Experimental identification of CO₂–oil–brine–rock interactions: Implications for CO₂ sequestration after termination of a CO₂-EOR project

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1 ABSTRACT

2 Carbon dioxide enhanced oil recovery (CO₂-EOR) has been widely applied to the process of
3 carbon capture, utilization, and storage (CCUS). Here, we investigate CO₂-oil-water-rock
4 interactions under reservoir conditions (100 °C and 24 MPa) in order to understand the fluid-rock
5 interactions following termination of a CO₂-EOR project. Our experimental results show that CO₂-rich
6 fluid remained the active fluid controlling the dissolution-precipitation processes in an
7 oil-undersaturated sandstone reservoir; e.g., the dissolution of feldspar and calcite, and the
8 precipitation of kaolinite as well as solid phases comprising O, Si, Al, Na, C, and Ti. Mineral
9 dissolution rates were reduced in the case that mineral surfaces were coated by oil. Mineral wettability
10 and composition, and oil saturation were the main controls on the exposed surface area of grains, and
11 mineral wettability in particular led to selective dissolution. In addition, the permeability of the
12 reservoir decreased substantially due to the precipitation of kaolinite and solid-phase particles, and
13 due to the clogging of less soluble mineral particles released by the dissolution of K-feldspar and
14 carbonate cement, whereas porosity increased. The results provide insight into potential formation
15 damage resulting from CO₂-EOR projects.

16
17 **Keywords:** CO₂-oil-brine-rock interaction, permeability, wettability, CCUS, Songliao Basin

18 19 1. Introduction

20 Carbon emissions as CO₂ from the combustion of fossil fuels (oil, coal, and natural gas) have
21 been considered the primary gases leading to greenhouse warming (IPCC, 2013). In an effort to limit
22 rising atmospheric CO₂ concentrations while meeting increasing global energy demands, carbon
23 capture, utilization, and storage (CCUS) projects have been carried out in many countries including
24 Canada, China, the Netherlands, Norway, and the USA (Pacala and Socolow, 2004; Surdam et al.,
25 2013; Cavanagh and Ringrose, 2014; Leeuwenburgh et al., 2014; Li et al., 2014). In CCUS projects,
26 carbon dioxide enhanced oil recovery (CO₂-EOR) has been widely applied because it effectively
27 enhances oil recovery while also contributing to a reduction in greenhouse gas emissions (Srivastava
28 and Huang, 1997; Barnhart et al., 1999; Leach et al., 2011; Kuuskraa et al., 2013; Lacy et al., 2013; Li
29 et al., 2014).

30 Underground porous media, such as oil reservoirs and saline aquifers, store CO₂ in various sites:
31 (1) in structural and stratigraphic traps, (2) trapped as a residual gas, (3) trapping by dissolution, and
32 (4) trapping within minerals (Chadwick et al., 2008; Gaus et al., 2008). Storage within minerals
33 involves the incorporation of CO₂ into immobile (and hence safe in terms of CO₂ storage) carbonate
34 minerals during interactions between the reservoir and CO₂-enriched formation water; this type of trap
35 can safely store CO₂ over timescales of millions to hundreds of millions of years (André et al., 2007;
36 Bachu et al., 2007; Shogenova et al., 2009; Klein et al., 2013). Thermodynamic analyses (Ryzhenko,
37 2006), numerical simulations of geochemistry (Bachu et al., 1994; Pearce et al., 1996; Gunter et al.,
38 1997; Xu and Pruess, 2001; Johnson et al., 2004; Xu et al., 2004; Knauss et al., 2005), and geological
39 observations (Baker et al., 1995; Moore et al., 2005; Golab et al., 2006; Liu et al., 2006; Worden, 2006;
40 Gao et al., 2009a; Liu et al., 2011) indicate that calcite, dolomite, magnesite, siderite, ankerite, and
41 dawsonite can form during interactions between reservoir minerals and CO₂-enriched water.

42 Precise knowledge of the CO₂-induced interactions between injected CO₂, saline formation fluid,
43 and reservoir sandstone under reservoir conditions, and of the resulting changes in the chemical and
44 physical properties of the reservoir, is a prerequisite for any secure operation of a storage site (Fischer
45 et al., 2010). In terms of operational technology, the recovery efficiency of CO₂-EOR is 15%–25%
46 (average 20%) (Godec et al., 2011), indicating that despite the process of enhanced recovery, a
47 significant amount of residual crude oil remains in the reservoir.

48 Previous experimental investigations have focused extensively on simulating the interactions
49 between CO₂, water solutions, and rock (sandstone and limestone) or minerals (feldspar and
50 rock-forming mineral concentrates) under various temperatures (25 °C to 300 °C) and pressures (6–80
51 MPa), and for a range of interaction times (~75 min to 450 d) (Rosenbauer et al., 2005; Bertier et al.,
52 2006; Wigand et al., 2008; Hangx et al., 2009; Ketzer et al., 2009; Sterpenich et al., 2009; Fischer et al.,
53 2010; Weibel et al., 2011; Luquot et al., 2012; Wilke et al., 2012; Yu et al., 2012; Iglauer et al.,

2014b; Farquhar et al., 2015). And the CO₂-oil-brine-rock interactions have been investigated by measuring the contact angles between rock or minerals slab and fluid under various temperatures, pressures and salinity (Ameri et al., 2013; Arif et al., 2016; Iglauer et al., 2015a). Unfortunately, few experimental studies have focused on the changes of minerals and petrophysical parameters during the CO₂-oil-brine-rock interactions under reservoir conditions.

