

1 **Transport properties of saline CO₂ storage reservoirs with**
2 **unconnected fractures from brine-CO₂ flow-through tests**

3 by

4 Andrea Muñoz-Ibáñez^{a*}

5 Ismael Himar Falcon-Suarez^b

6 Héctor Marín-Moreno^b

7 Jordi Delgado-Martín^a

8 &

9 Peter Mackin^c

10
11
12 ^aSchool of Civil Engineering, University of A Coruña, Campus de Elviña s/n, 15071
13 A Coruña, Spain

14 ^bNational Oceanography Centre, University of Southampton Waterfront Campus.
15 European Way, SO14 3ZH, Southampton, United Kingdom.

16 ^cUniversity of Southampton, Ocean and Earth Science, Southampton, SO14 3ZH,
17 UK

18
19
20 *Corresponding author: School of Civil Engineering, University of A Coruña, Campus
21 de Elviña s/n, 15071 A Coruña, Spain.

22 Phone: +34-981-167000 Office: 5415 e_mail: andrea.munoz@udc.es

1 **Abstract**

2 CO₂ storage in fractured reservoirs may lead to fast CO₂ flow through
3 interconnected fracture networks; but the role of isolated fractures on brine-CO₂
4 multiphase flow systems remains unclear. We present the results of a brine-CO₂ flow-
5 through experiment in which we assess the change in transport properties of a
6 synthetic sandstone plug (a surrogate of a saline siliciclastic CO₂ reservoir) containing
7 non-connected fractures aligned 45° from its axis. The test was performed at 40 MPa
8 of constant hydrostatic confining pressure and ~11 MPa of pore pressure, at room
9 temperature (~19.5°C), using pure liquid-CO₂ and 35 g L⁻¹ NaCl salt solution. The
10 injected CO₂-brine volume fraction was increased from 0 to 1 in 0.2 units-steps
11 (drainage). Upon achievement of the maximum CO₂ saturation ($S_{CO_2} \sim 0.6$), the plug
12 was flushed-back with the original brine (imbibition). During the test, we monitored
13 simultaneously pore pressure, temperature, axial and radial strains, and bulk electrical
14 resistivity. The fractured sample showed lower values of cross- and end-points in the
15 relative permeability curves to CO₂ compared to non-fractured samples, from
16 comparable experiments performed at similar pressure and brine salinity conditions,
17 but different temperature. Our results suggest that a non-connected fracture network
18 affects the mobility of the individual phases, favouring the trapping of CO₂ in the porous
19 medium and improving the storage efficiency of the reservoir. These evidences show
20 the need of a better understanding of fracture connectivity prior to discard fractured
21 reservoirs as unsuitable geological formations for CO₂ storage.

22
23 **Keywords:** CO₂ geosequestration; fractures; hydromechanics; electrical
24 resistivity; relative permeability.

1 **1. Introduction**

2 The success of large-scale CO₂ geosequestration and long-term storage highly
3 depends on the capacity of the reservoir to avoid potential CO₂ leakage to the surface
4 along permeable underground pathways. Depleted oil and gas reservoirs, saline
5 aquifers, and coal seams have been recognized as suitable formations for CO₂
6 storage (IPCC, 2005). Among them, saline aquifers are the most attracting sites due
7 to its worldwide distribution, high potential storage capacity and low reactivity to CO₂
8 (Bachu, 2015; Michael et al., 2010).

9 Enhanced chemical reactivity induced by the introduction of a non-resident fluid
10 into rocks can also lead to significant modifications of their porosity and permeability
11 (e.g., Canal et al., 2013). Even in reservoirs with low potential reactivity to CO₂ (e.g.,
12 sandstone), CO₂-induced salt precipitation can significantly affect the injection
13 efficiency in the CO₂ storage site, as observed in Ketzin (Baumann et al., 2014) or in
14 the Tubåen Formation at the Snøhvit Field (Grude et al., 2014). However, changes in
15 permeability caused by mineral dissolution/precipitation strongly depend on the
16 specific location where these processes occur (i.e. at open pore spaces or in necks or
17 throats; Canal et al. (2013); Stack et al. (2014)) in connection to the main flow paths.

18 Rock wettability in brine-CO₂ systems affects the efficiency of the CO₂ injection
19 process, the flow and distribution of fluids within the pore space, and the trapping
20 capacity during CO₂ storage (Al-Menhali and Krevor, 2014). The wetting phase (brine)
21 occupies the smallest pores while the non-wetting phase (CO₂) remains in the largest
22 cavities (Dullien, 1992). Then, residual CO₂ saturations are higher in strongly brine-
23 wet sandstones; while in CO₂-brine mixed-wet systems certain parts of the pore
24 surface are preferentially wetted by one of the both fluids, leading to a lower residual
25 trapping (Al-Khdheewi et al., 2017). A number of factors influence the wettability of

1 rock-fluid systems, such as pressure, temperature and brine salinity (Al-Khdheewi et
2 al., 2017). Water-wettability decreases (reciprocally, CO₂-wettability increases) with
3 pressure and brine salinity, and increases with temperature in the presence of
4 common sandstone minerals such as mica or quartz (Broseta et al., 2012; Chiquet et
5 al., 2007).

6 Capillary pressure is a key factor impacting fluid transport in the formation and
7 determines the ability of the wetting phase to prevent the non-wetting phase to flow
8 through the sample. It increases with the interfacial tension (IFT), decreases with the
9 pore radius (Chiquet et al., 2007), and also depends on wettability (e.g., Krevor et al.,
10 2015; Wang and Tokunaga, 2015). According to Bachu and Bennion (2009), IFT
11 increases with temperature and water salinity and decreases with pressure. Pore
12 shape and connectivity also influence CO₂ displacement at the pore scale. The relative
13 abundance of necks and throats in the overall rock framework constrains the capillary
14 threshold to be exceeded to initiate CO₂ migration (Zhu et al., 2016). The
15 heterogeneities in the pore space result in heterogeneous trapping of the non-wetting
16 phase (Tsuji et al., 2016).

17 The study of fluid mobility is commonly addressed by flow-through experiments
18 under reservoir conditions in the laboratory, typically complemented with non-intrusive
19 techniques such as computed tomography (CT) scanning (Akbarabadi and Piri, 2013;
20 Krevor et al., 2012), magnetic resonance imaging (Almenningen et al., 2018), or
21 electrical resistivity (Carrigan et al., 2013; Falcon-Suarez et al., 2016; Nakatsuka et
22 al., 2010). Electrical resistivity is also used as a remote sensing technique for
23 monitoring the CO₂ plume advance in saline aquifers (i.e., controlled-source
24 electromagnetic surveys – CSEM, e.g., Park et al. (2013)), due to the strong resistivity
25 contrast between brine (low resistivity) and CO₂ (high resistivity). The degree of brine

1 saturation can be inferred from electrical resistivity using Archie's law (Archie, 1942).
2 The application of Archie's law relies on the accurate resistivity estimate of the fully-
3 saturated rock, the resistivity of pore fluid, and the shape properties of the electrically-
4 connected porosity fraction (Cai et al., 2017). The resistivity-saturation conversion has
5 been previously used to map CO₂ distribution in partially saturated porous media in a
6 number of CO₂-brine flow-through tests (e.g., Alemu et al., 2013; Nakatsuka et al.,
7 2010; Z. Wang et al., 2009), as an alternative to X-ray CT-scanning (e.g., Berg et al.,
8 2013; Krevor et al., 2012).

9 To some extent, all CO₂ storage formations are fractured reservoirs (Iding and
10 Ringrose, 2010). Therefore, fracture density and distribution, orientation and
11 connectivity need to be precisely assessed to guarantee safe and long-term geological
12 storage of CO₂ (Bond et al., 2013). Different models have been proposed to describe
13 multiphase flow through an individual fracture (e.g. Huo and Benson (2016)), and
14 validated from experimental studies on artificial samples with ideal smooth and parallel
15 surfaces (Diomampo, 2001; Fourar and Bories, 1995). However, experimental studies
16 on natural rock samples with a single fracture highlight the limitations of the proposed
17 models when upscaling results to multiphase flow on real fractured reservoir
18 formations (Noriaki et al., 2015).

19 Assessing the fracture connectivity effect on multiphase flow is challenging both
20 in nature and laboratory scales. Interconnected fracture networks may act as path-
21 flow in low permeability formations (Nooraiepour et al., 2018). In principle, the high
22 hydraulic conductivity of the fractures would lead to preferential path-flows for CO₂,
23 diminishing the storage effectivity in the rock matrix and hampering the CO₂ migration
24 control (March et al., 2018). However, when a high density of non-connected fractures

1 exists in the reservoir, their effect on the hydrodynamic behaviour of CO₂ storage
2 systems is unclear, and yet to be investigated.

3 In this contribution, we deepen into this aspect and present the results of a brine-
4 CO₂ flow-through experiment performed on a synthetic sandstone sample containing
5 well-distributed non-connected fractures aligned at 45° from its axis. We focus on
6 assessing the transport properties of non-connected fractured saline siliciclastic CO₂
7 storage reservoirs, by analysing CO₂-induced changes in electrical resistivity and
8 relative permeability. The experiment is complemented with (i) post-test thin section
9 observations, (ii) reactive transport modelling, and (iii) comparison with previous
10 experiments performed under similar conditions but using non-fractured synthetic
11 sandstone samples.

12

13 **2. Materials and methods**

14 *2.1. Synthetic sandstone*

15 We used a 50 mm diameter 20 mm length silica-cemented synthetic sandstone
16 plug, with spread aligned fractures oriented at 45° from its axis. The sample belongs
17 to the same batch used by Tillotson et al. (2012), and later used by Amalokwu et al.
18 (2015) to study water saturation and stress effects on shear wave splitting at oblique
19 angles, using de-ionized water (DIW) as saturating fluid. Specific details concerning
20 its preparation are given therein, but we explain here the main aspects for
21 completeness. During the manufacturing process, aligned fractures were conformed
22 in a paralepipedic block at the time of sample manufacturing by horizontally spreading
23 2 mm-diameter, 200 µm-thick penny-shape aluminium elements (Al-discs), in four
24 layers with a vertical separation of ~4 mm. After the thermal (manufacturing) treatment,
25 the block was cored ensuring an angle of 45° for the Al-disc layers. The resulting

1 sample was flushed with 10% HCl solution to etch the fractures by leaching the
 2 aluminium. The morphology of the sample was checked by X-ray CT scan imaging,
 3 from which a fracture density $\varepsilon_f = 0.0289 \pm 0.0077$ was determined (Tillotson et al.,
 4 2012). Since ε_f is related to the number of fractures N with radius a per unit volume V
 5 as $\varepsilon_f = N a^3 V^{-1}$ (Mavko et al., 2009), we estimate the pore volume fraction of sample
 6 45A corresponding to fractures is $\sim 10\%$.

7 Before the brine-CO₂ flow-through (BCFT) test, porosity (ϕ_0) was measured by
 8 He-pycnometry and intrinsic permeability ($k_{gas,0}$) by N₂-permeameter under low
 9 confining pressure conditions (~ 0.5 MPa). Table 1 shows the main physical properties
 10 of the sample.

11 **Table 1.** Sample properties before test.

Sample	Length (mm)	Diameter (mm)	ϕ_0 (m ³ m ⁻³)	$k_{gas,0}$ (mD)	$^*\rho_b$ (kg m ⁻³)
45A	19.85	49.54	0.273	5.48	1812

12 $^*\rho_b$ is the bulk density

13 *2.2. Experimental setup*

14 The experimental rig (Figure 1) is designed around a modified Hoek-Franklin
 15 type triaxial core holder (previously described in Falcon-Suarez et al., 2016), which
 16 allows the simulation of reservoir conditions up to 65 MPa of confining and pore
 17 pressure. This system is capable to measure electrical resistivity and axial and radial
 18 strains simultaneously, during the co-injection of up to two different pore fluids.

