Experimental Characterization of Nonwetting Phase Trapping and Implications for Geologic CO₂ Sequestration

Elizabeth Harper Kimbrel¹, Anna L. Herring¹, Ryan T. Armstrong², Ivan Lunati³, Brian K. Bay⁴, Dorthe Wildenschild¹

¹*School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, OR*

²*School of Petroleum Engineering, University of New South Wales, NSW 2052 Sydney, Australia*

³*Institute of Earth Sciences, University of Lausanne, Lausanne, Switzerland*

⁴*School of Mechanical, Industrial and Manufacturing Engineering, Oregon State University, Corvallis, OR*

1.1 Corresponding Author

Anna L. Herring, PhD
103 Gleeson Hall
Oregon State University
Corvallis, OR 97331
herring@engr.orst.edu
(970) 629 3174

Abstract

Geological carbon sequestration is being considered worldwide as a means of mitigating anthropogenic emission of greenhouse gases. During sequestration, carbon dioxide (CO₂) gas effluent is captured from coal-fired power plants or other concentrated emission sources and injected into saline aquifers or depleted oil reservoirs for long term storage. In an effort to fully understand and optimize CO₂ trapping efficiency, the capillary mechanisms that immobilize

subsurface CO₂ were analyzed at the pore-scale. Pairs of proxy fluids representing the potential range of *in-situ* conditions of supercritical CO₂ (nonwetting fluid) and brine (wetting fluid) were used during experimentation. The two fluids were imbibed and drained from a flow cell apparatus containing a sintered glass bead core. Fluid parameters (such as interfacial tension and fluid viscosities) and flow rate were altered to characterize their relative impact on capillary trapping. Computed x-ray microtomography (microCT) was used to quantify immobilized nonwetting fluid volumes after imbibition and drainage events. MicroCT-analyzed data suggests that capillary trapping in sintered glass bead (a mildly consolidated porous medium) is dictated by the capillary number (Ca), the viscosity ratio (M), and the Bond number (Bo) of the system, reflecting that all three viscous, capillary, and gravity forces affect the displacement process to varying degree as their relative importance changes. The amount of residual trapped nonwetting phase was observed to increase with increasing nonwetting fluid viscosity, and with decreasing density difference of the fluids; this suggests that CO₂ sequestration can potentially be engineered for optimal trapping through alterations to the viscosity or density of supercritical CO₂.

1. Introduction

Carbon dioxide (CO₂) is emitted into the atmosphere through burning of fossil fuels for energy production. Combustion of fossil fuels accounts for approximately 75% of the atmosphere's total anthropogenic CO₂ emissions and is currently released into the atmosphere at a rate higher than it can be removed by natural sources (IPCC, 2005).

As a means of mitigating CO₂ emissions, carbon capture and storage (CCS) collects, concentrates, and transfers a stream of CO₂ from point sources of emissions to the injection site.

To optimize storage volume, CO₂ is injected into formations at depths of more than 800 meters; at this depth, CO₂ is above its critical point (the critical temperature and pressure are 31°C and 7.4 MPa, respectively) and in its supercritical state. The success of a CCS project depends on its ability to efficiently trap CO₂ in the subsurface for hundreds of years and longer, and in order to ensure security and prevent leakage, the physical and chemical mechanisms that trap CO₂ must be understood.

The focus of this work is on capillary (or residual) trapping in mildly consolidated media. Capillary trapping involves drainage and imbibition in the porous medium and is a consequence of hysteresis. CO₂ injection in a water-wet system is a drainage process during which the resident brine is displaced from the pores; during imbibition, which takes place when the resident brine returns to the formation after injection has stopped, or during an engineered waterflood, some of the injected CO₂ is trapped as a result of capillary interactions.

Capillary trapping is arguably the most advantageous form of trapping because of its high storage security (the risk of leakage into the atmosphere or of groundwater contamination is less than for hydrodynamic trapping, which relies on the integrity of a cap-rock) and relatively short time scales (Juanes et al., 2006). The capillary trapping mechanism also has the potential to contribute more to overall trapping than both dissolution or mineral trapping mechanisms (Kumar et al., 2013). Under specific formation and time constraints, significant quantities of the injected CO₂ can be potentially trapped by capillary forces (IPCC, 2005). Al Mansoori et al. (2009) showed that poorly consolidated media produced relatively low residual nonwetting phase saturations (0-15%), thus suggesting that highly consolidated media would be better suited for CO₂ injection scenarios. Yet, the saline formation used for CO₂ storage at the Sleipner CCS

project off the coast of Norway consists of unconsolidated sandstone and has stored approximately 1 Megaton (Mt) of CO₂ per year since 1996 (IPCC, 2005).

MicroCT imaging has now been used in a number of studies to explore the storage security of residually trapped nonwetting phase. Iglauder et al. (2011) measured trapped residual saturations of supercritical CO₂ of 25% in quartz sandstone cores (4.95 mm diameter, 9 mm length) and concluded that local capillary trapping is a safe and effective method of securing supercritical CO₂ in the subsurface. In larger consolidated Berea sandstone cores (diameter of 38.5 mm, length of 75.3 mm), Pentland et al. (2011) measured somewhat higher trapping capacities, that is 37% and 48% residual nonwetting phase saturation in brine-supercritical CO₂ and brine-oil experiments, respectively. More recently, Tanino and Blunt (2012) studied capillary trapping in sandstones and carbonates, in particular the dependence on pore structure. They measured the residual state established by water flooding at low capillary number and found that residual saturation decreased as conditions became less favorable for snap-off.

Our objective is to explore how CO₂ storage capacity can be optimized via capillary trapping. The results reported were obtained using proxy fluids and mildly consolidated media, and trapping was quantified using microCT imaging. Use of ambient condition proxy fluids greatly simplifies experimental conditions as compared to a supercritical CO₂ system, providing an opportunity to conduct a relatively large number of imaging experiments. While the use of proxy fluids does not exactly replicate the conditions of a supercritical CO₂-geologic medium system, it does allow for exploration of the combinations of IFT, viscosity and flow rate that are expected at reservoir conditions and provides insight into how variations of these fluid properties will impact capillary trapping during sequestration operations. The surrogate fluid approach has been used previously to predict supercritical CO₂ behavior, for example by Trevisan et al. (2014).

2. Background

2.1 Capillary, Viscous, and Gravitational Forces

In two-phase immiscible fluid systems, the capillary number (Ca) is a dimensionless number that is used to characterize relative strength of viscous to capillary forces and it is the variable that is commonly used as the predictor of trapping efficiency of the nonwetting phase. There are many different definitions of capillary number, some of which incorporate relative permeability; the simplest definition is as follows:

$$Ca = \frac{\text{viscous forces}}{\text{capillary forces}} = \frac{\mu \times v}{\sigma} = \frac{\mu \times \frac{Q}{A\eta}}{\sigma} \quad (1a)$$

where μ is the viscosity of the invading fluid, v is the average pore velocity of the invading fluid (as calculated by the volumetric flow rate, Q , divided by the cross sectional area of flow, A , and the core porosity, η) and σ is the interfacial tension between the two fluids (Chatzis and Morrow, 1984). The role of the invading or displaced fluid changes between imbibition and drainage events.

We note here that capillary forces are also dependent on medium properties, and particularly the wettability state of the porous medium. In an immiscible multiphase fluid-porous medium system, wettability describes the affinity of the medium for one fluid phase relative to the other. The wettability state of the medium can be quantified by measuring the contact angle (θ) formed by the intersection of the tangent of the fluid-fluid interface and the aqueous fluid-solid interface; generally, contact angle values (measured through the aqueous phase) from $0-75^\circ$ indicate a water-wet system, values from 75° to 105° indicate intermediate-wet conditions, and values of

105° to 180° indicate a non-water-wet system (e.g. an oil-wet or CO₂-wet system) (Treiber and Owens, 1972). In order to acknowledge the importance of wettability state on capillarity, some studies have incorporated contact angle into the definition of capillary number, e.g., Jamaloei et al. (2012):

$$Ca = \frac{\text{viscous forces}}{\text{capillary forces}} = \frac{\mu \times v}{\sigma \times \cos\theta} = \frac{\mu \times \frac{Q}{A\eta}}{\sigma \times \cos\theta} \quad 0 \leq \theta < 90^\circ \quad (1b)$$

To account for the viscosity differences between the two fluids, a second dimensionless number has to be introduced. The viscosity ratio (M) is used to compare the viscosities of the invading and displaced fluids and it is defined as:

$$M = \frac{\mu_i}{\mu_d} \quad (2)$$

where μ_i represents the viscosity of the invading fluid and μ_d represents the viscosity of the displaced fluid, in agreement with Lenormand et al. (1988) and Zhang et al. (2011). Notice that for the same fluid pair the viscosity ratio is different in drainage and imbibition because the invading fluid is the nonwetting fluid in the former case and the wetting fluid in the latter case.