The Songliao Basin is considered one of the six most suitable sites (in addition to the Zhungar, Tarim, Qaidam, Ordos, and Sichuan basins) for CO₂ aquifer storage projects in China (Wei et al., 2013), on the basis of a multi-criteria analysis (MCA) that considered four objectives: (1) storage optimization (capacity and injectivity); (2) risk minimization and storage security; (3) environmental restrictions regarding surface and subsurface use; and (4) economic feasibility. Currently, the main CCUS project in the Songliao Basin is in the Qing area of the Changling depression, where CO₂ has been considered to be stored safely for a long period after termination of the CO₂-EOR project (Xu et al., 2009). Here, we performed experiments on CO₂-oil-brine-sandstone interactions using a core flooding technique, to study the fluid-rock interactions that occur after termination of a CO₂-EOR project, to explore the CO₂ trapping mechanisms in oil reservoirs, and to provide basic geological information for other CO₂-EOR projects in China.

2. Geological setting

The Songliao Basin is the largest Mesozoic–Cenozoic continental sedimentary basin in China, as well as the largest oil-producing province (Fig. 1a; Liu et al., 2011). The basement of the Songliao Basin consists of Paleozoic metamorphic and granitic rocks, and is covered by Jurassic to Quaternary sediments (Himeno et al., 2001; Guo, 2007). The Changling depression is a secondary structural belt in the Central depression of the basin (Fig. 1b). The Changling depression is bordered by the Honggang step and the Western slope to the west, by the Huazijing step and the Fuxin uplift to the east, and by the Southwest uplift to the south.

Abundant crude oil exists in the first member of the Lower Cretaceous Qingshankou sandstone reservoir (Qing 1) in the Qing area of the Changling depression (Fig. 1c; Zhang, 2009), and a large amount of CO₂ has been released by human activity in this field (Xu et al., 2009). At present, a CCUS project is underway in the Qing 1 reservoir. The Qingshankou mudstones (maximum ~30–60 m for single layer), deposited during initial flooding of the southern Songliao Basin, are the main hydrocarbon source and cap rock of the basin (Zhang, 2009). A second period of flooding produced the Nengjiang mudstones (maximum ~50–80 m for single layer), the other significant cap rock of the Songliao Basin (Zhang, 2009). According to the evaluation, these two regional cap rocks provide a high level of security for CO₂ geological storage in the area for the huge thickness (total 500–550 m for Qingshankou and Nengjiang mudstones), perfect integrity and less fracture, etc. (Wei et al., 2013; Xu et al., 2009).

The Qing 1 reservoir comprises moderately well sorted, fine-grained sandstone and siltstone (Fig. 1S). The reservoir sediment comprises detrital quartz (26%–40%), feldspar (26%–40%), and rock fragments (26%–40%). Authigenic calcite, ankerite, quartz (as overgrowths and microcrystalline), albite, and clay are also present (Fig. 1S). Reservoir porosity ranges from 6% to 19% (avg. 13.6%), and permeability ranges from $0.1 \times 10^{-3} \mu\text{m}^2$ to $22 \times 10^{-3} \mu\text{m}^2$ (avg. $4.2 \times 10^{-3} \mu\text{m}^2$) (Chen, 2012).

3. Experiment

3.1 Sample descriptions and conditions

The samples for the experiment were collected from the Qing 1 Formation sandstone reservoir (1826m depth) of the CO₂ injected test site in Changling depression, Songliao basins. Six core samples (Q1–6; 2.5 cm in diameter) were drilled parallel to laminations. We used samples Q1–3 in Run 1, with a total core length (L) of 14.8 cm; we used Q4–6 in Run 2 (L = 13.4 cm; Table 1).

X-ray diffraction (XRD) analysis of Q1–6 revealed the presence of quartz (38%–50%), plagioclase (with compositions from albite to anorthite; 34%–40%), K-feldspar (9%–15%), carbonate minerals (1%–2%), and clay minerals (2%–6%) (Table 1). We cleaned oil residue from the samples prior to the experiment according to the Practices for Core Analysis standard (SY/T 5336-2006) of the petroleum and natural gas industry, to avoid interference from oil in the sandstone pores. Based on the

composition of Qing 1 Formation water, the experimental injection solution was prepared by dissolving 0.09 g/L CaCl_2 , 0.06 g/L MgCl_2 , 0.40 g/L Na_2SO_4 , 8.20 g/L NaCl , and 1.88 g/L NaHCO_3 in distilled water. We prepared a low-viscosity kerosene (1.81 mPa·s at 20 °C and atmospheric pressure) suitable for the sample pore structure; the C components of this kerosene ranged from C_7 to C_{12} (Table S1). A working temperature of 100 °C and pressure of 24 MPa were chosen to speed up reactions compared with in situ reservoir conditions (~80 °C, 20 MPa; Zeng, 1997; Ren et al., 2001).

3.2 Equipment and procedures

Experiments were conducted at the State Key Laboratory for EOR of the Research Institute of Petroleum Exploration & Development (RIPED), Beijing, China. These apparatus were connected by stainless steel tubing ($D = 1$ mm; Fig. 2S a and b).

