure 2. Illustration for defining larger and smaller pores associated with transverse relaxation times. The signal under the shaded region indicates signal that is decaying too fast to be resolved.

The FID sequence applies a single NMR RF pulse to excite the protons in the liquid H_2O in the sample and the free induction decay that is acquired immediately afterward can be directly correlated to the total water content of the rock sample [Callaghan, 1991].

The CPMG sequence consists of a 90° RF pulse followed by sequential 180° pulses that induce a train of spin echoes. These spin echoes create an exponential decay envelope which is determined by the transverse spin-spin T_2 relaxation [Callaghan, 1991]. For samples where multiple T_2 s are present, such as in porous media with different pore sizes, a multiexponential decay envelope is obtained. An inverse Laplace transform (ILT) algorithm is then used to obtain the distribution of T_2 values from within the sample [Hurlimann et al., 2003; Stingaciu et al., 2010; Washburn and Callaghan, 2006]. T_2 values can be correlated to pore sizes within the rock core [Hurlimann et al., 2003; Kleinberg, 1996; Mitchell et al., 2010; Song et al., 2008; Washburn and Callaghan, 2006]. The increased interactions of nuclei in small pores as well as surface relaxation effects contribute to the decrease of T_2 as pore sizes become smaller. Therefore, larger T_2 values (slower relaxation) can be attributed to larger pores and smaller T_2 values (faster relaxation) can be attributed to smaller pores, shown schematically in Figure 2. In order to be sensitive to the short T_2 s in the rock core, RF pulse durations shorter than the smallest relaxation times are required, and typically NMR can measure pore sizes in the range 0.2–100 μm . The lower limit is determined by the minimum echo time that is achievable with the NMR hardware and the upper limit is determined by the T_1 relaxation of the saturating fluid. In the 60 mm coil required in this work, 90 μs RF pulse was applied at max power (300 W) with 500 echoes covering the short T_2 decay with an echo spacing time τ of 140 μs for a total echo time of 70 ms. The range

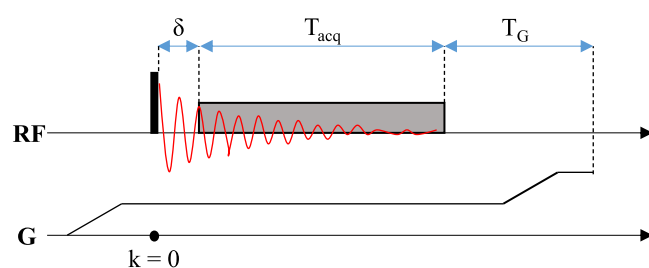


Figure 3. Three-dimensional ZTE pulse sequence used in experiments. A hard RF pulse is applied with a small tip angle after the gradient has been ramped up. The gradient represents all three directions and is changed before each RF pulse, thus it is a radial center-out acquisition with $k = 0$ at the middle of the RF pulse. Due to hardware limits, there is a delay, δ , for the coil to switch from transmit to receive mode before signal acquisition can begin. Consequently, there will be some missing k -space points at k -space center. The repetition time $TR = T_{RF} + \delta + T_{acq} + T_G$, the RF pulse time, the transmit/receive delay, the acquisition time, and the gradient ramp time.

2.2. Nuclear Magnetic Resonance

Three NMR pulse sequences were used to measure the saturation of the rock core: single-pulse free induction decay (FID), zero echo time 1-D imaging (ZTE), and Carr-Purcell-Meiboom-Gill (CPMG) 1-D T_2 relaxation [Callaghan, 1991; Garwood, 2013; Weiger et al., 2011, 2012]. The NMR signal is detected for the 1H protons so is not sensitive to CO_2 , air, fluorine, or any solid parts of the sample. The NMR measurements allow deduction of the trapping of the NW fluid through observations of the wetting (W) H_2O liquid, complementary to recent X-ray μCT [Andrew et al., 2014; Herring et al., 2013; Iglaue et al., 2011; Tanino and Blunt, 2012; Wildenschild et al., 2011; Zuo and Benson, 2014].

of T_2 values accessible by the current high-field NMR spectrometer, which is between 1 ms and 1 s, is illustrated in Figure 2.

The ZTE imaging sequence [Garwood, 2013; Weiger et al., 2011, 2012], depicted in Figure 3, has been specifically designed to allow the imaging of fast relaxing NMR signals of short T_2 values. This is achieved by switching on a readout gradient before any RF pulse excitation. A range of gradient values is ramped through, allowing acquisition of k -space data [Callaghan, 1991] in a 3-D radial center-out trajectory. By switching the gradient on before excitation, the dead time between acquisition

and RF excitation is minimized, limited only by the hardware dead time to switch between transmit and receive, denoted by δ . Therefore, more of the FID can be obtained at the cost of losing some initial k-space points due to the delay δ . The missing k-space points and Fourier transformed image reconstruction are dealt with through the use of an algebraic reconstruction and 3-D gridding algorithm [Kuethe et al., 1999; Weiger et al., 2011]. The sequence also utilizes short tip angle RF pulses to capture the fast decay.

Fourier transform of the full 3-D set of k-space data produces the 3-D image of the water in the sample, where intensity is proportional to the water saturation (W phase) in each volume element of the image. Image resolution is determined by bandwidth of the data acquisition in combination with the strength and duration of the applied gradient [Callaghan, 1991]. Increasing the bandwidth of the data acquisition will ensure faster sampling but also leads to more missing k-space points because faster sampling places more points within the dead time δ , where they are not acquired. Therefore, there is a trade-off between decreasing bandwidth which decreases resolution and missing k-space points which lead to poor image quality. It was found that any more than two missing k-space points leads to poor image quality and thus a maximum bandwidth of 200 kHz was used. An RF tip angle of 6.4° at maximum power yields a pulse time of $6.4 \mu\text{s}$. A repetition time (TR) of 3.84 ms was used and is greater than the needed TR, calculated from the Ernst angle equation [Callaghan, 1991; Weiger et al., 2011], thus giving adequate time for the longitudinal magnetization to recover. A FOV of $60 \text{ mm} \times 90 \text{ mm} \times 60 \text{ mm}$ with 64^3 pixels is adequate to image the rock core without creating any signal wrap-around artifacts. The spatial resolution these parameters set is $0.938 \text{ mm/pixel} \times 1.41 \text{ mm/pixel} \times 0.938 \text{ mm/pixel}$. This specified resolution can be less than the actual resolution due to susceptibility broadening from the short T_2 relaxation in the rock, however, imaging phantoms of varying size with equivalent T_2 s allowed an estimation of the actual resolution which was indeed similar to the specified resolution. The total scan time was $\sim 58 \text{ s}$ providing images of the real time process averaged over that time scale.

