

# Steady-state three-phase flow in a mixed-wet porous medium: A pore-scale X-ray microtomography study

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## ABSTRACT

We use three-dimensional X-ray imaging to investigate steady-state three-phase flow in a mixed-wet reservoir rock, while measuring both relative permeability and capillary pressure. Oil occupied the smallest pores, gas the biggest, while water occupied medium-sized pores. We report a distinct flow pattern, where gas flows in the form of disconnected ganglia by periodically opening critical flow pathways. Despite having capillary-controlled displacements, a significant fraction of the pore space was intermittently occupied by gas-oil and oil-water phases. Both types of intermittency occurred in intermediate-sized pores. Gas mainly displaces oil, and oil displaces water as the gas flow rate is increased, while oil displaces gas, and water displaces oil as gas flow is decreased. At the resolution of the images, no detectable gas was trapped in the rock due to its mixed-wettability which prevents either oil or water completely surrounding gas, suppressing snap-off and capillary trapping, which has significant implications for the design of gas storage in three-phase systems.

## 1. Introduction

While global consumption of fossil fuels has fallen over the last couple of years, they still remain the largest primary energy source, and therefore continue to play a dominant role in atmospheric CO<sub>2</sub> emissions (BP Statistical Review of World Energy, 2021; Allen et al., 2019). A solution where the produced CO<sub>2</sub> emissions are captured and stored – eliminating their impact on climate change – is therefore a practical and feasible component of efforts to prevent dangerous climate change (Bui et al., 2018; Bickle, 2009; Alcalde et al., 2018).

Geological carbon capture and storage (CCS) offers advantages in hydrocarbon reservoirs, where the injection infrastructure exists and the field is a known secure geological trap. Moreover, CO<sub>2</sub> injection can recover additional amounts of oil from depleted oilfields, providing the financial incentive needed to implement CCS (Brownsort et al., 2015; Blunt et al., 1993; Lake, 1989). When CO<sub>2</sub> is injected in oilfields, there is a simultaneous flow of three fluid phases – oil, water, and gas – in the pore space of the reservoir. Therefore, in order to maximize the amount of CO<sub>2</sub> stored and oil recovered in the reservoir, we need to improve our understanding of the pore-scale physics governing three-phase flow (Blunt, 2017).

The recent deployment of X-ray microtomography has accelerated

our understanding of multiphase flow in porous media (Blunt, 2017; Wildenschild and Sheppard, 2013; Blunt et al., 2013; Cnudde and Boone, 2013; Brown et al., 2014; Bultreys et al., 2016). The use of three-dimensional X-ray imaging has made it possible to visualize the flow of fluids inside micron-sized pore spaces to quantify pore-scale flow properties. Examples of these properties include *in situ* contact angles, interfacial areas and curvatures, saturation in micro-porosity, layer flow, connectivity and trapping events (Andrew et al., 2013, 2014, 2015; Singh et al., 2016, 2017; Lin et al., 2016, 2018; Armstrong et al., 2012; Rücker et al., 2015; Berg et al., 2013; Blunt et al., 2019; Gao et al., 2020; Alhammadi et al., 2017; Scanziani et al., 2018, 2017, 2018, 2019, 2020a, 2020b; Alhosani et al., 2019, 2020a, 2020b, 2020c, 2021a, 2021b; Blunt et al., 2021a, 2021b; Qin et al., 2021, 2019; Iglaier et al., 2019; Herring et al., 2019, 2017, 2015; Armstrong and Berg, 2013).

The coupling of X-ray imaging with steady-state two-phase flow techniques enables a complete quantification of two-phase flow properties through the simultaneous determination of relative permeability and capillary pressure in systems with various wettabilities (Lin et al., 2018; 2021; Alhammadi et al., 2020; Gao et al., 2020). Furthermore, it has helped delineate the boundary between linear (Darcy) flow and the non-linear (intermittent) flow regime (Gao et al., 2020, 2017; Zhang et al., 2021; Spurin et al., 2019a, 2019b; Gao et al., 2021). A linear

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relationship exists between pressure gradient and flow rate in the Darcy regime as opposed to the intermittent one for which a power-law scaling is found (Zhang et al., 2021). In two-phase flow, fluids flow through fixed pathways in the Darcy regime, where capillary-forces are dominant, while a more dynamic – periodically disconnected – pathway exists in the intermittent flow regime (Gao et al., 2020, 2021; Spurin et al., 2019).

In three-phase flow, X-ray imaging has been mostly performed during unsteady-state experiments (Scanziani et al., 2018, 2020; Alhosani et al., 2019, 2020, 2021a, 2021b; Qin et al., 2019; Iglauer et al., 2019; Scanziani et al., 2018). It was not until recently that Alhosani et al. (2021) successfully combined imaging with steady-state three-phase flow in a water-wet Bentheimer sandstone, acquiring measurements of three-phase relative permeabilities and capillary pressures. The authors discovered a unique flow pattern, that is gas, the most non-wetting phase, progressed through the pore space in the form of disconnected clusters by periodically opening critical flow pathways (Alhosani et al., 2021). Despite flowing under capillary-dominated conditions, intermittent gas-oil and oil-water phases were observed in the pore-scale images. This a distinct characteristic of three-phase flow made possible by double and multiple displacement events, where one displaced fluid phase can progress to displace another phase (or multiple phases) in the pore space. However, further work is needed to investigate the impact of wettability on steady-state three-phase flow.

In this work, we use X-ray imaging to investigate three-phase steady-state flow in a mixed-wet reservoir rock extracted from a large producing field in the Middle East. We study a saturation history where the gas fractional flow is first increased and then decreased. Our experiment is performed under capillary-dominated, immiscible gas-oil conditions, similar to previous work (Alhosani et al., 2021). A mixed wettability state, where the oil-water contact angle ( $\theta_{ow}$ ) is distributed both above and below  $90^\circ$ , is more representative of oil reservoirs where the existence of crude oil in parts of the pore space, at conditions of high temperature and pressure, over long periods of time renders some of the rock surfaces oil-wet (Blunt, 2017).

In our experiment, we measure three-phase relative permeabilities by recording the pressure drop across the sample at steady-state conditions for each set of gas, oil, and water fractional flows. We determine the saturations directly from the raw pore-scale images, without performing image segmentation, by extending the saturation analysis introduced by Lin et al. (2021), from two to three phases. We present a new image analysis technique to quantify the displacement of each phase when moving from one steady-state condition to another. In addition, we determine capillary pressures, pore occupancies, layer formation, interfacial areas, contact angles and fluid connectivity. We end with a discussion of the implications of this work on the design of carbon dioxide storage in oil reservoirs.

The averaged pore occupancy results indicate that the wettability order in our mixed-wet reservoir rock is oil-water-gas from most to least wetting. We observe disconnected gas flow across the system at steady-state conditions, similar to the observations of Alhosani et al. (2021) for a water-wet rock. Although displacements were capillary-controlled, we identified intermittent gas-oil and oil-water regions, where the phases alternatively filled the same pores. Unlike the water-wet system, oil-water intermittency is more significant here. As the gas fractional flow was increased, gas only filled the pores that were previously occupied by oil, and gas was mostly displaced by oil as the fractional flow was decreased. This work further supports previous work (Alhosani et al., 2021) that pore-scale steady-state conditions may never be attained in three-phase flow, despite, macroscopically, having a constant averaged saturation. Hence when we talk about steady-state conditions, we do not refer to a fixed configuration of fluids at the pore-scale, but more a dynamic situation where, while there are local fluctuations on the pore-scale arrangement of the phases, associated with rapid fluctuations in pressure drop across the system, when averaged over the period of a few hours, there is no trend, or change, in the

average pressure drop or the average saturation.

More significantly, at the image resolution we observed no gas trapping in this mixed-wet reservoir rock after gas injection has stopped, when only water and oil were injected ( $f_g = 0$  and  $f_{w,o} = 0.5$ ). This is different to the water-wet system, where a significant amount of gas was trapped in the pore centres surrounded by oil and water layers (Alhosani et al., 2021). This behaviour was ascribed to the mixed-wet nature of the surface which prevented either oil or water from completely surrounding the gas phase in the pore centres. This work suggests that a water-alternating-gas (WAG) injection strategy may not be favourable for carbon dioxide storage in oilfields since it can mobilize the gas possibly leading to its escape. Instead, an injection strategy of continuous gas injection is more effective since gas naturally gets disconnected once injection stops – there is no need to inject water to trap the gas.

## 2. Materials and methods

### 2.1. Rock and fluid properties

The rock sample selected was a reservoir carbonate extracted from a large producing oilfield in the Middle East, with a total porosity of 24.4%, characterised using differential imaging (Lin et al., 2016), and an absolute permeability ( $k$ ) of  $668 \pm 30$  mD ( $6.6 \times 10^{-13} \pm 0.3 \times 10^{-13}$  m<sup>2</sup>) – measured at the experimental conditions. These properties are typical for the reservoir as a whole. The mineralogically calcite-dominated sample was 42.9 mm in length and 12.3 mm in diameter. The pore and throat size distributions of the sample are plotted in Fig. S1 in the supplementary material.

The experimental fluids used to replicate gas, oil, and water phases were nitrogen ( $N_2$ ),  $n$ -decane ( $C_{10}H_{22}$ ), and deionized water ( $H_2O$ ), respectively. The oil and water phases were mixed with 20 wt.% iodo-decane ( $C_{10}H_{21}I$ ) and 30 wt.% sodium iodide ( $NaI$ ), respectively, in a process known as doping, to increase the contrast between the four phases – rock, gas, oil and water – in the X-ray images.

At the experimental conditions, 1 MPa pore pressure and 30 °C temperature, the dynamic viscosities of gas, oil and water were 0.017, 4.27, and 1.40 mPa·s, respectively (Alhosani et al., 2021; NIST 2019). Gas and oil were immiscible with an interfacial tension of  $11.2$  mN · m<sup>-1</sup> (Alhosani et al., 2021). The interfacial tensions between gas and water, and oil and water were 63.7 and 52.1 mN · m<sup>-1</sup>, respectively (NIST, 2019). These conditions are lower pressure and temperature than typical field conditions: the aim of this study though is to examine displacement processes rather than replicate a specific reservoir situation.

In our three-phase system, oil has a positive initial spreading coefficient (Alhosani et al., 2021) ( $C_{so} = +0.4$  mN · m<sup>-1</sup>) – calculated using  $C_{si} = \sigma_{jk} - \sigma_{ij} - \sigma_{ik}$ , where  $i, j$  and  $k$  denote the three fluid phases – which indicates oil will spread in layers sandwiched between gas and water in the rock pore space, as we will show later; gas and water both have a negative spreading coefficient.

### 2.2. Wettability alteration process

Prior to performing the steady-state experiment, the rock wettability was rendered mixed-wet: this process restores the initially water-wet state of the cleaned rock sample to conditions likely to be representative of subsurface conditions. Mixed-wettability means that certain parts of the pore-space are water-wet ( $\theta_{ow} < 90^\circ$ ), while the rest is oil-wet ( $\theta_{ow} > 90^\circ$ ) (Blunt, 2017). The wettability of a rock surface can be changed by placing it in contact with crude oil at high temperatures and pressures, during which asphaltene precipitation takes place (Alhammad et al., 2017; Alhosani et al., 2020; Salathiel, 1973; Kovscek et al., 1993). Asphaltenes deposition renders some of the solid surfaces oil-wet. The wettability alteration process is also known as ageing.

