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1 Experimental Study of Three-Dimensional CO₂-Water Drainage and
2 Fracture-Matrix Interactions in Fractured Porous Media

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10 **Highlights**

11 1. We imaged 3-D CO₂-water drainage in vertically stacked matrix-fracture columns that
12 are different from classic core-flood settings.

13 2. Capillary continuity in the fracture was key to water drainage and CO₂ invasion in the
14 matrix.

15 3. Fracture water saturation and capillary continuity were enhanced by the non-uniform
16 fracture capillary pressure and countercurrent flow across the fracture-matrix interface.

17

18 **Abstract:** Estimation of CO₂ storage capacity in fractured porous reservoirs requires a
19 better understanding of the CO₂-water flow fundamentals in fracture-matrix systems.
20 There are few core-flood experiments on three-dimensional CO₂-water drainage in a
21 fracture-matrix system, yet none have examined the impacts of the capillary continuity of
22 fractures and fracture-matrix interactions. In this study, twelve drainage experiments
23 were conducted in four fracture-matrix columns, each comprising a vertical stack of a
24 cylindrical rock core, a filter paper serving as an analog to a horizontal fracture, and a
25 ceramic plate. The core sample was surrounded by open space at the top and
26 circumferential sides to model fractures, allowing for 3-D CO₂-water drainage in the rock
27 core and displaced water draining across the horizontal fracture. X-ray computed
28 tomography was conducted to visualize the dynamic invasion/drainage processes in four
29 rock core samples showing contrasts in anisotropy, permeability, and heterogeneity.
30 Experimental results show (1) the equilibrium CO₂ saturations in the rock matrix vary
31 from 0.10 to 0.60 at controlled capillary pressures up to 200 kPa, (2) the CO₂ saturations
32 in the matrix increase with water saturation in the horizontal fracture resulting in better
33 capillary continuity for water to drain across the fracture, and (3) the fracture water
34 saturation can be enhanced by the non-uniform fracture capillary pressure and
35 countercurrent flow of CO₂ and water across the fracture-matrix interface. In the case of
36 high fracture water saturation, matrix CO₂ saturation largely depends on matrix
37 anisotropy and heterogeneity. The core-scale experimental results contribute to
38 understand the fracture-matrix interactions and CO₂ storage efficiency in fractured porous
39 media.

40 **Keywords:** Geological carbon storage, Fractured porous media, Two-phase flow, Core-
41 flooding, X-ray CT, Fracture-matrix interactions

1. Introduction

Two-phase flow characteristics of CO₂-water in subsurface fractured media are of great interest as fractured carbonate and sandstone reservoirs are increasingly considered as potential geological CO₂ sequestration (GCS) and simultaneous oil recovery locations because of their ubiquity in sedimentary basins (Agada et al., 2016). In saline aquifers, GCS in sandstone formations is also considerably influenced by the presence of fractures and faults, as reported from the currently world's largest onshore CO₂ storage site, the Krechba site within the In Salah gas field (Iding & Ringrose, 2010). It is also noted that fractures are a major source of uncertainty in subsurface media, and the existence of unidentified fracture networks should be incorporated with well-understood CO₂-water flow behaviors for risk analysis of storage projects (Narr et al, 2006; March et al., 2018).

The bulk of CO₂ storage in fractured reservoirs occurs in the interconnected pore volumes of the rock matrix because of its high porosity. Peters and Klavetter (1988) reported the fracture porosity three to five orders of magnitude lower than the matrix porosity, although the preferential and fast flow of injected CO₂ is expected to occur in fractures due to the overall higher fracture permeability than that of the (porous) rock matrix. CO₂ invasion into the rock matrix from fractures and brine drainage through matrix blocks are critical in establishing CO₂ storage in fractured reservoirs. Capillarity and gravity are usually major forces affecting the CO₂ invasion from fractures to the matrix, whereas viscous force may be more relevant in the near-well region, where large pressure gradients may impose viscous displacement inside the matrix blocks (March, 2018). Diffusion of dissolved CO₂ from fractures into the rock matrix could also be

64 pronounced, however, it may take a longer time for CO₂ diffusion to contribute to storage
65 capacity (Pruess et al., 1990; Zhou et al., 2017).

66 Figure 1. Conceptual model of CO₂-water displacement through a fracture-matrix system.
67 After injection, water desaturation in the fractures occurs first, followed by CO₂ invasion
68 into the blocks (e.g., the central block marked by the white dotted line). The thin blue
69 arrows indicate the preferential CO₂ flow in the fractures, while the thick blue arrows
70 refer to the subsequent CO₂ invasion from fractures to matrix. The red arrows represent
71 water drainage in neighboring matrix across portions of the fractures that may retain
72 water to an extent that water drainage across the fractures is available.

73

74 Figure 1 presents the conceptual model of CO₂-water flow in a fractured system
75 dominated by capillarity. After CO₂ injection, water desaturation in the largest flow
76 pathways (fractures) occurs first, followed by CO₂ invasion into matrix blocks (e.g., the

central block marked by the white dotted line). The invasion of CO₂ from fractures to matrix can only occur when water drainage from one matrix block to its neighboring blocks occurs. Countercurrent flow of CO₂ and water across the same fracture could happen in any direction, when (1) water is retained in portion of the fracture to an extent that water drainage across the fracture is available (red arrow in Figure 1), and (2) the capillary entry pressure of the water-wet matrix (or water-wet portion of the matrix) is lower than the capillary pressure in the fractures (thick blue arrows in Figure 1). For some of the fractured carbonates that may be either mixed wet or oil wet, CO₂ could be the wetting phase and spontaneously imbibing the rock matrix (Al-Menhali et al., 2016; Arif et al., 2017). Gravity may facilitate water bridging in horizontal fractures and favor water drainage between blocks (Horie et al., 1990). Extensive core-flood experiments have been conducted to investigate (1) the capillary pressure vs. saturation characteristics of fractures under in-situ conditions using X-ray computed tomography (CT) scanning (Reitsma and Kueper, 1994; Bertels et al., 2001, Huo and Benson, 2016), (2) the fracture-matrix transfer functions, which are the backbone of dual-porosity formulation in modeling of fluid flow in fractured porous media (Beckner et al., 1987; Gautam and Mohanty, 2004; Lim and Aziz, 1995; Rangel-German and Kovscek, 2005, 2006; Rangel-German et al., 2006; Penuela et al., 2002; Tao et al., 2019), and (3) the potential capillary continuity between matrix blocks established by liquid bridges across open fractures with varying wettability surfaces (Aspenes et al., 2008; Dejam and Hassanzadeh, 2010; Fernø et al., 2011). Common to all the studies above is that two-phase flow was prohibited through the sample circumferential surface because confining pressure was applied to the core, allowing displacement to occur only along the long-axis from inlet to outlet. To the

best of our knowledge, there are few core-flood experiments on three-dimensional CO₂-water drainage in a fracture-matrix system, and none have examined the impacts of the capillary continuity of fractures and fracture-matrix interactions.

