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Stefan Iglauer  
*Edith Cowan University*

Adriana Paluszny

Taufiq Rahman

Yihuai Zhang

Wolfgang Wülling  
*Edith Cowan University*

*See next page for additional authors*

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Residual Trapping of CO$_2$ in an Oil-Filled, Oil-Wet Sandstone Core: Results of Three-Phase Pore-Scale Imaging

Stefan Iglauer$^1$, Adriana Paluszny$^2$, Taufiq Rahman$^3$, Yihuai Zhang$^4$, Wolfgang Wülling$^1$, and Maxim Lebedev$^5$

$^1$School of Engineering, Edith Cowan University, Joondalup, Western Australia, Australia, $^2$Department of Earth Science and Engineering, Imperial College London, London, UK, $^3$Department of Petroleum Engineering, Curtin University, Kensington, Western Australia, Australia, $^4$Lyell Centre, Heriot-Watt University, Edinburgh, UK, $^5$Department of Exploration Geophysics, Curtin University, Kensington, Western Australia, Australia

Abstract  CO$_2$ geosequestration in oil reservoirs is an economically attractive solution as it can be combined with enhanced oil recovery (CO$_2$-EOR). However, the effectiveness of the associated three-phase displacement processes has not been tested at the micrometer pore scale, which determines the overall reservoir-scale fluid dynamics and thus CO$_2$-EOR project success. We thus imaged such displacement processes in situ in 3-D with X-ray microcomputed tomography at high resolution at reservoir conditions and found that oil extraction was enhanced substantially, while a significant residual CO$_2$ saturation (13.5%) could be achieved in oil-wet rock. Statistics of the residual CO$_2$ and oil clusters are also provided; they are similar to what is found in analogue two-phase systems although some details are different, and displacement processes are significantly more complex.

1. Introduction

CO$_2$ geostorage combined with enhanced oil recovery (CO$_2$-EOR) is an attractive and economic solution for reducing anthropogenic greenhouse gas emissions and mitigating global warming (Cantucci et al., 2009; Emberley et al., 2005; Intergovernmental Panel on Climate Change, 2005). The targeted oil reservoirs, however, are typically oil wet (Cuiec, 1991), which drastically reduces residual (Al-Khdheeawi et al., 2017; Al-Menhali et al., 2016; Al-Menhali & Krevor, 2016; Chaudhary et al., 2013; Iglauer, 2017; Krevor et al., 2015; Rahman et al., 2016) and structural (Naylor et al., 2011; Iglauer, Al-Yaseri, et al., 2015; Iglauer, Pentland, & Busch, 2015; Iglauer, 2017; Arif et al., 2017) trapping capacities and significantly accelerates vertical CO$_2$ migration (Al-Khdheeawi et al., 2017), which is detrimental as the injected CO$_2$ must not leak back to the surface.

It is, therefore, of key importance to quantify how much CO$_2$ can be safely stored in such oil reservoirs and how CO$_2$ migrates through the formation. However, such a three-phase (oil, water—which is always present in subsurface formations—and CO$_2$, which is injected for disposal) system has not been tested at the pore scale (micrometer scale), despite the fact that pore-scale flow determines hectometre-scale reservoir behavior (Bear, 1988; Sahimi, 2011; Blunt, 2017) and thus the success of any CO$_2$-EOR project.

Consequently, there is a serious lack of data and understanding of the fundamental in situ parameters and phenomena governing this process, which generates high uncertainty in terms of storage capacity and containment security predictions, translating into increased project risk.

We thus imaged such three-phase (oil/water/CO$_2$) displacement sequences via high-resolution in situ 3-D X-ray microcomputed tomography ($\mu$CT) at reservoir conditions and measured how much CO$_2$ is trapped as a residual phase in oil-wet rock and how much additional oil is produced. A statistical analysis of the residual phases is also provided. Results show that CO$_2$ effectively enhances oil production, remaining partially trapped in the core plug thereafter.

