Wettability effects on supercritical CO₂–brine immiscible displacement during drainage: Pore-scale observation and 3D simulation

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ABSTRACT

Wettability is an important factor controlling the displacement of immiscible fluids in porous media and therefore affects the flow and transport of supercritical (sc) CO₂ in geologic carbon sequestration. Because few studies have focused on the wettability effect in scCO₂–brine flow systems, we experimentally and numerically tested influences of wettability on drainage at the pore network scale. Using a high-pressure micromodel-microscopy system, we performed experiments of scCO₂ invasion into brine-saturated water-wet and intermediate-wet micromodels, and recorded the scCO₂ invasion morphology under reservoir relevant conditions. We also performed pore-scale numerical simulations to infer 3D details of fluid–fluid displacement processes. During drainage under intermediate-wet conditions, we found higher scCO₂ saturation, wider scCO₂ fingering, and more compact displacement patterns. The simulation results are qualitatively consistent with the experiments. Through quantitative analyses of the experiments, we found that the reduced wettability decreases the displacement front velocity, promotes non-wetting phase pore-filling events in the longitudinal direction, delays the breakthrough time of invading fluid, and increases the displacement efficiency. Simulated results also show that the fluid–fluid interface area follows a unified power-law relation with scCO₂ saturation, and show smaller interface area in intermediate-wet case which suppresses the mass transfer between the phases. These pore-scale results provide insights for the wettability effects on CO₂–brine immiscible displacement in geologic carbon sequestration.

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1. Introduction

Immiscible two-phase fluid flow in porous media is an important process in natural and engineering systems, including water infiltration through soils, geological carbon sequestration (Krevor et al., 2015; Pachauri et al., 2014), enhanced oil/gas recovery (Patzek et al., 2013; Simjoo et al., 2013), and groundwater contamination (Dawson and Roberts, 1997). The non-compact displacement pattern of fluid–fluid interfaces in porous media limits the efficiency of phase displacement. Understanding and controlling the immiscible displacement is vitally important for optimizing subsurface fluid management. In geological carbon sequestration (GCS), injection of CO₂ into deep geological formations displaces the native fluid (brine) from pore spaces (drainage) but only partially dis-

placement of brine due to the non-compact displacement pattern (e.g., Wang et al., 2012). In enhanced oil recovery, the oil recovery efficiency using water flooding (imbibition) is limited by the non-compact displacement pattern (Bikina et al., 2016; Godec et al., 2013; Nobakht et al., 2007; Orr and Taber, 1984).

Immiscible fluid flow in porous media has been studied in depth. When the gravitational effect can be neglected, the fluid–fluid displacement is governed by the competition between viscous and capillary forces (He et al., 1992; Lenormand et al., 1988; Wong, 1994; Zhang et al., 2011b), quantified by the capillary number Ca (defined as: $Ca = \mu_i v_i / \sigma$, where μ_i and v_i are the viscosity and characteristic velocity of the invading fluid, respectively, and σ is the interfacial tension), and viscosity ratio M (viscosity of the invading fluid divided by the viscosity of the defending fluid). The displacement patterns range from viscous fingering to capillary fingering to compact displacement (Lenormand et al., 1988). In addition to Ca and M , wettability of pore surface (represented by the contact angle θ of brine on the mineral surface) plays a critical role in govern-

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Fig. 1. (a) Schematic diagram of the high-pressure micromodel-microscopy system. Red line = scCO₂, blue line = brine. (b) The micromodel used for the experiments. (c) The finite volume mesh used in numerical simulations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ing the capillary force and directly impacts the interface stability (Holtzman and Segre, 2015). Most studies on wettability effects in flow behavior have been conducted on water-air and water-oil systems (Cottin et al., 2011; Holtzman and Segre, 2015; Trojer et al., 2015), and reported that increasing contact angle stabilizes the displacement interface under different flow rates, therefore increases the displacement efficiency. However, investigations into wettability impacts on the invasion morphology are largely limited to quasi-steady state conditions, due to long acquisition times required with micro-computed tomography (from 12 s to hours). The pressures and temperatures needed to represent storage conditions (at least 7.4 MPa and 31.1 °C) further limit the number of experimental studies conducted on geological carbon sequestration. Thus, dynamic invasion morphology and wettability effects need to be investigated under geological CO₂ storage conditions, particularly at the pore-scale.

Microscopy of micromodels is an effective method for investigating immiscible fluid flow and the morphology of dynamic invasion at the pore network scale. Although the micromodel is quasi-2D systems, it provides direct visualization of the physical displacement processes (Kazemifar et al., 2015; Kim et al., 2012; Roman et al., 2015), the immiscible fingering flow pattern (Cao et al., 2016; Karadimitriou et al., 2014; Lenormand et al., 1988; Wang et al., 2012; Zhang et al., 2011a,b), and the fluid–fluid interfacial areas (Cheng et al., 2004; Karadimitriou et al., 2014; Liu et al., 2011). Cottin et al. studied the wettability effect on the fingering flow pattern and reported that the front width of the invading fluid is larger under the complete wetting condition (Cottin et al., 2011). These previous studies indicate that pore scale quantitative analysis of the wettability impact on invading fluid morphology under supercritical CO₂ condition can be better understood through analyses of micromodel experiments.

It should be noted that although images obtained in micromodels are usually two-dimensional, the pores and throats can be engineered with etched depths similar to pore throat dimensions (Kim et al., 2012; Wan et al., 1996). Thus, information on the three-dimensional behavior of interfaces within micromodels can help better understand two-phase flow, and numerical simulations can help make this understanding more quantitative. Numerous modeling studies of the immiscible flow have been conducted, for example those using pore-network models (Joekar Niasar et al., 2009; Raeesi and Piri, 2009; Valvatne and Blunt, 2004; Yuan et al., 2016), computational fluid dynamic studies (CFD) (Ferrari et al.,

2015; Ferrari and Lunati, 2013; Hoang et al., 2013; Horgue et al., 2013; Raeini et al., 2015), Lattice Boltzmann methods (LBM) (Andrä et al., 2013; Jiang and Tsuji, 2015, 2016, 2017; Liu et al., 2015; Tsuji et al., 2016; Yamabe et al., 2014), and the smooth particle hydrodynamic method (SPH) (Bandara et al., 2013). The pore-network modeling is widely used due to its computational efficiency. The LBM and SPH are increasingly used because they are relatively easy to implement. However, the major disadvantage of these two methods is the need for calibration of model parameters (Ferrari and Lunati, 2013). In CFD, the Navier–Stokes equations are directly solved in a discretized form on an Eulerian mesh, and an interface capturing technique, such as the Volume of Fluid (VOF) method, is incorporated to track the movement of interfaces between the two fluids. In the modeling component of this study, direct numerical simulation of the full 3D Navier–Stokes equations with the VOF based on the finite volume method is used to represent the physical processes.

Here, we studied wettability impacts on scCO₂–brine two-phase fluid flow at pore network scale by combining micromodel experiments with numerical modeling. We performed drainage experiments of supercritical CO₂ displace brine in micromodel, at 8.5 MPa and 45 °C under three different flow rates. We also performed direct numerical simulations of the full Navier–Stokes equations for the drainage process under the same experimental conditions. The combination of experiment and simulation approaches were pursued in order to improve understanding of the wettability effect on the dynamic scCO₂ invasion morphology at pore- and pore network- scale under reservoir relevant conditions.

2. Experimental section

2.1. High-pressure micromodel-microscopy system

The high-pressure micromodel-microscopy system (Fig. 1a) consists of three high-pressure syringe pumps (Teledyne ISCO, 500HP and 65HP), a CO₂ cylinder connected to an ISCO pump, a stirred reactor (Parr, model 4560) for preparing the mutually saturated brine and CO₂ at 8.5 MPa and 45 °C, micromodel, and imaging system. ISCO pump B was used to fill the micromodel with scCO₂-saturated brine, and ISCO pump A was used to inject scCO₂ (pre-saturated with brine) into the micromodel in the drainage process. The imaging system has two modes: one is a CCD camera (Carl Zeiss, AxioCam MRC5) that records images at the pore

Table 1
Summary of experiment conditions.