To alter the wettability of the reservoir rock, we first saturated the rock sample with formation brine – a brine solution prepared with the same salt composition as the reservoir brine from which the rock was

extracted. Then, 100 pore volumes (PV) of crude oil, from the same reservoir, were injected at ambient conditions into the pore space with a flowrate of 0.1 mL/min. The injection of crude oil at a low flowrate is necessary to ensure that not all the formation brine is swept out and that some pores remain brine occupied, i.e., remain water-wet to achieve mixed-wettability. The sample was then taken out and placed in a crude oil bath at 80 °C for two months.

The Middle Eastern crude oil has a density and viscosity of 812 kg·m<sup>-3</sup> and 1.94 mPa·s, respectively, measured at 60 °C and 8 MPa, and is composed of 55.23% saturates, 38.07% aromatics, 6.22% resins and 0.46% asphaltenes (Alhammad et al., 2017).

### 3. Experimental procedure

After establishing the mixed-wet wettability state, the sample was prepared for the steady-state three-phase imaging experiment. A schematic of the three-phase flow and X-ray imaging apparatus is shown in Fig. 1. The sample was first wrapped with aluminium foil and inserted into a Viton rubber tubing. The Viton tubing was then connected to the injection and production ends of the coreholder, see Fig. 1. A full description of the X-ray transparent three-phase steady-state PEEK coreholder design can be found elsewhere (Alhosani et al., 2021). A Keller PD-33X pressure transducer, with an accuracy of ±0.03 KPa, was connected to the inlet and outlet of the sample to record the pressure drop during the experiment. The flow cell was then placed in a Zeiss Xradia 510 X-ray scanner, for pore-scale image acquisition throughout the flow experiment.

Five Teledyne Isco pumps were used in the experiment to inject the three fluid phases and apply confining and back pressures. The three fluid phases were injected from the bottom of the sample. A net confining pressure of 2 MPa was applied, while the back pressure was set to 1 MPa. The experiment was conducted at a temperature of 30 °C.

In the three-phase flow experiment, steady-state conditions were

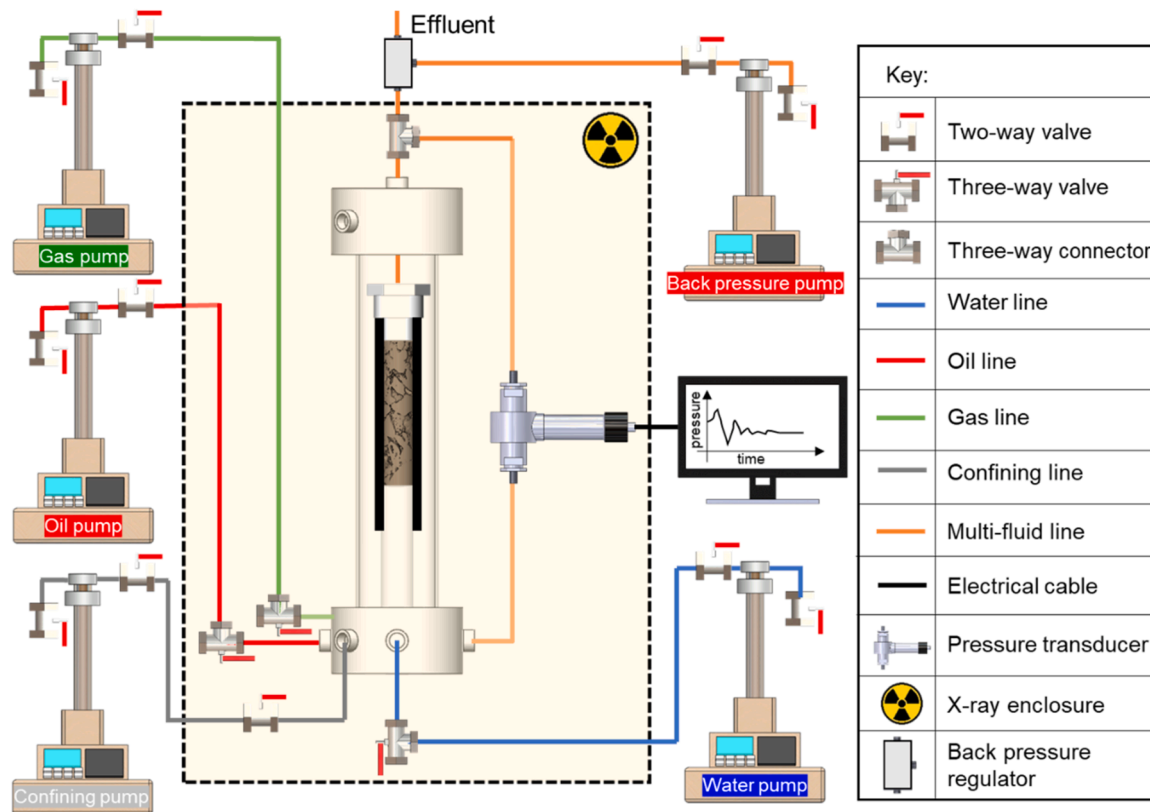
reached at various gas, oil, and water fractional flows ( $f_g$ ,  $f_o$  and  $f_w$ ) by keeping the fluid flow rates constant, with a total flow rate of  $Q_t = 0.8$  mL·min<sup>-1</sup>. The sets of fractional flows are listed in Table 1.

The selection of fractional flows was done prudently to investigate the impact of a saturation history, where the gas saturation is first increased and then decreased, on three-phase relative permeability. This saturation history is typically encountered in oil reservoirs (Lake, 1989). Furthermore, to avoid any switch from drainage to imbibition displacements between oil and water, we keep the oil and water saturation changes in the same direction – by keeping oil and water flow rates the same – and change the gas saturation in the opposite direction (Oak,

**Table 1**

The gas, oil, and water fractional flows at which steady-state conditions were reached in the three-phase flow experiment.  $Q$  and  $f$  refer to the flow rate and fractional flow, respectively. Subscripts  $g$ ,  $o$  and  $w$  refer to the gas, oil, and water phases, respectively. The total flow rate ( $Q_t$ ) was 0.8 mL·min<sup>-1</sup>. Five steady-state conditions were reached as  $f_g$  was increased (steps 4, 5, 6, 7 and 8), while only three steady-state conditions were reached when  $f_g$  was decreased (steps 9, 10 and 11).

| Flow Step | $Q_g$<br>mL·min <sup>-1</sup> | $Q_o$<br>mL·min <sup>-1</sup> | $Q_w$<br>mL·min <sup>-1</sup> | $f_g$ | $f_o$  | $f_w$  |
|-----------|-------------------------------|-------------------------------|-------------------------------|-------|--------|--------|
| 1         | 0                             | 0.8                           | 0                             | 0     | 1      | 0      |
| 2         | 0                             | 0                             | 0.8                           | 0     | 0      | 1      |
| 3         | 0                             | 0.4                           | 0.4                           | 0     | 0.5    | 0.5    |
| 4         | 0.3                           | 0.25                          | 0.25                          | 0.375 | 0.3125 | 0.3125 |
| 5         | 0.4                           | 0.2                           | 0.2                           | 0.5   | 0.25   | 0.25   |
| 6         | 0.5                           | 0.15                          | 0.15                          | 0.625 | 0.1875 | 0.1875 |
| 7         | 0.6                           | 0.1                           | 0.1                           | 0.75  | 0.125  | 0.125  |
| 8         | 0.8                           | 0                             | 0                             | 1     | 0      | 0      |
| 9         | 0.6                           | 0.1                           | 0.1                           | 0.75  | 0.125  | 0.125  |
| 10        | 0.4                           | 0.2                           | 0.2                           | 0.5   | 0.25   | 0.25   |
| 11        | 0.2                           | 0.3                           | 0.3                           | 0.25  | 0.375  | 0.375  |
| 12        | 0                             | 0.4                           | 0.4                           | 0     | 0.5    | 0.5    |



**Fig. 1.** A schematic diagram of the combined three-phase steady-state flow apparatus with the X-ray microtomography scanner. The black dashed line represents the X-ray scanner enclosure. The pumps, flow lines, valves, coreholder and pressure transducer were connected as shown in the diagram.

1990; Alizadeh and Piri, 2014; Oak et al., 1990; Saraf et al., 1982; Alizadeh and Piri, 2014). The minimum waiting time for each set of fractional flows to reach steady-state conditions was at least 12 hr. After which, we waited for the differential pressure signal to stabilize over a period of 3 hr to record the pressure drop and start the X-ray imaging process.

In flow step 1, see Table 1, oil (80 wt.% *n*-decane and 20 wt.% iododecane) was injected into the sample to replace the crude oil introduced during the wettability alteration process. Water was then injected in step 2 to reach the residual or remaining oil saturation. In step 3, both oil and water were injected simultaneously ( $f_w = 0.5$  and  $f_o = 0.5$ ) to initialize the sample for the three-phase steady-state experiment.

Gas was first injected into the sample in step 4. Five three-phase steady-state conditions were reached as  $f_g$  was increased (steps 4, 5, 6, 7 and 8), while only three steady-state conditions were reached when  $f_g$  was decreased (steps 9, 10 and 11). At  $f_g = 1$  (step 8), after reaching steady-state conditions at  $Q_g = 0.8 \text{ mL} \cdot \text{min}^{-1}$ , the gas flow rate was then increased to  $2 \text{ mL} \cdot \text{min}^{-1}$  to reach the maximum gas saturation and minimize the capillary end effect in the sample.

The absolute permeability ( $k$ ) =  $668 \pm 30 \text{ mD}$  ( $6.6 \times 10^{-13} \pm 0.3 \times 10^{-13} \text{ m}^2$ ) of the sample was measured using deionized water ( $\text{H}_2\text{O}$ ) prior to altering the wettability of the rock at the experimental conditions. A dry scan and a high contrast water saturated scan were also acquired at this point to characterize the porosity distribution, including sub-resolution porosity, of the sample using the differential imaging method (Lin et al., 2016).

The fluids were injected at low flow rates to ensure that displacements occur under capillary-dominated conditions, representative of field-scale flows. Capillary-controlled displacements are typically characterized by low capillary numbers ( $Ca$ ) (Blunt, 2017). For any fluid pair,  $Ca_{ij} = \mu_i q_i / \sigma_{ij}$ , where  $\sigma_{ij}$  is the interfacial tension between the two phases,  $\mu_i$  is the viscosity of the displacing fluid and  $q_i$  is its Darcy velocity. Table 2 lists the capillary numbers between the gas-oil and oil-water fluid pairs at each set of fractional flows. Since oil has an initial positive spreading coefficient ( $C_{so} = +0.4 \text{ mN} \cdot \text{m}^{-1}$ ), see Section 2.1, we expect it to spread in layers between gas and water preventing their direct displacement.

Three-dimensional images of the whole sample were acquired, with a voxel size of  $5.36 \mu\text{m}$ , using the Zeiss Versa 510 scanner, after reaching steady-state conditions at each set of fractional flows. To capture the whole length, images, of size  $12.45 \text{ mm} \times 12.45 \text{ mm} \times 10.23 \text{ mm}$ , were taken at four different locations of the sample, with an overlap of 25%. The X-ray source energy and power were set to 80 keV and 7 W, respectively, and a large flat panel was employed at the detector side.

