Co-sequestration of SO₂ with supercritical CO₂ in
Carbonates: An experimental study of capillary
trapping, relative permeability, and capillary pressure

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Abstract

In this study we performed three categories of steady- and unsteady-state core-flooding experiments to investigate capillary trapping, relative permeability, and capillary pressure, in a scCO₂+SO₂/brine/limestone system at elevated temperature and pressure conditions, i.e., 60°C and 19.16 MPa. We used a Madison limestone core sample acquired from the Rock Springs Uplift in southwest Wyoming. We carried out two sets of steady-state drainage-imbibition relative permeability experiments with different initial brine saturations to study hysteresis. We found that the final scCO₂+SO₂ drainage relative permeability was very low, i.e., 0.04. We also observed a rapid reduction in the scCO₂-rich phase imbibition relative permeability curve, which resulted in a high residual trapping. The results showed that between 62.8% to more than 76% of the initial scCO₂+SO₂ at the end of drainage was trapped by capillary trapping mechanism (trapping efficiency). We found that at higher initial brine saturations, the trapping efficiency was higher. The maximum initial and residual scCO₂-rich phase saturations at the end of primary drainage and imbibition were 0.525 and 0.329, respectively. Each

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drainage-imbibition cycle was followed by a dissolution process to re-establish $S_w=1$. The dissolution brine relative permeabilities for both cycles were also obtained. We characterized the $\text{scCO}_2+\text{SO}_2$ /brine capillary pressure hysteresis behavior through unsteady-state primary drainage, imbibition, and secondary drainage experiments. We observed negative imbibition capillary pressure curve indicative of possible wettability alteration throughout the experiments due to contact with $\text{scCO}_2+\text{SO}_2$ /brine fluid system. The trapping results were compared to those reported in literature for other carbonate core samples. We noticed slightly more residual trapping in our sample, which might be attributed to heterogeneity, different viscosity ratio, and pore-space topologies. The impact of dynamic effects, i.e., high brine flow rate imbibition tests, on trapping of the scCO_2 -rich phase was also explored. We performed two imbibition experiments with relatively high brine flow rates. The residual scCO_2 saturation dropped to 0.291 and 0.262 at the end of the first and second imbibition tests, i.e., 11.5% and 20.4%, respectively, compared to 0.329 under capillary-dominated regime.

Keywords:

CO_2+SO_2 co-sequestration, Madison limestone, Capillary trapping, Relative permeability, Capillary pressure, Hysteresis, Dynamic effect

1. Introduction

In 2012, worldwide energy-related CO_2 emissions increased by 1.4% in comparison with the previous year and reached the highest level of 31.6 Gt [1]. Power plants are the major producer of CO_2 , i.e., more than 78% of the total CO_2 emissions [2, 3]. It is also reported that the consumption of

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10 48 coal, which is responsible for 40% of the total CO₂ emissions globally, has
11 49 increased by 5% over the past decade while for natural gas and oil, these
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13 50 numbers were 2% and 1%, respectively [3]. In order to mitigate the CO₂
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15 51 emissions, the most viable option is carbon capture and storage (CCS) [2].

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17 52 The goal of CO₂ capture is to produce a high-concentration stream of
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19 53 CO₂ ready to be transported or to be stored [2, 4]. Captured CO₂ from
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21 54 various sources, e.g., refineries and steel industry, has been used for various
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23 55 purposes including Enhanced Oil Recovery (EOR). It can also be stored in
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25 56 different geologic formations [2, 5, 6].

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27 57 Geologic mitigation occurs through CO₂ injection into three different
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29 58 types of formations: 1) unmineable coal seams, 2) mature hydrocarbon reser-
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31 59 voirs, and 3) deep saline aquifers, among which the latter is known to have
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33 60 the highest total storage capacity [2, 5] and comprises about 90% of the
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35 61 global CO₂ storage space [7].

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37 62 In the mitigation process, CO₂ captured from commercial or industrial
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39 63 operations is injected into the saline aquifer that provides a medium in which
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41 64 CO₂ would be at supercritical state [8, 9], which means more mass of scCO₂
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43 65 can be stored into a given volume of the formation.

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45 66 It is reported that the risk of CO₂ leakage from deep saline formations
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47 67 through percolation of CO₂ towards the surface is fairly low as this upward
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49 68 mobilization might take thousands or even millions of years to occur [10].
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51 69 This is attributed to the storage of CO₂ in the pores of the hosting rocks
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53 70 with various trapping mechanisms. There are four different mechanisms to
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55 71 sequester CO₂ in the above-mentioned geologic formations: 1) structural and
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57 72 stratigraphic trapping, 2) capillary or residual trapping, 3) solubility trap-

ping, and 4) mineral trapping [2]. Studies have shown that capillary trapping of CO_2 is a very important short-term storage mechanism with a considerably low risk of leakage [11, 12, 13, 14, 15]. This mechanism also contributes to the effectiveness of the solubility and mineral trapping during later stages of the sequestration process [13]. Hence, it is critical to investigate trapping and relative permeability and capillary pressure hystereses that control this mechanism in CO_2 /brine systems.

In most cases, the CO_2 sources also emit impurities [16, 17]. Most North America coal-fired power plants emit large quantities of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) along with CO_2 [17, 18, 19]. Eliminating these by-products from the flue gas stream is expensive at commercial scale. Currently some power plants are employing coal gasification methods to remove sulfur contents from their flue gas emissions; and as a result, they are creating large amounts of elemental sulfur [4]. Co-sequestration of SO_2 with CO_2 might be a feasible substitute for removal procedures [2, 20]. The Weyburn EOR project in Canada, which stores CO_2 along with H_2S , another acid gas, captured from the Great Plains Synfuels Plant in North Dakota, is the only plant that uses this technique [2, 4].

Even though sequestering SO_2 and NO_x along with CO_2 may have economical advantages [21], the impact of these co-contaminants on the trapping of CO_2 in deep saline aquifers, and on the geologic formations is widely undiscovered [22]. There have been, however, some studies on the CO_2 - SO_2 -rock interactions to understand the impact of highly-acidic brine, resulting from the dissolution of CO_2 and SO_2 in aquifers, on different caprocks and on the reservoir integrity [16, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. The

studies show that scCO_2 and SO_2 react significantly with the minerals of the rock and alter the pore and matrix structures and also the wettability of the caprocks; whereupon they affect the maximum CO_2 storage pressure and capacity. For instance, SO_2 dissolution in brine drastically lowers the pH of the solution, which in turn decreases the hydrophilic property of the surface of the rock and makes it less water wet [27, 30, 35]. This leads to less trapping of the non-wetting phase, e.g., scCO_2 , as it can not be trapped easily in the larger pores [36] due to better hydraulic conductivity of the non-wetting phase.

