Capillary Trapping of CO_2 in Oil Reservoirs: Observations in a Mixed-wet Carbonate Rock

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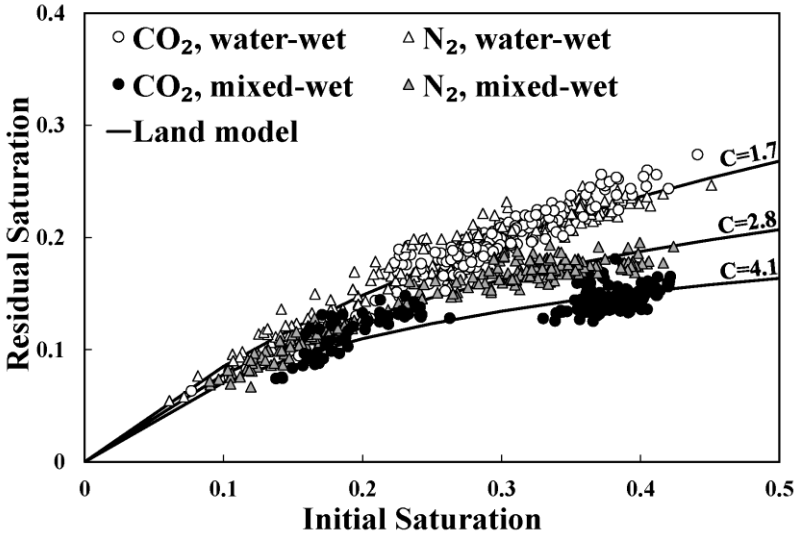
KEYWORDS

Residual trapping, capillary trapping, remaining saturations, mixed-wet, supercritical CO_2, CCS, EOR, X-ray, carbon utilization.

ABSTRACT

Early deployment of carbon dioxide storage is likely to focus on injection into mature oil reservoirs, most of which occur in carbonate rock units. Observations and modeling have shown how capillary trapping leads to the immobilization of CO_2 in saline aquifers, enhancing the security and capacity of storage. There are, however, no observations of trapping in rocks with a mixed-wet state characteristic of hydrocarbon bearing carbonate reservoirs. Here we found that residual trapping of supercritical CO_2 in a limestone altered to a mixed-wet state with oil was significantly

less than trapping in the unaltered rock. In unaltered samples, the trapping of CO_2 and N_2 were indistinguishable, with a maximum residual saturation of 24%. After altering the wetting state, the trapping of N_2 was reduced, with a maximum residual saturation of 19%. The trapping of CO_2 was reduced even further with a maximum residual saturation of 15%. Best fit Land model constants shifted from $C = 1.73$ in the water-wet rock, to $C = 2.82$ for N_2, and $C = 4.11$ for the CO_2 in the mixed-wet rock. The weakened trapping indicates that plume migration will be farther and the timescales for immobilization will be longer for CO_2 storage projects using oil fields compared with saline aquifers.



INTRODUCTION

The capture of carbon dioxide emitted from industrial processes and subsequent storage in subsurface geologic units has been identified as a key technology in the global reduction of anthropogenic CO_2 emissions to the atmosphere[1]. Capillary trapping, also called residual trapping, is one of the most significant physical mechanisms ensuring the permanence of CO_2

storage in the subsurface[1,2]. Capillary trapping limits the extent of CO_2 migration[3,4], underpins estimates of regional storage capacity[5-8] and controls the movement of the mobile sections of a subsurface plume through its relationship with fluid flow property hysteresis[4,9,10]. Thus a significant body of recent work has focused on observations characterizing capillary trapping[2], including in carbonate rocks[11].

Saline aquifer storage presents the largest potential for global CO_2 storage capacity[12] and the focus of the previous observations has been on the characterization of rocks unaltered by hydrocarbons. On the other hand, oil fields have a number of characteristics that could lead to their having an outsize importance during the early deployment of carbon storage. Commercial oil fields are well characterized, have a demonstrated fluid trap, and sometimes have infrastructure that can be repurposed for use with CO_2 injection[13,14]. Enhanced oil recovery with CO_2 injection may also provide for a significant revenue stream. These benefits are reflected in the dominance of enhanced oil recovery in the current portfolio of existing industrial scale sequestration projects[15].

The capillary properties of rocks typical of saline aquifer systems - unaltered by hydrocarbons - are considered water-wet with respect to CO_2-brine systems across wide range of reservoir conditions[16], although some important questions remain including the impact of chemical process kinetics on the wetting state[17,18]. In contrast, hydrocarbon reservoirs are characterized by a mixed-wet state, wherein chemical deposits from the hydrocarbon phase onto the surface of the pore mineral surfaces over geologic time have resulted in connected oil-wetting conduits to flow[19]. This has a significant impact on the flow properties of the system, including the capillary pressure, relative permeability, and residual trapping characteristic functions[20-22].