2. Experimental Procedure

2.1. Mimicking an Oil Reservoir at Laboratory Scale

It is well established that mimicking true reservoir conditions (i.e., high pressure and elevated temperature) in laboratory-scale experiments is required to achieve representative measurements (Iglauer & Lebedev, 2015).
Table 1

<table>
<thead>
<tr>
<th>Fluid-fluid system</th>
<th>Interfacial tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-CO$_2$</td>
<td>39.5</td>
</tr>
<tr>
<td>Water-1-Bromododecane</td>
<td>22.8</td>
</tr>
<tr>
<td>1-Bromododecane-CO$_2$</td>
<td>2.8</td>
</tr>
</tbody>
</table>

*Measured at 323 K and 10 MPa for 0.98 M (0.864 NaCl + 0.136 KCl) brine (Li et al., 2012).*  
*Measured at 330.89 K and 8.851 MPa for Ontario crude oil-Saskatchewan reservoir brine (4,270 mg/L total dissolved solids; Yang et al., 2005).*  
*Measured at 330.74 K and 13.362 MPa for Ontario crude oil (Yang et al., 2008a).*  

This is due to the CO$_2$ being in a supercritical state, in which it has an increased viscosity, a strongly increased density, and, importantly, also a strongly enhanced CO$_2$-rock wettability (e.g., Al-Yaseri et al., 2016a, 2016b; Span & Wagner, 1996; Yang et al., 2008a, 2008b).

Thus a sandstone oil reservoir at a depth of approximately 1,000 m (10-MPa pore pressure and 323-K temperature) was simulated in the laboratory. A clean homogeneous sandstone (Bentheimer) was selected, and small core plugs (5-mm diameter and 10-mm length) were drilled. The whole flood sequence was imaged for one miniature plug only. Porosity was 21.5% ± 0.5%, permeability 2,047 ± 27 mD (Saenger et al., 2016), and the rock consisted of 99 wt% quartz, 0.7 wt% kaolinite, and 0.3 wt% rutile. Initially, this rock was completely water wet at ambient conditions (0° water contact angle in air); however, oil reservoir rock is frequently oil wet (Cuiec, 1991). We thus rendered the plug oil wet (130° water contact angle measured at ambient conditions in air, cf. Rahman et al., 2016) by immersing it into slanie (Dodecyltriethoxysilane, ≥99.9 mol% purity, from Sigma-Aldrich) under vacuum and subsequently aged the plug for four weeks at ambient conditions (cp. Al-Anssari et al., 2016, Nwdee et al., 2016; Rahman et al., 2016). This process guarantees strongly oil-wet conditions in a highly reproducible way.

2.2. Pore-Scale μCT Imaging

The oil-wet plug was then placed into an X-ray transparent high-pressure μCT cell (Iglauer & Lebedev, 2018) and vacuumed for 4 hr to remove all air from the system. Subsequently oil (1-Bromododecane, which has a high CT contrast, purity ≥ 98 mol%, from Sigma-Aldrich) was injected so that the plug was fully oil saturated, and the pore pressure was raised to 10 MPa, the confining pressure to 15 MPa, and all flow lines and fluids were isothermally heated to 323 K. This was followed by injection of 50 pore volumes (PV) of water (using doped “dead” brine; i.e., 7 wt% NaI in deionized water; note that NaI is required for CT contrast) at a capillary number ($N_{\text{cap}} = \frac{\nu\delta}{\mu\gamma}$, where $\nu$ is the Darcy velocity of the injected fluid, $\mu$ is the viscosity of the injected fluid, and $\gamma$ is the fluid-fluid interfacial tension) of 3.72 × 10$^{-7}$, which was followed again by a second oil flood (50 PV of oil were injected again at a capillary number of 9.87 × 10$^{-6}$) so that a water-oil two-phase system was created, which represents an oil-wet oil reservoir at connate water saturation ($S_{\text{wc}}$) at approximately 1,000 m depth. The core plug was then imaged at $S_{\text{wc}}$ in 3D at a resolution of (3.4 μm)$^3$ with an Xradia VersaXRM μCT instrument. Afterwards 40 PV of supercritical (sc) CO$_2$ were injected at a flow rate of 0.1 mL/min, which corresponded to a capillary number of 6 × 10$^{-8}$, and the core was imaged again at initial CO$_2$ saturation ($S_{\text{og}}$). Finally 40 PV of CO$_2$-saturated “live” brine (i.e., brine thermodynamically equilibrated with CO$_2$ at 10 MPa and 323 K; El-Maghaby et al., 2012) were injected at a flow rate of 0.1 mL/min ($N_{\text{cap}} = 3.72 \times 10^{-7}$), and the sample was μCT imaged again at residual CO$_2$ saturation ($S_{\text{gr}}$). The interfacial tensions ($\gamma$) of the fluids used are tabulated in Table 1, and the related spreading coefficient of the oil was $S_{\text{spreading}} = \gamma_{\text{gw}} - \gamma_{\text{ow}} - \gamma_{\text{og}} = 13.9$ mN/m; thus, the oil tended to spread out on the water.