The mean fractional CO_2 (NW phase) saturation in a volume of interest is determined from the integrated MRI image intensity in that volume (I_V) and the image intensity in the region at 100% water saturation ($I_{V\text{sat}}$)

$$S_{\text{CO}_2} = \left(1 - \frac{I_V}{I_{V\text{sat}}} \right) \quad (2)$$

When evaluated postdraining by the CO_2 and postimbibition by the water, S_{CO_2} becomes the “initial” and “residual” fractions, S_I and S_R , respectively.

2.3. Experimental Process

Three separate drainage and imbibition experiments were performed on two different rock cores. Each experiment used either air, CO_2 , or scCO_2 as the nonwetting (NW) fluid and DI H_2O , doped with 0.4%-vol Magnevist (Gd^{3+} -DTPA) to enhance the signal, as the wetting (W) fluid. To keep experimental setup simple, the water was not presaturated with CO_2 . The density difference between water and water saturated with CO_2 has been previously presented in the literature to be less than 1% at the pressure and temperatures used [Hebach et al., 2004]. Additionally, the 0.5–1% error in the final trapping efficiencies will be similar for all imbibing fluids. The drainage and imbibition experiment was then repeated for each rock core for each NW fluid, yielding a total of six experiments for each rock core. This series of experiments allowed verification of the results for each rock core and demonstration of variations/similarities between rock cores. The results for each rock core are expected to be similar because the two cores were taken from the same block of well-characterized Berea sandstone which is known to be homogenous.

The protocol is the same for every experiment except for the specific NW fluid. Every experiment was conducted at 7584 kPa and 21°C for air/ CO_2 or 35°C in order for CO_2 to reach a supercritical state, scCO_2 . The experimental steps were as follows:

1. The core is wrapped with Teflon tape, heat shrunk in the FEP sleeve, and placed into the core holder which is then placed into the probe in the spectrometer and fluid lines attached. A ZTE image is taken with the core completely dry to obtain a background image of the probe and core holder material that is later used for background subtraction, since short T_2 protons in the probe and core are excited.
2. DI H_2O doped with Magnevist is pumped in saturating the core. It is then slowly pressurized to the desired 7584 kPa. Both the confining fluid pressure and the drainage/imbibition fluid pressures are ramped up simultaneously whilst maintaining the confining fluid pressure 1724 kPa above the drainage/imbibition

fluid pressure at all times. The saturation is monitored using the FID NMR sequence. Once the FID signal has stabilized, maximum saturation has occurred and a ZTE image and 1-D T_2 measurement are taken to define the full saturation state which can vary as indicated by the signal intensity of the red (solid) line in Figures 3 and 6.

3. Once pressure has equilibrated at 7584 kPa, pump A is isolated and the fluid is switched to the desired NW fluid (air, CO_2 , or scCO_2 for which the heating recirculation system is also turned on) and pumped into the core, simulating drainage, at 0.5 mL/min corresponding to very low Ca numbers ($\approx 2.72 \times 10^{-8}$ (air), 2.39×10^{-7} (CO_2), or 8.09×10^{-8} (scCO_2)). It is pumped in for ~ 15 min until the FID signal has reached a stable regime. Several ZTE images and 1-D T_2 s are obtained during the drainage process with the final one taken at maximum drainage when the FID signal stabilizes.
4. Pump A is isolated again and the fluid is switched to DI H_2O doped with Magnevist for the imbibition phase. The water is pumped in at 0.5 mL/min corresponding to low Ca numbers ($\approx 1.38 \times 10^{-6}$ (air), 3.21×10^{-6} (CO_2), or 3.50×10^{-6} (scCO_2)). The three Ca numbers are different from that for drainage because the invading fluid is now water and the dynamic viscosity of water is used instead of that of the NW. It is pumped in for ~ 10 min until the FID signal has stabilized. For both drainage and imbibition, the NMR signal was monitored and the process was stopped once the signal stabilized, therefore indicating that there was no more accumulation or removal of water occurring. For drainage, this corresponded to a flow of 0.5 mL/min for 15 min and a cumulative flow of 7.5 mL, which is equivalent to one pore volume for the 15% porosity rock. For imbibition, the total cumulative pore volume of flow was 5 mL, or 0.65 total pore volume. This amount of W fluid is slightly less than one pore volume, but despite the relatively small amount of fluid, imbibition with less than one pore volume is a common observation in Berea cores [Akbarabadi and Piri, 2013; Lu et al., 2013; Niu et al., 2015; Shell/Scottish Power CCS Consortium, 2011; Shi et al., 2011a, 2011b]. A ZTE image and 1-D T_2 are then taken after stabilization to measure the final imbibition saturation.
5. The core is then removed, oven dried, and placed in a vacuum in order to ensure all water and NW phase have been removed to ensure the initial conditions of the rock core are the same for every experiment.

3. Results and Discussion

3.1. ZTE Imaging

The ZTE image data were acquired at full saturation, several during the drainage process, and one at the end of the imbibition process. The three most important images, for calculating the fraction of residually trapped NW fluid and capillary trapping efficiency, are the full saturation image, the last drainage image, and the final imbibition image. Although 3-D ZTE images were obtained, it proved most useful for analysis to collapse the data into a 1-D profile along the length of the core. These profiles are shown in Figure 4 for air, CO_2 , and scCO_2 as the NW phase, respectively. These figures represent the most recent experiments on rock core #2. These data are representative of the other nine experiments. The profiles for the other nine experiments are not shown; however, the data analysis from all 12 experiments is compiled in Tables 1 and 2.