Of key importance for the security of CO_2 storage is that the capillary trapping of nonpolar fluids, like CO_2, have been observed to be significantly less in mixed wet rocks than trapping in water wet rocks typical of saline aquifers[23-25]. This issue has been largely ignored in the flow modelling literature for CO_2 storage and there are no observations characterizing the extent of capillary trapping that will take place with CO_2 in mixed-wet rocks. In this work we provide the first observations that a key trapping mechanism underpinning the security of CO_2 storage is significantly reduced in the very storage locations that are among the most economically appealing for the first generation of project development.

The key aim of this study was to evaluate the impact of the wetting state typical of carbonate oil reservoirs on trapping for CO_2 storage. We have done this by characterizing the trapping of supercritical CO_2 in a mixed-wet carbonate rock, comparing this with the degree of trapping in the same rock prior to alteration to the mixed wet state. We focused on a carbonate rock because of the prevalence of carbonate lithology in oil production[26,27]. To isolate the effects of wetting alteration from fluid-rock chemical reaction and mass transfer, the CO_2 and brine were equilibrated together with crushed samples of the rock prior to observations of trapping. Experiments were also performed with N_2 –water systems in unaltered and altered samples as a benchmark for comparison.

MATERIALS

Rock Samples, Fluids, and Test Conditions. A total of 14 core flood experiments were carried out on two Estaillades limestone core samples before and after alteration with a

76 hydrocarbon mixture. The sequence of experiments, fluid pairs, and drainage flow rates are
77 provided in Table 1.

78 Estaillades is a quarry carbonate limestone from the Estaillade Formation located in southeast
79 France[28]. The sample consists of 97.9% calcite and 2.1% quartz, measured by Weatherford
80 Laboratories, East Grinsted, UK. The faces of the core were machined flat to ensure contact with
81 the end-caps. Each sample was vacuum dried at 70 ^{o}C overnight before each test.

82 A single sample, E1, was used to compare trapping between water-wet and mixed-wet
83 systems. Observations were first made on the sample unaltered by hydrocarbon, and again after
84 altering the wetting state to a mixed-wet state using a procedure described in more detail below.
85 A second sample, E2, was used for a reproduction of observations in the unaltered rock. Both
86 samples were 3.8 cm in diameter and 12 cm in length. The absolute permeability of the E1 and
87 E2 samples to water were 138 and 148 mD, respectively. The average porosities as measured
88 with X-ray computed tomography (CT) were 28 and 29% for the E1 and E2 samples,
89 respectively.

90 Carbon dioxide and nitrogen were used as the non-polar fluid phases in the core-flooding
91 experiments, both with 99.9% purity (BOC Industrial Gases, UK). Nitrogen was used as the
92 benchmark nonwetting phase primarily because the thermophysical properties, including the
93 wetting state in unaltered carbonate rocks, was well constrained. There were other considerations
94 – the viscosity of N_2 is more similar to that of CO_2 than a typical benchmark hydrocarbon liquid
95 like decane. The use of N_2 allowed us to perform experiments in sequences alternating fluid pairs
96 without the need for a solvent based cleaning of the rock core, a process which may have altered
97 the wetting state and put further stress on the rock. The aqueous phase fluids used were

deionized water or brine consisting of deionized water and NaCl with total salt molality of 1 mol kg^{-1}. Arabian Medium crude oil (API=30.77°) and heptane with 99% purity (Sigma-Aldrich) were used for the wettability alteration and Amott tests[29]. Toluene with 99.8% purity (Sigma-Aldrich) was used as a solvent in the filtration experiments made prior wetting alteration to measure asphaltene precipitation of the crude oil.

All core flooding experiments were performed at 10 MPa pore pressure. The CO_2-brine experiments were performed at a temperature of 50 °C while N_2-water experiments were at 25 °C. The thermophysical properties of the fluids are provided as follows: The interfacial tension value of CO_2 and brine at the experimental condition was estimated to be 37 mN/m[30] while N_2 and water interfacial tension value was 67 mN/m[31]. The CO_2/brine and N_2/water viscosities were estimated to be 0.03/0.61 and 0.02/0.89 cP, respectively[32,33]. The CO_2/brine and N_2/water densities were estimated to be 0.39/1.02 and 0.11/1.01 g/cm^3, respectively[33].

Table 1. Initial-residual core flooding experiments and repeats in the chronological sequence that they were performed.