**Table 2**

The capillary numbers between oil-water, water-oil, gas-oil and oil-gas fluid pairs at different fractional flows during the steady-state three-phase flow experiment. An oil-water capillary number,  $Ca_{[ow]}$ , represents the number calculated when oil displaces water, with a similar definition for the other pairs. Capillary numbers were calculated using  $Ca_{ij} = \mu_i q_i / \sigma_{ij}$ , where  $\sigma_{ij}$  is the interfacial tension between the phases,  $\mu_i$  is the viscosity of the displacing fluid and  $q_i$  is its Darcy velocity. Refer to Table 1 for the fractional flows of each flow step.

| Flow Step | $Ca_{[ow]}$           | $Ca_{[wo]}$           | $Ca_{[go]}$           | $Ca_{[og]}$           |
|-----------|-----------------------|-----------------------|-----------------------|-----------------------|
| 1         | -                     | -                     | -                     | -                     |
| 2         | -                     | $6.34 \times 10^{-7}$ | -                     | -                     |
| 3         | $1.13 \times 10^{-6}$ | $3.17 \times 10^{-7}$ | -                     | -                     |
| 4         | $7.07 \times 10^{-7}$ | $1.98 \times 10^{-7}$ | $1.34 \times 10^{-8}$ | $5.26 \times 10^{-6}$ |
| 5         | $5.66 \times 10^{-7}$ | $1.58 \times 10^{-7}$ | $1.79 \times 10^{-8}$ | $3.29 \times 10^{-6}$ |
| 6         | $4.24 \times 10^{-7}$ | $1.19 \times 10^{-7}$ | $2.24 \times 10^{-8}$ | $2.63 \times 10^{-6}$ |
| 7         | $2.83 \times 10^{-7}$ | $7.92 \times 10^{-8}$ | $2.68 \times 10^{-8}$ | $1.97 \times 10^{-6}$ |
| 8         | -                     | -                     | $3.58 \times 10^{-8}$ | -                     |
| 9         | $2.83 \times 10^{-7}$ | $7.92 \times 10^{-8}$ | $2.68 \times 10^{-8}$ | $1.97 \times 10^{-6}$ |
| 10        | $5.66 \times 10^{-7}$ | $1.58 \times 10^{-7}$ | $1.79 \times 10^{-8}$ | $3.29 \times 10^{-6}$ |
| 11        | $8.49 \times 10^{-7}$ | $2.38 \times 10^{-7}$ | $8.95 \times 10^{-8}$ | $3.95 \times 10^{-6}$ |
| 12        | $1.13 \times 10^{-6}$ | $3.17 \times 10^{-7}$ | -                     | $5.26 \times 10^{-6}$ |

The exposure time was set to 1.60 s with a total of 3,201 projections taken at all sets of fractional flows. All the pore-scale images were then reconstructed, normalized, registered, and stitched as shown in Figs. 2 and 3.

### 3.1. Image processing and analysis

As mentioned in the introduction, we observe that a large fraction of the pore space is occupied by gas-oil and oil-water phases intermittently at three-phase steady-state conditions. Intermittency can take any grey-scale value in-between the grey-scale values of the two intermittent phases. This makes image segmentation almost impossible, and even if segmented there would be eight different phases in the image including rock, water, oil, gas, gas from gas-oil intermittency, oil from gas-oil intermittency, oil from oil-water intermittency, and water from oil-water intermittency.

Therefore, we decided not to segment the three-phase steady-state images with significant intermittency, and instead perform image analysis directly on the raw images. The analysis performed on the raw three-phase images includes saturation, pore occupancy and displacement.

Nonetheless, there was no/little intermittency in the pore-scale images acquired in flow steps 2, 3, 8 and 12, see Table 1. Hence, these images were segmented using the seeded watershed algorithm and used for the analysis of contact angles, capillary pressures, interfacial areas and connectivity. We also characterize the saturations in the segmented images and compare them to the saturations obtained directly from the raw images, see the next section. The segmentation procedure is detailed in Fig. S2 in the supplementary material.

#### 3.1.1. Saturation from grey-scale images

Since it was not possible to segment the three-phase steady-state images, we used an approach, developed by Lin et al. (2021), to find the fluid saturations directly from the raw (unsegmented) pore-scale images. We extend this approach from two to three fluid phases. Here, fluid saturations are determined using their grey-scale values in the pore-scale images. In this approach, the saturation of the intermittent region is added to the saturation of their respective phases, e.g., the contributions to the saturations of oil from gas-oil and oil-water intermittent regions are added to the oil saturation. We only considered the fluid saturations in the macro-porosity (porosity that was explicitly resolved in the images). Please refer to Lin et al., 2021 for the calculation of two-phase saturations directly from the pore-scale images.

The saturations, in the macro-porosity, at each set of three-phase fractional flows were obtained as follows:

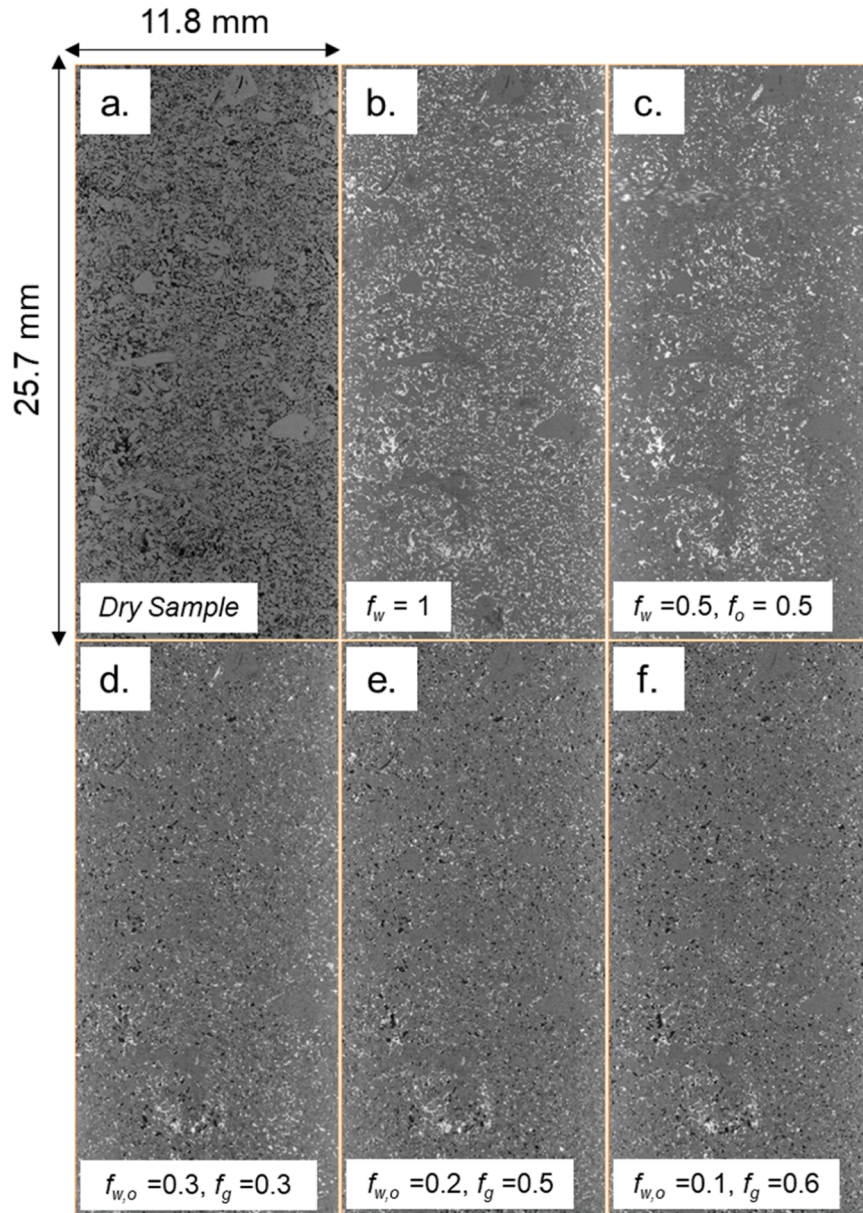
$$CT_{f_w, f_o, f_g} = S_w CT_w + S_o CT_o + S_g CT_g \quad (1)$$

where  $CT_{f_w, f_o, f_g}$  is the average grey-scale value in the macro-porosity of the three-phase steady-state image at each set of fractional flows,  $CT_w$  is the average grey-scale value in the macro-porosity of the water saturated image,  $CT_o$  is the average grey-scale value in the macro-porosity of the fully oil saturated image (acquired after flow step 1, see Table 1), and  $CT_g$  is the average grey-scale value in the macro-porosity of a fully gas saturated image (dry scan).  $S_w$ ,  $S_o$  and  $S_g$  refer to the water, oil and gas saturations, respectively.

Now, if we substitute ( $S_o = 1 - S_w - S_g$ ), Eq. (1) can be re-written as:

$$S_w = \frac{CT_o - CT_{f_w, f_o, f_g} + S_g CT_g - S_g CT_o}{CT_o - CT_w} \quad (2)$$

While  $CT_w$ ,  $CT_o$ , and  $CT_g$ , are constant,  $CT_{f_w, f_o, f_g}$  changes depending on the fluid saturations in the macro-porosity of each three-phase steady-state image. Eq. (2) can be solved linearly giving a range of  $S_w$  and  $S_g$  values; we limit this range by the minimum and maximum water and gas saturations that are obtained from the segmented images in flow steps 3, 8 and 12. Finally, the water and gas saturations are obtained by taking



**Fig. 2.** Vertical cross-sectional raw images of the whole sample acquired at steady-state conditions for different gas, oil, and water fractional flows. The gas, oil and water fractional flows ( $f_g$ ,  $f_o$ , and  $f_w$ ) are stated in each image. The black phase is gas, dark grey is oil, light grey is rock, and white is water.

the mid-point of their narrowed ranges at each set of fractional flows; oil saturation is then found from  $S_o = 1 - S_w - S_g$ .

### 3.1.2. Relative permeability

The gas, oil and water relative permeabilities were calculated using the multiphase Darcy law assuming a linear relationship between flow rate and pressure gradient (Blunt, 2017):

$$k_{rw} = \frac{q_w \mu_w L}{\Delta P k} \quad (3)$$

$$k_{ro} = \frac{q_o \mu_o L}{\Delta P k} \quad (4)$$

$$k_{rg} = \frac{q_g \mu_g L}{\Delta P k} \quad (5)$$

where  $k_r$  is the relative permeability (dimensionless),  $k$  is the permeability ( $\text{m}^2$ ),  $\mu$  is the viscosity (Pa.s),  $q$  is the Darcy velocity (flow rate per unit area,  $\text{m.s}^{-1}$ ),  $\Delta P$  is the pressure drop (Pa), and  $L$  is the sample length

