Pore-Scale Supercritical CO₂ Dissolution and Mass Transfer under Imbibition Conditions

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Abstract: In modeling of geological carbon storage, dissolution of supercritical CO₂ (scCO₂) is often assumed to be instantaneous with equilibrium phase partitioning. In contrast, recent core-scale imbibition experiments have shown a prolonged depletion of residual scCO₂ by dissolution, implying a non-equilibrium mechanism. In this study, eight pore-scale scCO₂ dissolution experiments in a 2D heterogeneous, sandstone-analogue micromodel were conducted at supercritical conditions (9 MPa and 40 °C). The micromodel was first saturated with deionized (DI) water and drained by injecting scCO₂ to establish a stable scCO₂ saturation. DI water was then injected at constant flow rates after scCO₂ drainage was completed. High resolution time-lapse images of scCO₂ and water distributions were obtained during imbibition and dissolution, aided by a scCO₂-soluble fluorescent dye introduced with scCO₂ during drainage. These images were used to estimate scCO₂ saturations and scCO₂ depletion rates. Experimental results show that (1) a time-independent, varying number of water-flow channels are created during imbibition and later dominant dissolution by the random nature of water flow at the micromodel inlet, and (2) a time-dependent number of water-flow channels are created by coupled imbibition and dissolution following completion of dominant imbibition. The number of water-flow paths, constant or transient in nature, greatly affects the overall depletion rate of scCO₂ by dissolution. The average mass fraction of dissolved CO₂ (dsCO₂) in water effluent varies from 0.38% to 2.72% of CO₂ solubility, indicating non-equilibrium scCO₂ dissolution in the millimeter-scale pore network. In general, the transient depletion rate decreases as trapped, discontinuous scCO₂ bubbles and clusters within water-flow paths dissolve, then remains low with dissolution of large bypassed scCO₂ clusters at their interfaces with longitudinal water flow, and finally increases with coupled transverse water flow and enhanced dissolution of large scCO₂ clusters. The three stages of scCO₂ depletion, common to experiments with time-independent water-flow paths, are

revealed by zoom-in image analysis of individual scCO₂ bubbles and clusters. The measured relative permeability of water, affected by scCO₂ dissolution and bi-modal permeability, shows a non-monotonic dependence on saturation. The results for experiments with different injection rates imply that the non-equilibrium nature of scCO₂ dissolution becomes less important when water flow is relatively low and the time scale for dissolution is large, and more pronounced when heterogeneity is strong.

Keywords: geological carbon storage, micromodel, imbibition, CO₂ dissolution, mass transfer, relative permeability

1. Introduction

Dissolution trapping, as well as residual trapping and structural trapping, is important to the long-term security of geological CO₂ injection and storage in saline aquifers (IPCC, 2005). The dissolution of injected supercritical CO₂ (scCO₂) occurs within scCO₂ plumes by local phase partitioning (e.g., Spycher and Pruess, 2005; Pruess and Spycher, 2007; Zhou et al., 2008, 2010) or beneath scCO₂ plumes by convection induced by the density difference between resident brine without and with dissolved CO₂ (dsCO₂) (e.g., Ennis-King and Paterson, 2003; Kneafsey and Pruess, 2010; Gasda et al., 2011; MacMinn et al., 2010, 2011; Agartan et al., 2015). In addition, scCO₂ dissolution occurs along immobile, tailing edges of scCO₂ plumes under the influence of ambient groundwater flow after scCO₂ injection ceases, as shown by Chang et al. (2014).

Recently, experiments on local scCO₂ dissolution have been conducted by injecting slightly dsCO₂-undersaturated brine (Akbarabadi and Piri, 2013; Berg et al, 2013) or dsCO₂-free water (Chang et al., 2013, 2014) into sandstone core samples during imbibition, and have shown that complete, post-imbibition depletion of residual scCO₂ is a prolonged process. Non-equilibrium dissolution has also been observed in a well-designed sequence of field tests at the CO₂CRC Otway site (Haese et al., 2013; Paterson et al., 2013). This type of dissolution contradicts the classic model of instantaneous phase partitioning and equilibrium that is usually used in numerical modeling (Pruess and Spycher, 2007; Zhou et al., 2008, 2010). The observed non-equilibrium dissolution is attributed by Chang et al. (2013, 2014) to non-uniform distribution of scCO₂ and water and slow mass transfer of dsCO₂ between displacing water and local dsCO₂-containing water. However, direct evidence and imaging of this non-equilibrium dissolution at the pore scale has not been provided to date.

For equilibrium dissolution, imbibition and dissolution are decoupled because dissolution is instantaneous. Experimentally or numerically, for non-equilibrium dissolution, dissolution can intentionally be decoupled from imbibition by injecting dsCO_2 -saturated water during imbibition followed by injection of dsCO_2 -undersaturated water or brine during dissolution. This process was used by Akbarabadi and Piri (2013) for core displacement experiments. They observed an increase in brine relative permeability with dissolution, caused by gradual reduction in the blockage of trapped scCO_2 bubbles. The interaction of displacement and dissolution of scCO_2 at pore scale was observed in a homogeneous micromodel by Buchgraber et al. (2012).

Similar coupling of dissolution and imbibition for non-aqueous phase liquid (NAPL) and water fluid pairs has been observed in experiments in heterogeneous sand boxes and columns packed with angular silica sands. The observed increase in NAPL dissolution rate with decrease in NAPL saturation has been attributed to the creation of new water-flow paths as NAPL is dissolved (Nambi and Powers, 2000, Zhang et al., 2002). In addition, dissolution fingering may occur at NAPL-water interfaces because of instabilities in NAPL saturation and water flow during dissolution, as observed in a homogeneous flow cell (Imhoff and Miller, 1996; Imhoff et al., 1996) and heterogeneous pore media (Farthing et al., 2012).

Pore-scale micromodels provide a direct way to observe scCO_2 -brine displacement and dissolution characteristics. Zhang et al (2011) studied water drainage by liquid CO_2 in a dual-permeability pore network and observed preferential flow of liquid CO_2 in the high-permeability regions. Wang et al. (2013) investigated unstable displacement of brine by injected scCO_2 under reservoir conditions, showing crossover from capillary to viscous fingering during drainage in a homogeneous pore network. Zuo et al. (2013) observed the process of CO_2 bubble nucleation and expansion during exsolution from carbonated water in a sandstone-analogue micromodel,

and significantly improved the understanding of exsolution obtained from their previous core-scale experiments (Zuo et al., 2012). Kim et al. (2012) found wettability alteration in a scCO₂-silica-brine system at pore scale. Common to all these micromodel studies is that scCO₂ dissolution and its effect on drainage/imbibition were ignored or disabled intentionally by using dsCO₂-saturated water and water-saturated scCO₂ in their experiments. By using water free of CO₂, Buchgraber et al. (2012) observed the disconnection and shrinkage of CO₂ bubbles in their imbibition experiments in a micromodel, which is geometrically and topologically similar to Berea sandstone. However, the influence of scCO₂ dissolution on water flow and two-phase relative permeability needs a comprehensive and systematical study.

In this study, by using a heterogeneous micromodel, we (1) imaged the non-uniform scCO₂-water distribution during imbibition and dissolution to improve the understanding of non-equilibrium dissolution, and (2) investigated the coupled imbibition and dissolution and the impact of water-flow paths on dynamic dissolution. Eight imbibition and dissolution experiments and two additional imbibition-only experiments, with different injection rates, inlet pore structures, and inlet initial fluid occupancies, were conducted in a heterogeneous, sandstone-analogue micromodel. During each experiment, high-frequency time-lapse images of scCO₂-water distributions were obtained using a fluorescent imaging system (with a fluorescent scCO₂-soluble dye). In a number of these experiments, differential pressure was measured between the inlet and outlet of the micromodel to calculate relative water permeability.

2. Experiments of CO₂ Dissolution under Imbibition Conditions

Eight imbibition and dissolution experiments were conducted to understand scCO₂ dissolution and mass transfer at the pore scale using a sandstone-analogue pore network. Before each experiment, the same experimental procedure including preparation and drainage, was

followed. During the experiment, time-lapse images of the distribution of scCO_2 were obtained using a fluorescence imaging system. These images were used to calculate scCO_2 saturation and depletion rate.

