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Pore-scale observations of supercritical CO\textsubscript{2} drainage in Bentheimer sandstone by synchrotron x-ray imaging

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\textbf{A B S T R A C T}

This work utilizes synchrotron-based x-ray computed microtomography (x-ray CMT) imaging to quantify the volume and topology of supercritical carbon dioxide (scCO\textsubscript{2}) on a pore-scale basis throughout the primary drainage process of a 6 mm diameter Bentheimer sandstone core. Experiments were performed with brine and scCO\textsubscript{2} at 8.3 MPa (1200 psi) and 37.5 °C. Capillary pressure–saturation curves for the scCO\textsubscript{2}–brine system are presented and compared to the ambient air–brine system, and are shown to overlay one another when pressure is normalized by interfacial tension. Results are analyzed from images with a voxel resolution of 4.65 μm; image-based evidence demonstrates that scCO\textsubscript{2} invades the pore space in a capillary fingering regime at a mobility ratio \( M \approx 0.03 \) and capillary number \( Ca \approx 10^{-4.6} \) to an end-of-drainage brine saturation of 9%. We provide evidence of the applicability of previous two-dimensional micromodel studies and ambient condition experiments in predicting flow regimes occurring during scCO\textsubscript{2} injection.

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\section{1. Introduction}

Geologic carbon sequestration has been proposed as a potential climate change mitigation strategy to prevent emissions of CO\textsubscript{2} to the atmosphere from large fossil-fuel burning point sources (IPCC, 2005). In geologic sequestration, supercritical CO\textsubscript{2} (scCO\textsubscript{2}) is injected into saline groundwater hosted in a porous aquifer (i.e., a brine \textit{drainage} process), thus producing an immiscible displacement scenario where scCO\textsubscript{2} is the non-wetting (NW) fluid and brine is the wetting (W) fluid. Subsequently scCO\textsubscript{2} is mobilized or trapped by capillary forces when brine reenters the pore space of the geologic matrix (i.e., the brine \textit{imbition} process) during water flooding or buoyant CO\textsubscript{2} migration. There are concerns associated with the long-term stability of a mobile subsurface CO\textsubscript{2} plume, so drainage and imbibition should be carefully engineered to facilitate favorable trapping conditions. Capillary trapping of scCO\textsubscript{2}, wherein the CO\textsubscript{2} is held within the pore structure of the geologic matrix by capillary forces, is a safer form of subsurface storage than hydrodynamic or structural trapping, which relies on a low permeability caprock to contain the buoyant CO\textsubscript{2} plume; additionally, capillary trapping occurs on vastly shorter timescales than reactive trapping methods (i.e. dissolution trapping and mineral trapping) (IPCC, 2005; Qi et al., 2009). To understand the multiphase physics of CO\textsubscript{2} transport and to make quantitative estimations of potential CO\textsubscript{2} capillary trapping in saline aquifers, it is necessary to study field, core, and pore-scale processes. Experiments at geological reservoir conditions at the core and pore-scale in combination with x-ray computed microtomography (x-ray CMT) allow for three-dimensional (3D) in situ visualization of fluid phases and the physical structure within a porous medium (Blunt et al., 2013; Ketcham and Carlson, 2001; Wildenschild et al., 2002) and have the potential to provide insight into the engineered process of geologic CO\textsubscript{2} sequestration to achieve high volume trapping of CO\textsubscript{2}. An overview of recent advances in pore-scale characterization of structure and flow processes via x-ray CMT technology can be found in Wildenschild and Sheppard (2013).

A number of studies have indicated that capillary trapping of scCO\textsubscript{2} may be maximized via manipulation of the temperature, pressure, salinity, and flow rates of the CO\textsubscript{2} and brine injections such that the CO\textsubscript{2}-brine interactions are most conducive to capillary trapping (Bachu and Bennion, 2008b; Wildenschild et al., 2011). Studies of general flow regimes in simple model systems, such as glass beads (Morrow et al., 1988; Polak et al., 2011) and two-dimensional (2D) micromodels (Lenormand et al., 1988; Wang et al., 2012; Zhang et al., 2011), have demonstrated the transitions...
between capillary, viscous, and gravity force-dominated regimes and the resulting effects on drainage flow patterns and capillary trapping. Although these works undoubtedly provide insight to the general field of transport in porous media, they may not all be analogous to a scCO$_2$–brine sequestration scenario because (a) some are not conducted at reservoir conditions, (b) results from simple model systems do not directly translate to geologic media, (c) the wettability condition of the scCO$_2$–brine–rock system is not the same as in analog systems, and (d) only the drainage (CO$_2$ injection) process has been analyzed so far. Confirmation of the applicability of the results of these analog model systems to a scCO$_2$ sequestration scenario is needed.