Experiment number[a]	Sample name / wetting state	Fluid pairs	Drainage flow rate[b] [ml min^{-1}]	Pore volumes injected during imbibition
1	E1 / water-wet	*N_2 / water*	0.5	0.25
2	E1 / water-wet	*N_2 / water*	20	0.17
3	E1 / water-wet	*N_2 / water*	-[c]	0.63
4a	E1 / mixed-wet	*N_2 / water*	20	0.2
5a	E1 / mixed-wet	*N_2 / water*	0.5	0.36
6a	E1 / mixed-wet	*CO_2 / brine*	20	0.2
7	E1 / mixed-wet	*CO_2 / brine*	0.5	0.63
4b	E1 / mixed-wet	*N_2 / water*	20	1.29
5b	E1 / mixed-wet	*N_2 / water*	0.5	1.71
8	E2 / water-wet	*N_2 / water*	20	0.45
9a	E2 / water-wet	*CO_2 / brine*	20	0.44

9b	E2 / water-wet	*CO_2 / brine*	20	0.98
10	E2 / water-wet	*CO_2 / brine*	0.5	0.23
6b	E1 / mixed-wet	*CO_2 / brine*	20	0.23

[a] Experiments with a common number indicate repeat tests on the same sample, at the same wetting state, and fluid flow condition, i.e., test 4b is a repeat of test 4a, but after the rock core has been exposed to CO_2 during tests 6a and 7.

[b] Imbibition was at 0.5 ml min^{-1} for all experiments

[c] Experiment 3 was initially fully saturated with N_2 instead of water. Water was subsequently injected at 0.5 ml min^{-1} to measure the initial-residual relationship at 100% initial gas saturation

Core-flooding Experimental Setup. Residual trapping measurements were conducted using a two fluid phase core flooding system described in detail in previous papers by the authors[16]. The experimental setup was designed to maintain temperature and pressure conditions of up to 120 ºC and 30 MPa. The system was modified for experiments with carbonates samples and included a stirred reactor to equilibrate fluids with ground sample of the solid (Parr Instruments Co., IL, USA). A schematic is provided in the supporting information.

METHOD

Core-flooding Test and Sequence. A core flooding technique[34] was applied in this work for the construction of initial-residual characteristic trapping curves. The technique combines the deliberate creation of capillary pressure gradients in the core with in-situ saturation monitoring to rapidly construct the initial-residual curve across a range of saturations. A detailed description of the startup and operation of the experiment is provided in the supporting information and summarized here.

To create the initial saturation, a primary drainage step was performed, injecting CO_2 or N_2 at a constant rate of either 0.5 or 20 ml min^{-1} into an initially water or brine-saturated core sample, Table 1. The choice of flow rate was made at different stages in the experiment to cover a particular range of the initial-residual curves – larger flow velocities during drainage result in larger initial saturations. X-ray scans were then performed to evaluate the initial saturation along the length of the rock core. Imbibition was then performed by injecting brine or water, pre-equilibrated with CO_2 and the limestone sample, at 0.5 ml min^{-1}. Saturations were calculated at each stage with X-ray CT using the standard approach[35] detailed in the supporting information. Several scans were taken to confirm measurements of imbibition and to reduce the uncertainty associated with the computed saturations.

To minimize the impact of calcite in the rock dissolving into the acidified brine, the brine was pre-equilibrated with both CO_2 and the rock material at the experimental conditions prior to the residual trapping test. The fluids were mixed vigorously together with crushed grains of the same rock in a Parr stirred reactor at experimental conditions for 24 hrs. Then, this CO_2 and brine were co-circulated at experimental conditions in a closed loop bypassing the core, but including circulation through the reactor. The dissolution of CO_2 into water was monitored by observing the volume balance of the fluid phases in the closed loop, maintained at constant pressure. X-ray imaging was used to confirm that the porosity was not changing during the tests. A comparison of the repeatability of the results of N_2 tests before and after CO_2 flooding tests also supported the view that the rock core, and its wetting state, were not significantly altered by the exposure to CO_2. The absolute permeability to water was measured before each experiment and varied less than 4% throughout the series of tests suggesting minimal changes in the pore structure of the core sample throughout the entire course of experiments. The slice average porosity along the entire length of

core was also measured at a resolution of 1 mm after each test with X-ray scanning providing another confirmation that rock properties were not significantly altered.

The sequence of tests were designed to test the impact of altering the wetting state and confirm that variations in observations were due to the change in wetting state. See Table 1. Tests 1-3 were used to construct the initial-residual curve for sample E1 using N_2 with the rock in the natural state, unaltered by hydrocarbon. The wetting state was altered as described below and subsequent tests characterizing the initial-residual curve were performed first using the N_2-water system (tests 4a, 5a) and then the CO_2-brine system (tests 6a, 7). Repeat tests were then performed with N_2 (tests 4b, 5b) to assess the impact, if any, of CO_2 exposure to the altered wetting state. A final repeat test was performed with CO_2 (6b) to test repeatability of the residual trapping at high initial saturation with CO_2.