In each figure, the red (solid) line indicates the maximum initial saturation with the W fluid, the blue (dotted) lines indicate the saturation changes during NW fluid-induced drainage with chronological order in the direction of decreasing signal and the green (dashed) line indicates the maximum saturation reached after imbibition of the W fluid postdrainage. All lines represent the signal associated with the wetting phase saturation so in order to obtain the NW phase saturation fraction the data are normalized to the initial saturation and the fractional difference in the final saturation level determines the NW phase within the pores. This analysis assumes that all the pores are initially full of the W phase and will actually be an undetermined fraction that are never imbibed with the W fluid (H_2O), a fraction of pores that remain gas filled and inaccessible to the wetting fluid. As these pores will not be accessible to the water and not participate in the draining and imbibing process, we normalize the results to define all subsequent saturations as a percentage of the initial saturation. Air displacement from the rock core during the saturation process is significant. Furthermore, any gas remaining in the rock in the fully saturated state will be compressed significantly as the pressure rises from 100 to 7500 kPa, and unable therefore to occupy more than 1% of its original volume. Air dissolution into the imbibing fluid at this pressure would further reduce the possibility of influence from any trapped air.

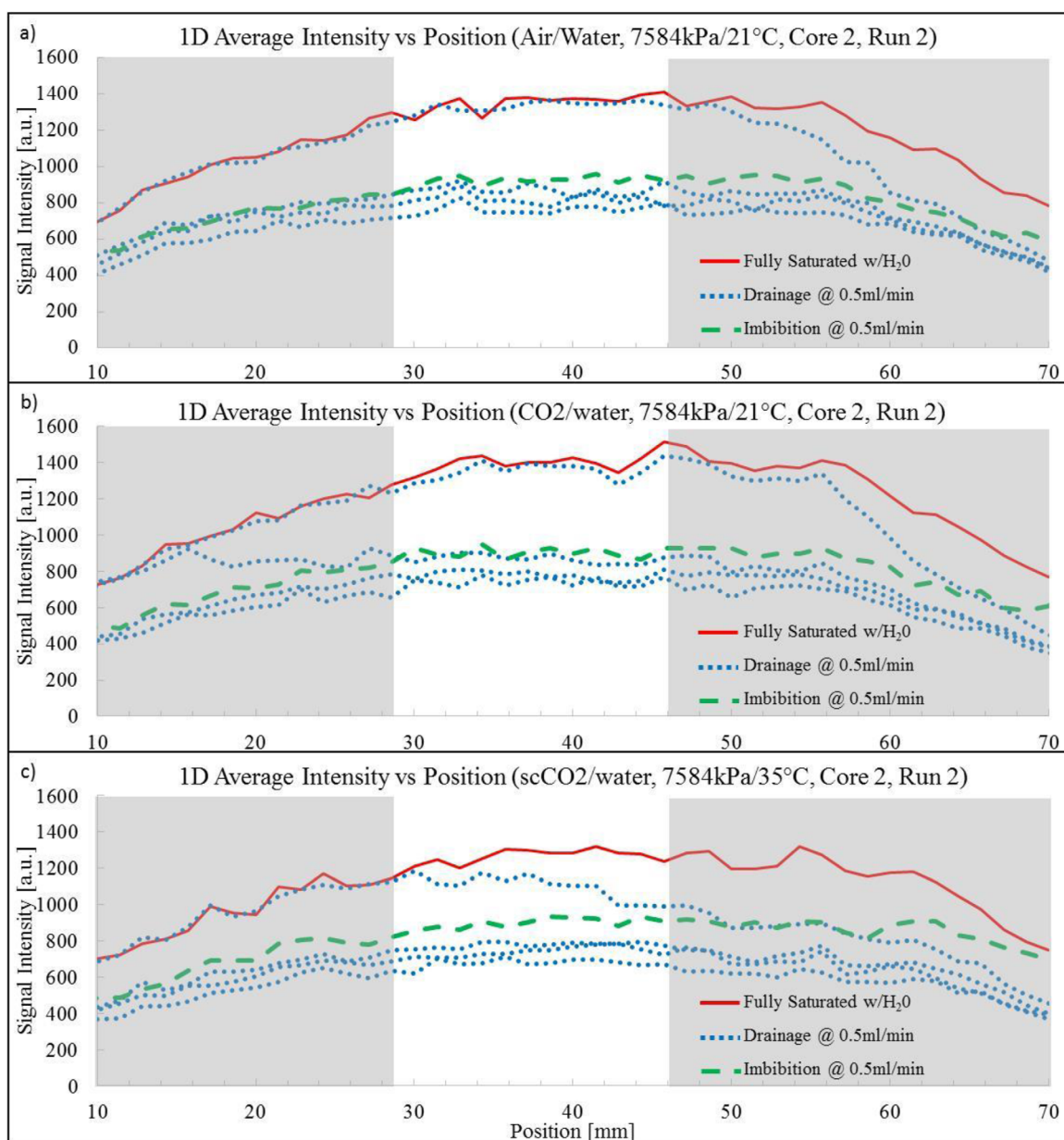


Figure 4. One-dimensional profiles for drainage/imbibition for (a) air/H₂O, (b) gas phase CO₂/H₂O, and (c) supercritical CO₂/H₂O indicating wetting phase along the length of the rock core after saturation (red-solid), during drainage process with NW fluid (blue-dotted), and after imbibition of W fluid H₂O (green-dashed). The residually trapped NW phase within the pores can be found by taking the difference between the red (solid) and green (dashed) lines. The data for the entire 90 mm length of the coil are shown consistent with the hardware specification. Roll-off in the data intensity in the shaded areas is due to power variation of the RF pulse at the coil ends.

Table 1. NW Phase Fraction in Berea Rock Core #1

Scan	Normalized Average 1-D Intensity From 28 to 54 mm (Indicating NW Phase Fraction)					
	Air		CO ₂		scCO ₂	
Fully saturated	0	0	0	0	0	0
Drainage-1	0.00	0.01	0.02	0.02	0.40	0.30
Drainage-2	0.30	0.22	0.36	0.43	0.44	0.40
Drainage-3	0.35		0.47	0.48	0.49	0.43
Drainage-4 (S_R)	0.41	0.42	0.51	0.51	0.51	0.47
Imbibition final (S_R)	0.28	0.32	0.36	0.37	0.27	0.30
Trapping efficiency (S_R/S_i)	0.68	0.76	0.71	0.73	0.53	0.64