Recent bulk-measurement-focused experiments (i.e. experiments wherein experimental parameters are measured at the inlet and outlet of the core, but not at individual points within the core) with scCO$_2$ at reservoir conditions have expanded knowledge of scCO$_2$ flow in porous media. Pentland et al. (2011a) measured the relationship between initial and residual (i.e. capillary trapped) scCO$_2$ saturation in Berea sandstone and found that the capillary-trapped amount of scCO$_2$ was less, although still significant, than that of an ambient condition analog (decane) in the same medium, with residual scCO$_2$ saturations occupying up to 35% of the pore space. Bachu and Bennion (2008b) demonstrated that pressure, temperature, and salinity conditions, as well as rock characteristics, have a significant impact on flow parameters such as capillary pressure, relative permeability, and interfacial tension (IFT) of scCO$_2$–brine systems. Others have investigated the wettability state of various scCO$_2$–brine–medium systems, e.g. in sand packs (Plug and Bruining, 2007), sandstone (Pentland et al., 2011b), and carbonates (El-Maghrawy and Blunt, 2012), and have shown that under primary drainage conditions the media behaves as strongly water-wet systems; however, during imbibition, sand and sandstone may transition to a more weakly water-wet or intermediate-wet system as a result of exposure to scCO$_2$. Other studies have shown that the CO$_2$–brine system can display a range of contact angles depending on the pressure, temperature, and composition of the solid surface (Broseta et al., 2012; Chalboud et al., 2009).

In addition to these bulk-measurement-focused experiments, x-ray CMT has been utilized from a pore-scale perspective to establish the feasibility of high-resolution visualization of reservoir pressure CO$_2$ (Silin et al., 2011); to confirm that residual trapping of scCO$_2$ is achievable in geologic media (Iglauer et al., 2011); and to investigate the influence of media properties such as geometry of natural and synthetic media (Pentland et al., 2012) and wettability and grain shape of synthetic media (Chaudhary et al., 2013) on scCO$_2$ flow. In addition, core-scale studies have investigated relative permeability (Akbarabadi and Piri, 2013; Perrin et al., 2009), pressure–saturation curves (Pini et al., 2012), as well as the relationship between initial and residual scCO$_2$ saturations (Akbarabadi and Piri, 2013).

In this work, we present a synchrotron tomography-based pore-scale analysis of the drainage processes of the scCO$_2$–brine system in Bentheimer sandstone with an in-house developed mobile high-pressure setup for operation at geological reservoir conditions using a core holder compatible with x-ray CMT. We present and compare the ambient (air-brine) and supercritical (scCO$_2$–brine) capillary pressure–saturation curves for primary drainage in Bentheimer sandstone; we show images of the scCO$_2$ within the Bentheimer sandstone at multiple points during the scCO$_2$ injection (drainage) process; and we analyze the evolution of connectivity of scCO$_2$ fluid clusters. The results indicate that ambient pressure or micromodel system experiments can accurately predict the dominant flow regime during scCO$_2$ drainage in Bentheimer sandstone and confirm that low mobility ratio (M) and low capillary number (Ca) flow during drainage results in capillary fingering displacement of the wetting fluid.

### Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>Viscosity (mPa·s)</th>
<th>Density (kg/m$^3$)</th>
<th>IFT w. Brine (mN/m)</th>
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<tr>
<td>scCO$_2$</td>
<td>0.03*</td>
<td>360</td>
<td>Approx. 38</td>
</tr>
<tr>
<td>Brine</td>
<td>1.13</td>
<td>1080</td>
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* National Institute of Standards and Technology (NIST) web database (http://webbook.nist.gov/chemistry/).

Interpolated from data by Bachu and Bennion (2008a).