At the outset of the study, we hypothesized that the N_2-brine and CO_2-brine initial-residual curves would match based on previous experience[34]. As will be discussed in the results, this turned out not to be the case for the initial residual curves obtained after altering the rock with hydrocarbon. To ensure that this effect was a result of the wetting state change, and not the propagation of a feature of CO_2 and N_2 trapping in unaltered carbonates, another set of tests was performed on a second sample of unaltered Estaillades rock comparing N_2 and CO_2 trapping, tests 8-10.

Injected pore volumes were kept to a minimum due to the corrosive nature of the fluids and the relative fragility of the rock under the test conditions. This is a particular difficulty of scientific studies using reservoir condition core floods – a single rock sample must endure a sequence of tests which place significant stress on the rock. In water wet systems, a single pore volume is

177 sufficient to achieve the residual saturation[34], whereas hundreds or even thousands of injected pore
178 volumes are required to achieve the true residual in mixed-wet systems[24]. In both water-wet and
179 mixed-wet systems there is an initial rapid desaturation of the non-wetting phase with less than
180 one pore volume of fluid injected. In the mixed-wet case, however, this is followed by a very slow
181 rate of desaturation during subsequent brine injection. In the tests performed in this work, the
182 initial rapid desaturation was monitored using X-ray scanning. The point of comparison of the
183 initial-residual curves was made using saturation measurements obtained following this initial
184 phase of rapid desaturation, generally between 0.25 and 1.5 pore volumes of brine injected, Table
185 1. The saturation of CO_2 in a mixed-wet system after such volumes of imbibition will be similar
186 to saturations in a field setting far from the well where the CO_2 has been injected. However, the
187 ultimate residual in the mixed-wet systems, should they ever be obtained, will be lower than the
188 reported values obtained in this work.

189 **Altering the Wetting State of the Rock.** After completing observations with the unaltered E1
190 sample, an aging technique using crude oil was applied to change the wetting state of the core
191 sample. An approach similar to Salathiel 1973[24] was performed by preparing a mixture of the
192 evacuated crude oil with an organic precipitant, heptane. The addition of heptane induces the
193 precipitation of asphaltene, leading to the alteration of the wetting state of mineral surfaces. Before
194 aging the rock, observations were made with crude oil-heptane mixtures to identify ratios of fluid
195 resulting in sufficient asphaltene precipitates to induce the wetting state change, but not so much
196 that permeability of the rock core is significantly reduced. A detailed description is provided in the
197 supporting information.

198 The core sample was fully saturated with evacuated brine and heated to 70 ^{o}C. A freshly made
199 oil mixture of 28% evacuated Arabian Medium crude oil and 72% heptane was heated to 70 ^{o}C

200 and injected into the core sample for a total of 20 pore volumes with the direction of flow reversed
201 midway to dynamically age the sample and speed the wetting alteration process[36]. The flow rates
202 ranged from 0.1 ml min^{-1} and up to 5 ml min^{-1}. The sample was then left for further static aging
203 (no flow) at 70 ^{o}C for 40 days. Then, the sample was cooled down to room temperature for at least
204 24hrs. The oil mixture was displaced with 5 pore volumes of heptane injected at 10 ml min^{-1} at
205 room temperature. The core sample was then vacuum dried at 100 ^{o}C for three days to remove
206 heptane and brine from the pore space by evaporating the fluids (heptane and water). Then the core
207 sample was cooled to room temperature. Degassed deionized water was flushed into the sample
208 for several pore volumes to remove salt that might have precipitated in the sample during drying.
209 The sample was vacuum dried again at 70 ^{o}C for 12 hours to remove water. Finally, to ensure
210 mobile oil was completely displaced, 5 pore volumes of CO_2 was injected at 20 MPa[37]. Next we
211 performed the initial-residual core flood tests.

212 After completing the initial-residual core flooding experiments, the wetting properties of the
213 mixed-wet (E1) and water-wet (E2) samples were measured by carrying out a standard Amott
214 test[29] using Heptane and brine. Details of the test are provided in the supporting information. The
215 Amott water ratio wettability index, δw, was measured to be $\delta w = 0.48$ and $\delta w = 0.89$ for E1 and
216 E2, respectively, after nine pore volumes of brine injected. The high δw value of E2 is indicative
217 of a strongly water-wet system where spontaneous imbibition leads to most of the oil in the sample
218 displaced by water. On the other hand, spontaneous and forced imbibition produced comparable
219 volumes of oil in the E1 sample resulting in a wettability index value similar to those measured in
220 giant carbonate oil fields in the Middle East characterized as mixed-wet systems[38]. Additionally,
221 the water-wet sample (E2) produced little oil after water breakthrough and quickly reached residual
222 oil saturation. On the other hand, in the mixed-wet sample (E1) oil production continued for the

entire nine pore volumes of water injected, and likely would continue with continued brine injection. The displacement followed the pattern of a rapid desaturation with less than a single pore volume of brine injected, followed by a slow rate of desaturation with continued brine injection.

