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Pore Scale Observations of Trapped CO₂ in Mixed-Wet Carbonate Rock: Applications to Storage in Oil Fields

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KEYWORDS

Residual trapping, CO₂ Storage, mixed-wet carbonate, Enhanced Oil Recovery, micro X-ray
CT, carbon utilization.

11

ABSTRACT

Geologic CO₂ storage has been identified as key to avoiding dangerous climate change.
Storage in oil reservoirs dominates the portfolio of existing projects due to favorable
economics. However, in an earlier related work, *Al-Menhali and Krevor (2016)*, it was
identified that an important trapping mechanism, residual trapping, is weakened in rocks with
a mixed wetting state typical of oil reservoirs. We investigated the physical basis of this
weakened trapping using pore scale observations of supercritical CO₂ in mixed-wet
carbonates. The wetting alteration induced by oil provided CO₂-wet surfaces that served as
conduits to flow. *In situ* measurements of contact angles showed that CO₂ varied from non-

21 wetting to wetting throughout the pore space, with contact angles ranging $25^\circ < \theta < 127^\circ$; in
22 contrast, an inert gas, N_2 , was non-wetting with a smaller range of contact angle $24^\circ < \theta <$
23 68° . Observations of trapped ganglia morphology showed that this wettability allowed CO_2 to
24 create large, connected, ganglia by inhabiting small pores in mixed-wet rocks. The connected
25 ganglia persisted after three pore volumes of brine injection, facilitating the desaturation that
26 leads to decreased trapping relative to water-wet systems.

morphologies of trapped CO_2 in carbonate rocks

29 INTRODUCTION

30 In this work we have observed the pore scale fluid displacement processes underlying the
31 trapping of CO_2 in carbonate rocks in the mixed-wet state characteristic of many oil fields^{1,2}.
32 The work has direct implications for CO_2 capture and storage in oil fields where capillary
33 trapping is seen as a key mechanism underpinning the permanence of sequestered CO_2 ³. In a
34 related work, observations reported in *Al-Menhali and Krevor* [2016]⁴ found that there was a
35 significant decrease in trapping when measured over centimetre lengths of rock, amounting to
36 the aggregate response of fluids in tens of thousands of pores. There was a much larger

37 decrease in CO₂ trapping than the N₂ trapping. A hypothesis was proposed for the varying
38 response of the fluids, relating changes in pore scale contact angle to the ratio of interfacial
39 tensions in the fluid systems. In this work pore scale observations of the fluids were made to
40 evaluate this hypothesis and further elucidate the processes underlying the decreased
41 trapping.

42 Carbon capture and storage in the subsurface has been identified as a key technology for
43 reducing CO₂ emissions and avoiding dangerous climate change⁵. Ensuring sequestration
44 through the residual trapping of CO₂ as microscopic immobilized droplets (ganglia) in the
45 rock pores is a key design component of storage projects. This trapping underpins confidence
46 in the safety and permanence of the storage and contributes the majority of estimated storage
47 capacity in regional assessments⁶⁻⁹. A large body of recent work has reported observations of
48 trapping in the laboratory¹⁰⁻¹² and modeling to analyze the implications for CO₂ migration¹³
49 and storage project engineering¹⁴. A review summarizing recent work on capillary trapping
50 for CO₂ storage has been published by *Krevor et al. (2015)*³.

51 The focus of these studies has been on CO₂ injection into brine filled aquifers, which are
52 estimated to contain the largest potential for global storage capacity¹⁵. The portfolio of
53 existing projects, however, is dominated by injection into mature oil fields¹⁶. Storage in oil
54 reservoirs brings commercial advantages such as enhanced oil recovery, infrastructure that
55 can be repurposed, existing site characterization, and established traps for buoyant fluids¹⁷⁻¹⁹.
56 Because of these benefits, and uncertainty around the practical storage capacity of saline
57 aquifers which are not well characterized, a number of analyses suggest that the use of oil and
58 gas fields will be a prevailing feature of the first generation of commercial carbon storage
59 projects²⁰.

60 Due to the presence of hydrocarbon, the fluid-rock chemico-physical properties of oil
61 reservoirs, including residual CO₂ trapping, are distinct from those of saline aquifers. In a
62 saline aquifer, core flood based observations on consolidated rocks suggest that the solid
63 surfaces are water-wetting in the presence of CO₂ under a wide range of conditions, leading
64 to significant trapping^{11,21,22}. However, some observations suggest this could evolve towards
65 more CO₂ wetting with exposure time²³ and that CO₂ may become the wetting phase on
66 surfaces contacted by oil²². These measurements^{22,23} though were made on homogeneous
67 sands and idealized flat surfaces, and hence do not necessarily replicate conditions within a
68 reservoir rock.