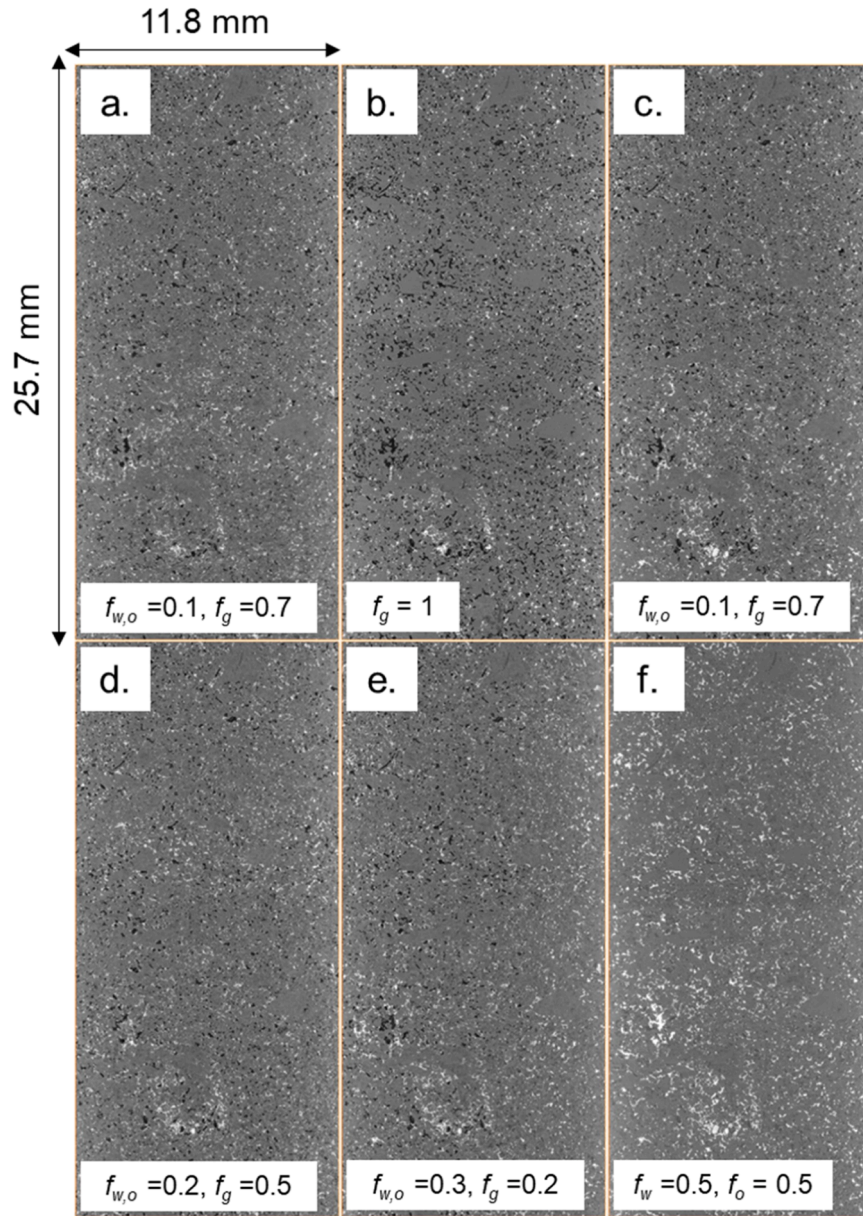
(m). Subscripts  $g$ ,  $o$  and  $w$  refer to the gas, oil and water phases, respectively.

Given that the pressure fluctuations were large at three-phase steady-state conditions, the average pressure drop was used to calculate the relative permeabilities.

### 3.1.3. Displacement analysis

To quantitatively assess the displacement processes in the three-phase mixed-wet system when moving from one steady-state condition to another, we developed an in-house algorithm that identifies the pores and throats occupied by a certain phase, at each set of fractional flows  $f_g(i)$ ,  $f_o(i)$  and  $f_w(i)$ , and then records the phases that occupy the same pores and throats at the next set of fractional flows  $f_g(i+1)$ ,  $f_o(i+1)$  and  $f_w(i+1)$ . Displacement is said to have taken place if the occupancy in the pore changes from one steady-state condition to another.

We use the network model code developed by Dong and Blunt (2009) and Raeini et al. (2017) to extract the pores and throats from the dry scan of the sample. Pores are defined as wide regions of the pore space,



**Fig. 3.** Vertical cross-sectional raw images of the whole sample acquired at steady-state conditions for different gas, oil, and water fractional flows. The gas, oil and water fractional flows ( $f_g$ ,  $f_o$ , and  $f_w$ ) are stated in each image. The black phase is gas, dark grey is oil, light grey is rock, and white is water.

that are connected by narrower regions, the throats. The pore diameter is the diameter of the largest sphere that can fit entirely in the pore, while the throat diameter is the diameter of the largest sphere that sits on the throat centre. We assume that the macro pore space can be occupied by five phases: (i) gas; (ii) oil; (iii) water; (iv) gas-oil intermittency; and (v) oil-water intermittency, at all three-phase steady-state conditions. For simplicity, we consider the intermittent regions as a single phase.

To determine the occupancy in the pores, we first set a range of grey-scale values for each phase, as shown in Fig. S3 in the supplementary material. Then, we find the average grey-scale value in the sphere we have extracted from the pores. Depending on what range the average grey-scale value falls in, the occupancy is assigned.

#### 4. Results and Discussion

In this section, we first measure the geometric fluid-fluid contact angles to confirm the mixed wettability state of the reservoir rock

(Section 3.1). Then, in Section 3.2, we show evidence of intermittent gas-oil and oil-water flow at three-phase steady-state conditions. We quantify pore occupancy in Section 3.3 to determine the wettability order in the system. In Sections 3.4 and 3.5, the connectivity of the fluids and interfacial areas are examined, respectively. Saturations are then quantified in Section 3.6 and plotted against the measurements of three-phase relative permeabilities in Section 3.7. Capillary pressures are characterized in Section 3.8. In Section 3.9, fluid-fluid displacements in the three-phase mixed-wet system are analyzed. Finally, in Section 3.10, we examine gas trapping and discuss the implications of pore-scale properties on the design of field-scale CO<sub>2</sub> storage and oil recovery.

##### 4.1. Wettability

The oil-water ( $\theta_{ow}$ ), gas-oil ( $\theta_{go}$ ) and gas-water ( $\theta_{gw}$ ) geometric contact angles were measured on subvolumes, of size 2.68 mm × 2.68 mm × 2.68 mm, on the segmented images (see Section 2.4 and Table 1 for the fractional flows of the segmented images). The geometric angles

were measured using the automated method developed by AlRatrou et al. (2017), see Fig. 4.

Fig. 4a shows measurements of the oil-water contact angle at two-phase flow conditions ( $f_w = 0.5$  and  $f_o = 0.5$ ), measured before and after gas injection (at the end of the experiment), denoted by subscripts  $b$  and  $a$ , respectively. We observe that  $\theta_{ow}$  has a wide distribution with angles both lower and higher than  $90^\circ$ , indicating the local existence of both water-wet and oil-wet regions which is the defining characteristic of mixed-wet media (Blunt, 2017). The mean oil-water contact angles, before and after gas injection, are  $82^\circ \pm 42^\circ$  and  $84^\circ \pm 39^\circ$ , respectively. This confirms that the wettability alteration protocol successfully achieved mixed-wet conditions. In contrast a dynamic ageing protocol, previously performed on the same reservoir rock in multiple studies, resulted in more oil-wet conditions with mean oil-water contact angles of  $112^\circ \pm 21^\circ$ ,  $118^\circ \pm 25^\circ$  and  $110^\circ \pm 20^\circ$  (Alhosani et al., 2020b, 2020c, 2021).

At  $f_g = 1$ , the measured mean oil-water contact angle is  $80^\circ \pm 41^\circ$ , see Fig. 4b. The consistency of the values indicates that the contact angle does not change within the uncertainty of the measurements during and after gas injection. The gas-oil and gas-water contact angles are  $66^\circ \pm 41^\circ$  and  $78^\circ \pm 40^\circ$ , respectively, suggesting that both oil and water are more wetting to the surface than gas. However, it is not possible to determine a clear wettability order in the system using the geometric contact angle measurements only.

#### 4.2. Three-phase intermittency

As mentioned previously, a large fraction of the pore space becomes occupied by gas-oil and oil-water phases intermittently at three-phase steady-state conditions, during which the two intermittent phases alternatively occupy the same pores. Intermittency is manifested in an intermediate grey-scale value in-between the grey-scale values of the two intermittent phases as shown in Fig. 5. This pore-scale phenomenon has been previously observed in two-phase flow albeit in the non-linear flow regime (Gao et al., 2020, 2017; Spurin et al., 2019, 2019; Reynolds et al., 2017; Gao et al., 2019). Nonetheless, it was also seen in a three-phase water-wet system under capillary-controlled conditions (Alhosani et al., 2021).

Fig. 5 shows the existence of two intermittent regions in the mixed-wet pore space: (i) a gas-oil region, and (ii) an oil-water region. We do not observe intermittent gas-water regions since the two phases do not come in direct contact due to the presence of oil layers. In contrast to the water-wet system, where gas-oil intermittency was clearly more

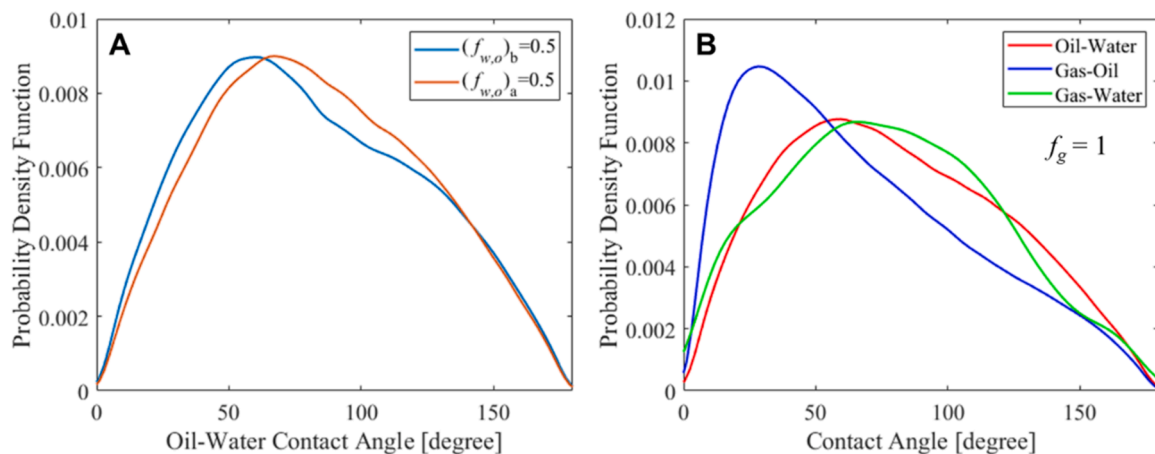
dominant (Alhosani et al., 2021), the oil-water and gas-oil intermittencies both occupy significant fractions of the pore space in the mixed-wet system. This is supported by the pore occupancy analysis in the next section.