Exp. #	Wettability	Volume flow rate, Q ($\mu\text{L}/\text{min}$)	Fluid velocity ^a , v_{inlet} (mm/s)	Time per PV ^b , t_{pv} (s/PV)	Apparent capillary number ^c , Ca
1–4	water-wet	12	0.5	10	2.2×10^{-5}
5–8	water-wet	48	2	2.5	8.7×10^{-4}
9–12	water-wet	120	5	1	2.2×10^{-3}
13–16	intermediate-wet	12	0.5	10	2.2×10^{-5}
17–20	intermediate-wet	48	2	2.5	8.7×10^{-4}
21–24	intermediate-wet	120	5	1	2.2×10^{-3}

^a The fluid velocity is the velocity at the inlet of micromodel, $v_{\text{inlet}} = Q/A_c$, where Q is the volume flow rate, A_c is the cross-section area at near-inlet, $A_c = W \times d$, where W , d are respectively the micromodel width and pore depth, $W = 10$ mm, $d = 40$ μm .

^b Time per PV is the time takes for one pore volume of fluid flowing through the micromodel, $t_{\text{pv}} = [Q/(Wd\phi)]^{-1}$, where L is the length of micromodel, $L = 20$ mm, ϕ is the porosity of micromodel ($\phi = 0.246$).

^c The apparent capillary number is calculated by $Ca = Q\mu/(Wd\phi\sigma)$, where μ is the viscosity of invading fluid and σ is the interfacial tension between brine and scCO_2 at the given pressure and temperature. The literature values of μ and σ used in calculations are listed in Table 2.

scale, and the other a DSLR camera (Nikon, 90D) installed over the stage of an inverted microscope (Carl Zeiss, Observer Z1.m) that records images of the full pore network of the micromodel. The whole experimental system was contained in an insulated enclosure, and the temperature was maintained with 45 ± 1 °C during experiments by 250 W infrared halogen heating lamps, connected to a PID controller (Cole Parmer, EW-89000-10) and thermocouples (Omega, Type T).

2.2. Micromodels

Fig. 1b shows the micromodel used in this study, with homogeneous pore network patterns etched on the fused silica plates. The porous network has a patterned area of 20 by 10 mm composed of 576 discoid silica grains (590 μm diameter). The pore throats are 50 μm wide and the depth of the pores and throats is 40 μm . The calculated pore volumes (PV) is 1.97 μL and the porosity of the micromodel is 0.246. To alter the wettability of a micromodel, a coating solution was prepared by diluting Aquaphobe-CM (PP1-AQCM, Gelest) with hexane (ACS grade, EMD). 5% (v/v) Aquaphobe-CM solution was used. The coating solution was injected into a micromodel at 1 mL/h for 2 h in order to saturate micromodel with the coating solution. Then, the inlets and outlets of the micromodel were kept closed for overnight at ambient pressure and temperature to allow enough time for the coating solution to react with the surface of micromodel. Then, the micromodel was washed with hexane by injecting 2 mL hexane into the micromodel at 0.2 mL/min 3 times. And then, 8 mL air was injected into the micromodel at 0.8 mL/min 3 times in order to remove the hexane remained in the micromodel. After that, the micromodel was dried and cured at 100 °C for 1 h. The average contact angle of the Aquaphobe-CM treated micromodels is about 90°, based on the direct observations obtained from the micromodel.

2.3. Experimental procedures

The brine (0.01 M NaCl) was prepared using deionized (DI) water (EMD Millipore, Milli-Q) and NaCl (Sigma-Aldrich, ACS grade). Pure CO_2 was used (Airgas, 99.9%). To prepare the mutually saturated brine and CO_2 , the degassed brine was injected into the Parr reactor (Fig. 1a), and then CO_2 was transferred to the Parr reactor and pressurized. After 24 h of stirring at 8.5 MPa and 45 ± 1 °C, the brine and scCO_2 were considered mutually equilibrated and ready for use. The scCO_2 -saturated brine stored in the stirred reactor was then injected to ISCO pump B (8.5 MPa and 45 ± 1 °C). A clean micromodel was assembled and fixed on the microscope stage. The ISCO pump C injected brine (non scCO_2 -saturated) into micromodel (flow path: E $\rightarrow$ D $\rightarrow$ C $\rightarrow$ B $\rightarrow$ F $\rightarrow$ H) with a flow rate of 12 $\mu\text{L}/\text{min}$ at the atmosphere pressure to completely displace the air. Once the

micromodel was fully saturated with brine, the three-way valve F was closed and the ISCO pump C increased pressure to the constant pressure of 8.5 MPa. After that the three-line valve F was connected to ISCO pump B and then the ISCO pump B injected the scCO_2 -saturated brine into micromodel to displace the initial brine (non scCO_2 -saturated) at a flow rate of 8.3 $\mu\text{L}/\text{s}$ for 20 min to ensure that the micromodel was saturated with CO_2 -saturated brine (flow path: G $\rightarrow$ F $\rightarrow$ B $\rightarrow$ C $\rightarrow$ D $\rightarrow$ E). The three-line valve B was then opened to the ISCO pump A. The system was then equilibrated at the same pressure and temperature for three hours. After three hours, the ISCO pump A injected scCO_2 into the micromodel at constant flow rates of 12, 48 and 120 mL/min for 80 s, during which the constant pressure mode (8.5 MPa) was applied in the ISCO pump C. During the drainage processes, images of scCO_2 distribution in the entire micromodel were recorded at 1 frame/s with the DSLR camera. Based on the observed scCO_2 invasion morphology and the calculated scCO_2 saturation of images, the drainage process approached quasi-steady conditions within several seconds of scCO_2 flooding. At the lowest flow rate of 12 $\mu\text{L}/\text{min}$, quasi-steady conditions for both the water-wet and intermediate-wet cases can be obtained at 6 s, at which the average changes for the scCO_2 saturation of the four replicate experiments became less than 0.1% per second. To clean a water-wet micromodel, distilled water was injected at the flow rate 120 $\mu\text{L}/\text{min}$ for about 5 min, the micromodel was burned at 650 °C for one hour, and then flushed with distilled water after it was cooled to the room temperature. Then the micromodel was oven dried at 65 °C. For the Aquaphobe-CM treated micromodel, the burning step was skipped.

Table 1 lists the sequence of experiments, showing that at the flow rates of 12, 48 and 240 $\mu\text{L}/\text{min}$, one PV of scCO_2 is injected within only 10 s, 2.5 s and 0.1 s, respectively. Each experiment was repeated four times in the water-wet and intermediate-wet micromodels. For both un-treated and Aquaphobe-CM treated micromodels, the contact angles of the silica surface within micromodel were measured with ImageJ software (Abramoff et al., 2004) combined with a contact angle plug-in (Marco Brugnara, marco.brugnara@ing.unitn.it) before and after the experiments. No significant wettability changes resulted from exposure to scCO_2 , indicating that our silica surfaces (untreated and treated) were stable under the experimental conditions (8.5 MPa and 45 °C). The measured contact angles are $22.4 \pm 1.1^\circ$ for the water-wet micromodel (non-treated) and $89.5 \pm 1.9^\circ$ for intermediate-wet (Aquaphobe-CM treated) micromodels. These two values (22° and 90°) were used in the numerical simulations. Although Kim et al. (2012) reported wettability change on an untreated micromodel from water-wet to intermediate-wet after drainage and a longer term exposure to scCO_2 flow, we did not observe this wettability change. Differences in wetting may reflect the very short exposure

time of the silica to scCO₂ in this study and the higher salinity (up to 5.0 M) used in the earlier study.