Some studies have shown that acidification of formation brine in the presence of SO_2 might take place due to hydrolysis, oxidation, and SO_2 disproportionation into the brine, among which the latter is suggested to be the predominant reaction [34, 28]. However, it is predicted that diffusion of SO_2 through the scCO_2 -rich phase plume leads to the retention of about 73 to 90% of SO_2 , which in turn limits the severe acidification of formation brine due to the SO_2 disproportionation [20, 21]. Therefore, its impacts on the caprock and reservoir integrity will be minimized. Furthermore, some studies indicate that the acidified brine might dissolve the walls of the pore space and widen the flow paths, thereby altering the pore-space topology and porosity and increasing the permeability of the rock sample [37, 31]. This causes less trapping of the non-wetting phase as its hydraulic conductivity is improved. However, it is also shown that in a fractured carbonate rock sample, the dissolution of minerals might lead to a decrease in the permeability due to different mechanisms such as blockage of the flow path by the mobilized grains and closure of the fracture aperture [34]. As it is evident, injection of

acidified brine impacts differently on the formation properties and generates complexity during core-flooding experiments. Hence, we eliminate the effect of mineral dissolution on the trapping of the scCO₂-rich phase.

In this study, we investigate capillary trapping of scCO₂ in the presence of SO₂ as an impurity. To simplify the experiments, we exclude the effect of mineral trapping by equilibrating the aqueous and scCO₂-rich phases with the minerals of the rock sample. We examine relative permeability and capillary pressure of the scCO₂/brine system in the presence of SO₂. In addition to these properties, we study the impact of dynamic effects on trapping of scCO₂+SO₂ mixture using high flow rate imbibition tests. Even though there have been a number of studies presenting findings on scCO₂/brine relative permeability and capillary pressure in sandstones [35, 36, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53] and in carbonates [42, 43, 54, 55, 56], to our knowledge, no experiments have been performed with SO₂+scCO₂ mixture in a carbonate core sample at elevated pressure and temperature conditions to investigate capillary trapping and drainage-imbibition relative permeability and capillary pressure hystereses. Okabe and Tsuchiya [54] carried out one set of unsteady-state drainage-imbibition scCO₂/brine experiment on a carbonate core sample obtained from a reservoir in the Middle East to measure the initial and residual scCO₂ saturations using an in-situ saturation measurement technique. Bennion and Bachu [55] performed series of unsteady-state drainage-imbibition scCO₂/brine core-flooding experiments at various pressure and temperature conditions on different carbonate core samples. They measured the initial and residual scCO₂ saturations using mass balance and calculated the relative permeabilities through his-

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10 tory matching. El-Maghraby and Blunt [56] reported the results of series
11 of unsteady-state scCO_2 /brine drainage-imbibition experiments performed
12 on an Indiana limestone core. The fluids in this work, unlike previous
13 studies, were equilibrated with the minerals of the Indiana limestone core
14 sample. The trapping results were obtained using an isothermal expansion
15 technique. The authors also reported the drainage capillary pressure versus
16 saturation curves for the Indiana limestone under gaseous and supercritical
17 conditions. Note that in all of these studies, the experiments were carried out
18 on horizontally-placed core samples. Table 1 lists these experimental studies
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28 In this work, a closed-loop, reservoir-conditions multi-phase flow core-
29 flooding apparatus was used to perform flow tests with aqueous and scCO_2 -
30 rich phases. The fluids were equilibrated with the minerals of the carbonate
31 rock sample to minimize the dissolution of the rock matrix into the highly-
32 acidic brine and also the impact of mineral dissolution on the trapping of
33 scCO_2 -rich phase. A medical CT scanner was utilized to determine the in-
34 situ saturations in the rock sample during the flow tests. All the experiments
35 were carried out at 60°C temperature and 19.16 MPa back pressure.
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44 In this paper, first, we provide detailed information on the rock sample,
45 fluids, and experimental conditions, apparatus, and procedures used in this
46 study. Next, we present the results of the trapping, relative permeability,
47 and capillary pressure experiments. This is then followed by the study of the
48 impact of high flow rate imbibition tests on the trapping of the scCO_2 -rich
49 phase. We then conclude the paper with a set of final remarks.
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2. Experiments

In this work, we performed three categories of experiments. In category A, we investigated relative permeability hysteresis of scCO₂-rich/brine fluid system in a Madison limestone sample in the presence of SO₂, as a co-contaminant, using the steady-state method. In category B, we used an unsteady-state (uss) technique to characterize the scCO₂+SO₂/brine capillary pressure. In categories A and B, we also examined trapping of the scCO₂+SO₂ mixture with variations in initial brine saturation (S_{wi}). In category C, we explored the impact of high brine flow rate displacement regime on the trapping of the scCO₂+SO₂ mixture. Table 2 lists all the experiments performed under this study. It also includes the technique used to carry out each experiment.

In the remainder of this section, we include information about the rock sample, fluids, and experimental conditions, apparatus, and procedure.

2.1. Rock Sample, fluids, and experimental conditions

The experiments were performed on a Madison limestone rock sample acquired from the Rock Springs Uplift in southwest Wyoming. This formation is currently being targeted as a potential site for storage of large quantities of CO₂. The layers of interest in this reservoir are Pennsylvanian Weber sandstone (equivalent to Tensleep sandstone) and Mississippian Madison limestone [57]. The core sample used in this study was 3.77 cm in diameter and 17.4 cm long. The porosity of the sample was measured 19.03% using an X-ray CT scanner. The other petrophysical properties of the sample are summarized in Table 3. The core was heterogeneous, and variation

of porosity along the length of the sample was considerable (see Figure 1). Before performing the main experiments listed in Table 2, a sacrificial core was used to equilibrate the fluids with the minerals of the rock. The details of this step are presented later in this paper. The main and sacrificial cores were cut from the same Madison limestone sample.

The main core was wrapped with a layer of Teflon shrink tube and several layers of Teflon tape. The sleeve used in this work was manufactured from a highly impermeable AFLAS material specifically manufactured for this study. The sleeve was wrapped with several layers of Teflon tape and Aluminum foil to provide further assurance against possible penetration of the $\text{scCO}_2 + \text{SO}_2$ mixture. The experiments were performed at 60°C and 19.16 MPa. At these experimental conditions, CO_2 and SO_2 were at the supercritical [9] and liquid states [58], respectively. We used a brine with 36500 ppm NaCl and 50000 ppm NaI salt concentrations as well as highly pure CO_2 and SO_2 gases for the flow tests.

We introduced 1200 ppm of SO_2 into the scCO_2 -rich phase in our experiments. This value represents the amount of SO_2 in the flue gas stream from the Jim Bridger coal-fired power plant in Wyoming [17] and lies within the range of the SO_2 concentration in mixtures that can be found in CCS processes [21]. The solubility of SO_2 in brine is extremely high [59], and a thermodynamic flash calculation indicated that we had formed a two-phase system [60], i.e., 1) a scCO_2 -rich phase, including CO_2 , SO_2 , and water vapor and 2) an aqueous phase, containing water, salts, CO_2 , and SO_2 . Throughout the text we will refer to these phases as scCO_2 -rich and aqueous phases, respectively.