2.1. Micromodel

A 2D heterogeneous micromodel was fabricated from images of a Mt. Simon sandstone core sample (Zuo et al., 2013) (Figure 1a) using microfabrication methods involving standard photolithography, coupled plasma-deep reactive ion etching (ICP-DRIE), thermal oxidation, and anodic bonding (Chomsurin et al., 2003; Willingham et al., 2008). The characteristics of the pore network are shown in Table 1. The $7.1 \text{ mm} \times 5.3 \text{ mm}$ pore network, $35 \text{ }\mu\text{m}$ in depth, consists of nine identical sub-networks in a 3×3 array, with a porosity of 0.35 and a permeability of $7.4 \times 10^{-13} \text{ m}^2$. The depth of the pore network was designed to facilitate observation of the fluorescent signal, similar to other pore-scale studies using micromodels (Chomsurin et al., 2003; Zhang et al., 2011; Wang et al., 2012; Zuo et al., 2013). The pore-size distribution of the network shown in Figure 1b was quantified using a local thickness plugin in ImageJ software (Hildebrand and Rüesgsegger, 1996; Rasband, 1997-2008). Three channels (C_1 to C_3) with large pore sizes along the flow direction are identified and marked. The width of each channel is $\sim 300 \text{ }\mu\text{m}$. At the right boundary, the average pore diameter is $27.5 \text{ }\mu\text{m}$, while at the left boundary it is $25.3 \text{ }\mu\text{m}$. The diameter of pore bodies varies from 24 to $84 \text{ }\mu\text{m}$, with an average value of $33 \text{ }\mu\text{m}$, while the width of pore throats varies from 3 to $24 \text{ }\mu\text{m}$, with an average value of $14 \text{ }\mu\text{m}$. These variabilities at the boundaries and in the micromodel may significantly affect flow at the micro-scale including imbibition and dissolution.

2.2. Experimental Procedure

An experimental setup with four high-pressure syringe pumps (Teledyne ISCO Inc., Lincoln, NE) was used for the drainage and imbibition experiments (Figure 2). The micromodel is assembled against the sapphire viewing window in a high-pressure cell. The cell is placed horizontally on an automated microscope stage with the pore network side facing down. The high-pressure cell and all the pump cylinders and fluid delivery pipelines are thermostatically controlled in a temperature chamber (In Vivo Scientific, St. Louis, MO) by circulating hot air and water using a water heater (Fisher Scientific). The inlet of the micromodel is connected to Pumps A and D via a three-way valve (Valve 1) for scCO₂ injection during drainage and subsequent deionized (DI) water injection during imbibition and dissolution. The outlet of the micromodel is connected to Pump B for back pressure control, and allows displaced fluid to flow out of the micromodel. Outside of the micromodel, the high pressure cell is filled with glycerol (Sigma-Aldrich Inc., St. Louis, MO) and is connected to Pump C for confining (overburden) pressure control.

Before experiments, the micromodel was cleaned by flowing the following sequence of fluids through it: (1) DI water, (2) Isopropanol, (3) DI water, (4) SC-1 solution (DI water: NH₄OH: H₂O₂ at 5:1:1) and (5) DI water. Gaseous CO₂ was first injected into the cleaned micromodel from a source tank to completely displace air from the micromodel and tubing. DI water was then injected using a syringe pump to dissolve and displace the gaseous CO₂ to obtain a fully water-saturated system. During these steps, the micromodel system was kept at atmospheric pressure.

Pump A was filled with dyed CO₂ at approximately 5.87 MPa while Valve 1 connecting Pump A to the micromodel was closed. The CO₂ was mixed with a fluorescent dye, Coumarin

153 (99.99%; Alfa Aesar, Ward Hill, MA), to facilitate visualization and quantification of CO₂ distribution and saturation in the micromodel using epifluorescent microscopy. Details of the fluorescent absorption and emission properties of Coumarin and the CO₂ staining processes can be found in Biswas et al. (1999) and Zhang et al. (2011). Pump A was then pressurized up to 9.00 MPa. The pressure in the micromodel and the confining pressure were gradually increased to 9.00 MPa and 9.58 MPa, respectively, by simultaneously pressurizing the back pressure pump and the confining pressure pump in increments of 0.21 MPa (30 psi) over 1.5 hours. All fluids were allowed to equilibrate to 40 °C for over 12 hours.

After the above preparatory steps were completed, a drainage experiment was conducted by injecting the dyed scCO₂ into the micromodel at a constant flow rate until a stable scCO₂ saturation was established that was not affected by further scCO₂ injection, monitored through the time-lapse images. The displaced water during drainage was collected in Pump C. At the completion of drainage (after ~6 hours), the scCO₂ distribution was imaged to calculate the baseline scCO₂ saturation.

After drainage, imbibition experiments with scCO₂ dissolution were conducted by injecting DI water at a constant flow rate until the scCO₂ in the pore network was completely depleted. During the imbibition experiments, the back pressure pump was maintained at a constant 9.00 MPa. A differential pressure transducer (Validyne Engineering Corporation, Northridge, CA) was connected to the inlet and outlet of the micromodel (see Figure 2) to monitor the differential pressure, allowing calculation of the relative water permeability (k_{rw}).

2.3. Fluorescence Imaging

Each of the micromodel images was acquired using a Nikon Eclipse TE2000-E epifluorescent microscope (Melville, NY) through a 4X inverted objective with a spatial resolution of 1.62 $\mu\text{m}/\text{pixel}$. The stained scCO_2 in the micromodel was observed through a Blue GFP filter set ($\lambda_{\text{ex}} = 379\text{-}401\text{ nm}$, $\lambda_{\text{em}} = 435\text{-}485\text{ nm}$). A single image that captured the entire pore network was formed by montaging 4×4 separate sub-images taken using a CoolSnap HQ2 monochrome CCD camera (Photometrics Inc., Tucson, AZ). The camera was controlled by a computer with imaging software (NIS-Elements, Nikon, Melville, NY).

The fluorescent signal intensity of dyed scCO_2 is significantly higher than that for silicon posts and pore spaces filled with water, with signal-to-noise ratio >10 . A threshold value can be unambiguously determined for each image to distinguish scCO_2 phase from others. By overlapping images of the dyed scCO_2 and the pore space, scCO_2 -water distribution in the pore network during imbibition and dissolution was obtained. During water imbibition, time-lapse images were obtained, and segmentation and analysis of these images were conducted to calculate time-dependent scCO_2 saturation by using ImageJ software (Rasband, 1997-2008).

The effect of the Coumarin dye on the surface properties is not significant. The reported water-Coumarin dyed CO_2 contact angle in micromodels fabricated using similar silicon wafers is approximately 15° for liquid CO_2 -water (Zhang et al.2012), and scCO_2 -water (Wang et al. 2012) displacement studies. These values indicate the strong water-wetting properties of micromodels with a silicon surface and are identical to observed values for fluid pairs without dissolved dye (Grate et al. 2013). The effect of dye on scCO_2 dissolution is likely to be minimal as demonstrated by the constant scCO_2 depletion rate during scCO_2 bubble dissolution (see

Figure 8a and Section 3.2) when the dye concentration is variable. This observation indicates that a significant change in scCO_2 dissolution due to the dye does not occur.

2.4. Description of Imbibition and Dissolution Experiments

Parameters for the 10 imbibition experiments are shown in Table 2. Four imbibition and dissolution experiments (Exp. A1 through A4) were conducted to investigate the fundamental mechanisms of scCO_2 dissolution and mass transfer by injecting dsCO_2 -free DI water from either side of the micromodel at the same constant rate of $50 \mu\text{L/h}$. The four experiments are used to show the impacts (i.e., boundary effects) of deterministic changes in pore structures and random changes in fluid occupancy at the micromodel inlets upon imbibition and dissolution occurring within the heterogeneous micromodel. As shown in Table 2, water was injected from the left-side inlet of the micromodel in Exp. A1, A2, and A4, and from the right-side inlet of the micromodel in Exp. A3. Experiments A1, A2, and A4 were conducted to investigate the effect of small, random perturbations of water occupancy at the left-side inlet and the repeatability of the imbibition and dissolution experiment. Exp. A3 was performed to check the effects of inlet pore structures because the pore structures at the left- and right-side inlets are different (see Figure 1 and Table 1).