Three cores from each assemblage (RUN1 and RUN2) were placed in a Teflon tube ($D = \sim 25$ mm) in the order of their permeability, and the tube was then placed into the Hassler core holder to generate a vacuum. We established a confining pressure (3 MPa higher than pore pressure) to prevent the reaction solution from flowing through the space between the core and Teflon tube. Then, the water solution and kerosene were injected into containers 1 and 2, respectively, and CO_2 gas and a water solution were injected into container 3, then swayed and stewed for about 24h to form the CO_2 -saturated water solution. Finally, we heated the apparatus in a high-temperature oven up to 100 °C. Experimental pressure (outlet pore pressure) was set to 24 MPa by adjusting the back pressure regulator (BPR). According to the records of St pump, 203ml for RUN1 and 205ml for RUN2 of CO_2 still left in the container 3 in steady state, indicated that the solution was saturated with CO_2 . This preparation process for CO_2 -saturated water solution under 100 °C and 24 MPa was also supported by the calculated equations given in Yu (2012). The water solution in container 1 was injected into the vacuumed pores of the core assemblages until saturated. Then the kerosene was injected into the cores to displace the water solution until no water flow out. According to records for both runs, 11.3ml water was injected into and 7.6ml was displaced by kerosene from cores for run1, and 10.9ml water was injected into and 5.8ml was displaced from cores for run2, so the irreducible brine saturation was almost 30-50% at the end of kerosene injection. Finally, the CO_2 -saturated water solution was injected (time zero) at a constant flow rate of 0.05 mL/min throughout both experiments (121.72 h for RUN1 and 104.15 h for RUN2). Residual oil saturation after the displacement by CO_2 -saturated water solution (9% for RUN1 and 21% for RUN2) was calculated from the volume of experimental record when the experiment was terminated (Table 2).

During each run, we continuously measured the reaction times, injected volumes, sampling measurements (including the volumes of water solution, kerosene, and gas), and influent and effluent pressures (Table 2).

3.3 Analytical methods

We measured the mineral composition, mineral morphology, porosity, and air permeability of the cores before and after each run. As shown in Fig. 2S c, three samples (A, B and C) were prepared from the core assemblage for analysis. Sample A was taken pre-experiment for mineral composition and mineral morphology, while sample B was taken for length, weight, porosity and air permeability for pre and post-experiment, sample C was taken for Mineral composition and mineral morphology for post-experiment.

Mineral compositions were determined using a Rigaku D/max-2500 XRD at the Petroleum Geology Research and Laboratory Center, RIPED, China National Petroleum Corporation, Beijing, China. Details of the XRD analytical procedures are given in the 'Analysis Method for Clay Minerals and Ordinary Non-Clay Minerals in Sedimentary Rocks by the X-ray Diffraction' standard (SY/T 5163-2010). Samples were powdered in an agate mortar and placed on a slide. XRD measurements were carried out at a scanning speed of $2\theta = 15^\circ/\text{min}$ (step width: $2\theta = 0.02^\circ$) over a range of $2\theta = 3^\circ - 70^\circ$. Pre- and post-reaction mineral morphologies were determined using a JEOL Corporation JSM6700F scanning electron microscope (SEM) fitted with energy-dispersive X-ray spectrometry (EDS) at the Research Center of Palaeontology and Stratigraphy, Jilin University, Changchun, China.

The porosity and air permeability of the cores were measured before and after each run using a helium porosimeter (PHI-220, Coretest Systems, CA, USA) and a gas permeameter (KA210, Coretest Systems), respectively. The core permeability was calculated continuously using Darcy's Law for

laminar flow, as follows:

$$K = \mu L Q / S \Delta P$$

where K is the permeability (m^2), μ is the dynamic viscosity of the brine ($\text{Pa}\cdot\text{s}$), L is the length of the sample (m), Q is the volumetric flow rate (m^3s^{-1}), S is the cross-sectional area of the sample (m^2), and ΔP is the displacement pressure (Pa).

After passing through the BPR, the effluent solution was collected continuously into a conical flask. The conical flask was replaced by a new one at every sampling time, and all the brine in conical flask was taken for volume and content analysis each time (Table 2). The CO_2 gas released from the effluent solution was measured using a gas flow meter. Contents of K, Na, Ca, Mg, Fe, Al, and Sr were measured using inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) at the China National Nuclear Corporation Beijing Research Institute of Uranium Geology, Beijing, China. The pH of the effluent solution was measured daily using a pH meter (Orion 4-STAR, Thermo Scientific, Cambridge, USA). The C components of the oil before and after the reaction were analyzed at the State Key Laboratory for EOR of RIPED using a gas chromatograph (7890A, Agilent, USA).

3.4 Simulation of solution chemistry

CO_2 was released from the effluent solution due to changing P-T conditions. We used the PHREEQC to calculate the speciation of the effluent. For each run, we used the values of the volume of CO_2 released from the solution that passed through the BPR to recalculate in situ pH, and the chemistry of the effluent solution was used to calculate the mineral saturation index (S.I.).

4. Results

4.1 Solution chemistry

Analytical results from the effluent solutions for both runs are listed in Table S2. Significant variation in solution chemistry (C_i , with $i = \text{K, Na, Al, Ca, Mg, Sr, or Fe}$) with reaction time are provided in Fig. 2.

During RUN1, K, Na, and Al showed similar variations (Fig. 2a–c). After injection, dissolved K, Na, and Al increased sharply from their initial values (1.04, 3626, and 0.028 mg/L, respectively) to maximum values (121, 4330, and 0.07 mg/L, respectively) after 14.3 h (Fig. 2a–c). However, concentrations dropped to 87.4, 3642, and 0.031 mg/L, respectively, at 19.15 h and then suddenly increased to 99.2, 3858, and 0.064 mg/L at 23.45 h. Subsequently, K and Na values remained around ~16 and 3700 mg/L, respectively, whereas Al values oscillated around 0.03 mg/L after a reaction time of ~100 h (Fig. 2a–c).