The effects of gravity on the system can be quantified by the Bond number (Bo), which estimates the relative importance of gravity to capillary forces and is typically defined as:

$$Bo = \frac{\text{gravity forces}}{\text{capillary forces}} = \frac{\Delta\rho \times g \times d^2}{\sigma} \quad (3a)$$

where $\Delta\rho$ is the density difference between the invading and displaced fluids, g is the gravitational constant, and d is a representative length scale (LOVOLL, 2005; Or, 2008) [13];

here, we define d to be the median bead or grain diameter (Herring et al., 2015). As was presented above for the capillary number, the Bond number can be modified in order to take into account the wettability state of the medium (Herring et al., *submitted*):

$$Bo = \frac{\text{gravity forces}}{\text{capillary forces}} = \frac{\rho \times g \times d^2}{\sigma \times \cos \theta} \quad 0 \leq \theta < 90^\circ \quad (3b)$$

The Bond number can be plotted inversely in combination with the capillary number to identify which of the three forces (capillary, viscous, or gravity forces) will dominate flow at the pore-scale during fluid displacement (e.g. Polak et al. (2011)).

2.2. Forces Balance Impacts on Nonwetting Phase Trapping

It is commonly accepted that the residual nonwetting phase saturation, S_R , depends on the capillary number during the imbibition stage (Chatzis and Morrow, 1984; Chatzis et al., 1988; Morrow et al., 1988). A significant body of research has shown that as capillary number increases (and thus, viscous forces dominate), residual trapping of the nonwetting phase decreases; typically a dramatic decrease in S_R is observed around a critical capillary number of 10^{-5} to 10^{-6} (e.g. Chatzis and Morrow (1984); Morrow et al. (1988); Ding and Kantzas (2007); Cense and Berg (2009)). This trend has been observed in many different types of consolidated porous media and is generally attributed to suppression of snap-off at larger Ca. The critical capillary number for wetting-phase trapping is generally measured in the range of 10^{-5} and 10^{-3} (Cense and Berg, 2009). However, the capillary number alone does not describe the complexity of trapping mechanisms because it does not carry information on the role played by viscous or gravitational forces when they dominate, which are described by the viscosity ratio or Bond number, respectively.

For two-dimensional (2D) systems where capillary forces and viscous forces dominate over gravitational forces (e.g. horizontal micromodels), consideration of both Ca and M is sufficient to describe flow. Using

these dimensionless ratios, three distinct flow regimes have been identified for a drainage process in 2D micromodels: viscous fingering, capillary fingering, and stable displacement (Lenormand et al., 1988; Wang et al., 2012; Zhang et al., 2011). These flow regimes are defined by their Ca and M values in reference to the so-called Lenormand phase diagram, wherein capillary numbers are plotted against mobility ratios on a log-log basis. Similarly, studies of drainage flow pattern in vertically oriented 2D systems have demonstrated that for a relatively less-dense nonwetting phase fluid injected into the top of a porous medium filled with more dense fluid, as gravity forces increase, the nonwetting phase injection displays a transition from fingering type invasion to stable displacement (Chau and Or, 2006; Méheust et al., 2002; Or, 2008). This transition in flow behavior is attributed to the fact that increasing gravity influence acts to prevent downward finger formation of the less dense phase.

However, these flow regimes (capillary fingering, viscous fingering, and stable displacement) have thus far only been studied with respect to the drainage process; whereas capillary trapping of nonwetting phase occurs during the imbibition process. We suggest that analogous flow regimes do indeed occur during imbibition, and should be studied in order to allow for more accurate prediction of nonwetting phase capillary trapping over a wide range of Ca , M , and Bo values. It is difficult to describe the interplay and combined effect of all three capillary, viscous, and gravity forces on mobilization of nonwetting phase during imbibition using one dimensionless ratio; and so Ca , M , and Bo should all be considered simultaneously for full physical understanding of fluid displacements in a three dimensional (3D) system.

For low Ca systems with negligible viscous and gravity forces, displacement is dominated by capillary forces, resulting in a capillary fingering pattern and snap-off-dominated nonwetting phase trapping. When Ca increases, viscous forces become more dominant and the front morphology (and thus trapping) is dictated by the viscosity ratio M (e.g. Lenormand et al. (1988); Ferrari and Lunati (2013)). For $M > 1$ the invading fluid (i.e. brine, during imbibition for a CO_2 sequestration scenario) is more viscous than the displaced fluid, the front is stable and tends to remain compact; therefore, trapping will decrease with increasing Ca . For $M < 1$ the invading fluid is less viscous, the front is destabilized by viscous effects and

thin, long fingers develop resulting in a significant amount of trapped nonwetting fluid; in this case, trapping will increase with increasing Ca (Ferrari and Lunati, 2013). In the petroleum engineering literature, where the amount of residual oil (the displaced fluid) is to be minimized, a viscosity ratio greater than one is also referred to as "favorable", while the term "unfavorable" is used when the viscosity ratio is less than one because the invading phase forms fingers that decrease the efficiency of oil recovery. This terminology was first introduced and discussed by Engelberts and Klinkenberg (1951) based on their experimental findings, and they coined the term viscous fingering to describe the fact that under unfavorable conditions the invading fluid flows only through sparse preferential flow paths.

Similarly, for a system with non-negligible gravity forces, as Bo increases (i.e. capillary forces are small relative to gravity), vertical flow patterns will demonstrate a transition from a fingering pattern to stable displacement (Or, 2008), and the relatively less dense nonwetting phase is more likely to mobilize upward and demonstrate reduced capillary trapping (Herring et al., *submitted*). The inverse relationship between nonwetting phase trapping and Bo (i.e. reduced trapping as capillary forces decrease and gravity forces increase) has been shown for water-oil and air-oil systems (Morrow et al., 1988), as well as tetrachloroethylene-water systems (Pennell et al., 1996).

The ultimate goal of CO_2 sequestration is to maximize the amount of trapped CO_2 in the subsurface in order to prevent migration to the surface. One can envision manipulating the parameters of a supercritical CO_2 injection (drainage), along with the following brine chase flood or natural groundwater flow (imbibition), such that the capillary number, viscosity ratio, and Bond number of the imbibition process are optimized to enhance residual trapping. Recent studies have explored the relative effect of *individual* fluid properties (interfacial tension, viscosity, density, medium contact angle, and flow rate) on residual trapping and their findings are summarized in the following sections.

2.3. Impact of Interfacial Tension, Viscosity, and Density on Trapping

Many ambient condition studies have investigated the impacts of interfacial tension, viscosity, and density on nonwetting phase capillary trapping (e.g., Chatzis and Morrow, 1984; Morrow et al., 1988; Pennell et al., 1996) and residual nonwetting phase morphology (e.g., Chao et al., 2000; Mayer and Miller, 1993). However, because it is experimentally difficult to isolate individual parameters and because various porous media systems are not necessarily comparable, these studies provide slightly contradictory results in terms of which parameters have the most impact on nonwetting phase mobilization.