Two different comparison and sensitivity analyses were conducted. The first analysis focused on dissolution mechanisms, while the second one focused on dissolution time. For the first sensitivity analysis, an experiment (Exp. B1) was conducted by initially having the micromodel fully-saturated with scCO_2 , followed by injecting dsCO_2 -free DI water at a rate of $20 \mu\text{L/h}$. This experiment was used to maximize the number of water-flow paths created by strong capillary suction and compare the dissolution results with those obtained under limited number of water-flow paths. Two additional experiments (B2 and B3) were conducted by

injecting dsCO₂-saturated DI water from left-side or right-side inlet of the micromodel at a constant rate of 50 μL/h. Before injection, scCO₂ and water were allowed to equilibrate in a mixing column for 12 h under experimental conditions, following Zuo et al. (2013). Comparisons between B2 and A1/A2/A4, and between B3 and A3 can help us better understand the interaction between imbibition and dissolution before a residual scCO₂ saturation and distribution is reached, after which dissolution is the only mechanism for scCO₂ depletion in the dsCO₂-free water injection experiments.

For the second sensitivity analysis, three imbibition and dissolution experiments (C1 through C3) were conducted to investigate the effect of water injection rate and dissolution time, with all other conditions identical to those in Exp. A1, A2, and A4. The injection rates (10, 50, 100, and 500 μL/h) were selected to shorten the duration of the experiments, even though their corresponding velocities, varying from 3.7 m/d to 185 m/d, are far greater than those under ambient groundwater gradients (e.g., 5 m/year). To allow for comparisons between experiments, we calculated the capillary number (Ca) using $Ca=v\mu/\sigma$, where v represents the average pore velocity of water, μ indicates water viscosity, and σ is the interfacial tension between scCO₂ and water.

3. CO₂ Dissolution and Mass Transfer

In this section, our analysis is focused on scCO₂ dissolution and depletion using the time-lapse images of scCO₂ distributions in Exp. A1 through A4. The four experiments show different number of water-flow paths that affect dynamic scCO₂ dissolution.

3.1. Pore-Network-Scale CO₂ Dissolution and Mass Transfer

For Exp. A1, an initial scCO₂ saturation of 0.68 was obtained after drainage was completed (see Table 2). It took approximately 10 min and 6.17 pore volumes (PV) of injected DI water for the imbibition process to complete, with a constant water injection rate of 50 µL/h and $\text{LogCa} = -5.34$, leading to a residual scCO₂ saturation of 0.55 (Table 3). Because of the short duration of this period, imbibition is expected to be dominant, even though scCO₂ dissolution is inevitably involved. As shown in the first scCO₂-water image in Figure 3a, a single, tortuous water-flow path (dark) is created along the lower high-permeability channel C₃ (see Figure 1b), with all injected water focusing in this path and bypassing the majority of the micromodel domain. After the imbibition is complete, scCO₂ dissolution is the dominant process for scCO₂ depletion with time. As shown by the scCO₂-water images in Figure 3a, scCO₂ depletion by dissolution is a prolonged process. In this experiment only one water-flow path was created during imbibition and lasted for the entire depletion phase. However, the width of the flow path increased with time until all scCO₂ dissolved after a total water injection time of 790 min. Some boundary effects can be observed in Figure 3a, showing that scCO₂ dissolution in the vicinity of both ends of the micromodel appears to be faster. This end effect is illustrated at different locations in Figure 4 for Exp. A1, showing higher water saturations (lower scCO₂ saturations) near both ends of the micromodel.

The prolonged dissolution process for the pore network manifests itself in the scCO₂ saturation as a function of time, as shown in Figure 5a. After imbibition, it takes 780 min for the complete depletion of residual scCO₂ (with a saturation of 0.55), while it would only take 2.83 min for equilibrium dissolution, assuming a CO₂ solubility of 1.225 mol/L under the experimental conditions (Spycher et al., 2003), to completely deplete the residual scCO₂. The

scCO₂ depletion rate, i.e., the depleted scCO₂ mass (gram) per unit time interval (min), decreases from 1.73×10^{-7} g/min at the beginning of dissolution to 8.65×10^{-8} g/min at 300 min, and then increases to 5.47×10^{-7} g/min at 760 min (see Figure 5b). The average CO₂ depletion rate for the entire depletion period is 1.72×10^{-7} g/min, which is only 0.38% of the equilibrium depletion rate of 4.49×10^{-5} g/min (see Table 3). In other words, the dsCO₂ concentration in the effluent water varies from 0.09% to 1.22% of the CO₂ solubility under the imposed experimental conditions. These scCO₂ depletion rates and effluent dsCO₂ concentrations, significantly smaller than those predicted from equilibrium phase partitioning, indicate that non-equilibrium scCO₂ dissolution occurs in the heterogeneous micromodel under a high flow rate. The non-equilibrium dissolution can be attributed to the non-uniform distribution of scCO₂ and mobile water and the limited interface area available for local scCO₂ dissolution and mass transfer of dsCO₂ at some distance away from the interfaces (see Figure 3a).

The depletion rate was calculated based on the scCO₂ volumes obtained from the image analysis and the scCO₂ density under the experimental conditions (9 MPa, 40 °C). The dsCO₂ concentration was calculated using the mass balance principle, assuming that dissolution and mass transfer account for scCO₂ depletion. It is noted that scCO₂ pressure, a Young-Laplace pressure, depends on the bubble size and shape (surface curvature), and is therefore likely to vary with dissolution and between bubbles. To validate the calculations, the pressure of scCO₂ bubbles with different sizes was calculated by the Young-Laplace equation (deGennes et al., 2004),

$$\Delta P = P_{inside} - P_{outside} = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (1)$$

where σ is the interfacial tension of the scCO₂ – water fluid pair and R_1 and R_2 are the principal radii of curvature. For scCO₂ bubbles/droplets in spherical shapes,

$$\Delta P = \frac{2\sigma}{R} \quad (2)$$

Using Eq. (2), we calculated the pressure of a CO₂ bubble with an initial radius of $10^4 \mu\text{m}$ that has dissolved into a smaller one with a final radius of $1 \mu\text{m}$. The calculated bubble pressure changes slightly from 9.00 to 9.05 MPa, with an interfacial tension of 26.2 mN/m (Bachu and Bennion, 2009). The corresponding scCO₂ density increases from 0.4855 to 0.4983 g/cm³, and the calculated scCO₂ density using the experimental pressure and temperature, 0.4855 g/cm³, is thus reasonable for our mass balance and depletion rate analysis.

It is of interest to distinguish three periods of scCO₂ dissolution and depletion (separated by hollow symbols in Figure 5b). During Period I (the first 150 min), the scCO₂ depletion rate decreases with time by dissolving trapped, discontinuous scCO₂ bubbles in the water-flow path, while little-to-no dissolution occurs in the scCO₂ region bypassed by the preferential flow path. After complete depletion of the trapped and discontinuous scCO₂, the scCO₂ depletion rate remains low during Period II (between 150 and 520 min). CO₂ dissolution occurs at the interface between the bypassed, immobile scCO₂ and the mobile water in the flow path, with mass transfer primarily occurring from the water-scCO₂ interface. Finally, in Period III, the scCO₂ depletion rate gradually increases with time until complete depletion of scCO₂ in the pore network. This time-dependent behavior of scCO₂ dissolution will be further discussed by detailed pore-scale image analysis in the next section.

The second experiment (Exp. A2) was conducted under the same conditions and procedures as in Exp. A1. However, a slightly different distribution of scCO₂ and water was

obtained before the imbibition and dissolution. In Exp. A2, a scCO₂ saturation of 0.72 (residual water saturation of 0.28) was obtained after the drainage process, compared to an initial scCO₂ saturation of 0.68 obtained in Exp. A1 (see Table 2). More importantly, the local scCO₂-water distribution at the left-side inlet of the micromodel is different from that in Exp. A1 (see Figures 3 and 6), due to the low viscosity ratio between scCO₂ and water, and the small depth variations of the micromodel. The water-filled pores near the micromodel inlet, marked by dashed line in Figure 6b, create an additional water-flow path along the central high-permeability channel C₂, while the flow path in the lower high-permeability channel C₃ is common for both experiments. These two water-flow paths developed during imbibition over the entire micromodel along channels C₂ and C₃ (see Figure 3b). As a result of better sweep efficiency, a scCO₂ saturation of 0.50 is obtained after the dominant imbibition is completed (see Table 3).

