Residual CO₂ imaged with X-ray micro-tomography

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[1] Carbon capture and storage (CCS), where CO₂ is injected into geological formations, has been identified as an important way to reduce CO₂ emissions to the atmosphere. While there are several aquifers worldwide into which CO₂ has been injected, there is still uncertainty in terms of the long-term fate of the CO₂. Simulation studies have proposed capillary trapping – where the CO₂ is stranded as pore space droplets surrounded by water – as a rapid way to secure safe storage. However, there has been no direct evidence of pore-scale trapping. We imaged trapped super-critical CO₂ clusters in a sandstone at elevated temperatures and pressures, representative of storage conditions using computed micro-tomography (μ-CT) and measured the distribution of trapped cluster size. The clusters occupy 25% of the pore space. This work suggests that locally capillary trapping is an effective, safe storage mechanism in quartz-rich sandstones. Citation: 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.

1. Introduction

[2] With increasing fossil-fuel consumption accounting for more than 80% of energy use [International Energy Agency, 2010], CCS is seen as a key technology to tackle greenhouse gas emissions directly at source [Intergovernmental Panel on Climate Change (IPCC) 2005]. Once captured and transported, the CO₂ is injected at depths of 800m or more where the CO₂ is in a dense supercritical (sc) state. Deep saline aquifers are likely to have the highest storage capacities because of their geographical abundance and large available volumes [IPCC, 2005]. The principal concern with CCS is to ensure that the CO₂ remains underground. There are four trapping mechanisms that prevent the CO₂ from escaping: a) stratigraphic, where a layer of caprock blocks the buoyant CO₂ from flowing upwards [Hesse et al., 2008]; b) dissolution into the formation brine, where the dense CO₂-saturated brine sinks through the aquifer [Riaz et al., 2006]; c) mineral trapping where dissolved CO₂ reacts with formation brine or host rock to form solid minerals [Xu et al., 2003] and d) capillary trapping [Hesse et al., 2008; Juanes et al., 2006; Qi et al., 2009]. In the fourth process, capillary trapping, the focus of this work, it is hypothesized that the CO₂ is immobilized by capillary forces as pore-space bubbles. When the injected CO₂ plume rises upwards it is followed by groundwater influx; at the trailing edge of the CO₂ plume the CO₂ is displaced by water and a fraction of the CO₂ is trapped. This process, analogous to the trapping of oil during waterflooding in hydrocarbon reservoirs, has been proposed as the most rapid and effective way to ensure safe storage that can be engineered through brine injection [Qi et al., 2009].

2. Experimental Procedure

[3] We imaged trapped clusters of scCO₂ directly in a homogeneous sandstone (Doddington) with a porosity of 20.7% and a brine permeability of 1.58 × 10⁻¹² m². Doddington consists of 98 wt% α-quartz, 2 wt% K-feldspar and traces of kaolinite (measured by X-ray diffraction on a Philips PW1830 diffractometer). A cylindrical core (9 mm length and 4.95 mm diameter) was drilled and placed in a specially developed μ-CT cell capable of operating at high pressure and elevated temperature (HPET). The novel HPET μ-CT cell is an assembly of an inner pressure module (core assembly) which housed the sandstone, and an outer carbon fiber vessel which contained confining fluid (Figure 1). Two stainless steel flow heads sealed the carbon fiber vessel so that pressure could be maintained constant. The core was wrapped in thin aluminium foil (50 μm thick) to prevent CO₂ from escaping. scCO₂ is an excellent solvent and would otherwise penetrate into the fluoropolymer elastomer (Viton) sleeve, which was placed around the foil. The sleeve was compressed by the confining fluid so that fluid bypassing around the core was prevented. This is essentially a miniaturized Hassler cell [Hassler, 1944] design. The apparatus guaranteed that confining fluid and pore fluids were hydraulically separated. Fluid injection occurred through the steel flow heads and into the sealed core through stainless steel tubing. The core assembly had an inlet and outlet for fluid injection and production.