In terms of supercritical condition studies using CO₂, it has been shown that increasing interfacial tension values was shown to increase residual CO₂ saturations in consolidated sandstone samples collected from a site in Alberta, Canada (Bachu and Bennion, 2008, 2009; B. Bennion and Bachu, 2013; D. B. Bennion and Bachu, 2013a, 2013b). Trapped CO₂ was also observed to increase with increasing viscosity ratio (with brine as the invading fluid and supercritical CO₂ as the displaced fluid) which was varied by changing experimental pressure and temperature conditions (Bachu and Bennion, 2008); this conflicts with the description of flow dynamics presented above. However, since interfacial tension and viscosity both vary with pressure, temperature, and salinity, it was not possible to isolate a potential viscosity effect in these studies, and instead the authors concluded that the increasing residual CO₂ trapping with viscosity ratio was related to the increasing interfacial tension trend. More recently, Reynolds et al. (2014) presented results of co-injection experiments of supercritical CO₂ and brine in sandstone cores which demonstrated that CO₂ viscosity was a main factor controlling CO₂ distribution, flow pattern, and relative permeability.

2.4. Impact of Porous Medium Contact Angle on Trapping

Medium wettability dictates the distribution of wetting and nonwetting fluids in a system. For a strongly water-wet system, the aqueous phase will generally reside in the smallest pore throats and crevices of the media, and will exist as thin films in the roughness and on the surfaces of the medium, while nonwetting phase can only easily invade the largest pore bodies (Blunt and Scher, 1995; Kumar et al., 2009). “Snap-off” occurs during imbibition as water refills the smallest pore spaces preferentially and water menisci touch in pore throats, encompassing and isolating nonwetting phase clusters. As thin films only exist in strongly wetting systems, the snap-off mechanism may be reduced or eliminated entirely in intermediate-wet media. This effect has been studied extensively for oil recovery applications, and it has been shown that residual nonwetting phase trapping is reduced as contact angle increases towards 90° (Amott, 1959; Anderson, 1987; Kennedy et al., 1955; Lorenz et al., 1974; Morrow, 1990). Additionally, Chaudhary et al. (2013) recently demonstrated reduced trapping of supercritical CO_2 in CO_2 -wet bead columns as compared to water-wet columns.

2.5. Impact of Flow Rate on Trapping

A consensus regarding the effects of flow rate on residual trapping has yet to be reached. Previous studies have generally been conducted for a single fluid pair, and thus the effect of the viscosity ratio on trapping mentioned previously, is not relevant. Blunt and Scher (1995) investigated the effects of flow rate on immiscible fluid displacement in a pore-network model for applications in oil reservoirs. They concluded that the dominant fluid displacement mechanism will change depending on flow rate due to fluid flow competition at the pore-scale. Nguyen et al. (2006) produced high residual nonwetting saturations through a numerical study of

the snap-off mechanism in the capillary fingering regime. Most research supports this finding, arguing that snap-off is suppressed and mobilization is enhanced at high flow rates; however, Wildenschild et al. (2011) showed a weakly increasing relationship between residual nonwetting phase and increasing flow rate; and Mohammadian et al. (2014) present results of trapped gas saturation which show no dependence on wetting phase velocity. This issue becomes more complicated at larger scales as pore-scale mechanisms compete with basin-scale flow patterns; for example, Juanes et al. (2006) simulated capillary trapping on a basin scale and predicted that supercritical CO₂ can be more effectively sequestered due to radical dispersion patterns induced by high injection flow rates.

2.6 Motivation

The impact of capillary forces (presented in terms of fluid flow rate, viscosity, and interfacial tension) on residual trapping were initially investigated by Wildenschild et al. (2011). Proxy fluid-pair experiments in glass bead packs showed that nonwetting phase trapping was optimized at high flow rates and with increasing nonwetting phase viscosity; however, because the trend was relatively weak, the authors concluded that further experimentation was required to substantiate these results.

To our knowledge, no additional work has been published that systematically examines *both* the isolated and combined impacts of the elements of Ca, M, and Bo as a means of optimizing CO₂ trapping efficiency. Further investigation is needed to bring clarity to issues related to capillary number, Bond number and viscosity ratio and their effect on imbibition flow regimes and residual trapping. Due to the experimental difficulties associated with isolating fluid parameters

of supercritical CO₂ (Bachu and Bennion, 2008), we report here on experiments using proxy fluids conducted under ambient conditions.

We emphasize that the focus of this study is on the relative importance of flow mechanisms that are in effect during imbibition, i.e. during an engineered waterflood that would take place after CO₂ injection has ceased. Thus, this work complements that of Herring et al. (2015, 2013) who focused on the mechanisms in effect during the initial state of the system, i.e. after CO₂ injection (before imbibition).

3. Materials and Methods

3.1 Experimental Set-Up

All experiments were performed in two sintered soda lime glass bead cores, approximately 5.7 mm inner diameter and 57 mm tall. The cores were a mixture consisting of 35% 600 μm, 35% 850 μm and 30% 1000-1400 μm size beads. The beads were sintered to a borosilicate glass pipette column using a graphite crucible in a muffle furnace at 760°C. The approximate porosity of each core was 34%. Following the terminology of Morrow et al. (1988), we will refer to this sintered glass bead core as a mildly consolidated medium.

Experiments were conducted using seven pairs of proxy fluids, chosen to obtain a range of interfacial tensions, viscosities, and flow rates which approximate the range of fluid property variation exhibited by supercritical CO₂ and brine during CCS injection at reservoir conditions. The injection characteristics of supercritical CO₂ and experimental proxy fluids are listed in Tables 1 and 2, respectively. Values presented in Table 1 demonstrate the approximate range and order of magnitude of viscosity, interfacial tension, and density of supercritical CO₂ as reported

by Freund et al. (2005). Experimental proxy fluid viscosities and fluid-fluid interfacial tensions presented in Table 2 were measured in the laboratory: fluid viscosities were measured using a Cannon Ubbelohde size 75 viscometer (air viscosity is assumed to be 0.018 mPa-s); fluid-fluid interfacial tensions were measured using a Fisher Surface Tensiometer Model 20 and a duNuoy ring. Contact angles (as measured through the wetting phase) for the fluid pairs on glass are reported from the literature; because these values are used to calculate dimensionless ratios describing imbibition, advancing contact angles are listed where available (static values are reported otherwise).

	IFT with brine (mN/m)	μ (mPa-s)	ρ (kg/m ³)
Supercritical CO ₂	25-50	0.025 – 0.15	200-1000

Table 1. Approximate values of interfacial tension (IFT), viscosity (μ), and density (ρ) of supercritical CO₂ (Freund et al., 2005).

In three pairs of proxy fluids, the wetting phase consisted of 1.0 mol·L⁻¹ potassium iodide (KI) brines (1:6 mass ratio of KI to deionized water). The solution ratio was tailored to facilitate good contrast in the x-ray tomographic images used for quantification by increasing the contrast of the wetting phase relative to the other constituents (nonwetting and solid phases). In these pairs, octane, air, and Soltrol were used as nonwetting phase. In the other four pairs of proxy fluids, Triton X-100 surfactant or glycerol were added to the KI brine at different concentrations (9.0×10^{-5} mol·L⁻¹ and 9.0×10^{-6} mol·L⁻¹ for solutions labeled Triton 1 and Triton 2, respectively) to modify the properties of the wetting phase. Triton X-100 was chosen to lower the interfacial tension (IFT) between the KI brine/air proxy pair because at very low concentrations it has a significant impact on the IFT value without affecting viscosity, thus allowing us to isolate

321 potential effects of interfacial tension on trapping. Glycerol (CAS-No:56-81-5), a water soluble
322 visco-thickener, was used to alter the viscosity of the wetting fluid without significantly altering
323 the IFT; mixing ratios (volume of glycerol to volume of brine) were 0.25 and 0.67 for solutions
324 labeled Glycerol 1 and Glycerol 2, respectively. All experiments with the altered wetting fluids
325 (solutions of KI brine and Triton X-100 or glycerol) were paired with air as a nonwetting fluid.