#### 4.3. Pore occupancy

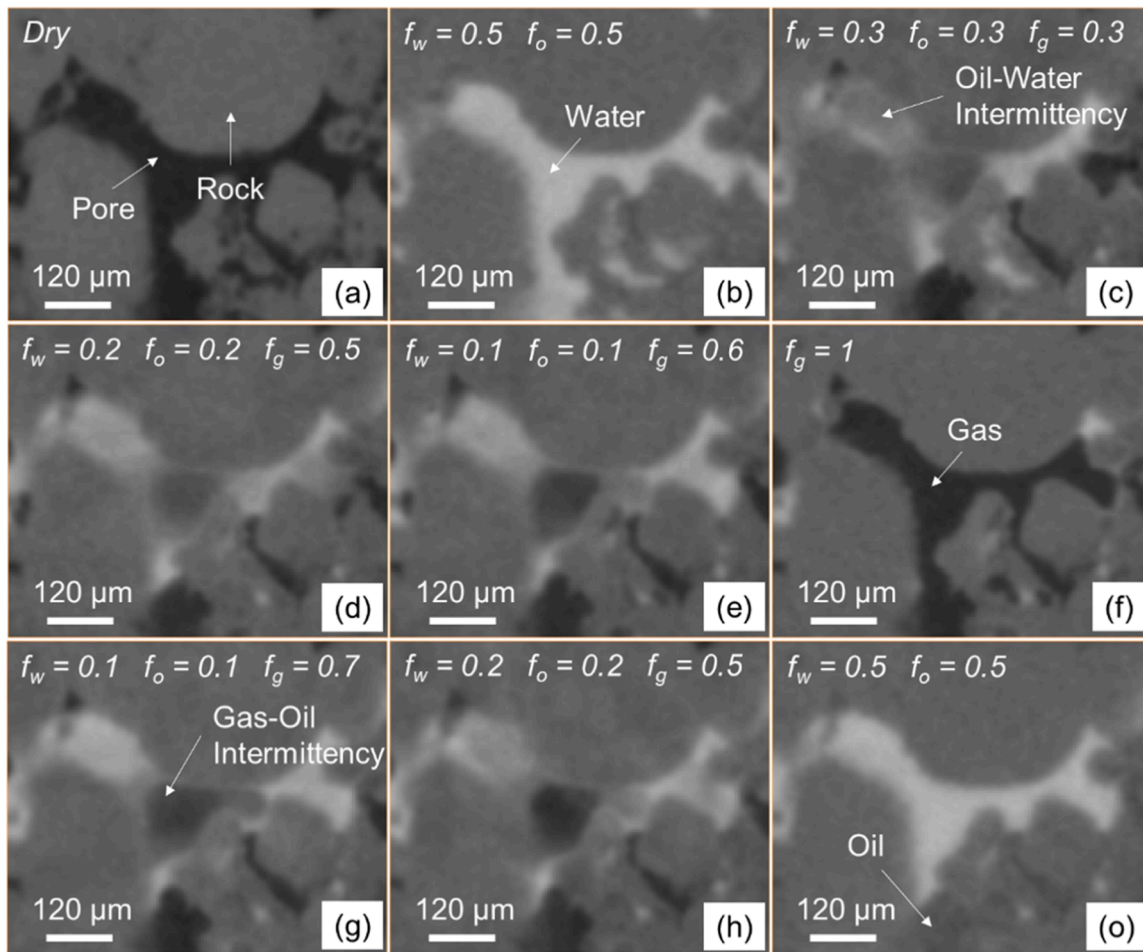
We characterized the pore occupancy – the size of the pores occupied by each fluid phase – directly from the raw two- and three-phase steady-state images of the whole sample, see Fig. 6. In two-phase flow, we divided the pore space into three phases: (i) oil; (ii) water; and (iii) oil-water intermittency, while we assigned five phases under three-phase steady-state conditions: (i) gas; (ii) oil; (iii) water; (iv) gas-oil intermittency; and (v) oil-water intermittency. We extract the pores using the pore-network model extraction (Dong and Blunt, 2009; Raeini et al., 2017), and then assign a unique occupancy dependent on the average grey-scale value in the pore; each phase is given a grey-scale value range and if the average value in the pore falls within this range then the pore is considered to be occupied by that phase, see Section 2.4.3.

Fig. 6a shows that at  $f_w = 0.5$  and  $f_o = 0.5$ , before gas injection, on average, oil flows in pores smaller than those occupied by water which suggests that oil is more wetting to the rock than water: it is favorable for the most wetting phase to reside close to the surface. Nonetheless, oil also flows in a large fraction of the big pores as well, away from the solid surfaces; this is ascribed to the mixed-wet nature of the surface. Furthermore, we notice that oil-water intermittency takes place mostly in the intermediate-sized pores as seen previously in two-phase flow experiments (Reynolds et al., 2017; Gao et al., 2019).

At three-phase steady-state conditions, as  $f_g$  is increased, and  $f_o$  and  $f_w$  are decreased, Figs. 6b to 6f, gas flows in the largest pores, oil the smallest, while water flows in the medium-sized pores. This suggests that the wettability order in the mixed-wet system is oil-water-gas from most to least wetting. This wettability order has been previously observed in weakly oil-wet rocks at immiscible gas-oil conditions (Scanziani et al., 2018). While one would expect more competition between oil and water to occupy the smallest pores, due to the mixed wettability, we believe that this is dictated by the filling order, since oil saturated the pore space first before water. We see that gas-oil and oil-water intermittency occurs in pores of similar, intermediate, size during the increasing  $f_g$ , and decreasing  $f_o$  and  $f_w$ , flow path. Gas tends to favour filling the larger pores, and oil the smaller ones, so they compete to occupy pores of intermediate size. Furthermore, as seen in two-phase flow, oil and water both occupy larger and smaller pores, since this is a



**Fig. 4.** Probability density function of the *in situ* measured geometric contact angles, at steady-state conditions, between (A) oil and water at  $f_w = 0.5$  and  $f_o = 0.5$ , before and after gas injection (flow steps 3 and 12), and (B) oil and water, gas and oil, and gas and water at  $f_g = 1$  (flow step 8). Refer to Table 1 for the details of each flow step. In (A), subscripts  $b$  and  $a$  refer to before and after gas injection (the end of the experiment), respectively. The contact angles were measured through the denser phase: water in the case of oil and water and gas and water, and oil in the case of gas and oil.  $f_w$ ,  $f_o$  and  $f_g$  refer to the water, oil and gas fractional flows, respectively.



**Fig. 5.** Two-dimensional unfiltered pore-scale images showing the occurrence of intermittent gas-oil and oil-water flow in the same pore under different three-phase steady-state conditions despite flowing in a capillary-force dominated displacement regime. Water is shown in white, rock in light grey, oil in dark grey, and gas in black. Intermittency appears with a grey-scale value that is in between the grey-scale values of the two intermittent phases.  $f_w$ ,  $f_o$  and  $f_g$  refer to the water, oil, and gas fractional flows, respectively.

mixed-wet system, and intermittency is seen in a range of pore sizes, and most commonly around the mode with intermediate radius.

The same wettability order persists during the decreasing  $f_g$ , and increasing  $f_o$  and  $f_w$ , flow path, see Figs. 6f to 6h. During this flow path, gas occupied increasingly smaller pores and oil and water larger pores. This is expected since the gas saturation decreases, while the oil and water saturations increase as we will show in Section 3.6. This pore occupancy behaviour is different to that observed in the water-wet system (Alhosani et al., 2021), where limited displacement was observed during the decreasing  $f_g$ , and increasing  $f_o$  and  $f_w$ , flow path due to double capillary trapping of gas by oil and water. Hence, this suggests that there is less gas trapping in the mixed-wet system at three-phase steady-state conditions. Therefore, it implies that the saturation history has little impact on the pore occupancy in a mixed-wet rock.

Finally, we observe that at  $f_w = 0.5$  and  $f_o = 0.5$ , after gas injection, Fig. 6i, only oil and water exist in the pore space – there is no gas. This will be discussed in more detail in Section 3.6. Nonetheless, we notice that a large fraction of oil has now moved into larger pores compared to before gas injection (Fig. 6a). We attribute this to the preferential displacement of gas by oil as we will show in Section 4.9.

#### 4.4. Connectivity

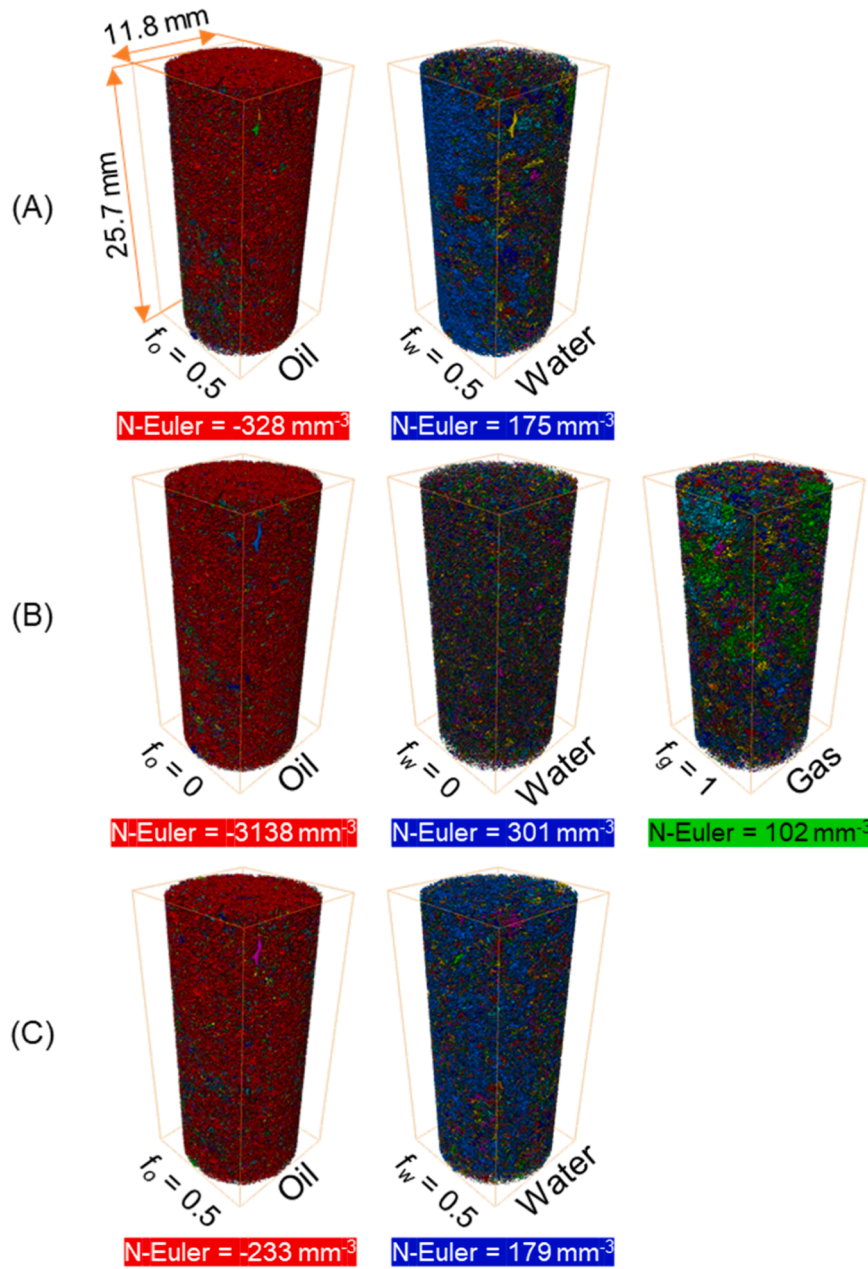
Here, we qualitatively and quantitatively assess the fluid connectivity on the segmented pore-scale images in flow steps 3, 8 and 12; see

Table 1 for their respective fractional flows. It was impossible to examine the fluid connectivity in the three-phase steady-state images as they could not be segmented due to the occurrence of intermittent gas-oil and oil-water flow, as explained in Section 2.4.

Fig. 7 shows the *in situ* three-dimensional connectivity of water, oil, and gas – a wide range of colours represents a poorly connected phase, while a narrow colour distribution indicates that the phase is well connected. Furthermore, the volume-normalized Euler characteristic of each phase is quoted to quantitatively evaluate its connectivity (Herring et al., 2015, 2013; Mecke and Wagner, 1991; Vogel and Kretzschmar, 1996; Vogel, 2002). A large positive Euler characteristic means that the phase is trapped into many discrete ganglia, while a large negative Euler characteristic implies a phase that is interconnected with many loops.

We observe that at  $f_w = 0.5$  and  $f_o = 0.5$ , before gas injection, oil is more connected than water, see Fig. 7a, supported by the negative Euler characteristic ( $-328 \text{ mm}^{-3}$ ). This implies that oil exists in thin wetting layers in the corners, and therefore, confirms that it is more wetting to the surface than water. However, the Euler characteristic of oil is still not in the range of Euler numbers measured on weakly and strongly oil-wet rocks from the same reservoir, where the oil number was much smaller than  $-1000 \text{ mm}^{-3}$  (Alhosani et al., 2021, 2021). This suggests that the rock surfaces are indeed mixed-wet.

