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Key Points:

- In situ capillary pressure was found by measuring interfacial curvature
- Trapping was examined by comparing local pore shape to capillary pressure
- We present a new formulation of capillary number based on pore-scale physics

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Pore-by-pore capillary pressure measurements using X-ray microtomography at reservoir conditions: Curvature, snap-off, and remobilization of residual CO₂

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Abstract X-ray microtomography was used to image the shape and size of residual ganglia of supercritical CO₂ at resolutions of 3.5 and 2 μm and at representative subsurface conditions of temperature and pressure. The capillary pressure for each ganglion was found by measuring the curvature of the CO₂-brine interface, while the pore structure was parameterized using distance maps of the pore space. The formation of the residual clusters by snap-off was examined by comparing the ganglion capillary pressure to local pore topography. The capillary pressure was found to be inversely proportional to the radius of the largest restriction (throat) surrounding the ganglion, which validates the imbibition mechanisms used in pore-network modeling. The potential mobilization of residual ganglia was assessed using a reformulation of both the capillary (N_{cmacro}) and Bond numbers (N_{bmacro}), rigorously based on a balance of pore-scale forces, with the majority of ganglia remobilized at N_{cmacro} around 1. Buoyancy forces were found to be small in this system ($N_{bmacro} \ll 1$), meaning the gravitational remobilization of CO₂ after residual trapping would be extremely difficult.

1. Introduction

Carbon capture and storage (CCS) could be a major contributor to the reduction of greenhouse gas emissions, potentially contributing 2.5 Gt/yr to total emission mitigation [IEA, 2012]. Geological CCS is the process where carbon dioxide (CO₂) is captured from large point sources, such as power plants or oil and gas installations, and injected into the subsurface, usually into porous rock. Here it displaces resident brines such that the CO₂ remains in the subsurface for hundreds to thousands of years. The four mechanisms available to immobilize CO₂ are stratigraphic, solubility, mineral, and residual trapping [Bachu, 2008]. Stratigraphic trapping refers to buoyant CO₂ which pools underneath an impermeable boundary formation, similar to hydrocarbon traps, and is thought to immobilize the vast majority of the CO₂ during the initial phase of CO₂ injection. Solubility trapping is when CO₂ dissolves into the resident formation brine surrounding the CO₂ plume [Ennis-King and Paterson, 2002]; this principally takes place over hundreds to thousands of years. Mineral trapping is where solid carbonate minerals are precipitated in the pore space of the rock [Lin et al., 2007] with a timescale of thousands to tens of thousands of years. Residual or capillary trapping occurs as CO₂ is held in place by surface forces as tiny droplets (ganglia) in the pore space of the rock; this process can be rapid—immobilizing a significant fraction of the CO₂ in a few years. This can occur either naturally, by the migration of brine into the CO₂ plume, or can be induced by the injection of chase brines [Qi et al., 2009].

Carbonate and sandstone saline aquifers represent important potential storage sites for CO₂ due to their large capacities and wide geographic spread. They are, however, associated with uncertainties in seal characterization and seismic risk [Hawkes et al., 2005; IPCC, 2007; Lackner, 2003]. Under these conditions, stratigraphic trapping becomes less reliable; however, engineered capillary trapping by chase-brine injection that fixes CO₂ in the porous space becomes extremely attractive, particularly over the short to medium term. It is, therefore, of great importance to address the security of the residual phase to prevent subsequent ganglia movement caused by viscous forces (due to a prolonged chase-brine injection) or by gravity forces (due to naturally occurring density differences). One of the main goals of our work is to examine the mechanisms by which ganglia may be remobilized on a pore-by-pore basis at reservoir conditions and present a methodology that yields an accurate description of the remobilization that can help design an injection strategy that maximizes capillary trapping.

Recent advances in microtomography have allowed for the noninvasive imaging of fluid distribution in rocks at conditions of pressure, temperature, and salinity representative of oil reservoirs and saline aquifers. This work has not only examined the distribution of residual saturation in different types of rocks [Andrew *et al.*, 2013, 2014b] but also started to examine the fundamental controls on multiphase flow in porous media with new tools to examine wettability and contact angle [Andrew *et al.*, 2014a]. Experiments examining multiphase flow in the supercritical (sc) CO₂-brine-rock system must be conducted at these conditions as petrophysical properties (such as surface tension and contact angle) are strongly pressure and temperature dependent [Espinoza and Santamarina, 2010; Li *et al.*, 2012; Spiteri *et al.*, 2008]. Recent results have shown significant differences in trapping behavior between ambient oil-water-rock systems, where 60–99% of the residual saturation is trapped in a single connected ganglion [Georgiadis *et al.*, 2013], and realistic scCO₂-brine-rock systems, where in most cases the largest single ganglion contributes less than 10% to the total residual saturation [Andrew *et al.*, 2013, 2014b].