Fluid Pair Designation	Wetting Fluid	Nonwetting Fluid	θ (°)	IFT (mN/m)	μ_w (mPa-s)	μ_{NW} (mPa-s)	$\Delta\rho$ (kg/m ³)	Ca (eqn. 1b)	M (eqn. 2)	Bo (eqn. 3b)
BA	Brine	Air	6.7 ^a	72	1.13	0.018	1079	$1.0 \times 10^{-6} - 2.5 \times 10^{-4}$	62.8	0.106
BS	Brine	Soltrol	43.5 ^a	25	1.13	4.82	286	$4.0 \times 10^{-6} - 4.0 \times 10^{-5}$	0.23	0.113
BO	Brine	Octane	5 ^b	37	1.13	0.540	377	$2.0 \times 10^{-6} - 2.0 \times 10^{-5}$	2.10	0.071
T1A	Triton 1	Air	34 ^c	37	1.13	0.018	1079	$2.4 \times 10^{-6} - 2.4 \times 10^{-5}$	62.8	0.249
T2A	Triton 2	Air	40 ^c	51	1.13	0.018	1079	$1.9 \times 10^{-6} - 1.9 \times 10^{-5}$	62.8	0.196
G1A	Glycerol 1	Air	26.5 ^d	66	1.86	0.018	1144	5.0×10^{-6}	102	0.137
G2A	Glycerol 2	Air	26.5 ^d	69	3.95	0.018	1206	$1.0 \times 10^{-5} - 4.1 \times 10^{-5}$	218	0.138

Table 2. Fluid properties for the seven experimental fluid pairs consisting of wetting (W) and nonwetting (NW) fluids: contact angle (θ) measured through the W phase (including advancing values where available, and static values otherwise), interfacial tension (IFT), viscosity (μ), and density (ρ); and resulting imbibition capillary number (Ca), viscosity ratio (M), and Bond number (Bo.)

- a. Advancing contact angle reported in Wei et al. (1993)
- b. Static contact angle reported in by Carré and Lacarrière (2006)
- c. Static contact angle reported by Szymczyk and Jańczuk (2008)
- d. Static contact angle reported by Alteraifi and Sasa (2006)

Experiments were conducted at standard temperature (22°C) and pressure (1 atmosphere). The sintered glass bead core was placed on top of a semi-permeable hydrophilic membrane (GE Nylon Membrane, 1.2 µm) which prevented the passage of nonwetting fluid into the wetting fluid tubing. The core and filter paper were secured to a plastic base with a set of threaded, plastic connectors and an O-ring. A Harvard PhD Ultra Syringe pump precisely injected wetting fluid into the glass bead core during imbibition, and pressure across the core was monitored via two pressure transducers with ranges of 22.5 cmH₂O and 55.6 cmH₂O (Validyne Engineering, Northridge CA, United States). During drainage the pump was reversed to extract the wetting fluid and draw in the nonwetting fluid from a reservoir connected to the top of the core (or from the atmosphere, for experiments where air was the nonwetting phase). For all flow processes, the boundary condition at the bottom of the core was a constant flow rate of wetting fluid, and the boundary condition at the top of the core was constant atmospheric pressure (for experiments where the nonwetting fluid was not air, the nonwetting fluid reservoir was open to the atmosphere). A schematic of the experimental set-up is shown in Figure 1.

Figure 1. Schematic of the experimental set-up showing the syringe pump, wetting and nonwetting fluid reservoirs, pressure transducers, and sintered glass core.

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350 The experimental set-up was assembled inside the hutch of a microCT scanner. Prior to each
351 experiment, the glass bead core was removed from the experimental apparatus and cleaned with
352 a series of fluids, each designed to dissolve and remove the preceding fluid from the core. The
353 cleaning procedure required flushing the bead core first with acetone, then ethanol, next
354 deionized water, and finally it was dried with compressed air. This procedure was repeated prior
355 to every experiment to ensure that the starting conditions were the same for each experiment.
356 The glass beads comprise a water-wet system for all fluid pairs in this study, see contact angle
357 vales in Table 2.

358 The clean, dry bead core was placed in the core holder and secured onto the x-ray stage prior to
359 the start of each experiment. The core was always imaged in its dry state before fluid injection to
360 simplify data processing.

361 **3.2 Experimental Procedure**

362 After the dry scan, a primary imbibition step was performed by injecting the wetting fluid into
363 the core at a relatively slow flow rate of 0.25 mL/hr to maximize the wetting phase saturation of
364 the core. This process was complete once the wetting fluid reached the top of the beads and the
365 pressure transducers indicated a zero capillary pressure. The fluids in the core were allowed to
366 equilibrate for 15 minutes after each pumping event (equilibration was confirmed by
367 approximately constant capillary pressure readings), and the core was imaged to measure the
368 *original* nonwetting-phase saturation (S_O).

After the primary imbibition scan, the bead core was drained at a flow rate of 1 mL/hr. This step mimics the drainage of the reservoir occurring during the CO₂ injection phase (see Figure 2). In experiments in which the nonwetting fluids were octane or Soltrol, a line of the nonwetting fluid was connected to the top of the bead core during drainage. When the capillary pressure decreased rapidly and reached approximately -980 Pa, the drainage process was stopped. After equilibration, the core was imaged again to measure the *initial* nonwetting phase saturation (S_i).

376 Figure 2. **Experimental process and analogy to reservoir CO₂ sequestration processes:**
377 (a) original state, S_0 : reservoir prior to CO₂ (nonwetting phase; NWP) injection;
378 (b) drainage: reservoir during CO₂ injection;
379 (c) initial state, S_I : reservoir just after CO₂ injection;
380 (d) imbibition: reservoir during waterflood injection or natural groundwater flow; and
381 (e) residual state, S_R : final reservoir state after migration of mobile CO₂ plume and reinvasion of
382 the pore space by wetting phase (WP).

Once the drainage scan was complete, wetting fluid was re-imbibed into the core in the third step (secondary imbibition). This step mimics an engineered waterflood or the natural migration of brine back into the drained reservoir region after CO₂ injection stopped. Fluid flow rates varied from 2-500 mL/hr, which corresponds to wetting phase capillary numbers of 10⁻⁶-10⁻⁴ depending on the proxy pairs (Table 2). Four pore volumes were flushed through the core to ensure capillary trapping. After a final 15 minute equilibration period, the secondary imbibition scan was captured to establish the *residual* nonwetting phase saturation (S_R).

Images were acquired using a microCT system in the School of Mechanical, Industrial and Manufacturing Engineering (MIME) at Oregon State University. The cone beam microCT system consists of a Microfocus FXE-160.20 x-ray source, a Medelelex 9" image intensifier (model: HXS-93/PS), and a 2448 x 2048 pixel 16 bit CCD Point Grey Grasshopper (model: GRAS-5055M) camera. The camera had a maximum resolution of 3.45 microns and a frame rate of 15 frames per second (fps). All experiments were operated at a voltage of 100 kilovolts (kV) and a current of 78 microamps (μ A). Images were collected over a rotation of 360° in 1440 increments, averaging 4 projections per increment. The approximate spatial resolution of each image was 13 microns per pixel and the height of the imaged region of the bead core was 20 millimeters, however, this region varied slightly due to small changes in stage location between experiments.

3.3 Image Processing

The images collected from each scan were saved in the form of 2D radiographs. Due to the nature of the microCT image detection configuration, the raw 2D images are inherently distorted,

and were corrected using a distortion correction algorithm implemented in the Java-based program ImageJ. The distortion corrected 2D images were then reconstructed into three dimensional volumes using a cone-beam reconstruction algorithm in Octopus 8.5, a commercial software program for image reconstruction. A commercially available imaging software (Avizo FireTM) was used to prepare the 3D volumes for further analysis.

The goal of the image processing is to convert the collected grayscale images to images with three distinct phases (solid, wetting, and nonwetting fluids) for quantitative analysis. The segmented images can then be used to calculate a variety of desired system characteristics, in the present case, porosity and fluid saturations. The nonwetting phase saturation after the primary scan is defined as the original saturation, S_O , while the nonwetting phase saturation after the drainage scan is defined as the initial saturation, S_I , and the nonwetting phase saturation after the secondary imbibition scan is defined as the residual saturation, S_R (Figure 2).

Exactly the same region of the core was analyzed in all three scans within the same experiment. However, from experiment to experiment, this region changed slightly due to variation in the vertical positioning of the core inside the core holder, and of the stage. The final calculated saturations from each scan represented a vertical subsection of the total core of approximately 10 mm.

A target goal of 98% original wetting saturation was set for each experiment; however data analysis of initial experiments indicated that this goal was not consistently achieved as some air was trapped in the core initially. A trend of increasing *residual* nonwetting phase saturation with increasing *original* non-wetting phase saturation emerged (Harper and Wildenschild, 2012). Because many CO₂ sequestration injection sites will consist of depleted oil or gas reservoirs (e.g.