A similar pattern is evident for Ca, Sr, Mg, and Fe concentrations, which peaked at ~20 h (479, 1.72, 63.9, and 253 mg/L, respectively; Fig. 2d–g). These concentrations then decreased with reaction time to relatively constant values (~450, 1.08, 26, and 50 mg/L, respectively) within 100 h (Fig. 2d–g). However, in contrast to Sr, and Mg, the Ca concentrations peaked at 23.45 h (similar to the peak times of K, Na, and Al), and dropped slightly to the constant values (~450 mg/L; Fig. 2f) after a reaction time of ~100 h. The pH also increased with reaction time before maintaining a steady value of ~4.3 (Fig. 2h).

During RUN2, the K, Na and Al contents oscillated (peaked at 16.35 h) before a reaction time of ~23 h (Fig. 24a–c). Then K and Na values remained around ~16 and 3650 mg/L, respectively, whereas Al values also oscillated around 0.03 mg/L after a reaction time of ~100 h (Fig. 2a–c).

The contents of Sr, Mg and Fe rapidly increased to peaks at ~20 h (Fig. 2d, e and g), and then decreased with reaction time to relatively constant values until the end of the run (1.01–1.45, 25.1–40.2, and 19.5–59.5 mg/L, respectively; Fig. 2d, e and g). The contents of Ca peaked (381 mg/L) at 23.45 h and remained around 412 mg/L to the end of experiment (Fig. 2f).

The concentrations in RUN2 changed at similar times to those in RUN1 (Fig. 2). However, the maximum contents of K, Na, and Al in RUN2 were lower than those in RUN1 (~53%, 45%, and 57%, respectively), while the maximum contents of Ca, Sr, and Mg were similar to those in RUN1 (Fig. 2).

4.2 Mineralogy

4.2.1 Mineral dissolution

Scanning electron photomicrographs of cores used in both runs, as well as the original cores, are

shown in Figure 5. Mineral surface changes were only observed for plagioclase, K-feldspar, calcite, and ankerite. The surfaces of pre-injection K-feldspars were smooth, but became serrated after the experiments (Fig. 3a–c). Dissolution textures developed on the surfaces of detrital albite grains but were not observed in pre-injection samples (Fig. 3d–f). Before the experiment, calcite and ankerite grains had smooth, step-like structures on their surfaces (Fig. 3g and h), but after the experiment corrosion pits were evident at grain boundaries (Fig. 3i and j).

4.2.2 Mineral precipitation

We identified the kaolinite that more likely precipitated during the experiments using the high-magnifying SEM (Fig. 3k and l) and (Fig. 4). The main characteristics of newly precipitated kaolinite were as follows. (1) EDS analysis showed that the mineral contained O, Si, and Al, consistent with kaolinite. (2) The presence of hexagonal-platelet, euhedral crystals consistent with those of kaolinite that precipitates in sandstones and volcanoclastic rocks, and indicative of kaolinite that forms during fluid–rock interactions. (3) Crystals with a sub-micron diameter (~150–300 nm; Fig. 3k and l). The diameters of kaolinite crystals precipitated in prior experiments were ~200 nm (Luquot et al., 2012) and 10 μm (Hangx and Spiers, 2009; Ketzer et al., 2009). Our experiments and those of Luquot et al. (2012) were run for <130 h, perhaps explaining why the diameters of kaolinite crystals were less than those reported by Ketzer et al. (2009) and Hangx and Spiers (2009). (4) As opposed to the vermiform masses of diagenetic kaolinite, the hexagonal-platelet kaolinite in the experiment indicates the precipitation time was insufficient. (5) Precipitation of kaolinite in the dissolved, intragranular, or intergranular pore spaces within or adjacent to feldspar grains (Fig. 3k and l), indicating that these kaolinite crystals formed as a result of interaction between CO_2 -rich fluids and feldspar. (6) The lack of gaps on the surface of precipitated kaolinite (Fig. 3k), indicating that these kaolinite crystals were not of clastic sedimentary origin.

Notably, a long, acicular solid phase (possibly a mineral phase) was observed by SEM. EDS analysis showed that the composition of this solid phase is heterogeneous (Fig. 5) and that it contains O, Si, Al, and Na at all points, and in central parts also contains C and Ti (at only four points; Fig. 5).

Although the solid-phase component was rare during RUN1 and RUN2, similar precipitation of a solid phase was reported during experiments between CO_2 -rich fluid and rock by Pearce et al. (1996), Lin et al. (2006), Hangx and Spiers (2009), Ketzer et al. (2009), Luquot et al. (2012), and Yu et al. (2012). There are three possible origins for the solid phase: (1) new minerals precipitated during the interaction between CO_2 -rich fluid and rock (Lin et al., 2006; Hangx and Spiers, 2009; Ketzer et al., 2009; Luquot et al., 2012; Yu et al., 2012); (2) poorly crystallized carbon (Luquot et al., 2012); and (3) the salts related to post-experiment drying (Pearce et al., 1996; Yu et al., 2012). However, according to EDS analysis, the C contents are low (2.82%–7.49%) and no Cl element was detected (Fig. 5). Therefore, the solid phase was not poorly crystallized carbon or salts precipitated during post-experiment drying, and is most likely a new mineral phase related to interactions between CO_2 -rich brine and sandstone during the experiments.