The MATLAB Image Processing Toolbox was used to binarize images by thresholding. With the binary image, the overall scCO₂ saturation (S_{CO_2}) and the average longitudinal saturation profiles ($S_{CO_2,x}$) were directly calculated.

3. Numerical simulation

3.1. Basic assumptions

Before introducing the numerical method, the following assumptions were made for simplification: (1) the two fluids (scCO₂, and brine) are assumed to be incompressible; (2) there is no mass exchange at the interface of scCO₂ and brine, i.e. the dissolution effect is neglected; (3) the two fluids have reached thermal equilibrium; (4) the gravity effect is neglected because the height of micromodel (40 μ m) is small; (5) the wettability effect is represented by the static contact angle; in this study, the dynamic effect of contact angle and the hysteresis of contact angle are not considered. Assumptions 1 through 4 are reasonable because, both the pressure and temperature remained constant and the two phases were pre-saturated with each other. Note that a dynamic contact angle, or the contact hysteresis may influence the displacement processes, but will be left for further study.

3.2. Governing equations

The processes of scCO₂ invasion into brine saturated micromodels can be captured by the Navier–Stokes, i.e. the conservation of

$$\begin{aligned} \frac{\partial(\rho(\alpha)\mathbf{u})}{\partial t} + \nabla \cdot (\rho(\alpha)\mathbf{u}\mathbf{u}) &= -\nabla p + \nabla \cdot [\mu(\alpha)(\nabla\mathbf{u} + \nabla^T\mathbf{u})] - \sigma \cdot \nabla \cdot \left(\frac{\nabla\alpha}{\|\nabla\alpha\|} \right) \cdot \nabla\alpha \\ \nabla \cdot \mathbf{u} &= 0 \\ \frac{\partial\alpha}{\partial t} + \nabla \cdot (\alpha\mathbf{u}) + \nabla \cdot (\alpha \cdot (1-\alpha)\mathbf{u}_r) &= 0 \end{aligned} \quad (8)$$

momentum:

$$\frac{\partial(\rho\mathbf{u})}{\partial t} + \nabla \cdot (\rho\mathbf{u}\mathbf{u}) = -\nabla p + \nabla \cdot [\mu(\nabla\mathbf{u} + \nabla^T\mathbf{u})] + \mathbf{f}_s \quad (1)$$

with the conservation of mass:

$$\nabla \cdot \mathbf{u} = 0 \quad (2)$$

where $\mathbf{u}$ is the fluid velocity, p is the pressure, μ is the viscosity, $\mathbf{f}_s$ represents the source term of the momentum due to the surface tension at the interface between the two fluids. $\mathbf{f}_s$ can be expressed as:

$$\mathbf{f}_s = \sigma \cdot \kappa \cdot \mathbf{n} \quad (3)$$

where σ is the surface tension, κ is the curvature, $\mathbf{n}$ is the normal vector of the interface. Therefore $\mathbf{f}_s$ is nonzero at curved interfaces and represents the effect of the Young–Laplace pressure.

The volume of fluid method (VOF) is used to track the evolution of the scCO₂–Brine interface. A volume fraction α is introduced as an indicator function to represent the volume fraction of fluid within cells, as mentioned:

$$\alpha = \begin{cases} 0 & \text{in the nonwetting fluid} \\ 1 & \text{in the wetting fluid} \\ 0 < \alpha < 1 & \text{on the interface} \end{cases} \quad (4)$$

Table 2
Densities, viscosities, and interfacial tension used in simulations.

45 °C and 8.5 MPa	Brine (0.01 mol/L)	scCO ₂
Density (kg/m ³)	993.9 ^a	281.8 ^b
Viscosity (kg/(s m))	5.972×10^{-4b}	2.2758×10^{-5b}
interfacial tension (N/m)	$(33.1 \pm 0.5) \times 10^{-3c}$	

^a The NaCl brine density was calculated based on the regression equations of Batzle and Wang (1992).

^b The density and viscosity of scCO₂ were obtained from CO₂ phase diagram in the National Institute of Standards and Technology (NIST) web-based database. available at <http://webbook.nist.gov/chemistry/fluid/>. The viscosity of brine (0.01 mol/L) was set as the same value of water at the same temperature and pressure.

^c Interfacial tensions for scCO₂–brine were measured in our laboratory using the pendant drop method (Moebius and Or, 2012).

The evolution of α is given by an advection equation:

$$\frac{\partial\alpha}{\partial t} + \nabla \cdot (\alpha\mathbf{u}) + \nabla \cdot (\alpha \cdot (1-\alpha)\mathbf{u}_r) = 0 \quad (5)$$

where $\mathbf{u}_r$ is an artificial compression velocity to limit numerical diffusion (Greenshields, 2015; Rusche, 2003). Therefore the density and the viscosity in the whole domain can be expressed as:

$$\begin{aligned} \mu &= \alpha\mu_w + (1-\alpha)\mu_{nw} \\ \rho &= \alpha\rho_w + (1-\alpha)\rho_{nw} \end{aligned} \quad (6)$$

Given that $\mathbf{n} = \nabla\alpha$, the source term $\mathbf{f}_s$ can be expressed in alternative form (Brackbill et al., 1992):

$$\mathbf{f}_s = \sigma \cdot \kappa \cdot \nabla\alpha \cdot \delta_\Gamma = -\sigma \cdot \nabla \cdot \left(\frac{\nabla\alpha}{\|\nabla\alpha\|} \right) \cdot \nabla\alpha \quad (7)$$

Finally the two-phase immiscible flow was determined by solving the following equations:

Numerical simulation considers the wettability effect on the fluid flow by imposing an additional constraint on α at the intersection between the interface and solid surface (e.g., Ferrari and Lunati, 2013):

$$\left. \frac{\nabla\alpha}{\|\nabla\alpha\|} \right|_{\mathbf{x} \in \text{wall}} := \mathbf{n} = \mathbf{n}_s \cos \theta + \mathbf{n}_t \sin \theta \quad (9)$$

where $\mathbf{n}_s$ is the unit normal pointing into the solid and $\mathbf{n}_t$ is the unit tangent to solid points into the wetting phase.

3.3. Direct simulations

Direct solution for the governing equations (Eq. (8)) has been implemented in an open-source library software OpenFOAM (Greenshields, 2015). The main advantage of direct solutions of Navier–Stokes equations is that relatively few model parameters are required (listed in Table 2). However, larger computing resources are required for the simulation. We performed the simulation on the Lawrence Livermore cluster, a platform for the Condo Cluster Computing program in Lawrence Berkeley National Laboratory. We set up a 3D computational model of the 20 mm $\times$ 10 mm micromodel (Fig. 1b), with relatively uniform meshes comprised of 2,712,905 nodes and 1,962,924 cells (Fig. 1c) to permit stable and fast solution. The third dimension (orthogonal to the plane of the micromodel) was discretized into four cells. The static contact angle (22° for water-wet and 90° for intermediate-wet) was used in OpenFOAM to consider the wettability of micromodels. The following boundary conditions were applied: the inlet was

Fig. 2. The observed (representative of the four replicate experiments, a–c and g–i) and simulated scCO_2 phase distributions (d–f and j–l) at 1 s of drainage in water-wet (a–f) and intermediate-wet (g–l) micromodels. In the experiment, the dark color is scCO_2 and the light color is brine. In simulations, red color is scCO_2 and gray color represents brine. Three apparent capillary numbers are shown along the top edges and their corresponding flow rates are provided in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. The observed (representative of the four replicate experiments, a–c and g–i) and simulated scCO_2 phase distributions (d–f and j–l) at 6 s of drainage in water-wet (a–f) and intermediate-wet (g–l) micromodels. In the experiment, the dark color is scCO_2 and the light color is brine. In simulations, red color represents scCO_2 and gray color represents brine. The enlarged images of the selected regions (a', d', g' and j') are given in Fig. 4. Three apparent capillary numbers are shown along the top edges and their corresponding flow rates are provided in Table 1. The scCO_2 saturation values for these figures are listed Table 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fixed with constant velocity, zero gradient pressure and constant α value ($\alpha = 1$); the outlet was fixed with zero gradient velocity, constant zero pressure and zero gradient α . We added a buffer layer with width of $100 \mu\text{m}$ at attached onto the inlet to improve the convergence rate of simulation. The initial time step is set as

2.5×10^{-5} s and the Maximum Courant number and the Maximum Alpha Courant number are both set as 1.0.