Saeedi and Rezaee (2012)), this phenomenon is likely to be observed in natural settings and we chose to examine the effect, and correct for it, as opposed to trying to achieve complete original saturation (i.e. $S_O = 100\%$ saturation).

Additional details regarding image reconstruction and segmentation can be found in the supplementary materials, available online.

4. Results

The experimental results are discussed in terms of the wetting/nonwetting fluid pairs which are described in Table 2. The experiments using different nonwetting fluids are defined as Brine-Air (BA), Brine-Soltrol (BS), and Brine-Octane (BO). Experiments using altered wetting fluids (through addition of either the surfactant, Triton X-100, or visco-thickener, glycerol) are defined as Triton 1-Air (T1A), Triton 2-Air (T2A), Glycerol 1-Air (G1A) and Glycerol 2-Air (G2A) in this section. We first present trapping as a function of the dimensionless ratios Ca , Bo , and M in Section 4.1, 4.2, and 4.3, respectively; then the individual parameters that comprise these ratios are examined in Section 4.4. Results of t-test analyses (using t-values as calculated by equation A.1, see supplementary materials, available online) on the linear regressions of investigated parameters are presented in Table 3.

Dimensionless Ratio	R ² value of linear regression	Number of data points, n	Degrees of Freedom, d.f. (n-2)	t-value	Student's t-test two tailed p-value
Capillary Number (Ca) for M >>1	0.03	23	21	0.79	0.34
Capillary Number (Ca) for M=0.23	0.17	9	7	1.19	0.27
Viscosity ratio (M)	0.30	35	33	3.72	<0.001
Bond Number (Bo)	0.16	35	33	2.48	0.018
Experimental Parameter					
Flow Rate	0.04	35	33	1.10	0.28
Interfacial Tension (IFT)	0.16	23	21	0.75	0.46
Contact Angle (θ)	0.25	35	33	3.38	0.002
Wetting Phase Viscosity (μ_w)	0.03	35	33	1.07	0.29
Nonwetting Phase Viscosity (μ_{nw})	0.80	35	33	11.58	<0.001
Wetting/Nonwetting Phase Density Difference ($\Delta\rho$)	0.77	35	33	10.45	<0.001

Table 3. Results of Student's t-test analysis on the linear regressions of trapped residual nonwetting (NW) phase saturation as a function of individual fluid parameters.

4.1 S_R vs. Capillary Number

We present results in terms of residual nonwetting phase saturation (S_R) as a function of imbibition Ca . Values shown in Figure 3 correspond to the experimental properties (flow rate and viscosity) of the invading (wetting) fluid during secondary imbibition and range from approximately 10^{-4} to 10^{-6} . As trapping cannot be predicted solely based on Ca , in Figure 3 we present the data for unstable ($M < 1$) and stable ($M \gg 1$) displacement in separate plots. The error bars in this and in the following figures reflect standard deviation around the mean when multiple experiments were performed for the same experimental conditions.

Figure 3. Residual nonwetting (NW) phase saturation as a function of imbibition capillary number (Ca). Fluid pairs presented in (a) exhibit viscosity ratio that indicates stable displacement ($M \gg 1$); results of brine-Soltrol experiments are shown in (b), the viscosity ratio of these experiments indicates unstable displacement ($M = 0.23$).

Measured S_R vs. Ca values are presented in Figure 3a for fluid pairs (BA, T1A, T2A, G1A, and G2A) with a viscosity ratio of $M \gg 1$ (stable displacement, as the invading wetting phase is more

viscous than the displaced phase; see Table 2 for M values for each fluid pair); the expected trend of decreasing S_R with increasing imbibition Ca is not evident. Most previously published data of S_R as a function of imbibition Ca represents consolidated rock cores, typically sandstone (Bachu and Bennion, 2008; Chatzis and Morrow, 1984; Chatzis et al., 1988; Ding and Kantzas, 2007; Kantzas et al., 2013; Shen et al., 2010; Suekane et al., 2008), and residual nonwetting phase trapping in high porosity, unconsolidated, or mildly consolidated media is not necessarily expected to follow the same trends as firmly consolidated media. However, Morrow et al. (1988) also reported sintered bead pack capillary trapping data that indicated a decrease in residual trapped oil with increasing capillary number (over a range of capillary numbers of 10^{-4} - 10^{-2}). The scatter observed in the relationship between S_R and Ca in this study implies that imbibition Ca does not fully describe the physics dominating this experimental system, and that other experimental parameters may contribute more to trapping. A t-test analysis (using t-values as calculated by equation A.1 presented in the supplementary materials, available online) on the linear regression of all data points of all fluid pairs with $M \gg 1$ comprising residual nonwetting saturation as a function Ca results in a p-value of 0.45, indicating no statistical significance of the linear relationship between S_R and Ca for $M \gg 1$ (Table 3).

The same quantities for the experiments with a low viscosity ratio of $M=0.23$ (unstable displacement; the invading wetting phase is less viscous than the displaced solvent phase) are plotted in Figures 3b and a relatively high amount of residual trapping is observed. As a consequence of the unstable flow regime ($M < 1$), the observed residual saturations are generally higher than other published residual saturation in glass bead packs, e.g. a maximum residual nonwetting saturation of approximately 3.5% for a water-nitrogen gas system reported by Suekane et al. (2010), and 16% for a water-oil system reported by Morrow et al. (1988). The

trend of increasing nonwetting phase saturation in the unstable viscous regime ($M=0.23$) is however, supported by simulations by Ferrari and Lunati (2013); yet, very little experimental data exists in which the viscosity ratio of the fluids was varied during *imbibition* experiments. Zhang et al. (2011) and Wang et al. (2012) did study trapping using different fluid pairs with varying viscosity ratios, but focused on drainage to assess the effect these properties have on the initial saturation of CO_2 obtained during the injection stage. A t-test analysis on the linear regression of BS data points comprising residual nonwetting saturation as a function Ca (for $M=0.23$) results in a p-value of 0.27, indicating no statistical significance of the linear relationship between S_R and Ca for $M<1$ (Table 3).

4.2 S_R vs. Bond Number

Measured S_R vs. Bo values for all seven fluid pairs are presented in Figure 4. As Bo increases and gravity forces become dominant over capillary forces in the experimental system, trapped nonwetting phase decreases due to the upward mobilization of the less-dense nonwetting phase. This is consistent with previous works; e.g. Morrow et al (1988). For each fluid pair investigated in this study, the nonwetting phase was the less dense fluid, which is representative of a supercritical CO_2 sequestration operation. The relationship between residual nonwetting saturation and Bo is quantitatively more significant than the relationship between residual nonwetting saturation and imbibition Ca , with a t-test analysis on the linear regression resulting in a p-value of 0.018, indicating strong significance of the relationship between Bo and S_R (Table 3); thus, buoyant transport must be considered in this system.

Figure 4. Residual nonwetting (NW) phase saturation as a function of Bond number (Bo) for all seven experimental fluid pairs.

4.3 S_R vs. Viscosity ratio

Viscosity ratios for the imbibition process (i.e. invading wetting phase viscosity divided by displaced nonwetting viscosity) are summarized in Table 2, and Figure 5 shows the effect of viscosity ratio on residual nonwetting phase trapping. Figure 5 demonstrates decreasing residual saturation with increasing viscosity ratio. Bachu and Bennion (2008) explain that as the viscosity ratio increases (lowering the nonwetting phase viscosity), the invading wetting fluid experiences less resistance while flowing in the pore space. In these instances, the wetting phase is more likely to dislodge nonwetting phase, and also will prevent nonwetting phase immobilization or trapping. A t-test analysis on the linear regression of the relationship between M and S_R indicates high statistical significance (p-value <0.001, see Table 3).

Figure 5. Residual nonwetting (NW) phase saturations as a function of experimental viscosity ratio (M) of the imbibition process, defined as invading (wetting) phase viscosity (μ_i) divided by displaced (nonwetting) phase viscosity (μ_d) for seven proxy fluid pairs.