In this study, we conducted water drainage experiments in four fracture-matrix columns to investigate the 3-D CO₂-water drainage across a horizontal fracture between two neighboring matrix blocks. Each column was composed of a water-wet rock core, a filter paper that provides an analog for horizontal fracture, and a water-wet ceramic plate that was located at the bottom of the vertical stack. Four rock core samples (5 cm diameter and ~10 cm long) with contrasts in foliation anisotropy, permeability, and heterogeneity were used as the upper matrix block. Two types of ceramic plates were selected as the lower matrix block to allow control of the capillary pressure applied to the upper matrix block, without changing the hydraulic continuity downstream of the horizontal fracture. The changes in fracture water saturation (thus the capillary continuity and water relative permeability) at applied capillary pressures (P_c), the displacement efficiency and the drainage time scale in the upper matrix block were investigated through frequent X-ray CT scans.

2. Material and methods

2.1 Rock cores

Four rock core samples, with a diameter of 5.0 cm and a length varying from 9.5 to 10 cm, were used for the stacked-column tests. Samples #1 and #2 were cut from a Carbon Tan sandstone block from outcropped Late Cretaceous formation, Utah, US, with bedding layers orthogonal and parallel to the long axis (Kocurek Industries, TX). Their

average porosities were calculated from CT images and Eq. (1) as 0.16 and 0.15, respectively. For each sample, four thin disks (5.0 cm diameter and 1.0 cm thickness) were oven-dried and weighed, followed by saturating with deionized (DI) water under 101kPa for over 6 hours. The water-saturated disks were then weighed, and the porosity of each disk was measured gravimetrically. The measured porosities for Samples #1 and #2 is 0.16 ± 0.0012 and 0.15 ± 0.0011 , similar to the values obtained from CT images of 10 cm long cores. The absolute air permeabilities of Sample #1 and #2 were measured as 46 and 51 mD. More details on the permeability measurements of the samples can be seen in the supporting information (Figure S1 of SI). Sample #3 was cut from a Kentucky sandstone block (Virginia, US) with the long axis parallel to the bedding layers (Kocurek Industries, TX). The porosity of Sample #3 measured from CT images is 0.14, while the value from thin discs is 0.13 ± 0.0012 . The air permeability is measured as 6.67 mD. Sample #4, a Duperow dolostone, was obtained from a depth of 1260 m from the Wallewein 22-1 well, a planned injection well for a CO₂ geological storage test at Kevin Dome, Montana. The porosity of Sample #4 was measured by water saturating under 101 kPa for 3 days, until the time-lapse CT images showed a constant porosity at 0.042 ± 0.0012 . The absolute air permeability for the sample was measured at 0.17 mD. Table 1 lists the size, porosity and permeability measurements on the four core samples. Figure 2a depicts the profile (by blue curve) of the average porosity of 0.625 mm horizontal slices derived from X-ray CT scans along the long-axis, with the background image showing the porosity distribution of a 2-D cross section along the central axis. The porosity distribution of Sample #4 by the X-ray CT image indicates (1) a low-porosity (0.02 to 0.04) portion “P1” (0-35 mm) with two tight fractures, (2) a low-porosity (0.02

to 0.04) portion “P2” (35 to 55 mm) with one open fracture, and (3) a higher porosity (0.04 to 0.06) portion “P3” (55 to 95 mm) with one tight fracture. These fractures are marked by the white arrows in Figure 2a and further discussed in Section 3.3. The absolute water permeability of each sample in Table 1 was converted from air permeability measurements considering Klinkenberg effect (Klinkenberg, 1941; Jones and Owens, 1980). To quickly represent the sample characteristics, we use high (H), medium (M), and low (L) permeability, and bedding/fracture orthogonal (O) to or parallel (P) to the water drainage path to redefine Sample #1 (HO), #2 (HP), #3 (MP) and #4 (LO). We combine the sample name with the applied capillary pressure (e.g., HO13.8 at an imposed capillary pressure of 13.8 kPa) to denote an experiment. Water flow experiments were conducted in these samples with frequent X-ray CT imaging to better understand the dynamic invasion/drainage processes of CO₂-water and impacts of matrix properties.

With an aim to quantify the surface wettability of each sample, we conducted contact angle measurements of a water droplet on the sample surface at ambient conditions. The measured air-water contact angles (i.e., $21 \pm 2.6^\circ$, $22 \pm 2.0^\circ$, $22 \pm 0.7^\circ$ and $46 \pm 0.9^\circ$ for HO, HP, MP, and LO, respectively) indicate that the four samples are water wet (see more details in Figure S2 of SI). The sandstone rocks (HO and HP) are composed mainly of quartz (90%) and non-swelling kaolinite (7%), and we do not expect considerable changes of pore geometry after sample exposure to deionized (DI) water. Sample MP is composed of quartz (61%), feldspar (12%), montmorillonite (15%) and non-swelling illite (12%). Although montmorillonite may potentially swell and reduce the matrix porosity and permeability, its impacts on the CO₂-water flow in the fracture-matrix

system may not be pronounced due to the large contrast of capillary pressure-saturation characteristics between fracture and matrix. Also note that we measured the sample porosities, and characteristic curves (P_c - S relations) and conducted all of the water drainage experiments after fully saturating with DI water, thus the potential impacts from clay swelling have been compensated for. Sample LO is composed of calcite (70%), dolomite (20%), anhydrite (4%), and clay (0.3%), thus the impacts from exposure to DI water were expected to be very small (see more details on the sample mineralogy in Table S1 and S2 of SI).

2.2 Experimental setup and procedures

Figure 2b presents a schematic of the experimental setup, consisting of a reaction vessel and a pressure system that allows for CO₂ and water flow limited to a gauge pressure of 1035 kPa. Rocks were cored and end faces were sawn flat and sanded as smooth as necessary to fit into the acrylic core holder with an inner diameter of 5.08 cm and a length of 14 cm. The core samples were maintained dry in an oven at 60 °C prior to use. The rock core was then pressed against a filter paper disk in contact with the capillary ceramic plate. This arrangement was stabilized by a stiff spring at the top of the custom core holder. Two different types of ceramic plates (Soilmoisture Equipment Corp., CA) were used for Samples HO and HP and Samples MP and LO. Ceramics I and II have a porosity of 0.45 and 0.34, a water absolute permeability of 6.0 and 0.17 mD, and a capillary entry pressure of 100 and 300 kPa, respectively (see Table 1). The space between the vessel walls and the rock represents vertical fractures surrounding the matrix. A single sheet of filter paper disk (Glass microfiber filter GF/D, Whatman) between the core bottom and the ceramic plate was used to simulate a horizontal fracture

191 between the matrix blocks, similar to Stone et al. (1992). The fracture thickness and
 192 porosity are 0.8 mm and 0.6, respectively, while the fracture capillary pressure vs. water

193 saturation relations were measured and the dynamic CO₂ invasion into the top matrix
 194 block was monitored through frequent X-ray CT scans (see Section 2.3).

195 **Figure 2.** (a) 2-D porosity maps derived using X-ray CT scans and profiles (blue lines)
 196 of slice-average porosity for the four core samples. Brighter color indicates higher
 197 porosity as depicted by the color bar. The white dotted lines for #4 in (a) marked the

boundary of the three portions indicated by the porosity distribution from the X-ray CT image. The white arrows indicate the natural fractures in each portion. (b) Schematic of the experimental setup that allows for CO₂ invasion (blue arrows) from the horizontal fracture and from the vessel open space (representing fractures) next to the top and side of the core sample, and for downward water drainage (red arrow) through the horizontal fracture.