For Exp. A2, scCO₂ dissolution first occurs within the two separate water-flow paths, then at their interfaces with bypassed scCO₂ clusters, gradually depleting the scCO₂ cluster between the two paths, and finally at the interface between the merged flow path and the remaining scCO₂ cluster, as shown in Figure 3b. It takes 575 min to completely deplete residual scCO₂, which is shorter than the 780 min in Exp. A1 (see Figure 5a). This faster dissolution and depletion can also be seen from the higher depletion rate over most of the depletion time than in Exp. A1 (see Figure 5b). The scCO₂ depletion rate varies from 7.3×10^{-8} to 5.1×10^{-7} g/min, corresponding to an effluent dsCO₂ mass fraction of 0.16% to 1.14% of the scCO₂ solubility under the experimental conditions. The average depletion rate is 2.14×10^{-7} g/min and the average effluent concentration is 0.48% of solubility (see Table 3), which are higher than 1.72×10^{-7} g/min and 0.38% in Exp. A1, respectively. The higher dissolution and depletion rate in Exp. A2 can be attributed to the two water-flow paths and their increased interface area between mobile water

and immobile scCO_2 . As with Exp. A1, three different periods of dissolution can be distinguished (Figure 5b): the depletion rate decreases with time until residual scCO_2 bubbles are completely dissolved within the two water-flow paths at 100 min (Period I), then remains relatively low until 405 min (Period II), and finally gradually increases with time (Period III).

The observed scCO_2 depletion rates in both Exp. A1 and A2 can be attributed to the time-dependent interaction between (1) water flow and (2) scCO_2 dissolution and mass transfer. For instance, during Period I of Exp. A1 and A2, scCO_2 dissolution and mass transfer dominate the scCO_2 depletion as stable water flow establishes in the high permeability channel(s). As the scCO_2 mass and interface area were reducing during dissolution, the scCO_2 depletion rate decreased over time. After complete removal of the CO_2 blobs/clusters and during Period II, scCO_2 depletion rate remained low with dissolution occurring at the interfaces between the bypassed, immobile scCO_2 and the mobile water in the flow paths. Under these conditions, mass transfer primarily occurred from the scCO_2 -water interfaces. During this period, transverse water flow into the boundary layers slowly develops but minimally affects the scCO_2 depletion rate. During Period III, transition of the dominating mechanism from scCO_2 dissolution to transverse water flow occurred. The development of the latter and the coupled water flow and dissolution at the pore scale enhanced the dissolution rate at the pore-network scale. Further discussion on this phenomenon of enhanced dissolution is given in the next section.

In Exp. A3, the fluids were injected into the right-side inlet of the pore network at the same flow rate as in Exp. A1 and A2, where the pore structures are different from those at the left-side one. In Exp. A3, a scCO_2 saturation (0.73) was obtained after drainage, slightly higher than for Exp. A1 and A2. A single water-flow path was initiated and developed along the central high-permeability channel (C_2) within 1 min of imbibition, as shown in Figure 3c. At 3 min, a

second water-flow path over the micromodel length developed along the upper high-permeability channel (C_1), and a third water-flow path of a limited length initiated in the lower high-permeability channel (C_3). In addition, a smaller, local path developed connecting the C_1 path with the C_2 path. At 22 min, the C_3 path diverted from the C_2 path at the inlet and connected again with the C_2 path, allowing injected water to flow along all the three global paths. While the C_2 path was created by the imbibition process at early times, all the additional flow paths, global or local, were initiated by dissolution and then developed by coupled imbibition and dissolution.

The dissolution-imbibition coupling and the dynamically created multiple flow paths significantly enhance overall scCO_2 dissolution and reduce scCO_2 depletion time to 118 min, compared to Exp. A1 (780 min) and A2 (575 min). In this experiment, the CO_2 depletion rate almost monotonically decreases from 1×10^{-5} to 4.96×10^{-7} g/min, with an order of magnitude reduction during the first 10 min (Figure 5c). This behavior of depletion rate is different from that of three stages observed in Exp. A1 and A2 where the number of water-flow paths remains unchanged before merging by dissolution. In Exp. A3, the average depletion rate and the average effluent dsCO_2 concentration are 1.22×10^{-6} g/min and 2.72% solubility, respectively (Table 3), which are almost one order of magnitude higher than those in Exp. A1 and A2.

In Exp. A4, conducted using the same conditions and procedures as in Exp. A1 and A2, two water-filled pores at the left-side inlet, marked by dashed lines in Figure 6c, were created during drainage, and result in two water-flow paths during imbibition (see Figure 6f) that developed over the entire micromodel (not shown). The time-dependent depletion rate and scCO_2 saturation are almost identical to those obtained in Exp. A2 (see Figure 5). This indicates that the micromodel experimental results are reproducible as long as the number of water-flow paths after drainage is similar at the micromodel inlet. Different initial distributions of scCO_2 -

water along with natural channels with large pores can impact the number of water-flow paths, affecting the dissolution process.

This series of experiments, conducted with the same injection rate and experimental procedure, show that the dissolution of scCO_2 in a heterogeneous pore network is controlled by the number and extent of water-flow paths that are effective during the dissolution process over the micromodel. The varying number of flow paths may be initiated by the heterogeneity at the micromodel inlet (e.g., Exp. A1, A2, and A4 vs. Exp. A3) or by the different scCO_2 -water distribution (i.e., fluid occupancy) before imbibition and dissolution at the same inlet of the same heterogeneity (Exp. A1 vs. Exp. A2 and A4). More statically or dynamically developed water-flow paths result in an increased scCO_2 -water interface area and therefore faster scCO_2 dissolution. In contrast to the observed water fingering flow, stable displacement with uniform scCO_2 -water distribution and ubiquitous scCO_2 -water interfaces will accelerate the depletion of residual scCO_2 , as assumed in the equilibrium dissolution.

3.2. Pore-scale CO_2 Dissolution and Mass Transfer

To better understand the imbibition and dissolution phenomena at the pore-network scale presented in the above section, we first analyze dynamic scCO_2 dissolution in four selected scCO_2 -filled pores or pore clusters within a water-flow path using time-lapse scCO_2 -water images, and then present time-dependent dimensionless mass statistics (representing dynamic dissolution and depletion) for over 70 scCO_2 -filled pores or pore clusters in the water-flow path. Finally, we investigate how small water-flow paths are created by dissolution and how dissolution is enhanced by enlarged scCO_2 -water interface area, by zooming on the scCO_2 boundary layer (with mobile water flow) of a large bypassed scCO_2 -filled region. All these analyses are based on the dissolution process in Exp. A1.

Figure 7 shows the progressive dissolution of isolated scCO₂ bubbles and bubble clusters within the water-flow path for Exp. A1 at different times after the start of water injection. Three single scCO₂ bubbles (referred to as P1, P2, and P3) with different surrounding scCO₂-water conditions and one cluster (referred to as P4) of multiple bubbles within the water-flow path are selected. Figure 8 shows selected time-lapse images of the scCO₂-water distributions for each pore or cluster. The first image is obtained at the end of imbibition (i.e., 10 min), while the last image is used to show the near-depletion of the scCO₂ bubble(s). Also shown in Figure 8 is the average depletion rate for each pore or cluster calculated using two consecutive images. For each image of a pore or cluster, the interfacial area between immobile scCO₂ and mobile water is calculated (see Figure 9). Note that the color of scCO₂ changes from purple to bright yellow with the increase in dye concentration and intensity as scCO₂ is dissolved with time.

For the four selected bubbles or bubble cluster, three modes of pore-scale scCO₂ dissolution are identified. In the first mode (Mode 1), scCO₂ dissolution occurs in the direction of a long pore throat or a long, narrow pore with a relatively constant interface area between scCO₂ and water, and the resulting depletion rate is relatively constant. In this mode, diffusion-dominated mass transfer is the main cause of scCO₂ dissolution and depletion, while no imbibition and advection occur along the pore or throat. For example, the time-lapse scCO₂-water images in Figure 8a show the gradual depletion of the scCO₂ bubble (P1 marked by a dashed line), linearly from one end to the other. The depletion rate is relatively stable at 1.7×10^{-9} g/min over the 80 min dissolution period (see Figure 8a), with a relatively constant interfacial area of approximately $1700 \mu\text{m}^2$ (Figure 9). Note that there is no dissolution occurring at the opposite end of this bubble. For the L-shaped long pore (P2) in Figure 8b, the time-lapse images show the scCO₂ bubble breaks by dissolution into two small bubbles, with a spike in scCO₂-

water interface area from 2530 to 3640 μm^2 and depletion rate from 2.09×10^{-9} to 3.57×10^{-9} g/min (see Figure 8f and 9), while for most of the dissolution time the depletion rate is relatively stable at 1.7×10^{-9} g/min.