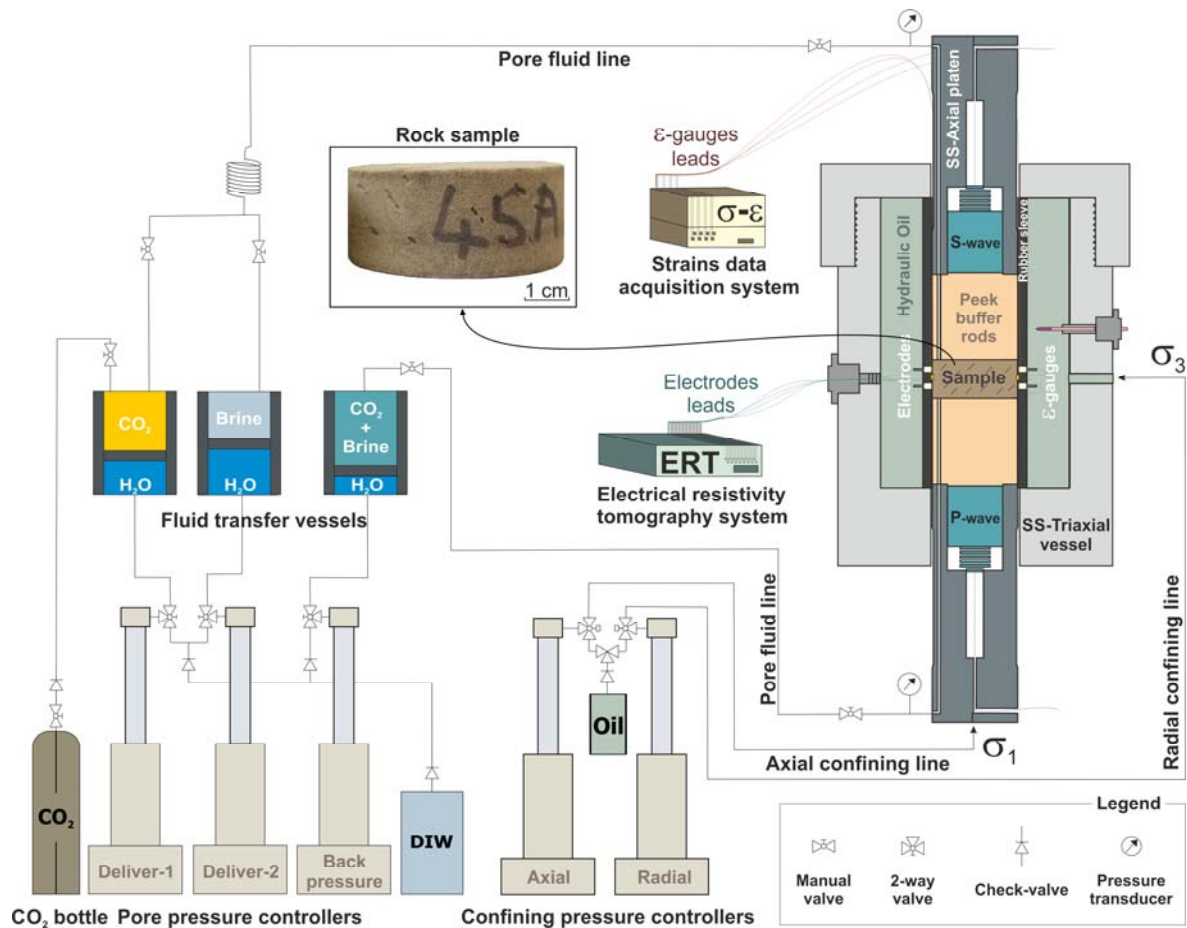


Figure 1. Experimental setup and synthetic sandstone with non-connected fractures aligned at 45° from its axis (sample 45A).

1

2 To track the axial and radial displacements occurring during the experiment, a
 3 rosette of two 350-ohm strain gages (90° configuration) was epoxy-glued onto the
 4 lateral surface of the sample. Inside the triaxial cell, a 6 mm thick, 190 mm height
 5 nitrile-hydrogenated butadiene rubber (NHBR) sleeve isolates the sample plug from
 6 the mineral oil used to deliver confining pressure. The sleeve is equipped with 16
 7 stainless steel electrodes arranged in two rings around the plug that provide electrical
 8 resistivity measurements, once in contact with the sample. The system uses a tetra-
 9 polar electrode configuration to minimize electrode polarization artefacts. For any
 10 single operational run, the electrical resistivity tomography (ERT) system acquires 208
 11 individual tetra-polar measurements using various permutations of current injection

1 and potential difference sensing electrode pairs. The whole acquisition lasts ~20 s.
2 The gathered data are then inverted using software based upon EIDORS (Adler and
3 Lionheart, 2006) MATLAB toolkit for a uniform/homogeneous isotropic resistivity and
4 heterogeneous isotropic resistivity distribution. Both inversion schemes employ a finite
5 element forward model of the sample and electrodes (further details in North et al.,
6 2013). For this test, the system was configured to discard the measurements at the
7 electrodes nearby the strain gauges, providing an accurate result for the bulk resistivity
8 but hampering the tomography inversion. Under our experimental *P-T*- fluid salinity
9 conditions and sample permeability, the associated resistivity error is ~1% (for
10 frequencies between 1 and 500 Hz), for homogenous and isotropic rock samples in
11 the electrical resistivity range 1 to 100 Ω m. Above this resistivity and for the case of
12 non-isotropic materials, the error may rise up to 5% (North et al., 2013).

13 Axial stress is applied through two stainless-steel platens, which allow pore fluid
14 circulation through the sample via thru-holes. The platens are specially designed to
15 bypass the leads from the strain gauges glued to the sides of the plug, which are then
16 connected to a 4-channel data acquisition system (Vishay-Model D4).

17 The experiment was conducted under hydrostatic confining stress condition (σ_1
18 = σ_2 = σ_3) automatically controlled with a dual ISCO EX-100D system. Upstream pore
19 pressure was also controlled with an additional ISCO EX-100D system, configured to
20 independently deliver brine and CO₂. A third ISCO ED100 pump was used as
21 backpressure regulator downstream of the sample. In order to prevent the controller
22 from potential damage due to direct contact with the corrosive brine and CO₂ solutions,
23 the pore fluids are indirectly delivered/received using fluid transfer vessels (FTVs). For
24 this experiment, two FTVs supplied pure liquid-CO₂ and 35 g L⁻¹ NaCl salt solution,
25 respectively, while a third one received the resulting fluid downstream. Additionally,

1 two piezo-resistive pressure transmitters (Keller model PA-33X) placed very close to
2 the inlet (upstream) and outlet (downstream) ports allowed accurate control of the pore
3 pressure.

4

5 *2.3. Experimental procedure: Brine-CO₂ flow-through test*

6 The test simulates a CO₂ injection scenario in a siliciclastic saline reservoir with
7 non-connected aligned fractures. We performed a brine-CO₂ flow-through (BCFT) test
8 using the steady-state technique (Dullien, 1992), with drainage (i.e., the progressive
9 displacement of a resident saline fluid with CO₂) and imbibition (i.e., the back-
10 displacement of CO₂ by saline fluid) episodes, similar to the experimental approach
11 described in Falcon-Suarez et al. (2018, 2017, 2016).

12 Before starting the experiment, the plug was oven-dried at 60 °C for 24 h and
13 then saturated with a 35 g L⁻¹ NaCl deaired aqueous solution (brine), representing
14 the resident fluid in a potential reservoir. The dry sample was placed in the saturation
15 chamber and subjected first to brine imbibition under vacuum ($\sim 10^{-4}$ Pa), followed by
16 a 5 MPa pore fluid pressurization to enhance the dissolution of any remaining air in
17 the porous media. The test was performed at constant confining pressure (P_c) of 40
18 MPa at room temperature (~ 19.5 °C), while pore pressure downstream (P_{down}) was set
19 to 9.5 MPa. Because the experiment was performed under constant flow conditions,
20 pore pressure upstream (P_{up}) was not constant and, on average, it attained a value of
21 11 ± 1 MPa during the experiment. The pore pressure difference up- and downstream
22 ($\Delta P_p = P_{up} - P_{down}$) of the sample, temperature (T), and axial (ϵ_a) and radial (ϵ_r) strains
23 were measured every second. Electrical resistivity was systematically measured at
24 least every one sample pore volume (1PV ~ 10 ml) time of flow-through.

1 During the drainage stage of the experiment the volume fraction of CO₂ ($X_{CO_2} =$
2 $V_{CO_2} / (V_{CO_2} + V_{H_2O})^{-1}$; being fraction of brine $X_w = 1 - X_{CO_2}$) was increased from 0 to 1 in
3 0.2 X_{CO_2} units, stepwise. For the imbibition, we set up a continuous flow-through with
4 brine. From Batzle and Wang (1992) relationships, the density and viscosity for CO₂
5 are 864 kg m⁻³ and 8.64 10⁻⁵ Pa s, respectively, and 1026 kg m⁻³ and 1.084 10⁻³ Pa s
6 for the brine, for the physicochemical (*P-T*-salinity) conditions imposed in the test. We
7 imposed a condition of maximum $\Delta P_p = 2$ MPa, to keep CO₂ viscosity and density
8 variations across the sample below 5%. To satisfy this condition, in the beginning of
9 each flow-through episode the total flow ($Q_{T,IL} = Q_w + Q_{CO_2}$; the subscript 'IL' refers to
10 flow inlet) was regulated between 0.1 and 0.5 mL min⁻¹ (accepted values for field flow
11 rates (Berg et al., 2013)), and kept constant until the next episode.

12 The injection of pure fluids (either brine or CO₂) was possible with dedicated
13 pumps and the fluid transfer vessels described above. To inject the mixed fluid we
14 used a ~4.5 m of 1/16" stainless steel high pressure tubing (0.1651 mm ID). The length
15 of the pipe coupled with its inner surface roughness and its sinuosity (coil-type)
16 enhance homogeneous mixing and sufficient time of interaction (El-Maghraby et al.,
17 2012; Farajzadeh et al., 2009). The reciprocal solubilities of CO₂ and brine for the
18 physicochemical conditions prevailing in the test are ~6.8 vol.% CO₂ in brine, and <
19 0.1 vol.% brine in CO₂ (Canal et al., (2013), based on the equations of Duan et al.
20 (2006)). Considering these values, the actual X_{CO_2} and X_w were corrected by
21 subtracting the corresponding dissolved mass components, whereas the criterion for
22 steady state was assumed by the condition of corrected inflow equal to outflow
23 (Dullien, 1992).

24

1 3. Permeability, electrical resistivity and degree of saturation

2 3.1. Absolute and relative permeability

3 The absolute permeability (k_{abs}) to brine was calculated at the initial brine-CO₂
4 flow episode ($X_w = 1$) before starting CO₂ injection. During this period the sample was
5 completely saturated with brine. k_{abs} was derived using the steady-state flow method
6 based on Darcy's law:

$$k_{\text{abs}} = \frac{\mu QL}{\Delta P_p A}, \quad (1)$$

7 where μ is the dynamic viscosity of the fluid (Pa s), Q is the volumetric flow rate (m³ s⁻
8 ¹), ΔP_p is the pressure drop across the sample (Pa), A and L are the cross sectional
9 area (m²) and the length (m) of the sample, respectively.

10 We calculated relative permeability to brine and CO₂ (denoted hereafter as $k_{r,w}$
11 and k_{r,CO_2} , respectively) by simultaneously circulating both fluids (with different volume
12 ratios) at controlled pore pressure and flow rates, using a two-phase multiphase flow
13 system (Dullien, 1992):

$$k_{r,i}(S_i) = \frac{\mu_i Q_i L}{\Delta P_p A k_{\text{abs}}} \quad (2)$$

14 In Eq. (2), the relative permeability of each phase (denoted with the subscript i)
15 is a function of their partial contribution to the total saturation, inferred from the
16 electrical resistivity of the sample as explained below. Partial fluid mobility is controlled
17 by the relative permeability of each fluid phase.

18

19 3.2. Two-phase relative permeability models

20 Multiphase flow properties are needed to characterize the mobility of the CO₂
21 plume, the injection pressure, the extent of the residual CO₂ trapping and the far-field
22 pressure distribution (Krevor et al., 2012; Müller, 2011).

1 Several empirical relationships for relative permeability in multiphase systems
2 have been developed. The Brooks-Corey's model is the one more generally used to
3 describe relative permeability curves in water-CO₂ systems (e.g., Krevor et al. (2012),
4 Bachu (2013)), although the Corey's (Corey, 1954), Purcell's (Purcell, 1949) or van
5 Genuchten's (van Genuchten, 1980) models are also applied (e.g. Li and Horne
6 (2006), Oostrom et al. (2016)). Multiphase flow simulators such as TOUGHREACT
7 (Xu et al., 2017), ICSSM (Shi et al., 2007) or METSIM2 (Shi et al., 2011), use van
8 Genuchten and Corey models to solve relative permeabilities to water and gas,
9 respectively.

10 Purcell's model tends to give better fits for the wetting phase, while Corey's and
11 Brooks-Corey's models seem to be appropriate for both phases (Li and Horne, 2006).
12 Based on this, we compare our experimentally obtained relative permeability curves
13 to those from the modified version of Brooks-Corey in Krevor et al. (2012) for the
14 wetting (brine) and non-wetting (CO₂) phases, with the Purcell and van Genuchten
15 models for the wetting phase, and the Corey model for the non-wetting. These models
16 use the normalized water saturation (S_w^*) to calculate the relative permeability:

$$S_w^* = \frac{S_w - S_{wr}}{S_e}, \quad (3)$$

17 where S_w is the degree of water saturation, S_{wr} is the residual water saturation, and S_e
18 is the effective saturation, that is, the saturation in the sample within the range which
19 is still available to be saturated. For drainage $S_e = 1 - S_{wr}$, while for imbibition $S_e = 1 -$
20 $S_{wr} - S_{CO_2r}$, where S_{CO_2r} is the residual CO₂ saturation. At S_{wr} , the relative permeability
21 to CO₂ is maximum. During imbibition, as water saturation increases, k_{r,CO_2} decreases
22 until it reaches its minimum at S_{CO_2r} . The equations and parameters of each model are
23 presented in Table 2.