Table 4 shows the estimated physical properties of the fluid phases used in this work at experimental conditions with and without impurity. The values were obtained from literature and also thermodynamic flash calculations [60].

2.2. Core-flooding apparatus

The experiments were carried out using a reservoir-conditions core-flooding system that includes a ten cylinders Hastelloy Quizix pumping system, a medical CT scanner (Universal HD-350E-V) modified for petrophysical applications, a Hassler-type Aluminum core holder, 3500 cm³ three-phase separator, two 2000 cm³ Hastelloy accumulators, and a pressure array system with Rosemount differential pressure transducers. To maintain a uniform temperature throughout the setup, three mechanical convection ovens were used to contain the pumps, the separator, and the accumulators. Several thermocouples were inserted at different locations of the apparatus, such as the inlet and the outlet of the core holder, to monitor the temperature. The wetted parts of the set up are made of Hastelloy to minimize corrosion. We also used special AFLAS seal kits with the equipment to leakproof the system at high pressure and temperature with the fluids mentioned earlier. Figure 2 presents a schematic diagram of the core-flooding system [67].

To prepare for the experiments, the apparatus was thoroughly cleaned and vacuumed for several hours to remove any trapped air in the lines. The separator and accumulators were then filled with brine using pump 3 (P3), see Figure 2. We added 1200 ppm SO₂ to the separator and accumulators using the brine pump (P1). After saturating the setup with the appropriate fluids, the system was pressurized by injecting CO₂ using pump 2 (P2). At the same time, the ovens were turned on to heat the equipment to 60°C. This

also helped with pressurization of the system.

After establishing the pre-specified temperature and pressure, the fluids were re-circulated (by-passing the core sample) to achieve thermodynamic equilibrium. P1 and P2 were retracting brine and $\text{scCO}_2 + \text{SO}_2$ mixture from the separator, respectively, and injecting them at constant flow rate to point P (see Figure 2) at which two phases were mixed and retracted by the back pressure regulation (BPR) pump (P3). We used the Constant Pressure Receive mode in P3 to retract effluent mixture from the core holder at a constant back pressure. This mode allowed us to establish a very stable boundary condition, which was essential for the experiments as the fluids were highly miscible. Variations in the back pressure could introduce inaccuracies into the experimental results (e.g., in-situ saturations).

It is important to note that all the experiments listed in Table 2 were carried out in a closed-loop system in which we maintained the equilibrium between the phases and minimized the amount of mass transfer between them in the core. A dual cylinder 5000 Quizix pump was utilized to adjust the overburden pressure on the core at 21.37 MPa. Additional details about the core-flooding setup can be found elsewhere [51].

2.3. Experimental procedure

As it is listed in Table 2, steady- and unsteady-state techniques were used to carry out different series of experiments. In this section, first, we explain the preparation steps taken prior to the main tests. We then describe the procedures used to perform three different categories of flow experiments.

Before initiating the main experiments, a sacrificial core was prepared to equilibrate the fluids with the minerals of the limestone core. The fluids

(i.e., $\text{scCO}_2 + \text{SO}_2$ mixture and brine) were injected into the sacrificial core and re-circulated throughout the system to achieve the thermodynamic equilibrium. This stage was necessary as the interactions between the minerals of the carbonate rock and the acidic fluids prevented matrix dissolution during the main core-flooding experiments. Therefore, the core used in the main experiments remained intact.

The main core was placed in the core holder and flushed with dry CO_2 to displace trapped air in the pore space and lines. The sample was then vacuumed for several hours and pressurized using P2 by injecting pure CO_2 . At this stage, when temperature and pressure were 60°C and 19.16 MPa, respectively, the outlet of the core was connected to the BPR pump (P3). We then started, using P2, to inject water-saturated scCO_2 into the core while P3 was retracting the effluent mixture from the core holder. After injecting about 15 pore volumes of scCO_2 -rich phase, the core was imaged to obtain the reference scan (CT_{gc}) for saturation calculations. Thereafter, the core was flushed with fresh brine.

A 1000 cm^3 of fresh brine was prepared and equilibrated with the minerals of the crushed Madison limestone rock in a separate cell placed in an oven maintained at 60°C and 19.16 MPa. The fresh brine was re-circulated through the crushed minerals at the pressure and temperature of the experiments. It was then injected into the core using a 6000 Quizix cylinder. More than 20 pore volumes of the brine was injected to displace and dissolve all the $\text{scCO}_2 + \text{SO}_2$ mixture to establish $S_w=1$; the core was then scanned. The main goal of this step was to obtain a reference scan (CT_{fb}) for comparison in later stages of the study. The core was then subjected to injection of

scCO₂-saturated brine using P1. After injection of about 20 pore volumes of the brine, the core was imaged to find another reference scan (CT_{wc}). CT_{wc} was identical to CT_{fb}. At this point, the first drainage-imbibition cycle was started.

2.3.1. Porosity, permeability, and in-situ saturation measurements

The resolution per slice of the scanner was 250 μm . Throughout the experiments, the core was scanned with 4 mm slice thickness and 2 mm spacing, producing 44 slices. The porosity was calculated using the CT numbers obtained from the scanner:

$$\phi = (CT_{wc}^* - CT_{gc}^*) / (CT_w - CT_g) \quad (1)$$

where CT_{wc}^{*} and CT_{gc}^{*} are the CT numbers of the core fully saturated with fresh brine and CO₂ at ambient temperature and 0.14 MPa pressure, respectively, whereas CT_w and CT_g were obtained by scanning the core holder while it was filled with brine and CO₂, respectively.

The permeability of the sample was calculated using the relationship between flow rate and pressure drop in Darcy's law. To measure the absolute permeability, when the core was saturated with scCO₂-saturated brine, we recorded steady-state pressure drops at several brine flow rates. The permeability was obtained by calculating the slope of the line generated by plotting the pressure drop data versus the flow rate values.

To calculate two in-situ fluid phase saturations, the core was scanned at one energy level (130 kV, 100 mA) during the experiments, and also when it was fully saturated with each of the fluids to obtain the reference scans. The saturations were determined using:

$$S_w = (CT_c - CT_{gc}) / (CT_{wc} - CT_{gc}) \quad (2)$$

$$S_g = 1 - S_w \quad (3)$$

where CT_c is the CT number of the core containing two fluid phases during the experiments, and CT_{wc} and CT_{gc} are the CT numbers of the core fully saturated with aqueous and $scCO_2$ -rich phases at the temperature and pressure of the experiments, respectively.