Before each experiment, the oven-dried rock core, filter paper, and ceramic plate were first stacked and CT-scanned in the reaction vessel. The vessel was connected to vacuum at -101 kPa for over 2 hours, followed by DI water injection through the bottom valve until the sample core was completely submerged in water. The bottom valve was then closed, and vacuum was maintained for 1-3 days depending on the samples used. After saturating with water, the ceramic plate established a threshold pressure for CO₂ invasion, below which the plate will be fully saturated with water. During the tests, the pressure difference between CO₂ and water (at atmospheric pressure) was controlled and maintained higher than the capillary entry pressure of the rock core, while lower than the value of the ceramic plate. In this way, the bottom ceramic plate was maintained fully water saturated (verified by CT images) at room pressure. Thus only downward drainage of water from the stacked column to the outlet through the bottom ceramic (marked by the red arrow in Figure 2b) is expected.

During each experiment, water between the rock core and vessel drained first, allowing for CO₂ invasion at the top and from the circumferential surfaces of the rock core. Water desaturation in the horizontal fracture could also occur, depending on the

221 applied gauge pressures of CO₂ and capillary entry pressure of the fracture. Water was
 222 drained through the ceramic plate and the outflow tube into an outflow reservoir
 223 containing DI water at the bottom. The water outflow mass was monitored by weighing
 224 the outflow reservoir on a balance. CO₂ was supplied to the vessel via a precise pressure
 225 regulator (Parker Hannifin Corp., US) at a resolution of 1.4 kPa from a 500D ISCO pump
 226 (Teledyne ISCO, NE) operated in a constant pressure mode. The setup allows frequent X-
 227 ray CT scans without disconnecting the reaction vessel from the pressure and drainage
 228 lines. The vessel containing the core sample was oriented vertically to investigate
 229 potential gravity effects, and positioned horizontally for very brief (when compared to the
 230 time needed for drainage) durations when an X-ray CT scan was conducted. A GE
 231 LightSpeed 16 CT Scanner was used to visualize the 3-D CO₂ distribution, and image
 232 data were used to calculate CO₂ saturation at a voxel size of 0.1925×0.1925×0.625 mm³.
 233 Scans in each experiment were performed at 120 kV and 160 mA. Each CT scan took
 234 24s, which is short in relative to the time scale of fluid migration in the rock samples.

235 The sample porosity (ϕ) and CO₂ saturation (S_{CO_2}) in the rock core and the horizontal
 236 fracture during each test were obtained from background and experimental scans, as
 237 given in the followings:

$$238 \quad \phi = \frac{CT_{watersat} - CT_{dry}}{CT_{water} - CT_{air}} \quad (1)$$

$$239 \quad S_{CO_2} = \frac{CT_{watersat} - CT_{exp}}{CT_{watersat} - CT_{dry}} \quad (2)$$

240 where CT is the CT number in Hounsfield units computed for each voxel and that
 241 includes contributions from each pure component material present in the system (i.e., air,
 242 DI water, CO₂, and rock). The $CT_{watersat}$ and CT_{dry} refer to the CT values for each voxel of

water-saturated and oven-dried core, while CT_{exp} is the CT value obtained at different times during each CO_2 displacement experiment. The CT numbers of the two pure reference fluids, water ($CT_{water} = 0$) and air ($CT_{air} = -998$) are known from previous calibration. Note that the two equations are derived originally from the linear attenuation coefficients, μ (the truly measurable quantity by X-ray absorption), and uses $CT \propto (\mu - \mu_{water}) / \mu_{water}$ (Akin and Kavscek, 2003). They also imply that the CT number of a voxel can be expressed as the linear combination of the CT numbers associated with the volume fractions of each of its components. This assumption is justified by the linear attenuation coefficient (thus the CT number) is proportional to the bulk density of materials for X-ray energies above 100 keV (Wellington and Vinegar, 1987; Peters and Hardham, 1990; Pini and Madonna, 2016). In Eq. (2), the CT numbers of air-saturated and CO_2 -saturated core are assumed be equal since the similar density of CO_2 and air at the low imposed pressures in this study.

Applying equations (1) and (2) to each voxel, X-ray CT images have been widely used during core-flood experiments to better understand the CO_2 -water flow and displacement characteristics at the core- and sub-core scales (Perrin and Benson, 2009; Shi et al., 2011; Krevor et al., 2012; Berg et al., 2013; Zhang et al., 2014; Xu et al., 2020). In this study, slice-averaged properties were calculated using CT numbers averaged over a circular cross section (slice). The core porosity determined from X-ray CT scans was comparable to that calculated gravimetrically from core mass changes at dried and saturated conditions.

2.3 Gas intrusion capillary pressures of matrix cores and fracture

We cut thin disks (5.0 cm diameter and 1.0 cm thickness) from core samples of each rock described above, and measured their gas intrusion capillary pressures using the pressure plate method (Dane and Hopmans, 2002; Tokunaga et al., 2017). A 1500 kPa chamber (Soilmoisture Equipment Corp., US) was used, and compressed nitrogen was supplied to the chamber via a two-stage pressure regulator. The outflow tube from the pressure plate led into the bottom of an outflow reservoir containing DI water, and the free surface of this reservoir was kept at the same level as the plate. This method is well-suited for directly controlling P_c via changing pressure differences above a porous ceramic plate. We assume no considerable impact of gases (CO_2 or N_2) on P_c - S_w measurements because of the similar interfacial tensions for CO_2 -water (71.03 mN/m at 100 kPa, 25 °C) and N_2 -water (71-72 mN/m at <12 MPa, 25-30 °C) at the experimental pressure and temperature conditions (Massoudi and King, 1974, Chun and Wilkinson, 1995). The sample disks were initially saturated with DI water, and the applied P_c and corresponding water saturations in the disks were monitored using a precise pressure gauge and by frequently weighing the disks. The equilibrium water saturation in a sample for a particular P_c was then determined at constant mass. Figures 3a and 3b display the P_c - S_w functions for Samples HO, HP and MP, with error bars obtained from multiple sample disks. For Sample LO, two thin disks were obtained from the rock plug at locations next to P1 and P3, while sampling from P2 was difficult due to the open fracture.

Figure 3c shows the very different P_c - S_w functions for P1 and P3 induced by potential micro-fractures within the centimeter scale core sample. Mirzaei and Das (2007) performed a comprehensive modeling sensitivity analysis on the micro-heterogeneity

287 effects on P_c - S_w functions, and conducted a non-linear correlation between them,
 288 depending highly on the distribution of micro-heterogeneity. For larger scale fracture-
 289 matrix systems, the CO₂-water flow and CO₂ storage efficiency would be collectively
 290 affected capillary and gravity forces (Ide et al., 2007). In these systems, impacts from
 291 fracture orientation, connectivity, and transmissibility relative to the matrix will be more
 292 pronounced.

293 **Figure 3.** Measurements of the P_c - S_w functions for (a) Samples #1 (HO) and #2 (HP), (b)
 294 Sample #3 (MP), and (c) Sample #4 (LO) using 1.0 cm thick disks (black symbols) and
 295 9.5-10 cm long whole core samples (color symbols). The error bars (black) in (a) and (b)
 296 were obtained from multiple disk measurements. P1 and P3 in (c) denote the top and
 297 bottom portions of Sample LO shown in Figure 1. (d) Measurements of the P_c - S

functions for the horizontal fracture, with the error bars obtained from two repeated tests. The colored bars in (b) and (c) indicate the range of water saturations in the long core samples measured from water drainage tests. The dashed lines in (d) bound the range of fracture water saturations during the water drainage experiments in the different rock samples. The red arrows indicate the capillary entry pressure measured for core samples and the bottom fracture.