Capillary pressure, defined as the difference in pressure between a nonwetting and wetting phase in a porous medium, is fundamentally a pore-scale phenomenon arising from the equilibrium pressure difference across a curved interface separating two immiscible fluids

$$P_c = P_{nw} - P_w \quad (1)$$

where P_c is the capillary pressure, P_{nw} is the nonwetting phase pressure, and P_w is the wetting phase pressure. The wetting phase adheres most readily to the rock surface and the nonwetting phase adheres least readily. If interfacial and pressure forces are balanced, this pressure difference can be related to the geometry of the interface, specifically the interfacial curvature, by the Young-Laplace equation

$$P_c = 2\sigma\kappa = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

where σ is the interfacial tension, κ is the mean curvature, which can be determined using the two principal radii of curvature R_1 and R_2 .

If we consider a simple capillary tube geometry, the interfacial curvature can be related to the contact angle and tube diameter (d)

$$\kappa = \frac{2\cos\theta}{d} \quad (3)$$

where θ is the contact angle. In real systems, however, curvature cannot be determined analytically, as it is formed by a combined effect of arbitrarily complicated pore morphology and contact angle. The full information on curvature has, therefore, been previously inaccessible in natural rock at reservoir/aquifer pressures and temperatures and its examination is therefore one of the primary objectives of this paper.

At the macroscale capillary pressure is usually defined such that the values of capillary pressure uniquely determine nonwetting phase saturation for a given displacement sequence. This relationship between capillary pressure and saturation can be determined experimentally using different coreflood experimental techniques, such as mercury injection capillary pressure [Purcell, 1949], porous plate coreflooding [El-Maghraby and Blunt, 2013; Pentland *et al.*, 2011], and quasi steady state flooding [Pini *et al.*, 2012]. These, however, rely on external pressure measurements, and so can only determine interface pressure differences around phase clusters connected to a pressure transducer. This means that the full information on capillary pressure distribution present in disconnected nonwetting phase clusters has remained a challenge. Recent work has, however, correlated the externally derived capillary pressure measurements with direct pore-scale measurements of interface curvature [Armstrong *et al.*, 2012]. In our previous work, we examined cluster size distributions in a wide range of rocks, showing that the structure of the pore space and its connectivity play a vital role in the capillary trapping process, with better connected pore spaces having more large clusters relative to small clusters, and vice versa [Andrew *et al.*, 2014b]. Despite these advances, further work is needed to fully examine the pore-scale processes associated with the formation and remobilization of these residual ganglia on a pore-by-pore basis at reservoir conditions.

In this paper, we use in situ X-ray microtomographic imaging coupled with new interface curvature measurement tools to examine the capillary pressure distribution at the end point of the CO₂ trapping process. We

Figure 1. Experimental apparatus. (a) The pumps used to control fluid flow and the seating of the cell within the μ CT enclosure. (b) Detail of the flow cell, heating apparatus, and the seating of the core assembly. (c) Detail of the core assembly, showing a triple aluminium wrap around the core, preventing diffusive CO_2 exchange across the Viton sleeve.

relate these measurements to the local pore space topography that is responsible for the snap-off of the nonwetting phase. Moreover, we use a combination of experiment and pore-scale modeling analysis to present a new methodology to examine how trapped CO_2 could be remobilized by either viscous or gravitational forces, with specific reference to the importance of local pore space structure.

2. Materials and Methods

The experimental apparatus is shown in Figure 1; the rock and fluids were imaged using a Versa XRM-500 X-Ray Microscope (www.zeiss.com). The experiments were conducted on a single carbonate quarry sample, Ketton Oolite, from the

Upper Lincolnshire Limestone Member from Ketton, Rutland, UK, which was deposited 169–176 million years ago. Helium porosimetry (Weatherford Laboratories, East Grinstead, UK) shows the rock to have a porosity of 23.37% and a gas permeability of $2.807 \times 10^{-12} \text{ m}^2$. X-ray diffraction analysis shows the rock to be composed of >99% calcite.

Ketton limestone was chosen as a sample rock type as it is an oolitic grainstone with large intergranular pores. This makes tracing fluid-fluid and fluid-rock interfaces simpler than in more complex bioclastic carbonate. It still has, however, a realistic flow and transport signature of natural rock, similar to sandstone samples and dissimilar to sandpacks and synthetic porous media such as bead packs [Bijeljic *et al.*, 2011, 2013a, b].

Samples were drilled into cylindrical cores 4–6.5 mm in diameter and 10–30 mm in length. Sample preparation procedures and further details of the apparatus are provided elsewhere [Andrew *et al.*, 2014b]. The ionic salt used in the brine was potassium iodide (KI) with a salinity of 0.42 mol kg^{-1} (7 wt %). KI was used as it has a higher linear X-ray attenuation coefficient than other solutes (such as NaCl), making it an effective contrast agent. The salinity was chosen such that the X-ray absorption of the brine was intermediate between the absorption of the rock grains and that of the scCO_2 .