In the second mode of dissolution (Mode 2), a single scCO_2 bubble (P3 marked by a dashed line in Figure 8c) sits next to immobile water in a large, wide pore whose throats are mainly blocked by four smaller scCO_2 bubbles (b1, b2, b3, and b4 in Figure 8c); the immobile water is believed to be saturated with dsCO_2 , resulting in no further dissolution of the large bubble from 10 to 20 min. The small bubble on the left (b1) is completely dissolved at 20 min, and mobile dsCO_2 -undersaturated water is then able to communicate with the bubble by dsCO_2 diffusion and advection. The large bubble starts to shrink with time by dissolution. At 35 min, the small bubble at the bottom (b2) is completely dissolved, and the water body in the pore is then connected through two throats with mobile water. The dissolution is accelerated as shown by the increasing depletion rate (Figure 8g), leading to the complete dissolution of the separated bubble at the top throat at 40 min. The shrinkage of the large bubble is accelerated until it almost disappears at 60 min. It is interesting to note that the small bubble at the right (b3) remains stable during the entire dissolution process of P3. In this mode, the accelerated dissolution of the large bubble in the large and wide pore indicates the importance of (1) dissolution of small bubbles at pore throats and creation of small flow paths, allowing for advection to play a role, and (2) the resulting mixing of dsCO_2 -saturated water near the bubble with mobile water. For example, the scCO_2 depletion rate increases by more than one order of magnitude from 2.4×10^{-10} to 7.5×10^{-9} g/min over 60 min. In this mode the interfacial area between scCO_2 and water is not the dominant factor, as shown in Figure 9.

The final mode (Mode 3) is used to show the dynamic dissolution process occurring in a cluster (P4) of multiple scCO₂-filled pores, with connected scCO₂ in pore bodies and throats, surrounded by mobile and immobile water in the water-flow path. This cluster may contain isolated immobile water inside as shown in Figure 8d. The dissolution is initiated from the largest scCO₂ bubble in the cluster (as shown by the white arrow in the first image at 10 min) by water flow through a water-filled throat. This bubble is quickly dissolved after 10 min at relatively high and stable depletion rate of 1.62×10^{-8} g/min, leaving four small bubbles at the remaining pore throats. This relatively large rate can be attributed to the large scCO₂-water interface area ($\sim 7200 \mu\text{m}^2$) in the large pore and water invasion into the depleted pore through the water-filled throat. The dissolution continues along four scCO₂-filled throats, following the processes outline in Mode 1 in multiple areas. The different depletion rate among these throats is caused by their different width (i.e., scCO₂-water interface area). The overall depletion rate decreases with time to a lower stable value at 90 min. Finally the remaining large, long bubble is continuously dissolved following Mode 1, with a stable depletion rate of 5.19×10^{-9} g/min and an interface area of $3451 \mu\text{m}^2$. For the entire dissolution process in this mode, only one scCO₂-water interface is available for dissolution in any scCO₂-filled pore or pore throat (marked by white arrows) and diffusion-dominated mass transfer of dsCO₂ from this moving interface to mobile water is likely the key mechanism for continuous dissolution.

For the three pore-scale scCO₂ dissolution modes discussed, we can conclude that the one-end dissolution in a single scCO₂-filled pore or throat (Mode 1) or in a cluster of scCO₂-filled pores and pore throats (Mode 3) is dominated by diffusion and mass transfer with the scCO₂-water interfacial area as the key parameter controlling the dissolution rate. For example, the depletion rate for the pore cluster (P4) linearly depends on the scCO₂-water interface area

over the entire dissolution process, as shown in Figure 9. For the areal dissolution in a large scCO₂-filled pore (Mode 2), with multiple water-filled throats allowing for mobile water to flow along the scCO₂-water interface, the non-proportionality between depletion rate and interface area (see Figure 9 for P3) may be caused by the change in flow rate of mobile water as scCO₂ blobs dissolve. Quantifying the local velocity of water flow is not possible with the current experimental method and setup.

Second, to understand the wide range of dissolution and depletion rates in a statistical manner, the time-dependent, dimensionless scCO₂ mass, normalized by the scCO₂ mass at 10 min, was calculated for each of over 70 scCO₂-filled pores or clusters within the water-flow path in Exp. A1 (see Figure 7). As shown in Figure 10, the depletion rate of the dimensionless mass varies significantly, which can be attributed to (1) the scCO₂ mass in each selected pore or cluster, (2) the mode of pore-scale dissolution, and (3) the flow rate of mobile water along scCO₂-water interface. For small scCO₂-filled pores or pore throats, the curves are more or less like those for P1 and P2, while for many other pores, their curves are similar to the curve for P3 in that a slow dissolution and depletion is followed by an accelerated dissolution. For a few scCO₂-filled pore clusters, their curves look like that of P4. The curves for all individual pores and clusters are bounded by the curve for scCO₂ dissolution in the entire pore network under the equilibrium dissolution assumption (black dashed line) and by the curve for the observed dissolution of bypassed scCO₂ (i.e., out of the water-flow path) during Periods II and III (red dashed line). In other words, it takes a longer time to dissolve the individual CO₂ bubbles in pores or clusters less than 0.5 mm × 0.5 mm than equilibrium dissolution for the entire pore network; it takes much longer time to dissolve the large bypassed scCO₂ mass. For example, all the individual scCO₂ bubbles in the water-flow path are completely dissolved in 200 min (see

Figures 7c and 10), while the bypassed scCO₂ mass is completely dissolved in 780 min. Note that the dissolution of the isolated bubbles in the water-flow path occurs within dissolution Period I for the pore network. During this period, many bubbles undergo accelerated dissolution, but the overall dissolution rate for the pore network decreases with time because less scCO₂ mass is involved in the dissolution.

Finally, we focus on the enhanced dissolution in the boundary layer of the large, bypassed scCO₂ region with the main water-flow path to understand the increased dissolution rate with time during Period III in the pore network. Figure 11 shows the large, bypassed scCO₂ body with the water-flow path, with different colors (not associated with dye intensity) to show the fraction of scCO₂ bubbles dissolved within different time intervals from 500 min to 790 min. Also shown in this figure are the time-lapse images of scCO₂ bubbles (associated with light intensity) in two boxes within the boundary layer. In the left (1.2 mm × 1.1 mm) box, dissolution is initiated at a small bubble at a pore throat, then spreads to a large bubble in a large pore, and finally proceeds upward and left-ward. Once the connected bubbles are broken at a location, mobile flow may occur upward (see the flow lines), thus accelerating dissolution. The same accelerated dissolution occurs in the other (0.7 mm × 0.7 mm) box after a small water-flow path developed, cutting the bubbles into three smaller clusters. The coupled water flow and dissolution at the pore scale increases the dissolution rate at the pore-network scale, shortening the total depletion time. Note that the depletion rate in Exp. A1 increases by a factor of about five, from 1.00×10^{-7} at 500 min to 5.47×10^{-7} g/min at 760 min, showing enhanced dissolution by pore-scale water flow and dissolution coupling. This coupling is caused by transverse water flow perpendicular to the boundary layer into the boundary layer, rather than longitudinal water flow along the boundary layer in the main water flow path.

4. Experimental Comparison

In this section, the effects of (1) the number of water-flow paths and (2) the coupling between dissolution and imbibition on the overall dissolution behavior presented in the previous section are further discussed using three experiments with dsCO₂-free water injection into an initially scCO₂-saturated micromodel (Exp. B1), and dsCO₂-saturated water injection for imbibition without dissolution (Exp. B2 and B3). Then, the effect of dissolution time is discussed using three additional experiments (Exp. C1 through C3) conducted using different flow rates to provide a context on how to link the pore-network-scale dissolution to a field-scale dissolution with smaller groundwater flow velocities. The comparison between equilibrium and non-equilibrium is discussed using dissolution rates over time. Finally, the water relative permeability measured under imbibition and dissolution is compared to classic model results for imbibition conditions only.