Table 2. NW Phase Fraction in Berea Rock Core #2

Scan	Normalized Average 1-D Intensity From 28 to 54 mm (Indicating NW Phase Fraction)					
	Air		CO ₂		scCO ₂	
Fully saturated	0	0	0	0	0	0
Drainage-1	0.10	0.03	0.01	0.04	0.19	0.18
Drainage-2	0.35	0.36	0.34	0.39	0.42	0.40
Drainage-3	0.38	0.40	0.41	0.44	0.44	0.42
Drainage-4 (S_i)	0.40	0.44	0.47	0.48	0.49	0.48
Imbibition final (S_R)	0.30	0.32	0.33	0.35	0.29	0.29
Trapping efficiency (S_R/S_i)	0.75	0.73	0.70	0.73	0.59	0.60

Examining each of the 1-D profiles for air, CO₂, and scCO₂, it is clear that they have similar spatial profiles and intensities. Roll-off in the data intensity at the ends of the observation window, the shaded gray areas, is due to nonuniformity of the RF coil pulse power at the ends. The NW phase fractions are calculated based on the signal only in the most linear region of the profiles, from 28 to 54 mm, the ~30 mm unshaded area where the RF power is uniform. The NW phase fraction data (S) for each 1-D profile are given in Tables 1 and 2, and are calculated using the average MRI signal intensity in the region of interest (I_V) according to equation (2) for the associated fully saturated, drainage, or imbibition profiles. The trapping efficiency is calculated as S_R/S_i where S_i is the final drainage NW phase fraction, thus giving an indication as to the amount of NW phase that has remained trapped in the core after imbibition. The average NW saturation and trapping efficiency values for all four runs for each NW fluid (air, CO₂, and scCO₂) are shown in Table 3. It should be noted that at the experimental conditions of 7564 kPa and 20°C, there will be some CO₂ dissolution into the water, ~0.03 mol fraction CO₂ into the water phase [Spycher *et al.*, 2003]. This mass transfer has the potential to slightly increase both the S_i and S_R values listed in Table 3 for scCO₂ but have little impact of the calculation of the trapping efficiency. Preequilibration of the water with CO₂ would eliminate this error source.

The data in Table 3 indicate that both CO₂ and scCO₂ drain the core to a higher NW phase saturation than air in the same period of time, as indicated in the drainage-4 line. After imbibition, CO₂ is observed to fill the greatest percentage of the rock core with NW phase, as determined from analysis of the imbibition final line. The CO₂ and air have similar trapping efficiencies but differ in both the amount of NW phase drained and the residual amount of NW phase trapped. The scCO₂ has similarities to air in the amount of residual NW phase trapped and similarities to CO₂ in the maximum amount of NW phase drained but it has significantly lower trapping efficiency when compared to both air and CO₂. The scCO₂ trapping efficiency is found to be ~10% less than the values reported in Andrew *et al.* [2014] for similar sandstones of Bentheimer and Doddington. However, the trapping efficiency for air and CO₂ are on par with their reported results [Andrew *et al.*, 2014]. This decrease in the quantity of capillary trapping for scCO₂ is more in agreement with the results obtained in Iglauer *et al.* [2011] and Pentland *et al.* [2011], where scCO₂ has a lower residual saturation than for an analogue strongly water-wet system, octane-brine. They are also in agreement with the lower end of the range of values found by Manceau *et al.* [2015] for a Triassic sandstone.

While the trapping efficiency does provide some indication of the amount of NW phase that can be residually trapped, it is a function not only of the rock-fluid system, but also on the initial NW saturation, which may itself depend on the type of NW fluid. By plotting the residual versus initial NW phase saturation values

Table 3. Summary of NW Phase Fractions^a

Scan	Average Values for All Four Runs of Air, CO ₂ , and scCO ₂ With Standard Deviation (Indicating NW Phase Fraction)		
	Air	CO ₂	scCO ₂
Drainage-4 (S_i)	0.42 ± 0.02	0.49 ± 0.02	0.49 ± 0.02
Imbibition final (S_R)	0.31 ± 0.02	0.35 ± 0.02	0.29 ± 0.01
Trapping efficiency (S_R/S_i)	0.73 ± 0.04	0.72 ± 0.02	0.59 ± 0.05

^aThe three primary conclusions are: CO₂ and scCO₂ drain a higher percentage of the W fluid than air does; CO₂ traps the largest residual amount of the NW phase than air and scCO₂ do; air and CO₂ have similar trapping efficiencies whereas scCO₂ is on the order of 13% less than both air and CO₂.

from Tables 1 and 2, we obtain the IR plot of Figure 5, which also includes equation (1) plotted with average Land constant C for all three NW fluids. While certainty in the general trends is limited because the initial saturation was not expressly varied, this is the best means to make a simple comparison of air, CO₂, and scCO₂, which exhibit significantly different initial saturations. Notably, these curves suggest that air and CO₂ exhibit similar IR characteristics ($C \sim 0.81 - 0.89$)

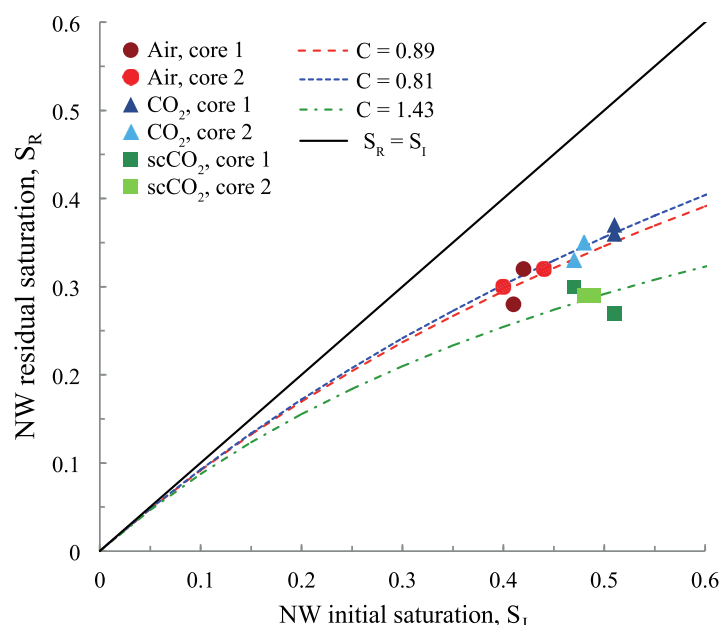


Figure 5. Initial/residual plot for all rock cores and NW fluids. Symbol size is representative of experimental standard deviation. Solid black line indicates the maximum possible residual saturation, while dashed lines represent equation (1) with average Land constant C for each NW fluid.

while the scCO_2 data on average lie near a curve with a higher constant ($C = 1.43$). All of these values are consistent with results from a meta-analysis of a large number of CO_2 trapping experiments in Berea sandstone where C ranged from 0.7 to 2.0 [Krevor *et al.*, 2015]. The variation is generally seen to be due to differences in the pore structure. In the context of this experiment, where repeated measurements were made on the same cores, it suggests a less efficient trapping mechanism for scCO_2 than for the other NW fluids. The lower S_R for scCO_2 as compared to CO_2 has been observed before, and is also attributed to a difference in the wetting state of the two fluids with water [Akbarabadi and Piri, 2013].