4.3 Mineral saturation

The changes in mineral S.I. with reaction time are shown in Figure 7. The S.I. of carbonates (e.g., calcite, dawsonite, dolomite, magnesite, and siderite) and silicate minerals (e.g., feldspar, albite, and anorthite) was mostly negative during RUN1 and RUN2. However, effluent solutions were supersaturated (positive S.I.) with respect to kaolinite, gibbsite, and boehmite (Table S3; Fig. 6). The S.I. indices demonstrate that carbonates and most silicate minerals were dissolved, while kaolinite, gibbsite, and boehmite were precipitated under the experimental fluid conditions.

4.4 Porosity and permeability

The weight and permeability of the cores decreased, while the porosity increased after each experiment (Table S4; Fig. 7). The weighted value of porosity in RUN1 increased from 16.99% to 19.34%, the permeability decreased by 36.59% (from 7.4 to 4.69 mD), and the weight decreased by 2.1 g (from 157.31 to 155.21 g). The weighted value of porosity in RUN2 increased from 15.56% to 16.56%, the permeability decreased 34.72% (from 2.83 to 1.85 mD), and the weight decreased by 8.09 g (from 143.74 to 135.65 g). The water-phase relative permeability, calculated using Darcy's Law, decreased with reaction time (Table 2; Fig. 7).

4.4 Oil component

No changes in the oil component were observed during or after the experiments (TableS1; Fig. 8). Before the experiments, the oil was composed of C₇ (3.11 mol%), C₈ (10.62 mol%), C₉ (30.11 mol%), C₁₀ (37.17 mol%), C₁₁ (12.41 mol%), and C₁₂ (2.01 mol%). After RUN1, the oil composition included C₇ (3.12–3.21 mol%), C₈ (10.49–10.79 mol%), C₉ (29.32–30.80 mol%), C₁₀ (36.6–37.33 mol%), C₁₁ (11.79–12.80 mol%), and C₁₂ (1.99–2.03 mol%); after RUN2, the oil composition included C₇ (3.16–3.25 mol%), C₈ (10.46–10.88 mol%), C₉ (29.55–30.85 mol%), C₁₀ (36.3–37.01 mol%), C₁₁ (11.55–12.44 mol%), and C₁₂ (1.96–2.00 mol%).

5. Discussion

5.1 CO₂–oil–brine–sandstone interactions

Evidence for the dissolution of feldspar and carbonates, such as the serrated structures on feldspars (Fig. 3a–c) and the corrosion pits on carbonates (Fig. 3d–f), was observed under SEM for RUN1 and RUN2. These observations, combined with the increase in solution concentration after the experiment (Fig. 2a–d), leads us to conclude that the carbonates and most silicate minerals were altered in the CO₂–oil–brine–sandstone system.

Petroleum is an organic compound composed of liquid hydrocarbons. Therefore, petroleum and brine interact as a two-phase fluid in the micropores of the sandstone, controlled by oil–water interfacial tension (William and McCain, 1990; Qin et al., 2006). According to the work of Worden et al. (1998), the formation of new minerals during the interaction between fluid and sandstone occurs over three steps: the supply of ions, transportation, and precipitation. However, in a CO₂–oil–brine–sandstone system, the existence of oil reduces the interaction between CO₂-rich brine and sandstone minerals (Gluyas et al., 1993; Worden et al., 1998). A previous geochemical study indicated that the interaction rates between fluid and rock are significantly reduced with increasing oil saturation, as when the rock was saturated with oil, and water saturation decreased to irreducible water saturation (S_{wi}), and then water–rock interactions ceased (Worden et al., 1998). Moreover, because authigenic illite growth stops when the sandstone becomes oil saturated, the dating of petroleum emplacement by authigenic illite (⁴⁰Ar/³⁹Ar or K/Ar) has been applied in many petroliferous basins of the world (Pevear, 1999; Che, 2002; Shi et al., 2011; Clauer et al., 2012).

In the present study, the experiment design and sample pore structure mean that the oil saturation was low (9% for RUN1 and 21% for RUN2; Table. 2), and the concentration of the solution increased with mineral dissolution. These results indicate that interactions occurred between CO₂-rich brine and the minerals with low oil saturation. In terms of CO₂-EOR operations, water-alternating gas technology is used to increase the CO₂ sweep area and to reduce the CO₂ fingering effect (Christensen et al., 2001); e.g., the DUWAG technology of the Royal Dutch Shell Group of Companies and the HYBRIDWAG technology of Unocal Corporation (Rogers and Grigg, 2001). This indicates that plenty of water would be injected into the pores to replace the oil, and suggests that CO₂ could be captured by minerals during interaction in the CO₂–oil–brine–sandstone system.

5.1.1 Feldspar

Similar K, Na, and Al concentrations were recorded during both runs of the present experiments (Fig. 2a–c), and the correlation coefficients of these concentrations (>0.5; Table. 3) indicate that the behavior of these ions was controlled by the same reaction. In addition, K-feldspar and plagioclase were the main potassic and sodic silicates in these samples (Table. 1), and the dissolution of K-feldspar and plagioclase observed by SEM (Fig. 3–f) indicates that the dissolution of K-feldspar and plagioclase was the primary reason for changes in the concentrations of K, Na, and Al. However, there was a contradiction between XRD results (Fig. 4) and K-feldspar dissolution volume (0.023 cm³ and 0.017 cm³, respectively) calculated by the K content of solution (section 5.2; Fig. 9a–b). And this contradiction suggested that the samples for XRD have a inevitable heterogeneity. The dissolution mechanism of feldspar and plagioclase in CO₂-rich fluids has been studied in detail by Shiraki and Dunn (2000), Gao et al. (2007), and as follows:

According to Eqs. 1–3, kaolinite is precipitated with the dissolution of feldspar. Worden and Burley (2009) reported that the precipitation of kaolinite and other kaolin aluminosilicates requires low pH and low ionic strength water. Therefore, in sedimentary basins the precipitation of kaolinite from the alteration of feldspars occurs mainly in acidic and open systems, such as pore fluids related to the injection of meteoric water (Worden and Burley, 2009; Qu et al., 2012). During the present experiments, the effluent solution was collected continuously with the injection of saturated CO₂ brine, so the fluid environment of the core assemblages was open and the pH was maintained at ~4.3 (Fig. 2h). XRD analysis shows that the kaolinite content increased after the experiments (Fig. 4). Moreover, the PHREEQC calculations indicate that the feldspars were undersaturated and that the kaolinite was supersaturated (Table S3; Fig. 6). Different from the steady K concentration, the Al concentration was more wavy in equilibrium state (30h after the injection of CO₂). These indicated the Al was consumed after it was dissolved from K-feldspar and suggested the dissolution of K-feldspar and the precipitation of kaolinite occurred at the same time for both runs. Experiments on CO₂–brine–rock interactions (Shiraki and Dunn, 2000; Bertier et al., 2006; Wigand et al., 2008; Hangx and Spiers, 2009; Ketzer et al., 2009; Fischer et al., 2010; Zemke et al., 2010; Wandrey et al., 2011; De et al., 2012; Yu et al., 2012; Farquhar et al., 2014), numerical simulations of geochemistry (Xu and Pruess, 2001; Xu et al., 2004; Zerai et al., 2006), and geological observations (Liu et al., 2011; Zhou et al., 2014) also confirm this mechanism. In conclusion, the CO₂–brine remains the active fluid causing dissolution–precipitation in a sandstone reservoir with low oil saturation.

5.1.2 Carbonate

The Mg, Ca, and Sr concentrations of the effluent changed in parallel with each other (Fig. 2e–h), and the correlation coefficients of Mg and Sr are >0.5 (Table 3), indicating that the evolution of these ionic concentrations originated with the dissolution of a single mineral. The major elements Mg and Ca, and the trace element Sr are dominant in carbonates, and the dissolution of these carbonates can account for the increasing Mg, Ca, and Sr concentrations during CO₂ injection.

The dissolution of carbonates in the early stages after injection of CO₂ has been reported in CO₂–brine–rock interaction experiments (Shiraki and Dunn, 2000; Weibel et al., 2011; Yu et al., 2012) and numerical simulations of geochemistry (Xu and Pruess, 2001; Xu et al., 2004; Zerai et al., 2006). However, with continued reactions the pH increased with the consumption of H⁺ and the increase in Ca²⁺, and the carbonates re-precipitated. The pH is a key factor in determining whether carbonates dissolve or precipitate in CO₂-rich fluid. The precipitation of carbonates has been documented in experiments by Pearce et al. (1996) and Ketzer et al. (2009), where new microcrystalline carbonates precipitated on mineral surfaces after 3–8 months and 100 h, respectively. However, under the experiment conditions of RUN1 and RUN2, the fluid–rock system was open and pH was maintained at ~4.3, thus allowing for carbonate dissolution.

Besides, the Ca concentrations was similar to, but not identical to (similar to the peak times of K, Na, and Al; Fig. 2f), the Sr and Mg implied that the dissolution of carbonates was not the only mechanism for the increase of Ca. According to the results of XRD, the experiment samples contains significant amounts of plagioclase (34%–40%), and the dissolution of plagioclase (anorthite end-member) also increase the Ca concentration by the mechanism given in Eq. 3 (Wawersik et al., 2001) after the injection of CO₂. So the combined effect of these two reaction mechanisms (the dissolution of plagioclase and carbonates) would be the mainly reason for the Ca concentrations changed with reaction time.

5.1.3 Extraction of crude oil by CO₂ injection

Although CO₂ is inorganic, it is supercritical (at T > 31.3 °C, P > 7.3 MPa) at experimental P–T conditions (100 °C, 24 MPa), and can dissolve in and extract the lighter oil components, leading to deasphalting of the oil (Nobakht et al., 2008; Gao et al., 2009b; Zanganeh et al., 2011; Kavousi et al., 2014). Based on a detailed petrographic analysis of the southern Songliao Basin, Yu et al. (2014) reported that the density of crude oil dropped from 0.8299–0.8550 g/cm³ to 0.7972–0.8063 g/cm³ due to extraction by supercritical CO₂. Similar deasphalting has been reported in CO₂ flooding

experiments and reservoirs where oil co-exists with mantle CO₂ (Nobakht et al., 2008; Gao et al., 2009b; Zanganeh et al., 2011; Cao et al., 2013; Kavousi et al., 2014).

However, no obvious changes in the oil components were observed during or after RUN1 and RUN2 (Table S1; Fig. 8), perhaps due to the kerosene components in these experiments. According to experiments by Li et al. (2005), CO₂ dissolved and extracted the lighter components in (especially <C₂₀) crude oil. Similar experimental results were reported by Nobakht et al. (2008), Qin et al. (2010), and Cao et al. (2013). Here, the pore structure of the sandstones required the use of low-viscosity kerosene (1.81 mPa·s at 20 °C and atmospheric pressure). The C components of this experimental kerosene included C₇ to C₁₂ (Table S1), meaning the C components would be extracted entirely without fractionation.