### 2. Experimental equipment and methods

#### 2.1. Porous medium and fluid characteristics

Two 6 mm diameter Bentheimer sandstone cores, denoted B1 (length of 37.1 mm) and B2 (length of 39.6 mm), were used during supercritical drainage experiments. Drainage of core B1 was stopped at seven points during drainage to allow for equilibration and scanning (“quasi-static”), while core B2 was drained continuously, but not scanned, allowing for comparison of the quasi-static scanned and continuous unscanned capillary pressure–saturation curves. A third core, B3, was drained continuously under ambient conditions with air as the nonwetting phase following the methods of Herring et al. (2013). Porosity of B1, derived from a dry scan of the core with voxel resolution of 4.65 μm, was 16%. The petrophysical properties of Bentheimer sandstone have been previously reported by Maloney et al. (1996) and Øren et al., 1998. The wetting (W) fluid was a brine of 1:6 by mass potassium iodide (which produces good x-ray contrast) and deionized water. Relevant fluid properties at supercritical experimental conditions ($T = 37.5 \, ^\circ C, P = 8.3 \, MPa$) are shown in Table 1.

#### 2.2. Supercritical experimental set up

The mobile experimental set up (Fig. 1) was designed to allow for both core-scale and pore-scale flow experiments at pressures up to 13.75 MPa (2000 psi) in combination with synchrotron and bench top x-ray imaging. All components are connected via 3.18 mm (1/8") O.D. 316 stainless steel tubing (Swagelok, Solon OH, United States) and are mounted upon heavy-duty rolling carts. The aluminum Hassler–sleeve type core holder (Phoenix Instruments, Splendora, TX, United States) has a wall thickness of 0.127 cm and can accommodate cores up to 6.35 mm in diameter and 7.6 cm in length (Fig. 2). Overburden pressure was applied to the core via a Buna-N Nitrile sleeve accommodated inside the core holder. The core was assembled with a stainless steel spacer, Viton o-ring, and two layers of hydrophilic nylon membrane with 1.2 μm pore size (General Electric Company, Fairfield, CT, United States) at the base of the core and a Viton o-ring and a 316 stainless steel washer at the top of the core. The entire core assembly is wrapped in aluminum foil to prevent uptake of the scCO$_2$ by the Buna-N nitrile overburden sleeve, and then wrapped in Teflon tape (Fig. 2). Core temperature is maintained via incandescent lamps and continuously monitored with external thermocouples (Omega Engineering Inc, Stamford, CT, United States).

Fluid flow rates and pressures, including the overburden pressure, were controlled by high precision, high pressure syringe pumps (Teledyne ISCO, Lincoln, NE, United States). The 400 ml fluid separator (Fig. 1) (manufactured in-house) allows complete mixing of the fluids and is monitored by a differential pressure transducer with a range of ±14.0 kPa (±2 psi) (Validyne Engineering, Northridge, CA, United States). Three other Validyne pressure transducers are connected in parallel with the core holder to allow pressure measurements during flow experiments: two pressure transducers measure absolute pressure above and below the
core (pressure range: ±8.6 MPa (±1250 psi)), and one pressure transducer measures differential (i.e. capillary) pressure across the core (pressure range: ±14.0 kPa). The 450 ml brine and CO₂ accumulators and fluid separator, the temperature sensitive pressure transducers, as well as all other temperature-sensitive components of the setup are housed in a temperature-controlled and monitored environment (oven and external compartment), as indicated in Fig. 1.

2.3. Supercritical experimental process

Before filling and pressurizing the high-pressure system, the CO₂ flow paths and fluid separator components assigned to hold and transport CO₂ were cleared of air by repeatedly flushing with gaseous CO₂. The brine accumulator and the connections for brine were filled with degassed brine and taken up to working pressure (8.3 MPa or 1200 psi). Approximately 150 ml of brine at ambient pressure was pumped into the separator; then CO₂ was pumped into the separator until working pressure was achieved.