4.4 S_R vs. Individual Fluid Parameters

From the analysis of S_R as a function of the dimensionless ratios Ca , Bo , and M ; the experimental system investigated here is dependent on all three capillary, viscous, and gravitational forces to varying extent. In this section we investigate fluid parameters individually to determine the dominant controls on the S_R response (Figure 6). Even if they are often used when reporting and analyzing the results of laboratory experiments, the dependence of residual trapping on these individual parameters (density, viscosity, contact angle, IFT, wetting and nonwetting phase viscosities) may become noisy and obscure due to the fact that, for the same value of one parameter, the interplay among the different forces may significantly vary.

Figure 6. Average residual nonwetting (NW) phase saturation (S_R) as a function of (a) imbibition flow rate, (b) invading wetting (W) phase viscosity, (c) displaced NW phase (viscosity, (d) interfacial tension, (e) contact angel, and (f) W-NW density difference for the seven fluid pairs.

4.4.1 S_R vs. Imbibition Flow Rate

Contrary to findings of other studies (e.g. Herring et al. (2013)), injection flow rate did not have a distinct isolated impact on the amount of trapped residual nonwetting phase (Figure 6a). This finding is, however, consistent with recent work by Mohammadian et al. (2014). A t-test analysis on the linear regression of all data points of all fluid pairs comprising residual nonwetting saturation as a function of flow rate results in a p-value of 0.28, indicating no statistical significance of the relationship between the dependent (S_R) and independent (flow rate) variables (Table 3). If flow rate were increased beyond the parameters of this study, it is likely that desaturation of nonwetting phase would indeed occur.

4.4.2 S_R vs. Wetting Phase Viscosity

Glycerol was added to the brine solution to isolate the impact of *wetting* fluid viscosity (invading phase viscosity) on residual trapping. Two glycerol solutions (G1A and G2A) were prepared

with viscosities that were approximately two and four times greater than the original brine solution, respectively. Figure 6 shows the wetting phase viscosities and the resulting S_R values.

The BA, BS, BO, T1A and T2A experiments all had wetting phase viscosities of 1.13 mPa-s. The G1A experiment had a viscosity of 1.86 mPa-s and a corresponding S_R of 5.10%, while the G2A experiment had a viscosity of 3.95 mPa-s and S_R values that ranged from 0-12.4%. Figure 6b shows that altering the wetting phase viscosity (by factors of two and four) does not increase trapping, i.e., the two glycerol solutions have a similar effect on residual trapping as the original brine solutions. Additionally, a t-test on the linear regression between S_R and wetting phase viscosity indicates that the relationship is not significant (p-value of 0.29, Table 3).

4.4.3 S_R vs. Nonwetting Phase Viscosity

Three nonwetting fluids (displaced phase) with viscosities varying by two orders of magnitude were used in experiments; air at 0.018 mPa-s, octane at 0.54 mPa-s, and Soltrol at 4.82 mPa-s. Nonwetting phase S_R values are plotted against these nonwetting phase viscosities in Figure 6c.

All of the proxy fluid pairs using air as the nonwetting fluid (BA, T1A, T2A, G1A and G2A) resulted in low residual nonwetting phase saturations between 0-12.4%. The three BO experiments have distinctly higher residual saturations (14.3-17.8%), and at the highest nonwetting phase viscosity, the BS fluid pair produced the highest residual nonwetting saturations of 21-38.5%. Despite some noise in the data, a distinct trend of increasing nonwetting phase residual saturation with increasing nonwetting phase viscosity was observed (R^2 value of 80%). Notice, however, that the trend is dictated by the results of experiments in which the viscosity of the brine is constant (i.e. BO and BS experiments), such that the trend in

564 nonwetting phase viscosity indeed corresponds to a trend in the viscosity ratio M , thus
565 confirming the relevance of the latter to determine the amount of trapping.

566 The statistical significance of the linear regression line of nonwetting residual saturation as a
567 function of nonwetting phase viscosity was also evaluated by a t-test. The resulting p-value was
568 less than 0.001 (Table 3), indicating that the relationship between residual saturation and
569 nonwetting phase viscosity is highly significant.

570 To further illustrate this trend, isosurfaces were created for the trapped nonwetting phase
571 resulting from displacement using different nonwetting phase viscosities. Figure 7 shows this
572 trapped nonwetting phase after secondary imbibition at 2 mL/hr in BA, BO and BS experiments.
573 The residual saturations increase from 4.20% for BA to 20.9% for BS with increasing
574 nonwetting phase viscosity, and the isosurfaces show that trapping is distributed uniformly
575 throughout the (imaged section of the) core for all three viscosities, eliminating potential
576 concerns about preferential flow paths that might emerge at higher nonwetting phase viscosity
577 (or lower viscosity ratio).

578

Figure 6d: 3D visualization of nonwetting phase trapping for experiments with brine and air (BA), brine and octane (BO), and brine and soltrol (BS), for an imbibition flow rate (Q) of 2 mL/hr. Values for interfacial tension (IFT, σ), displaced NW phase viscosity (μ_{NW}), fluid pair density difference ($\Delta\rho$), and residual saturation (S_R) are provided.

4.4.4 S_R vs. Interfacial Tension

The effect of IFT on nonwetting residual trapping (S_R) was also examined (Figure 6d). As stated above, wetting phase viscosity had no significant effect on trapping (Section 4.4.2) while nonwetting phase viscosity had a highly significant effect on trapping (Section 4.4.3); thus, fluid pairs with different nonwetting phase viscosity (i.e. BO and BS data) were excluded from

585 analysis. IFT values for the remaining five proxy fluid pairs (BA, T1A, T2A, G1A, and G2A)
586 ranged 37 – 72 mN/m.

587 For systems with low IFT, capillary forces are reduced and NW phase can more easily pass
588 through pore throats and therefore migrate through the sample; this is demonstrated by the slight
589 increase in S_R with increasing IFT (Figure 6d). This trend is in agreement with Bennion and
590 Bachu (2008) who found a modest increase in nonwetting phase trapping during imbibition with
591 increasing IFT (note that in the experiments of Bennion and Bachu viscosity was altered
592 simultaneously with IFT). However, the t-test analysis of the linear relationship between S_R and
593 IFT results in a p-value of 0.46, indicating that the relationship is not statistically significant
594 (Table 3).

595 To emphasize the necessity of consideration of fluid parameters other than IFT, isosurfaces of
596 residually trapped nonwetting fluid are presented in Figure 8. The T1A and BO experiments both
597 exhibit IFT of 37 mN/m; however, the fluid pairs exhibit distinct differences in trapped
598 nonwetting volume and spatial arrangement; with S_R values of 5.91% and 15.4% at 2 mL/hr, and
599 2.12% and 17.8% at 20 mL/hr for the T1A and BO experiments, respectively. If IFT alone
600 controlled residual trapping, then we would expect fluid pairs with the same IFT to produce
601 similar nonwetting phase saturations; however, this was clearly not the case. Based on the lack of
602 clear trend between S_R and IFT, as described above, we conclude that IFT alone is unable to
603 explain the variations in residual saturations because viscous and gravity effects are important
604 for the injection parameters considered here.

Figure 8. Residual (capillary trapped) nonwetting (NW) phase isosurfaces for experiments with Triton 1 and air (T1A) and brine and octane (BO), both of which exhibit an interfacial tension (IFT) of 37 mN/m. Experiments are shown for (a) imbibition flow rate of 2 mL/hr and (b) imbibition flow rate of 20 mL/hr. Values for interfacial tension (σ), displaced NW phase viscosity (μ_{NW}), fluid pair density difference ($\Delta\rho$), and residual saturation (S_R) are provided.

4.4.5 S_R vs. Contact Angle

Residual saturation shows no clear dependence on medium contact angle (Figure 6e). When a linear regression is applied to the data, it indicates a positive trend (i.e. increasing contact angle results in increasing trapping); this relationship is contradictory to a large body of previous literature (e.g. the studies presented in Section 2.4). From Figure 6e, it is apparent that the linear regression is skewed due to the inclusion of the Soltrol-Air data, which is also affected by high nonwetting phase viscosity (Section 4.4.3) and low wetting/nonwetting density difference (Section 4.4.5, below). Consequently, although the t-test analysis for nonwetting phase trapping as a function of contact angle results in a p-value of 0.002 (indicating the relationship is significant at a $p < 0.05$ level), we conclude that the influence of contact angle in these

experiments is overshadowed by other effects; and indeed, contact angle is not a significant parameter determining nonwetting phase trapping for this experimental system.