1 **Table 2.** Relative permeability models (A: Purcell (1949); B: Corey (1954); C: Krevor
 2 et al. (2012); D: van Genuchten (1980)). In models A and D, λ is the pore size
 3 distribution index; in model C, N_w and N_{CO_2} are the Corey exponents for the wetting
 4 and non-wetting phase, respectively. See the text for explanation of other parameters.

Models	Wetting phase (brine, $k_{r,w}$)	Non-wetting phase (CO ₂ , k_{r,CO_2})
Purcell (A)	$k_{r,w} = (S_w^*)^{\frac{2+\lambda}{\lambda}}$	
Corey (B)		$k_{r,CO_2} = (1 - S_w^*)^2 [1 - (S_w^*)^2]$
Brooks-Corey (C)	$k_{r,w} = (S_w^*)^{N_w}$	$k_{r,CO_2} = k_{r,CO_2}^{\max} (1 - S_w^*)^2 [1 - (S_w^*)^{N_{CO_2}}]$
van Genuchten (D)	$k_{r,w} = \sqrt{S_w^*} \left[1 - (1 - S_w^{*1/\lambda})^\lambda \right]^2$	

5

6 3.3. *Electrical resistivity*

7 Archie's first and second laws (Archie, 1942) allow to relate electrical resistivity
 8 to brine saturation in variably saturated clean (clay-free) reservoir rocks (Mavko et al.,
 9 2009). Archie's first law relates the formation factor of the rock, F_0 , to the porosity (ϕ)
 10 of the porous medium when fully saturated, as follows:

$$F_0 = \frac{R_0}{R_w} = \phi^{-m}, \quad (4)$$

11 where R_0 and R_w are the resistivities of the (fully saturated) rock and pore fluid,
 12 respectively, and m the cementation exponent.

13 Archie's second law extends the previous relationship to partially saturated
 14 rocks, through the following expression:

$$S_w = \left(\frac{R_w}{\phi^m R_b} \right)^{1/n}, \quad (5)$$

15 where R_b is the bulk electrical resistivity of the rock, and n is the saturation
 16 exponent. The empirical exponents m and n usually adopt values close to 2 for

1 sandstones (Mavko et al., 2009). This relationship is useful to describe fluid
2 substitution in brine-CO₂-rock systems initially saturated with the conducting fluid
3 (brine), where the resistivity increases when brine is replaced by the non-conductive
4 CO₂ phase. CO₂ saturation (S_{CO_2}) is computed as the reciprocal of brine saturation
5 (i.e., $S_{CO_2} = 1 - S_w$).

6 For a reservoir with low chemical reactivity to CO₂ (e.g., silicic sandstones), R_w
7 can be assumed to be constant. Then, we can normalize the bulk resistivity in terms
8 of partial formation factors (F_i), as follows:

$$F = \frac{F_0}{F_i} = \frac{R_0}{R_b} = S_w^n, \quad (6)$$

9 Our normalized formation factor F is the inverse of the resistivity index (e.g.,
10 Dullien (1992)). Using Eq. (6), the S_w in the conventional relative permeability curves
11 can be directly replaced by the measured property (F), by adjusting the saturation
12 exponent n (e.g., Li (2008)). In this contribution, we analyse our experimental results
13 from this angle, assuming that the system remains chemically non-reactive to CO₂-
14 brine-rock interaction, so that the bulk electrical resistivity of the rock is solely function
15 of the partial saturation of each fluid phase in the porous medium.

16 Some models account for the excess of conductivity induced by the presence of
17 clay minerals by introducing an additional term into Archie's law (Mavko et al., 2009).
18 However, here we neglect this effect due to the practical absence of clays, which is
19 limited to the kaolinite used to make the rock and practically consumed in the
20 manufacturing process (Tillotson et al., 2012).

21

1 4. Results

2 Pore pressure difference (ΔP_p) progressively increases (the pressure upstream,
3 P_{up} , goes up; the pressure downstream, P_{down} , remains constant) as the volume
4 fraction of CO₂ (X_{CO_2}) increases (Figure 2), during the first two fractional flow episodes
5 (up to $X_{CO_2} = 0.4$). Thereafter, the inlet flow rate ($Q_{T,IL}$) is reduced by 50% down to
6 0.25 mL min⁻¹ to satisfy our imposed condition of $\Delta P_p < 2$ MPa and keep the CO₂
7 variations in density and viscosity below 5% across the sample. The reduction in the
8 inlet flow rate decreases the ΔP_p for the next three drainage episodes. During
9 imbibition, we imposed the same flow rate as that used during the first ($X_{CO_2} = 0$)
10 injection episode (i.e. 0.5 mL min⁻¹). However, ΔP_p is higher during imbibition than
11 during the original drainage (100% brine) episode (i.e., more energy required to flow-
12 through), which can be related to the presence of a residual CO₂ fraction in the porous
13 medium. During drainage, the presence of CO₂ increases the data dispersion of the
14 resulting flow downstream ($Q_{T,OL}$; the subscript 'OL' refers to flow outlet), which
15 decreases towards the end of each episode, eventually satisfying the condition $Q_{T,OL}$
16 = $Q_w + Q_{CO_2}$ (after discounting mutual phases dissolution fractions).

17 Assuming a good gauge-rock function during the test (i.e., no visual damage
18 evidences), volumetric strain (ϵ_v) was inferred from axial (ϵ_a) and radial (ϵ_r) strains (ϵ_v
19 = $\epsilon_a + 2\epsilon_r$). We observe no significant changes in the dimensions of the sample during
20 the major part of the experiment, although some axial and minor radial increase were
21 recorded after attaining $X_{CO_2} = 0.6$. At the end of the experiment, the maximum
22 volumetric strain computed reached ~0.13% (i.e., axial and diametrical enlargement
23 of ~0.06 and ~0.025%, respectively; Figure 2). At the sample scale, that corresponds
24 to an apparent swelling of ~12 μ m in both the axial and diametric directions. Strains

1 remained constant during imbibition. The magnitude of the swelling is small and rather
2 intriguing, considering the significant confining pressure and nearly constant (average)
3 pore pressure conditions, and the absence of swelling minerals.

4 The resistivity gradually increases with CO₂, by ~300% at the end of the $X_{CO_2} =$
5 0.8 episode (Figure 2). Then, the sharpest increase (~500%) occurs with pure CO₂
6 flowing through the sample ($X_{CO_2} = 1$), indicating that high CO₂ saturations are needed
7 to effectively block the conductive connections. This behaviour is different to the
8 gradual transition reported by Falcon-Suarez et al. (2017) for a sample with
9 homogeneous pore shapes. During imbibition, brine partially refills the pore space and
10 resistivity drops down to ~10% above its original value, likely related to CO₂ trapping
11 in the porous medium.

12

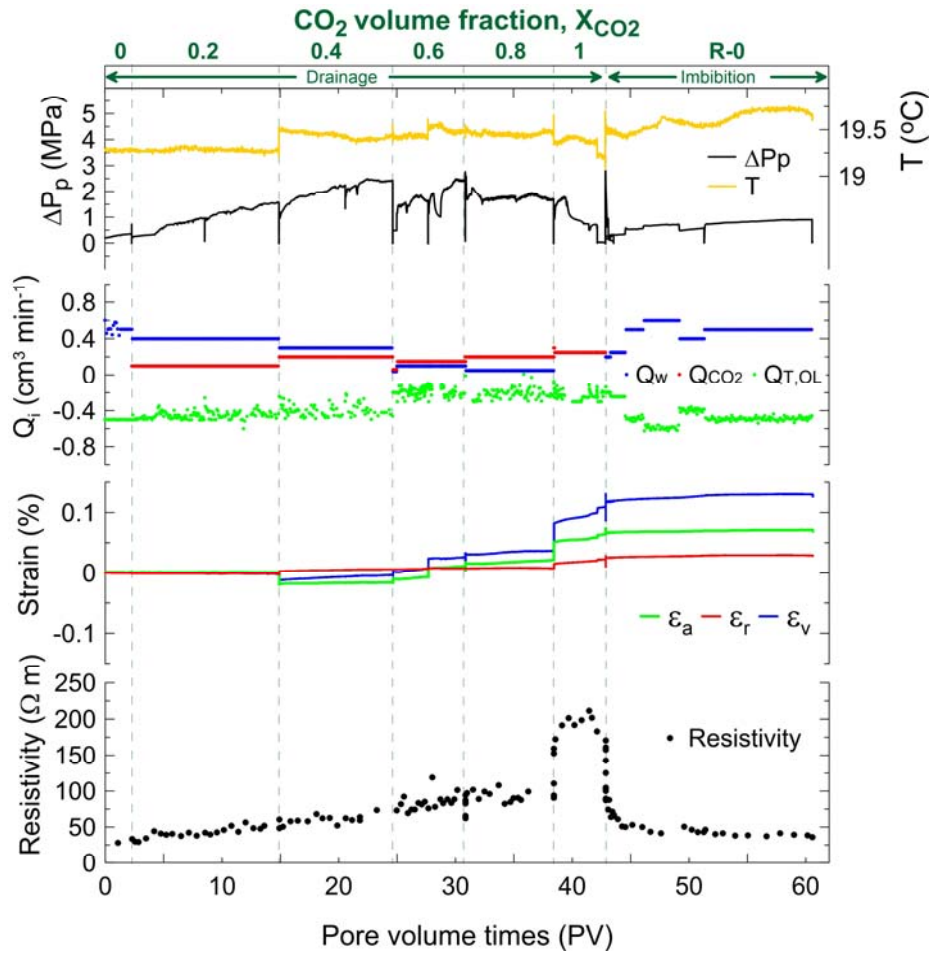


Figure 2. Brine-CO₂ flow-through test on 45A synthetic sandstone with a controlled distribution of non-connected fractures. Pore pressure difference (ΔP_p), temperature (T), partial flows for CO₂ (Q_{CO_2}), brine (Q_w) set upstream and the resulting fluid flow outlet ($Q_{T,OL}$) downstream, axial, radial and volumetric strains (ϵ_a , ϵ_r and ϵ_v , respectively), and electrical resistivity for seven consecutive brine-CO₂ injection stages denoted as volume fractions of CO₂ (X_{CO_2} , see text for details), covering six drainage (from $X_{CO_2} = 0$ to $X_{CO_2} = 1$) and a forced imbibition ($X_{CO_2} = R-0$) episodes, plotted versus pore volume (PV). Vertical dashed lines separate consecutive brine-CO₂ stages. Notice that we only show effective flow time; interludes between two consecutive episodes are omitted. The duration of the interludes varied from one episode to the next, as follows: $X_{CO_2,[0-0.2]}$ ~ 0.1 h; $X_{CO_2,[0.2-0.4]}$ ~ 15 h; $X_{CO_2,[0.4-0.6]}$ ~ 0.1 h; $X_{CO_2,[0.6-0.8]}$ ~ 13 h; $X_{CO_2,[0.8-1]}$ ~ 13 h; and transition from drainage to imbibition, $X_{CO_2,[1-R-0]}$, ~ 40 h.

1 5. Data assessment

2 5.1. Relative permeability versus resistivity

3 Both the wetting (brine) and non-wetting (CO₂) phase curves (Figure 3) fit power-
4 functions of the form $k_{r,i} = aF^b$, where a and b are the fitting parameters (Table 3) and
5 the subscript i denotes the fluid phase. The relative permeability curves estimated by
6 Purcell (P), Brooks-Corey (BC) and Van-Genuchten (vG) models for the wetting
7 phase, and by Corey (C) and Brooks-Corey (BC) models for the non-wetting phase,
8 were obtained (sample 45A; Table 3) by using $S_w = F^{1/n}$ with a saturation exponent n
9 of 2, a value commonly accepted for sandstones (Mavko et al., 2009).

10 For the wetting phase, Brooks-Corey and Purcell models are in a better
11 agreement with our experimental data than the van Genuchten model; for the non-
12 wetting phase, only Brooks-Corey model fits reasonably well (Figure 3). Nonetheless,
13 differences between the theoretical models and the experimental fits can be related to
14 the heterogeneous distribution of pore shapes in our sample, an aspect neglected by
15 these models (Müller, 2011).