[4] The core was initially fully saturated with brine, then CO₂ was injected (primary drainage), representing the initial migration of CO₂ through the aquifer. This was followed by a waterflooding step, where brine saturated with CO₂ was injected. This represents the trailing edge of an advancing CO₂ plume, or when brine is artificially injected: some CO₂ is displaced, leaving behind an immobile residual fraction. Experimental flow, pressure and temperature conditions in the core were representative of a deep saline aquifer at approximately 1000 m depth (T = 323 K [= 50°C], 9 MPa pore pressure and 11.75 MPa overburden pressure).

[5] Specifically, the μ-CT experiment consisted of following steps (Figure 1a):

[6] 1. The core was vacuumed and then fully saturated with brine (10wt% potassium iodide, KI, was dissolved in deionized water to enhance the CT contrast; NaCl brine would have resulted in low CT contrast between brine and CO₂).

[7] 2. The space between core assembly and carbon fiber vessel was filled with deionized water, which acted as a confining fluid. This confining space was connected through...
the steel heads with thermally isolated steel tubing to two syringe pumps. One pump pumped confining fluid into the confining space and the second pump received confining fluid while maintaining constant high pressure conditions (11.75 MPa). The confining fluid was continuously heated in both pumps so that isothermal conditions in the core were achieved (323 K). In addition a heating jacket was placed around the top end of the carbon fiber vessel to support isothermal conditions.

[8] 3. Two syringe pumps which were connected with thermally isolated steel tubing to the core assembly’s inlet and outlet then increased the pore pressure to 9 MPa.

[9] 4. Once the viscoelastic rubber sleeve relaxed to the pressure and the core and the pore fluids were heated to 323 K, the 10wt% KI brine was displaced with 10wt% KI brine which was saturated with scCO$_2$ at the same thermophysical conditions (323 K, 9 MPa) in a separate mixing reactor.

[10] 5. After pumping at least 1000 pore volumes (PV) of CO$_2$-saturated brine through the core, scCO$_2$ was injected in a primary drainage process, again at constant thermophysical conditions. Approximately 1000 PV of scCO$_2$ were injected at a flow rate of 2 mL/min (which corresponds to a capillary number $N_{cap} = \frac{2}{\nu_c}$ with the Darcy velocity $\nu$, the scCO$_2$ viscosity $\mu = 2.1 \times 10^{-5}$ Pa.s) [Fenghour et al., 1998] and the scCO$_2$-brine interfacial tension $\sigma = 36.0$ mN/m [Chalbaud et al., 2009]).

[11] 6. The core was scanned with a GE phoenix l X-ray microtomography system v/tome/x to obtain an image for the initial scCO$_2$ saturation and distribution in the core at a nominal resolution of 13.156 $\mu$m. This experiment (starting with step 1) was repeated three times to check reproducibility. Similar results were obtained for each scan and reproducibility was good.

[12] 7. In the waterflooding step approximately 50 PV of CO$_2$-saturated brine were injected at isothermal and isobaric conditions and at a flow rate of 2 mL/min which corresponded to a capillary number of $2.45 \times 10^{-5}$ (CO$_2$ saturated brine viscosity = $5.1 \times 10^{-4}$ Pa.s) [Bando et al., 2003]. The brine was CO$_2$ saturated so as not to dissolve the scCO$_2$ phase. Changes in scCO$_2$ saturation were only due to immiscible displacements within the pore space.

[13] 8. The sample was scanned with the $\mu$-CT instrument at a nominal resolution of 13.682 $\mu$m. Three complete independent experiments were repeated to check reproducibility; tomographic images were similar for each replicate and gave the same average residual saturations and cluster size distributions.