The μCT images were filtered with a 3-D nonlocal means algorithm (Buades & Morel, 2005) and segmented with a watershed algorithm (Schluter et al., 2014). Petrophysical properties were then measured on the 3-D images; see below.

3. Results and Discussion

3.1. Fluid Saturation and Pore-Scale Configurations

For CO$_2$ geostorage project assessment it is crucial to know how much CO$_2$ can be stored as a residual phase (Krevor et al., 2015). Indeed, some geostorage projects have been approved solely on the basis of this storage mechanism (Stalker et al., 2013). Similarly, it is vital to know how much additional oil can be produced by CO$_2$ injection (Lake, 2010). This information forms the basis of economic decisions in terms of whether CO$_2$-EOR schemes are feasible (Green & Willhite, 1998; Lake, 2010). Technically, this information is quantified by the fluid saturation $S$ (i.e., the volume fraction a fluid occupies in the pore space of the rock) and $S$ can be measured on the μCT images for the three fluids (oil: $S_{\text{oil}}$; water: $S_{\text{w}}$; CO$_2$: $S_{\text{CO}_2}$), Iglauer and Lebedev (2018).
Initially, the plug contained 64.5% oil (Table 2 and Figures 1 and S1 in the supporting information) in the pore space at connate water saturation ($S_w$). This was mainly due to the strongly oil-wet rock surface, which led to oil (the wetting phase) residing in the smallest pores and thus a high oil saturation ($S_o$). Water was present only in the large pores as it was the nonwetting phase (Oren & Pinczewski, 1995; Piri & Blunt, 2004; Soll et al., 1993); however, due to its residence in the larger pores, water saturation was significant ($S_w = 35.5\%$). The roundish shape of the water drops was caused by interfacial forces, which minimized the droplet's surface areas (sometimes distorted by pore geometry) and with that the (Gibbs) energy of the system.

This configuration represents an oil-wet oil reservoir where the capillary pressure of water is relatively low, that is, more at the top or in the center of the oil column (Watts, 1987). During CO$_2$ injection (CO$_2$ is the intermediate-wetting phase; cf Figure 1), most of these water drops were displaced by scCO$_2$. The scCO$_2$ moved into large but also intermediate-sized pores, so that an initial scCO$_2$ saturation of 41.3% was achieved, and a significant amount of oil (oil recovery factor $R_{CO_2\text{-}flood} = \frac{S_o \text{ produced by CO}_2\text{-flood}}{S_{o\text{ initial}}}$ = 29.6%) was recovered. The CO$_2$ bubbles were again roundish due to interfacial forces. From Figure 1 it can be inferred that two-pore-scale displacement processes occurred, namely, (a) a two-phase direct drainage process, where CO$_2$ directly displaced oil, and (b) a three-phase double-drainage process (Oren & Pinczewski, 1994, 1995), where CO$_2$ displaced water, which again displaced oil. This is similar to displacement processes found in N$_2$ injection processes once the ranking of the fluid phases with respect to their mineral surface wetting affinity is taken into account (i.e., N$_2$ is the nonwetting phase there and water is the wetting phase if the rock is water-wet; Scanziani et al., 2018; Khishvand et al., 2016; Iglauer et al., 2013, 2016).

Subsequently, when water was injected to residually trap CO$_2$ and to produce more oil, approximately 70% of the CO$_2$ was displaced by the water, and water remained mainly in spaces, which were previously occupied by CO$_2$ (Figure 1). This, in combination with the CO$_2$ phase morphology (cf. Figure S1), indicates that CO$_2$—as the intermediate-wet phase—is sandwiched between the oil and water phases. Thus, CO$_2$ has a layer-like structure, which has also been observed previously for the intermediate-wetting phase in analogue systems (e.g., Iglauer et al., 2013; Scanziani et al., 2018); it is therefore possible that more of this CO$_2$ is displaced as such layers can attain very thin thicknesses, although the relative permeability of such a thin layer would be very low (Keller & Chen, 2003). In addition, it is apparent from Figure 1 that now three displacement processes occurred, namely, (a) water displaced CO$_2$ directly in a two-phase drainage process, (b) water also displaced additional oil directly in a two-phase drainage process, and (c) water displaced CO$_2$, which again displaced more oil in a double-drainage process. This is somewhat different to what has been observed previously for N$_2$ systems, as there waterflooding corresponds to an imbibition process (Scanziani et al., 2018). Note that oil is hydraulically connected throughout all flooding sequences. Overall, however, significant amounts of residual CO$_2$ (13.5%) were stored, and a substantial amount of additional oil (18.6%) was recovered by waterflooding ($R_{water\text{-}flood} = \frac{S_o \text{ produced by waterflooding}}{S_{o\text{ initial}}}$ = 18.6%; Table 2).