16 The crossing point of the relative permeability curves (i.e., $k_{r,CO_2} = k_{r,w}$) is a
17 function of the wettability of the sample (Reynolds, 2016). In our experiment, it occurs
18 at $F \sim 0.23$ (Figure 3), equivalent to $S_{CO_2} \sim 0.52$, which suggests that the non-wetting
19 phase preferentially adheres to the grain surface (Reynolds et al., 2018). The
20 extremely low k_{r,CO_2} end-point also suggests low mobility, which may be indicating
21 either a high IFT between CO₂ and brine and/or a pore structure less favourable for
22 uniform displacement (Bennion and Bachu, 2006). The imbibition data evolution in
23 Figure 3 reflects that the formation factor increases with very low relative permeability
24 variations. Since the injected brine is unsaturated in CO₂, this trend would be indicating

- 1 fast CO₂ dissolution (< 3 PV, equivalent to < 1 h at the experimental conditions; Figure
- 2 2) until the residual CO₂ saturation is achieved ($S_{CO_2,r} \sim 0.15$).
- 3

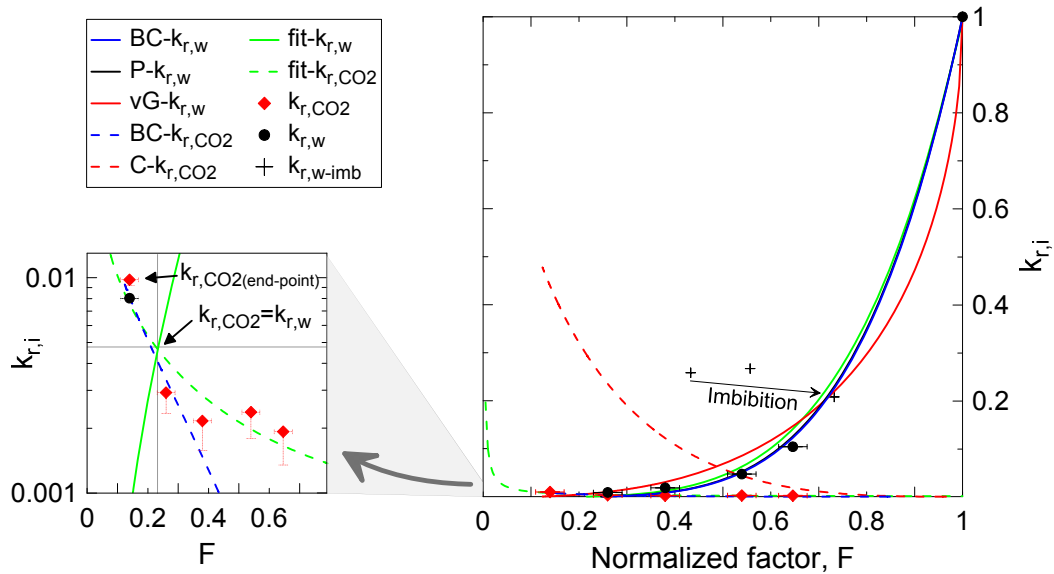


Figure 3. Brine-CO₂ relative permeability ($k_{r,i}$) versus normalized formation factor (F), from drainage (dots for $k_{r,w}$; diamonds for k_{r,CO_2}) and imbibition (crosses for $k_{r,w-imb}$; the arrow labelled “imbibition” indicates the data evolution) experimental data for the fractured synthetic sandstone. The graph includes the best fit curves for the wetting (fit- $k_{r,w}$) and non-wetting (fit- k_{r,CO_2}) phases based on the experimental data, together with the best fit curves for Brooks-Corey (BC- $k_{r,w}$), Purcell (P- $k_{r,w}$) and van Genuchten (vG- $k_{r,w}$) models for the wetting phase, and Brooks-Corey (BC- k_{r,CO_2}) and Corey (C- k_{r,CO_2}) models for the non-wetting phase, with best-fit parameters given in Table 3. The inset plot shows the crossing point for $k_{r,w}$ and k_{r,CO_2} based on the experimental data. The error cross bars arising from the experimental data correspond to the uncertainty propagation from the electrical resistivity measurements (horizontally) and the CO₂ dissolution and viscosity variations across the sample in the relative permeability (vertically).

- 4
- 5 The specific dimensions of the sample, together with the experimental procedure
- 6 applied, may be affecting our observations. We expect significant capillary end effects
- 7 (Leverett, 1941) because of the low length-to-diameter ratio (slenderness) of our rock

1 sample, which result in heterogeneous pore pressure and fluid distributions across the
2 plug. Based on the characterization developed by Jackson et al. (2018), neglecting
3 this boundary effect can lead to a crossing point underestimation of up to one order of
4 magnitude in relative permeability and ~5% in saturation, for our experimental
5 conditions. This aspect limits the extrapolation of our observations regarding the
6 fractures effect on fluid mobility and CO₂ storage capacity to samples with similar
7 geometric characteristics tested at similar experimental conditions.

8 We compare our results to those obtained from three previous experiments
9 (Falcon-Suarez et al., 2017, 2016; Papageorgiou et al., 2018) performed with non-
10 fractured synthetic sandstones using a similar experimental approach. The datasets
11 of these tests are available at the <http://www.bgs.ac.uk/discoveryMetadata/>. These
12 synthetic sandstones were made using similar manufacturing conditions and materials
13 to those employed in this study, but with variable sand-to-cement ratios.
14 Consequently, the resulting samples S026 (Falcon-Suarez et al., 2016), S038 (Falcon-
15 Suarez et al., 2017) and S045 (Papageorgiou et al., 2018), have different porosities
16 (0.26, 0.38 and 0.45, respectively) and permeabilities (1, 50 and 500 mD,
17 respectively). Considering that all samples have the same grain size and that they
18 were subjected to the same consolidation during manufacturing, the pore size
19 distribution of the three non-fractured samples should be similar but with different
20 cumulative distribution (Falcon-Suarez et al., 2019). Then, the main difference in terms
21 of transport properties should be the presence of fractures. All the experiments were
22 performed at the same brine salinity (35 g L⁻¹ NaCl). The main differences with respect
23 to our test are the temperature, which was set above 31 °C and the variable pore
24 pressure from 7 to 12 MPa (seeking for supercritical-CO₂ conditions). The latter
25 condition caused significant data scattering in the relative permeability values (Falcon-

- 1 Suarez et al., 2016). Also, although the three experiments present drainage episodes,
- 2 imbibition is only available for S038 (Falcon-Suarez et al., 2017).

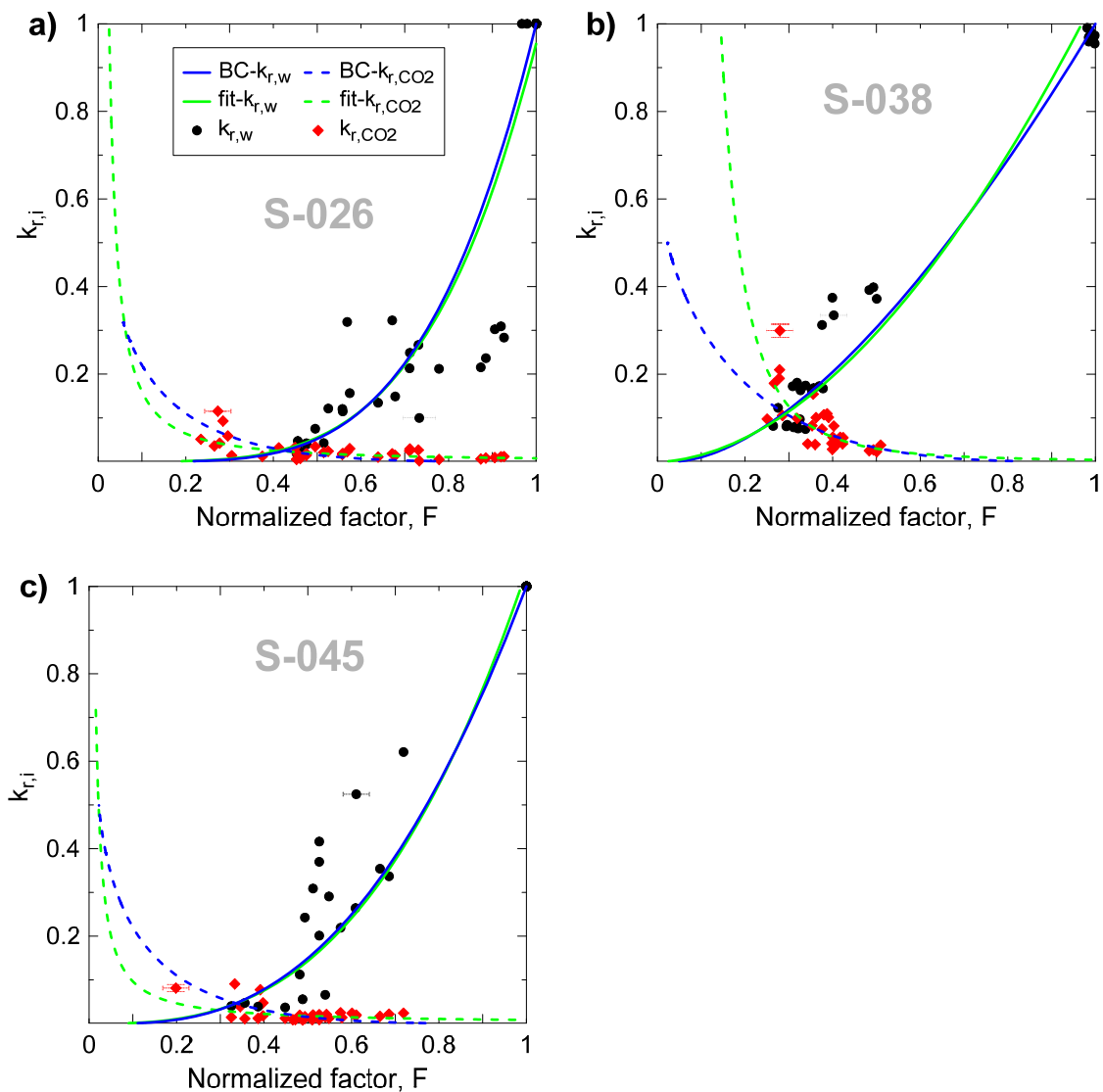


Figure 4. Brine-CO₂ relative permeability ($k_{r,i}$) versus normalized formation factor (F). Experimental data for the brine ($k_{r,w}$) and CO₂ (k_{r,CO_2}) phases for the three non-fractured synthetic sandstones: (a) S026; (b) S038; (c) S045 (Falcon-Suarez et al., 2017, 2016; Papageorgiou et al., 2018). The plot includes the best fit curves for the wetting (fit- $k_{r,w}$) and non-wetting (fit- k_{r,CO_2}) phases based on the experimental data, together with the best fit curves for Brooks-Corey for the wetting (BC- $k_{r,w}$) and non-wetting phases (BC- k_{r,CO_2}), with best-fit parameters given in Table 3. To facilitate the visualization, only one error cross bar is displayed: The horizontal bar covers the error associated with the electrical resistivity; the vertical bar, the influence of the (neglected) dissolved CO₂ in the relative permeability.

1 As above, we fit the data using power-functions of the kind $k_{r,i} = aF^b$ for both the
 2 wetting and non-wetting phases (Table 3 and Figure 4). Based on the results obtained
 3 for the fractured sample, we only account for Brooks-Corey to fit the non-fractured
 4 samples data. For S038 and S045 the measured relative permeabilities are higher
 5 than those from the models for intermediate F values (within the range 0.35 - 0.75).

6 **Table 3.** Fitting parameters for Brooks-Corey (BC), Purcell (P) and van Genuchten
 7 (vG) models for the fractured sample (45A), the BC for the three non-fractured
 8 samples (S026, S038, S045), and power-function experimental fitting for the four
 9 samples.

*Fitting parameters	Fractured sample		Non-fractured samples					
	45A	S026	S038	S045				
Brooks-Corey								
N_w	7.5	7	2.8	4.5				
N_{CO_2}	0.1	0.7	1.8	0.7				
Purcell								
λ_P	0.3							
van Genuchten								
λ_{vG}	0.55							
BC, P, vG								
S_{wi}	0.1							
k_{r,CO_2}	0.4							
Experimental fit ($k_{r,w} k_{r,CO_2}$)								
a	0.95	1×10^{-3}	0.97	3×10^{-3}	1.05	7×10^{-5}	1.05	1×10^{-3}
b	4.02	1.38	4.13	-2.30	1.84	-6.82	2.87	-3.48
R^2	0.97	0.27	0.91	0.26	0.90	0.70	0.88	0.30

10 * The values were derived from an iterative, error constrained least square fitting.

11

12 5.2. Hydrodynamic modelling

13 In Falcon-Suarez et al. (2017), the geochemical analysis of the pore fluid
 14 revealed a gradual reduction of the major cation Na with increasing CO_2 , interpreted
 15 as salt precipitation phenomena during CO_2 -injection. To assess the hydrodynamics

1 of our test, including potential CO₂-induced salt precipitation/dissolution effects, we
2 performed a 2D axisymmetric radial numerical simulation of our experiment using
3 TOUGHREACT v3.3 code (Xu et al., 2017). TOUGHREACT is a non-isothermal
4 reactive transport code that introduces reactive chemistry into the existing multi-phase
5 fluid and heat flow code TOUGH2 (Xu et al., 2017, 2004). TOUGHREACT uses a fluid
6 property module called ECO2N designed for applications to CO₂ storage in saline
7 aquifers (Pruess, 2005). This module reproduces fluid properties of H₂O-NaCl-CO₂
8 mixtures under temperature, pressure and salinity conditions typically encountered in
9 storage reservoirs of interest ($10^{\circ}\text{C} \leq T \leq 100^{\circ}\text{C}$; $P \leq 60 \text{ MPa}$; salinity up to halite
10 saturation). Here, we consider that the system is chemically non-reactive to CO₂-brine-
11 rock interaction and only solve the multiphase fluid transport processes (find the
12 details of the modelling in Appendix A).