69 Trapping in the previous related work and other works has been observed to be
70 significantly less in rocks altered by the presence of hydrocarbons^{4,24}. The trapping was less
71 for CO₂ than for another non-aqueous phase, N₂⁴. In this work we report an analysis of the
72 pore-scale ganglion distribution and contact angles of trapped CO₂ and N₂ in the same rock
73 samples used in the previous work⁴, before and after a wetting alteration with hydrocarbon.

74 The term mixed-wet is used to describe permeable rocks with non-uniform wetting
75 properties²⁵. During initial emplacement in reservoir rocks, oil preferentially fills connected
76 pore networks with larger pore throats due to capillarity. Chemical deposits from the
77 hydrocarbon phase onto the mineral surfaces of the pores alter the local contact angle at the
78 oil-water-solid interface. This results in a pore network that contains connected oil-wet
79 pathways to flow alongside water-wet pathways where hydrocarbon did not alter the surface
80 properties. This is a common oil field wetting state and it has a significant impact on flow
81 properties, especially for carbonate lithologies prevalent in oil production^{1,2}. Recent technical
82 advances in X-ray micro-tomography have allowed for the direct observation of the fluid

83 distribution in the pores. Observations using this technique have largely validated this
84 conceptual picture^{25,26}.

85 A fundamental control on multiphase fluid displacement, and the degree of trapping, is the
86 pore-scale distribution of contact angle²⁷⁻³¹. In this work we measure contact angles of fluid
87 ganglia in the rock pores after waterflooding. This is performed in samples before and after a
88 wetting alteration procedure is applied with hydrocarbons. We also show how the
89 morphology of the trapped CO₂ ganglia respond to the wetting alteration. The observations of
90 the pore scale displacement processes provides an explanation for the related core-scale
91 measurements where CO₂ trapping decreased in rocks after wetting alteration to the mixed-
92 wet state⁴.

93 MATERIALS

94 Rock Samples, Fluids, and Test Conditions

95 Miniature core flood experiments were performed on cylindrical samples of Estailades
96 limestone that were 5 mm diameter and 15-16 mm in length. These samples were obtained
97 from the conventional sized rock core samples, 3.8 cm diameter and 12 cm in length, used in
98 previous work⁴ where the characterization of the wetting state and trapping before and after
99 wetting alteration were reported. The absolute permeability of the water-wet and mixed-wet
100 core scale samples to water were 148 and 138 mD, respectively. The porosities, measured
101 with X-ray computed tomography (CT), were 29 and 28%, respectively.

102 Estailades limestone is a quarry carbonate limestone from the Estailade Formation in
103 Southeast France³². The sample consisted of 97.9% calcite and 2.1% quartz, measured by
104 Weatherford Laboratories, East Grinstead, UK. Estailades limestone exhibits a bimodal pore

size distribution with intergranular macro-pores and intragranular micro-pores, Figure S2 and S3 in the supporting information.

Carbon dioxide and nitrogen were used as the non-aqueous fluid phases in the core-flooding experiments, both with 99.9% purity (BOC Industrial Gases, UK). Nitrogen was used as a benchmark non-wetting phase to compare with results obtained using CO₂. Nitrogen was chosen because the thermophysical properties are well constrained, the viscosity is closer to CO₂ than liquid hydrocarbons, and repeat measurements did not require a cleaning step between observations. The aqueous phase fluid in each case was brine consisting of deionized water and 7 wt% Potassium Iodide (KI). For the wettability alteration, we used Arabian Medium crude oil (density=872 kg/m³ at 15 °C) with an organic precipitant, heptane with 99% purity (Sigma-Aldrich), as explained in the following section.

Core-Flooding Experimental Apparatus. The experimental apparatus is shown in Figure S1 in the supporting information. In each test, the core plug was wrapped with a layer of aluminum foil then placed in a Viton sleeve that was attached to 5 mm diameter steel end-caps placed on both sides of the sample connecting it to flow lines. The Viton sleeve was then wrapped with two extra layers of aluminum foil to prevent CO₂ from diffusing from the core sample through the Viton sleeve. This was then placed within a custom built high-pressure high-temperature carbon fiber core-holder (Airborne, The Hague, Netherlands). The core holder was wrapped with an external flexible heater (Omega Engineering, Manchester, UK, Model KH Series). The heater was connected to a custom-built PID controller and a thermocouple was fitted in the confining fluid annulus of the core-holder (Omega Engineering, Manchester, UK, Model: LMTSS-IM025U-300). The core-holder was firmly secured to a rotating stage and the flow lines were connected to the rest of the flow apparatus. The fluid flow lines were made of flexible PEEK (Kinesis, St. Neots, UK) allowing free and

stable sample rotation during image acquisition. The images were acquired using a micro CT (μ CT) scanner (Versa XRM-500 X-Ray Microscope, Zeiss X-Ray Microscopy, CA, USA).