4.1. Comparison on Dissolution Mechanisms

In Exp. B1, the micromodel was initially fully saturated by scCO₂ ($S_{g,i}=1$) and dsCO₂-free DI water was then injected from the right-side inlet at a constant rate of 20 $\mu\text{L/h}$ (Table 2). Figure 12a shows time-lapse images of scCO₂ for this experiment. As shown in the upper left image of Figure 12a, injected water migrates quickly into the micromodel due to high capillary pressure and then spreads extensively in the upgradient region of the network. In this region, the strong suction results in film flow along grain walls accumulating at pore throats of higher capillarity where initially continuous scCO₂ is snapped off into isolated bubbles that shrink by local dissolution. During the imbibition coupled with dissolution, there are no major paths that can be distinguished in this region. In the downgradient region, two main water-flow paths

develop along channels C_1 and C_3 to the outlet, leading to two large bypassed $scCO_2$ clusters. The residual $scCO_2$ saturation after 10 min injection for the entire network is 0.46.

Three dissolution periods can be distinguished for time-dependent $scCO_2$ saturation and depletion rate (see Figure 13). In Period I, the depletion rate is relatively high because of the interaction between dissolution and water flow in the upgradient region. The CO_2 depletion rate increases with increased interaction after 50 min (12 PV), then spikes at 75 min (18.5 PV) because of the strongest interaction between pervasive water flow and dissolution, and finally remains relatively stable. In Period II (between 185 and 345 min marked by hollow symbols in Figure 13), the $scCO_2$ depletion rate remains stable at a low level of 1×10^{-7} g/min, which is similar to the values in Exp. A1 and A2, because dissolution mainly occurs at the interfaces between $scCO_2$ clusters and water-flow paths. In Period III, the depletion rate is also at a relatively high level, because of enhanced dissolution by transverse water flow as discussed in the previous section. The average $scCO_2$ depletion rate and effluent $dsCO_2$ concentration for the entire dissolution process are 2.13×10^{-7} g/min and 1.19% of solubility, respectively (see Table 3). It is noted that at the very beginning in Period I (i.e., before 10 PV water injection), the depletion rate is small, possibly because water flow may still occur as film water around grain walls. The stable depletion rates in Periods I and III are higher than those in Exp. A1 and A2, even though the injection rate is smaller. This enhanced dissolution may be attributed to the many small water-flow paths initially induced by strong capillary forces and later by coupled water flow and dissolution (see Figure 12b). By comparing the many small flow paths in the upgradient region in Exp. B1 (Figure 12) to the one or two main paths in Exp. A1 or A2 (Figure 3) and their associated dissolution rates, we can improve the understanding of the effect of the number of flow paths on overall dissolution, which is one of the key mechanisms of dissolution.

Experiments B2 and B3 were conducted by injecting dsCO₂-saturated DI water from the left-side (B2) and right-side (B3) inlet of the micromodel at a constant rate of 50 μ L/h, respectively. As shown in Figure 14, the water-flow paths develop in the first 10 min, and then remain relatively stable over the remaining experiment time, even though scCO₂ saturation decreases slightly from 0.48 at 10 min to 0.38 at 100 min in Exp. B2 and from 0.45 to 0.36 in Exp. B3.

Comparing Exp. B2 and A2 with water injection from the left-side inlet, two preferential water flow paths develop and remain stable along two high-permeability channels. The main difference is that the two flow paths are along channels C₁ and C₂ in Exp. B2, while they are along channels C₂ and C₃ in Exp. A2. More importantly, the two tortuous flow paths in Exp. B2, with smaller vertical paths connecting them, are compared to the two straight ones in Exp. A2. This indicates that the imbibition with dissolution has a lower displacement efficiency than the imbibition without dissolution, as also shown by their residual scCO₂ saturations (see Table 3). In other words, with dissolution, displacement is more focused and has a less effective sweep.

Experiments B3 and A3, both with injection from the right-side inlet, have different water-flow paths during imbibition. In Exp. B3, two water-flow paths are developed along channels C₁ and C₂, with a better sweep efficiency and a lower residual saturation of 0.36. In Exp. A3, however, a single water-flow path develops along channel C₂ within the first minute of imbibition and two water-flow paths develop in the next two minutes along channels C₁ and C₃. The above comparisons indicate that with dissolution, imbibition is less effective in sweep and results in larger residual scCO₂ saturation for dissolution to deplete.

4.2. Comparison on Dissolution Rate and Time

Three imbibition-dissolution experiments (Exp. C1 through C3) were conducted by injecting water at a rate of 10, 100 and 500 $\mu\text{L/h}$, while all other conditions were kept the same as in Exp. A1 and A2. Time-lapse images of scCO_2 distribution and water-flow path development are shown in Figures 15a-c, respectively. Like in Exp. A1 and A2, preferential flow of water develops along the high-permeability channels in all the three experiments. In Exp. C1, one water-flow path is initiated and developed along the central high-permeability channel C_2 , while in Exp. C2 and C3, conducted at higher injection rates, three water-flow paths develop along channels C_1 , C_2 , and C_3 . As a result, the residual scCO_2 saturation after imbibition is 0.54 in Exp. C1, 0.40 in Exp. C2, and 0.37 in Exp. C3, even though their initial condition after drainage is very similar.

Figure 16 shows the scCO_2 depletion rate for all the experiments (A1-A2 and C1-C3), with water injection from the left-side inlet and LogCa values from -6.04 to -4.34. Initially, scCO_2 depletion rates are higher with larger water injection rates. The depletion rate during this time is the highest in Exp. C3, and lowest in Exp. C1. This result is understandable in that advection and diffusion are the two fundamental mechanisms contributing to the mass transfer of dsCO_2 from the two-phase interface to the displacing water in water-flow paths. With an increase in water flow rate, advection of dsCO_2 from phase interfaces in individual scCO_2 -filled pores and clusters may enhance dissolution at the phase interfaces. During Period III, Exp. A1, A2, and C1 share similar highest depletion rate (in time), around $3\text{-}4 \times 10^{-7}$ g/min. This is also understandable in that diffusion and transverse water flow (not longitudinal flow) enhance scCO_2 dissolution rate and result in the increase in CO_2 depletion rate during Period III.

4.3. Discussion on Equilibrium and Non-Equilibrium Dissolution

We first focus on the time-dependent effluent dsCO_2 concentration and its variation range for Exp. A1-A4, B1, and C1-C3 to measure the effectiveness of water in dissolving scCO_2 . Figure 17a shows the effluent dsCO_2 concentration as a function of injected water PV for five experiments (A1, A2, C1, C2, and C3). The concentration is calculated from the depleted scCO_2 mass and the total injected water volume between two consecutive imaging times. For each experiment, the fluctuation of effluent concentration over PV of injected water indicates the dynamic dissolution occurring in the micromodel. For example, the fluctuation is more than one order of magnitude in Exp. A1. The total PV needed for complete dissolution represents the effectiveness of dissolution per unit volume of water. The effectiveness inversely depends on injection rate and is positively correlated with the number of water-flow paths. For example, 490 PV of injected water is needed for complete dissolution in Exp. A1 because of less effectiveness caused by the only one water-flow path, while only 360 PV of injected water is needed in Exp. A2 when two water-flow paths are created.

Figure 17b shows the range of the time-dependent effluent concentration and the average concentration over the entire dissolution process for the eight experiments with dissolution. The maximum effluent concentration varies from 0.46% of solubility for Exp. C3 to 22% of solubility for Exp. A3. The minimum concentration varies from 0.06% solubility in Exp. C3 to 1.11% solubility in Exp. A3. For all these experiments, the highest obtained concentration is 22% of solubility, indicating that equilibrium dissolution never happens under the imposed experimental conditions and at the pore-network scale. The average concentration over the entire dissolution time varies from 0.25% to 2.72% of the scCO_2 solubility. The two highest average concentrations correspond to Exp. A3 with the most dynamic water-flow paths and Exp. C1 with

the lowest injection rate; the two lowest average concentrations correspond to Exp. A1 with the fewest water-flow paths and Exp. C3 with the highest injection rate. All the lower-than-solubility effluent concentrations indicate prolonged dissolution times. For example, the observed dissolution times in Exp. C1, C2, and C3 are 750, 220 and 70 minutes, respectively, while the associated equilibrium dissolution would take only 15.01, 1.11 and 0.19 minutes for the complete depletion of residual scCO_2 , respectively.