13 CO₂ extends laterally and vertically from the injection point, and after the first
14 CO₂ injection episode ($X_{\text{CO}_2} = 0.2$), the upward migration of CO₂ occurs quickly and
15 S_{CO_2} reaches ~ 0.15 . The maximum S_{CO_2} of ~ 0.35 is achieved after the last drainage
16 episode ($X_{\text{CO}_2} = 1$) (Figure 5). The model reported no evidences of salt precipitation at
17 the experimental conditions. The maximum S_{CO_2} obtained in the model ($S_{\text{CO}_2} \sim 0.35$)
18 significantly differs from that estimated from electrical resistivity, $S_{\text{CO}_2} \sim 0.55$. From this
19 20% difference, the combined effect of the resistivity error and the empirical saturation
20 factor ($n = 2$) used for the conversion (see above) could explain $\sim 10\%$ variability in
21 saturation. The remaining 10% could be related to the pore fabric of the rock. Since
22 the model does not reproduce the non-connected fractures, we interpret this 10%
23 represents CO₂ preferentially trapped in the fractures (see discussion below).

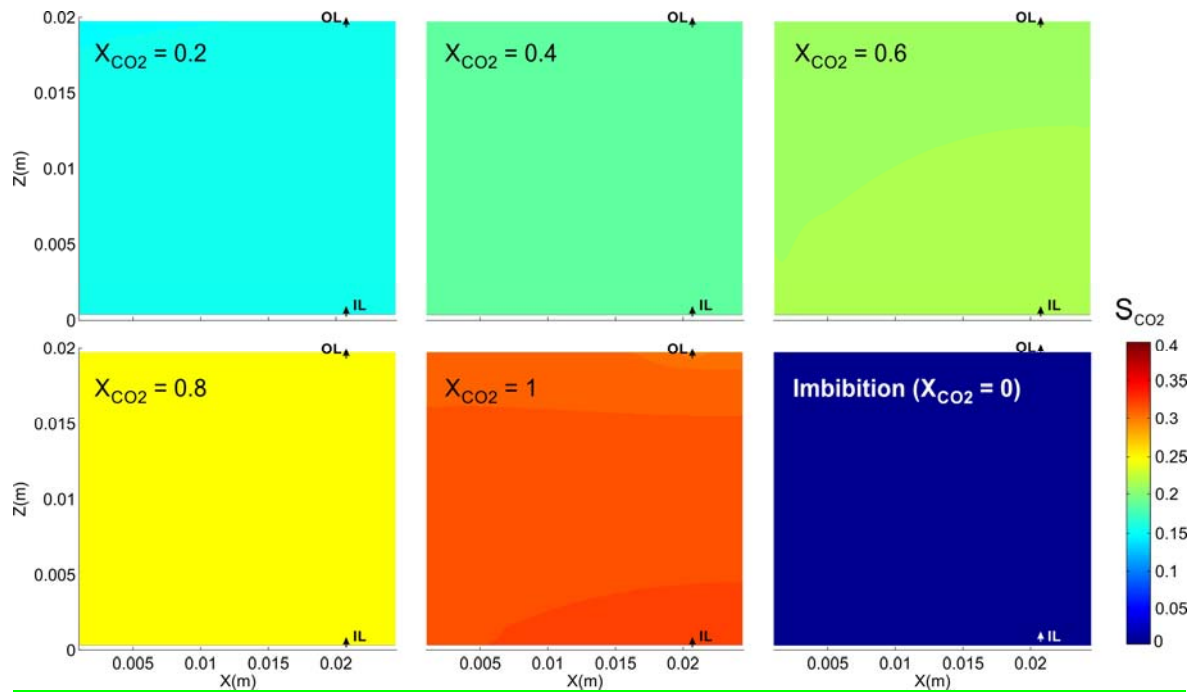


Figure 5. Distribution of CO₂ saturations (S_{CO_2}) within the sample after five drainage episodes (from $X_{CO_2} = 0.2$ to $X_{CO_2} = 1$). For the first drainage episode and imbibition ($X_{CO_2} = 0$ in both cases) the sample was fully saturated in brine. The horizontal (x) and vertical (z) axis are the sample radius and thickness, respectively. The symmetry axis of the sample is placed at $x = 0$, and the flow inlet (IL) and outlet (OL) points are ~ 21 mm far from it, at the bottom and the top of the sample, respectively.

1

2 6. Discussion

3 6.1. Hydro-mechanical interpretation

4 The reactivity of our synthetic sample is very low, but may be able to induce an
 5 increase in porosity and permeability (Hangx et al., 2015). Post-test porosity (ϕ) and
 6 gas permeability ($k_{gas,f}$) were measured after a week of immersion in DIW; porosity
 7 increased from 0.273 to 0.296 ($\sim 8\%$ increment) and permeability increased from 5.5
 8 to 12.1 mD ($\sim 54\%$ increment). These changes indicate rock weathering during the
 9 flow-through experiment, linked to the dissolution of mineral phases or to mechanical
 10 damage associated with crack propagation; probably both (e.g., Hangx et al., 2015).

1 In principle, the low-concentrated (10% HCl) acid solution used originally for
2 dissolving aluminium disks in the sample to create the fractures, should have had a
3 minor effect on the rock matrix, composed by quartzose grains and silica cement.
4 However, this sample was previously used to study stress-induced changes and
5 partial saturations effects on ultrasonic properties of fractured media (Amalokwu et al.,
6 2015; Tillotson et al., 2012). The variable stress history applied in those experiments
7 may have also contributed to develop localized weak points in the microstructure,
8 resulting in grain-to-grain bounds weakening from one test to the next, explaining the
9 porosity and permeability variations.

10 To characterize the microstructure of the sample, we segmented it into smaller
11 portions to obtain two oriented thin sections: normal and parallel to the dip direction of
12 the cracks (Figure 6). The thin sections reveal distinct stress-induced features. For
13 instance, section A-A" (Figure 6b), which represents the dip direction of the crack,
14 illustrates that, locally, the major axis of the crack ellipsoid has been enlarged by a
15 factor of 2 with respect to its original nominal size. This effect might be attributed to Al-
16 disk overlapping during the manufacturing process (Tillotson et al., 2012), but also to
17 crack propagation. Eventhough the cracks have grown, they remain non-connected.
18 This observation suggests the permeability changes from before to after the test are
19 not related to flow paths enhancement, or at least they would be very difficult to explain
20 using a continuum media approach (Lee et al., 1999). Grain scale arching effects are
21 also present (Figure 6c), indicating local heterogeneous load distribution (Falcon-
22 Suarez et al., 2019). We also observe that some small-scale horizontal cracks appear
23 to have formed at or close to the crack tips (Figure 6b).

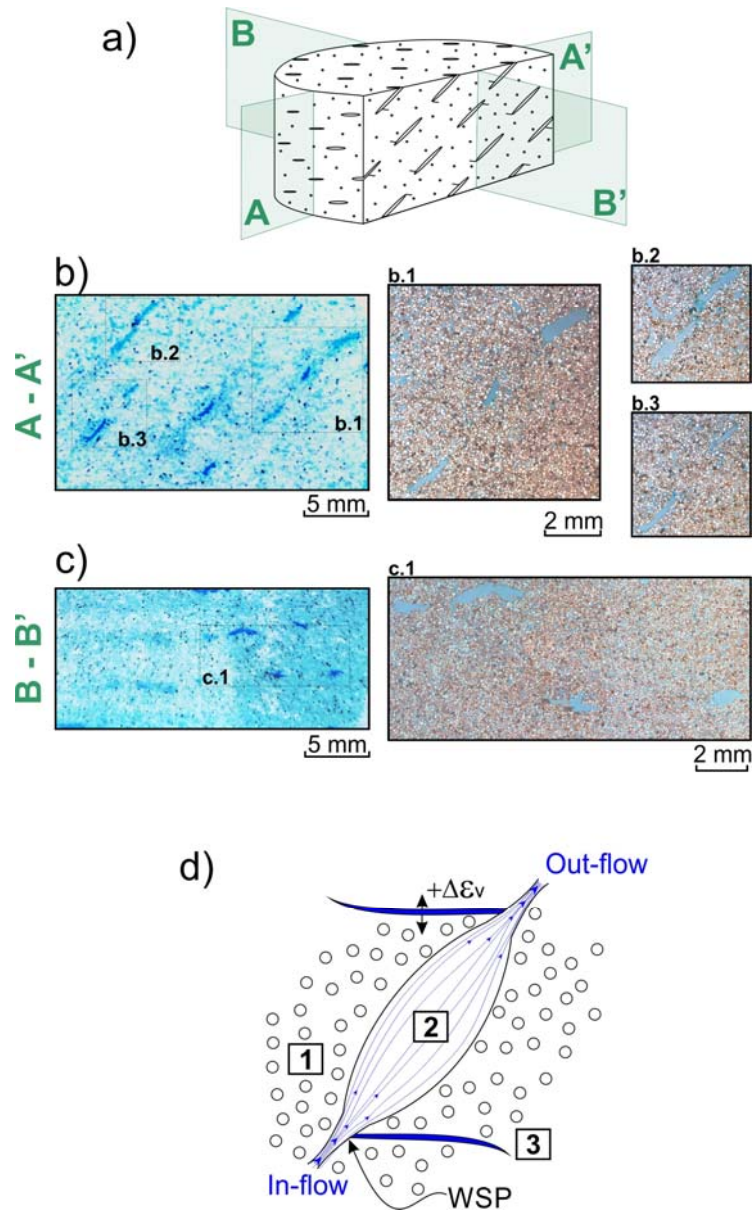


Figure 6. (a) Schematic of the synthetic sample with a controlled distribution of non-connected fractures aligned at 45° from its axis. (b) Thin section parallel to fracture dip and (c) thin section perpendicular to fracture plane. (d) Conceptual model of the porous medium, consisting of three different pore families: (1) porosity, (2) aligned penny-shape fractures, and (3) microcracks.

1

2 Based on the previous observations, we describe a conceptual model for brine-
 3 CO₂ multi-flow through non-connected fractured rocks (Figure 6d). The model
 4 identifies three pore families: (1) intergranular space (i.e., catenary pores); (2) non-

1 connected, aligned penny-shaped voids or isolated cracks; and (3) microcracks,
2 associated with stress-variations from the original formation properties.

3 The dimensions and distribution of the fractures, and the matrix porosity were
4 prescribed by the manufacturing process. However, additional microcracks could have
5 been also generated during block coring and/or along the various stress-paths to
6 which the plug was submitted prior to our experiment (Amalokwu et al., 2015; Tillotson
7 et al., 2012). Abrupt geometric changes, such as the transitions between pores and
8 fractures (Pollard and Aydin, 1988), may cause a localized increase in stress. At these
9 weak structural points (WSP, Figure 6d), microcracks are also prone to develop and
10 propagate when the level of stress reaches the critical strength of the material.

11 The observed volumetric deformation ($\sim 0.12\%$) is within the 0.7% porosity
12 fraction commonly attributed to microcracks (Fortin et al., 2007). Microcracks partially
13 close during loading as the confining stress is gradually increased (Fjaer et al., 2008).
14 When the sample is originally saturated in brine, the microcracks turn into capillary
15 fringes while closing. If the closure process is incomplete, then the brine in the capillary
16 fringes remains immobile during CO₂ injection, due to the high surface tension of the
17 wetting phase (Kim et al., 2013). Then, effective stress changes within the sample
18 could explain the strain evolution observed during the test.

19 During CO₂ injection, when pore pressure increases for a constant confining
20 stress, the drop in effective stress may result in rock dilatancy and crack movement.
21 The former can explain the axial strain increase, while the latter would lead to a more
22 complex deformation pattern, preferentially affecting the radial deformation. For
23 hydrostatic stress conditions the orientation of our artificial cracks (45°) should be
24 adequate to compensate in an equally proportioned way the fluctuations in pore
25 pressure. However, misalignments in the manufacturing process may have result in

1 crack orientation at angles different to 45° that could lead to variable stress
2 concentration effects along the sample, and eventually to radial strain increase.

3

4 *6.2. Effects and implications of non-connected fractures in CO₂ storage reservoirs*

5 A number of methods have been developed to measure the wettability of a rock-
6 fluid system (Castillo et al., 2011). Among them, relative permeability curves can be
7 used to qualitatively assess strong changes in wettability, although minor differences
8 may remain unnoticed (Dandekar, 2013). Our fractured sample (45A) shows a relative
9 permeability cross point at $F \sim 0.23$ (Figure 3), which may be indicating a weaker water-
10 wet behaviour than the non-fractured samples (S026, S038 and S045) with F values
11 within the range of 0.32-0.38 (Figure 4). This observation suggests the pore
12 morphology may affect the wettability of the sample, although the differences between
13 the cross points may be insufficient to guarantee this behaviour. The residual trapping
14 is also indicative of wettability. Our data for residual trapping are only available for
15 samples S038 (Falcon-Suarez et al., 2017) and 45A, with $S_{CO_2r} \sim 0.16$ and ~ 0.15 ,
16 respectively. These two close values would indicate similar wettability in both cases,
17 although the lack of imbibition data for S026 and S045 limit any further interpretations.