Solubility issues make experiments at high capillary numbers extremely difficult as rapid fluid flow not only makes temperature control more challenging, but also the large number of pore volumes passed through the core mean any small differences in solubility state between the core and the reactor during flow (due to, for example, small differences in temperature) could result in exsolution or dissolution of CO_2 from brine, resulting in a change in saturation without viscous displacement. When scCO_2 is injected into a saline carbonate aquifer it will dissolve into the resident brine, forming a highly reactive carbonic acid, which will in turn start to dissolve any calcite present. To prevent this, and represent conditions present in the aquifer far away from the injection site, the brine was pre-equilibrated with scCO_2 by vigorously mixing the two fluids together with small particles of the host rock in a stirred and heated reactor (Parr Instruments Co., IL, USA).

2.1. Flow Strategy and Image Acquisition

Scans were taken of residual scCO_2 , which was achieved through the following steps:

1. The pressure and temperature of the reactor were raised to the desired pressure and temperature of the pore fluid during the experiment (50°C and 10 MPa) and were vigorously mixed until no further change

- in pump volume was seen, taking typically 1 h. Fluids and solid were then mixed for an additional 12 h before the start of each experiment to ensure chemical equilibrium.
2. A confining pressure of 11 MPa was established in the cell.
 3. The pore space was filled with KI doped brine that had not been equilibrated with scCO₂. This brine was then raised to the same pressure and temperature as the reactor, dissolving any CO₂ or other gases which had not been removed by miscible displacement.
 4. More than 1000 pore volumes of equilibrated brine were flushed through the core to miscibly displace the unequilibrated brine, ensuring 100% initial brine saturation.
 5. One milliliter (around 20 pore volumes) of scCO₂ was passed through the core at very low flow rates ($1.67 \times 10^{-9} \text{ m}^3/\text{s}$). This corresponds to a traditional capillary number:

$$N_c = \mu q / \sigma \quad (4)$$

where μ is the brine viscosity, q is the Darcy velocity, and σ is the wetting-nonwetting phase interfacial tension) of around 9×10^{-7} , well within the capillary dominated regime. Two-dimensional (2-D) projections were continually taken in order to observe the point when scCO₂ displaces brine in the pore space.

6. One milliliter (around 20 pore volumes) of equilibrated brine was passed through the core at the same low flow rate, causing scCO₂ to become trapped as a residual phase in the pore space.

After step 6, 1600 projections were taken of the sample at regular angular intervals, taking approximately 75 min to acquire. Fluid rearrangement during the scan was minimized by allowing the system to re-equilibrate for 20 min before the scan. These projections were then reconstructed into a three-dimensional (3-D) volume using proprietary software on the Versa system, creating a reconstructed volume of 1000³ voxels. Two experiments were performed, one using a 4 mm diameter core imaged with a voxel size of 2.013 μm and one with a 6.5 mm diameter core imaged with a voxel size of 3.533 μm . The higher resolution experiment was used to test the impact of resolution on the curvature measurement, while the lower resolution experiment was used to examine the viscous and gravitational remobilization of ganglia. The analyzed volume for the lower resolution scan was more than five times larger than for the high resolution experiment, allowing for more ganglia to be examined and a more statistically representative sample to be collected, with very little change to the observed capillary pressure (see section 2.3).

2.2. Image Processing and Analysis

After acquisition, the images were filtered using a nonlocal means edge preserving filter [Buades *et al.*, 2005, 2008] before being corrected for any beam hardening or softening artifacts created during acquisition by subtracting a fitted second-order polynomial surface, assumed to be constant in the Z direction, to the image. The segmentation of images containing a partial saturation of multiple fluids is significantly more complicated than the segmentation of dry images, so the use of simple gray scale universal thresholding was insufficient [Sheppard *et al.*, 2004]. The image was segmented into three phases (rock grains, brine, and scCO₂) by the use of a seeded watershed algorithm, where a seed was generated using a 2-D histogram of both the gray scale and the gray scale gradient images [Jones *et al.*, 2007]. This seed was then grown using a watershed algorithm on the gray scale gradient image. The segmented image was then analyzed in 3-D to identify each unique disconnected ganglion, which was then labeled (Figure 2). A detailed description of these image processing techniques is beyond the scope of this paper; however, an excellent recent review can be found in Schluter *et al.* [2014].