Comparing CO_2 and air, the difference in saturation values, where CO_2 has a higher initial and residual NW phase saturation, can be explained by the difference in surface tension. The surface tension between CO_2 and water is nearly half that between air and water [Bachu and Bennion, 2009]. Where the capillary entrance pressure of a pore in the rock is defined as $P_{cap} = 2\gamma \cos \theta / r$ where γ is the interfacial tension, θ is the wetting angle, and r is the pore radius, a lower surface tension will lead to lower overall capillary entrance pressures within the pores of the rock [Blunt and Scher, 1995; Pentland *et al.*, 2011]. With a lower capillary entrance pressure than that for the air/water system but with the same flow rate, the viscous forces are stronger in comparison to the capillary forces, and CO_2 invades more pores leading to higher initial NW phase saturation.

The curve describing the scCO_2 data appears to have Land constant C greater than that for air and CO_2 . The initial NW phase saturation is similar to CO_2 , due to the similar surface tension values [Bachu and Bennion, 2009]. As the contact angle increases, snap-off is less favored and gives way to a more piston-like advance. With the suppression of snap-off, there is decrease in residual saturation [Blunt and Scher, 1995; Iglaier *et al.*, 2011; Pentland *et al.*, 2011]. Therefore, this supports that scCO_2 /water is slightly less strongly water-wet, leading to larger contact angles, a decrease in snap-off, and therefore a lower residual saturation.

3.2. T_2 Distributions

Distributions of T_2 relaxation times were obtained by Laplace transformations of the 1-D CPMG T_2 data in MATLAB. The results from the three most recent experiments of air, CO_2 , and scCO_2 on rock core #2 are shown in Figure 6, and are representative of the results observed in rock core #1. Although it is well known that high-field NMR can introduce artifacts in T_2 distributions due to susceptibility [Mitchell *et al.*, 2010], the results presented here provide evidence that such measurements can provide insight into the pores that participate in capillary trapping. Future experiments will be conducted in a new low field spectrometer which will provide more accurate insight into pore saturation distributions.

In all the T_2 distributions for the 12 samples, there appear to be two main distributions, which can be loosely associated with the larger or the smaller pore sizes [Jorand *et al.*, 2011; Liaw *et al.*, 1996; Tanino and Blunt, 2012]. The lack of any signal with a T_2 larger than 200 ms is confirmation that the largest pores are about 100 μm and that there are no large cracks or vugs present. Some of the water is in small pores less than 3 μm with relaxation times less than 1 ms; below that which is accessible with the current instrument [Song, 2003]. T_2 values less than 1 ms cannot be resolved because the minimum CPMG echo time is limited

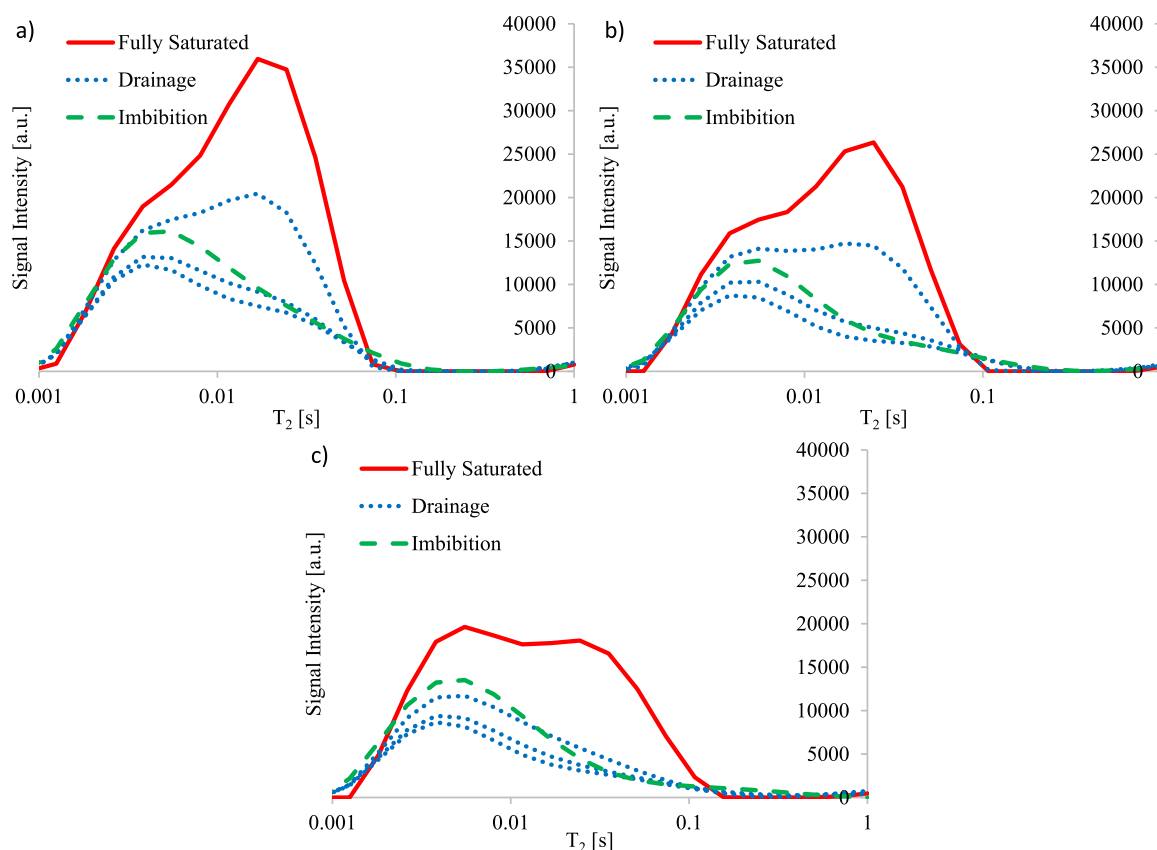


Figure 6. Evolution of T_2 distributions for drainage/imbibition for (a) air/ H_2O at 7584 kPa and 21°C in core #2 run #2, (b) gas phase CO_2/H_2O at 7584 kPa and 21°C in core #2 run #2, and (c) supercritical CO_2/H_2O at 7584 kPa and 35°C in core #2 run #2.