2.3.2. *Relative permeability, capillary pressure, and dynamic-effects experiments*

To perform the category A of the experiments, fully brine-saturated core was flooded with both fluid phases simultaneously to perform a test using the steady-state technique. In this approach, the ratio of $scCO_2$ -rich and aqueous phase flow rates (Q_{CO_2}/Q_w) was monotonically increased and decreased during drainage and imbibition processes, respectively. At each fractional flow, the saturation distribution was carefully monitored and pressure difference along the length of the core was recorded. When the difference between two consecutive measurements of the saturation distribution and pressure difference were less than 1%, the step was considered at steady state. The core was scanned, and the flow rates were changed. Meanwhile, we used capillary number at each step to select the flow rates in such a way that the process was always under the capillary-dominated displacement regime (i.e., $N_c \leq 10^{-5}$). It was calculated using:

$$N_c = \frac{k_{rw} * K_{abs} * \Delta P}{\phi * \sigma_{gw} * L} \quad (4)$$

where k_{rw} , K_{abs} , ϕ , σ_{gw} , ΔP , and L are brine relative permeability, absolute permeability, porosity, interfacial tension between $scCO_2$ and brine, pressure drop, and length of the core, respectively. The flow rates of each phase and the fractional flows used in this study during steady-state experiments are listed in Table 5.

After establishing the maximum $scCO_2$ saturation ($S_{CO_2}^{max}=1-S_{wi}$) at the end of drainage test, the imbibition experiment was started. It was performed analogous to the drainage test with this difference that the Q_{CO_2}/Q_w was monotonically decreased during the experiment until Q_{CO_2} became zero. At this point, small increases in Q_w did not affect the saturations. After completing the imbibition and determining the residual $scCO_2$ saturation (S_{CO_2r}), the Q_w was increased gradually to dissolve all the trapped $scCO_2+SO_2$, and re-establish $S_w=1$. We then started a new drainage-imbibition cycle with shorter saturation span. After the second cycle, the dissolution process was carried out again. As a result of the thermodynamic equilibrium established between the phases, the dissolution was a time-consuming process. Each dissolution run took about 7 days to be completed. About 250 pore volumes of brine were injected to re-create a fully brine-saturated core. After the second steady-state drainage-imbibition cycle, the capillary pressure measurement experiments (category B) were performed. This category included primary drainage, imbibition, and secondary drainage tests using the unsteady-state approach.

In category B, to accomplish primary drainage, $scCO_2$ -rich phase was

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10 365 injected at a low flow rate, i.e., $0.025 \text{ cm}^3/\text{min}$ into a fully brine saturated
11 366 core. After reaching the steady state, the brine saturation was measured.
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13 367 The pressure difference was also recorded throughout the whole process. This
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15 368 information was then processed to obtain capillary pressure as we will explain
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17 369 later in this document. For the next point, the scCO_2 flow rate was increased,
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19 370 and similar procedure was repeated until upon increasing the scCO_2 flow rate,
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21 371 no significant decrease in brine saturation was observed. At this point, we
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23 372 had constructed a full drainage capillary pressure curve.

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25 373 To establish an imbibition capillary pressure curve, one can use two dif-
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27 374 ferent methods: 1) spontaneous imbibition in which the capillary pressure
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29 375 is decreased gradually to zero to allow the wetting phase to imbibe and 2)
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31 376 forced imbibition that can be created by decreasing the capillary pressure
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33 377 from zero to a potentially large negative number [68]. In this study, we used
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35 378 the latter where the imbibition process was started just after the primary
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37 379 drainage step with a very low brine flow rate ($0.005 \text{ cm}^3/\text{min}$). This process
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39 380 was continued by increasing the brine flow rate in small increments. When
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41 381 slight increase in brine flow rate did not change the saturation profile, the im-
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43 382 bibition process was considered complete, and the residual scCO_2 saturation
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45 383 was determined. This allowed us to build an imbibition capillary pressure
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47 384 curve. After accomplishing the imbibition test, the secondary drainage was
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49 385 started by injecting scCO_2 at a much lower flow rate, i.e., $0.005 \text{ cm}^3/\text{min}$,
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51 386 compared to that of the primary drainage. The procedure was identical to
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53 387 the primary drainage process to construct the capillary pressure curve and
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55 388 ultimately establish the same S_{wi} as primary drainage (i.e., ~ 0.49).

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57 389 Following the secondary drainage, in order to perform the last group of
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experiments (category C), an imbibition test was started with a relatively high brine flow rate of $1.01 \text{ cm}^3/\text{min}$, which corresponded to $N_c=1.3 \times 10^{-5}$. After reaching the steady-state condition, we recorded the pressure drop and measured the S_{CO_2} . This imbibition test was then followed by another set of drainage and imbibition experiments, with this difference that we used an even higher brine flow rate, i.e., $2.02 \text{ cm}^3/\text{min}$. Before each imbibition test, we made sure that S_{wi} was similar to previous imbibition tests. All the saturation values used in this study were averaged over the entire length of the core, unless stated otherwise.

3. Results and discussions

In this section, first, we present the capillary trapping results obtained from experiments 1-8, see Table 2, followed by the results of the relative permeability tests using steady- and unsteady-state methods; then we explain the characteristics of the capillary pressure curves (exp.7-9), and finally we demonstrate the results of the high brine flow rate imbibition experiments (exp.9-12).

3.1. Capillary trapping

Two steady-state (experiments 1, 2, 4, and 5) and one unsteady-state drainage-imbibition cycles (experiments 7 and 8) were performed on the Madison limestone core sample under capillary-dominated displacement regime.

Figure 3 demonstrates the variation of the CO_2 saturations across the core sample during steady-state experiment. This figure also shows the effect of heterogeneity on the saturation profiles along the length of the core

sample. Figure 4 exhibits the variation of the $S_{\text{CO}_2\text{r}}$ with $S_{\text{CO}_2}^{\text{max}}$ for these series of experiments. In this figure, the results are compared with the Spiteri et al. [69] empirical correlation and Land model [70], which provide a relationship between initial and residual non-wetting phase saturations. The results compare well using the model parameters listed in Table 6. The coefficients α and β were calculated through fitting the experimental data into the quadratic equation provided by Spiteri et al. [69]. Note that each point in this figure represents the slice-averaged saturations obtained along the length of the core sample. For the first steady-state drainage-imbibition cycle, the $S_{\text{CO}_2}^{\text{max}}$ was about 0.32. The subsequent waterflood led to $S_{\text{CO}_2\text{r}}$ of about 0.245, meaning that approximately 76.3% of the initial scCO_2 was trapped permanently through capillary trapping. The $S_{\text{CO}_2}^{\text{max}}$, $S_{\text{CO}_2\text{r}}$, and trapping efficiency ($S_{\text{CO}_2\text{r}}/S_{\text{CO}_2}^{\text{max}}$) for the second cycle were 0.164, 0.126, and 76.8%, respectively. For the last drainage and imbibition cycle, i.e., experiments 7 and 8, these values were 0.525, 0.329, and 62.7%, respectively. Figure 5 illustrates the trapping efficiency obtained from each slice along the length of the Madison limestone core sample. It indicates that significant fractions of scCO_2 -rich phase can be trapped, i.e., from 62.7 to 76.8%, due to chase brine flooding. It also shows that as the initial brine saturation increases, the trapping efficiency improves. The scatter in the data is attributed to the heterogeneity of the sample. The trapping results obtained from the second cycle of steady-state experiments with low $S_{\text{CO}_2}^{\text{max}}$ are particularly significant due to the fact that at reservoir scale, initial CO_2 saturation in grid blocks away from the injection wells may not be high. This reduces the saturation span that those blocks experience during a drainage-imbibition cycle.