18 Although water-wet rocks are desirable CO₂ reservoirs, the degree of trapping
19 also depends on other aspects besides wettability, such as pore to throat size ratio,
20 connectivity and flow rate. The pore scale physics of trapping is governed by the
21 competition between snap-off of wetting layers and piston-like advance (Krevor et al.,
22 2015). During piston-like filling, a displacing phase progressively fills the pores and
23 throats, gaining space over the other phase and forcing it to exit the pore space. Snap-
24 off occurs as the wetting phase on the pore wall and corners swells and separates two
25 pores filled with the non-wetting phase, disconnecting and trapping the non-wetting

1 phase in the centre of the pores. This process only occurs if the movement of the
2 wetting phase is prevented by very large pores (Krevor et al., 2015), as in our 45A
3 sample. Accordingly, we interpret that the poorly connected fracture network of our
4 45A sample facilitates the isolation of the non-wetting phase and benefits the CO₂
5 trapping in the porous medium, when compared to non-fractured samples.

6 The data of the four samples compared here were obtained from experiments
7 performed at the same brine salinity (35 g L⁻¹ NaCl), but different *P-T* conditions. The
8 mean pore pressure observed in the 45A test (i.e., $P_p = 11 \pm 1$ MPa) is within the upper
9 P_p range (7 to 12 MPa) applied for the tests performed on the three non-fractured
10 samples S026, S038 and S045 (Papageorgiou et al., 2018). Therefore, the most
11 significant difference between experiments is the temperature: room temperature at
12 19 °C for the 45A sample, 35 °C for S026 and S045, and 32 °C for S038 (i.e.,
13 supercritical CO₂ conditions for the non-fractured samples). Hence, a relatively lower
14 water wettability might be expected in the 45A sample because the temperature
15 difference between experiments would decrease the CO₂-brine interfacial tension by
16 ~15% (Bachu and Bennion, 2009). The higher IFT of the non-fractured samples would
17 lead to increase the convexity of the relative permeability curves (Bachu and Bennion,
18 2008), and to lower the endpoint relative permeability value (Bennion and Bachu,
19 2006). However, we observe the contrary, which suggests the IFT might have a minor
20 effect on our results.

21 The end-point relative permeability to CO₂ significantly controls injectivity
22 (Yoshida et al., 2016). The extremely low k_{r,CO_2} in the 45A sample suggests that the
23 presence of fractures is affecting the mobility of the individual phases (brine and CO₂),
24 when compared to the non-fractured samples. This interpretation agrees with the
25 observations reported by Reynolds and Krevor (2017), of CO₂ preferentially filling high

1 porosity layers in heterogeneous cores. In our experiment, in essence, the lower
2 capillary entry pressure of the large pores (fractures) benefits the displacement of the
3 wetting phase by the non-wetting one, allowing the CO₂ to fill the large fractures,
4 preferentially. During imbibition, the CO₂ would remain trapped in the fractures due to
5 their lower capillary pressure, provided that they are non-connected.

6 With certain limitations (arising from sample size and the non-random orientation
7 of fractures), we speculate our fractured sample represents a scaled-down ideal
8 reservoir with non-connected fractures. Our experimental results suggest that this type
9 of reservoirs could potentially isolate the CO₂ fraction in the central section of the
10 fractures. This finding might have significant implications in the storage efficiency.
11 Although CO₂ mobility would be reduced in non-connected fractured systems, the
12 fractures would be acting as small reservoirs, enhancing the overall CO₂ storage
13 efficiency of the system. Based on these observations, an ideal configuration for a
14 potential CO₂ storage site could be a reservoir in which (i) the bottom part of the
15 formation (injection point) has high CO₂ mobility (i.e., a porosity/permeability formation,
16 which could contain interconnected fractures), to guarantee an adequate injectivity
17 and distribution of the CO₂ plume, and (ii) the top part has non-connected fractures
18 that would act as vertical flow barriers, helping to immobilize the CO₂ plume and
19 enhancing the whole trapping efficiency of the reservoir (Figure 7).

20

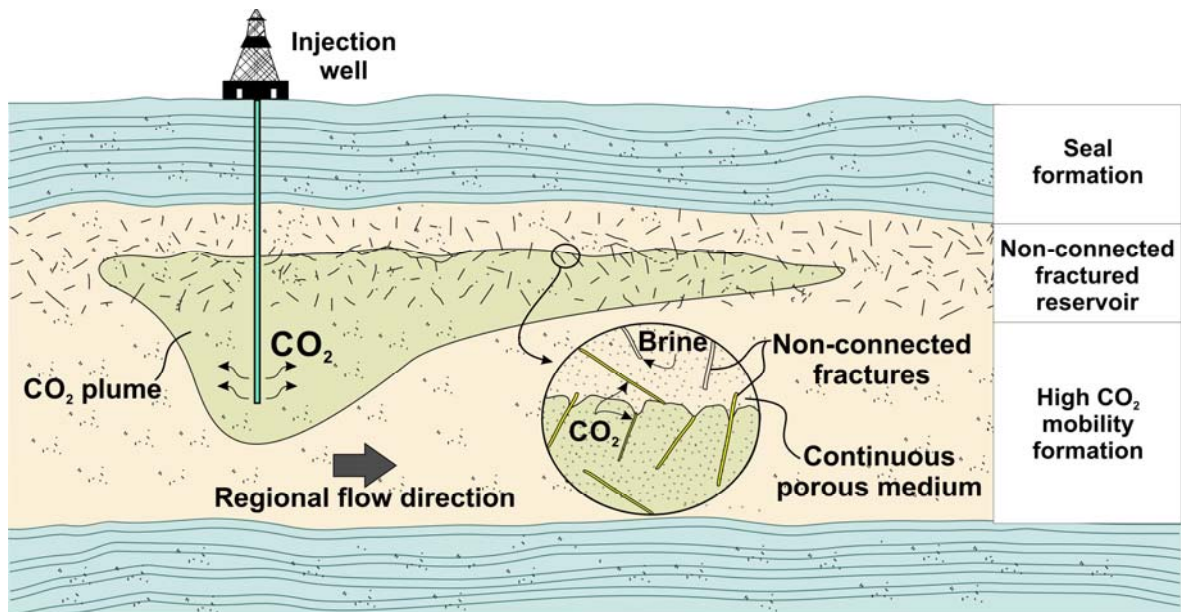


Figure 7. Schematic diagram of an ideal CO₂ storage reservoir, showing CO₂ injection and plume migration. The bottom part of the reservoir is a non-fractured formation with high CO₂ mobility, allowing efficient injection and distribution of CO₂. Above this formation, a non-connected fractured layer with high CO₂ trapping capacity immobilises the CO₂ plume.

1

2 7. Conclusions

3 We have performed a brine-CO₂ flow-through experiment using a synthetic sandstone
 4 sample with oblique aligned cracks while monitoring electrical resistivity and relative
 5 permeability. The experimental results have been compared to previous experiments
 6 in which similar synthetic samples without cracks were tested under similar conditions.
 7 Based on the newly obtained experimental data, the integration of previous results
 8 and rationale described in the text we conclude that:

- 9 • The presence of non-connected fractures may hamper the mobility of CO₂ in
 10 the porous medium and slightly increase the residual CO₂ trapping.
- 11 • In a weak water-wet sample, large fractures may prevent the movement of the
 12 wetting phase and facilitate the partial isolation of the non-wetting phase in the

1 centre of pores (snap-off process). Further experiments to investigate the
2 wettability on fractured samples are required for more robust interpretations.

3 • Heterogeneities within the porous medium may lead to differences among the
4 various relative permeability models. The Brooks-Corey's model can be used
5 to describe relative permeability curves for the wetting and non-wetting phase,
6 in both fractured and non-fractured systems.

7 • The fractures remain unconnected, even though we found evidences of
8 mechanical deformation. Associated microcracks developed at weak structural
9 points would remain saturated in brine during CO₂ injection due to the higher
10 surface tension of the wetting phase.

11
12 **Funding:** We have received funding from the UK's Natural Environment Research
13 Council (grant NE/R013535/1 GASRIP and grant NE/N016041/1 CHIMNEY), the
14 European Union's Horizon 2020 research and innovation programme (grant No.
15 654462 STEMM-CCS), the project BIA2017-87066-R (MINECO/AEI/FEDER, UE), the
16 Xunta de Galicia and the European Union (European Social Fund – ESF).

17
18 **Acknowledgments:** The experiment was conducted at the NOC Rock Physics
19 Laboratory in Southampton. The authors thank Dr Laurence North for his support in
20 the laboratory.

21
22 **Author contributions:** A.M.I. contribution roles include data curation, formal analysis,
23 investigation, software, validation, visualization and writing – original draft; I.F.S.
24 contribution roles include conceptualization, funding acquisition, methodology, project
25 administration resources, supervision, visualization and writing – original draft; H.M.M.

1 contribution roles include conceptualization, formal analysis, software, validation and
2 writing – review & editing; J.D.M. contribution roles include resources and writing –
3 review & editing; P.M. contribution roles include formal analysis.

4

5 **Declarations of Interest:** The authors declare no conflict of interest. The funders had
6 no role in the design of the study; in the collection, analyses, or interpretation of data;
7 in the writing of the manuscript, and in the decision to publish the results.

8

1 **Appendix A**

2 Reactive transport modelling has been extensively applied to predict the
3 behaviour of aquifers during and after CO₂ sequestration (e.g., Xu and Pruess (2001),
4 Pruess and Müller (2009), André et al. (2010), Sung et al. (2014)).

5 The TOUGHREACT code has been previously used to simulate brine-CO₂ multi-
6 flow processes in continuum idealized porous media (e.g. Pruess and Müller, 2009).
7 We did not consider transport by molecular diffusion and performed an isothermal
8 analysis. In addition, and although this program couples thermal, hydrologic and
9 chemical (THC) processes, reactive transport was not considered since our siliciclastic
10 sample is likely to remain chemically unaltered when exposed to brine and CO₂.

11 We developed a 2D axisymmetric radial model (20 mm thickness; 25 mm radius)
12 of 500 grid elements. Cells between 0.5 and 2 mm wide were distributed in vertical
13 layers of 1 mm, with a mesh refinement around the injection point and flow outlet to
14 capture more precisely the processes occurring around them. An initial equilibrium
15 simulation was performed to establish the initial pressure and temperature conditions
16 for the BCFT simulation. In this equilibrium simulation, the grid blocks along the right,
17 top, and bottom boundaries are kept constant at $P = 100$ bar; $T = 19.6^{\circ}\text{C}$; salinity =
18 3.5%; no CO₂ mass fraction. During the BCFT simulation, only the flow outlet element
19 was kept at a constant pressure of 95 bar. The volume of the cell representing the
20 injection point matches that of the diffusor pathway to better capture the injection
21 velocities of the experiments. We used van Genuchten models (van Genuchten, 1980)
22 for both water relative permeability and capillary pressure and Corey's model (Corey,
23 1954) for CO₂ relative permeability. Residual liquid and gas saturation values were
24 obtained from experimental data. The simulation covers the six drainage stages and

1 the imbibition episode. Injection rates and partial flows varied according to the
 2 experimental conditions. Table A.1 shows the parameters adopted in this model.