Three high precision high pressure syringe pumps (Teledyne Isco, Lincoln, NE, USE, Model: 250XD) were used to apply confining pressure and control very low flow rates, discussed below in the Core-Flooding Test section, and maintain the pressure of a Hastelloy reactor with entrainment stirrer (Parr Instruments Co., IL, USA) at experimental pressure.

METHODS

Core-flooding. All core flooding experiments were performed at 10 MPa pore pressure. Observations were made with either CO₂ and water or N₂ and water as the two fluid phases. The CO₂ experiments were performed at a temperature of 50 °C while N₂ experiments were performed at 25 °C. Observations were made of the ganglion distribution of N₂-brine or CO₂-brine systems after an initial supercritical (sc)CO₂ or N₂ flooding stage, partially saturating the core with the non-aqueous phase, and again after waterflooding, where the remaining gas ganglia were imaged. One set of observations was made on samples that were unaltered by hydrocarbon and another set was made on samples altered to a mixed-wet state using a procedure described in the next section.

Prior to the residual trapping tests, CO₂ and brine were mixed vigorously with crushed grains of Estailades limestone in the stirred reactor at experimental conditions to equilibrate brine with CO₂ and calcite. The equilibration process minimized the potential of sample dissolution during the injection of acidified brine and represented flow in the reservoir some distance from the injection point. In each test, the core sample was placed inside the μ CT enclosure and mounted to the rotation stage and flow assembly. Then the core sample was

vacuumed to remove all air in the pore space while applying 1 MPa confining pressure. Carbon dioxide was then injected through the sample and flow lines. The CO₂ inside the pore space was then dissolved by injecting over 1000 pore volumes of brine through the sample. At this stage, the sample was fully saturated with brine and was pressurized at stages to 10 MPa, a confining pressure of 13 MPa and heated to experimental conditions, 50 °C. The brine in the pore space of the sample was then displaced with at least 500 pore volumes of brine from the reactor that was fully equilibrated with CO₂ and rock. This allowed for immiscible CO₂ displacement during residual trapping core-flooding tests.

The flow rates were 0.1 ml min⁻¹ and 0.3 ml min⁻¹ for CO₂ and N₂, respectively. Brine was injected at a lower flow rate of 0.01 ml min⁻¹. The flow rates applied during N₂, CO₂ and brine flooding resulted in similar capillary numbers, $N_c \sim 10^{-7}$. These are within the range of capillary numbers associated with oil production and groundwater flow ($10^{-9} < N_c < 10^{-6}$). These were also similar to the capillary number used in the core scale observations⁴. About 30 pore volumes (~2.5 ml) of CO₂ or N₂ were injected, and 3 pore volumes of equilibrated brine during subsequent waterflooding. This was selected to be typical of waterflooding and migration processes over the lifetime of a carbon sequestration project, on the order of 10-100 years. Two-dimensional X-ray projections were constantly taken during core flooding in order to observe fluid breakthroughs.

Rock Aging for Mixed-Wet Conditions. To alter the wetting state of the limestone core sample, an aging technique using crude oil was applied along with Amott³³ wettability measurements that have been described in detail⁴ and summarized here. The following steps were performed on the conventional sized core sample used in *Al-Menhali and Krevor* [2016]⁴.

Similar to the work of *Salathiel* [1973]³⁰ evacuated crude oil was mixed with an organic precipitant, heptane, to induce the precipitation of asphaltene, leading to the alteration of the wetting state of mineral surfaces. Before aging the rock, asphaltene precipitation observations were made with crude oil–heptane mixtures to identify an optimal ratio for inducing asphaltene precipitation, but avoiding permeability changes in the rock. The addition of heptane also improved the stability of asphaltene precipitation, preventing changes to the wetting state from washing out the deposited oil layers after multiple waterfloods. The oil mixture was made of 28% evacuated Arabian Medium crude oil and 72% heptane. Then the core sample was placed in a Hassler type core holder that was placed in an oven. A confining pressure of 1.5 MPa was applied to the sample then it was saturated with evacuated brine and heated to 70 °C. A freshly made oil mixture was heated to 70 °C and injected into the core sample at flow rates ranging from 0.1 – 5 ml min⁻¹ for 20 pore volumes with the direction of flow reversed midway. This dynamic aging technique speeds up the wetting alteration process³⁴. Saturation was not measured directly during the ageing process. The pressure differential was measured to approximately 0.1 MPa during the dynamic ageing. Using that as a constraint on the capillary pressure³⁵, from the measured capillary pressure by Hg porosimetry (see below), the oil saturation, S_o , was estimated to be in the range $0.45 < S_o < 0.60$ accessing pores down to a radius of approximately 1 µm. The Amott water ratio wettability index³³ after wettability alteration was measured to be 0.48 after nine pore volumes of brine were injected. The sample was then left (no flow) at 70 °C for 40 days for further static aging. After aging, the sample was cooled down to lab temperature for at least 24 h. Five pore volumes of heptane were then injected into the sample at room temperature at 10 mL min⁻¹ to displace the oil mixture. Heptane and brine were evaporated from the pore space of the sample by vacuum-drying the core sample at 100 °C for 3 days. Then, the sample was cooled down to lab temperature for at least 24 h. Salt that might have precipitated