to $2\tau = 280 \mu s$ in the 60 mm RF coil. These extremely fast relaxing spins are associated with the connate water fraction, as microporosity clay-bound water [Jorand *et al.*, 2011; Tanino and Blunt, 2012]. The low mobility of this water makes an insignificant contribution to the acquired signal and participates minimally in the macroscale drainage and imbibition process. Similarly, the other NMR techniques are insensitive to this connate water fraction, and it is excluded from all determinations of initial/residual saturation.

All the T_2 distributions exhibit a similar bimodal trend, although it is clear that susceptibility artifacts from slight variations in the rock core loading each time, produce some variability on the features in the initial T_2 distribution. As discussed above, all values range between 1 and 100 ms with intensities that are bimodal with two populations centered on 5 and 25 ms, respectively. Pore sizes in a Berea sandstone can be easily characterized by NMR and range from 1 to 100 μm [Mitchell *et al.*, 2010; Song, 2003]. Therefore, in Figure 6, the left population can be associated with the mesoporosity, pore sizes between 3 and 10 μm , and the right population can be associated with the macroporosity, pore sizes between 10 and 100 μm . However, the T_2 measurements are not a direct correlation to pore size. Rather than indicating that a higher percentage of smaller pores are filled than were originally, we believe the shift to lower T_2 times after imbibition is due primarily to the effect of gas/water interfaces and the susceptibility that this induces in the sample. Future work will focus on determining how much quantitative information can be pulled out from the T_2 distributions. Operating at a lower magnetic field will reduce susceptibility effects and may be necessary for the T_2 distributions to be quantitatively interpreted.

As described above, the microporosity, with pore sizes less than 3 μm are not accessible with the Super-Wide Bore NMR hardware required to obtain supercritical sample conditions with the rock core sample system. The conclusion that can be drawn from these distributions is that during imbibition it appears only the mesoporosity is filling with water whereas the macroporosity remains the same. This can be concluded as there is no change from the final drainage line (blue, dotted) to the imbibition line (green, dashed) within the macroporosity region whereas there is an increase in saturation in the mesoporosity. It can therefore be

concluded that the NW phase is preferentially trapped in the larger pores. This is consistent with the fact that NW fluids minimize their contact area with the solid and that the pore-throat aspect ratio, i.e., the ratio of the pore body radius to the throat radius, is greater in the macroporosity giving rise to more favorable snap-off conditions [Al-Raoush and Willson, 2005; Herring et al., 2013; Iglaue et al., 2011; Wardlaw and Li, 1988].

4. Conclusions

This work demonstrates the usefulness of NMR in measuring the residually trapped NW phase as well as providing insight into the pores in which the NW phase is preferentially trapped. The results provide a comparison between the different NW phases used as well as characterizing the capillary trapping of each NW phase. Several conclusions are apparent when comparing each NW phase:

1. scCO_2 and CO_2 drain the core to a higher NW phase fraction than air. This is in part due to the higher interfacial tension of these fluids compared to air.
2. CO_2 traps the largest residual amount of NW phase.
3. scCO_2 traps the lowest residual amount of NW phase and has a trapping efficiency about 13% less than CO_2 and air.
4. Air and CO_2 follow a linear trend where a higher initial NW phase saturation leads to a higher residual NW phase saturation with a trapping efficiency of around 72%.

Since scCO_2 has a lower residual NW phase saturation than air and CO_2 , it can be concluded that scCO_2 /water is not as strongly water-wet. This is consistent with scCO_2 /water having larger contact angles which lead to a suppression of snap-off and therefore a lower residual NW phase saturation [Blunt and Scher, 1995; Iglaue et al., 2011; Pentland et al., 2011]. The data indicate that CO_2 in its supercritical state leads to a reduction in capillary trapping relative to gas phase CO_2 or air so using air as a proxy for scCO_2 sets an upper bound for capillary trapping of scCO_2 .

Lastly, the T_2 relaxation distribution data show that the NW phase, regardless of whether air, CO_2 , or scCO_2 , is preferentially trapped in the larger pores. This result is supported by the findings of Al-Raoush and Willson [2005] and Wardlaw and Li [1988] indicating that snap-off conditions are more favorable in the rock macroporosity, due to the larger pore aspect ratio limiting piston-like flow.

Acknowledgments

The data for this paper are available by contacting the corresponding author. The authors would like to thank the members of the Magnetic Resonance Laboratory at Montana State University for assistance and support. S.L.C. acknowledges support by the National Science Foundation under CBET grant 1335534. S.L.C. acknowledges support from the Department of Energy under grant DE-FE000397. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Department of Energy or the National Science Foundation and the M.J. Murdock Charitable trust.