Mixing of fluids occurs within the fluid separator which has ports that are flush with the endcaps at the top and bottom of the vessel as well as a bored-thorugh port at the bottom with a line that reaches approximately the midpoint of the vessel. Fluids are pushed back and forth using the high pressure pumps; scCO₂ is pushed through the flush bottom port while a mixture of fluids is allowed to be retracted through the midpoint line, then the mixture of fluids is pushed back into the cylinder via the midpoint line while the scCO₂ phase is allowed to retract from the top flush port. Pushing in the buoyant scCO₂ through the bottom port allows the scCO₂ to travel through the brine phase as it migrates to the top of the separator vessel, and pushing the mixture of fluids through the midpoint line allows brine in the mixture to cascade down through the scCO₂ phase, facilitating complete mixing. This mixture process was performed at least three cycles. Finally, brine phase was pulled from the bottom flush port then pushed through the midpoint line multiple times, while scCO₂ was allowed to flow in or out of the cylinder via the top port. This step clears the midpoint and lower brine lines of scCO₂, replacing it with a pure phase of CO₂-saturated brine.
Temperatures were set to 37.5 °C, and fluids allowed to reach chemical and thermal equilibrium, a process requiring 12–16 h. Temperature was continuously monitored by thermocouples inside the temperature-controlled space. Equilibrium was assumed to be reached when the CO₂ pump, set to maintain constant pressure, maintained a constant volume, indicating no further fluid volume changes, and the pressure across the separator maintained a constant value.

The core assembly was attached to the system and vacuum-degassed brine was used to wet the hydrophilic membrane and flush the core, with an applied overburden pressure of 1.4 MPa (200 psi). Vacuum was applied at the upper outlet of the core holder in order to completely saturate the core with brine. The core was gradually brought to the working pressure (8.3 MPa), while the overburden pressure was concurrently raised to approximately 4.1 MPa (600 psi) in excess of the core pressure, and the core temperature (37.5 °C) was established using incandescent lamps. Once the core reached a stable temperature, the core was flushed with CO₂-saturated brine at 8.3 MPa and 37.5 °C until CO₂ gas was confirmed to exit at the core holder back-pressure regulator (BPR) (see Fig. 1). This filling process ensured that the brine within the core was saturated with CO₂ and that the drainage process was truly immiscible (i.e. the scCO₂ displaced the brine rather than dissolving into it). At this point, scCO₂ was introduced into the line above the core holder and the CO₂ and brine phases were separated by a single valve (labeled “S1” in Fig. 1), and the core system was allowed to equilibrate. Equilibration was established when the differential pressure transducer across the core maintained a constant pressure.

The brine pump was used to control flow rate from the bottom of the core, while the CO₂ pump provides a constant pressure boundary at the top of the core. The brine pump was set to retract at a constant volumetric flow rate of 0.100 ml/h, while the scCO₂ pump was set to a constant pressure setting of 8.3 MPa (1200 psi). Absolute and differential pressures were continuously monitored and recorded. For both continuous and quasi-static (scanned) experiments, pumping of brine continued until a differential pressure of approximately 14.0 kPa (the pressure transducer range) was achieved, indicating that the NW fluid had reached the hydrophilic membrane. For scanning, the pumps were stopped at seven points during the drainage process, the system was allowed to equilibrate for 45 min and a scan was acquired of the core. A scan was also taken of the dry core.

For the scanned experiment, scCO₂ saturation was derived from the images. Nonwetting phase saturation for the unscanned, continuous curves was calculated from the pore volume of the rock (which is estimated using the dimensions and mass of the vacuum dried core) and the brine flow rate. The start point of drainage within the core (rather than the line above the core) is evident as a sharp decrease in pressure and saturation is calculated as a function of time from that start point.

2.4. Synchrotron x-ray CMT imaging and data processing

Tomographic imaging was performed at the bending magnet beam-line at sector 13 (GSECARS) at the Advanced Photon Source at Argonne National Laboratory. The beam-line specifications have been described in detail in previous works (Rivers et al., 1999; Wildenschild et al., 2005; Wildenschild et al., 2002). All scans were performed at a monochromatic energy level of 37.0 keV, significantly above the K-shell photoelectric absorption edge of iodine (33.17 keV), resulting in high x-ray attenuation by the 1.6 by weight potassium iodide-doped brine and thus allowing for separation of the wetting and non-wetting fluids in the reconstructed images. This higher energy was used to overcome the attenuation due to the core holder, overburden pressure fluid, and aluminum foil surrounding the core. Images were captured at 720 angles, with a horizontal field of view of 6.47 mm, a vertical field of view of 4.83 mm, and a resulting voxel resolution of 4.65 μm, as a result of utilizing local tomography. For each point on the drainage curve (subsequently labeled A to G, e.g. in Fig. 5), two scans were acquired at different heights in the core with a vertical overlap of 0.5 mm.