A subvolume around each CO₂ ganglion was then extracted and resegmented into three phases using the same 2-D histogram-based watershed method detailed above. Local segmentation was likely to be more accurate than global segmentation as the polynomial artifact correction process described above may not remove all variations in gray scale across an image. The scCO₂ phase was then extracted and a smoothed surface was generated across it using a generalized marching cubes algorithm [Hege *et al.*, 1997; Stalling *et al.*, 1998]. The magnitude of smoothing across the ganglion surface could be altered by changing the size of the kernel of a modified Gauss filter used to compute probability weights during the surface assignment. The impact of the size of this kernel, and so the amount of smoothing, is examined later in section 2.3. The surface was labeled as either the CO₂-brine interface or the CO₂-grain interface by the use of the Sobel edge detection filter [Engel *et al.*, 2006].

Figure 2. The image processing workflow. (a) The raw reconstructed image. CO_2 is the darkest phase, rock grains are the lightest phase, and brine is the intermediate phase. (b) The raw image has been filtered using a nonlocal means edge preserving filter. (c) A higher resolution subsection of the raw reconstructed image. The ganglion shown here is the same shown in Figures 2h–2j, 3, and 7. (d) A high resolution subsection of the filtered image. (e) The watershed seed image used for the initial segmentation step. (f) The expanded label image, found by growing the labeled voxels in Figure 2e using a watershed algorithm. (g) A map of the ganglia present within the segmented image. (h) A subvolume of the unsegmented filtered data, as shown by the white square in Figure 2g. (i) The data were resegmented using the same 2-D seeded watershed algorithm, then a surface was generated using a generalized marching cubes algorithm. (j) The curvature of this surface was found by creating best fit quadratic surfaces across the interface.

The curvature of this surface is found by approximating the surface locally as a quadratic form. The eigenvalues and eigenvectors of this quadratic form represent the principal curvature values and the directions of principal curvature, respectively. A surface scalar field is produced where the principal radii of curvature are averaged and assigned to each element across the interface. This method was originally described in *Armstrong et al.* [2012]. The distribution of curvature seen across the CO_2 -brine interface of a representative ganglion is shown in Figure 3.

The distribution clearly shows a single, well-defined peak, representing a single capillary pressure across the entire CO_2 -brine interface. This distribution is then fitted using a trust region algorithm [Conn et al., 2000] to estimate the peak position from which peak position the pressure difference across the CO_2 -brine interface—the microscopic capillary pressure—is calculated using the Young-Laplace equation (equation (2)). The CO_2 -brine interfacial tension is estimated by linearly interpolating between measurements found in *Georgiadis et al.* [2010] and *Li et al.* [2012], for a given pressure, temperature, and salinity, and a value of

Figure 3. (a) A histogram of the curvature of the CO₂-brine interface for a single ganglion. The blue line represents a fitted Gaussian distribution, giving an objective estimation of peak position. (b) The curvature map across a single ganglion. Blue colors represent the low curvatures and yellow colors represent the high curvatures. Gray areas represent the regions of the CO₂ ganglion which are in contact with the rock grain and which are ignored in the analysis.

0.0339 N/m was used in this study (see Table 1 for this and other fluid properties). Ganglion volume was measured by counting voxels and interfacial area was calculated measuring the area of the surface labeled as the CO₂-brine interface.

The CO₂ and brine labels of the whole segmented image were then joined together, so that the entirety of the pore space could be analyzed as a single unit. The pore space was separated into individual pores by finding the watershed catchment basins of a Euclidian distance map of the pore space (Figure 4) [Beucher and Lantuejoul, 1979; Wildenschild and Sheppard, 2013].

These pores were then individually labeled, and the interfaces between them defined as throats. Each throat was given a “radius” equivalent to the maximum of a Euclidian distance evaluated around the throat plane, equivalent to the radius of the maximum inscribed circle through the throat plane. The viscous remobilization criterion proposed in this work is stated as when the viscous pressure drop across a ganglion is larger than the difference between the static capillary pressure and the capillary pressure required to pass through the largest of the adjacent throats. The largest adjacent throat was used as we do not know exactly through which throat a ganglion may be remobilized, so the most cautious case was chosen, that of the largest adjacent throat. A total of 433 pores were analyzed in this sample, connected by 1943 throats. Twenty-one ganglia were analyzed, occupying a total of 46 pores, surrounded by 484 throats. The largest single ganglion contributes only 25% of the total residual CO₂—a relatively small fraction, indicating that the ganglion distribution is statistically well represented in this system.

The viscous pressure drop was calculated by simulating incompressible viscous flow directly through the wetting phase. The volume conservation equation and the Navier-Stokes equation were solved for the wetting phase flow in the voxelized pore space by the method presented in Bijeljic *et al.* [2013a] and Raeini *et al.* [2012] that is based on the finite-volume code in OpenFoam. The spatial discretization was achieved by creating a finite-volume mesh through converting each image voxel into a grid block. We apply constant pressure boundary conditions at the inlet and outlet faces and zero-gradient boundary condition for velocity on the lateral sides. A no-slip boundary condition is used at solid voxel boundaries and at the interface between fluid phases. Mass and momentum balance equations are solved through an iterative scheme based on Pressure Implicit with Splitting of Operators (PISO) algorithm Issa [1986], until the velocity field becomes steady state.