References

- Akbarabadi, M., and M. Piri (2013), Relative permeability hysteresis and capillary trapping characteristics of supercritical CO_2 /brine systems: An experimental study at reservoir conditions, *Adv. Water Resour.*, 52, 190–206, doi:10.1016/j.advwatres.2012.06.014.
- Al-Raoush, R. I., and C. S. Willson (2005), A pore-scale investigation of a multiphase porous media system, *J. Contam. Hydrol.*, 77(1–2), 67–89, doi:10.1016/j.jconhyd.2004.12.001.
- Andrew, M., B. Bijeljic, and M. J. Blunt (2014), Pore-scale imaging of trapped supercritical carbon dioxide in sandstones and carbonates, *Int. J. Greenhouse Gas Control*, 22, 1–14, doi:10.1016/j.jggc.2013.12.018.
- Bachu, S. (2008), CO_2 storage in geological media: Role, means, status and barriers to deployment, *Prog. Energy Combust.*, 34(2), 254–273, doi:10.1016/j.pecs.2007.10.001.
- Bachu, S., and D. B. Bennion (2009), Interfacial tension between CO_2 , freshwater, and brine in the range of pressure from (2 to 27) MPa, temperature from (20 to 125) degrees C, and water salinity from (0 to 334 000) mg/L(–1), *J. Chem. Eng. Data*, 54(3), 765–775, doi:10.1021/je800529x.
- Benson, S. M., and D. R. Cole (2008), CO_2 sequestration in deep sedimentary formations, *Elements*, 4(5), 325–331, doi:10.2113/gselements.4.5.325.
- Blunt, M. J., and H. Scher (1995), Pore-level modeling of wetting, *Phys. Rev. E*, 52(6), 6387–6403, doi:10.1103/PhysRevE.52.6387.
- Callaghan, P. T. (1991), *Principles of Nuclear Magnetic Resonance Microscopy*, vol. XVII, 492 pp., Clarendon, Oxford, U. K., doi:10.1002/ange.19931050256.
- Carles, P. (2010), A brief review of the thermophysical properties of supercritical fluids, *J. Supercritical Fluid*, 53(1–3), 2–11, doi:10.1016/j.supflu.2010.02.017.
- Deng, W., M. B. Cardenas, and P. C. Bennett (2014), Extended roof snap-off for a continuous nonwetting fluid and an example case for supercritical CO_2 , *Adv. Water Resour.*, 64, 34–46, doi:10.1016/j.advwatres.2013.12.001.
- Gammer, D., A. Green, S. Holloway, and G. Smith (2011), The Energy Technologies Institute's UK CO_2 Storage Appraisal Project (UKSAP), in *Offshore Europe Oil & Gas Conference and Exhibition*, SPE 148426, pp. 1045–1058, Curran Assoc. Inc., N. Y.
- Garwood, M. (2013), MRI of fast-relaxing spins, *J. Magn. Reson.*, 229, 49–54, doi:10.1016/j.jmr.2013.01.011.[10.1016/j.jmr.2013.01.011]
- Halland, E. K., I. T. Gjeldvik, W. T. Johansen, C. Magnus, I. M. Meling, S. Pedersen, F. Riis, T. Solbakk, and I. Tappel (2011), *CO2 Storage Atlas Norwegian North Sea*, Norwegian Petroleum Directorate, Stavanger, Norway.
- Hebach, A., A. Oberhof, and N. Dahmen (2004), Density of water + carbon dioxide at elevated pressures: Measurements and correlation, *J. Chem. Eng. Data*, 49(4), 950–953, doi:10.1021/je034260i.
- Herring, A. L., E. J. Harper, L. Andersson, A. Sheppard, B. K. Bay, and D. Wildenschild (2013), Effect of fluid topology on residual nonwetting phase trapping: Implications for geologic CO_2 sequestration, *Adv. Water Resour.*, 62, 47–58, doi:10.1016/j.advwatres.2013.09.015.