The acquired radiographs were reconstructed into three-dimensional (3D) volumes via the programming language IDL™ (Research Systems Inc.) and the subsequent image processing and analysis was performed using Avizo® Fire (FEI Visualization Sciences Group, Burlington Massachusetts, United States).

To reduce noise and blur, the grayscale 3D datasets (Fig. 3a) were processed with an anisotropic diffusion filter applied with a diffusion threshold value of 350 and 50 iterations (Fig. 3b).
3. Results and discussion

3.1. Primary drainage pressure–saturation relationship

The drainage process of the scCO₂-brine system in Bentheimer sandstone, at geological reservoir conditions, was imaged at the pore-scale using x-ray synchrotron tomography. Capillary pressure–saturation ($P_c$–$S$) curves measured with the supercritical experimental system are shown in Fig. 4(a); a continuous drainage curve (from core B2) is overlain with the equilibrium pressure–saturation points from the scanned drainage experiment (core B1) showing consistent behavior between the stepped equilibrium data and the continuously scanned measurements. The scanned points from core B1 are labeled A–G, corresponding to the data presented in Section 3.2. Note that the pressures of points B and C are estimated by comparison to the continuous drainage curve, due to inadequate equilibration during the first two scanning periods. Point A was collected prior to the start of drainage. However, temperature fluctuations within the core (temperature ranged from 36.9 to 38.8°C prior to the start of data collection) caused exsolution of dissolved CO₂ and the resulting data is shifted

Fig. 3. Image processing steps for segmenting supercritical CO₂ (scCO₂) within Bentheimer sandstone. The raw data (a) is cropped and an anisotropic diffusion filter is applied (b). The filtered image is segmented according to the grayscale histogram local minimum, resulting in a binary image (c) and noise is removed applying a size exclusion filter (d). The anisotropic diffusion filter facilitates the histogram-based segmentation process by separating the peaks that differentiate two phases: the non-wetting phase scCO₂ and a combination of the wetting phase and solid (Fig. 3a and b). We segmented the resulting grayscale image by applying a universal intensity threshold to all volumes at a grayscale value of 62.5 (Fig. 3c). To remove the remaining noise, we applied a size exclusion filter that removes all NW phase-labeled clusters smaller than 250 voxels (Fig. 3d). The size of these clusters corresponds to the volume of a spherical pore with a radius of 18.2 μm; removal of clusters smaller than this size is justified given the pore-size distribution of the Bentheimer sandstone (Maloney et al., 1990). The two vertical scan sections were then merged to form an 8.0 mm tall volume, and all quantitative measures are calculated on this final volume using analysis tools available in Avizo® Fire: total number and density of NW-labeled voxels and individual volume of distinct NW voxel clusters. These values were normalized by the corresponding values for the respective core in its dry state.

Fig. 4. Primary drainage (a) capillary pressure–saturation ($P_c$–$S$) curves and (b) capillary pressure normalized by interfacial tension–saturation ($P_t$/$\sigma$–$S$) curves for the two scCO₂-brine experiments (continuous and quasi-static) and for a continuous ambient air-brine drainage experiment. The quasi-static points are labeled with their scan designation in (a). Uncertainty bars indicate the range of pressure variation during equilibration. The hollow supercritical quasi-static points indicate estimated pressure values.
toward lower brine saturation (i.e. less than 1.0) (e.g. Fig. 4, point A; and Fig. 7a).

For comparison with the scCO₂-brine system, an ambient air-brine \( P_r-S \) curve was measured on a third core, B3, following the methods described in Herring et al. (2013) and is also shown in Fig. 4(a). The decrease in NW phase entry pressure between the ambient air and supercritical CO₂ curves is due to decreased interfacial tension (IFT) between scCO₂ and brine as compared to air and brine (see Table 1). This result is similar to the shift between supercritical and ambient pressure–saturation curves reported by Plug and Bruining (2007). This interpretation is confirmed by the curves shown in Fig. 4(b), wherein the capillary pressures of the systems are normalized by their respective interfacial tension values; as shown, primary drainage for the scCO₂-brine and air-brine systems can be successfully described by a single \( P_r-T \) relationship. This finding provides support for use of analog fluids in flow experiments to simulate primary drainage of scCO₂.