At  $f_g = 1$ , see Fig. 7b, both water and gas appear disconnected, with positive Euler number, while the oil connectivity is significantly improved. The enhanced oil connectivity under three-phase conditions is attributed to the spreading of oil in connected layers in the presence of



**Fig. 7.** Three-dimensional maps of oil, water, and gas connectivity in the pore-space of the mixed-wet rock at steady-state conditions. A wide range of colours represents a poorly connected phase, while a narrow colour distribution indicates that the phase is well connected. Gas, water and oil fractional flows ( $f_g$ ,  $f_w$ , and  $f_o$ ) are stated. N-Euler refers to the normalized Euler characteristic of each phase.

gas as seen previously in water-wet experiments (Scanziani et al., 2019, 2018; Alhosani et al., 2021). In contrast, gas exists in disconnected clusters even when injected alone in the mixed-wet system unlike the water-wet case (Alhosani et al., 2021). This behaviour has significant implications for gas storage applications; it means that the re-injection of water to trap gas is unnecessary. This gas behaviour has been previously observed in oil-wet rocks, extracted from the same reservoir, under unsteady-state conditions (Alhosani et al., 2020, 2021).

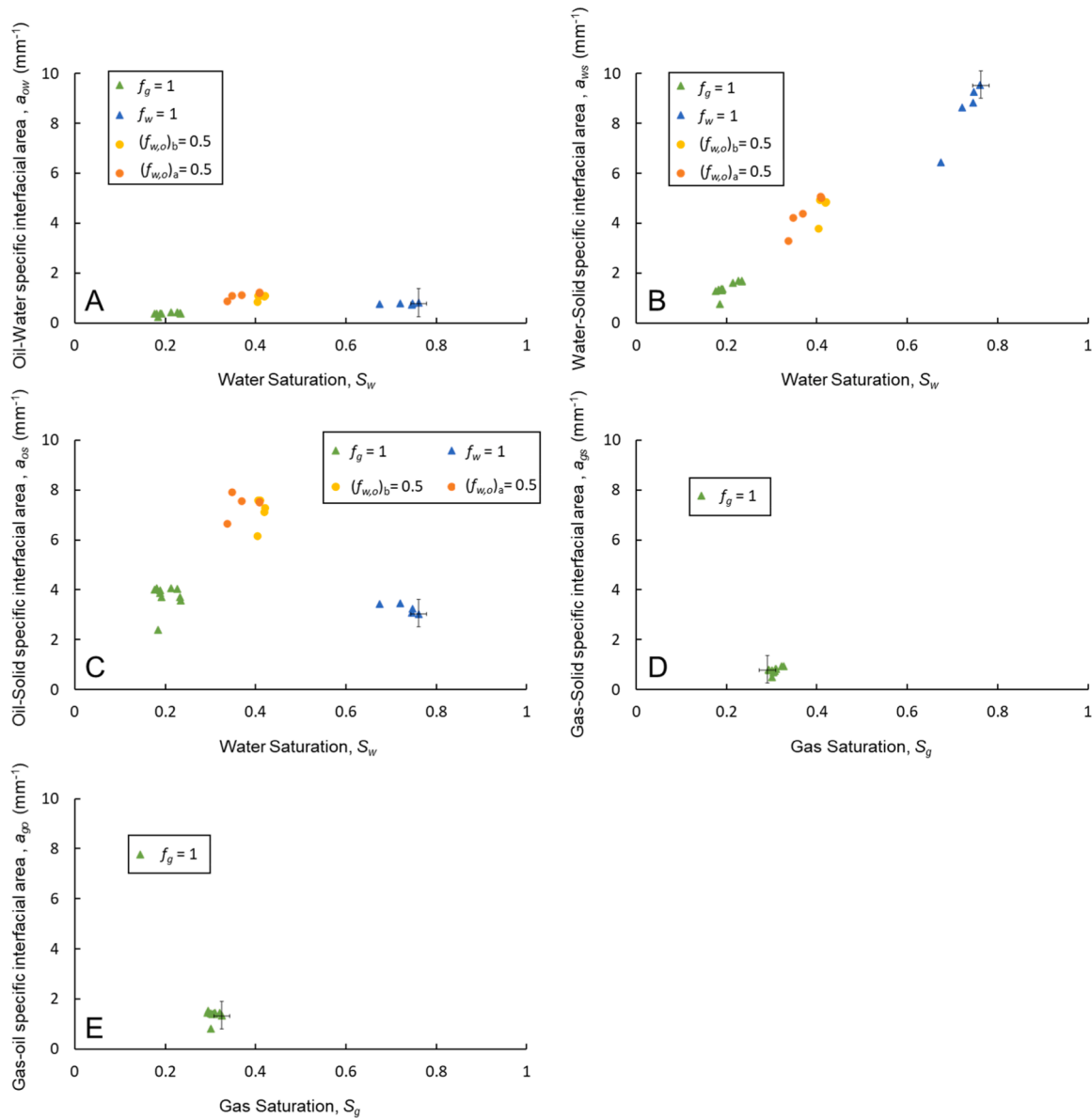
Furthermore, at three-phase steady-state conditions, we suspect that all three phases have a poor connectivity due to their intermittent behaviour. This can lead to each phase having a dynamic connectivity, where it is momentarily connected and then disconnected at steady-state conditions.

#### 4.5. Specific interfacial areas

The fluid-fluid and fluid-solid specific interfacial areas – area per unit total volume (pore and grain) – were measured only on the segmented images of the sample, see Fig. 8.

The oil-water interfacial area remains almost constant under two- and three-phase conditions, with values around  $1 \text{ mm}^{-1}$ , see Fig. 8a. The same behaviour was observed for the area between oil and water in the water-wet system (Alhosani et al., 2021). This is because oil and water are respectively the most and intermediate wetting phases in both systems; the oil-water area is dominated by their contact in the smaller sized pores next to the solid surface.

The water-solid and oil-solid interfacial areas are the largest, see Fig. 8b and c, with the oil-solid area being slightly higher. This indicates that there are more oil-wet regions compared to water-wet regions in the



**Fig. 8.** Specific interfacial areas between (a) oil and water, (b) water and solid, (c) oil and solid, (d) gas and solid, and (d) gas and oil measured on the segmented images of the sample.  $f_g$ ,  $f_w$ , and  $f_o$  refer to gas, water, and oil fractional flows, respectively. Subscripts b and a in the legends of (a), (b) and (c) refer to before and after gas injection, respectively. Error bars represent the uncertainty in the measurements.

mixed-wet pore space. In contrast, the gas-solid area is much lower; this is ascribed to oil spreading around gas reducing its contact with the solid surface. Furthermore, oil spreading prevents any direct contact between gas and water.

The gas-oil interfacial area is higher than that of the oil-water under three-phase conditions ( $f_g = 1$ ), with values around  $2 \text{ mm}^{-1}$ , see Fig. 8a and e. This is a consequence of the spreading of oil in layers around gas in the large pores.

It was not possible to determine the dependence of fluid-fluid and fluid-solid interfacial areas on the saturation history since the three-phase steady-state images could not be segmented.

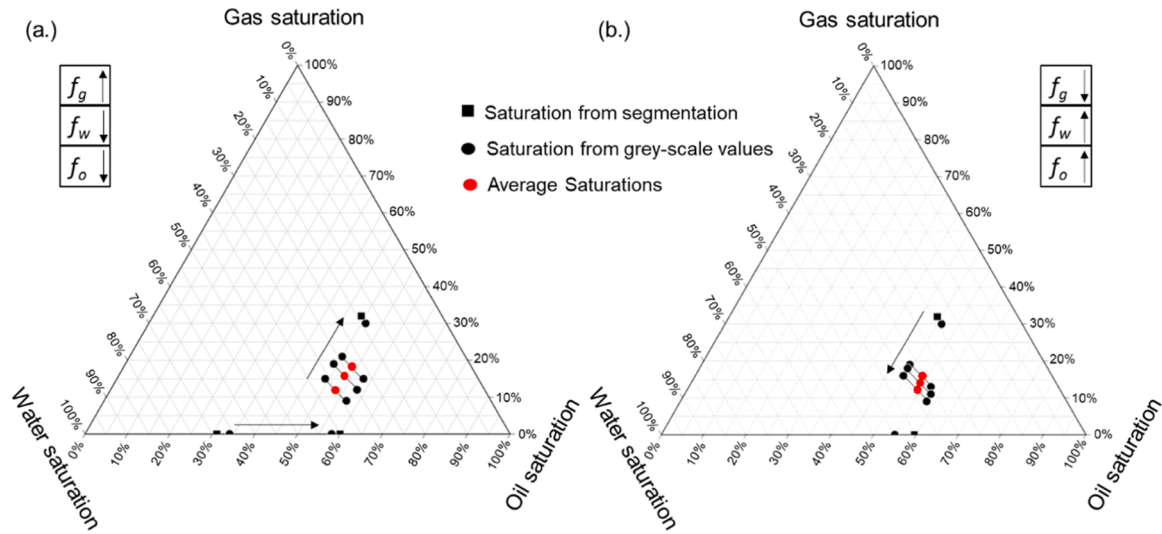
#### 4.6. Saturation

The gas, oil and water saturations, in the macro-pores, were quantified directly from the raw two- and three-phase steady-state images using the approach described in Section 2.4.1, see Fig. 9. This calculation gives a range of gas and water saturations for each three-phase

steady-state image (represented by the line connecting the black circles in Fig. 9); therefore, to obtain the average saturation across the whole sample we assume it is the mid-point of that range (shown in red circles). Fig. 9 is divided into two parts. Part (a) shows the saturations for the increasing  $f_g$ , and decreasing  $f_o$  and  $f_w$ , flow path, while, part (b), shows the saturations for the decreasing  $f_g$ , and increasing  $f_o$  and  $f_w$ , path. The saturations from the segmented images in flow steps 2, 3, 8 and 12, see Table 1 for their fractional flows, are also plotted (shown in black squares).

On average, Fig. 9 displays that there is a good agreement between the saturations obtained from the raw and segmented images, with an uncertainty of  $\pm 5\%$ . However, for consistency, we will only quote the saturations obtained from the raw images in the text.

The first step of the experiment involved the injection of water into the oil-saturated sample, at  $f_w = 1$ , to reach the remaining oil saturation in the mixed-wet system. While a value of 0.34 may seem high, it is still much lower than the values reached in the same reservoir rock but under oil-wet conditions, where the irreducible oil saturations were 0.54 and

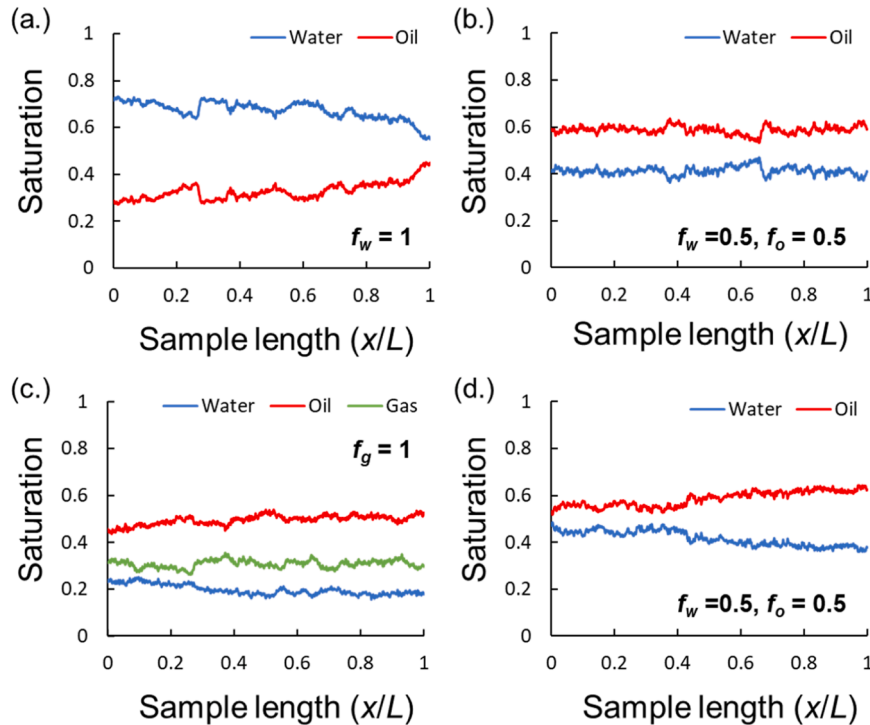


**Fig. 9.** Ternary diagrams showing the saturations obtained at (a) increasing gas fractional flow – decreasing oil and water flow – and (b) decreasing gas fractional flow – increasing oil and water – during the steady-state three-phase experiment in the mixed-wet reservoir rock. Black circles represent the saturations obtained directly from the raw images. Red circles are the averaged saturations obtained from the raw images. Black squares are the saturation obtained from the segmented images in flow steps 2, 3, 8 and 12, see Table 1 for their respective fractional flows.  $f_g$ ,  $f_w$ , and  $f_o$  refer to gas, water, and oil fractional flows, respectively.