from brine in the sample during drying was flushed by degassed deionized water with several pore volumes. The sample was vacuum-dried again at 70 °C for 12 h to remove water. The dry core sample was placed in a core holder and the pore fluid was pressurized to 20 MPa with CO₂ while applying 3 MPa differential confining pressure. Five pore volumes of CO₂ were injected at 20 MPa, above the minimum miscibility pressure with heptane³⁶, to displace any heptane that might have been in the pore space by means of miscible displacement. The sample was depressurized to the lab pressure and a miniature rock sample was then cored from the conventional sized sample for the pore-scale observations.

The potential for the CO₂ itself to alter the wetting state by dissolving surface agents was of primary concern in the design of the tests. In our previous work on conventional core samples⁴, alternating tests with N₂ and CO₂ were made to test if the CO₂ itself was changing the wetting state of the sample. It was found that the trapping observations were precise through several alternating cycles with CO₂ and N₂, suggesting that the wetting state was not altered by CO₂⁴.

Image Acquisition. Three-dimensional X-ray scans were taken at 4.9 μm voxel size of the entire core sample while dry (3200 projections) and after gas injection and waterflooding (800 projections) to image the initial and remaining saturations. Approximately one hour was allowed for equilibration before the ~2 hours wet scans for the entire length of the core samples with a 4.9 μm voxel size. Subsequent interior scans were taken at a smaller voxel size of 2 μm at the central location of the sample while dry (3200 projections) and after waterflooding (1600 projections) to measure advancing contact angles *in situ*. Approximately three hours were allowed for equilibration prior to the ~5 hours scans used to analyse contact angles to avoid interface relaxation during the scans. The increased number of projections for the contact angles scans were required to precisely resolve fluid-

fluid interfaces and reduce the poor signal to noise ratio inherent in taking interior tomographies. On the other hand, the lower number of projections for the wet scans (gas and waterflooding) greatly reduced the time required for image acquisition and decreased the risk of interface movement during scanning. Short scan times are especially important for CO₂ tests where long scan times could result in CO₂ diffusion through PEEK flow lines. So scan time should be minimised, but there are direct trade-offs with image quality. The settings applied here was found to be the best balance between image quality and scan time. It allowed for the acquisition of high quality images when combined with dry scans for accurate three-phase segmentation, explained in detail in the following section.

The 4.9 μm voxel size for imaging initial and residual saturations allowed for a field of view covering the entire diameter of the core sample. The entire length of the core samples (15 and 16 mm) were imaged at the same resolution by sequentially acquiring four 3D overlapping images of the sample that were then constructed and stitched together, as described in the following section. The images were then cropped vertically so that only the central 11 mm of each sample was used to avoid using data that might have been affected by inlet and outlet boundary effects, removing at least 2mm from the inlet and outlet. There may have been some impact of the sleeve boundaries where the wetting state was possibly different. For the contact angle measurements, only imagery from the central 2mm of the rock core were used, mitigating possible sleeve boundary effects. The quantitative analysis was restricted to the resulting image size of $5 \times 5 \times 11$ mm. For visualization, the images were cropped to a cuboidal volume of $550 \times 550 \times 2200$ voxels resulting in the image size of approximately $2.8 \times 2.8 \times 11$ mm.

Image Processing. The raw images were first reconstructed using a software with the Zeiss Versa XRM-500 μCT imaging system. The grey level range was manually fixed for