4.4.6 S_R vs. Density Difference

Residual nonwetting phase saturation decreases as the difference in density between the two fluid pairs increases (Figure 6f). In these experiments, all nonwetting fluids were the less dense fluid of the proxy fluid pair investigated and the imbibition process was carried out in the upward vertical direction. Thus, as density difference between the fluid pairs increases, nonwetting fluid is more likely to be mobilized upward, out of the column. This is analogous to a geologic CO₂ sequestration operation, where buoyant CO₂ will migrate upward in the storage reservoir.

A t-test analysis of the linear relationship between S_R and the wetting/nonwetting density difference results in a p-value <0.001, indicating that the relationship is strongly statistically significant (Table 3).

4.5 Discussion of the Interplay between the Three Forces

In these drainage-imbibition experiments in sintered glass bead columns, strong relationships were found between nonwetting phase residual trapping (S_R) and Bond number (Bo) and viscosity ratio (M) of the experiments. When analyzing the effect of the individual parameters independently, as it is customary in many studies, nonwetting-phase viscosity and wetting/nonwetting fluid density difference appeared the most important physical parameters influencing residual trapping: volume of trapped nonwetting phase consistently increased with increasing nonwetting proxy fluid viscosity and with decreasing difference in fluid densities. Note that in these experiments nonwetting phase viscosity, density difference, and imbibition

flow rate were altered by two orders of magnitude (from 0.0180 mPa-s to 4.82 mPa-s for nonwetting viscosity, 290 kg/m³ to 1206 kg/m³ for density difference, and 2 ml./hr to 500 ml/hr for imbibition flow rate); by comparison, viscosity of the wetting fluids were varied only between 1.13 mPa-s and 3.95 mPa-s, IFT between 25 mN/m and 72 mN/m, and contact angle from 5° to 45°. The largest residual nonwetting phase saturation was approximately 40%, significantly higher than previously published saturations for sintered or loose-packed glass bead packs (at imbibition Ca ranging from 10^{-4} – 10^{-2}).

To further evaluate the dominant forces at play in the imbibition process, Figure 9 provides evaluation of the inverse Bond number (Bo^{-1}) and the imbibition capillary number. For this analysis, Ca and Bo have been calculated as defined in equations 1b and 3b, respectively, in order to take into account medium contact angle. The product of the inverse Bond number (ratio of gravitational to viscous forces) and the imbibition capillary number (ratio of viscous to capillary forces) yields a ratio of viscous to gravitational forces ($'Bo^{-1} \cdot Ca'$); a similar analysis was previously presented by Polak et al. (2011) and Herring et al. (2015). Since Bo is dependent on grain size, the median bead size of 850 µm was used in the Bo calculations represented by the data points in Figure 9. Polak et al. (2011) and Herring et al. (2015) used this type of plot to identify the relative dominance of capillary, viscous and gravitational forces. The dominance of each force is indicated by the force arrows in Figure 9.

Figure 9. Force diagram showing the relative importance of capillary, viscous, and gravitational forces in an experimental system, with the experiments of this study (denoted as Harper et al. 2012) and two other studies from the literature presented. Inverse bond number (Bo^{-1}) represents the ratio of capillary to gravitational forces, and the product of imbibition capillary number to inverse Bond number ($Ca \cdot Bo^{-1}$) represents the ratio of viscous to gravitational forces during the imbibition process.

Findings from two additional fluid flow studies are also depicted in Figure 9. The Chatzis et al. (1988) data represents experiments conducted in consolidated sandstone cores and are located in the upper right-hand corner of the figure with relatively large Bo^{-1} and $Bo^{-1} \cdot Ca$ values (10^3 and $10^{-3} - 10^{-1}$, respectively). The results obtained by Herring et al. (2013) in consolidated media (although not represented in Figure 9) show similar trends as Chatzis et al. (1988), with data located in the capillary and viscous dominated regimes.

The second data set is from Mayer and Miller (1993) who performed fluid flow experiments in unconsolidated glass bead packs; the resulting Bo^{-1} and $Bo^{-1} \cdot Ca$ values from these experiments are located closer to our data towards the lower left-hand corner of Figure 9, indicating a slightly more gravity-dominated regime than our data. Our experimental results, which demonstrate significant dependence on nonwetting phase viscosity (or viscosity ratio) and wetting/nonwetting density differences (or Bond number), are perfectly complemented by Figure 9 which shows that our flow system spans the gravitational and viscous dominated regimes, with reduced influence due to capillarity (as is indicated by the limited effects of imbibition Ca , contact angle and altering IFT).

To account for the combined effects of viscous and gravity forces we introduce the modified capillary number (Ca^*):

$$Ca^* = \frac{1}{f} \left(1 - \frac{1}{M} \right) Ca + Bo, \quad (4)$$

where the coefficient f is a dimensionless permeability that describes the fact that the viscous force depends on the invading structure formed by the wetting phase, which affects the drag exerted by the porous medium; the incorporation of permeability in formulations of capillary number to properly describe viscous forces has been suggested by previous work (e.g., Armstrong et al. (2014)). In analogy to the criterion introduced by Saffman and Taylor (1958) for an analogous problem in a Hele-Shaw cell, Ca^* describes the stability of the flow, which is stable if $Ca^* > 0$ and unstable if $Ca^* < 0$. Notice that, in all experiments reported here, the denser fluid was injected from the bottom of the column; therefore, Bo was always positive and gravity acted to stabilize the flow. In contrast, viscous forces stabilized the flow if $M > 1$, but resulted in a

destabilizing force if $M < 1$. This duality of viscous forces is described by the prefactor in parenthesis, i.e., $(1-1/M)$, which ensures that the viscous term is negative when the flow is viscously unstable.

To estimate the dimensionless permeability coefficient, f , we used the Kozeny-Carman equation (Bear, 1972) in which we replaced the porosity by the volume fraction occupied by the wetting phase. This yields:

$$f = \frac{1}{n} \frac{1}{180} \frac{[n(1-S_R)]^3}{[1-n(1-S_R)]^2} \quad (5).$$

Notice that the prefactor $(1/n)$ appears in equation 5 because the capillary number was defined as the mean pore velocity and not as the Darcy velocity. The residual nonwetting phase saturation is plotted as a function of the modified capillary number, Ca^* , in Figure 10. The values of Ca^* presented in Figure 10 incorporate Ca and Bo as calculated in equations 1b and 3b, respectively, which include medium contact angle in the equation formation. A very clear trend can be noticed: the residual nonwetting phase saturation increases when the modified capillary number decreases as a result of the decreased stability of the flow, which promotes the formation of fingers, leaving more nonwetting fluid behind the invading front.

5.0 Application to Geologic Sequestration of Supercritical CO₂

The results presented in this study represent greatly simplified conditions relative to supercritical CO₂ sequestration scenarios in geologic reservoirs wherein complex system properties such as medium surface chemistry and mass transfer must be considered. Nevertheless, the results of this study do provide insight into the immiscible fluid flow behavior of geologic sequestration scenarios, particularly those *in which gravitational or viscous forces* are determined to dominate over capillary forces (as per the force balance analysis presented in Figure 9, (Herring et al., 2015; Polak et al., 2011)); for such systems, imbibition viscosity ratio (M) and Bond number (Bo) should be minimized in order to increase capillary trapping of supercritical CO₂. For example, injection pressure and temperature could be manipulated in order to increase the viscosity or density of the CO₂, or storage reservoirs could be selected such that reservoir pressure and temperature are conducive to a high viscosity and high density CO₂ state (i.e. relatively high pressure, relatively low temperature (Bachu, 2003)). Unfortunately, the range of CO₂ viscosity variation available for conditions of potential storage reservoirs is small (e.g., using pressure-temperature conditions of potential storage reservoirs reported by Bachu (2003)) compared to the range of nonwetting phase viscosity investigated in this study. However, recent studies of co-injection of brine and supercritical CO₂ have noted CO₂ viscosity as a crucial parameter controlling supercritical CO₂ flow patterns, distribution, and relative permeability; and have demonstrated a transition in these properties for CO₂ viscosity changes as small as 0.02 to 0.06 mPa·s (Reynolds et al., 2014). Additionally, the use of CO₂ with engineered viscosity is being explored, for instance nanoparticle-stabilized CO₂ for EOR [45]. Alternatively, increased trapping can also be achieved by decreasing the viscosity ratio of the fluids, i.e., by decreasing

the viscosity of the wetting phase. It is not feasible to decrease the viscosity of reservoir brine, but reservoirs of low salinity (and thus lower viscosity and density) could be preferentially selected. Further, for scenarios where a chase water or brine flood would be utilized, use of low salinity brine or water injections would decrease the wetting phase viscosity and density.