With the above pore-network-scale experimental findings, we can infer that equilibrium dissolution can only be achieved when a large number of water-flow paths are available, with sufficient interface area between scCO_2 and mobile water for local dissolution to occur. Indeed, the equilibrium of phase partitioning assumes that scCO_2 and water are in contact everywhere (i.e., an infinite number of flow paths) and dissolution occurs instantaneously. Alternatively, equilibrium dissolution can be achieved by taking a long time of dissolution, as we follow the trend of the average effluent concentration as a function of flow velocity (Table 3). When a limited number of water-flow paths are developed, non-equilibrium dissolution is generally observed.

At the core scale, the non-equilibrium dissolution has been observed during imbibition and dissolution experiments by imaging the limited number of water-flow paths (Akbarabadi and Piri, 2013) and by inferring from effluent dsCO_2 concentration that is far less than solubility (Chang et al., 2013; 2014). At the field scale of tens meters, this phenomenon has been observed in the well-designed sequence of field tests at the CO2CRC Otway site (Haese et al., 2013; Paterson et al., 2013). In all these laboratory and field experiments, imbibition has been induced by water injection with a large water-flow velocity. For a reservoir-scale scCO_2 plume after cessation of injection, the ambient groundwater flow is relatively small and the duration for local

dissolution to occur is long; this effect tends to approach equilibrium dissolution. On the other hand, a natural reservoir is always heterogeneous, and the scCO₂ plume follows sand and high-permeability channels and diffuses into low-permeability regions (e.g., Birkholzer et al., 2015). The ambient groundwater flow may follow the same channels to dissolve residual scCO₂ after imbibition is complete. For the portion of scCO₂ plume in those low-permeability regions, scCO₂ dissolution is expected to be a lengthy process because of limited interface for mobile water and immobile scCO₂. The combined effect of low ambient groundwater flow and strongly heterogeneity-limited interface areas between the groundwater flow and scCO₂ plume will decide on the reservoir-scale dissolution behavior.

4.4. Relative Permeability under Dissolution

The differential pressure (in cm H₂O) between the inlet and outlet of the micromodel was measured over the imbibition and dissolution periods in Exp. A1, A2, and C2, and only over the imbibition period for Exp. B3. The measured differential pressure of these experiments is shown in Figure 18a. The water relative permeability (k_{rw}), calculated using an absolute permeability of $7.4 \times 10^{-13} \text{ m}^2$, is shown in Figure 18b. Note that the water injection rate is 50 $\mu\text{L/h}$ in Exp. A1, A2 and B3, and 100 $\mu\text{L/h}$ in Exp. C2.

For Exp. A1, k_{rw} is 0.15 after the main water-flow path develops and imbibition has been completed at 10 min. After that, k_{rw} increases to 0.4, as the trapped scCO₂ bubbles/clusters that partially block water flow within the water-flow path are gradually dissolved, leading to a water saturation (S_w) of 0.53 at the end of dissolution Period I (labeled by the left hollow square symbol). After that, k_{rw} remains approximately constant until S_w reaches 0.65 (indicated by the right hollow square symbol), as the slow dissolution of the large, bypassed scCO₂ cluster in Period II contributes little to the water flow. Finally, k_{rw} increases with S_w up to unity at $S_w = 1.0$.

as the bypassed scCO₂ cluster is gradually dissolved with enhanced dissolution and transverse water flow in Period III (see Section 3.2). A similar k_{rw} pattern is also observed for Exp. A2, with considerably higher relative permeabilities: $k_{rw} = 0.27$ at $S_w = 0.51$ and $k_{rw} = 0.77$ at $S_w = 0.63$ at the two end times of Period I. This pattern of k_{rw} growth is not observed in Exp. C2 with a higher injection rate. In this experiment, water-flow paths are developed in all three high-permeability channels after imbibition is completed, leading to an initially high k_{rw} of 0.55 at $S_w = 0.6$. For Exp. B3, with only imbibition, k_{rw} monotonically increases with S_w from 0.13 at 10 min to 0.40 at 100 min of water injection.

The observed non-monotonic k_{rw} in Exp. A1 and A2 is caused by (1) bi-modal permeability with three high-permeability channels and low-permeability regions between them in the highly heterogeneous micromodel and (2) non-uniform distribution of scCO₂ bubbles and bubble clusters in the high-permeability channels after imbibition is complete. The k_{rw} value at the end of imbibition depends on the number of water-flow paths (i.e., 0.15, 0.27, 0.55 for Exp. A1, A2, and C2 with 1, 2, and 3 water-flow paths, respectively). k_{rw} increases with time by dissolving scCO₂ bubbles and bubble clusters in the high-permeability channels, and then remains stable or slightly decreases with dissolution of scCO₂ between the channels. k_{rw} may increase again with water saturation if additional water-flow paths and dissolution of their isolated scCO₂ bubbles get involved, for example, in Exp. A1 and A2.

The non-monotonic k_{rw} observed under both imbibition and dissolution is quite different from the classic models of k_{rw} that show a monotonic function of S_w under imbibition only, such as for Exp. B3. A large number of core-flooding experiments have been conducted to measure k_{rw} under imbibition for the scCO₂-water fluid pair (Shi et al., 2011; Krevor et al., 2012; Akbarabadi and Piri, 2013; Pini et al., 2013; Levine et al., 2014), and the measured k_{rw} relations

generally fit the Brooks-Corey model (Burdine, 1953; Corey, 1954; Brooks and Corey, 1964) or the van Genuchten-Mualem model (Mualem, 1976; van Genuchten, 1980). The key parameter of these models is the pore-size distribution index. The Brooks-Corey model assumes a bundle of long capillary tubes of different sizes (Burdine, 1953), while the van Genuchten-Mualem model assumes a bundle of capillary tubes each of which consists of in-series tube segments of two different sizes (Mualem, 1976). The non-monotonic k_{rw} pattern observed in this study indicates that isolated non-wetting phase bubbles and bubble clusters in high-permeability channels may significantly reduce k_{rw} , while the by-passed non-wetting phase regions out of the three high-permeability channels has a little to do with k_{rw} . Dissolution of the former significantly increases k_{rw} , while dissolution of the latter does not change k_{rw} .

5. Conclusions

Dissolution of scCO₂ and mass transfer of dsCO₂ were investigated by a series of imbibition and dissolution experiments conducted in a sandstone-analogue micromodel with three large pore-size channels, fabricated from images of a real Mt. Simon sandstone core. All the imbibition-dissolution experiments were conducted at 9.0 MPa and 40 °C, with a wide range of water injection rates and $LogCa$ values from -6.04 to -4.34. For each experiment, time-lapse images of scCO₂-water distributions were obtained using the fluorescence imaging system developed in this study, providing direct evidence on non-uniform displacement of scCO₂ by preferential water flow and subsequent dynamic scCO₂ dissolution. The images were used for calculating scCO₂ saturation and depletion rate to investigate dynamic and non-equilibrium dissolution.

The overall scCO₂ dissolution at the pore-network scale is controlled by (1) the number of water-flow paths developed during imbibition, and (2) the velocity of water flow or

dissolution time. The varying number (1, 2, and 3) water-flow paths in different experiments developed along the three high-permeability channels of the heterogeneous micromodel, and a dynamic number of paths developed by strong coupling between dissolution and imbibition in one experiment. The number and nature of the flow paths depend on the heterogeneity and initial fluid occupancy near micromodel inlets, as well as water injection rate. We observed that (1) more flow paths result in faster depletion of the residual scCO_2 by dissolution, and (2) a lower water-flow velocity (with a smaller injection rate for higher dissolution time) results in dsCO_2 concentration closer to scCO_2 solubility. Under the various experimental conditions in this study, equilibrium dissolution was *never* reached because of the limited scCO_2 -water interface area available for dsCO_2 mass transfer and limited residence time (or dissolution time). The equilibrium phase partitioning assumes that scCO_2 and water are in contact anywhere (i.e., an infinite number of flow paths) and dissolution occurs instantaneously.