248 composite images to allow for precise segmentation on the stitched images. The rest of the
249 image processing was made using Avizo 9 software (FEI, Hillsboro, Oregon, USA). The
250 composite overlapping 3D images were registered, resampled and stitched together using
251 Lanczos interpolation. Then the stitched images were filtered using a non-local means edge
252 preserving filter^{37,38}. The images were then segmented using a watershed-based algorithm
253 implemented in Avizo 9³⁹. Precise three phase segmentation of scCO₂, brine and the complex
254 rock of Estailades limestone was only possible by registering the wet scan image with the
255 dry scans images of each rock sample and make two phase segmentation for each set. To
256 eliminate arbitrary voxel misidentification between rock and brine in the 800 projection wet
257 scans, the wet scan images were segmented into just two phases, with CO₂ being treated as
258 one phase and the brine and the rock as other phase. Then, the higher quality dry images were
259 registered and segmented into two phases, with solid material being one phase and the air in
260 the pore space the other phase. These two sets of segmented images were then combined for
261 the final three-phase segmentation with the difference between the segmented images being
262 the brine phase. The image processing workflow is shown in Figure S4 in the supporting
263 information. The segmented data were processed for quantifying spatial distribution and
264 volume of each phase. A sensitivity analysis of the segmentation process was made to
265 estimate the error in saturation measurements by varying the intensity thresholds within the
266 visually permissive range. In all cases, the error in saturation attributed to segmentation
267 approaches were less than 0.01. Uncertainty in the initial-residual saturation relationship was
268 dominated by precision in the flooding technique. The N₂ coreflooding tests were repeated.
269 The saturation measurements were reproducible and the variation was within ± 0.02 . The
270 average of the repeats were used and the uncertainty for all the measurements was based on
271 the precision of the repeated N₂ measurements, Figure 1.

272 **Capillary Trapping Measurement.** The volume of the remaining CO₂ was calculated by
273 counting the number of voxels of the CO₂ phase in the segmented image of the scan after
274 waterflooding. This was then converted to a remaining saturation value, $S_{CO_2,r}$, by dividing
275 this volume by the total porosity of each sample as measured by μ CT and discussed in the
276 following section.

277 **Macro and Micro Porosity Segmentation.** The apparent porosities from the dry images
278 measured by the μ CT were 10 and 14% for the water-wet and mixed-wet samples,
279 respectively. These are significantly lower than the ~29% average porosity of the same
280 samples at the core scales obtained by X-ray CT. The total porosity obtained from Hg
281 porosimetry was 30%. This large difference in total porosity is due to the presence of
282 significant sub-resolution micro-porosity in the Estailades limestone samples. At 2 μ m voxel
283 size, only the macro-pores, with average pore throat diameter of 7 μ m, are completely
284 captured by μ CT, Figure S2 in the supporting information. Both macro-pores and micro-
285 pores are apparent from mercury porosimetry. The maximum possible capillary entry
286 pressure applied during the core flooding tests were less than 0.01 MPa and well below the
287 capillary entry pressure of the micro-pores (>0.1 MPa) of the water-wet sample, so these are
288 assumed to remain saturated with brine. On the other hand, CO₂ can preferentially fill some
289 of the smaller pores that have undergone a wettability alteration, down to a 1 μ m size – these
290 may not be resolved in the scan.

291 To measure saturation from μ CT images for such rock types, the measured volume should
292 be divided by the total porosity, including that not resolved by the μ -CT scan. The total
293 porosity was estimated for each sample by segmenting the dry images into three phases,
294 namely solids, micro-pores and macro-pores, Figure S5 in the supporting information. Since
295 the carbonate samples have a monomineral matrix, the image porosity was expressed as

296 $\phi_{img} = (g_s - g_m)/(g_s - g_v)$ where g_m is the mean gray level of the filtered image and g_v
297 and g_s are the peaks' gray levels of void and the solid phases, respectively⁴⁰. The porosity
298 estimation from the μ CT images were 28 and 30% for water-wet and mixed-wet samples.
299 These are in good agreement with the 29 and 28% average porosities of the core scale water-
300 wet and mixed-wet samples, respectively, obtained using medical X-ray CT.

301 **Contact Angle Estimation.** Contact angle measurements were taken using the scans with a
302 2 μ m voxel size with 1600 projections of the central section of each sample after
303 waterflooding. The smaller voxel size resulted in a smaller field of view but allowed more
304 accurate identification of the phase interfaces. The raw images were then reconstructed,
305 filtered and segmented using a set of wet and dry scans as described in the previous sections.
306 A sub-volume was then extracted around each unique ganglion that is adjacent to an
307 apparently relatively flat surface. Then the measurements were made using a visual method
308 described in *Andrew et al.*, [2014]⁴¹ and summarized here. The segmented image was
309 processed to identify the three-phase contact line that was then projected onto the filtered
310 image. Then the filtered image was rotated to obtain a plane perpendicular to the contact line.
311 The image alignment was made where the contact line was approximately straight for a
312 perpendicular line. Finally, the apparent contact angle was measured from the resampled
313 filtered image at the point where the plane was rotated, Figure S7 in the supporting
314 information.