6. Conclusions

The optimization of the capillary trapping mechanism was investigated by proxy fluid pair experiments in a mildly consolidated glass bead pack. Alterations were made to fluid flow rate, wetting and nonwetting fluid viscosity, nonwetting fluid density, and interfacial tension to determine the combined and individual effectiveness of these variables on residual nonwetting phase trapping efficiency.

The effects of the imbibition capillary number on residual trapping have been extensively studied, observing, in general, that the trapped nonwetting phase will increase with decreasing capillary number. However, considering only capillary number does not provide a complete picture of the displacement process; the viscosity ratio of the fluids involved also needs to be taken into account, particularly at relatively high capillary numbers, for which viscous effects dominate; and in a three-dimensional (3D) system, gravity forces must be considered as well. Our residual saturation data, which was collected from experiments that altered and isolated the individual elements of imbibition capillary number, viscosity ratio, and Bond number show that consideration of all three ratios Ca , M , and Bo is necessary to provide a coherent explanation of the results. Contrary to other studies which show that capillary trapping is highly dependent on imbibition Ca , IFT, and porous medium contact angle (as discussed previously), we find that our system is dominated by gravitational and viscous forces (Figure 12), exhibiting strong

relationships between residual nonwetting phase saturation (S_R) and imbibition M and Bo.

Further analysis demonstrates that nonwetting phase viscosity and wetting/nonwetting density difference are the most important factors affecting nonwetting phase capillary trapping for this experimental system.

The fluid parameters which will have the most impact on capillary trapping of supercritical CO₂ in a geologic setting will likely vary, and depend on which forces dominate in a given system (Herring et al., 2015). The most appropriate numbers to describe the flow are a combination of Bo, Ca, and M; and rather than focusing on individual parameter values, it is always safer to characterize the flow by the dimensionless numbers, which more fully describe the interplay among the forces. We have introduced a modified Capillary number formulation (Ca^* , equation 4), which takes into account all the fluid parameters contributing to the three capillary, viscous, and gravitational forces; and which also includes a dimensionless permeability term to fully describe the dependence of the viscous force on the invading structure of the wetting phase as it moves through channels defined by the pore space and trapped nonwetting phase.

Although we acknowledge that the ambient condition system considered in this study is not fully representative of reservoir conditions, our results suggest that for geologic systems which demonstrate viscous and gravitational dominance over capillarity, capillary trapping of supercritical CO₂ could be enhanced by minimizing the Bond number and imbibition viscosity ratio of the system. To achieve low Bo and M values, supercritical CO₂ density and viscosity should be elevated (via manipulation of injection or reservoir pressure and temperature conditions), or wetting phase (brine) density and viscosity should be minimized by use of low salinity reservoirs and/or chase brine floods.

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944 2 Supplementary Materials

945 A.1. Materials and Methods

946 All of the primary imbibition, drainage and secondary imbibition scans were aligned to the dry
947 scan such that the wetting and nonwetting fluid phases could be more easily isolated from the
948 glass beads, which remain constant throughout each phase of the experiment. After the images
949 were aligned, the reconstructed volumes were converted from 16-bit grayscale images (with
950 voxel values ranging from 0 to 65535) to trinary segmented images in which each voxel is
951 assigned a value of 0, 1 or 2, thus making the phases (and thereby wetting and nonwetting fluid
952 saturations) more easily quantifiable.

953 To accurately and reliably threshold (and thus segment) the images, the upper and lower
954 intensity values of the wetting and nonwetting fluids were first defined. In the following we refer
955 to the dry scan as the “dry” volume and the primary imbibition, drainage, and secondary
956 imbibition scans as the “wet” volumes. Figure A1 is a sample histogram showing voxel intensity
957 information from example dry and wet scans. Voxel values represent x-ray absorption intensity
958 and appear in the histogram according to the frequency in which they appear in each volume.

Figure A1. Sample histogram containing voxel intensity values and the frequency in which they occur in a dry and wet grayscale volume.

The dry volume, containing only nonwetting phase (air) and glass beads, has two distinct peaks, whereas the wet volume, containing nonwetting phase (air), wetting phase (brine) and glass beads, has three less well-defined peaks as shown by the histogram. The image threshold boundaries (i.e. binary limits) are associated with the first local minima of each curve (at approximately 34000 voxel intensity for the dry and wet scans in Figure A1).

The threshold boundaries for segmentation should be selected based on the identified local minima from image histograms. However, for our data, minima identification from a histogram does not produce accurately segmented images due to noise in the transition areas between the nonwetting, wetting and solid phases. This is evident in Figure A2 which shows a sample reconstructed grayscale image and a profile of the intensity values across the identified line. The resulting intensity profile shows that the difference between the intensity values associated with

975 solid phase and wetting phase are not as distinct as the difference between the nonwetting phase
976 and the solid phase.

977
978
979 **Figure A2. Plot profile of sample slice indicating the noise between the boundaries of the**
980 **nonwetting, solid and wetting phases**

Due to the ambiguity between the phases, the solid phase and wetting phase can potentially be misidentified during segmentation when only the local minima of the histogram are utilized (“*histogram minima segmentation*” method). Alternately, the local minima were manually located and adjusted to identify *only* the glass beads in the dry volume, and *all* of the wetting phase and some of the glass beads in the remaining wet volumes. This method (“*overestimation segmentation*”), while overestimating the location of the local minima slightly, ensured that the nonwetting phase was completely isolated in both the dry and wet images, thus reducing the possibility of misidentified phases and error during segmentation and, ultimately, in the final results. The difference between the two thresholding methods is shown by a comparison of two final segmented images of the same slice, along with the original grayscale image, in Figure A3.

Figure A3. A grayscale image (a) segmented by both (b) the histogram minima segmentation method, and (c) the overestimation segmentation method

An isolated glass bead in the upper left hand corner of the grayscale image in Figure A3 is surrounded by nonwetting phase in black (air). However, the histogram minima method in the middle image of Figure A3 misidentifies the phase surrounding the isolated bead as wetting phase (brine) shown in black. The final image on the right of Figure A3 is an example of the overestimation segmentation method. This method produced a more accurate nonwetting, wetting and solid phase segmentation.

1001 All of the volumes were median filtered to remove noise in the data prior to being segmented.
 1002 Once the dry and wet volumes were binarized, solid phase and the oversegmented nonwetting
 1003 phase was combined to create an image with each phase being assigned a value of 0, 1, 2 or 3.
 1004 The volumes are then processed to reassign oversegmented voxels to the correct value associated
 1005 with the solid phase. A final segmented image with three distinct phases is thus produced.

1006 After segmentation, the extra space surrounding the glass core was removed from the image. The
 1007 remaining pixels were labeled and the total number of voxels associated with each of the three
 1008 markers: glass beads, wetting phase and nonwetting phase were calculated.

1009 A.2 Statistical Analysis

1010 **Linear relationships between residual nonwetting phase saturation and individual fluid parameters**
 1011 **are evaluated by a two-tailed student's t-test, where the t-value is determined by equation A.1:**

$$1012 \quad t = R \sqrt{\frac{n-2}{1-R^2}} \quad (\text{A.1})$$

1013 **where R^2 is the coefficient of regression of the linear trendline and n is the number of data points**
 1014 **comprising the data set. In this study, a p-value of <0.001 is considered to be a strongly significant**
 1015 **correlation.**