Thus, in summary, when compared with analogous two-phase (water/CO$_2$) experiments (Al-Menhali et al., 2016; Andrew et al., 2013, 2014; Chaudhary et al., 2013; Iglauer et al., 2011; Rahman et al., 2016), it is clear that overall less CO$_2$ can be stored in oil-wet rock by residual trapping; however, it was demonstrated on the miniature core plug used here that a similar amount of CO$_2$ can be stored in three-phase systems (i.e., oil reservoirs, as opposed to aquifers). The 3-D fluid morphologies reflect this (Figure S1 in the supporting information); these phase structures were further statistically analyzed in detail in section 3.2 below.

3.2. Residual Cluster Statistics

3.2.1. Oil and CO$_2$ Cluster Size Distributions

Subsequently, the oil and CO$_2$ cluster size distributions were analyzed as they are related to remobilization and mass transfer effects. Larger clusters can be remobilized more easily (Herring et al., 2013), and they have a smaller surface area-to-volume ratio, which slows down mass transfer (Iglauer & Wülling, 2016; Jiang et al., 2016). Note that remobilization of CO$_2$ needs to be avoided (as it increases leakage risk), and mass transfer needs to be accelerated to maximize dissolution trapping—a safe storage mechanism where CO$_2$ dissolves in formation brine and sinks deep into the reservoir (Al-Khdheewai et al., 2017; Emami-Meybodi et al., 2015).
We thus analyzed these cluster distributions by counting the number $N$ of oil or CO$_2$ clusters of size (volume) $V$. The normalized frequency ($=N$/total number of oil/CO$_2$ clusters) is plotted against cluster size for each saturation state, Figure 2.

Clearly, $N$ always dropped rapidly with increasing cluster size $V$, consistent with observations made in similar experiments (e.g., Iglauer et al., 2010, 2011, 2013, 2016; Iglauer & Wülling, 2016; Georgiadis et al., 2013; Andrew et al., 2014; Geistlinger et al., 2014; Geistlinger & Mohammadian, 2015). These cluster size distributions followed power law correlations ($N \sim V^{-\tau};$ Table 3). More smaller oil clusters were counted after each flooding step, and, related to that, the cluster size distribution exponent $\tau$ significantly increased (from 1.09 to 1.35 after waterflooding, Table 3). This indicates that during the floods, larger oil clusters were split into smaller clusters, consistent with the images shown in Figures 1 and S1. A similar effect was observed for the CO$_2$ clusters. The initially largest CO$_2$ cluster was reduced from 1.45 × 10$^9$ μm$^3$ to 3.47 × 10$^7$ μm$^3$ after waterflooding, while the cluster size exponent $\tau$ increased from 1.10 to 1.20 (Table 3). Note that an increased $\tau$ value implies a higher frequency of smaller CO$_2$ bubbles, which dissolve quicker in the oil or water phase due to the increased surface-to-volume ratio (Iglauer & Wülling, 2016), thus accelerating dissolution and mineral CO$_2$ trapping.

### 3.2.2. Oil and CO$_2$ Cluster Surface Areas

The cluster surface area-volume relationship is another morphological descriptor of the individual fluid phases, and they provide information directly relevant for any mass transfer considerations (see above). Thus, the interfacial areas $A$ for each CO$_2$ and oil cluster were measured and plotted against their volume $V$; from the (log-log) graphs power law relations are evident ($A \sim V^p$; Figure 2) and as with all other measurements of this kind (Iglauer et al., 2013; Karpyn et al., 2010; Pentland et al., 2012), $p$ was always ~0.8. Note that $p = 2/3$ for a sphere, the most compact object, while it is $p = 1$ for a percolation-like cluster (Stauffer, 1979). The fluid clusters are therefore less compact than spheres as they can occupy more than one pore (cf. Figures 1 and S1) but less ramified than percolation clusters. Furthermore, $p$ was independent of the fluid and process step.

It is interesting to note that the power law exponents measured ($\tau$ and $p$) are significantly lower than predicted by percolation theory [which predicts $\tau = 2.189$ and $p \approx 1$; Stauffer, 1979; Lorenz & Ziff, 1998]. We thus conclude that simple percolation models are unlikely to deliver reliable predictions; see also Iglauer and Wülling (2016).