The brine saturation at the end of primary drainage ("initial" brine saturation) measured here (scan G, \( S_w = 9\% \)) is relatively low compared with other scCO₂ flow experiments. For example, Iglauer et al. (2011) measured an initial brine saturation of approximately 50% in homogenous Doddington sandstone cores of 9 mm length and 4.95 mm diameter, and Akbarabadi and Piri (2013) measured initial brine saturations ranging from 30% to 75% in Berea and Nugget sandstone cores of approximately 15 cm length and 3.8 cm diameter. Similarly, Krever et al. (2012) reports initial brine saturations of 41–54% in a variety of 5 cm diameter, 10 cm length sandstone and reservoir rock samples; however, Krever et al. state that the minimum achievable end-of-drainage brine saturation is dependent on the capillary pressure achieved in the experiment, and the authors indicate that lower brine saturations should be attainable at sufficiently high capillary pressure. The difference in initial brine saturation values between these previous studies and the value reported here is due to our use of a hydrophilic membrane at one end of the core (the works mentioned above use co-current flow, and do not include a membrane in the experimental design). A similar effect is shown by Pentland et al. (2011a) who achieved initial brine saturations of approximately 10% with the use of a semi-permeable disk in their experimental set-up. The hydrophilic membrane (or semi-permeable disk) prevents scCO₂ breakthrough, thus approximating a semi-infinite geologic media, and allows higher capillary pressures (and consequently, lower brine saturations) to be achieved. As a result of this experimental design, we have presented a more complete pressure–saturation curve for primary drainage, derived from real-time measurements of capillary pressure across the core coupled with x-ray tomography based saturation information.

3.2. Connectivity and topology of scCO₂ front during drainage

The connectivity of NW fluid after drainage plays a significant role in controlling the amount of residual trapping of the NW fluid that is achieved after the subsequent imbibition of W fluid back into the pore space (Herring et al., 2013; Wardlaw and Yu, 1988). Here, the connectivity of the CO₂ is investigated via \( \Gamma_{scCO₂} \) (Renard and Allard, 2013):

\[
\Gamma_{scCO₂} = \frac{1}{n_{scCO₂}} \sum_{i=1}^{N_{scCO₂}} \left( \frac{n_{scCO₂}}{n_i} \right),
\]

where \( n_i \) is the number of connected scCO₂ voxels of each individual \( i \)th scCO₂ cluster (i.e. the size of each individual scCO₂ cluster, in voxels), \( X_{scCO₂} \) is the set of all scCO₂ voxels, and \( n_{scCO₂} \) is the total number of scCO₂ clusters. The relative fraction of connected scCO₂ clusters increases as drainage proceeds and brine saturation decreases (Fig. 5). The relative fraction of connected scCO₂ clusters approaches unity even at relatively high brine saturation (0.60); this indicates that the scCO₂ invades the core largely as one connected component, rather than multiple distinct fingers emanating from distinct sources.

The high connectivity of the scCO₂ is confirmed by investigating the distribution of the scCO₂ cluster sizes (Fig. 6). Fig. 6(a) demonstrates that throughout the drainage process, the number of small clusters (clusters of approximately 0.01 mm³ and smaller) first increases (points A to E), then decreases (points E to G). These small clusters are present due to snap-off, which occurs when pumping is paused during scanning. The number of small clusters
first increases as more scCO$_2$ enters the pore space, then decreases as pumping continues and scCO$_2$ saturation increases and connects individual clusters via pore throats. Fig. 6(b) is a truncated plot, showing the size distribution of the medium (0.01–1 mm$^3$) and large (>1 mm$^3$) clusters, which establishes that for drainage points B-G, there exists precisely one large cluster that increases in volume from points B-G. Comparison of Fig. 6(b) with Fig. 6(c) establishes that this one large scCO$_2$ cluster makes up the great majority of the total scCO$_2$ volume within the pore space (90% of the total scCO$_2$ volume for point B, and increasing as drainage proceeds) for every drainage point (excluding point A, which was measured before the start of drainage).