5.2 Mineral dissolution rates

Reaction rates were determined from mass-balance calculations using the influent and effluent solution chemistry, as well as the mineral compositions of the cores. First, we assumed that the variation in the K concentration of the fluid was due solely to K-feldspar dissolution, and that the Mg concentration of the fluid was controlled solely by ankerite dissolution. Second, we calculated the volume of dissolved minerals by multiplying the molar amount of each mineral's constituent elements by the molar volume of each mineral (64.3 cm³/mol for ankerite and 109 cm³/mol for K-feldspar; Robie et al., 1978; Helgeson et al., 1981; Shiraki and Dunn, 2000). The reaction rates for mineral dissolution using the K and Mg solution concentration curves are shown in Figure 10.

The effective dissolution rate constant, K_r^* , is defined as

$$K_r^* = K_r(A/\emptyset) \quad (\text{Eq. 3})$$

where K_r is the dissolution rate constant, A is the mineral area exposed per unit volume of rock, and $\emptyset$ is the porosity (Lasaga and Kirkpatrick, 1981).

The calculated dissolution rates for K-feldspar and ankerite in RUN1 both peak at ~15 h (1.34×10^{-5} cm³/min and 5.09×10^{-6} cm³/min, respectively), then gradually decrease to 2.71×10^{-6} cm³/min and 9.85×10^{-7} cm³/min at ~30 h and maintain steady values between 1.76×10^{-6} cm³/min and 1.31×10^{-6} cm³/min over a reaction time of ~100 h (Fig. 9c-d). The concentrations in Run 2 changed at similar times to those in Run 1. The dissolution rates for K-feldspar and ankerite in RUN2 increased to a maximum value (7.41×10^{-6} cm³/min and 5.41×10^{-6} cm³/min, respectively), then decreased to maintain relatively constant values (1.79×10^{-6} cm³/min and 1.26×10^{-6} cm³/min, respectively) over the last stage of the run ($t > 100$ h; Fig. 9 c-d).

Taken as a whole, the mineral dissolution rate involves two stages of its development. In stage one, the rate changed sharply within ~ 30 h for the reason that the status between rock and fluid was changed after the injection of CO₂. The ions released by the interaction between minerals and CO₂-rich fluid would not only increased the concentration of solutions but also flow out from the outlet of BPR before reached to the equilibrium concentration(<30h). Moreover, the different dissolution rate of K-feldspar in stage one indicates that the interaction between K-feldspar and CO₂-rich was still restrained by the oil in the pore(Worden et al., 1998) even though the oil saturation was only 9-21%. In stage two, the “new balance” between rock and CO₂-rich fluid under this flow-through experiment condition was build after the ~ 30 h reaction, the ions released by the dissolution of minerals only flow out from the outlet of BPR. Restricted by the low flow rate of (0.05 mL/min) and low oil saturation(9% for RUN1 and 21% for RUN2), the concentrations of injected CO₂-saturated brine reached the “equilibrium” concentration before flow out from the outlet of BPR. The dissolution rate of K-feldspar was different for each run, while we did not observe a difference in dissolution rates for ankerite between the two runs (Fig. 9). The occurrence of variable dissolution rates for the same mineral under different oil saturations indicates that the presence of oil leads to selective dissolution reactions between fluids and minerals. Wettability is the tendency of a fluid to spread along a solid surface in the presence of an immiscible fluid (Crocker and Marchin, 1988), and it is a function of the characteristics of the rock and fluid in the oil reservoir (Barclay and Worden, 1997). Based on contact angle measurements on the ideal mineral substrate, the feldspar was more hydrophilic than calcite in a CO₂-water system(Iglauer et al., 2015a). But the wettability of minerals in micropore was also strongly affected by the sorting, sphericity, pore structure, clay particles and fluid

properties of reservoir sandstones (Sincock and Black, 1988; Dullien et al., 1990; Fassi-Fihri et al., 1991; Dijke et al., 2001). So an ideal sketch model was drawn to describe our results according to the experiment conditions (low permeability), oil may coat K-feldspar while the calcite surfaces have a thin water coating (Fig. 10a). With the injection of CO₂ in our experiments, the interaction between CO₂-rich fluid and K-feldspar is inhibited at the oil-coated K-feldspar surfaces, while interactions between fluid and calcite would not be significantly reduced by thin water coatings (Fig. 10b and c). Therefore, the dissolution rate of K-feldspar decreased for less exposed surface area with the increasing of oil saturation (RUN1 to RUN2), while no obvious impacts for that of carbonate minerals. And these imply that the interaction between CO₂-rich fluid and water-wet reservoir was more violent than oil-wet reservoir.

In the present study, the dissolution rate of K-feldspar was higher than that calculated by Yu et al. (2012), an indication that in our experiments more K-feldspar was exposed per unit volume of sandstone. The content of K-feldspar in RUN1 and RUN2 was 10% higher than that in the experiment of Yu et al (2012), while the porosity was similar. However, the dissolution rate of ankerite varied only slightly between RUN1 and RUN2, and the run in Yu et al. (2012), which indicates that wettability and mineral content were the main controls on dissolution in the oil–CO₂–brine environment.

5.3 Porosity and permeability

5.3.1 Porosity

Porosity increased (Table S4; Fig. 7) in accordance with the dissolution of feldspar and calcite by CO₂-rich fluid (Fig. 2 and 3). Similar results have been reported in both experiments (Shiraki and Dunn, 2000) and numerical simulations of geochemistry (Xu et al., 2005), which showed that the porosity increased adjacent to a CO₂ injection well.