0.61 (Alhosani et al., 2020, 2021). Again, this behaviour confirms that our system is mixed-wet. After that, oil and water were injected at  $f_w = 0.5$  and  $f_o = 0.5$ , and the initial saturations of oil and water, before gas injection, were 0.58 and 0.42, respectively.

At the first three-phase steady-state condition, the gas saturation was 0.12, with oil and water saturations of 0.53 and 0.35, respectively, see Fig. 9a. As the gas fractional flow was increased, finally reaching  $f_g = 1$ , the maximum gas saturation only reached 0.32, with 0.49 and 0.19 oil and water saturations, respectively. The first observation here is that the gas saturation never exceeds 0.32 despite increasing the gas flow rate.

This has been previously seen in other unsteady-state and steady-state three-phase flow imaging studies (Scazziani et al., 2019, 2020, Alhosani et al., 2020, 2021b, Alhosani et al., 2021c; Scazziani et al., 2018). Hence, we suggest that, under three-phase capillary-dominated conditions, with immiscible gas and oil phases, the maximum gas saturation that can be reached in this reservoir rock is approximately 32–40% regardless of the rock wettability. The second observation at  $f_g = 1$  is the high remaining oil saturation, see Fig. 9a. We note that gas mainly replaces water in this mixed-wet rock, which will be discussed in more detail in Section 3.9.



**Fig. 10.** Steady-state fluid saturation profiles obtained from the segmented images at (a)  $f_w = 1$ , (b)  $f_w = 0.5$  and  $f_o = 0.5$ , (c)  $f_g = 1$ , and (d)  $f_w = 0.5$  and  $f_o = 0.5$  in the mixed-wet rock plotted along the length of the sample. Fluid saturations in the macro-pores only are considered.  $f_g$ ,  $f_w$ , and  $f_o$  refer to gas, water, and oil fractional flows, respectively.

As the flow path is reversed, decreasing  $f_g$  and increasing  $f_o$  and  $f_w$ , the gas saturation decreases and the oil and water saturations increase, see Fig. 9b. This suggests that, unlike the water-wet system (Alhosani et al., 2021), gas does not get trapped in the pore centres by oil and water; instead, it is produced as more oil and water are injected. While there is a hysteresis in the saturation path of the two flow paths in the mixed-wet experiment, we conclude that fluid saturations are less impacted by the saturation history compared to the water-wet system (Alhosani et al., 2021).

More significantly, we observe that the gas saturation, in the resolvable macro-pores, reaches zero when the gas injection is stopped (at  $f_w = 0.5$  and  $f_o = 0.5$ ), see Fig. 9b, i.e., no gas is trapped in the mixed-wet system. This implies that the stored gas can escape in the case of a water re-injection in mixed-wet reservoir. We will discuss this in more detail in Section 3.10.

Fig. 10 shows the saturation profiles across the sample obtained from the segmented images in flow steps 2, 3, 8 and 12, see Table 1 for their respective fractional flows. While a saturation gradient is seen in 3 of the 4 cases, there is no evidence for a significant capillary end-effect (retention of the wetting phase) at the outlet ( $x/L = 1$ ).

#### 4.7. Three-phase relative permeability

We recorded the pressure drop across the sample at two- and three-phase steady-state conditions to calculate the relative permeabilities in our mixed-wet reservoir rock, see Section 2.4.2. The measured pressures were stable in two-phase flow but continuously fluctuated between two pressure values in three-phase steady-state conditions. We believe that these fluctuations are caused by the intermittent behaviour of fluids which continuously altered the pressure needed for displacement at steady-state conditions.

The pressure fluctuations are significantly larger in the mixed-wet system compared to the water-wet one (Alhosani et al., 2021). We attribute this behaviour to the larger fraction of oil-water intermittency in the mixed-wet system. Furthermore, these observations imply that true steady-state conditions are never attained at the pore-scale in three-phase flow, and that the fluid arrangement is constantly fluctuating between locations of local capillary equilibrium.

Nonetheless, the average of the two pressure values, between which the pressure drop fluctuated, was used to calculate the three-phase relative permeabilities at all the fractional flows. Fig. 11 shows measurements of gas, oil, and water three-phase relative permeabilities in

the mixed-wet system for the increasing  $f_g$  – decreasing  $f_o$  and  $f_w$  – and decreasing  $f_g$  – increasing  $f_o$  and  $f_w$  – flow paths. The relative permeability of each phase is plotted as a function of its own saturation; the fluid saturations in the macro-pores were obtained directly from the raw pore-scale images as described in Section 3.6.

The water relative permeability is lower than that of oil, but higher than gas, see Fig. 11. The low water relative permeability is attributed to the poor water connectivity, as shown in Section 3.4; water flow is limited to medium-sized pores as shown in the pore occupancy (Section 3.3). In contrast, the oil relative permeability is highest due to its improved connectivity in wetting and spreading layers, see Fig. 11c.

Fig. 11b shows that the gas relative permeability is very low. This is ascribed to two reasons: (i) gas progresses in the form of disconnected clusters in the pore centres; and (ii) gas invasion is mostly limited to pores occupied by oil as we will show in Section 3.9.

Fig. 11c shows that the saturation history has a little impact on the oil relative permeability. This is expected since oil is considered the most wetting phase in our system; oil flows in smaller pores and spreading layers regardless of the flow path. On the other hand, water and gas relative permeabilities show a clear dependency on the saturation history since their flow is impacted by the relative presence of another phase in the medium and large pores.

#### 4.8. Capillary pressures

The capillary pressures ( $P_c$ ) were calculated from the interfacial curvature ( $\kappa_{ij}$ ) between the fluid pairs using the Young-Laplace law (Blunt, 2017; Armstrong et al., 2012; Akai et al., 2019):  $P_{c,ij} = \sigma_{ij}\kappa_{ij}$ . The interfaces between the fluids were constructed and smoothed, kernel size = 5, from the segmented images in flow steps 3, 8 and 12, see Table 1, before measuring their curvatures. Fig. 12 shows the measured oil-water and gas-oil capillary pressures in the mixed-wet rock; it was not possible to measure the gas-water capillary pressure since spreading oil layers prevented direct gas-water contact.

The two- and three-phase oil-water capillary pressures are negative, with values around -0.5 kPa, demonstrating the dominance of oil-wet regions over water-wet regions in the mixed-wet reservoir sample, see Fig. 12a. The two-phase oil-water capillary pressure is slightly higher after gas injection, denoted by subscript  $a$  in Fig. 12a, compared to that from before, denoted by subscript  $b$ . We attribute this behaviour to the shift in oil pore occupancy to larger pores after gas injection as we have shown in Section 3.3. As expected, the gas-oil capillary pressure is

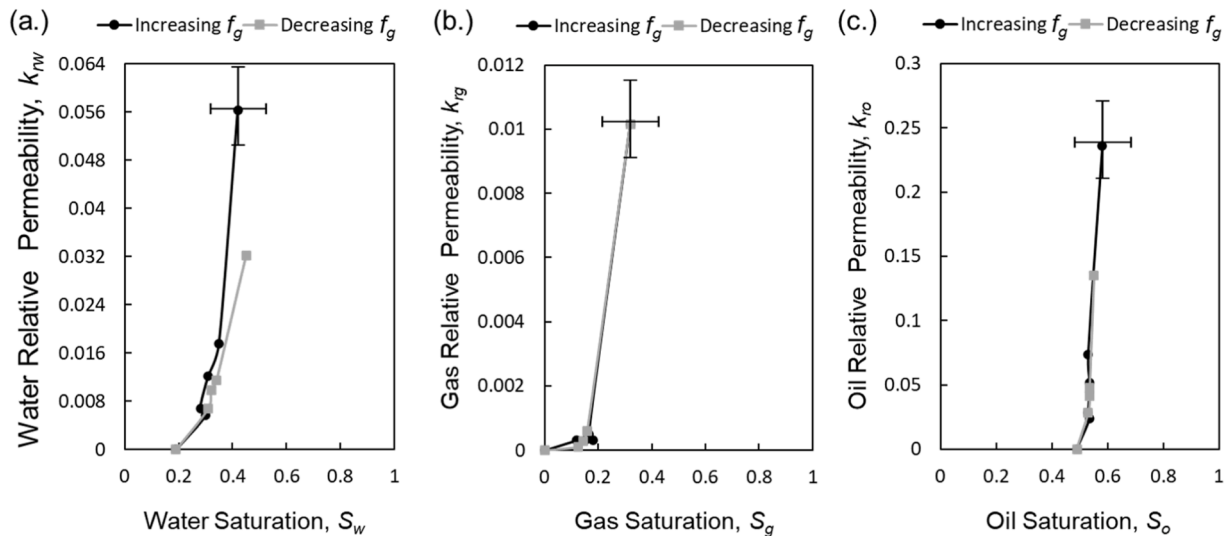
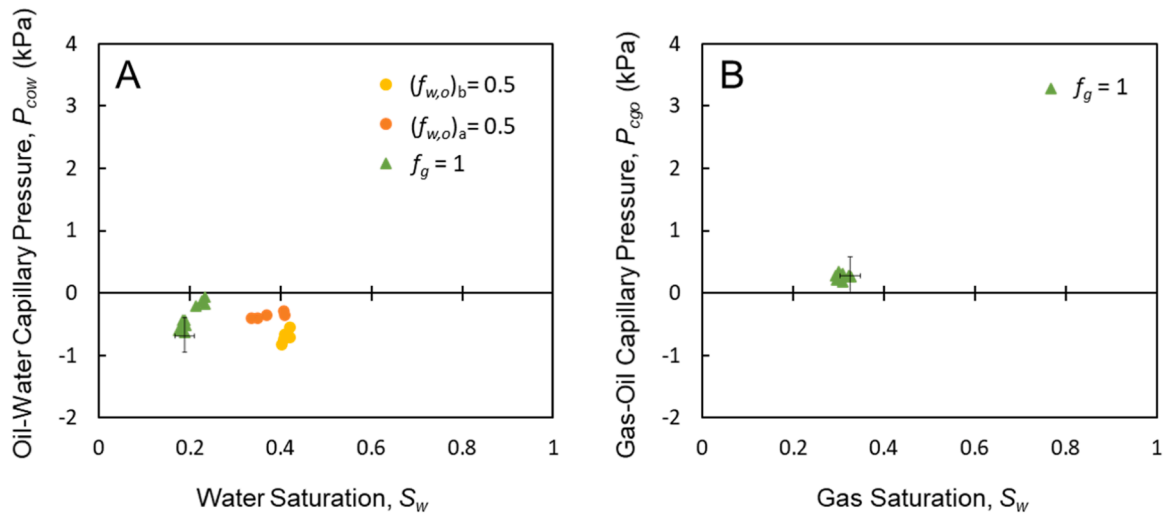


Fig. 11. Three-phase relative permeability of (a) water, (b) gas, and (c) oil during the increasing gas fractional flow – decreasing oil and water fractional flows – and decreasing gas fractional flow – increasing oil and water – in the mixed-wet reservoir rock. Error bars indicate the uncertainty in the measurements for all the points; both in the estimate of saturation and the determination of average pressure drop.