We used 96 cores (four cluster nodes) at a clock speed of 2.6 GHz to perform parallel computing for each case (6 in total) respectively. As noted in Experimental Procedures, even at the lowest flow rate

Fig. 4. The phase distribution at $Ca = 2.2 \times 10^{-5}$ and $Q = 12 \mu\text{L}/\text{min}$ within multiple pores (a', d', g' and j') and single pore (a'', d'', g'' and j'') recorded with the microscope, corresponding to the marked regions (a–d) in Fig. 3. The bright yellow and red are scCO_2 in the experiment and in simulation, respectively. Flow is from left to right. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. The evolution of scCO_2 saturation with injected scCO_2 pore volumes and with drainage time at different Ca and flow rates of (a) $Ca = 2.2 \times 10^{-5}$, $Q = 12 \mu\text{L}/\text{min}$, (b) $Ca = 8.7 \times 10^{-5}$, $Q = 48 \mu\text{L}/\text{min}$, and (c) $Ca = 2.2 \times 10^{-4}$, $Q = 120 \mu\text{L}/\text{min}$. The solid (●, ◆, ▲) and open (○, ◇, △) symbols indicate respectively the water-wet and intermediate-wet cases. These symbols indicate the average saturation of four replicate experiments, and the error bars indicate standard deviations. The solid and dashed lines are the simulation for the water-wet and intermediate-wet cases, respectively. The arrows and the circles denote respectively the breakthrough time at water-wet and intermediate-wet cases, and the values of breakthrough time are presented in Table 3. At 6 s, the injected PVs of scCO_2 are 0.6, 2.4 and 6, respectively.

of $12 \mu\text{L}/\text{min}$ the drainage processes can approach the quasi-steady conditions with 6 s of scCO_2 flooding. To save computing resources, we performed parallel computations for the first 6 s of drainage processes, and the parallel computations were terminated if the change in pressure drop between inlet and outlet, and the scCO_2 saturation are no more than 0.01 kPa per 0.1 s and 0.01% per 0.1 s, respectively. After that time, the simulated scCO_2 distribution did not change, and steady-state conditions were considered reached. The parallel computations required roughly 4, 7 and 10 days for the

flow rates of 120, 48 and $12 \mu\text{L}/\text{min}$, and total cost was about 96,000 CPU hours.

4. Results and discussion

4.1. Comparison between experiments and simulations

As noted earlier, the scCO_2 invasion processes approached quasi-steady state in less than 6 s in experiments. Thus, we com-

pared the scCO_2 -brine displacement patterns between experiment and simulation within the range of 0 to about 6 s of drainage. Given the maximum capture rate (1 s/frame) for high-resolution photographs obtainable with the DSLR camera, the flow pattern was captured every second. Here we selected the invasion pattern at 1 s of drainage as a representative example, shown in Fig. 2. It illustrates the fingering of scCO_2 invasion and the resultant non-compact displacement. The wider fingering was clearly and consistently observed in intermediate-wet case comparing with the water-wet case in both experiment and simulation. The observed and simulated scCO_2 flow patterns at 6 s are shown in Fig. 3. Together, Figs. 2 and 3 indicate the finger growth towards the outlet and no backward movement of the displacement front, which are main features of viscous fingering patterns. However, according to the classic phase diagram by Lenormand et al. (1988), the experiment conditions (denoted by Ca and M) are located in the crossover zone including both capillary fingering and viscous fingering, whereas the conditions are located in capillary fingering zone from the diagram by Zhang et al. (2011b). The classical phase diagram provides a qualitative presentation only, because the boundaries of displacement pattern are not only dependent on Ca and M , but also highly depend on the pore structure and wettability. The phase diagram of Lenormand et al. (1988) and Zhang et al. (2011b) is based on the conditions that the invading fluid is the strong wetting phase. In another words, the phase diagram is more suitable for the water-wet experiments in this work. Currently, extension of the classic phase diagram (Lenormand et al., 1988) to elucidate the wettability effect has been reported (Holtzman and Segre, 2015; Jung et al., 2016; Trojer et al., 2015; Zhao et al., 2016).

Fig. 4a–d shows pore scale images recorded by the microscope. Again the wider fingering with multiple pores was observed in intermediate-wet case. The average cross-sectional width of scCO_2 fingering in water-wet case is in the range of 1 grain diameter ($\sim 590 \mu\text{m}$), whereas in intermediate-wet case the fingering spans up to 3 grain diameters ($\sim 1770 \mu\text{m}$). Governed by the wettability of pore surface, the curvature of the scCO_2 -brine interface is very small in intermediate-wet case (Fig. 4g', g'') and larger interface curvature exists in water-wet case (Fig. 4a', a''). Through 3D numerical simulation, we can observe the curve interface in the third dimension, which cannot be captured by the imaging system. The interface is planar in the third direction in the case of intermediate-wet micromodel (Fig. 4j', j''), whereas in the water-wet case the interface is concaved to the phase of brine (Fig. 4d', d'').

The measurements of scCO_2 saturation within 6 s of drainage were obtained based on the analysis of 144 captured images. Fig. 5 shows the observed and simulated scCO_2 saturations (S_{CO_2}) with respect to injected scCO_2 PV and drainage time. In accordance with mass balance of fluids, the scCO_2 saturation increases linearly with time before scCO_2 phase breakthrough, strictly following $\Delta S_{\text{CO}_2}/\Delta t = 1/t_{\text{PV}}$, as indicated in Fig. 5. Due to the image capture rate limitation (maximum capture rate was 1 frame/s), the invasion morphology before breakthrough can only be captured at 1 s at the flow rate condition of $12 \mu\text{L}/\text{min}$, as shown in Fig. 2a and g. The measured S_{CO_2} at 1 s under such flow rate condition are 0.088 ± 0.030 for water-wet case and 0.092 ± 0.027 for intermediate-wet case, whereas the predicted values are both 0.10. As the scCO_2 continues to inject, scCO_2 phase breaks through the micromodel. The 1 s per frame of image collection prevented accurate capture of the scCO_2 phase breakthrough time, but predicted finer resolution behavior can be examined in the simulations. The displacement efficiency is usually defined as the scCO_2 saturation at its breakthrough time (e.g., Xu et al., 2014). Table 3 lists the breakthrough times (t_b) and the corresponding scCO_2 saturation (S_{CO_2}), indicating larger displacement efficiencies and longer breakthrough times

Table 3The scCO_2 saturation at the breakthrough time by simulation.