- Hurlimann, M. D., M. Flaum, L. Venkataramanan, C. Flaum, R. Freedman, and G. J. Hirasaki (2003), Diffusion-relaxation distribution functions of sedimentary rocks in different saturation states, *Magn. Reson. Imaging*, 21(3–4), 305–310, doi:10.1016/S0730-725X(03)00159-0.
- Hussain, R., T. R. R. Pintelon, J. Mitchell, and M. L. Johns (2011), Using NMR displacement measurements to probe CO₂ entrapment in porous media, *AIChE J.*, 57(7), 1700–1709, doi:10.1002/aic.12401.
- Iglauer, S., A. Paluszny, C. H. Pentland, and M. J. Blunt (2011), Residual CO₂ imaged with X-ray micro-tomography, *Geophys. Res. Lett.*, 38, L21403, doi:10.1029/2011GL049680.
- Jorand, R., A. Fehr, A. Koch, and C. Clauser (2011), Study of the variation of thermal conductivity with water saturation using nuclear magnetic resonance, *J. Geophys. Res.*, 116, B08208, doi:10.1029/2010JB007734.
- Juanes, R., C. MacMinn, and M. Szulczewski (2010), The footprint of the CO₂ plume during carbon dioxide storage in saline aquifers: Storage efficiency for capillary trapping at the basin scale, *Transp. Porous Media*, 82(1), 19–30, doi:10.1007/s11242-009-9420-3.
- Kleinberg, R. L. (1996), Utility of NMR T₂ distributions, connection with capillary pressure, clay effect, and determination of the surface relaxivity parameter rho 2, *Magn. Reson. Imaging*, 14(7–8), 761–767, doi:10.1016/S0730-725X(96)00161-0.
- Klusman, R. W. (2003), Evaluation of leakage potential from a carbon dioxide EOR/sequestration project, *Energy Conversion Manage.*, 44(12), 1921–1940, doi:10.1016/S0196-8904(02)00226-1.
- Krevor, S., M. J. Blunt, S. M. Benson, C. H. Pentland, C. Reynolds, A. Al-Menhali, and B. Niu (2015), Capillary trapping for geologic carbon dioxide storage—From pore scale physics to field scale implications, *Int. J. Greenhouse Gas Control*, 40, 221–237, doi:10.1016/j.ijggc.2015.04.006.
- Kuethe, D. O., A. Caprihan, I. J. Lowe, D. P. Madio, and H. M. Gach (1999), Transforming NMR data despite missing points, *J. Magn. Reson.*, 139(1), 18–25, doi:10.1006/jmre.1999.1767.
- Land, C. S. (1968), Calculation of imbibition relative permeability for two and three-phase flow from rock properties, *Soc. Pet. Eng. J.*, 8(2), 149, doi:10.2118/1942-PA.
- Liaw, H. K., R. Kulkarni, S. H. Chen, and A. T. Watson (1996), Characterization of fluid distributions in porous media by NMR techniques, *AIChE J.*, 42(2), 538–546, doi:10.1002/aic.690420223.
- Liu, Y., Y. Zhao, J. Zhao, and Y. Song (2011), Magnetic resonance imaging on CO₂ miscible and immiscible displacement in oil-saturated glass beads pack, *Magn. Reson. Imaging*, 29(8), 1110–1118, doi:10.1016/j.mri.2011.05.009.
- Lu, J., M. Kordi, S. D. Hovorka, T. A. Meckel, and C. A. Christopher (2013), Reservoir characterization and complications for trapping mechanisms at Cranfield CO₂ injection site, *Int. J. Greenhouse Gas Control*, 18, 361–374, doi:10.1016/j.ijggc.2012.10.007.
- Manceau, J. C., J. Ma, R. Li, P. Audigane, P. X. Jiang, R. N. Xu, J. Tremosa, and C. Lerouge (2015), Two-phase flow properties of a sandstone rock for the CO₂/water system: Core-flooding experiments, and focus on impacts of mineralogical changes, *Water Resour. Res.*, 51, 2885–2900, doi:10.1002/2014WR015725.
- Mitchell, J., T. C. Chandrasekera, and L. F. Gladden (2010), Obtaining true transverse relaxation time distributions in high-field NMR measurements of saturated porous media: Removing the influence of internal gradients, *J. Chem. Phys.*, 132(24), 244705, doi:10.1063/1.3446805.
- Neufeld, J. A., M. A. Hesse, A. Riaz, M. A. Hallworth, H. A. Tchelepi, and H. E. Huppert (2010), Convective dissolution of carbon dioxide in saline aquifers, *Geophys. Res. Lett.*, 37, L22404, doi:10.1029/2010GL044728.
- Niu, B., A. Al-Menhali, and S. C. Krevor (2015), The impact of reservoir conditions on the residual trapping of carbon dioxide in Berea sandstone, *Water Resour. Res.*, 51, 2009–2029, doi:10.1002/2014WR016441.
- Pentland, C. H., E. Itsekiri, S. K. Al Mansoori, S. Iglauer, B. Bijeljic, and M. J. Blunt (2010), Measurement of nonwetting-phase trapping in sand-packs, *SPE J.*, 15(2), 274–281, doi:10.2118/115697-PA.
- Pentland, C. H., R. El-Maghraby, S. Iglauer, and M. J. Blunt (2011), Measurements of the capillary trapping of super-critical carbon dioxide in Berea sandstone, *Geophys. Res. Lett.*, 38, L06401, doi:10.1029/2011GL046683.
- Rassi, E. M., S. L. Codd, and J. D. Seymour (2012), MR measurement of critical phase transition dynamics and supercritical fluid dynamics in capillary and porous media flow, *J. Magn. Reson.*, 214, 309–314, doi:10.1016/j.jmr.2011.09.045.
- Roof, J. G. (1970), Snap-off of oil droplets in water-wet pores, *Soc. Pet. Eng. J.*, 10(1), 85, doi:10.2118/2504-PA.
- Rossen, W. R. (2000), Snap-off in constricted tubes and porous media, *Colloids Surf. A*, 166(1–3), 101–107, doi:10.1016/S0927-7757(99)00408-2.
- Shell/Scottish Power CCS Consortium. (2011), UK Carbon Capture and Storage Demonstration Competition Design HSE Case. [Available at http://www.decc.gov.uk/en/content/cms/emissions/ccs/ukccscomm_prog/feed/feed.aspx]
- Shi, J. Q., Z. Q. Xue, and S. Durucan (2011a), Supercritical CO₂ core flooding and imbibition in Berea sandstone—CT imaging and numerical simulation, *Energy Proc.*, 4, 5001–5008, doi:10.1016/j.egypro.2011.02.471.
- Shi, J. Q., Z. Q. Xue, and S. Durucan (2011b), Supercritical CO₂ core flooding and imbibition in Tako sandstone-influence of sub-core scale heterogeneity, *Int. J. Greenhouse Gas Control*, 5(1), 75–87, doi:10.1016/j.ijggc.2010.07.003.
- Song, Y. Q. (2003), Using internal magnetic fields to obtain pore size distributions in porous media, *Concept Magn. Reson. A* 18A(2), 97–110, doi:10.1002/cmra.10072.
- Song, Y. Q., H. Cho, T. Hopper, A. E. Pomerantz, and P. Z. Sun (2008), Magnetic resonance in porous media: Recent progress, *J. Chem. Phys.*, 128(5), 052212, doi:10.1063/1.2833581.
- Spycher, N., K. Pruess, and J. Ennis-King (2003), CO₂-H₂O mixtures in the geological sequestration of CO₂, *Geochim. Cosmochim. Acta*, 67(16), 3015–3031, doi:10.1016/S0016-7037(03)00273-4.
- Stingaciu, L. R., L. Weihermuller, S. Haber-Pohlmeier, S. Stapf, H. Vereecken, and A. Pohlmeier (2010), Determination of pore size distribution and hydraulic properties using nuclear magnetic resonance relaxometry: A comparative study of laboratory methods, *Water Resour. Res.*, 46, W11510, doi:10.1029/2009WR008686.
- Tanino, Y., and M. J. Blunt (2012), Capillary trapping in sandstones and carbonates: Dependence on pore structure, *Water Resour. Res.*, 48, W08525, doi:10.1029/2011WR011712.
- Wardlaw, N. C., and Y. Li (1988), Fluid topology, pore-size and aspect ratio during imbibition, *Transp. Porous Media*, 3(1), 17–34, doi:10.1007/BF00222684.
- Washburn, K. E., and P. T. Callaghan (2006), Tracking pore to pore exchange using relaxation exchange spectroscopy, *Phys. Rev. Lett.*, 97(17), 175502, doi:10.1103/PhysRevLett.97.175502.
- Weiger, M., K. P. Pruessmann, and F. Hennel (2011), MRI with zero echo time: Hard versus sweep pulse excitation, *Magn. Reson. Med.*, 66(2), 379–389, doi:10.1002/mrm.22799.
- Weiger, M., K. P. Pruessmann, A. K. Bracher, S. Kohler, V. Lehmann, U. Wolfram, F. Hennel, and V. Rasche (2012), High-resolution ZTE imaging of human teeth, *NMR Biomed.*, 25(10), 1144–1151, doi:10.1002/nbm.2783.
- Wildenschild, D., R. T. Armstrong, A. L. Herring, I. M. Young, and J. W. Carey (2011), Exploring capillary trapping efficiency as a function of interfacial tension, viscosity, and flow rate, *Energy Proc.*, 4, 4945–4952, doi:10.1016/j.egypro.2011.02.464.
- Zuo, L., and S. M. Benson (2014), Process-dependent residual trapping of CO₂ in sandstone, *Geophys. Res. Lett.*, 41, 2820–2826, doi:10.1002/2014GL059653.