315

316 RESULTS

317 **Capillary Trapping.** The total averaged initial CO₂ saturations in the micro cores ($S_{CO_2,i}$)
318 were similar in both unaltered and mixed-wet samples (~29% of the pore volume) but the

319 remaining – after waterflooding – saturation ($S_{CO_2,r}$) in the mixed-wet sample ($\sim 14\%$) was
320 significantly lower than the saturation in the water-wet sample ($\sim 21\%$). The initial and
321 residual nitrogen saturations in the water wet sample were 33 and 24%, respectively,
322 comparable to CO_2 in the water-wet sample. On the other hand, the initial nitrogen saturation
323 in the mixed-wet system was 20% with a remaining saturation of 13%. Two repeat
324 measurements were made for N_2 -brine systems. The saturation measurements were
325 reproducible with a variation within ± 0.02 . The values were within the uncertainty range for
326 the initial-residual correlation measured in the larger scale rock cores, Figure 1.

327

328

329 **Figure 1.** Initial and remaining CO_2 and N_2 saturations measured in this study, colored
330 points, compared to saturations measured on the same samples at the core scale from *Al-
331 Menhali and Krevor, [2016]⁴ The solid lines show the best fit Land trapping model⁴² with
332 their respective values for the parameterization constant, C .

333

334 **Ganglia Morphology and Distribution.** None of the CO₂ ganglia, defined as clusters
335 of adjacent CO₂-filled voxels in the image, appeared connected across the water-wet sample
336 at the resolution of the micro-CT scan; instead we see many disconnected ganglia with a wide
337 range of sizes after both gas injection and waterflooding. Since the gases have a high mobility
338 compared to the displaced brine, the initial saturations are relatively low and the injected
339 phase is therefore poorly connected. The initial distribution appears disconnected for two
340 reasons: firstly, connections through pores below the resolution of the scan will not be seen;
341 and secondly, fluid rearrangement during and after injection may allow for snap-off⁴³ which
342 fragments the injected gas into disconnected cluster. In contrast, Figure 2, for the mixed-wet
343 rock some larger ganglia are seen. The morphology is also different, with thinner and more
344 extensive, almost sheet-like, trapped ganglia when compared to the water-wet cases, Figure 3.
345 As we show below, in these cases some of the pore space is CO₂-wet, which means that CO₂
346 preferentially invades the smaller pores, as opposed to the water-wet case where the larger
347 pores are filled.

348 In the mixed-wet sample, the largest ganglion of the initial CO₂ saturation was
349 $1.5 \times 10^9 \mu\text{m}^3$ accounting for 33% of the total volume of initial saturation compared to 4.7×10^8
350 μm^3 accounting for just 5% in the water-wet sample. In the water-wet rock, the largest
351 residually trapped CO₂ ganglion had a volume of $1.8 \times 10^8 \mu\text{m}^3$, but it accounted for only 2%
352 of the total volume of residual CO₂ in the water-wet sample. On the other hand, for the
353 mixed-wet sample, the largest remaining CO₂ ganglion volume was smaller, $1.0 \times 10^8 \mu\text{m}^3$,
354 but accounted for 3% of the total volume.

Figure 2. Three-dimensional rendering of the initial and remaining CO₂ saturations and their values in the water-wet and mixed-wet limestone core samples. Each CO₂ cluster is given a different color.

Figure 3. Morphologies of the largest initial and remaining supercritical CO₂ ganglia in Estailades limestone. Red represents the CO₂ ganglion inside the rock pore. The rock is rendered semitransparent while brine and smaller CO₂ ganglia are rendered transparent. (A) Initial in water-wet ($4.7 \times 10^8 \mu\text{m}^3$, 5% of the total volume of initial CO₂ saturation), (B) Residual in water-wet ($1.8 \times 10^8 \mu\text{m}^3$, 2% of the total volume of residual CO₂ saturation), (C) Initial in mixed-wet ($1.5 \times 10^9 \mu\text{m}^3$, 33% of the total volume of initial CO₂ saturation), (D) Remaining in mixed-wet ($1.0 \times 10^8 \mu\text{m}^3$, 3% of the total volume of remaining CO₂ saturation).

Ganglia size distributions were calculated from the images after waterflooding for CO₂ and N₂, in both the water-wet and mixed-wet samples. Figure 4 shows the frequency distributions of these ganglia [μm^3] normalized to the average pore body [μm^3] of each sample to account for local heterogeneity between the two samples. The pore body volumes were measured from the segmented images of dry samples at 4.9 μm voxel resolution so only the macro-porosity was captured, see Figure S2 in the supporting information. The pore bodies were separated at the pore throats using the Separate Objects module in Avizo 9 software (FEI, Hillsboro, Oregon, USA) and the average volume of the separated pore bodies was used to normalize the ganglion distribution. Image processing is described in detail in the methods section.