These results show that the maximum initial scCO₂-rich phase saturation obtained at the end of unsteady-state experiments (i.e., 0.525) is less than its counterparts in Berea and Nugget SS cores, i.e., 0.59 and 0.68, respectively [51]. The lower initial saturation may be attributed to higher drainage capillary pressure needed. Furthermore, compared to sandstone rock samples, less amount of scCO₂-rich phase is trapped in the Madison limestone, which might be attributed to the latter being less water wet leading to better hydraulic conductivity of the scCO₂-rich phase. In Figure 4, we also plot our data against the trapping results of the various carbonate rock samples reported in the literature. In some cases, higher residual trapping observed in our study may be attributed to heterogeneity [35], lower viscosity ratio between two phases under our experimental conditions as well as different pore-space topologies impacting pore-scale displacement mechanisms responsible for trapping. In Table 7, the initial and residual scCO₂ saturations measured on different carbonate rock samples presented in the literature are compared to those of this study. It can be seen that our results lie within the range of data that have been reported by other researchers (see also Figure 4). This could be in part owing to the fact that small amount of SO₂ did not affect parameters such as IFT and contact angle, significantly, [65] and hence SO₂+scCO₂ trapping results compare favorably with those without SO₂. This is consistent with the results of another study suggesting that small amount of SO₂ does not decrease the volume of the scCO₂-rich phase trapped in the rock sample [16]. Note that to simplify this work, the fluid phases were equilibrated with the minerals of the rock sample to minimize the impact of acidic brine on the trapping of scCO₂-rich phase, for instance,

by altering the pore and matrix structures.

3.2. Relative permeability measurements

In this section, we demonstrate the results of two sets of drainage-imbibition relative permeability experiments with different saturation spans in the Madison limestone core sample (category A). We also present the brine relative permeability results generated through dissolution processes.

3.2.1. Steady-state experiments

Figure 6 illustrates the results of the drainage-imbibition relative permeability tests for both cycles. As it is shown in this figure, the initial and residual scCO_2 saturations for the first and second cycles were 0.321, 0.245 and 0.164, 0.136, respectively. We observe rather rapid reduction of scCO_2 -rich phase relative permeability during imbibition. Furthermore, $\text{scCO}_2+\text{SO}_2$ relative permeability at the end of drainage reaches relatively small values, e.g., 0.04. This is consistent with the results reported by various research groups in the literature [39, 46, 48, 49, 51, 55]. The low scCO_2 -rich phase relative permeability in scCO_2 /brine system at the end of the steady-state drainage processes might be attributed to several factors, such as heterogeneity of the sample, viscosity ratio, interfacial tension, and wettability of the rock [71].

It is clear that unlike the results of the drainage-imbibition relative permeability experiments on, for instance, Berea sandstone core [51], we do not observe a sharp decrease in brine relative permeability during drainage. This might be attributed to poor pore-level connectivity of large brine-filled elements that get invaded by $\text{scCO}_2+\text{SO}_2$ compared to those of the scCO_2 /brine

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10 487 system in the Berea SS core. This figure suggests that the brine maintained
11 488 a good hydraulic conductivity while the non-wetting phase gradually invaded
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13 489 the pores. The trends observed in this category agree well with those of the
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15 490 carbonate core samples published in the literature [43, 55].

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17 491 For the imbibition process we noticed that for a given brine saturation,
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19 492 the drainage brine relative permeability is slightly smaller than that of the
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21 493 imbibition. This phenomenon was also observed in the results presented by
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23 494 Akbarabadi and Piri [51], Bennion and Bachu [43, 55], and Oak et al. [72] and
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25 495 might have been caused by slight re-configuration of pore fluid occupancy.
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27 496 Numerical values of the measured steady-state relative permeabilities for
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29 497 experiments 1, 2, 4, and 5 are listed in Table 8.

31 498 3.2.2. *Dissolution experiments*

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33 499 An unsteady-state dissolution step was performed as an approach to re-
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35 500 establish $S_w=1$, and initiate a new set of experiments. At the end of each dis-
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37 501 solution test, the core was fully scanned and CT numbers were compared with
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39 502 both CT_{fb} and CT_{wc} . Comparing the scans showed that we had successfully
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41 503 re-established $S_w=1$. The end-point dissolution brine relative permeability
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43 504 for both cycles are demonstrated in Figure 8. The slight difference between
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45 505 the results of the two dissolution experiments might have been caused by
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47 506 the vastly different brine flow rates used for dissolution in experiment 3 com-
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49 507 pared to those in test 6. The difference in brine flow rate may have resulted
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51 508 in a slightly different order by which $scCO_2+SO_2$ -filled pores were invaded
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53 509 by brine through dissolution of the mixture. This may have then led to a
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55 510 different fluid occupancy at the pore scale for a given saturation producing
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57 511 different relative permeability.

3.3. Capillary pressure

In this section, we present the results of the capillary pressure measurement experiments performed on the Madison limestone core using the unsteady-state method. We used *inlet* saturations to characterize the capillary pressure behavior of the rock sample. The method of using the inlet saturations during the 100% non-wetting phase injection to calculate relative permeability and capillary pressure was first introduced by Leas [73] and Ramakrishnan and Capiello [74], and then adopted by Pini et al. [35, 52] to study the capillary pressure versus saturation of the scCO₂/brine core-flooding experiments.

During unsteady-state core-flooding experiments, scCO₂-rich phase is injected at a constant flow rate (Q_{CO_2}) into the fully brine-saturated core. The boundary conditions are: 1) $P|_{x=L} = P_{\text{back pressure}} = \text{constant}$ (Back pressure is kept constant using back pressure regulation pump) and 2) $Q_{\text{CO}_2}|_{\text{inlet}} = \text{constant}$ (Inlet flow rate is constant). Therefore, a pressure gradient exists along the length of the core. The inlet and outlet pressures, as well as pressure drops, are carefully monitored and recorded. At the steady state, there is no brine production and the pressure drop is constant. This means that brine pressure in the core reaches to a fixed value, i.e., $dP_w/dx = 0$, and $P_w|_{x=0} = P_w|_{x=L}$. As long as brine remains a continuous phase across the outlet face of the core, which is a valid assumption for the wetting phase, the CO₂ flow creates the pressure drop across the core. At this point, if CO₂ stays as a continuous phase across the upstream of the core, it can be assumed that $P_{\text{inlet}} = P_{\text{CO}_2}$ and $P_{\text{outlet}} = P_{\text{brine}}$. This means that before reaching to zero capillary pressure outside outlet face of the core, P_c takes a

finite value at the end faces, i.e., $P_c|_{x=0}$ and $P_c|_{x=L} \neq 0$.