Trapping Model. A large number of models have been developed for describing the initial-residual relationship[39]. The Land model was used to fit the trapping data. It is one of the earliest and most widely used trapping models[40]. The residually trapped non-wetting phase saturation after imbibition, $S_{CO_{2,r}}$ is an increasing function of the maximum non-wetting phase saturation achieved during drainage, $S_{CO_{2,i}}$,

$$S_{CO_{2,r}} = \frac{S_{CO_{2,i}}}{1+CS_{CO_{2,i}}}, \quad (1)$$

where C is a constant known as the Land coefficient and is equal to or greater than zero. Larger values of the constant indicate less trapping. Some models, e.g., the model of Spiteri et al. (2008)[41] have been proposed specifically for mixed-wet systems. In this case we found the Land model to fit our observations well. The data can in principle be fit using any of the alternatives.

RESULTS

Figure 1 shows examples of the slice average saturation along the rock core with corresponding two dimensional saturations maps of a central slice of the core for three of tests with high drainage flow rates. These graphs were generated for each experiment and used to quality check the results. The saturation maps show that CO_2 and N_2 were uniformly distributed in the core sample in central

parts of the core where the residual trapping was characterized, and not affected by mass transfer or gravity segregation. The slice averaged saturations of the water-wet systems showed a declining trend towards the outlet due to the capillary end effect. On the other hand, the saturation profiles in the same rock sample after wetting state alteration exhibited an end-effect behavior, either with no decline or increasing non-wetting phase saturation, characteristic of the mixed-wet state. The drainage profiles were relatively uniform and saturation increased towards the outlet during imbibition. Data from the central ~60 mm of the rock core were used to construct the initial-residual curves to avoid the interference of the boundary affects.

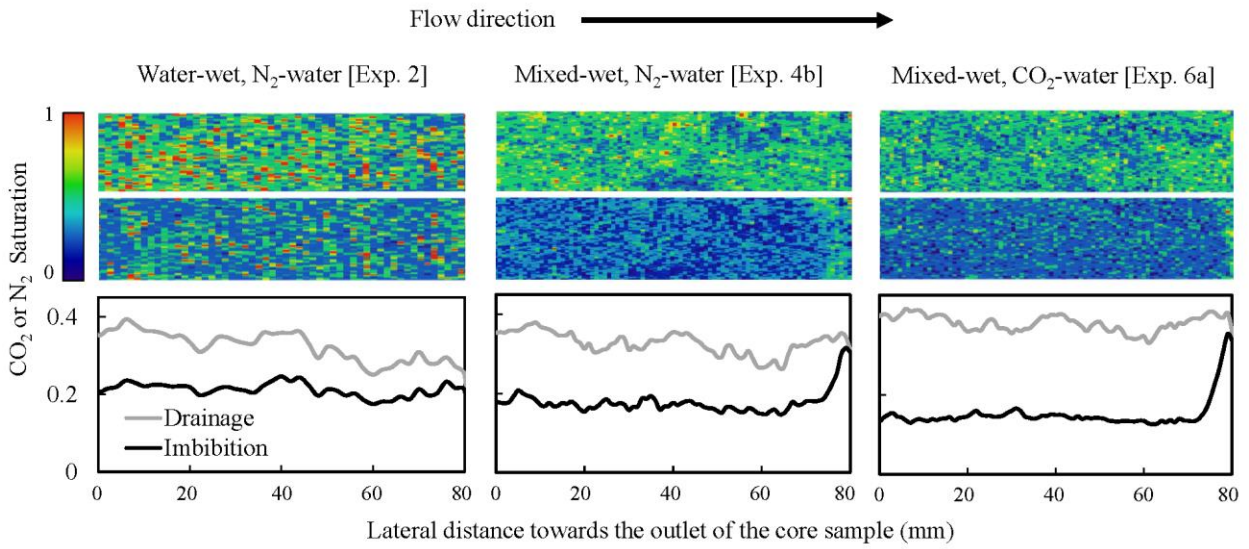


Figure 1. 2D saturation maps of the central slice of the core after drainage (top) and imbibition (middle) for three experiments on the same sample. The core average saturation of the final section of the core sample is shown in the lower graphs. The end-effect changes after the wettability alteration.

In previous work it was confirmed that residual trapping in the water wet case was obtained rapidly, with less than a pore volume of brine injected, and remained stable for more than 40 pore

volumes of subsequent brine injection[34]. In this work the initial rapid desaturation was again observed in tests with both the water wet and hydrocarbon altered rock. The subsequent stability of the residual saturation in the water-wet rock, and the slow and persistent desaturation of non-wetting phase in the altered rock, was then confirmed with the forced injection part of the Amott test shown in Figure 2.