3 **Table A.1.** Modelling parameters

<i>Rock property</i>	<i>Symbol</i>	<i>Value</i>	<i>References</i>
Sample diameter (m)	\emptyset	0.05	
Sample thickness (m)	T	0.02	
Rock grain density (kg m ⁻³)	ρ_s	2600	
Porosity	Φ	0.273	Experimental
Horizontal permeability (m ²)	K_H	5.410x10 ⁻¹⁵	Experimental
Vertical permeability (m ²)	K_V	5.410x10 ⁻¹⁶	Experimental
Rock thermal conductivity (W m ⁻¹ °C ⁻¹)	K	2	Eppelbaum et al. (Eppelbaum et al., 2014)
Rock specific heat (J kg ⁻¹ °C ⁻¹)	C	840	Eppelbaum et al. (Eppelbaum et al., 2014)
Pore compressibility (Pa ⁻¹)	c_p	8.69E-10	
<i>Relative permeability parameters</i>			
M		0.457	Pruess et al. (Pruess and Müller, 2009)
Residual liquid saturation	S_{wi}	0.1	Experimental
Liquid saturation		1.000	
Residual gas saturation	S_{CO_2i}	0.07	Experimental
<i>Capillary pressure parameters</i>			
$m = 1 - 1/n$		0.457	Pruess et al. (Pruess and Müller, 2009)
Residual liquid saturation	S_{wi}	0.1	Experimental
$1/P_0$		5.1E-5	Pruess et al. (Pruess and Müller, 2009)
P_{max} (Pa)		1E7	
Liquid saturation		0.930	Experimental

4

5

6

1 **References**

- 2 Adler, A., Lionheart, W.R.B., 2006. Uses and abuses of EIDORS: an extensible
3 software base for EIT. *Physiol. Meas.* 27, 25–42. [https://doi.org/10.1088/0967-](https://doi.org/10.1088/0967-3334/27/5/S03)
4 3334/27/5/S03
- 5 Akbarabadi, M., Piri, M., 2013. Relative permeability hysteresis and capillary trapping
6 characteristics of supercritical CO₂/brine systems: An experimental study at
7 reservoir conditions. *Adv. Water Resour.* 52, 190–206.
8 <https://doi.org/10.1016/j.advwatres.2012.06.014>
- 9 Al-Khdheawi, E.A., Vialle, S., Barifcani, A., Sarmadivaleh, M., Iglauer, S., 2017.
10 Impact of reservoir wettability and heterogeneity on CO₂-plume migration and
11 trapping capacity. *Int. J. Greenh. Gas Control* 58, 142–158.
12 <https://doi.org/10.1016/j.ijggc.2017.01.012>
- 13 Al-Menhali, A., Krevor, S., 2014. Effective wettability measurements of CO₂-brine-
14 sandstone system at different reservoir conditions. *Energy Procedia* 63, 5420–
15 5426. <https://doi.org/10.1016/j.egypro.2014.11.572>
- 16 Alemu, B.L., Aker, E., Soldal, M., Johnsen, Ø., Aagaard, P., 2013. Effect of sub-core
17 scale heterogeneities on acoustic and electrical properties of a reservoir rock: a
18 CO₂ flooding experiment of brine saturated sandstone in a computed
19 tomography scanner. *Geophys. Prospect.* 61, 235–250.
20 <https://doi.org/10.1111/j.1365-2478.2012.01061.x>
- 21 Almenningen, S., Gauteplass, J., Fotland, P., Aastveit, G.L., Barth, T., Ersland, G.,
22 2018. Visualization of hydrate formation during CO₂ storage in water-saturated
23 sandstone. *Int. J. Greenh. Gas Control* 79, 272–278.
24 <https://doi.org/10.1016/j.ijggc.2018.11.008>
- 25 Amalokwu, K., Chapman, M., Best, A.I., Sothcott, J., Minshull, T.A., Li, X.-Y., 2015.

1 Experimental observation of water saturation effects on shear wave splitting in
2 synthetic rock with fractures aligned at oblique angles. *Geophys. J. Int.* 200, 17–
3 24. <https://doi.org/10.1093/gji/ggu368>

4 André, L., Azaroual, M., Menjöz, A., 2010. Numerical simulations of the thermal
5 impact of supercritical CO₂ injection on chemical reactivity in a carbonate saline
6 reservoir. *Transp. Porous Media* 82, 247–274. [https://doi.org/10.1007/s11242-](https://doi.org/10.1007/s11242-009-9474-2)
7 [009-9474-2](https://doi.org/10.1007/s11242-009-9474-2)

8 Archie, G.E., 1942. The Electrical Resistivity Log as an Aid in Determining Some
9 Reservoir Characteristics. *Trans. AIME* 146, 54–62.
10 <https://doi.org/10.2118/942054-G>

11 Bachu, S., 2015. Review of CO₂ storage efficiency in deep saline aquifers. *Int. J.*
12 *Greenh. Gas Control* 40, 188–202. <https://doi.org/10.1016/j.ijggc.2015.01.007>

13 Bachu, S., 2013. Drainage and imbibition CO₂/brine relative permeability curves at in
14 situ conditions for sandstone formations in western Canada. *Energy Procedia*
15 37, 4428–4436. <https://doi.org/10.1016/j.egypro.2013.07.001>

16 Bachu, S., Bennion, B., 2009. Dependence of CO₂ -brine interfacial tension on
17 aquifer pressure, temperature and water salinity. *Energy Procedia* 1, 3157–
18 3164. <https://doi.org/10.1016/j.egypro.2009.02.098>

19 Bachu, S., Bennion, B., 2008. Effects of in-situ conditions on relative permeability
20 characteristics of CO₂-brine systems. *Environ. Geol.* 54, 1707–1722.
21 <https://doi.org/10.1007/s00254-007-0946-9>

22 Batzle, M., Wang, Z., 1992. Seismic properties of pore fluids. *Geophysics* 57, 1396–
23 1408. <https://doi.org/10.1190/1.1443207>

24 Baumann, G., Henniges, J., De Lucia, M., 2014. Monitoring of saturation changes
25 and salt precipitation during CO₂ injection using pulsed neutron-gamma logging

1 at the Ketzin pilot site. *Int. J. Greenh. Gas Control* 28, 134–146.
2 <https://doi.org/10.1016/j.ijggc.2014.06.023>

3 Bennion, B., Bachu, S., 2006. The impact of interfacial tension and pore size
4 distribution/capillary pressure character on CO₂ relative permeability at reservoir
5 conditions in CO₂-brine systems, in: 2006 SPE/DOE Symposium on Improved
6 Oil Recovery. Tulsa, Oklahoma, U.S.A., 22–26 April.
7 <https://doi.org/10.2523/99325-MS>

8 Berg, S., Oedai, S., Ott, H., 2013. Displacement and mass transfer between
9 saturated and unsaturated CO₂-brine systems in sandstone. *Int. J. Greenh. Gas*
10 *Control* 12, 478–492. <https://doi.org/10.1016/j.ijggc.2011.04.005>

11 Bond, C.E., Wightman, R., Ringrose, P.S., 2013. The influence of fracture anisotropy
12 on CO₂ flow. *Geophys. Res. Lett.* 40, 1284–1289.
13 <https://doi.org/10.1002/grl.50313>

14 Broseta, D., Tonnet, N., Shah, V., 2012. Are rocks still water-wet in the presence of
15 dense CO₂ or H₂S? *Geofluids* 12, 280–294. [https://doi.org/10.1111/j.1468-](https://doi.org/10.1111/j.1468-8123.2012.00369.x)
16 [8123.2012.00369.x](https://doi.org/10.1111/j.1468-8123.2012.00369.x)

17 Cai, J., Wei, W., Hu, X., Wood, D.A., 2017. Electrical conductivity models in
18 saturated porous media: A review. *Earth-Science Rev.* 171, 419–433.
19 <https://doi.org/10.1016/j.earscirev.2017.06.013>

20 Canal, J., Delgado, J., Falcón, I., Yang, Q., Juncosa, R., Barrientos, V., 2013.
21 Injection of CO₂-saturated water through a siliceous sandstone plug from the
22 Hontomin test site (Spain): Experiment and modeling. *Environ. Sci. Technol.* 47,
23 159–167. <https://doi.org/10.1021/es3012222>

24 Carrigan, C.R., Yang, X., LaBrecque, D.J., Larsen, D., Freeman, D., Ramirez, A.L.,
25 Daily, W., Aines, R., Newmark, R., Friedmann, J., Hovorka, S., 2013. Electrical

1 resistance tomographic monitoring of CO₂ movement in deep geologic
2 reservoirs. *Int. J. Greenh. Gas Control* 18, 401–408.
3 <https://doi.org/10.1016/j.ijggc.2013.04.016>

4 Castillo, S.C., Skjaeveland, S., Fjelde, I., 2011. Water and surfactant flooding at
5 different wettability conditions. *Mycotoxin Res.* 6, 77.
6 <https://doi.org/10.1007/BF03192151>

7 Chiquet, P., Broseta, D., Thibeau, S., 2007. Wettability alteration of caprock minerals
8 by carbon dioxide. *Geofluids* 7, 112–122. [https://doi.org/10.1111/j.1468-](https://doi.org/10.1111/j.1468-8123.2007.00168.x)
9 [8123.2007.00168.x](https://doi.org/10.1111/j.1468-8123.2007.00168.x)

10 Corey, A.T., 1954. The interrelation between gas and oil relative permeabilities.
11 *Prod. Mon.* 19, 38–41.

12 Dandekar, A.Y., 2013. *Petroleum Reservoir Rock and Fluid Properties*, Second
13 Edition. CRC Press. <https://doi.org/10.1201/b15255>

14 Diomampo, G.P., 2001. Relative permeability through fractures. Stanford University,
15 Stanford, USA. <https://doi.org/10.2172/896520>

16 Duan, Z., Sun, R., Zhu, C., Chou, I.M., 2006. An improved model for the calculation
17 of CO₂ solubility in aqueous solutions containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and
18 SO₄²⁻. *Mar. Chem.* 98, 131–139. <https://doi.org/10.1016/j.marchem.2005.09.001>

19 Dullien, F.A.L., 1992. *Porous media: fluid transport and pore structure*. Second
20 edition. Academic Press Inc. [https://doi.org/doi.org/10.1016/B978-0-12-223651-](https://doi.org/doi.org/10.1016/B978-0-12-223651-8.50001-8)
21 [8.50001-8](https://doi.org/doi.org/10.1016/B978-0-12-223651-8.50001-8)

22 El-Maghraby, R.M., Pentland, C.H., Iglauer, S., Blunt, M.J., 2012. A fast method to
23 equilibrate carbon dioxide with brine at high pressure and elevated temperature
24 including solubility measurements. *J. Supercrit. Fluids* 62, 55–59.
25 <https://doi.org/10.1016/j.supflu.2011.11.002>

1 Eppelbaum, L., Kutasov, I., Pilchin, A., 2014. Thermal properties of rocks and
2 density of fluids, in: Applied Geothermics. Lecture Notes in Earth System
3 Sciences. Springer, Berlin, Heidelberg, pp. 99–149. [https://doi.org/10.1007/978-](https://doi.org/10.1007/978-3-642-34023-9_2)
4 [3-642-34023-9_2](https://doi.org/10.1007/978-3-642-34023-9_2)

5 Falcon-Suarez, I., Marín-Moreno, H., Browning, F., Lichtschlag, A., Robert, K., North,
6 L.J., Best, A.I., 2017. Experimental assessment of pore fluid distribution and
7 geomechanical changes in saline sandstone reservoirs during and after CO₂
8 injection. *Int. J. Greenh. Gas Control* 63, 356–369.
9 <https://doi.org/10.1016/j.ijggc.2017.06.019>

10 Falcon-Suarez, I., North, L., Amalokwu, K., Best, A., 2016. Integrated geophysical
11 and hydromechanical assessment for CO₂ storage: shallow low permeable
12 reservoir sandstones. *Geophys. Prospect.* 64, 828–847.
13 <https://doi.org/10.1111/1365-2478.12396>

14 Falcon-Suarez, I., Papageorgiou, G., Chadwick, A., North, L., Best, A.I., Chapman,
15 M., 2018. CO₂-brine flow-through on an Utsira Sand core sample: Experimental
16 and modelling. Implications for the Sleipner storage field. *Int. J. Greenh. Gas*
17 *Control* 68, 236–246. <https://doi.org/10.1016/j.ijggc.2017.11.019>

18 Falcon-Suarez, I.H., Amalokwu, K., Delgado-Martin, J., Callow, B., Robert, K., North,
19 L., Sahoo, S.K., Best, A.I., 2019. Comparison of stress-dependent geophysical,
20 hydraulic and mechanical properties of synthetic and natural sandstones for
21 reservoir characterization and monitoring studies. *Geophys. Prospect.* 67, 784–
22 803. <https://doi.org/10.1111/1365-2478.12699>

23 Farajzadeh, R., Zitha, P.L.J., Bruining, J., 2009. Enhanced mass transfer of CO₂ into
24 water: Experiment and modeling. *Ind. Eng. Chem. Res.* 48, 6423–6431.
25 <https://doi.org/10.1021/ie801521u>

- 1 Fjaer, E., Holt, R.M., Horsrud, P., Raaen, A.M., Risnes, R., 2008. Petroleum related
2 rock mechanics. 2nd edition. Elsevier. [https://doi.org/10.1016/0148-](https://doi.org/10.1016/0148-9062(93)92632-Z)
3 [9062\(93\)92632-Z](https://doi.org/10.1016/0148-9062(93)92632-Z)
- 4 Fortin, J., Guéguen, Y., Schubnel, A., 2007. Effects of pore collapse and grain
5 crushing on ultrasonic velocities and V_p/V_s . *J. Geophys. Res.* 112, B08207.
6 <https://doi.org/10.1029/2005JB004005>
- 7 Fourar, M., Bories, S., 1995. Experimental study of air-water two-phase flow through
8 a fracture (narrow channel). *Int. J. Multiph. Flow* 21, 621–637.
9 [https://doi.org/10.1016/0301-9322\(95\)00005-I](https://doi.org/10.1016/0301-9322(95)00005-I)
- 10 Grude, S., Landrø, M., Dvorkin, J., 2014. Pressure effects caused by CO₂ injection in
11 the Tubåen Fm., the Snøhvit field. *Int. J. Greenh. Gas Control* 27, 178–187.
12 <https://doi.org/10.1016/j.ijggc.2014.05.013>
- 13 Hangx, S., Bakker, E., Bertier, P., Nover, G., Busch, A., 2015. Chemical–mechanical
14 coupling observed for depleted oil reservoirs subjected to long-term CO₂ -
15 exposure – A case study of the Werkendam natural CO₂ analogue field. *Earth*
16 *Planet. Sci. Lett.* 428, 230–242. <https://doi.org/10.1016/j.epsl.2015.07.044>
- 17 Huo, D., Benson, S.M., 2016. Experimental investigation of stress-dependency of
18 relative permeability in rock fractures. *Transp. Porous Media* 113, 567–590.
19 <https://doi.org/10.1007/s11242-016-0713-z>
- 20 Iding, M., Ringrose, P., 2010. Evaluating the impact of fractures on the performance
21 of the In Salah CO₂ storage site. *Int. J. Greenh. Gas Control* 4, 242–248.
22 <https://doi.org/10.1016/j.ijggc.2009.10.016>
- 23 IPCC, 2005. Carbon dioxide capture and storage. Special report. Cambridge
24 University Press.
- 25 Jackson, S.J., Agada, S., Reynolds, C.A., Krevor, S., 2018. Characterizing Drainage