5.3.2 Permeability

We observed three main permeability trends: (1) the water-phase relative permeability of RUN1 was higher than that of RUN2; and (2) the water-phase relative permeability for both runs decreased with reaction time by ~40% (Fig. 7).

Oil residue in the pores was the main reason that the water-phase relative permeability of RUN1 was higher than that of RUN2. In a multi-phase fluid environment, any single-phase relative permeability was lower than the permeability of sandstone, and the single-phase relative permeability increased with increasing fluid saturation (Amyx et al., 1960). In the present study, an oil residue remained in the pores after the injection of CO₂, and the water-phase relative permeability for both runs was lower than the measured permeability before the experiments (Table S4; Fig. 7). Because the oil saturation in RUN2 was higher than that in RUN1, the water-phase relative permeability of RUN1 was also higher than that of RUN2.

Many previous CO₂ flooding experiments (including equilibrium CO₂ solution and supercritical CO₂) reported a reduction in permeability after the experiments (Sayegh et al., 1990; Shiraki and Dunn, 2000; Yu et al., 2012; Iglauer et al., 2014b). The largest decrease (by ~60% compared with original sample) in the permeability of sandstone was reported by Sayegh et al. (1990), for experiments performed with the Cretaceous Cardium sandstones of Alberta, Canada; The decrease in permeability was attributed to three mechanisms: (1) the precipitation of new minerals (kaolinite and solid phases) due to interactions between the equilibrium CO₂ solution and sandstones (Yu et al., 2012); (2) the release of clay particles by the dissolution of minerals (Sayegh et al., 1990; Yu et al., 2012; Ellis et al., 2013; Mangane et al., 2013; Iglauer et al., 2014b; Luquot et al., 2014); and (3) the dissolution of critical fracture asperities that resulted in mechanical aperture closure (Polak et al., 2003; Yasuhara et al., 2006). According to SEM and XRD analyses, the kaolinite and solid-phase particles precipitated in pores and pore throats (Fig. 3k and l; Fig. 5); however, the small amount of precipitation of new minerals (at ~110–120 h experimental time) means that such precipitation played a limited role in the reduced permeability. Given the dissolution of detrital minerals (K-feldspar and plagioclase) and cement (carbonate), large amounts of relatively insoluble minerals (clay particles) would have been transported in the fluid flow and accumulated at pore throats during the injection of CO₂-rich solution. Thus, the particles in the core are responsible for the changes in permeability. Given that the cores are not fractured, we rule out mechanism (3).

It is worth noting that the permeability of the core assemblage decreased substantially, while the

porosity increased after CO₂ flooding. This result was common in the experiments between CO₂ and oolitic limestone(Mangane et al., 2013) or sandstone (Shiraki and Dunn, 2000; Luquot et al., 2014). And this inconsistent tendency between porosity and permeability would result from that the new dissolution pore might not offset the damage of permeability by the particles after CO₂ flooding during the experiment time-scale(several days). As the geochemistry simulation shown(Jin et al., 2016), the permeability of reservoirs reduction obviously after the injection CO₂. and the permeability at the advancing front at 5000 days reduces to about 1/3 to 1/2 of its initial value. So the damage of permeability by the injection of CO₂ might be a long time-scale. However, Luhmann et al. (2014) and Menke et al. (2015) reported the increasing permeability due to dissolution after reaction between CO₂-saturated brine and carbonatite under reservoir conditions. Different from high quantities of clay particles in oolitic limestone (Ellis et al., 2013; Mangane et al., 2013) and sandstone(Sayegh et al., 1990; Yu et al., 2012; Iglauder et al., 2014b; Luquot et al., 2014), the particles in dolomite for the experiment carried by Luhmann et al. (2014) was scarce. Although the Menke et al. (2015) study cannot be directly compared with our permeability data (the permeability is five orders of magnitude higher than in our samples), their report also imply that the low permeability reservoir was more sensitivable to the injecton of CO₂(Luo., 1999). So it is essential to evaluated the sensitivity of CO₂ storage reservoir, especially the low permeability and high particle quantities reservoir, and develop a specific reservoir protection scheme for the CCUS project.

6. Conclusions

We performed two oil saturation experiments under simulated reservoir conditions (100 °C and 24 MPa), providing new insights into the fluid–rock interactions that occur after termination of a CO₂-EOR project.

The dissolution of K-feldspar, albite, calcite, and ankerite, the precipitation of kaolinite and solid phases (comprising O, Si, Al, Na, C, and Ti), and the increase in solution concentration after both runs indicated that the CO₂-rich fluid remained the active fluid controlling the dissolution and precipitation processes in the low-oil-saturated sandstone reservoir.

Mineral dissolution rates were reduced in the case that exposed mineral surface areas were coated with oil. Mineral wettability, oil saturation, and mineral content were the main controls on the surface area exposure of minerals. The dissolution rates of K-feldspar were strongly affected by oil because the K-feldspar is more hydrophobic than calcite.

No obvious changes in the oil component were observed after the injection of CO₂. The lighter kerosene C components (C₇–C₁₂) were the main reason that kerosene was extracted by CO₂ without fractionation.

The permeability of the core assemblage decreased substantially, while the porosity increased. The loss of permeability resulted from the precipitation of new minerals (kaolinite and solid-phase particles) and the clogging of relatively insoluble mineral particles released by the dissolution of minerals (K-feldspar and carbonate cement). The increased porosity resulted from mineral dissolution.

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