Table 1. List of Key Fluid and Rock Properties Used in This Study

Darcy Velocity (m s ⁻¹)	σ^a (N m ⁻¹)	μ^b (Pa s)	Permeability (m ²)	Wetting Phase Relative Permeability
4.87×10^{-5}	0.0339	6.24×10^{-4}	3.59×10^{-12}	0.283

^aTaken from Li *et al.* [2012].

^bTaken from Batzle and Wang [1992].

Figure 4. Ganglion occupying two pores. (a) A rendering where each pore close to the ganglion shown in Figures 4b–4d, as found using the watershed basins of the distance map of the pore space, is rendered in a different color. (b) The ganglion surface in purple. (c) The ganglion is situated within two pores, with pore 1 colored yellow and pore 2 colored red. The narrow pore throat is indicated. (d) The pressure field calculated using finite-volume method in OpenFOAM [Bijeljic et al., 2013b; Raeini et al., 2012]. Blue regions represent the low pressure and red regions represent the high pressure. The maximum viscous pressure drop across the ganglion was found by finding the maximum and minimum pressure in the wetting phase adjacent to the ganglion.

The viscous pressure drop across each ganglion was then calculated by finding the maximum and minimum pressure of the wetting phase voxels in contact with the ganglion (Figure 4). The system was simulated at low Reynolds numbers; the pressure drop across a ganglion scaled linearly with the total pressure drop across the simulated volume, which in turn is proportional to the Darcy flow rate. Using Darcy's law, the absolute permeability was calculated from the simulations on the image fully saturated with water. The wetting phase relative permeability was then computed from the ratio of the absolute permeability calculated for fully saturated flow to that calculated through the imaged wetting phase at the end of the experiment. The relative permeability of 0.28 (see

Table 1) indicates that the ganglia restrict flow through some of the larger pore spaces, but that there is still significant connectivity of the wetting phase.

2.3. Measurement Error

To quantitatively address potential measurement error for the image analysis process described above, we conducted two sensitivity studies. First, we address the impact that voxel size has on calculated ganglion curvatures, then we examine the impact that different amounts of smoothing during surface generation have on resulting curvature distributions. In order to examine the impact of voxel size on measured curvature data from a high resolution experiment (with a voxel size of $2\ \mu\text{m}$) was artificially coarsened to a voxel size of $4\ \mu\text{m}$ by binning the data from around 1000^3 to 500^3 . The surface generation and curvature extraction procedure described above were then applied at both resolutions (Figure 5).

Figure 5. The variation of fitted curvature with voxel size. The peak curvature position measured at a $2\ \mu\text{m}$ voxel size is indicated on the x axis, and the peak curvature position measured on a subsampled lower resolution image is shown on the y axis. The black line shows a 1:1 correspondence.

Figure 6. The impact of the smoothing kernel size on curvature distribution for a surface generated from a ganglion extracted from the larger voxel size ($3.533 \mu\text{m}$) image. The curvature peak position remains almost unchanged.

For this system, coarsening to a $4 \mu\text{m}$ voxel size has little effect on the peak curvature position, so the experiment with a larger voxel size ($3.533 \mu\text{m}$) was used for all subsequent analysis, since many more ganglia could be sampled. To examine the impact of smoothing on resulting curvature at larger voxel sizes, surfaces were generated across a representative ganglion multiple times using different smoothing kernel sizes (Figure 6).

The peak curvature value changes very little with an increasing amount of surface smoothing (Figure 7). As the magnitude of the principal radii of curvature of the CO_2 -brine interface is around 100 times the voxel size, smoothing across these curvatures has a relatively small impact on their distribution.

3. Results and Discussion

3.1. Snap-Off

The interface curvature and the corresponding ganglion capillary pressure are observed to be a strong function of local pore topography, as measured by the maximum throat radius adjacent to the ganglion (Figure 8). Ganglia that have smaller maximum

adjacent throat radii are characterized by higher calculated capillary pressures.

This is explained by the process of snap-off [Roof, 1970]. During capillary-driven wetting phase ingress (imbibition), the capillary pressure decreases along a hysteretic capillary pressure curve. As the capillary pressure decreases, the wetting phase (brine) layers in throat corners will swell until the CO_2 -brine interface becomes unstable, causing the throat to rapidly fill with water. If this throat is the only connection between a volume of CO_2 that may become isolated and the connected CO_2 phase, its filling will result in the formation of a disconnected CO_2 ganglion that

Figure 7. (a) The variation of fitted curvature peak position with smoothing kernel size for a surface generated from a ganglion extracted from the larger voxel size ($3.533 \mu\text{m}$) image. Once more than a small amount of smoothing is applied, the curvature peak position remains unchanged. (b–e) The same ganglion rendered with different amounts of smoothing across the CO_2 -brine interface. (b) 1 voxel kernel size, (c) 1.5 voxel, (d) 5 voxel, and (e) 9 voxel.