1 Multiphase Flow in Heterogeneous Sandstones. *Water Resour. Res.* 54, 3139–
2 3161. <https://doi.org/10.1029/2017WR022282>

3 Kim, M., Sell, A., Sinton, D., 2013. Aquifer-on-a-Chip: understanding pore-scale salt
4 precipitation dynamics during CO₂ sequestration. *Lab Chip* 13, 2421–2662.
5 <https://doi.org/10.1039/c3lc00031a>

6 Krevor, S., Blunt, M.J., Benson, S.M., Pentland, C.H., Reynolds, C., Al-Menhali, A.,
7 Niu, B., 2015. Capillary trapping for geologic carbon dioxide storage – From
8 pore scale physics to field scale implications. *Int. J. Greenh. Gas Control* 40,
9 221–237. <https://doi.org/10.1016/j.ijggc.2015.04.006>

10 Krevor, S.C.M., Pini, R., Zuo, L., Benson, S.M., 2012. Relative permeability and
11 trapping of CO₂ and water in sandstone rocks at reservoir conditions. *Water*
12 *Resour. Res.* 48, W02532. <https://doi.org/10.1029/2011WR010859>

13 Lee, J., Choi, S.-U., Cho, W., 1999. A comparative study of dual-porosity model and
14 discrete fracture network model. *KSCE J. Civ. Eng.* 3, 171–180.
15 <https://doi.org/10.1007/BF02829057>

16 Leverett, M.C., 1941. Capillary Behavior in Porous Solids. *Trans. AIME* 142, 152–
17 169. <https://doi.org/10.2118/941152-G>

18 Li, K., 2008. A new method for calculating two-phase relative permeability from
19 resistivity data in porous media. *Transp. Porous Media* 74, 21–33.
20 <https://doi.org/10.1007/s11242-007-9178-4>

21 Li, K., Horne, R.N., 2006. Comparison of methods to calculate relative permeability
22 from capillary pressure in consolidated water-wet porous media. *Water Resour.*
23 *Res.* 42, W06405. <https://doi.org/10.1029/2005WR004482>

24 March, R., Doster, F., Geiger, S., 2018. Assessment of CO₂ storage potential in
25 naturally fractured reservoirs with dual-porosity models. *Water Resour. Res.* 54,

1 1650–1668. <https://doi.org/10.1002/2017WR022159>

2 Mavko, G., Mukerji, T., Dvorkin, J., 2009. The rock physics handbook. Tools for
3 seismic analysis of porous media. Second edition. Cambridge University Press.
4 <https://doi.org/10.1017/CBO9780511626753>

5 Michael, K., Golab, A., Shulakova, V., Ennis-King, J., Allinson, G., Sharma, S.,
6 Aiken, T., 2010. Geological storage of CO₂ in saline aquifers—A review of the
7 experience from existing storage operations. *Int. J. Greenh. Gas Control* 4, 659–
8 667. <https://doi.org/10.1016/j.ijggc.2009.12.011>

9 Müller, N., 2011. Supercritical CO₂-brine relative permeability experiments in
10 reservoir rocks—Literature review and recommendations. *Transp. Porous Media*
11 87, 367–383. <https://doi.org/10.1007/s11242-010-9689-2>

12 Nakatsuka, Y., Xue, Z., Garcia, H., Matsuoka, T., 2010. Experimental study on CO₂
13 monitoring and quantification of stored CO₂ in saline formations using resistivity
14 measurements. *Int. J. Greenh. Gas Control* 4, 209–216.
15 <https://doi.org/10.1016/j.ijggc.2010.01.001>

16 Nooraiepour, M., Bohloli, B., Park, J., Sauvin, G., Skurtveit, E., Mondol, N.H., 2018.
17 Effect of brine-CO₂ fracture flow on velocity and electrical resistivity of naturally
18 fractured tight sandstones. *Geophysics* 83, WA37–WA48.
19 <https://doi.org/10.1190/geo2017-0077.1>

20 Noriaki, W., Keisuke, S., Takuya, I., Yutaka, O., Tetsuya, T., Masahiko, Y.,
21 Noriyoshi, T., 2015. New v-type relative permeability curves for two-phase flows
22 through subsurface fractures. *Water Resour. Res.* 51, 2807–2824.
23 <https://doi.org/10.1002/2014WR016515>

24 North, L., Best, A.I., Sothcott, J., MacGregor, L., 2013. Laboratory determination of
25 the full electrical resistivity tensor of heterogeneous carbonate rocks at elevated

1 pressures. *Geophys. Prospect.* 61, 458–470. <https://doi.org/10.1111/j.1365->
2 [2478.2012.01113.x](https://doi.org/10.1111/j.1365-2478.2012.01113.x)

3 Oostrom, M., White, M.D., Porse, S.L., Krevor, S.C.M., Mathias, S.A., 2016.
4 Comparison of relative permeability–saturation–capillary pressure models for
5 simulation of reservoir CO₂ injection. *Int. J. Greenh. Gas Control* 45, 70–85.
6 [https://doi.org/https://doi.org/10.1016/j.ijggc.2015.12.013](https://doi.org/10.1016/j.ijggc.2015.12.013)

7 Papageorgiou, G., Falcon-Suarez, I., Chapman, M., Best, A., 2018. Pressure-varying
8 CO₂ distribution affects the ultrasonic velocities of synthetic sandstones. *Int. J.*
9 *Greenh. Gas Control* 74, 1–8. <https://doi.org/10.1016/j.ijggc.2018.03.022>

10 Park, J., Fawad, M., Viken, I., Aker, E., Bjørnarå, T.I., 2013. CSEM sensitivity study
11 for Sleipner CO₂-injection monitoring. *Energy Procedia* 37, 4199–4206.
12 <https://doi.org/10.1016/j.egypro.2013.06.322>

13 Pollard, D.D., Aydin, A., 1988. Progress in understanding jointing over the past
14 century, in: *General Society of America Bulletin*. pp. 1181–1204.
15 <https://doi.org/10.1130/SPE253-p313>

16 Pruess, K., 2005. ECO2N: A TOUGH2 fluid property module for mixtures of water,
17 NaCl, and CO₂. Berkeley, CA. <https://doi.org/10.2172/877331>

18 Pruess, K., Müller, N., 2009. Formation dry-out from CO₂ injection into saline
19 aquifers: 1. Effects of solids precipitation and their mitigation. *Water Resour.*
20 *Res.* 45, 1–11. <https://doi.org/10.1029/2008WR007101>

21 Purcell, W.R., 1949. Capillary pressures - Their measurement using mercury and the
22 calculation of permeability therefrom. *J. Pet. Technol.* 1, 39–48.
23 <https://doi.org/10.2118/949039-G>

24 Reynolds, C., Krevor, S., 2017. Capillary limited flow behavior of CO₂ in target
25 reservoirs in the UK. *Energy Procedia* 114, 4518–4523.

1 <https://doi.org/10.1016/j.egypro.2017.03.1568>

2 Reynolds, C.A., 2016. Two-phase flow behaviour and relative permeability between
3 CO₂ and brine in sandstones at the pore and core scales. Imperial College
4 London.

5 Reynolds, C.A., Blunt, M.J., Krevor, S., 2018. Multiphase flow characteristics of
6 heterogeneous rocks from CO₂ storage reservoirs in the United Kingdom. *Water*
7 *Resour. Res.* 54, 729–745. <https://doi.org/10.1002/2017WR021651>

8 Shi, J.-Q., Xue, Z., Durucan, S., 2011. Supercritical CO₂ core flooding and imbibition
9 in Berea sandstone — CT imaging and numerical simulation. *Energy Procedia*
10 4, 5001–5008. <https://doi.org/10.1016/j.egypro.2011.02.471>

11 Shi, J.-Q., Xue, Z., Durucan, S., 2007. Seismic monitoring and modelling of
12 supercritical CO₂ injection into a water-saturated sandstone: Interpretation of P-
13 wave velocity data. *Int. J. Greenh. Gas Control* 1, 473–480.
14 [https://doi.org/10.1016/S1750-5836\(07\)00013-8](https://doi.org/10.1016/S1750-5836(07)00013-8)

15 Stack, A.G., Fernandez-Martinez, A., Allard, L.F., Bañuelos, J.L., Rother, G.,
16 Anovitz, L.M., Cole, D.R., Waychunas, G.A., 2014. Pore-size-dependent calcium
17 carbonate precipitation controlled by surface chemistry. *Environ. Sci. Technol.*
18 48, 6177–6183. <https://doi.org/10.1021/es405574a>

19 Sung, R.-T., Li, M.-H., Dong, J.-J., Lin, A.T.-S., Hsu, S.-K., Wang, C.-Y., Yang, C.-N.,
20 2014. Numerical assessment of CO₂ geological sequestration in sloping and
21 layered heterogeneous formations: A case study from Taiwan. *Int. J. Greenh.*
22 *Gas Control* 20, 168–179. <https://doi.org/10.1016/j.ijggc.2013.11.003>

23 Tillotson, P., Sothcott, J., Best, A.I., Chapman, M., Li, X.-Y., 2012. Experimental
24 verification of the fracture density and shear-wave splitting relationship using
25 synthetic silica cemented sandstones with a controlled fracture geometry.

1 Geophys. Prospect. 60, 516–525. <https://doi.org/10.1111/j.1365->
2 2478.2011.01021.x

3 Tsuji, T., Jiang, F., Christensen, K.T., 2016. Characterization of immiscible fluid
4 displacement processes with various capillary numbers and viscosity ratios in
5 3D natural sandstone. *Adv. Water Resour.* 95, 3–15.
6 <https://doi.org/10.1016/j.advwatres.2016.03.005>

7 van Genuchten, M.T., 1980. A closed-form equation for predicting the hydraulic
8 conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44, 892–898.
9 <https://doi.org/10.2136/sssaj1980.03615995004400050002x>

10 Wang, S., Tokunaga, T.K., 2015. Capillary Pressure–Saturation Relations for
11 Supercritical CO₂ and Brine in Limestone/Dolomite Sands: Implications for
12 Geologic Carbon Sequestration in Carbonate Reservoirs. *Environ. Sci. Technol.*
13 49, 7208–7217. <https://doi.org/10.1021/acs.est.5b00826>

14 Wang, Z., Gelius, L.-J., Kong, F.-N., 2009. Simultaneous core sample
15 measurements of elastic properties and resistivity at reservoir conditions
16 employing a modified triaxial cell - a feasibility study. *Geophys. Prospect.* 57,
17 1009–1026. <https://doi.org/10.1111/j.1365-2478.2009.00792.x>

18 Xu, T., Pruess, K., 2001. Modeling multiphase non-isothermal fluid flow and reactive
19 geochemical transport in variably saturated fractured rocks: 1. Methodology.
20 *Am. J. Sci.* 301, 16–33. <https://doi.org/10.2475/ajs.301.1.16>

21 Xu, T., Sonnenthal, E., Spycher, N., Pruess, K., 2017. TOUGHREACT V3.32
22 Reference manual: A parallel simulation program for non-isothermal multiphase
23 geochemical reactive transport, Report LBNL-Draft. Berkeley, California.
24 <https://doi.org/10.1016/j.cageo.2005.06.014>

25 Xu, T., Sonnenthal, E., Spycher, N., Pruess, K., 2004. TOUGHREACT user's guide:

1 A simulation program for non-isothermal multiphase reactive geochemical
2 transport in variable saturated geologic media. Earth Sciences Division,
3 Lawrence Berkeley National Laboratory, Berkeley, CA.
4 <https://doi.org/10.2172/834237>

5 Yoshida, N., Levine, J.S., Stauffer, P.H., 2016. Investigation of uncertainty in CO₂
6 reservoir models: A sensitivity analysis of relative permeability parameter
7 values. *Int. J. Greenh. Gas Control* 49, 161–178.
8 <https://doi.org/10.1016/j.ijggc.2016.03.008>

9 Zhu, Q., Zhou, Q., Li, X., 2016. Numerical simulation of displacement characteristics
10 of CO₂ injected in pore-scale porous media. *J. Rock Mech. Geotech. Eng.* 8,
11 87–92. <https://doi.org/10.1016/j.jrmge.2015.08.004>
12