Under water-wet conditions, with trapping controlled by snap-off⁴³ we expect to see a power-law distribution of ganglion size consistent with percolation theory: $n(s) \sim s^{-\tau}$ where s is the ganglion size, $n(s)$ is the number of ganglia of this size and $\tau = 2.2$ is the percolation (Fisher) exponent⁴⁴. This relationship has been observed for a wide range of samples⁸ and matches our water-wet data for intermediate sizes. There is less trapping of smaller ganglia thanks to cooperative pore filling⁴⁵. The large ganglion sizes were at least as big as predicted by the percolation theory with some trapping of larger-than-expected ganglia^{22,46-48}. This may be caused by incomplete displacement of the non-wetting phase or finite-size effects.

For the altered wettability samples, we see a different distribution, with far fewer smaller clusters, but similar numbers of larger ganglia. This is consistent with a model of little pore-space trapping. Carbon dioxide as a wetting phase retains connectivity through large ganglia occupying the smaller pore spaces or wetting layers, as seen in pore-scale images of oil-wet media^{24,26,46}. If anything, we are likely to under-estimate the size of the larger ganglia: CO₂ may preferentially fill some of the smaller pores that have undergone a

392 wettability alteration, down to a 1 μm size – these may not be resolved in the scan. Indeed, it
 393 is likely that the larger ganglia are still connected across the rock, allowing further
 394 displacement to even lower saturation were waterflooding to continue³⁰.

395

396 **Figure 4.** Frequency distributions of the ganglion volume of remaining (after imbibition)
 397 CO₂ saturations in the water-wet sample (white circles) and mixed-wet sample (black
 398 circles). The ganglion distribution is normalized to the average pore body of each sample.
 399 The dotted line plotted against the ganglion distribution in the water-wet sample represent the
 400 percolation theory power-law distribution with the Fisher exponent, $\tau = 2.2$, for comparison.

401 **Contact Angles.** Contact angles were estimated from the X-ray images at the end of
 402 waterflooding at a 2 μm voxel resolution. A total of 55 angles were measured following the
 403 approach of *Andrew et al.*, [2014]⁴¹ and described in the methods section. The distributions of
 404 angles observed for the different wetting states are shown in Figure 5. Contact angle
 405 measurements of CO₂ in the water-wet sample had an average value of 34°, as measured in
 406 the water phase, and a standard deviation of 8°. Nitrogen contact angles were slightly larger

on average, 45°, with a standard deviation of 7°. Both cases represent water-wet conditions, consistent with previous measurements⁴¹.

Figure 5. *In situ* contact angle measurements (black circles) and their average (red stars) for each fluid pair in the water-wet and mixed-wet samples. (B) Six contact angles measured in the CO₂ phase (yellow lines) with their corresponding values in the brine phase (white text), showing a wide distribution of contact angle values for trapped CO₂ in the mixed-wet limestone sample with (B1 and B2) strongly water-wet, (B3 and B4) intermediate-wet and (B5 and B6) wetting to CO₂.

There was an increase in both the value and range of contact angles for both N₂ and CO₂ systems in the altered wettability rock. The measurements of CO₂ in the mixed-wet rock had the widest distribution, $25^{\circ} < \theta < 127^{\circ}$ (angles measured through the aqueous phase), ranging from strongly water-wet to CO₂-wet, with an average of 94°, and standard deviation of 30°, Figures 5 and 6. The N₂ system was less significantly impacted by the wetting state alteration with average contact angle value of 50° and a standard deviation of 13°, indicating that the system remained water-wet to N₂ in this case.

Figure 6. Six contact angles measured in the CO₂ phase (yellow lines) with their corresponding values in the brine phase (white text), showing a wide distribution of contact angle values for trapped CO₂ in the mixed-wet limestone sample with (1 and 2) strongly water-wet, (3 and 4) intermediate-wet and (5 and 6) wetting to CO₂.

The contact angles of the CO₂ and N₂ systems were compared at the same location in the rock for surfaces both altered and unaltered by hydrocarbon, Figure 7. The CO₂ was more wetting on the altered surface, whereas less wetting in the unaltered surface when compared to N₂ contact angles. The main finding though is that for a rock whose wettability has been altered by crude oil, a wide range of contact angle for CO₂ is seen, from water-wet to CO₂-wet. The pore-scale manifestation of this effect is shown in Figure 7.

Figure 7. Contact angles measured in the brine phase comparing CO₂ and N₂ wetting strengths at the same location in the two samples, A and B. (A1) Contact angle of CO₂-brine in the water-wet sample measured at 28°. (A2) Contact angle of N₂-brine in the water-wet sample measured at 44°. (B1) Contact angle of CO₂-brine in the mixed-wet sample measured at 117°. (B2) Contact angle of N₂-brine in the mixed-wet sample measured at 43°.