Figure 8. The variation of ganglion capillary pressure with maximum adjacent pore throat radius.

preserves the capillary pressure at which it became immobilized. This process can be best understood by considering a set of throats surrounding a region of the pore space filled with CO_2 . These throats can be represented by a set of hypothetical elements with cross sections consisting of scalene triangles, with corner half angles β_1 , β_2 , and $\beta_3 (=180 - (\beta_1 + \beta_2))$ (Figure 9), defined such that $\beta_1 \leq \beta_2 \leq \beta_3 < \pi$ [Mason and Morrow, 1991]. The elements maintain both the maximum inscribed radius, r , of the original throats with a shape factor G , such that $G = \frac{A}{P^2}$, where A is the cross-sectional area of the throat and P is its perimeter.

Snap-off will occur when two of the wetting phase corner regions swell until they come into contact, after which the CO_2 -brine interface becomes unstable and the throat rapidly fills with brine. If all three interfaces swell concurrently, this will occur between the interfaces in the two corners with the smallest half angles at a threshold capillary pressure [Valvatne and Blunt, 2004]:

$$P_{c-so} = \frac{\sigma}{r} \left(\cos \theta_a - \frac{2 \sin \theta_a}{\cot \beta_1 + \cot \beta_2} \right) \quad (5)$$

As β_1 and β_2 are not uniquely defined by inscribed radius and shape factor, the snap-off capillary pressure is also nonuniquely defined. It is therefore useful to consider the case where $\beta_1 = \beta_2 = \beta$, so equation (5) reduces to

$$P_{c-so} = \frac{\sigma}{r} (\cos \theta_a - \sin \theta_a \tan \beta) \quad (6)$$

Figure 9. Throats can be represented as idealized triangular elements. (a) The half angles and maximum inscribed circle for a pore throat. (b) During imbibition the brine layers swell until two layers come into contact, making the CO_2 -brine interface unstable and causing the throat to rapidly fill with brine in the process of snap-off.

For a given shape factor and radius, the snap-off capillary pressure is now uniquely defined, and should scale approximately with the inverse of the inscribed throat radius. If local capillary equilibrium is maintained, and the throat half angle is constant, as capillary pressure decreases, connected throats will snap-off in order of radius size. The final throat to snap-off, disconnecting a residual ganglion, will therefore have the largest inscribed radius, and the resulting ganglion should preserve the capillary pressure at which this throat snapped off. As capillary equilibrium is maintained beyond a single pore, a CO_2 ganglion can span multiple pores. This occurs if snap-off in adjacent pores causes the ganglion to be isolated from the rest of the connected CO_2 phase before all the throats adjacent to a single pore have snapped off.

A correlation can be seen between the capillary pressure of a ganglion and the maximum inscribed radius of the adjacent pore throats (Figure 10).

Figure 10. The variation of ganglion capillary pressure with the inverse of the maximum adjacent pore throat radius.

This correlation is only approximate as real throats may not maintain a constant shape factor with size, and even if they did, they may not be perfectly represented by idealized triangular elements. Contact angle in this system has been examined by *Andrew et al.* [2014a], finding a contact angle distribution of $45 \pm 10^\circ$. This variation in contact angle may contribute to any deviation from the inverse correlation between capillary pressure and adjacent throat radius. Despite this, the correlation between maximum adjacent pore throat radius and ganglion capillary pressure provides evidence that at the flow rates used in these experiments the snap-off rules used in network models are realistic. A linear model was fitted using a trust region algorithm [Conn et al., 2000], finding a coefficient of 0.017 ± 0.002 Pa m, corresponding to a half angle of 15° for a contact angle of 45° , which can be used to assign the capillary pressure for snap-off in network models.

3.2. Viscous Remobilization

The adjacent pore throats are a strong control on the viscous pressure drop required for ganglion remobilization (Figure 11). The ganglion volume, however, is not well correlated to the adjacent pore throat radius. This is because ganglia can occupy multiple adjacent pores connected by relatively large pore throats which had not fulfilled the criteria for snap-off during wetting phase invasion.

The ganglion volume is, nevertheless, important for cluster remobilization. Traditional examinations of capillary desaturation have focused on the conventional capillary number, equation (4).

With this representation of the relative effect of viscous forces versus surface tension, remobilization tends to occur above $N_c \sim 10^{-5}$ [e.g., Dullien, 1979]. This is unsatisfactory as, if the capillary number is to reflect

Figure 11. The variation of viscous pressure drop required for ganglion remobilization with maximum adjacent pore throat radius.