The P_c - S_w function of the horizontal fracture in the stacked columns was quantified through water drainage tests. The fracture water saturations ($S_{w,f}$) under different applied P_c were determined through X-ray CT images. Figure 3d displays the P_c - $S_{w,f}$ relation, with error bars obtained from two repeated tests at 13.8, 68.9 and 200 kPa.

The capillary pressure characteristics of both matrix cores and the horizontal fracture can be described by the van Geuchten (1980) model as follows:

$$P_c = \frac{1}{\alpha} \left[\left(\frac{S_w - S_{w,r}}{1 - S_{w,r}} \right)^{\frac{1}{m}} - 1 \right] \quad (3)$$

where $S_{w,r}$ refers to the residual water saturation, and α and m are fitting parameters. Table S3 of the SI lists the fitting parameters of the van Genuchten (1980) model, with R^2 values higher than 0.99. The capillary entry pressure refers to the minimum P_c required for CO₂ intrusion into the water-saturated core sample or fracture, which corresponds to the inflection point identified by the red arrows in the P_c - S_w relations in Figure 3. The values for Samples HO, HP and MP are measured as 13.8, 13.8, 135 kPa. The pore size interpreted from the capillary entry pressures ranges from 1-10 μ m, which are consistent with the sandstone classifications from Nelson (2009). For Sample LO, the capillary entry pressures are 135 and 66 kPa for P1 and P3, respectively, while the value for the

horizontal fracture is 41.4 kPa. In the stacked column tests at $P_c > 68.9$ kPa, we expect considerable fracture desaturation and concomitant reduction of capillary continuity between the top and bottom matrix blocks (See Section 3.2).

The non-zero, non-constant, and porous-medium-like capillary pressure of the horizontal fracture in this study is representative of certain types of natural fractures, due to (1) the large variations of fracture apertures, (2) the complex geometry of a fracture network, and (3) the wide presence of mineralization in fractures. Ramsay (1980) reported the observations of tectonically deformed crustal rocks and cracks and fissures filled with silicate or carbonate mineral. The open microfractures filled with crystalline material derived from pressure solution in the rock matrix and chemical transfer of this material into the low-pressure fluid-filled space, a mechanism termed ‘crack-seal’. Morrow et al. (1990) further reported the permeability measurements of the mineral-filled fractures in the Mesaverde formation rock samples, which were of the same order as the surrounding matrix and presented water-saturation dependent behavior, similar to the porous matrix. Parry (1998) presented the fault-fluid compositions and solubilities of the fracture-sealing minerals, while Fletcher and Merino (2001) summarized the published insights into the mineralization and crystal growth in rock fractures, and proposed models on the coupling between mineral growth kinetics and mechanical response of the rock. In summary, the wide presence of mineralization in natural fractures and the resulting changes in fracture properties (e.g., permeability, capillary pressure and chemistry) impose fracture P_c - S_w functions similar to porous media, resulting in a large range of contrast with matrix. The CO₂-water flow fundamentals in these fractured porous media are of importance to GCS and other subsurface processes.

Also note the capillary entry pressure of the fracture in the stacked columns is higher than that of the matrix in Samples HO and HP. This may reduce the effect of the water-flow barrier of the fracture and help highlight the importance of capillary continuity. The experiments still allow us to focus on CO₂-water displacements in these fracture-matrix systems.

2.4 Water Drainage Experiments

Twelve water drainage experiments were conducted to investigate the CO₂-water displacements with controlled P_c up to 200 kPa (see Table 2). Five tests in the column stacked with Samples HO (HO13.8, HO30.7, HO27.6, HO41.4 and HO68.9) were conducted to investigate the fundamentals of CO₂-water flow and CO₂ saturation in matrix with high fracture water saturation, thus high capillary continuity. Tests under varying imposed capillary pressures (from 13.8 to 68.9 kPa) were used to understand the impacts of capillary pressures.

Two different comparison and sensitivity analyses were conducted. The first analysis focused on the effects of bedding orientation by two experiments with Sample HP (HP13.8 and HP41.4) maintaining similarly high capillary continuities in fracture. For the second sensitivity analysis, experiments were conducted targeting at water drainage across the single desaturated fracture (thus reduced capillary continuity) in Sample MP (MP150, MP200a, MP200b), as well as water drainage across multiple desaturated fractures in Sample LO (LO150, LO200).

During the experiment, the impacts of CO₂ dissolution and mass transfer is expected to be minimal, because of (1) the low CO₂ solubility in water (0.068 mol/L, from Zhao et al., 2015) under the low pressure (≤ 200 kPa) and temperature (25 °C) conditions in this

study, and (2) the very small impacts of CO₂ dissolution and mass transfer on two-phase displacement and distribution under drainage conditions. For instance, in a previous study (Chang et al., 2017), we investigated supercritical CO₂ (scCO₂)-water displacement and dissolution in an mm-scale micromodel at 9 MPa and 40 °C, and monitored the CO₂ dissolution and mass transfer into residual water. Results showed overall constant CO₂ saturation after drainage and stable two-phase distribution in the micromodel due to the continuous inflow of CO₂, although CO₂ dissolution occurred at the two-phase interface is considerably higher (1.225 mol/L) at the elevated pressure and temperature.

3. Results

3.1 CO₂-water flow in the matrix with high fracture water saturation

Five drainage experiments were conducted in Sample HO at varying P_c from 13.8 to 68.9 kPa. During each experiment, dynamic CO₂ invasion and water drainage were monitored by frequent X-ray CT scans and the images were used to calculate both slice- and core-average CO₂/water saturations at a number of times until a capillary quasi-equilibrium was reached. According to the P_c - $S_{w,f}$ characteristics of the fracture in Figure 3d, fracture water desaturation to 0.68-0.96 is expected, depending on the imposed P_c values.

3.1.1 Dynamic water drainage and CO₂ saturation

Figure 4a shows selected time-lapse images of 3-D CO₂ distribution (purple color) in test HO13.8. The numbers in the parentheses are experimental time and core-average CO₂ saturations, respectively. Also displayed in the figure (the last sub-image) is the 3-D porosity distribution for comparison. The temporal CO₂ distributions indicate preferential

389 CO₂ uptake along multiple high-porosity layers in contact with the circumferential
390 surface. The variations of the slice-averaged CO₂ saturation along the core sample from
391 top to bottom shown in Figure 4b are overall consistent with those of porosity (not in a
392 perfect correlation however, indicating porosity and pore size are not necessarily
393 correlated). The inconsistencies in correlation and offset of the peak CO₂ saturation vs.
394 porosity at some portions of the sample (e.g., marked by the red dotted lines at 50 mm, 70
395 mm and 78 mm from the sample top in Figure 4b) could be attributed to the competition
396 between different CO₂ fingers from the circumferential surface. As shown in Figure 4a,
397 CO₂ fingers developed preferentially along the high porosity layer at 38 mm, which
398 induced drainage of resident water towards the core bottom and resulted in the other CO₂
399 fingers to develop slightly beneath the peak porosity positions at 50 mm, 70 mm and 78
400 mm. At the bottom portion of the core (e.g., at 90 mm and close to the outlet), the
401 variations of CO₂ saturation are more consistent with those of porosity as water drainage
402 pathway was shortest and easiest towards the outlet. The core-average CO₂ saturation
403 increased with time for 78 hours, and remained relatively constant at 0.15 ± 0.006 after
404 exposure to CO₂ until 288 hours, when the experiment was stopped.