The pore-scale imaging analysis indicates that dissolution at the pore-network scale may be enhanced by (1) the enlarged scCO_2 -water interface area for local dissolution of trapped, discontinuous scCO_2 bubbles and bubble clusters within water-flow paths, and (2) coupled transverse water flow and local dissolution within the boundary layer of large bypassed scCO_2 clusters, in contrast to the slow dissolution of large bypassed scCO_2 clusters by longitudinal water flow with a limited interface area. The enhanced dissolution in the water-flow paths and the boundary layers results in an increase in the measured water relative permeability with reduced scCO_2 saturation, while the slow dissolution between the enhanced dissolution periods contributes little to the water relative permeability in spite of reduction in scCO_2 saturation. The measured non-monotonic relative permeability caused by bi-modal permeability and dissolution

of residual scCO_2 in high-permeability channels may indicate a limitation of the classic models showing a monotonic relationship between relative permeability and saturation.

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Figure 1. (a) Micromodel pore network with silicon posts in black and pore space in white, consisting of nine identical sub images in a 3×3 array, indicated by the red dash lines, (b) pore size distribution quantified by the Local Thickness plugin in Imagej software. Three channels with large pores (C_1 to C_3) are distinguished and marked by white dotted boxes.

Figure 2. Schematic of the experimental setup.

Figure 3. Time-lapse images of scCO₂ phase (bright) at different times for Exp. A1 (a), A2 (b) and A3 (c), with the injection at the left side of these images marked by the blue arrow. The silicon posts are shown in blue, water in black and scCO₂ in bright colors-purple to white. Note that the images for Exp. A3 with right-side injection are flipped horizontally to facilitate comparisons. The white box in (a) indicates the region selected for local dissolution analysis in Figure 7. The white box in (b) indicates the region used for analyzing the effect of small, random perturbations of water occupancy in Exp. A1, A2 and A4 as shown in Figure 6. The white dotted lines in (c) show boundaries of water-flow paths and scCO₂-filled clusters.

Figure 4. Temporal change in CO₂ saturation at different locations of the pore network. The location is normalized by the length of the pore network.

Figure 5. (a) Temporal change in scCO₂ saturation for Exp. A1 through A4, (b) scCO₂ depletion rate as a function of water injection time for Exp. A1, A2, A4, and (c) scCO₂ depletion rate for Exp. A3. The hollow symbols in (b) indicate the data points at period boundaries.

Figure 6. Sub-images showing different scCO₂-water occupancy in the vicinity of micromodel inlet before the start of water imbibition for Exp. A1 (a), A2 (b) and A4 (c), and at 10 min after water injection starts for Exp. A1 (d), A2 (e), and A4 (f). The difference in the initial phase occupancies (see the region marked by the white dotted lines) between different experiments

results in different water flow path(s) (indicated by the white arrows) developed during imbibition and dissolution.

Figure 7. Sub-images of scCO₂-water distributions showing the progressive dissolution of isolated scCO₂ bubbles and bubble clusters within the water-flow path for Exp. A1 at (a) 10 min, (b) 50 min and (c) 200 min after the start of water injection. Also shown are the four selected scCO₂ bubbles and bubble clusters (P1, P2, P3, and P4) used for interpreting mechanisms of scCO₂ dissolution and mass transfer.

Figure 8. Time-lapse scCO₂-water sub-images for (a) bubble P1, (b) bubble P2, (c) bubble P3, and (d) bubble cluster P4 marked by white dotted lines, and their associated time-dependent scCO₂ depletion rates in (e) through (h) respectively. White arrows indicate the direction of water flow and green arrows indicate the newly created water flow paths during scCO₂ dissolution.

Figure 9. Correlation between time-dependent scCO₂ depletion rate and scCO₂-water interfacial area for P1 to P4. For P4, the depletion rate is linearly correlated with the interfacial area.

Figure 10. Dimensionless scCO₂ mass (normalized by scCO₂ mass at 10 min) as function of water injection time for more than 70 scCO₂-filled bubbles and bubble clusters within the water-flow path in Exp. A1 (see Figure 7), including the four selected bubbles/clusters (P1 through P4), shown in bold solid lines. Also shown are the curve (in black dash line) for equilibrium dissolution for the entire pore network and the curve (in red dash line) for the large, bypassed scCO₂ cluster during Period II and III.

Figure 11. Dynamic dissolution and depletion of the large, bypassed scCO₂ cluster during Period III in Exp. A1, with different portions, marked by different colors, depleted at different time intervals. The silicon posts are dark blue and water is black. Also shown are the time-lapse sub-

images of two regions (marked in boxes) selected to show the transverse water flow and enhanced dissolution. The white arrows indicate the newly created water flow along the micromodel inlet and in the local pores.

Figure 12. (a) Time-lapse images of scCO₂-water phase in Exp. B1, with white dotted lines showing the boundary of bypassed scCO₂ clusters, and (b) time-lapse sub-images of the region (marked by the white box in Figure 12a) selected to show newly created water flow marked by white arrows and enhanced dissolution.

Figure 13. CO₂ saturation and depletion rate as a function of time (min) in Exp. B1, with the three separate dissolution periods marked by hollow symbols.

Figure 14. Time-lapse images of scCO₂ phase for imbibition experiments without dissolution in Exp. B2 (a) and B3 (b). The white dotted lines show the boundary of water-flow paths and bypassed scCO₂ clusters.

Figure 15. Time-lapse images of scCO₂ phase for DI water injection for Exp. C1 (a), C2 (b) and C3(c).

Figure 16. CO₂ depletion rate as a function of water injection time for Exp. C1, C2, and C3, in comparison with that for Exp. A1 and A2.

Figure 17. (a) Effluent dsCO₂ concentration as function of water injection volume for five experiments with the left-side inlet and (b) the range of effluent dsCO₂ concentrations in eight dissolution experiments.

Figure 18. (a) Transient differential pressure (in cm H₂O) measured between the inlet and outlet of the micromodel and (b) calculated water relative permeability for Exp. A1, A2, B3, and C2. The hollow symbols indicate the water saturation at both end times of Period II in Figure 5b. Differential pressure is recorded every 10 seconds and the water relative permeability is

951 calculated by averaging the pressure data for imaging intervals (with 2 min duration) with the
952 error bar showing the variations.

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954

Table 1. Summary of the pore network characteristics

Pore network characteristics	
Length (cm)	0.71
Width (cm)	0.53
Depth (μm)	35
Porosity	0.35
Permeability (m ²)	7.4×10 ⁻¹³
Average pore size at left boundary (μm)	25.3
Average pore size at right boundary (μm)	27.5
Grain size range (area equivalent diameter, μm)	5-106
Average grain size (area equivalent diameter, μm)	31
Pore body diameter range (μm)	24-84
Average pore body diameter (μm)	33
Pore throat width range (μm)	3-24
Average pore throat width (μm)	14

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Table 2. Summary of the imbibition/dissolution experiments

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Exp. #	Q ($\mu\text{L}/\text{h}$)	v (m/d)	$\text{Log}Ca$	$S_{g,i}$	Inlet boundary	Imbibition fluid
A1	50	18.5	-5.34	0.68	Left	DI water
A2	50	18.5	-5.34	0.72	Left	DI water
A3	50	18.5	-5.34	0.73	Right	DI water
A4	50	18.5	-5.34	0.69	Left	DI water
B1	20	7.40	-5.74	1.00	Right	DI water
B2	50	18.5	-5.34	0.73	Left	CO ₂ -saturated water
B3	50	18.5	-5.34	0.75	Right	CO ₂ -saturated water
C1	10	3.70	-6.04	0.70	Left	DI water
C2	100	37.0	-5.04	0.68	Left	DI water
C3	500	185.0	-4.34	0.71	Left	DI water

966

Table 3. Results of the imbibition/dissolution experiments

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Exp. #	S_{gr}	Imbibition time (min)	Dissolution time (min)	$Q_d \times 10^7$ (g/min)	$C/C_s \times 10^2$
A1	0.55	10	780	1.72	0.38
A2	0.50	10	575	2.14	0.48
A3	0.59	1.0	118	12.23	2.72
A4	0.50	10	550	1.94	0.43
B1	0.46	10	535	2.13	1.19
B2	0.38	100	0	8.03	----
B3	0.36	100	0	8.97	----
C1	0.54	10	750	1.77	1.97
C2	0.40	10	220	4.48	0.50
C3	0.37	1.0	70	11.43	0.25

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