Wettability	Variables	Volume flow rate, Q ($\mu\text{L}/\text{min}$)		
		12	48	120
Water-wet	t_b (s)	1.68	0.64	0.42
	S_{CO_2} (–)	0.17	0.26	0.42
Intermediate-wet	t_b (s)	2.16	1.06	0.55
	S_{CO_2} (–)	0.22	0.43	0.55

Fig. 6. The measured and simulated scCO_2 saturation at 6 s of drainage under the constant flow rates of $12 \mu\text{L}/\text{min}$ ($Ca = 2.2 \times 10^{-5}$), $48 \mu\text{L}/\text{min}$ ($Ca = 8.7 \times 10^{-5}$) and $120 \mu\text{L}/\text{min}$ ($Ca = 2.2 \times 10^{-4}$). (a) comparison of experimental and numerical results. The bars for experiments indicate the average values of four replicate experiments, and the error bars indicate standard deviations. (b) the error (ϵ) of numerical results with respect to the measurement is calculated by $S_{\text{CO}_2, \text{sim}} - S_{\text{CO}_2, \text{exp}}$, where $S_{\text{CO}_2, \text{sim}}$ and $S_{\text{CO}_2, \text{exp}}$ denote the measured and simulated scCO_2 saturation, respectively.

were simulated in the intermediate-wet cases, and the displacement efficiency increases as the flow rate increases.

The measured and predicted steady state S_{CO_2} (at 6 s of drainage) are compared in Fig. 6. Fig. 6a shows that the predicted S_{CO_2} values are 0.209, 0.332 and 0.527 for the water-wet case, 0.288, 0.513, and 0.639 for the intermediate case, with the increased values as the flow rate increasing. However, the measured steady state S_{CO_2} values are 0.169 ± 0.025 , 0.282 ± 0.025 , and 0.408 ± 0.019 for the water-wet case, and 0.336 ± 0.012 , 0.475 ± 0.017 , and 0.545 ± 0.015 for the intermediate-water case. As shown in Fig. 6b, discrepancies (ranging from -0.05 to 0.12) exist between the measured and predicted values. The relative errors, $\epsilon_r = (S_{\text{CO}_2, \text{sim}} - S_{\text{CO}_2, \text{exp}})/S_{\text{CO}_2, \text{exp}}$, are 23.7%, 17.7% and 29.1% for the flow rates of 12, 48 and $120 \mu\text{L}/\text{min}$ in water-wet condition, and are -14.3% , 8.0% and 17.2% under intermediate-wet condition.

Figs. 5 and 6 summarize the discrepancies between experiment and simulation. Large discrepancies in saturation (0.12 for water-wet case and 0.09 for intermediate-wet case) were observed at the high flow rate condition of $120 \mu\text{L}/\text{min}$. Note that the flow rate of $120 \mu\text{L}/\text{min}$ will induce 1 PV injection into micromodel within one second (Table 1). The finite time needed for the ISCO pump to increase the flow rate from $0 \mu\text{L}/\text{min}$ (equilibrium state before scCO_2 injection) to $120 \mu\text{L}/\text{min}$ is an important factor that complicates experiment-simulation comparisons. At the very beginning of the scCO_2 invasion processes, the actual injecting rate delivered by ISCO pump is slower than $120 \mu\text{L}/\text{min}$. However, in numerical simulation, a constant flow rate condition is applied at the inlet with $120 \mu\text{L}/\text{min}$. This difference in boundary conditions may contribute higher scCO_2 saturation in simulations. Ferrari et al. (2015) presented a detailed comparison of pore-scale simulations with experiments of air invasion into water-saturated micromodel. As reported by Ferrari et al. (2015), the errors can be attributed to the

Fig. 7. The average longitudinal saturation profiles at 6 s of drainage for experiment (a, c, e) and simulation (b, d, f). The apparent capillary numbers of 2.2×10^{-5} , 8.7×10^{-5} and 2.2×10^{-4} correspond to flow rates of 12, 48 and 120 $\mu\text{L}/\text{min}$, respectively, as listed in Table 1. The data points indicate the average saturation of four replicate experiments, and the error bars indicate standard deviations. The lines are the simulation results.

Fig. 8. The dependence of displacement pattern on wettability at the flow rate of 48 $\mu\text{L}/\text{min}$. (a) The simulated relation between the scCO_2 saturation (S_{CO_2}) and the normalized displacement front location (ξ^*) at the flow rate of 48 $\mu\text{L}/\text{min}$ for water-wet and intermediate-wet cases. The fit lines are expressed by $S_{\text{CO}_2} = k_\xi \xi^*$, $k_\xi = 0.26$ ($r^2 = 0.99$) for the water-wet cases, and by $S_{\text{CO}_2} = k_\xi \xi^*$, $k_\xi = 0.43$ ($r^2 = 0.99$) for the intermediate-wet cases. (b)–(d) The dimensionless variable k_ξ is a measure of displacement pattern. As k_ξ increases, the displacement pattern becomes more compact.

difference of pore space geometry, the difference of initial phase configuration and the three-dimensional effects. They focused on the invaded area and the interfacial length at the breakthrough and showed that even when the initial invasion structure was taken the same as that of the experiment, the relative error for interfacial length can grow up to 32.4% at the breakthrough time, and this relative error is even larger (39.5%) if the initial invasion structure was not initialized. In this study, without initialization of the invasion structure, the maximum relative error for the saturation at the steady-state is 29.1%.

As discussed above, the lower flow rate can eliminate the errors induced by the ISCO pump. However, immiscible flow with lower injection flow rate (the capillary number lower than 10^{-5}) cannot be simulated accurately by the current simulation techniques. This is because under such lower capillary number, the capillary force is dominant and so-called ‘parasitic’ velocities at the fluid–fluid interface reduce the accuracy of simulation results (Roman et al., 2015). Raeini et al. (2012) reported filtering methods to avoid non-physical velocities, which can improve the accuracy of simulation results for pore-scale two-phase immiscible fluid flow.

The overall scCO_2 saturation is an integrated variable that does not provide any information on scCO_2 distribution. Here we compare the simulated average longitudinal saturation profile with experimental results, as shown in Fig. 7. Although the simulated profile of average longitudinal saturation is higher than the measurement in most cases (except Fig. 7b), the simulation is able to capture the whole trend of longitudinal saturation profile: it tends to decrease with the increasing distance from the inlet, similar to results reported for core-flooding experiments (Al-Menhali et al., 2015; Niu et al., 2015).

4.2. Quantitative analysis of wettability effects

We performed quantitative analysis to gain insight into how wettability impacts invasion morphology. Given the limitation of the imaging system, the quantitative analysis is conducted based on the numerical simulation that can generally capture the main features of the drainage processes. We characterize the displacement pattern by introducing a dimensionless variable, k_ξ , representing the increasing rate of scCO_2 saturation with respect to the distance of displacement front to inlet, expressed by:

$$k_\xi = \frac{\partial S_{\text{CO}_2}}{\partial \xi^*} \quad (10)$$

where ξ^* is the normalized distance of displacement front to inlet, $\xi^* = \xi / L$, ξ is the distance of scCO_2 front to the inlet, L is the length of the micromodel, $L = 20$ mm. For completely compact displacement pattern, $k_\xi = 1$, whereas the displacement pattern becomes less compact (an unstable fluid–fluid interface) as k_ξ decreases.

Fig. 9. The displacement front propagation within the drainage time interval of 0.5 s and 0.51 s at the flow rate of 48 $\mu\text{L}/\text{min}$ in water-wet (a, a', c) and intermediate-wet (b, b', d) cases. (a)–(b), the scCO_2 invasion morphology at 0.5 s of drainage and the pore filled zone is marked by blue in (a', b') with the filling direction represented by the arrows. (c)–(d), the variation of pressure drop (ΔP) between inlet and outlet within the 0.01 s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As indicated in previous section, higher flow rate amplifies the error induced by ISCO pump whereas lower flow rate presents a challenge for the numerical simulation. Comparison of experiment and simulation shows that relatively smaller error was observed at the flow rate of 48 $\mu\text{L}/\text{min}$. Thus, based on the simulation results at this flow rate, we plot the relation between S_{CO_2} and ξ^* , as shown in Fig. 8a. It shows that S_{CO_2} increases roughly linearly with ξ^* , indicating a constant k_ξ during the drainage processes. Fitting data of S_{CO_2} and ξ^* yields $k_\xi = 0.26$ for water-wet case and $k_\xi = 0.43$ for intermediate-wet case. As shown in Figs. 8b–d, k_ξ captures the stabilizing effect of wettability on displacement pattern: as the pore surface becomes less water-wetting, a more compact displacement pattern is expected. As the contact angle continues to increase ($\theta > 90^\circ$), the scCO_2 is wetting phase and the displacement process is imbibition. Micromodel experiments using water-oil system (Zhao et al., 2016) reported that increasing θ from 90° to 120° , the effective finger width continues to increase. It indicated that the fluid–fluid displacement pattern becomes more stable and the variable k_ξ increases (but $k_\xi < 1$). However, if θ continues from 120° to 180° , incomplete pore-scale displacement occurs by thin film of wetting fluid (scCO_2) that propagates along the solid surfaces and the defending fluid (brine) is left in the pore body (Zhao et al., 2016), resulting in a smaller k_ξ . Giving the focus of this study is the scCO_2 –brine drainage processes, the wettability effect on imbibition processes is left to the further study.