### 3.3. CO$_2$ and Oil Cluster Capillary Pressure Distributions

Finally, the capillary pressures ($p_c$)—which strongly influence the multiphase flow behavior through the rock (Blunt, 2017; Øren et al., 1992; Sahimi, 2011; Soll et al., 1993)—of all oil and CO$_2$ clusters were determined. Thus, the curvature ($C$) of each cluster was measured on the μCT images, and the associated capillary pressures ($p_c = \gamma C$) were calculated using the CO$_2$-oil and water-oil interfacial tensions (Table 1), as both, CO$_2$ and water, were (mainly) surrounded by oil. The accuracy of these measurements is discussed in the supporting information; note that due to the voxelized image acquired in a μCT experiment, a measurement bias is introduced that results in a high count of zero curvatures (and thus zero capillary pressures). This is thus an artifact of the μCT technology and should not be interpreted as a mixed-wet condition (the core is strongly oil wet, see section 2.1).

The capillary pressure distributions were roughly axially symmetric and bell tower shaped and always showed a narrow and high peak at zero capillary pressure (Figure 3), consistent with data reported for oil-water (Armstrong et al., 2012) and three-phase oil-water-gas (Iglauer et al., 2016) systems. Interestingly, the $p_c$ range for the oil clusters at $S_{wc}$ approximately doubled after CO$_2$ flooding, from approximately...
Figure 1. Two-dimensional slices through the rock and various fluids at different saturation states. In the raw and filtered images, oil is white, CO₂ is black, brine dark gray, and sandstone is light gray. Oil is red, brine blue, gas yellow, and rock is brown in the segmented images.
−100 to 200 kPa to −350 to 350 kPa but then stayed constant after waterflooding; this is clearly related to a broadening in curvature values of the oil drops. The $p_c$ range for the CO$_2$ clusters did not significantly change and remained at −40 to 40 kPa. Note that the interfacial curvatures were similar for CO$_2$ and oil (ranging

Figure 2. Oil (a) and scCO$_2$ (b) cluster size distribution for each saturation state. Surface area versus cluster volume for each (c) oil and (d) CO$_2$ cluster and production step. Oil (e) and CO$_2$ (f) droplet capillary pressures. Measured at 323 K and 10-MPa pore pressure.
from −15 to 15 μm²/m³); thus, the large difference in the nominal values of the CO₂ and oil capillary pressures were caused by the significantly lower CO₂-oil interfacial tension.

### 3.4. Limitations

This study was conducted at typical μCT scale; that is, the observed volume was only several cubic millimeters (cf., e.g., Blunt et al., 2013 or Iglauer & Lebedev, 2018). At field scale, additional factors including geological reservoir features, or gravity effects play a significant role, and also need to be considered (e.g., Moorat et al., 2011). Furthermore, the core was initially completely filled with oil (note that due to the strong hydrophobicity of the core it was not possible to 100% saturate it with water), which is only approximately representative of an oil reservoir core which also contains some water initially. However, the error in saturations is small. The subsequent coreflood sequence mimicked a scenario where CO₂ is directly injected into an oil reservoir, and the large number of PV used during the different flooding steps represents more the situation closer to the wellbore, while a smaller number of PV are expected to sweep deeper through the reservoir. This is, however, a limitation of the small sample used (as required by the μCT technology; Iglauer & Lebedev, 2018), and the associated very small fluid volumes (1 × PV = 40 μl). Note that no comparative study was conducted on an analogue water-wet sample (where different flow patterns are expected, e.g., Iglauer et al., 2013, Blunt, 2017), and only one full coreflood sequence was imaged with μCT.

### 4. Conclusions and Implications

CO₂ geosequestration in oil reservoirs is an attractive solution to dispose anthropogenic CO₂ while simultaneously enhancing oil recovery (Cantucci et al., 2009). However, the effectiveness of the three-phase (micro-meter) pore-scale displacement mechanism, when CO₂ is injected into a formation, and additional oil is mobilized, is only poorly understood. We thus imaged such a displacement sequence at high resolution in situ in 3-D via X-ray μCT at reservoir conditions in an outcrop sandstone core. Significant amounts of residual CO₂ saturations were achieved in an oil-wet rock (13.5%), while oil production was enhanced substantially (~50% total oil recovery was achieved). Furthermore, the residual oil and CO₂ cluster size distributions, and the cluster surface area-volume relationships followed power law distributions, similar to the situation in two-phase flow despite three-phase flow being dramatically more complex (e.g., Øren et al., 1992). We conclude that, at the pore-scale, CO₂-EOR is an efficient method to residually trap CO₂ and recover significant incremental oil.

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