The topology of the scCO$_2$ can be investigated from a qualitative perspective (Fig. 7). Three dimensional (3D) isosurfaces and two dimensional (2D) binary X-Z oriented slices of the scCO$_2$ show the extent of temperature-induced scCO$_2$ phase separation out of the brine prior to drainage (Fig. 7, scan designation A). We note here that such exsolution may occur in any experiment using CO$_2$-saturated brine, which highlights the importance of maintaining temperature uniformity throughout the experimental system. The tomographic data show the increase of scCO$_2$ saturation during the progression of drainage (Fig. 7, scan designations B, D, and G). A subsection of these binary X-Z oriented slices overlain on the original grayscale data (Fig. 7) demonstrates the evolution of the scCO$_2$ front on the pore scale. As shown by all three image types, although scCO$_2$ was injected at the top of the core, the scCO$_2$ does not move in a uniform, stable front. Rather, it first invades the largest pores, gradually filling smaller pores as drainage proceeds, and traveling in all directions.

For a drainage process in 2D micromodels, three flow regimes have been identified: capillary fingering is characterized by flow through a single interconnected flow path with a width of tens of pore bodies; viscous fingering presents several disconnected flow paths with widths of 1–3 pore bodies; and stable displacement occurs when the NW fluid advances as a solid front (Lenormand et al., 1988; Zhang et al., 2011). The characteristics of these flow regimes are not as clearly defined in 3D porous media; however, the quantitative measures demonstrating high connectivity dominated by a single scCO$_2$ fluid cluster (Figs. 5 and 6) and qualitative data illustrating the evolution of the scCO$_2$ front (Fig. 7) we present here provide evidence that during this drainage experiment, scCO$_2$ invades the sandstone via capillary fingering. This is expected; given the low mobility ratio $M = \mu_{CO_2}/\mu_{brine} = 0.03$ and low capillary number $Ca = (\mu_{CO_2} v_{CO_2})/\sigma = 10^{-8.6}$ of this drainage experiment (Fig. 8). The agreement between previous studies on 2D systems and the supercritical 3D system investigated here provides support that the flow regimes developed by examination of 2D micromodels (Lenormand et al., 1983; Wang et al., 2012;
fingering flow regime using sandstone at reservoir conditions and indicate that 2D and ambient system experiments can be used to approximate scCO₂ flow processes during primary drainage.

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**Fig. 8.** Flow regime phase diagram for drainage. The flow regimes are defined based on the capillary number (Ca) and mobility ratio (M) of the drainage process; solid lines indicate boundaries defined by Lenormand et al. (1988) and dashed lines indicate boundaries defined by Zhang et al. (2011). Conditions of the scanned supercritical CO₂ (scCO₂) drainage experiment within Bentheimer sandstone are represented by the red diamond. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Zhang et al., 2011) are relevant to 3D systems with geologic porous media and supercritical conditions.

**4. Conclusions**

We have presented unique capillary pressure–saturation (Pc–S) curves for supercritical CO₂ (scCO₂) and brine at reservoir conditions, i.e. 37.5 °C and 8.3 MPa, where the saturation data is calculated from x-ray CMT images paired with bulk measurements of capillary pressure via pressure transducers. We have compared the scCO₂ Pc–S curve to an ambient Pc–S curve and normalization of the capillary pressure curves by the air-brine and scCO₂-brine interfacial tensions (σ) results in a single Pc/σ-S curve that describes primary drainage for both ambient and supercritical conditions. We have shown that quasi-static equilibrium capillary pressure data overlap that obtained in continuous pressure experiments of the primary drainage process of scCO₂ in Bentheimer sandstone at reservoir conditions and low flow rate. We have obtained much lower initial saturations of brine in our system (9%) than reported in other studies (30–75%), which, because of our use of a hydrophilic membrane at the brine outlet, better approximates a semi-infinite geologic medium, and which we believe is a more realistic characterization of CO₂ storage capacity during drainage. These experiments have highlighted the importance of temperature uniformity throughout the experimental system due to the possibility of scCO₂ exsolution due to temperature variation. Additionally, we have investigated the connectivity of the scCO₂ front on a pore-scale basis and provided both quantitative and qualitative evidence demonstrating scCO₂ invasion via capillary fingering, which is consistent with mobility ratio/capillary number-based predictions obtained at ambient pressure (Lenormand et al., 1983; Zhang et al., 2011) and in homogenous (2D) high-pressure CO₂ system micromodel studies (Wang et al., 2012). Our results show a very complete drainage process of scCO₂ displacing brine (to a brine saturation of 9% at the end of primary drainage) in a capillary
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