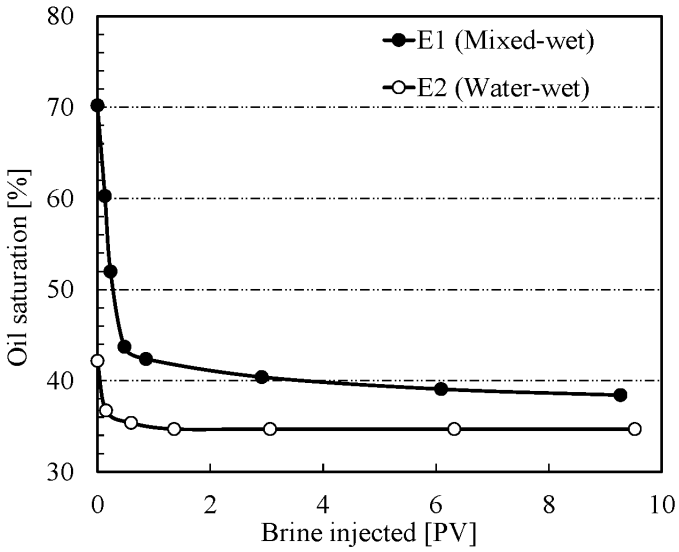


Figure 2. Results from the forced imbibition part of the Amott test showing oil saturation as a function of the pore volumes (PV) of brine injected, applied after 30 days of spontaneous imbibition. The water-wet sample (E1) produced little oil after water breakthrough while the mixed-wet sample (E2) continued oil production with a reducing remaining oil saturation trend as a function of PV injected.

Figure 3 shows initial-residual characteristic curves measured in this study with best fit curves using the Land model, Equation 1. Table 2 shows the best fit parameters for the Land hysteresis model. The trapping of CO_2 and N_2 in the unaltered samples, Experiments 1-3, 9-10, were indistinguishable, with best fit Land constants equivalent within the uncertainty bounds, Table 2.

This was consistent with earlier work[34] characterizing CO_2 trapping in unaltered sandstone rocks and suggests that the wetting state is similar for the two systems[16], but contrasts with observations made using a different technique in which more trapping was observed for supercritical CO_2 relative to gaseous CO_2 in an unaltered limestone [11]. The best fit Land constant for all of the data (both CO_2 and N_2) in the water wet tests was $C = 1.73$. At the highest initial saturations observed, 42% of the pore space, the residual saturation obtained was 24%.