Figure 12. The fraction of CO₂ remobilized as a function of N_c and N_{macro} . Most ganglia fulfill the remobilization criteria around $N_{macro} = 1$, and around $N_c = 10^{-5}$.

the balance between viscous and surface forces, desaturation should occur at capillary numbers around 1. New formulations of capillary number [Armstrong *et al.*, 2014; Hilfer and Oren, 1996; Melrose and Brandner, 1974] have incorporated the increased impact of viscous shear across an extended nonwetting-wetting phase interface by adding a term incorporating cluster length, only available through pore-scale experiments. The most recent re-examination [Armstrong *et al.*, 2014] of this issue also requires relative permeability, computed through pore-scale simulation. The use of ganglion cluster length is only valid if it is proportional to the pressure drop across the ganglion. In a uniform flow field this is the case; however, the flow field through the wetting phase at residual saturation is highly heterogeneous. These new formulations are also divorced from the direct physics of the remobilization process. In this study, we propose a new definition for capillary number rigorously based on the pore-scale physics of the desaturation process.

The capillary number is defined as the ratio between viscous and surface forces, or the ratio between the viscous pressure drop across a ganglion and the capillary pressure, both acting over the ganglion interfacial area. Each ganglion is assigned a unique microscopic capillary number N_{micro} :

$$N_{micro} = \frac{\text{Viscous pressure drop across ganglion}}{\text{Capillary Pressure}} = \frac{\Delta P}{P_c} \quad (7)$$

The viscous pressure drop (ΔP) is computed directly by solving for flow in the wetting phase, as discussed previously in section 2.1—this value is proportional to the imposed total Darcy velocity (flow rate). The capillary pressure (P_c), as described in section 2.2, is found from the maximum curvature of the ganglion interface with the wetting phase.

This capillary number definition can then be upscaled to a macroscopic capillary number (N_{macro}) using a volume-weighted average of the ratio of N_{micro} over k ganglia

$$N_{macro} = \frac{\sum_{j=0}^k V_g^j N_{micro}^j}{\sum_{j=0}^k V_g^j} \quad (8)$$

where V_g^j is the volume of the j th ganglion. Volumetric averaging was used so that the ganglia dominating the saturation would dominate the macroscopic capillary number. Using this definition, the fraction of ganglia fulfilling the desaturation criterion is shown in Figure 12 as a function of the macroscopic capillary number N_{macro} , equation (8) and N_c , equation (6). A ganglion is considered to be remobilized when the viscous pressure drop across it is equal to or greater than the difference between the ganglion's capillary pressure and the capillary pressure required to pass through the largest of the adjacent pore throats, $N_{micro} > 1$. Remobilization is achieved through increasing the wetting phase flow rate.

Figure 13. The relationship between the ganglion volume and the macroscopic capillary number N_{macro} required for remobilization of that ganglion.

The vast majority of the ganglia fulfill the remobilization criteria at N_{macro} around 1, and traditional capillary numbers (N_c) of around 10^{-5} . This demonstrates that this overall formulation for N_{macro} and the defined averaged parameters provide a reasonable representation of the local flow, whereas the traditional formulation for capillary number does not correctly represent the local balance between viscous and surface forces. While other formulations of capillary number, particularly that presented by *Armstrong et al.* [2014], have achieved similar results for homogeneous samples, these methods tend to rely on the assumption of a uniform fluid flow field since they assume that the ganglion cluster length is proportional to the viscous pressure drop. A major advantage of our method is that it makes no assumptions about the pore-scale flow field, and so could be more appropriate for more heterogeneous samples, such as those commonly found in the subsurface.

Recent results addressing a large range of rock types [*Andrew et al.*, 2013, 2014b] show that the distribution of ganglia sizes at residual saturation is controlled by pore space structure and connectivity. Well-connected rocks tend to have more large clusters relative to small clusters and vice versa. In this context, it is interesting to examine the relationship between ganglion volume and remobilization. We would expect larger volume ganglia to have a larger cluster length along the direction of the viscous pressure drop, and so should be easier to remobilize than smaller ones. This is the case with spherical ganglia, however, as nonspherical ganglia (particularly long thin ganglia with high aspect ratios) may not be aligned with the direction of flow so any relationship between ganglion volume and remobilization of high aspect ratio ganglia would be inexact. Ganglion snap-off (as discussed above) is controlled by local pore topography, which is isotropic through the sample, so ganglia have no preferred orientation upon formation. On the other hand, remobilization is controlled by the viscous pressure field, which is highly directional. The relationship between the macroscopic capillary number (N_{macro}) required to remobilize each ganglion and the ganglion volume is presented in Figure 13.

Large ganglia tend to be remobilized at smaller N_{macro} than small ganglia. This is critical in understanding the differences between remobilization in different rock types as local pore topography and connectivity are controlling factors in ganglia size distributions [*Andrew et al.*, 2014b], so they should be a controlling factor in viscous remobilization.