405 **Figure 4.** (a) Images of 3-D CO₂ saturation from core top to bottom acquired during the
 406 water drainage experiment in Sample HO at $P_c=13.8$ kPa, as well as the 3-D porosity
 407 distribution in the last sub-image. Brighter color indicates higher CO₂ saturation and
 408 porosity as depicted by the color bar. (b) Slice-averaged porosity and CO₂ saturations

change with time. The numbers in the parenthesis in (a) denote exposure time and core-
average CO₂ saturation or the core-average porosity. Water saturation in the bottom
fracture maintained high at 0.96 during the experiment. The red dotted lines in (b) mark
the offset of the peak CO₂ saturation vs. porosity.

Figure 5. Images of 3-D CO₂ saturation from core top to bottom at (a) early time (1 hour)
and (b) the quasi-equilibrium state during drainage experiments in Sample HO at P_c -
=13.8, 20.7, 27.6, 41.4 and 68.9 kPa. The numbers in each parenthesis denote applied P_c

and core-average CO_2 saturation. (c) Core-average CO_2 saturation vs. exposure time acquired at different P_c , and (d) CO_2 saturation variations along the core from the top at quasi-equilibrium state for different cases. The inserted sub-image in Figure 5c presents the temporal changes of specific CO_2 saturation, the ratio between temporal CO_2 saturation and CO_2 saturation at capillary equilibrium, under different imposed capillary pressures. Note water saturation in the bottom fracture decreased from 0.96 to 0.68 with increasing capillary pressures during these experiments.

3.1.2 *Effects of capillary pressure*

The P_c effects on CO_2 -water displacement in Sample HO were investigated by specifying CO_2 pressures of 20.7, 27.6, 41.4 and 68.9 kPa, while keeping water drainage pressure at atmospheric. X-ray CT images were obtained during each experiment until the CO_2 distribution and saturation in the core were stable with time. Figures 5 shows the CO_2 distributions at early time (Figure 5a, 1 hour) and quasi-equilibrium state (Figure 5b) under the five capillary pressures. When P_c was increased above the capillary entry pressure of the core (13.8 kPa), most CO_2 invaded into the rock along its circumferential surface, preferentially through the higher porosity layers (again, not perfectly correlated). This dominant circumferential inflow of CO_2 from the surrounding fractures can be attributed to the larger circumferential area compared to that of the top surface and reduced water drainage pathway towards the bottom fracture than axial flow from top. For instance, we observed high CO_2 saturations in the bottom portion of the core at 1 hour, where the water drainage pathway was shortest towards the outlet. Figures 5c and

5d depict the core-average CO₂ saturations vs. time and variations of slice-average values along the core at the quasi-equilibrium state for each case. We may infer that the core-scale CO₂ saturations increase with increasing P_c with more CO₂ uptake in the low-porosity layers, smoothing the CO₂ saturation variations along the core sample. We also define a specific CO₂ saturation, the ratio between temporal CO₂ saturation vs. CO₂ saturation at capillary equilibrium, and present the temporal changes of the value in the inserted sub-image in Figure 5c. As the imposed capillary pressures are higher than the capillary entry pressure ($P_c > 13.8$ kPa), the temporal increases in the specific CO₂ saturation follow the similar trend and time scale to converge at the capillary equilibrium saturation, as the dominant CO₂ invasion from the circumferential surface and water drainage in the normal direction. This is different from 1-D two-phase flow, where confining pressure is applied and CO₂-water flow is prohibited across the circumferential surface. The quasi-equilibrium P_c vs. water saturation generally follows the P_c - S_w curve obtained from disk measurements in Figure 3a.

3.2 Effects of bedding orientation

Two flow experiments (HP13.8 and HP41.4) were conducted in Sample HP to better understand the impacts of matrix bedding orientations on CO₂-water displacement. Sample HP was cut parallel to the bedding with porosity variations from 0.15 to 0.16 along the long axis. During these experiments, high water saturations (>0.60) were maintained in the horizontal fracture (Table 2), resulting in high capillary continuity for water drainage across the fracture.

461

462

463 **Figure 6.** Images of 3-D CO₂ saturation from core top to bottom during the water

464 drainage experiments in Sample HP at (a) $P_c = 13.8$ kPa and (b) 41.4 kPa, as well as the 3-

D porosity distribution in the last sub-image. (c) Core-average CO_2 saturation vs. exposure time at different P_c . The numbers in each parenthesis denote the exposure time and core-average CO_2 saturation or the core-average porosity, while the white arrows show the direction of CO_2 invasion. Water saturation in the bottom fracture is 0.96 and 0.80, respectively, in (a) and (b).

Figures 6a and 6b present the dynamic CO_2 saturations and distributions in Sample HP during the two experiments. In both cases, CO_2 preferentially invaded the core sample from one side (high porosity), and displaced resident water toward the opposite side (low porosity), where the displaced water migrated downward under single-phase water flow condition during most of the experiment duration. The core-average CO_2 saturation was stable at 0.11 after 120 hours in HP13.8 and 0.50 after 43 hours in HP41.4 (see Figure 6c). These quasi-equilibrium CO_2 saturations are close to those (0.15 and 0.56) obtained in Sample HO at the same P_c values as should be expected. The parallel bedding in Sample HP, however, facilitated downward drainage of water, and greatly shortened the time scale to reach equilibrium compared to that in Sample HO at the same $P_c=41.4$ kPa (see Table 2).

3.3 Water drainage across single desaturated fracture and fracture-matrix interactions

CO_2 -water displacements after fracture desaturation were investigated in the column stacked with Sample MP, with a higher capillary entry pressure (135 kPa) relative to the horizontal fracture (69 kPa). For the two experiments (MP150 and MP200a), we expected (1) larger water desaturation in the fracture than that in the matrix (see Figure 3b and d),

488 and (2) considerable reduction in the capillary continuity of the fracture with increased
 489 water drainage resistance, due to the blockage of water flow (thus decrease of water
 490 relative permeability) across the bottom fracture by invaded CO_2 .

491 **Figure 7.** (a) Images of 3-D CO₂ saturation from core top to bottom during the water
 492 drainage experiment in Sample MP at $P_c=150$ kPa (MP150), (b) slice-averaged variations
 493 of porosity and CO₂ saturation along the core from the top at different exposure times,
 494 and (c) core-average CO₂ saturation vs. exposure time. Water saturation in the bottom
 495 fracture is 0.50 during the experiment. The numbers in the parentheses in (a) denote the
 496 exposure time and core-average CO₂ saturation.