For a CO₂/brine system, the capillary pressure is calculated using:

$$P_c = P_{CO_2} - P_{brine} \quad (5)$$

Using the above-mentioned boundary conditions with equation 5, the final P_c^{dra} can be found through pressure drop measurement:

$$P_c^{dra}|_{x=0} = P_{inlet} - P_{outlet} = \Delta P \quad (6)$$

To calculate the capillary pressure during the imbibition process, we only injected brine and implemented the following procedure: at the steady-state condition, we use equation 5 where the pressures are measured at the inlet face of the core. Considering the pore-scale physics of the displacement mechanism during the imbibition tests: $P_{CO_2}^{inlet} = P_{back\ pressure} + \Delta P_{max}^{dra}$ and $P_{brine}^{inlet} = P_{back\ pressure} + \Delta P^{imb}$, where ΔP_{max}^{dra} is the maximum pressure drop at the end of the primary drainage process preceding imbibition and ΔP^{imb} is the pressure drop at the end of each imbibition step. Hence, the final equation would be:

$$P_c^{imb}|_{x=0} = \Delta P_{max}^{dra} - \Delta P^{imb} \quad (7)$$

Therefore, through measuring the inlet saturation using the CT scanner and repeating this procedure for various CO₂ and brine flow rates, the capillary pressure versus saturation curves can be constructed [52].

Two sets of experiments were performed on the Madison limestone core sample to characterize the scCO₂+SO₂/brine primary drainage, imbibition, and secondary drainage capillary pressures versus saturation. In category C,

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10 559 to obtain more accurate values for the saturations, the inlet face of the core
11 560 was scanned 20 times after reaching steady state, and the final value was
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13 561 calculated through averaging.

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15 562 Figure 9 depicts the results of the $\text{scCO}_2+\text{SO}_2$ /brine capillary pressure
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17 563 data obtained using the core-flooding apparatus. As it is illustrated, the
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19 564 maximum initial and residual scCO_2 saturations are 0.692 and 0.532, respec-
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21 565 tively. These values agree well with the trend shown in Figure 4.

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23 566 During the imbibition process, if the sample was strongly water-wet, imbi-
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25 567 bition would establish the final residual CO_2 saturation at capillary pressures
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27 568 close to zero; otherwise, additional CO_2 could be displaced by more brine in-
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29 569 jection [68]. This phenomenon was observed in the Madison limestone core
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31 570 sample. Our results show that the wettability of the core sample might have
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33 571 been altered due to being in contact with $\text{scCO}_2+\text{SO}_2$ mixture. This is con-
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35 572 sistent with the observations reported in Chiquet et al. [26], Chalbaud et al.
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37 573 [27], and Be [30]. The numerical values of the primary drainage, imbibition,
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39 574 and secondary drainage capillary pressure versus saturation are presented in
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41 575 Table 9.

42 43 576 3.4. *Dynamic effects*

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45 577 To investigate the impact of dynamic effects, corresponding to viscous-
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47 578 dominated displacement regime, on the trapping of the scCO_2 -rich phase,
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49 579 two separate imbibition tests with relatively high brine flow rates (i.e., 1.01
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51 580 and $2.02 \text{ cm}^3/\text{min}$) were conducted. The initial scCO_2 saturation for both
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53 581 tests were identical (i.e., ~ 0.49). Figure 10 displays the $\text{scCO}_2+\text{SO}_2$ trap-
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55 582 ping results for each individual slices for both experiments in the Madison
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57 583 limestone core. We also compared these results with those obtained from

the capillary-dominated experiments as well as the Spiteri et al. [69] empirical correlation. The results compare well utilizing the models parameters listed in Table 6. We observed that the scCO_2 -rich phase saturation was significantly reduced because of the dynamic effects. The average residual scCO_2 saturation decreased from 0.329 at the end of experiment 8 to 0.291 and 0.262 at the end of experiments 10 and 12, respectively. It means that the residual scCO_2 -rich phase dropped about 11.5% for the first and 20.4% for the second imbibition test. This decline is attributed to high brine flow rates producing a considerable pressure drop across the core. Under these conditions, brine invades accessible scCO_2 -filled pores not only based on the pore threshold capillary pressure but also the viscous pressure drops associated with each displacement. This creates displacements similar to frontal piston-like advance, which significantly reduces trapping. These reductions were more significant specifically through the first half of the core. One could imagine the possibility of high pressure brine, created by high flow rate, at the inlet side of the core dissolving some of the scCO_2 -rich phase and releasing it at the second half of the core, which was at a much lower pressure due to considerable heterogeneity. This phenomenon, however, is expected to have negligible impact on the saturation difference observed in the first half of the core, because the difference in pressure values could not create a meaningful difference in additional dissolution and hence saturations. Flash calculations [60] showed that only 0.3% and 0.5% (saturation percentage) reductions in residual saturation during the above-mentioned experiments were due to additional dissolution of scCO_2 -rich phase in brine as a result of pressure increase. Note that this amount represents the maximum disso-

lution when the pressure is at its highest value, i.e., at the inlet of the core sample. This pressure gradient decreases significantly towards the outlet of the sample, leading to even less additional dissolution of the $\text{scCO}_2+\text{SO}_2$ in brine. Furthermore, the reservoir core sample used in this study had a lower porosity and permeability in the middle (see Figure 1); therefore, this created a significant pressure gradient in the first half of the core sample while the rest of the sample did not experience large pressure drop. This led to more decrease in saturation through the first half of the core.

3.5. Conclusions

A heterogeneous Madison limestone core sample acquired from Rock Springs Uplift in southwest Wyoming was used to perform reservoir-conditions core-flooding experiments with $\text{scCO}_2+\text{SO}_2$ /brine fluid system at 60°C temperature and 19.16 MPa pressure. A state-of-the-art experimental apparatus was utilized to carry out three categories of flow tests to characterize relative permeability, capillary pressure, and capillary trapping of $\text{scCO}_2+\text{SO}_2$ mixture using steady- and unsteady-state techniques. We also investigated the impact of dynamic effects on capillary trapping of the above-mentioned mixture due to chase brine injection.

The results of three different categories of experiments were presented and discussed. In category A, we employed a steady-state method to perform two drainage-imbibition relative permeability cycles. At the end of each cycle, a dissolution process was implemented to re-establish $S_w=1$. The comparison between the dissolution scans and the fresh brine scans confirmed the $S_w=1$ state. Different ranges of fractional flow during drainage experiments were applied to establish various initial scCO_2 -rich phase saturations for the sub-

sequent imbibition process. The results showed that 62.7% to 76.8% of the initial $\text{scCO}_2 + \text{SO}_2$ volume was trapped through capillary trapping, meaning that significant portion of the CO_2 in-placed at the end of the drainage process will be trapped permanently due to chase brine injection with the lowest risk of leakage. The amount of scCO_2 -rich phase trapping was comparable to those of pure CO_2 in other carbonates reported in the literature. This might be in part due to the fact that small amount of SO_2 did not affect IFT, contact angles, and storage capacity of the rock sample, which was also reported by other researchers. Note that in this study, the impact of mineral dissolution into the acidified brine caused by SO_2 disproportionation was almost eliminated as we equilibrated the fluid phases with the minerals of the rock sample.