3.3. Gravitational Remobilization

Another potential mechanism for remobilization is the gravitational force arising from the density difference between the nonwetting phase and the wetting phase. This is traditionally defined using the Bond number (N_b), given by the ratio of gravitational forces to surface forces acting on some characteristic length scale L :

$$N_b = \Delta\rho g \frac{L^2}{\sigma} \quad (9)$$

where g is the acceleration due to gravity, $\Delta\rho$ is the density difference between the wetting and nonwetting phase and σ is the interfacial tension. Similarly to the analysis presented for the capillary

Figure 14. The variation of surface area/ganglion volume ratio with ganglion volume. The smaller ganglia have higher volume/surface area ratios, while larger ganglia show relatively little variation.

number, it is possible to reformulate the Bond number to rigorously reflect the ratio between the buoyancy and capillary forces at the pore scale. Each ganglion of volume V_g has a hydrostatic buoyancy force acting on it equal to $\Delta\rho g V_g$ and capillary force equal to the capillary pressure acting on the interfacial area:

$$N_{b\text{micro}} = \frac{\text{Gravitational Forces}}{\text{Capillary Forces}} = \Delta\rho g \frac{V_g}{A_s P_c} \quad (10)$$

where A_s is the CO₂-brine interfacial area for an individual ganglion, computed by counting the number of faces between wetting and non-wetting phases in the segmented image.

The distribution of microscopic Bond numbers $N_{b\text{micro}}$ calculated from this experiment is relatively narrow ($5.2 \pm 1.4 \times 10^{-4}$) and shows that at residual saturation capillary forces are far stronger than gravitational forces. Ganglion volume to surface area ratios would have to increase, or capillary pressures decrease, by more than 3 orders of magnitude in order to start the gravitational remobilization of the residual CO₂. Although there are mechanisms for such a process, such as Ostwald Ripening [Voorhees, 1985], these rely on larger clusters having correspondingly lower surface energies, due to lower surface areas at a given saturation. This can be examined in this system by looking at the ganglion surface area to volume ratio (A_s/V_g), which decreases with ganglion volume up to a certain point, as shown in Figure 14. As ganglia span more and more pores, however, interfacial area increases almost linearly with ganglion volume, meaning their ratio A_s/V_g changes little, if at all. As larger clusters inside a porous medium are not as energetically favorable as they are in a free liquid (where volume to surface area ratios decrease as ganglion volume increases) there is no energy gradient to drive the process of Ostwald Ripening.

If saturation were to increase, the non-wetting phase connectivity would correspondingly increase, decreasing total surface area. This would, however, require significant remobilization, which is difficult, as discussed above. As microscopic capillary pressure is unlikely to decrease by 3 orders of magnitude given fixed pore topographies and contact angles, the gravitational remobilization of residual CO₂ seems extremely difficult, a positive result for capillary trapping efficiency in carbon capture and storage.

Following the approach of the previous section, this microscopic Bond number can be upscaled to a macroscopic Bond number by using a volume-weighted average:

$$N_{b\text{macro}} = \frac{\sum V_g^j N_{b\text{micro}}^j}{\sum V_g^j} \quad (11)$$

The upscaled Bond number in this system at residual saturation was 6.14×10^{-4} , confirming that gravitational remobilization for disconnected ganglia is extremely difficult.

4. Conclusions

We present a new method for examining and assessing the formation, displacement and remobilization of a residual phase on a pore-by-pore basis at pressures and temperatures representative of flow in subsurface aquifers and oil and gas reservoirs (10 MPa and 50°C). At residual saturation, capillary pressure was found by extracting interface curvature from the CO₂-brine interface surface. This was then compared to local pore topography by the use of a watershed algorithm on the distance map of the pore space in order to examine snap-off, and viscous and gravitational remobilization of the residual CO₂. Capillary pressure was found to be a strong function of local pore topography, explained during imbibition by the timing of snap-off events, where small pore throats are snapped off early in the imbibition process and large pore throats are snapped off later. The viscous pressure drop across each ganglion was found by direct modeling of flow through the wetting phase, and this information was used to develop a new, physically based, capillary number definition. This showed that most ganglia fulfilled the remobilization criteria at capillary numbers around 1. Similarly a new formulation of the Bond number is proposed and it is shown that the gravitational remobilization of capillary trapped CO₂ is extremely difficult. This is an important result for assessing the security of residual trapping as a mechanism for the long term immobilization of CO₂ in the subsurface.

The method for assessing fluid behavior on a pore-by-pore basis has an application to a wide range of problems in porous media, and future work will focus on the application of this technique to both dynamic (time resolved) tomographic systems and more complicated pore structures typically found in the subsurface.

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