The dimensionless variable, k_ξ also relates the dimensionless velocity of displacement front, v_ξ , given by:

$$v_\xi = \frac{\partial \xi^*}{\partial t^*} \quad (11)$$

where t^* is the scaled time variable, $t^* = t \cdot v_{\text{inlet}} / L$, t is the time of scCO_2 injection, v_{inlet} is the fluid velocity at the inlet of micromodel (shown in Table 1). Substituting Eqs. (10) into (11) leads to $v_\xi = \frac{\phi}{k_\xi}$, ϕ is the porosity. Therefore, we have:

$$v_\xi \propto \frac{1}{k_\xi} \quad (12)$$

Eq. (12) shows that the dimensionless velocity of displacement front (v_ξ) is inversely related to k_ξ . Therefore, higher k_ξ and lower v_ξ reflect the stabilizing effect of wettability on fluid–fluid displacement pattern. Radial air–water (Trojer et al., 2015), and water–oil

(Zhao et al., 2016) displacement experiments under ambient conditions also demonstrated this stabilizing effect. In these works, the fractal dimension of the fluid–fluid interface and the effective finger width were introduced for characterize the stabilizing effect. In the water–oil system, the fractal dimension exhibits a monotonic relation with respect to the contact angle (Zhao et al., 2016), whereas in the air–water system, as the effective finger width continues to increase as the wettability of invading fluid increases (Trojer et al., 2015).

The 3D simulation enables us to investigate the immiscible displacement behavior within the time interval similar to time step of iteration ($\sim 10^{-5}$ s), which is shorter than the Haines jump time of $\sim 10^{-3}$ s (e.g., Berg et al., 2013b). Fig. 9 presents the displacement front propagation within the drainage time interval of 0.5 s and 0.51 s at the flow rate of 48 $\mu\text{L}/\text{min}$. From Fig. 9a and b, within 0.01 s, although the same volume of scCO_2 is injected into micromodel meaning the same incremental value of S_{CO_2} , the forward travel distance of displacement front is longer in water-wet case ($\Delta \xi = \sim 261 \mu\text{m}$) than that in intermediate-wet case ($\Delta \xi = \sim 240 \mu\text{m}$), as expected by the front velocity given in Eq. (11). This indicates that intermediate-wetting promotes pore-filling in the longitudinal direction, relative to the water-wet case. On the other hand, from Fig. 9a', we can clearly see the Haines jump event (Berg et al., 2013b; Yamabe et al., 2014), with the scCO_2 phase invading from pore throat to pore body. However, because we selected the same time scale, $t \in [0.5, 0.51]$, in the intermediate-wet case, Fig. 9b' did not capture the full range of the Haines jump event. Nevertheless, the fluctuation of pressure drop (ΔP) between inlet and outlet shown in Fig. 9c and d reflects this pore-scale flow behavior. High frequency of this fluctuation suggests more pore-filling events in intermediate-wet condition. The larger ΔP in water-wet case (~ 350 Pa) is due to interfaces with higher curvature providing larger capillary pressures. In summary, we can conclude that reducing the pore surface wettability reduces the displacement front velocity, delays the breakthrough time, promotes the pore-filling in the longitudinal direction, and thus stabilize the displacement pattern.

To gain additional insight on effects of wettability effects on displacement pattern, we calculated the variation of fluid–fluid interface area with respect to the scCO_2 saturation. The simulated specific interface area ($a_{\text{nw}} = A_{\text{nw}} / (dWL\phi)$), where A_{nw} is the area

Fig. 10. The simulated relation between the specific scCO_2 -brine interface area (a_{nw}) and scCO_2 saturation (S_{CO_2}) for water-wet (●, ◆, ▲) and intermediate-wet cases (○, ◇, △) at the flow rates of 12 $\mu\text{L}/\text{min}$ (●, ○), 48 $\mu\text{L}/\text{min}$ (◆, ◇) and 120 $\mu\text{L}/\text{min}$ (▲, △). The breakthrough points are labeled with the dash circles. Fitting of data provides a power-law relation between a_{nw} and S_{CO_2} (given by Eq. (13)).

calculated from the 3D shape of fluid–fluid interface) follows a power-law relation with S_{CO_2} :

$$a_{\text{nw}} = a_0 S_{\text{CO}_2}^\beta \quad (13)$$

where a_0 and β are fitting parameters. The relation shown in Eq. (13) is consistent with the simulation (Liu et al., 2014) and experimental results (Zhang et al., 2011a). As shown in Fig. 10, this relation (Eq. (13)) is independent of flow rate and is also valid after the scCO_2 phase breakthrough. In water-wet case, $a_0 = 1.11 \text{ mm}^{-1}$, $\beta = 1.37$ ($r^2 = 0.99$), whereas $a_0 = 0.35 \text{ mm}^{-1}$, $\beta = 1.02$ ($r^2 = 0.98$), for intermediate-wet case. Fig. 10 also illustrates that as a given scCO_2 saturation, the specific interface area is higher in water-wet case than that in intermediate-wet case, similar to the simulation results in rock fractures (Dou et al., 2013).

In addition to Eq. (13), we introduced another parameter (k_a) to characterize the displacement pattern via the interface area (A_{nw}) normalized by the invaded volume (V_{invd}):

$$k_a = \frac{A_{\text{nw}}}{V_{\text{invd}}} = \frac{a_{\text{nw}}}{S_{\text{CO}_2}} = a_0 S_{\text{CO}_2}^{\beta-1} \quad (14)$$

This variable k_a is a measure of the interface instability. An irregular interface provides higher k_a value whereas smaller k_a indicates more smooth and compact interface (Holtzman and Segre, 2015). The values of a_0 and β ($\beta > 1$) in water-wet case are both larger than those in intermediate-wet case. Therefore, it can be seen from Eq. (14) that a larger k_a value is always higher in water-wet condition than in intermediate-wet condition for the same scCO_2 saturation, reflecting a more irregular interface and reduced displacement efficiency.

5. Conclusions

We elucidated the wettability effect on the scCO_2 -brine displacement pattern in drainage by performing a series of micromodel experiments under reservoir-relevant condition, combined with 3D numerical simulations. Through the micromodel experiment, high resolution images of scCO_2 phase distribution from pore-network to multiple pores to single pores were obtained, and the 3D pore-scale simulation qualitatively agrees with our experimental results, showing wider fingering, more compact displacement pattern, and higher scCO_2 saturation in intermediate-wet condition. Numerical simulations provided detailed information about the immiscible displacement in three dimensions, as well as the pore filling behavior resolved within milliseconds. Quantitative analysis based on pore-scale simulation suggested that the reduced wettability reduces the displacement

front velocity, promotes the pore-filling events in the longitudinal direction, and increases displacement efficiency. Simulated results also show smaller scCO_2 -brine interface area in intermediate-wet case, which suppresses the mass transfer between the phases. This work provides a more detailed understanding how the wettability affects the displacement pattern at the pore scale. Our work is important for GCS, because the surfaces of reservoirs and caprocks range from strongly water wetting to intermediate wetting (Akbarabadi and Piri, 2013; Berg et al., 2013a; Chiquet et al., 2005; Iglaue et al., 2015). Moreover, transitions from strongly water wetting to intermediate wetting may occur during exposure to CO_2 under reservoir conditions (El-Maghraby and Blunt, 2012; Kim et al., 2012; Plug and Bruining, 2007; Tokunaga and Wan, 2013; Wang and Tokunaga, 2015). Given that a homogenous pore-network pattern was used in this study, the effects of pore and pore network heterogeneity need to be investigated to determine the generality of our findings.