The results show that the higher initial brine saturations led to higher trapping efficiencies. We found that the final scCO_2 -rich phase drainage relative permeability was very low, i.e., 0.04, which is consistent with the results that have been reported by other research studies. We observed a rapid reduction in imbibition relative permeability of the scCO_2 -rich phase, resulting in high residual trapping. For the imbibition process, we noticed that for a given brine saturation, the imbibition brine relative permeability is higher than that of the drainage. This might be due to the re-configuration of the fluid occupancy. The end-point dissolution brine relative permeabilities were also obtained for two dissolution experiments. A slight difference between the dissolution results may be attributed to difference in brine flow rates used, resulting in a different order by which $\text{scCO}_2 + \text{SO}_2$ -filled pores were invaded by brine through dissolution of the mixture, in turn leading to a different

fluid occupancy at the pore scale for a given saturation. This result indicates that dissolution plays an effective role on the permanent mitigation of the scCO₂-rich phase at the later stages of the geological storage process.

In category B of the experiments, unsteady-state technique was used to perform primary drainage, imbibition, and secondary drainage tests to measure scCO₂+SO₂/brine capillary pressures. The results showed that the lowest initial brine saturation we could establish in the Madison limestone core sample was 0.475. The subsequent imbibition process resulted in 0.329 residual scCO₂ saturation, meaning that more than 62% of the scCO₂-rich phase was trapped through capillary trapping mechanism. By comparing the trapping results (i.e., initial and residual saturations, and trapping efficiency) obtained from both categories (A and B) of experiments in this study to those available in the literature for other rock samples (e.g., Berea and Nugget sandstones and different carbonates), it can be concluded that the capacity of the rock sample to receive scCO₂-rich phase during the drainage was slightly lower in the Madison limestone compared to those of the sandstones, furthermore, the residual saturations of the scCO₂-rich phase also decreased. This could be due to the fact that Madison limestone is less water wet than the above-mentioned sandstone rock samples. However, in comparison with the results of carbonate cores, our data showed slightly higher residual scCO₂-rich phase saturations. This might be attributed to heterogeneity, different viscosity ratio, and dissimilar pore-space topologies impacting pore-scale displacement mechanisms responsible for trapping. The imbibition capillary pressure curve showed a negative value at the residual scCO₂ saturation, which is an indication of wettability alteration of the rock

sample. This was consistent with findings of other authors reported in the literature.

In category C, two imbibition tests with relatively high brine flow rates were conducted to study the impact of dynamic effects on capillary trapping. Brine flow rates during the first and second fast imbibition tests were 1.01 and 2.02 cm³/min. Residual scCO₂ saturations at the end of each imbibition test were reduced by 11.5% (0.291) and 20.4% (0.262) compared to 0.329 obtained under capillary-dominated displacement regime. This phenomenon can be attributed to the large viscous pressure drop, created by high brine flow rate, along the core, causing the sweeping of the scCO₂-rich phase from the pores. The extra scCO₂ was produced by weakening the non-wetting phase trapping processes. This was done by changing the order by which the displacement mechanisms take place at the pore scale, which in turn is achieved by changing their relative threshold pressure values. Flash calculations showed that only 0.3% and 0.5% (saturation percentage) of the reductions in residual saturation during the first and second fast imbibition tests were due to high pressures created by high brine flow rates. Therefore, the contribution of the dissolution to the overall reduction in trapping was relatively insignificant.

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TABLES

Table 1: Experimental studies with CO₂/brine flow in carbonate rock samples; ss: steady-state, uss: unsteady state, Cat.:Category.

Item	Reference	Fluids	Experimental conditions	Method	Saturation measurement technique	Rock samples	Measured parameters	Process	Pre rock-mineral equilibrium
1	Okabe & Tsuchiya [54]	scCO ₂ , Brine (14 wt% NaI)	40°C, 9.8 MPa	uss	In-situ measurement	Carbonate from Middle East	Initial and residual sat.	Drainage Imbibition	No
2	Bennion & Bachu [43, 55]	scCO ₂ , Brine (103701-320847) (ppm)	36-56°C 8.73-18.8 MPa	uss	Mass balance	Redwater Leduc and Wabamun limestone Cooking lake, Nisku, Morinville Leduc & Grosmont dolomite	Initial and residual sat. Relative perm.	Drainage Imbibition	No
3	El-Maghraby & Blunt [56]	scCO ₂ , gCO ₂ Brine	50°C, 4.2, 9.0 MPa	uss	Isothermal expansion	Indiana limestone	Initial and residual sat. Capillary pres.	Drainage Imbibition	Yes
4	This study	scCO ₂ +SO ₂ Brine(NaI, NaCl) (86500 ppm)	60°C, 19.16 MPa (Cat. A)	ss	In-situ measurement	Madison limestone	Residual sat. Relative perm.	Drainage Imbibition Dissolution	Yes
5	This study	scCO ₂ +SO ₂ Brine(NaI, NaCl) (86500 ppm)	60°C, 19.16 MPa (Cat.B & C)	uss	In-situ measurement	Madison limestone	Residual sat. Capillary pres.	Drainage Imbibition	Yes

Table 2: Experiments performed in this study; RP: relative permeability.

Item	Experiment No.-Category No.	Process	Experiment	Technique
1	Exp.1-A	Drainage	1st RP cycle	ss
2	Exp.2-A	Imbibition	1st RP cycle	ss
3	Exp.3-A	Dissolution	1st RP cycle	uss
4	Exp.4-A	Drainage	2nd RP cycle	ss
5	Exp.5-A	Imbibition	2nd RP cycle	ss
6	Exp.6-A	Dissolution	2nd RP cycle	uss
7	Exp.7-B	Drainage	Capillary pressure	uss
8	Exp.8-B	Imbibition	Capillary pressure	uss
9	Exp.9-B	Drainage	Capillary pressure	uss
10	Exp.10-C	Imbibition	Dynamic effects	uss
11	Exp.11-C	Drainage	Dynamic effects	uss
12	Exp.12-C	Imbibition	Dynamic effects	uss

Table 3: Dimensions and petrophysical properties of the Madison limestone core sample used in this study.

Sample	Length (cm)	Diameter (cm)	Avg. porosity (%) (X-ray)	$K_{abs,brine}$ (mD)	Pore volume (cm ³)
Madison limestone	17.4	3.77	19.03	13.6	36.96

Table 4: Properties of the fluid phases used in this study at 60°C and 19.16 MPa [9, 60, 61, 62, 63, 64, 65, 66].