[14] During each scan, at the end of primary drainage and waterflooding, 720 radiographs were obtained and reconstructed. The raw $\mu$-CT images were cleaned of ring artefacts by applying a stripe removal algorithm based on combined wavelet—Fourier filtering [Münch et al., 2009]. No median filter was applied during this process. Salt-and-pepper noise was removed using an anisotropic regularization filter [Tschumperlé and Deriche, 2003]. The phases were segmented according to their CT contrast using multithresholding, i.e., by identifying peaks in the gray-level histogram of each image based on Otsu’s algorithm [Otsu, 1979]. Primary drainage images are shown in Figure 2.
Images taken after waterflooding are shown in Figure 3; the end sections contained significant noise and were cropped. Animations (Animations S1–S3) of Figures 2c, 3c and the largest trapped scCO$_2$ cluster are available in the auxiliary material.

3. Results and Discussion

[15] We measured porosity, initial CO$_2$ saturations (after primary drainage) and residual CO$_2$ saturations (after waterflooding) on the $\mu$-CT images; these are consistent with literature results measured with Helium pycnometry [Iglauer et al., 2010] and standard core floods on larger samples [Pentland et al., 2011; Suekane et al., 2008] (Table 1).

[16] The amount of trapping is controlled by the competition between snap-off and piston-like advance [Blunt and Scher, 1995]. In a strongly water-wet medium (a wetting phase-non-wetting phase contact angle close to zero), water flows along the roughness in wetting layers and during waterflooding these layers swell, filling the narrowest regions of the pore space in order of size by snap-off [Roof, 1970]. This is a percolation-like process that leads to trapping of the non-wetting phase in the larger pores. Percolation theory predicts that there is a power-law distribution of the number of trapped clusters of size $s$: $N \sim s^{-\tau}$ with an exponent $\tau = 2.189$ [Lorenz and Ziff, 1998]. As the contact angle increases, snap-off is less favoured and the dominant mode of displacement is cooperative piston-like advance, where a water front moves through the system; when snap-off is completely suppressed there is little or no trapping [Blunt and Scher, 1995]. As discussed below scCO$_2$/brine/sandstone is not strongly water-wet; this results in less capillary trapping (less snap-off) and a nominally reduced power law coefficient $\tau$, with fewer small residual CO$_2$ clusters.

[17] Figures 2 and 3 illustrate that scCO$_2$ is the non-wetting phase under these conditions; brine contacts the rock surface and fills the smaller pores; CO$_2$ preferentially resides in the centers of the larger pore spaces and is trapped in clusters of different size, surrounded by brine. During primary drainage, the CO$_2$ is connected in large clusters; some snap-off to maintain local capillary equilibrium is observed that breaks up the injected phase [Roof, 1970; Lenormand et al., 1988]. The residual scCO$_2$ saturation, composed of clusters of all sizes, is consistent with values measured in larger scale core floods [Pentland et al., 2011; Suekane et al., 2008]. However, the residual CO$_2$ saturation (24.9%) measured is lower than in the case of an analogue, strongly water-wet, Doddington sandstone-n-octane-brine experiment where a residual oil saturation of 35% was observed [Iglauer et al., 2010] (Table 1). Based on the discussion above, this implies an increased water contact angle on the quartz surface at high pressures, as observed on smooth surfaces [Chiquet et al., 2007] and in relative permeability experiments [Berg et al., 2011].