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References

- Abbramoff, M.D., Magalhães, P.J., Ram, S.J., 2004. Image processing with ImageJ. *Biophotonics Int.* 11 (7), 36–42.
- Akbarabadi, M., Piri, M., 2013. Relative permeability hysteresis and capillary trapping characteristics of supercritical CO_2 /brine systems: an experimental study at reservoir conditions. *Adv. Water Resour.* 52, 190–206.
- Al-Menhali, A., Niu, B., Krevor, S., 2015. Capillarity and wetting of carbon dioxide and brine during drainage in Berea sandstone at reservoir conditions. *Water Resour. Res.* 51 (10), 7895–7914.
- Andrá, H., Combaret, N., Dvorkin, J., Glatt, E., Han, J., Kabel, M., Keehm, Y., Krzikalla, F., Lee, M., Madonna, C., 2013. Digital rock physics benchmarks—part II: computing effective properties. *Comput. Geosci.* 50, 33–43.
- Bandara, U., Tartakovsky, A.M., Oostrom, M., Palmer, B.J., Grate, J., Zhang, C., 2013. Smoothed particle hydrodynamics pore-scale simulations of unstable immiscible flow in porous media. *Adv. Water Resour.* 62, 356–369.
- Batzle, M., Wang, Z., 1992. Seismic properties of pore fluids. *Geophysics* 57 (11), 1396–1408.
- Berg, S., Oedai, S., Ott, H., 2013a. Displacement and mass transfer between saturated and unsaturated CO_2 -brine systems in sandstone. *Int. J. Greenh. Gas Control* 12, 478–492.
- Berg, S., Ott, H., Klapp, S.A., Schwing, A., Neiteler, R., Brussee, N., Makurat, A., Leu, L., Enzmann, F., Schwarz, J.-O., 2013b. Real-time 3D imaging of Haines jumps in porous media flow. *Proc. Natl. Acad. Sci. U. S. A.* 110 (10), 3755–3759.
- Bikkina, P., Wan, J., Kim, Y., Kneafsey, T.J., Tokunaga, T.K., 2016. Influence of wettability and permeability heterogeneity on miscible CO_2 flooding efficiency. *Fuel* 166, 219–226.
- Brackbill, J., Kothe, D.B., Zemach, C., 1992. A continuum method for modeling surface tension. *J. Comput. Phys.* 100 (2), 335–354.
- Cao, S.C., Dai, S., Jung, J., 2016. Supercritical CO_2 and brine displacement in geological carbon sequestration: micromodel and pore network simulation studies. *Int. J. Greenh. Gas Control* 44, 104–114.
- Cheng, J.T., Pyrak, L.J., Nolte-Nolte, D.D., Giordano, N.J., 2004. Linking pressure and saturation through interfacial areas in porous media. *Geophys. Res. Lett.* 31 (8), L08502.
- Chiquet, P., Broseta, D.F., Thibaut, S., 2005. Capillary alteration of shaly cap rocks by carbon dioxide. *SPE* 94183 (1), 1–10.
- Cottin, C., Bodiguel, H., Colin, A., 2011. Influence of wetting conditions on drainage in porous media: a microfluidic study. *Phys. Rev. E* 84 (2), 026311.
- Dawson, H.E., Roberts, P.V., 1997. Influence of viscous, gravitational, and capillary forces on DNAPL saturation. *Ground Water* 35 (2), 261–269.