497

Figures 7a and 7b show the selected images of CO₂ distribution and CO₂ saturation along the core at different times for MP150. It can be seen that CO₂ initially invades the higher porosity portion of the core at the bottom close to the horizontal fracture and propagates upwards in the matrix. This process may retard CO₂ invasion from the circumferential surface. The core-average CO₂ saturation increases with time and stabilizes at 0.24 after 264 hours (Figure 7c). The pair of specified P_c and measured core-scale CO₂ saturation follows the P_c - S curve measured from 1 cm thin disks in Figure 2b. The slice-average CO₂ saturation shown in Figure 7b, however, varies greatly from the top (0.18) to the bottom (0.30), indicating the impact of sub-core scale heterogeneity in the 10 cm long core. By the end of the experiment, water saturation in the bottom fracture is 0.50, considerably higher than the value of 0.26 measured for the fracture P_c - $S_{w,f}$ function in Figure 3d. Also note the pronounced difference in equilibrium matrix CO₂ saturation between Samples HO and HP vs. Sample MP. At similar porosities and when maintaining sufficient fracture water saturation (≥ 0.5), the maximum storage capacity in Samples HO and HP (0.60 at 68.9 kPa) could be as much as 2.5 times higher than that in Sample MP (0.24 at 150 kPa).

The unexpectedly high fracture water saturation in MP150 can be attributed to the countercurrent flow of CO₂ and water across the fracture-matrix interface, i.e., CO₂ invades the matrix core from the bottom fracture and water drains from the matrix core across the same interface. To better understand the process, we compared the CO₂ distribution in the bottom portion of the core next to the horizontal fracture (Figures 8a and 8b), with the water distribution within the fracture (Figures 8c and 8d) at early time (1 hour) and the end of the experiment (264 hours). Once exposed to CO₂, the bottom

fracture is invaded by CO₂ and resident water is partially displaced, as indicated by the two black patches representing low fracture water saturations in Figure 8c. P_c in these patches may exceed the capillary entry pressure of the matrix core above, thus CO₂ invasion into the rock matrix is available. At the same time, drainage of water occurs downward next to the CO₂ flow pathway, resulting in a high water saturation patch in the bottom fracture in Figure 8c (see the bright band in the middle). Note the consistent geometry of the high $S_{w,f}$ patch vs. CO₂ plume in the bottom portion of the core. This high $S_{w,f}$ patch hydraulically bridges the top core and bottom ceramic plate, providing an efficient water drainage pathway across the fracture and allowing for continuous CO₂

invasion of fracture,

CO₂ in the fracture,

resulting in a high $S_{w,f}$ patch.

invasion of fracture,

CO₂ in the fracture,

resulting in a high $S_{w,f}$ patch.

Figure 8. Images of 2-D average CO_2 saturation within the bottom portion (30 mm above the horizontal fracture) in Case MP150 at (a) early time and (b) quasi-equilibrium state, and images of 2-D fracture water saturation at (c) early time and (d) quasi-equilibrium

average CO₂ saturation increased slowly with time, and we stopped the test at 1222 hours before reaching the capillary equilibrium. By the end of the experiment, the core-average CO₂ saturation is 0.16, lower than the value in MP150 (0.24), although a higher P_c was applied and maintained for a significant longer time (see Figure 9c). We then conducted an additional drainage test (MP200b), in which the same P_c (200 kPa) was applied, while the junctions between the surrounding and horizontal fractures were partially sealed by epoxy coating around the circumferential surface of the horizontal fracture. The seal was not perfect as a crack developed within the thin epoxy layer when pressed the core against the ceramic plate, but was able to reduce CO₂ invasion and increase fracture water saturation to 0.30. Figure 9b and 9c show the faster CO₂ invasion and higher CO₂ saturation in the core, when compared to Case MP200a under the same P_c . The three drainage experiments indicate that efficient CO₂ uptake in the matrix and water drainage across fracture are only possible when sufficient water saturation (thus capillary continuity and water relative permeability) is maintained in the horizontal fracture. The capillary continuity of the fracture can be greatly enhanced by fracture-matrix interactions through a countercurrent flow between CO₂ and water, when (1) the P_c and CO₂-water distribution are non-uniform in the fracture, and (2) the local P_c exceeds the capillary entry pressure of matrix at the interface.

3.4 CO₂-water drainage across multiple desaturated fractures

We investigated the CO₂ uptake in the matrix and water drainage across a single fracture from a number of cases (Samples HO, HP and MP). In this section, we present CO₂-water drainage across multiple horizontal fractures from two experiments (LO150 and LO200) in the naturally fractured Duperow dolostone Sample LO. Sample LO is

characterized by three alternating fracture-matrix portions with capillary pressure contrasts shown in Figure 3c.

Figures 10a and 10b show the temporal changes in core density (relative to the initially water-saturated condition) after CO₂ exposure at $P_c=150$ and 200 kPa. Calculating CO₂ saturations for each pixel Using Eq. (2) resulted in considerable noise due to the low porosity nature of the core. Some pixels or portions of the sample were too tight to have distinguishable CT signal changes between $CT_{watersat}$ and CT_{dry} , $CT_{watersat}$ and CT_{exp} . Noise was further amplified as $CT_{watersat} - CT_{dry}$ (=0 or negative) was in the denominator of Eq. (2). To reduce the noise, we converted $CT_{watersat}$ and CT_{exp} to density $\rho_{watersat}$ and ρ_{exp} through a pre-established correlation function, and calculated density changes ($\Delta\rho = \rho_{exp} - \rho_{watersat}$) to represent the CO₂ invasion and water drainage. In both figures, brighter color refers to larger density reduction, thus higher CO₂ saturation. As shown in Figures 10a and b, density reduction started in the four fractures at early time (8.5 hours at $P_c=150$ kPa and 6 hours at 200 kPa), followed by matrix density reduction until the end of experiments at 701 and 841 hours. A larger matrix density reduction was also observed in the bottom portion of the core at later times (e.g., 262.5 hours in Figure 10a and 264 hours in Figure 10b). In Sample LO, the low matrix porosity and permeability, and high capillary entry pressure hindered fracture-matrix interaction at the interface. The fracture water saturations during the two experiments were measured at 0.26 and 0.21, following the fracture P_c - $S_{w,f}$ relation shown in Figure 3d.

We also calculated the slice-average CO₂ saturation using Eq. (2) by averaging the CT_{exp} , $CT_{watersat}$, CT_{dry} values over 50,000 voxels in each slice, and showed in Figure 10c the variations along the core at the end of the two experiments. From the figure, we

observed (1) higher CO₂ saturations in the four fractures validating the initial assumption of drainage occurring first in the fractures (see the peaks marked by the black arrows), (2) the overall CO₂ saturation in P3 was higher than that in P1 and P2, and (3) CO₂ saturation in P3 increases with increasing P_c , while it remained constant in P1 and P2, independent of the P_c applied. At P_c =200 kPa, the average CO₂ saturation in P3 was stable at 0.44 after 841 hours exposure to CO₂, similar to the value of 0.45 obtained from thin disk P_c - S_w measurements (marked by the blue dashed line in Figure 10c). This indicated capillary equilibrium state in P3. The average CO₂ saturation in P1, however, remained low (0.10) by the end of the two experiments. Note the gas saturation measured from thin disks at the capillary equilibrium state is higher at 0.25 (marked by the blue dashed lines for P1 in Figure 10c). For water drainage from P1, the multiple desaturated fractures (including the two in P2, P3 and the one beneath the matrix) increased water flow resistance along the pathway, thus considerably reduced the drainage efficiency at the experimental time scale. At this point, the fractures served as barriers for further CO₂ invasion into matrix, similar to the modeling results from Bogdanov et al. (2003), who concluded that fractures can act as obstacles to the flow in their normal directions due to capillary effects. By the end of the experiments, the core-average CO₂ saturations were measured as 0.29 and 0.19 at P_c = 150 and 200 kPa (see Figure 10d).