The pore-scale explanation of the behavior comes from the Bartell-Osterhof equation⁴⁹ that relates interfacial tensions and contact angles: $\sigma_{gw}\cos\theta_{gw} = \sigma_{go}\cos\theta_{go} + \sigma_{ow}\cos\theta_{ow}$, where σ is the interfacial tension, θ the contact angle, while o labels the oil phase, w the water (brine) phase and g the N₂ or CO₂. It is generally assumed that N₂ or CO₂ is non-wetting to oil such that $\sigma_{go}\cos\theta_{go} > 0$; however, at reservoir conditions, oil and CO₂ may become partially miscible meaning that σ_{go} is much lower for CO₂ than for N₂. Furthermore, σ_{gw} is also lower for CO₂ (37 mN/m, as opposed to 67 mN/m for N₂)^{50,51}. On an altered wettability surface, the solid is coated with oil-like components and in places we see $\cos\theta_{ow} < 0$. For N₂, the higher value of the gas/oil interfacial tension appears to retain water-wet conditions, $\sigma_{gw}\cos\theta_{gw} > 0$, while for CO₂ $\sigma_{gw}\cos\theta_{gw}$ may become negative, giving an apparently CO₂-wet surface.

At reservoir conditions, oil and CO₂ may become partially miscible, lowering the interfacial tension between gas and oil. The minimum miscibility pressure will likely be in the range of 8-17 MPa at 50 °C for a light oil, generally suitable for CO₂ enhanced oil recovery^{52,53}. Light oil was also used in the aging experiments and this ensured that the gas-oil interfacial tension was much lower for CO₂ than for N₂. In the case of the trapping experiments of this study there were only two mobile phases at a given time, CO₂ or N₂ and brine. The use of the oil-phase here is to obtain information about the contact angles of CO₂-water and N₂-water relative to each other on an oil-wet surface, but we emphasize that the

hypothesis does not require three flowing phases: if gas and oil are indistinguishable, then wherever a surface is wetting to oil, then will be wetting to the gas phase as well.

The exact nature of the wettability alteration will depend subtly on the local conditions and pore-scale morphology²⁵ meaning that we expect a range of contact angle. The larger contact angles measured for CO₂ prevent snap-off⁴⁵, leading to relatively less trapping of small ganglia, as seen in Figure 4, and may allow the formation of CO₂ layers, which accommodate slow drainage down to low saturation.

Environmental Implications. In this work we have shown that a wide variation in pore scale contact angles co-exist in rocks with mixed wettability. The previously hypothesized⁴ relationship of contact angle change to interfacial tension of the N₂ and CO₂-brine systems was found to be too simple to explain the response observed at the pore scale. It was confirmed that trapping of both CO₂ and N₂ in the altered rock decreased due to an increased wetting of the surfaces by N₂ and CO₂. It was also shown that CO₂ trapping decreased more than N₂ trapping because CO₂ became more wetting than N₂ in the altered rocks. On the other hand, no contact angles were found identifying N₂-wet surfaces as contact angle is conventionally measured and interpreted. The impacts of the change in contact angles allows for CO₂ to form long connected flow pathways through smaller channels that persist after several pore volumes of brine injection, in contrast to the water-wet system where snap off quickly isolates the ganglia from flow. These are the conduits for continued desaturation of the CO₂ that lead to the significant decreases in capillary trapping.

There are significant opportunities presented by the use of existing hydrocarbon reservoirs for CO₂ storage¹⁶⁻²⁰. In this work we have evaluated trapping at capillary numbers (fluid flow rates) and under reservoirs conditions typical of reservoirs targeted for CO₂ enhanced oil recovery. Given the central role that capillary trapping has played in assessments and the

development of CO₂ storage³, it is important to analyze the performance of the reservoir system in the context of significantly weakened capillary trapping.

ASSOCIATED CONTENT

Supporting Information. A schematic of the experimental apparatus. Mercury porosimetry of the sample. Images of Estailades limestone sample at different scales from μ CT, thin section and SEM. A figure summarizing three phase image segmentation sequence of the wet scans aided by the dry scans. A figure summarizing three phase segmentation sequence of the dry scans of carbonate rock samples to account for micro porosity. A figure showing an example of μ CT central cross sectional images before and after segmentation. A figure explaining the contact angle estimation process. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

A.A. and S.K. conceived the study and designed the experimental programme. A.A. carried out the tests with H. M. assisting with micro CT imaging. A.A. carried out the analysis in discussion with S.K. and M.B. A. A. led the writing of the paper with input and review from all of the authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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morphologies of trapped CO₂ in carbonate rocks

Water-wet

Mixed-wet