- Dou, Z., Zhou, Z., Sleep, B., 2013. Influence of wettability on interfacial area during immiscible liquid invasion into a 3D self-affine rough fracture: Lattice Boltzmann simulations. *Adv. Water Resour.* 61, 1–11.
- El-Maghraby, R.M., Blunt, M.J., 2012. Residual CO₂ trapping in Indiana limestone. *Environ. Sci. Technol.* 47 (1), 227–233.
- Ferrari, A., Lunati, I., 2013. Direct numerical simulations of interface dynamics to link capillary pressure and total surface energy. *Adv. Water Resour.* 57, 19–31.
- Ferrari, A., Jimenez-Martinez, J., Borgne, T.L., Méheust, Y., Lunati, I., 2015. Challenges in modeling unstable two-phase flow experiments in porous micromodels. *Water Resour. Res.* 51 (3), 1381–1400.
- Godec, M.L., Kuuskraa, V.A., Dipietro, P., 2013. Opportunities for using anthropogenic CO₂ for enhanced oil recovery and CO₂ storage. *Energy Fuel* 27, 4183–4189.
- Greenshields, C., 2015. OpenFOAM User Guide. Version 2.4.0. OpenFOAM Foundation Ltd.
- He, S., Kahanda, G.L., Wong, P.-z., 1992. Roughness of wetting fluid invasion fronts in porous media. *Phys. Rev. Lett.* 69 (26), 3731.
- Hoang, D.A., van Steijn, V., Portela, L.M., Kreutzer, M.T., Kleijn, C.R., 2013. Benchmark numerical simulations of segmented two-phase flows in microchannels using the Volume of Fluid method. *Comput. Fluids* 86, 28–36.
- Holtzman, R., Segre, E., 2015. Wettability stabilizes fluid invasion into porous media via nonlocal, cooperative pore filling. *Phys. Rev. Lett.* 115 (16), 164501.
- Horgue, P., Augier, F., Duru, P., Prat, M., Quintard, M., 2013. Experimental and numerical study of two-phase flows in arrays of cylinders. *Chem. Eng. Sci.* 102, 335–345.
- Iglauer, S., Pentland, C., Busch, A., 2015. CO₂ wettability of seal and reservoir rocks and the implications for carbon geo-sequestration. *Water Resour. Res.* 51 (1), 729–774.
- Jiang, F., Tsuji, T., 2015. Impact of interfacial tension on residual CO₂ clusters in porous sandstone. *Water Resour. Res.* 51 (3), 1710–1722.
- Jiang, F., Tsuji, T., 2016. Numerical investigations on the effect of initial state CO₂ topology on capillary trapping efficiency. *Int. J. Greenh. Gas Control* 49, 179–191.
- Jiang, F., Tsuji, T., 2017. Estimation of three-phase relative permeability by simulating fluid dynamics directly on rock-microstructure images. *Water Resour. Res.* 53, 11–32.
- Joekar Niasar, V., Hassanizadeh, S., Pyrak-Nolte, L., Berentsen, C., 2009. Simulating drainage and imbibition experiments in a high-porosity micromodel using an unstructured pore network model. *Water Resour. Res.* 45 (2), 1944–1973.
- Jung, M., Brinkmann, M., Seemann, R., Hiller, T., Sanchez de La Lama, M., Herminghaus, S., 2016. Wettability controls slow immiscible displacement through local interfacial instabilities. *Phys. Rev. Fluids* 1, 074202.
- Karadimitriou, N., Hassanizadeh, S., Joekar-Niasar, V., Kleingeld, P., 2014. Micromodel study of two-phase flow under transient conditions: quantifying effects of specific interfacial area. *Water Resour. Res.* 50 (10), 8125–8140.
- Kazemifar, F., Blois, G., Kyritsis, D.C., Christensen, K.T., 2015. A methodology for velocity field measurement in multiphase high-pressure flow of CO₂ and water in micromodels. *Water Resour. Res.* 51, 3017–3029.
- Kim, Y., Wan, J., Kneafsey, T.J., Tokunaga, T.K., 2012. Dewetting of silica surfaces upon reactions with supercritical CO₂ and brine: pore-scale studies in micromodels. *Environ. Sci. Technol.* 46 (7), 4228–4235.
- Krevor, S., Blunt, M.J., Benson, S.M., Pentland, C.H., Reynolds, C., Al-Menhali, A., Niu, B., 2015. Capillary trapping for geologic carbon dioxide storage—From pore scale physics to field scale implications. *Int. J. Greenh. Gas Control* 40, 221–237.
- Lenormand, R., Touboul, E., Zarcone, C., 1988. Numerical models and experiments on immiscible displacements in porous media. *J. Fluid Mech.* 189, 165–187.
- Liu, Y., Nolte, D., Pyrak-Nolte, L., 2011. Hysteresis and interfacial energies in smooth-walled microfluidic channels. *Water Resour. Res.* 47 (1), W01504.
- Liu, H., Valocchi, A.J., Werth, C., Kang, Q., Oostrom, M., 2014. Pore-scale simulation of liquid CO₂ displacement of water using a two-phase lattice Boltzmann model. *Adv. Water Resour.* 73, 144–158.
- Liu, H., Ju, Y., Wang, N., Xi, G., Zhang, Y., 2015. Lattice Boltzmann modeling of contact angle and its hysteresis in two-phase flow with large viscosity difference. *Phys. Rev. E* 92 (3), 033306.
- Moebius, F., Or, D., 2012. Interfacial jumps and pressure bursts during fluid displacement in interacting irregular capillaries. *J. Colloid Interface Sci.* 377 (1), 406–415.
- Niu, B., Al-Menhali, A., Krevor, S.C., 2015. The impact of reservoir conditions on the residual trapping of carbon dioxide in Berea sandstone. *Water Resour. Res.* 51 (4), 2009–2029.
- Nobakht, M., Moghadam, S., Gu, Y., 2007. Effects of viscous and capillary forces on CO₂ enhanced oil recovery under reservoir conditions. *Energy Fuel* 21, 3469–3476.
- Orr, F., Taber, J., 1984. Use of carbon dioxide in enhanced oil recovery. *Science* 224, 563–569.
- Pachauri, R.K., Allen, M., Barros, V., Broome, J., Cramer, W., Christ, R., Church, J., Clarke, L., Dahe, Q., Dasgupta, P., 2014. Climate Change 2014: Synthesis Report Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.
- Patzek, T.W., Male, F., Marder, M., 2013. Gas production in the Barnett Shale obeys a simple scaling theory. *Proc. Natl. Acad. Sci. U. S. A.* 110 (49), 19731–19736.
- Plug, W.-J., Bruining, J., 2007. Capillary pressure for the sand–CO₂–water system under various pressure conditions. Application to CO₂ sequestration. *Adv. Water Resour.* 30, 2339–2353.
- Raeesi, B., Piri, M., 2009. The effects of wettability and trapping on relationships between interfacial area, capillary pressure and saturation in porous media: a pore-scale network modeling approach. *J. Hydrol.* 376 (3), 337–352.
- Raeni, A.Q., Blunt, M.J., Bijeljic, B., 2012. Modelling two-phase flow in porous media at the pore scale using the volume-of-fluid method. *J. Comput. Phys.* 231, 5653–5668.
- Raeni, A.Q., Bijeljic, B., Blunt, M.J., 2015. Modelling capillary trapping using finite-volume simulation of two-phase flow directly on micro-CT images. *Adv. Water Resour.* 83, 102–110.
- Roman, S., Soulaire, C., AlSaud, M.A., Kovscek, A., Tchepeli, H., 2015. Particle velocimetry analysis of immiscible two-phase flow in micromodels. *Adv. Water Resour.* 95, 199–211.
- Rusche, H., 2003. Computational Fluid Dynamics of Dispersed Two-phase Flows at High Phase Fractions. PhD Thesis. Imperial College, London, UK.
- Simjoo, M., Dong, Y., Andrianov, A., Talanana, M., Zitha, P., 2013. CT scan study of immiscible foam flow in porous media for enhancing oil recovery. *Ind. Eng. Chem. Res.* 52 (18), 6221–6233.
- Tokunaga, T.K., Wan, J., 2013. Capillary pressure and mineral wettability influences on reservoir CO₂ capacity. *Rev. Mineral. Geochem.* 77 (1), 481–503.
- Trojer, M., Szulczewski, M.L., Juanes, R., 2015. Stabilizing fluid–fluid displacements in porous media through wettability alteration. *Phys. Rev. Appl.* 3, 054008.
- Tsuji, T., Jiang, F., Christensen, K.T., 2016. Characterization of immiscible fluid displacement processes with various capillary numbers and viscosity ratios in 3D natural sandstone. *Adv. Water Resour.* 95, 3–15.
- Valvatne, P.H., Blunt, M.J., 2004. Predictive pore-scale modeling of two-phase flow in mixed wet media. *Water Resour. Res.* 40 (7), 1944–1973.
- Wan, J., Tokunaga, T.K., Tsang, C.-F., Bodvarsson, G.S., 1996. Improved glass micromodel methods for studies of flow and transport in fractured porous media. *Water Resour. Res.* 32, 1955–1964.
- Wang, S., Tokunaga, T.K., 2015. Capillary pressure-saturation relations for supercritical CO₂ and brine in limestone/dolomite sands: implications for geologic carbon sequestration in carbonate reservoirs. *Environ. Sci. Technol.* 49 (12), 7208–7217.
- Wang, Y., Zhang, C., Wei, N., Oostrom, M., Wietsma, T.W., Li, X., Bonneville, A., 2012. Experimental study of crossover from capillary to viscous fingering for supercritical CO₂–water displacement in a homogeneous pore network. *Environ. Sci. Technol.* 47 (1), 212–218.
- Wong, P.-z., 1994. Flow in porous media: permeability and displacement patterns. *MRS Bull.* 19 (5), 32–38.
- Xu, W., Ok, J.T., Xiao, F., Neeves, K.B., Yin, X., 2014. Effect of pore geometry and interfacial tension on water–oil displacement efficiency in oil-wet microfluidic porous media analogs. *Phys. Fluids* 26 (9), 093102.
- Yamabe, H., Tsuji, T., Liang, Y., Matsuo, T., 2014. Lattice Boltzmann simulations of supercritical CO₂–water drainage displacement in porous media: CO₂ saturation and displacement mechanism. *Environ. Sci. Technol.* 49 (1), 537–543.
- Yuan, C., Chareyre, B., Darve, F., 2016. Pore-scale simulations of drainage in granular materials: finite size effects and the representative elementary volume. *Adv. Water Resour.* 95, 109–124.
- Zhang, C., Oostrom, M., Grate, J.W., Wietsma, T.W., Warner, M.G., 2011a. Liquid CO₂ displacement of water in a dual-permeability pore network micromodel. *Environ. Sci. Technol.* 45 (17), 7581–7588.
- Zhang, C., Oostrom, M., Wietsma, T.W., Grate, J.W., Warner, M.G., 2011b. Influence of viscous and capillary forces on immiscible fluid displacement: pore-scale experimental study in a water-wet micromodel demonstrating viscous and capillary fingering. *Energy Fuel* 25 (8), 3493–3505.
- Zhao, B., MacMinn, C.W., Juanes, R., 2016. Wettability control on multiphase flow in patterned microfluidics. *Proc. Natl. Acad. Sci. U. S. A.* 113 (37), 10251–10256.