Fluids	Density ρ (kg/m ³)	Viscosity μ (m.Pa.s (cP))	scCO ₂ /Brine IFT (mN/m)
scCO ₂ -rich phase	0.70	0.0692	28.1
Aqueous phase	1.05	0.635	-
scCO ₂	0.70	0.0582	29.8
Brine	1.05	0.597	-

Table 5: Aqueous and scCO₂-rich phases flow rates (cm³/min) and the fractional flows used during steady-state experiments (1, 2, 4, and 5).

Item	Drainage	Imbibition
Aqueous phase flow rate	0.03-0.2	0.03-0.16
scCO ₂ -rich phase flow rate	0-0.1	0-0.08
Fractional flow	0.05-3.33	0.06-2.67

Table 6: Parameters used with Spiteri [69] empirical correlation and Land model [70].

Sample	Experiment	Fluid system	α	β	$S_{\text{CO}_2\text{r}}^{\text{max}}$	C
Madison limestone	Exp. 1,2,4,5,7, and 8	scCO ₂ +SO ₂ /Brine	0.85	0.35	0.62	0.613
Madison limestone	Exp. 9 and 10	scCO ₂ +SO ₂ /Brine	0.80	0.42	-	-
Madison limestone	Exp. 11 and 12	scCO ₂ +SO ₂ /Brine	0.70	0.40	-	-

Table 7: Initial and residual scCO_2 saturations measured in various carbonate rock samples obtained from the literature.

Rock sample	Porosity (%)	K_{abs} (mD)	Temperature ($^{\circ}\text{C}$)	Pressure (MPa)	Viscosity ratio (μ_w/μ_{nw})	Initial scCO_2 saturation	Residual scCO_2 saturation	Reference
Wabamun#3	15.4	54.3	41	11.9	15.41	0.148	0.045	[42, 43]
Nisku#2	10.4	21.02	56	17.4	11.80	0.508	0.218	[42, 43]
Nisku#3	10.9	74.4	56	17.4	11.80	0.603	0.207	[42, 43]
Grosmont	11.8	153.9	41	11.9	-	0.480	0.365	[42, 43]
Morinville Leduc	11.6	371.9	40	11.4	-	0.470	0.131	[42, 43]
Redwater Leduc	16.8	353.6	36	9.2	-	0.335	0.208	[42, 43]
Cooking Lake#2	16.7	4.87	55	15.5	15.43	0.431	0.268	[42, 43]
Slave Point	9.9	0.217	43	18.8	-	0.454	0.256	[42, 43]
Winnipegosis	14.8	3.09	36	8.73	-	0.789	0.415	[42, 43]
Carbonate from Middle East	14.0	6.7	40	9.8	-	0.400	0.230	[54]
Indiana	19.7	244	50	9.0	3.0	0.730	0.230	[56]
Madison	19.03	13.6	60	19.16	9.18	0.475	0.329	This study

Table 8: Steady-state relative permeability data of experiments 1, 2, 4, and 5.

	Experiments 1,2			Experiments 4,5		
	S_w	k_{rw}	k_{rg}	S_w	k_{rw}	k_{rg}
Drainage	1.000	1.000	0.000	1.000	1.000	0.000
	0.8274	0.32712	0.0106	0.9039	0.5361	0.0035
	0.7892	0.2340	0.0152	0.8873	0.4669	0.0061
	0.7509	0.1980	0.0205	0.885	0.4629	0.0067
	0.7254	0.1266	0.0263	0.8727	0.4213	0.0096
	0.6792	0.0825	0.0357	0.8364	0.3779	0.0131
Imbibition	0.6792	0.0825	0.0357	0.8407	0.3830	0.0099
	0.6848	0.0958	0.0331	0.8511	0.4063	0.0070
	0.6887	0.1035	0.0307	0.8539	0.4093	0.0066
	0.7004	0.1161	0.0215	0.8653	0.4181	0.0034
	0.7145	0.1383	0.0179	0.8744	0.4381	0.0000
	0.7278	0.1400	0.0109			
	0.7429	0.1556	0.0061			
	0.7554	0.1797	0.0000			

Table 9: Capillary pressure data of experiments 7 to 9.

Primary drainage				Imbibition				Secondary drainage			
Q_g (cm ³ /min)	ΔP (kPa)	$S_{w-inlet}$		Q_w (cm ³ /min)	ΔP (kPa)	$S_{w-inlet}$		Q_g (cm ³ /min)	ΔP (kPa)	$S_{w-inlet}$	
0.000	0.00000	1.0000		0.0100	8.29710	0.35740		0.005	12.1876	0.4651	
0.025	20.5374	0.5486		0.0150	-2.86230	0.40040		0.009	15.0733	0.4140	
0.040	21.8607	0.4294		0.0200	-12.1661	0.40980		0.013	14.9520	0.3932	
0.050	22.2994	0.3959		0.0250	-20.7562	0.43430		0.017	16.2138	0.3756	
0.065	23.6311	0.3741		0.0275	-22.2562	0.45880		0.022	17.6727	0.3592	
0.075	24.7552	0.3620		0.0300	-26.7706	0.46770		0.030	18.4670	0.3380	
0.085	25.3560	0.3467						0.035	18.9899	0.3300	
0.100	26.9562	0.3476						0.040	19.6030	0.3218	
0.120	27.7999	0.3315						0.045	20.0791	0.3197	
0.140	29.4642	0.3103						0.055	21.5183	0.3093	
0.175	30.8489	0.3098						0.065	22.6772	0.3054	
0.200	32.6594	0.3086									

FIGURES

Figure 1: Porosity distribution of the Madison limestone core sample measured using an X-ray CT scanner.

Figure 3: scCO₂ saturation profiles along the length of the Madison limestone core sample at the end of Experiments 1, 2, 4, and 5.

Figure 4: Variation of S_{CO_2r} with $S_{CO_2}^{max}$ for capillary-dominated experiments on the Madison limestone core sample.

Figure 5: Variation of trapping efficiency with $S_{CO_2}^{max}$ for capillary-dominated experiments on the Madison limestone core sample.

(a)

52 (b)

Figure 6: scCO₂+SO₂/brine drainage-imbibition relative permeability results generated using steady-state method on the Madison limestone sample for (a) first (b) second cycles.

(a) scCO₂-rich phase

(b) Aqueous phase (brine phase)

Figure 7: Comparison between the relative permeability data of this study and those from the literature.

Figure 8: End-point dissolution brine relative permeability for experiments 3 and 6 performed on the Madison limestone core sample.

Figure 9: $scCO_2+SO_2$ /brine capillary pressure versus saturation curves for the Madison limestone core sample.

Figure 10: Variation of S_{CO_2r} with $S_{CO_2}^{max}$ for high flow rate brine floods and comparison with the capillary-dominated counterparts.