[18] We explored the implication of a lower overall residual saturation on the distribution of trapped clusters by...
counting the number of disconnected scCO₂ clusters \( N(s) \) of size \( s \) in voxels. We define the cumulative cluster size distribution \([Dias and Wilkinson, 1986]\)
\[
S(s) = \sum_{n=1}^{\infty} \frac{n(s)}{s^{-\tau+2}}
\]
where \( n(s) = N(s)/N_v \) and \( N_v \) is the total number of pore-space voxels. \( S(s) \) represents the contribution to the trapped CO₂ saturation of clusters larger than a size \( s \); \( S(1) \) is the residual saturation. Figure 4 shows \( n(s) \) and \( S(s) \) compared to results obtained in the same rock for trapped oil \((n-octane)\) at ambient conditions \([Iglauer et al., 2010]\). Other authors have imaged residual saturation and measured the cluster-size distribution for ambient-condition experiments \([Kumar et al., 2010; Prodanović et al., 2007; Karpyn et al., 2010]\). In a strongly water-wet system \((oil-brine)\), we find an approximately power-law size distribution with \( \tau = 2.05 \), close to the prediction from percolation theory \([Blunt and Scher, 1995]\); \( S(s) \) only drops sharply when the clusters begin to span the system, which represents the largest sizes we can see in the experiment. With scCO₂ (Figure 4) we see a lower residual saturation and fewer small residual clusters; the best fit to the data gives \( \tau = 2.01 \). We see fewer clusters occupying one or a small number of pores \((s \sim 30)\), with a larger contribution from bigger clusters \((spanning 10 or more pores; s > 300)\) than in the strongly water-wet system. It would appear that locally snap-off is suppressed, but there are still – at larger scales – many isolated clusters, implying that filling of some of the very narrowest pore spaces with brine during imbibition is sufficient to trap a significant fraction of the non-wetting CO₂ phase. At the capillary numbers studied, capillary forces still dominate the displacement over the length of the volume imaged \([Hilfer and Øren, 1996]\) and so we do not expect the results to be affected by viscous mobilization of the largest clusters.

Table 1. Porosities and CO₂ Saturations

<table>
<thead>
<tr>
<th>Porosity ( \mu)-CT [%]</th>
<th>Porosity He [%]</th>
<th>CO₂ Saturation ( \mu)-CT [%]</th>
<th>CO₂ Saturation Coreflood [%]</th>
<th>Oil Saturation ( \mu)-CT [%]</th>
<th>Oil Saturation Coreflood [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary drainage</td>
<td>20.5</td>
<td>20.7</td>
<td>48.0 (initial)</td>
<td>50 (initial)</td>
<td>not measured (initial)</td>
</tr>
<tr>
<td>Waterflooding</td>
<td>20.8</td>
<td>20.7</td>
<td>24.9 (residual)</td>
<td>25 (residual)</td>
<td>35.0 (residual)</td>
</tr>
</tbody>
</table>

*Measured via Helium pycnometry on a larger core sample of the same rock \([Iglauer et al., 2010]\).

*Measured with the porous plate method on a Berea sandstone core \((porosity = 0.22 \text{ and brine permeability} = 4.6 \times 10^{-13} \text{ m}^2)\) \([Pentland et al., 2011]\).

*Measured in a similar \( \mu\)-CT experiment with the same rock with n-octane at ambient conditions \([Iglauer et al., 2010]\).
Figure 4. The normalized cluster size distribution \( n(s) \) and \( S(s) \), the fractional pore volume occupied by clusters larger than a size \( s \), as a function of cluster size on doubly logarithmic axes. \( S(s) \) indicates the contribution to residual saturation from clusters of size \( s \) or greater. Data for scCO\(_2\) are compared to analogue experiments on the same rock type performed at ambient conditions for a strongly water-wet octane-brine system [Iglauer et al., 2010]. A cluster size \( s = 30 \) represents, approximately, a cluster filling a single pore.

Furthermore, the principal contribution to residual saturation comes from clusters that are significantly smaller than the system size: it is possible that poor sampling of the largest clusters could lead to an error of around 2% in the estimate of large-scale residual saturation.

[19] Future research will focus on investigating the role of rock type on capillary trapping. We show here that CO\(_2\) can be trapped in a relatively clean quartz rich sandstone. Carbonate rocks and sandstones containing clays and other mineral impurities may show different trapping behavior due to the influence of surface chemistry on contact angle and hence snap-off.

### 4. Conclusions

[20] We have used a novel high-pressure elevated-temperature micro-flow cell to image trapped clusters of super-critical CO\(_2\) at the pore scale confirming that capillary trapping of scCO\(_2\) is locally a viable CCS mechanism in clean sandstones. While there is a lower residual saturation than for an analogue strongly water-wet system, with fewer small clusters, there are clusters of all sizes, up to the system size, providing a large surface area for dissolution and reaction [Hirai et al., 1997] leading, again, to reduced CO\(_2\) leakage risk.

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### References


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