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637

638 **Figure 10.** Images of 3-D density changes from core top to bottom in Sample LO during
 639 water drainage experiments at (a) $P_c=150$ kPa and (b) $P_c=200$ kPa. (c) Slice-average CO₂
 640 saturation at the end of the two experiments, and (d) core-average CO₂ saturation vs.
 641 exposure time. The numbers in the parenthesis in (a) and (b) denote the exposure time
 642 and core-average CO₂ saturation. In (c), the black arrows mark the multiple peaks of CO₂

saturation in core fractures, the black dashed lines bound the three portions, while the blue dashed lines indicate the average gas saturations in P1 and P3 from the P_c - S_w relation measured with thin disks of Sample LO. Water saturation in the bottom fracture is 0.26 and 0.21, respectively in (a) and (b).

4. Discussion

In Section 3.1 and 3.2, we investigated the CO₂-water flow in fracture-matrix systems with high capillary continuity in the fracture. In Section 3.3 and 3.4, two different comparison and sensitivity analyses were conducted with reduced capillary continuities in the fracture and core samples having different properties. These experiments were motivated by the long consideration of the assumption of the on-off fashion and constant capillary entry pressure of natural fractures. The single-block concept has been widely adopted for modeling multiphase flow in fractured reservoirs through the well-known dual-porosity model (Warren and Root, 1963). In the model, the drainage of matrix blocks by invading fluid occurs independently so that the performance of a stack of blocks is equal to the performance of a single block multiplied by the number of individual blocks. Theoretical analysis and examination of the field performance of some fractured reservoirs, however, indicate the existence of some capillary continuity between matrix blocks as (1) the existence of formation rocks that are not completely separated or isolated from other blocks by open natural fractures (Festoy and van Golf-Racht, 1989; Liu and Rutqvist, 2010), and (2) bridging of matrix blocks by residual water in fractures that creates potential hydraulic connections for water drainage across the fractures (Sulak 1990; Hermansen et al. 1997; Agarwal et al. 1999; Rangel-German and Kovscek, 2006;

665 Rangel-German et al., 2006; Firoozabadi, 2000; De la Porte et al., 2005; Fernø et al.,
666 2011). Through a series of stacked-block experiments, Horie et al. (1990) and Stones et
667 al. (1992) reported that the fracture capillary pressure is water-saturation dependent, and
668 might have a functional form similar to that of a matrix. Reitsma and Kueper (1994)
669 measured the capillary pressure vs. saturation in a single, rough-walled fracture, which
670 was well represented by a Brooks-Corey porous media capillary pressure function with a
671 distinct entry pressure observed. The errors introduced when ignoring nonlinear k_r curves
672 and non-zero P_c in fractures were demonstrated by de la Porte et al. (2005), who
673 presented that displacement efficiency could be underestimated by a factor of two when
674 fracture capillary pressure was set to zero. A detailed investigation is required, which is
675 one of the objectives in this study, to better understand the impacts of the non-constant,
676 porous-like capillary pressure of fractures on CO₂-water drainage and CO₂ saturations in
677 fracture-matrix systems.

678 **Figure 11.** The relations between matrix CO₂ saturation vs. applied capillary pressure in
 679 the twelve water drainage experiments. The colored bars bound the standard deviations of
 680 CO₂ saturation along the matrix cores, calculated from each X-ray CT image slice at
 681 0.625 mm thickness. The number in each parenthesis represents the fracture water
 682 saturation at steady state. *Note the fracture water saturation of 0.30 in MP200b was
 683 induced by reducing the peripheral area of fracture exposure to CO₂ through an epoxy
 684 sealing treatment.

685

686 Figure 11 summarizes the relationships of average matrix CO₂ saturation vs. applied
 687 capillary pressure in stacked fracture-matrix systems. The bars bound the standard
 688 deviations of CO₂ saturation along the matrix cores, calculated from each CT image slice
 689 (0.625 mm thickness). The numbers in parenthesis in the figure represent the

690 corresponding water saturations in the bottom fracture at steady state. Overall, there
691 exists a range of critical capillary pressure values below and above which the matrix CO₂
692 saturation vs. capillary pressure relations are considerably different. Here, when P_c is low
693 (<100 kPa) and fracture water saturations are high (>0.6), the matrix CO₂ saturations in
694 Samples HO and HP increase with increasing P_c , depending on the matrix P_c - S_w
695 characteristics. Note the matrix CO₂ saturations vary by a larger span in Sample HO
696 (indicated by the bars), where the bedding layers are normal to the water drainage
697 direction. Also recall the faster water drainage to the capillary quasi-equilibrium state (43
698 hours) in Sample HP at P_c = 41.4 kPa where bedding is parallel to the water drainage
699 pathway, compared to 145 hours required for Sample HO (Table 2). In Sample HP, CO₂
700 and water maintain high saturation along their individual pathways (see Figure 6) and
701 thus high relative permeabilities for both fluids. With frequent CT imaging, we directly
702 visualized the 3-D CO₂-water drainage in the stacked columns, and indicated the impacts
703 of matrix bedding orientations relative to the fracture that maintains high capillary
704 continuity (e.g., 0.50 to 0.96).

705 When P_c is higher and fracture water desaturation occurs (e.g., > 100 kPa in this
706 study), the reduced capillary continuity of the fracture hinders water drainage from and
707 CO₂ invasion into the top matrix core. Thus matrix CO₂ saturation in Sample MP
708 decreases from 0.24 at a fracture water saturation of 0.50 in MP150, to 0.16 at a fracture
709 water saturation of 0.19 in MP200a, even when a higher P_c was applied to the latter (see
710 Figure 11). In MP150, the spatial and temporal changes in fracture water saturation vs.
711 matrix CO₂ saturation indicate the countercurrent flow of CO₂ and water at the fracture-
712 matrix interface. Compared to MP200b, the fracture water saturation, thus the capillary

continuity of the fracture and matrix CO₂ saturation were enhanced by (1) the non-uniform CO₂-water distribution in the fracture, and (2) the lower capillary entry pressure of matrix relative to portions of the fracture (see Section 3.2). The highest matrix CO₂ saturation presented in MP200b, when fracture water saturation and capillary pressure increased simultaneously by reducing the circumferential surface of fracture available to CO₂ invasion. Results from MP150, MP200a and MP200b indicate the complex CO₂-water flow across the fracture-matrix interface, and the importance of fracture and matrix properties (e.g., the capillary entry pressures) in determining CO₂-water flow in fractured porous media.