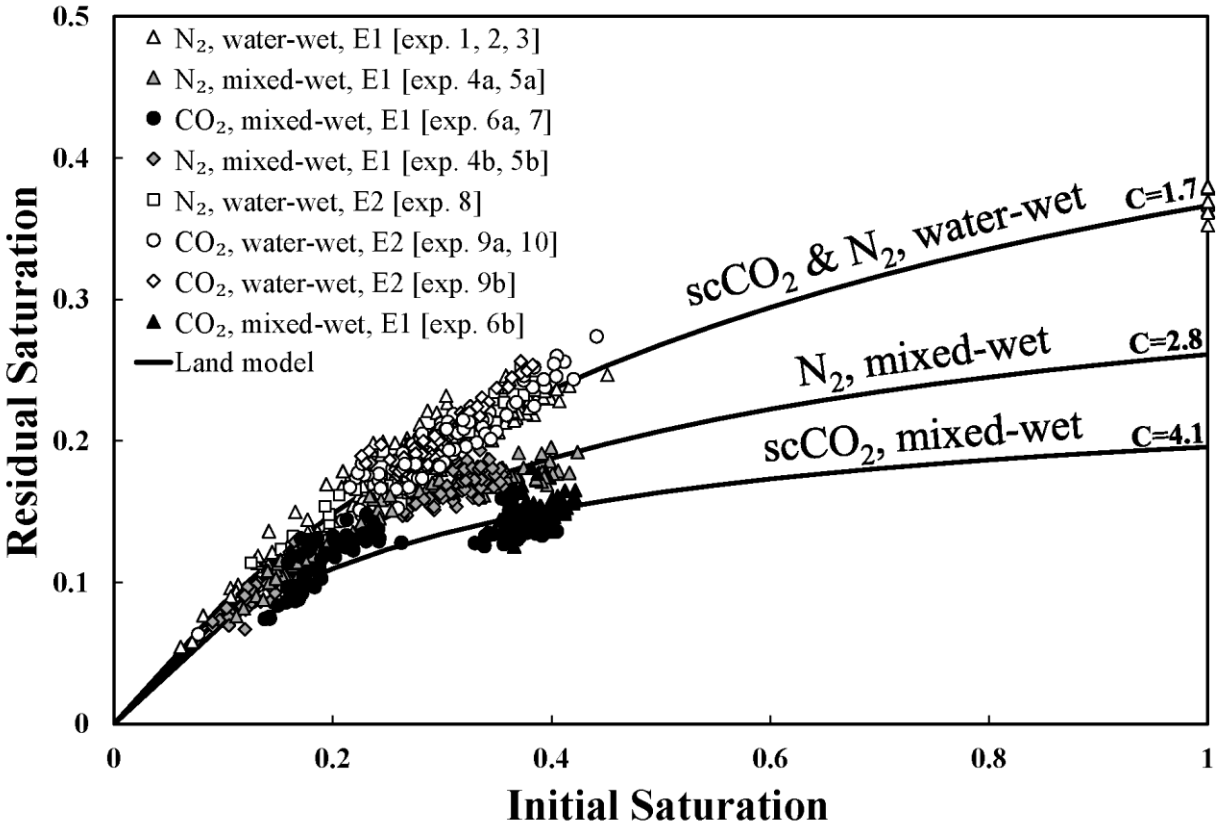


Figure 3. Initial and residual CO_2 and N_2 saturations measured in this study. White symbols are observations from the unaltered rock. Grey symbols are observations of N_2-water from the mixed-wet rock. Black symbols are observations of CO_2-brine from the mixed-wet rock. The solid lines show the best fit Land trapping model with their respective values for the parameterization

284 constant, C. The order of the experiments in the legend shows the sequence in which the
285 observations were made.

286 After alteration of the wetting state of the rock sample with the crude oil-heptane mixture, less
287 trapping was observed with both N_2 and CO_2, Experiments 4-7. The value of the best fit Land
288 constant increased from 1.68 to 2.83 for N_2 after 0.2 – 1.7 pore volumes of brine injected into the
289 core. The initial-residual relationship for N_2 was obtained in repeated tests before (Experiments 4a
290 and 5a) and after (Experiments 4b and 5b) tests with CO_2. The data were indistinguishable, with
291 Land constants $C = 2.86 \pm .06$ and $2.80 \pm .06$ from the datasets obtained before and after exposure
292 of the altered rock to CO_2, respectively. This suggests that exposure to CO_2 did not alter the wetting
293 state of the rock sample.

294 The trapping of CO_2 was reduced even further compared to N_2. The best fit Land constant for
295 CO_2 increased to a value of 4.11 after 0.2 – 0.6 pore volumes of brine injected, with slow
296 desaturation continuing up to 1.6 pore volumes of injected brine (see the supporting information).
297 At the measured initial saturation of 42% the remaining CO_2 was reduced to 15% compared with
298 19% for the N_2 system. This observation was repeated with experiment 6b after exposure to N_2,
299 showing both the precision in the measurement and that the rock core was not substantially altered
300 through multiple measurements obtained in the same sample.

301 **Table 2.** Best fit Land residual trapping hysteresis model coefficient

Experiment number	Wetting state	Trapped gas	$C*$
1, 2, 8	water-wet	N_2	1.68 ±0.05
9a, 9b, 10	water-wet	CO_2	1.74 ±0.05
1, 2, 8, 9a, 9b, 10	water-wet	CO_2, N_2	1.73 ±0.03
4a, 4b, 5a, 5b	mixed-wet	N_2	2.83 ±0.04

6a, 6b, 7	mixed-wet	CO_2	4.11 ±0.08

* C values ± error calculated as two times the standard deviation of best fit C

DISCUSSION

The results for the unaltered rocks show the same degree of trapping for CO_2 and N_2. The Land constant is larger, indicating less trapping, than values obtained characterizing CO_2 trapping in Berea sandstone[2]. The source of the difference may be due to pore structure and/or wetting state differences[2], although the similarity of the N_2 and CO_2 observations in this study suggests pore structure differences to be the likely explanation. The equivalence of the CO_2 and N_2 is consistent with past observations with Berea sandstone[34], but contrasts with observations made in a different carbonate rock in which more trapping was observed for supercritical CO_2 as compared with gaseous CO_2 in a different carbonate rock[11]. The contrasting results could be due to differences in rock structure leading to different sensitivities to contact angle changes, or experimental procedure, and is discussed further below.

In the mixed-wet sample the trapping of N_2 and CO_2 systems were significantly less than the trapping in the unaltered rocks. As discussed in the introduction, this result was consistent with past observations evaluating the impact of the mixed-wet state on the capillary trapping of hydrocarbon liquids[23-25,42]. This is generally thought to result from oil-wet surfaces providing connected pathways for thin film drainage of non-polar fluids[24,40].

The trapping was also specific to the fluid pair, with less CO_2 remaining in the pore space than N_2 upon secondary imbibition. The observations with N_2 and CO_2 were alternated and repeated with the same result, indicating that the difference was not due to chemical reaction between the

fluids and the rock, or altered wetting surfaces. This suggests that the difference was due to the impact of a difference in contact angle between the CO_2-brine and N_2-water on the surfaces with an altered wetting state, with the CO_2 more wetting of the altered surfaces than N_2.