In previous modeling work, we investigated the impacts of capillary continuity/connectivity on CO₂ storage capacity and efficiency in meter scale stacked columns (Bandilla et al., 2019). Numerical simulations were conducted on stacked homogeneous matrix blocks with varying matrix-matrix connectivities at 0%, 30% and 100%. Modeling results showed no considerable difference of CO₂ saturation distribution in the stacked columns for the cases of 30% and 100% matrix-matrix connectivities, while significant difference in CO₂ saturation distribution was observed between the 0% case and the 30 to 100% cases. Similar to the modeling results, we showed that when capillary continuity determined by fracture water saturation is equal and over 0.3 (Case MP150 and MP200a), CO₂ saturations in the top matrix are not considerably affected by the fracture, whereas when the fracture water saturation is less than 0.3 (Case MP200b), the matrix CO₂ saturation is greatly hindered over a longer period of time. Meanwhile, our lab observations indicated a more complicated counter-current flow at the fracture-matrix interface, as well as the pronounced impacts of matrix heterogeneity and

anisotropy. All these need to be considered for a more accurate predication of CO₂ storage efficiency. In addition, Tene et al. (2017) investigated the two-phase flow in fractured porous media using a Projection-based Embedded Discrete Fracture Model (pEDFM), considering the fracture-matrix coupling terms by a cross-media transmissibility. Modeling results indicate the impacts of fracture positions and the cross-media conductivity contrasts. Kim et al. (2011) examined the experimental P_c - S_w functions of heterogeneous carbonate rock samples, and concluded that Leverett J-function cannot accurately describe the carbonate rocks due to heterogeneous pore systems with fractures and vugs. The X-ray CT images from this study directly visualized the dependence of CO₂-water flow and P_c - S_w functions on fractures and matrix, and indicated that single Leverett J-function may not be applicable in scaling P_c - S_w functions for field-scale studies, considering the orders of magnitude difference between fracture and matrix permeability.

At last, differing from the columns stacked with a single fracture (Samples HO, HP and MP), tests in Sample LO with multiple horizontal fractures present (1) the largest variations of CO₂ saturation within the core (Figure 11), and (2) the four fractures, orthogonal to the water drainage direction, served as conduits for CO₂ invasion at early time. They, however, hindered water drainage across and further CO₂ invasion from these fractures into neighboring matrix (Figure 10). These can be attributed to the increased water flow resistance (thus decreased water relative permeability) across the desaturated fractures. While the CO₂-water flow within a fracture or fracture network has been investigated by laboratory experiments and modeling (Shukla et al., 2010; Perera et al., 2011; Oh et al., 2013; Celia et al., 2015; March et al., 2018; Tao et al., 2019), cross-

fracture flow is worthy of a systematic and detailed investigation. Results from Sample LO imply the spatial and temporal dependent role of fractures for 3-D CO₂-water flow, the importance of fracture network (e.g., distribution, orientation, connectivities, and transmissibility characteristics with respect to the matrix) in determining CO₂ distribution and storage efficiency.

Common to all cases above is the observed higher CO₂ saturation at the bottom portion of the matrix cores (1) in Samples HO and HP with high fracture continuity, regardless of matrix anisotropy and applied P_c (e.g., Figure 5 and 6), and (2) in Samples MP and LO, where fractures were desaturated and capillary continuity was considerably reduced (Figures 7 and 10). This cannot be predicted by the dual-porosity approach that assumes zero capillary continuity through the fracture (Warren and Root, 1963), or observed by the classic core-flood experiments where confining pressure is applied and CO₂-water flow is prohibited across the circumferential surface (Perrin and Benson, 2000; Krevor et al., 2012; Chang et al., 2013, 2014; Pini and Benson, 2013). In our experiments, the 3-D displacement enables CO₂ invasion through the bottom fracture into matrix and countercurrent water drainage from the matrix. This may benefit the fracture-matrix flow and mass transfer and CO₂ storage efficiency in fractured reservoirs.

5. Conclusions and implications

Recent modeling results have demonstrated significant CO₂ storage efficiency in fractured reservoirs when preferentially drained fractures retain certain hydraulic/capillary continuity. In this study, we investigated the CO₂-water flow across an mm-scale fracture and storage efficiency in rock matrix at room temperature and

controlled capillary pressures up to 200 kPa. Frequent X-ray CT scans provided direct observations on the processes and show the importance of fracture capillary continuity and fracture-matrix interactions. We observed the increase of displacement efficiency in the matrix with increasing fracture water saturation (capillary continuity), and presented that the fracture water saturations could be enhanced by the non-uniform fracture capillary pressure and countercurrent flow of CO₂ and water across the fracture-matrix interface. The displacement efficiency was also affected by matrix heterogeneity and anisotropy, when high fracture water saturations (>0.6) were maintained. In naturally fractured reservoirs, the interfacial tension of CO₂-water is expected to be considerably lower than that under the experimental conditions in this study. In addition, fractures develop with a wider range of apertures from microns to much larger, while individual fractures may also contain spatially variable apertures (microns to millimeters). These might collectively result in spatially variable and a larger span of capillary pressure contrasts between fractures vs. matrix. While cautions are needed before applying the experimental results to the field, this study implies that tight fractures and tight portions of a rough fracture may sustain high water saturation, allowing for water drainage across multiple matrix blocks and CO₂ invasion from large fractures. The cross-fracture flow of water may bridge the preferentially drained fractures ahead of the CO₂ plume and enhance CO₂ storage efficiency in matrix. In summary, adequate capillary continuity of fractures and fracture-matrix interactions may result in continuous displacement that occurs over multiple matrix blocks, to an extent that the single-block based dual porosity model may greatly underestimate the CO₂ storage efficiency in fractured reservoirs.

804 **Supporting Information (SI)**

805 More detailed information on air permeability, contact angles and mineral compositions
806 of the rock core samples, as well as the fitting parameters of the van Genuchten (1980)
807 Model for both rock cores and the fracture are provided in the SI.

808

809 **Notes**

810 The authors declare no competing financial interest.

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1014

1015 Table 1 Properties of the core samples and ceramic plates used for the stacked columns

Samples and ceramic plates		#1 (HO)	#2 (HP)	Ceramic I	#3 (MP)	#4 (LO)	Ceramic II
Diameter×length (cm×cm)		5×10	5×10	5×0.7	5×10	5×9.5	5×0.7
Porosity		0.16	0.15	0.45	0.14	0.042	0.34
Absolute air permeability (mD)	CASE	46.00	Fracture	/	Matrix	0.17	/
	P_c (kPa)	40	Water saturation	1.0	CO ₂ saturation	0.038	equilibrium (hrs)
Absolute water permeability (mD)		13.8	13.8	100	0.185	135	(P1); 66 (P8)
Capillary entry pressure (kPa)		13.8	13.8	100	0.185	135	(P1); 66 (P8)
Sample HO	HO20.7	20.7	0.93		0.38		102
	HO27.6	27.6	0.90		0.45		56
	HO41.4	41.4	0.80		0.56		145
	HO68.9	68.9	0.68		0.59		58
Sample HP	HP13.8	13.8	0.96		0.11		106.5
	HP41.4	41.4	0.80		0.50		43
Sample MP	MP150	150	0.50*		0.24		216
	MP200a	200	0.19		0.16		>1222
	MP200b	200	0.30*		0.36		>956
Sample LO	LO150	150	0.26		0.19		>701
	LO200	200	0.21		0.29		841

1017 Note: H, M, L = High, Medium, and Low permeability; O, P = bedding/fracture

1018 Orthogonal to, Parallel to the water drainage path.

1019 Table 2. The twelve water drainage experiments conducted with four core samples, and
 1020 corresponding fracture water saturations, matrix CO₂ saturations and time to reach system
 1021 equilibrium obtained by the end of each experiment.

1022

1023 Note: * indicates the observed fracture water saturations that deviate from the measured
 1024 P_c - $S_{w,f}$ relation due to fracture-matrix interactions in MP150 and the reduced
 1025 circumferential surface of fracture exposure to CO₂ in MP200b.

1026

1027