This response is predicted by theoretical considerations of contact angles on smooth surfaces[43]. With a contact angle, θ [rad], measured in the aqueous phase, the relationship between the CO_2-brine and N_2-brine angles are dependent on the ratio of their respective values of interfacial tension, σ, [mN/m], through the relationship $\cos\theta_{CO_2-w} \propto \frac{\sigma_{N2-w}}{\sigma_{CO2-w}} \cos\theta_{N_2-w}$. A derivation is included in the supporting information. The interfacial tension of N_2 and gaseous CO_2 systems are much larger than that of the supercritical CO_2 system[30,31], predicting a larger contact angle for CO_2 (more CO_2-wetting) on oil-wet surfaces and smaller contact angles for CO_2 (less CO_2-wetting) on water-wet surfaces.

In practice, small changes in contact angle do not usually manifest in changes in flow properties due to the counterbalancing effects of pore structure and mineral roughness[20,21]. The differences in how this is manifest in trapping in the water-wet (equivalent CO_2 and N_2 trapping) and mixed-wet (less CO_2 trapping) states may be due to the values of the contact angles (the pore scale force balance changes as $\frac{d(\cos\theta)}{d\theta} = -\sin\theta$), or due to mineral wall roughness smoothed out by asphaltene deposition in the mixed-wet rock. It is notable that the difference in trapping of gaseous and supercritical CO_2 observed in an unaltered carbonate in El-Maghraby and Blunt (2012)[11] also follows the theoretical argument. Thus it is possible that the difference between those observations and the observations in unaltered rock reported here are not contradictory, but rather due to a difference in sensitivity of the flow properties to changes in contact angle in the respective rocks.

Finally, the decreased trapping values obtained in the altered rocks are conservative – it is likely that the irreducible residual saturation is lower. The Amott test indeed showed continued slow desaturation of the non-wetting phase with continued brine flooding of the core. It is evident that the residual trapping of CO_2 in mixed-wet carbonate reservoirs will be significantly less than in reservoir units that have not been exposed to hydrocarbon.

IMPLICATIONS

On the one hand, there are a number of attributes of the use of commercial oil fields that contribute significantly to the safety and success of storage projects. The fields are well characterized. The fields also have a demonstrated fluid trap and are not as dependent on capillary and dissolution trapping as the majority of CO_2 storage sites [13,14].

On the other hand, it is important that large scale assessments, e.g., of storage capacity take into account the difference in flow physics controlling storage in oil fields relative to those of saline aquifers. A simple example using the analytic model of Juanes et al. 2010[44] illustrates the significance of the weakened capillary trapping for CO_2 flow at the regional scale. Consider a depleted oil reservoir with a thickness of 100 m with the same petrophysical properties of the Estaillades limestone used in this study – a permeability and porosity of 138 md and 0.28, respectively. The model was used to estimate the ultimate footprint of a CO_2 plume migrating horizontally below a confining caprock layer, and the timescale required for immobilization through capillary trapping. Consider 100 Mt of CO_2 injected every year using 100 wells, with an interwell spacing of 1 km, for a period of 5 years. The connate water saturation and k_{rg} was assumed to be 0.4 and 0.6, respectively[45]. The model accounts for gravity override, capillary

366 trapping, natural groundwater flow, and the shape of the plume during the injection period but
367 does not account for reservoir heterogeneity and changes to relative permeability due to changes
368 in the wetting state.

369 In the water wet system, an initial CO_2 saturation of 42% corresponded to a 24% residual
370 saturation. This resulted in a migration of the plume ~ 50 km prior to immobilization in ~ 5,000
371 years. For the same initial CO_2 saturation, only 15% was trapped in the mixed-wet system,
372 corresponding to a migration path of ~ 130 km and immobilization in ~ 16,000 years.

373 Our results show that one of the key processes for maximizing CO_2 storage capacity and security
374 is significantly weakened in many hydrocarbon reservoirs relative to saline aquifers. We anticipate
375 this work to highlight a key issue for the early deployment of carbon storage – that those sites
376 which are economically most appealing as initial project opportunities are the very locations in
377 which the contribution of capillary trapping to storage security will be minimized. This should
378 serve as a starting point for modelling studies to incorporate the reduced impact of capillary
379 trapping on CO_2 injection projects using hydrocarbon reservoirs.

380

381 ASSOCIATED CONTENT

382 **Supporting Information**. Tables listing all IR results and corresponding 2D saturation maps of
383 all tests are included. Derivation of the relationship between contact angles. Further information
384 on experimental procedures, porosity and saturation measurements, a schematic of the
385 coreflooding rig, asphaltene precipitation measurement, wetting alteration procedure, wetting
386 state assessment, rock samples, remaining CO_2 saturations as a function of pore volume injected

of brine in mixed-wet system. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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ABBREVIATIONS

CO_2 carbon dioxide

N_2 Nitrogen

C Land model coefficient

sc supercritical

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