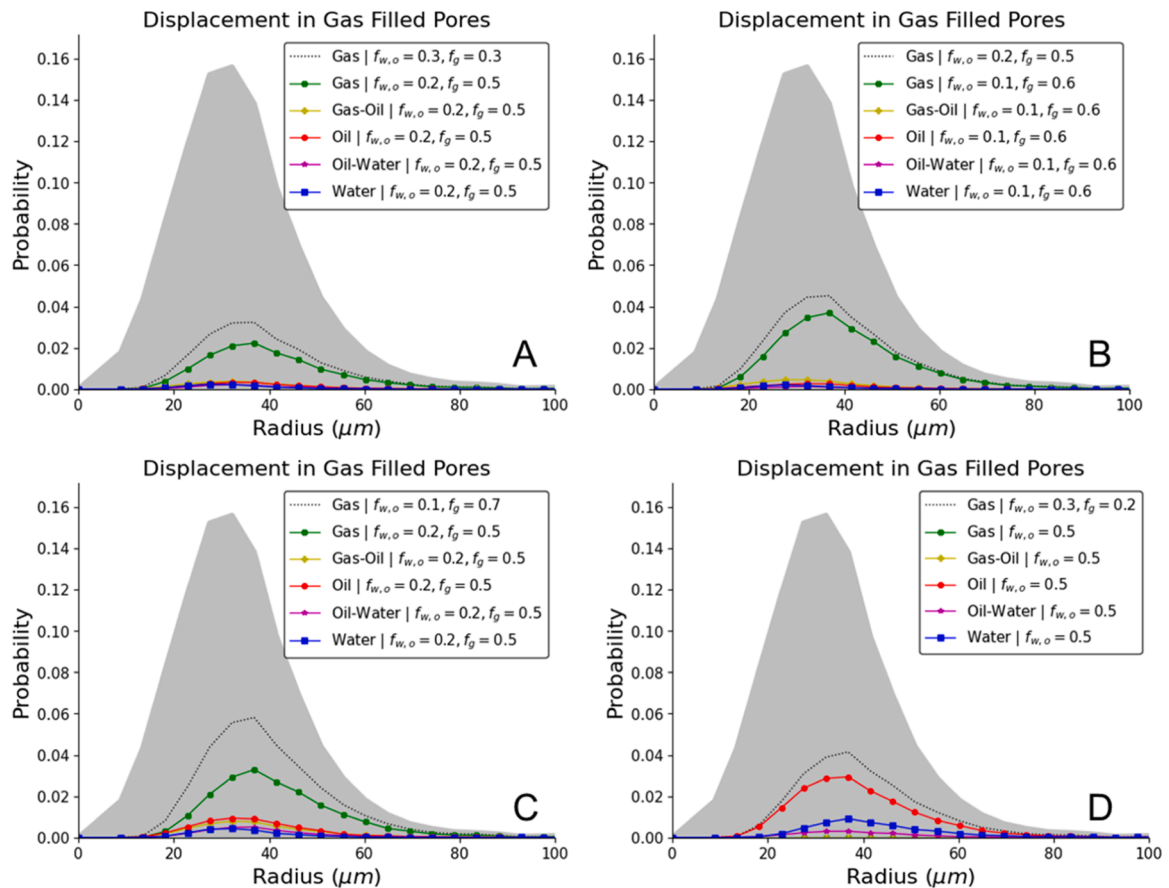
**Fig. 12.** The curvature-based capillary pressure between (a) oil and water, and (b) gas and oil measured on the segmented images and plotted as a function of water and gas saturations, respectively.  $f_g$ ,  $f_w$ , and  $f_o$  refer to gas, water, and oil fractional flows, respectively. Subscripts b and a in the legend of (a) refer to before and after gas injection (at the end of the experiment), respectively. Error bars represent the uncertainty in the measurements.

positive, with values around +0.25 kPa, indicating that oil is wetting to gas, see Fig. 12b.

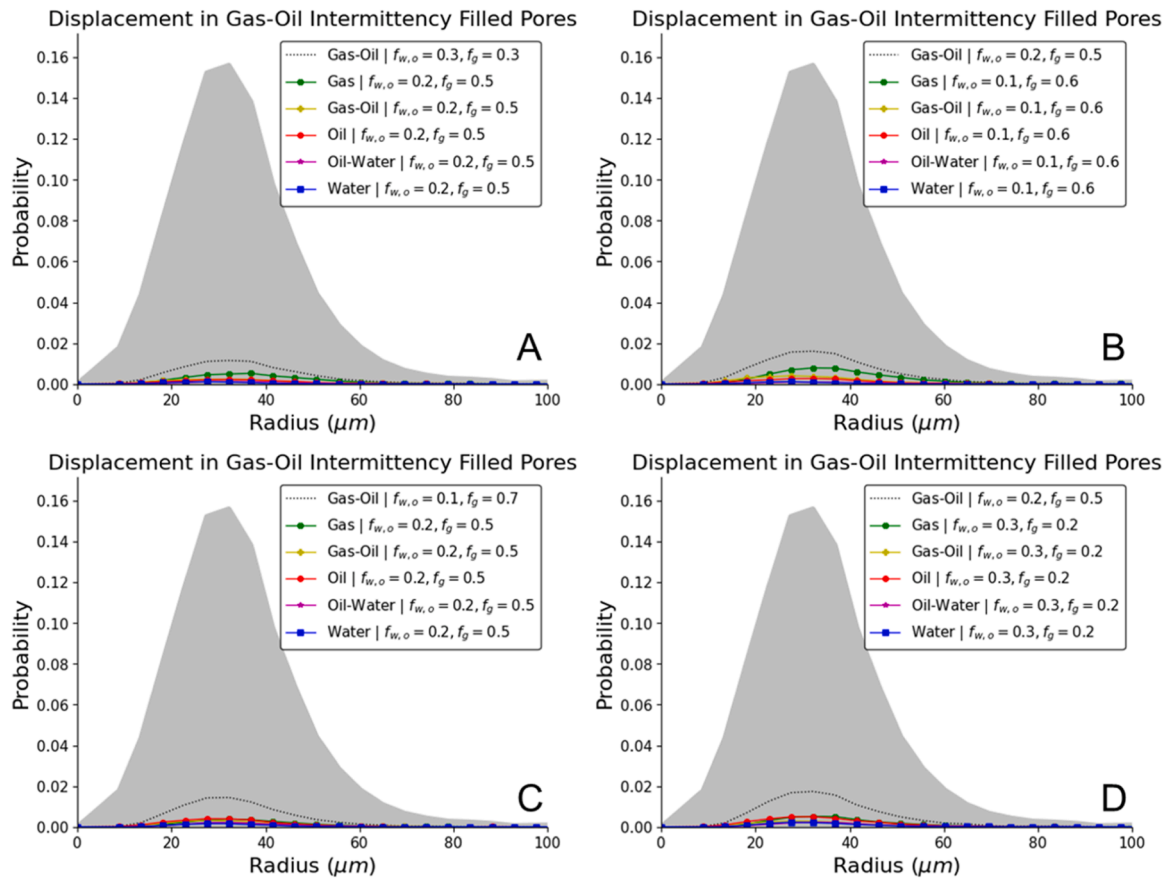
#### 4.9. Three-phase displacements

We quantify the fluid-fluid displacement when moving from one

steady-state condition to another on the raw pore-scale images as described in Section 2.4.3. Similar to pore occupancy, we consider the existence of five phases in the pores of the rock: gas, oil, water, gas-oil intermittency, and oil-water intermittency. Figs. 13, 14 and 15 show the displacement in the pores filled with gas, gas-oil intermittency, and oil at different fractional flows, respectively.



**Fig. 13.** Displacement in the gas-filled pores at different fractional flows in the mixed-wet rock during (a) and (b) increasing gas fractional flow, decreasing oil and water fractional flows, and (c) and (d) decreasing gas fractional flow, increasing oil and water fractional flows, plotted as a function of pore size. Displacement here refers to the change in volume-weighted pore occupancy from one fractional flow to another. Gas, oil and water fractional flows ( $f_g$  and  $f_{w,o}$ ) are stated.



**Fig. 14.** Displacement in the gas-oil intermittency-filled pores at different fractional flows in the mixed-wet rock during (a) and (b) increasing gas fractional flow, decreasing oil and water fractional flows, and (c) and (d) decreasing gas fractional flow, increasing oil and water fractional flows, plotted as a function of pore size. Displacement here refers to the change in volume-weighted pore occupancy from one fractional flow to another. Gas, oil and water fractional flows ( $f_g$  and  $f_{w,o}$ ) are stated.

Fig. 13a and b show that during the increasing  $f_g$ , and decreasing  $f_o$  and  $f_w$ , flow path, the gas-filled pores – represented by the dotted black line – remain mostly occupied by gas; there is very little displacement of gas as  $f_g$  increases.

In contrast, when  $f_g$  is decreased, and  $f_o$  and  $f_w$  are increased, Fig. 13c, we notice that gas is mostly displaced by oil, especially when gas injection stops (Fig. 13d). Gas is produced since it does not get trapped in the pore centres; the displacement of gas by oil is piston-like. While one would expect a percolation-like displacement, with snap-off, we suspect that it is suppressed by the mixed-wet nature of the surface which prevents continuous oil flow and snap-off of gas by oil. The preferential displacement of gas by oil shifts the oil occupancy towards larger pores as seen in Section 4.3.

Fig. 14 shows the displacement in the gas-oil intermittency-filled pores at different fractional flows. We observe that as  $f_g$  is increased, and  $f_o$  and  $f_w$  are decreased, most of the gas-oil intermittency occupied pores are filled with gas, see Fig. 14a and b. In contrast, when  $f_g$  is decreased, and  $f_o$  and  $f_w$  are increased, the gas-oil intermittency occupied pores become filled with oil. This suggests that intermittent regions of the pore space are transitional occupancies waiting for displacement to occur in the direction of the phase with the increasing fractional flow.

In the case of oil-water intermittency, the intermittent pores were equally displaced by oil and water at different fractional flows, regardless of the flow path. This is because the oil and water flow rates were kept in the same direction and had the same value throughout the experiment; see Table 1 for the flow rates. The change in the oil-water intermittency-filled pores is shown in Fig. S4 in the supplementary material.

The displacement in oil-filled pores during the increasing  $f_g$ , and

decreasing  $f_o$  and  $f_w$ , flow path is shown in Fig. 15a and b. Oil is mostly displaced by gas. However, this contradicts the saturation results in Section 3.6, where mostly the water saturation decreased as the gas saturation increased. This phenomenon will be explained later in this section. Furthermore, we note that most of the oil displacement occurs in the bigger pores; there is a little displacement of oil in the smallest pores. This is due to the strongly oil-wet nature of the smaller pores that are filled with oil in our mixed-wet system, where a very high capillary pressure is needed to displace the oil out.

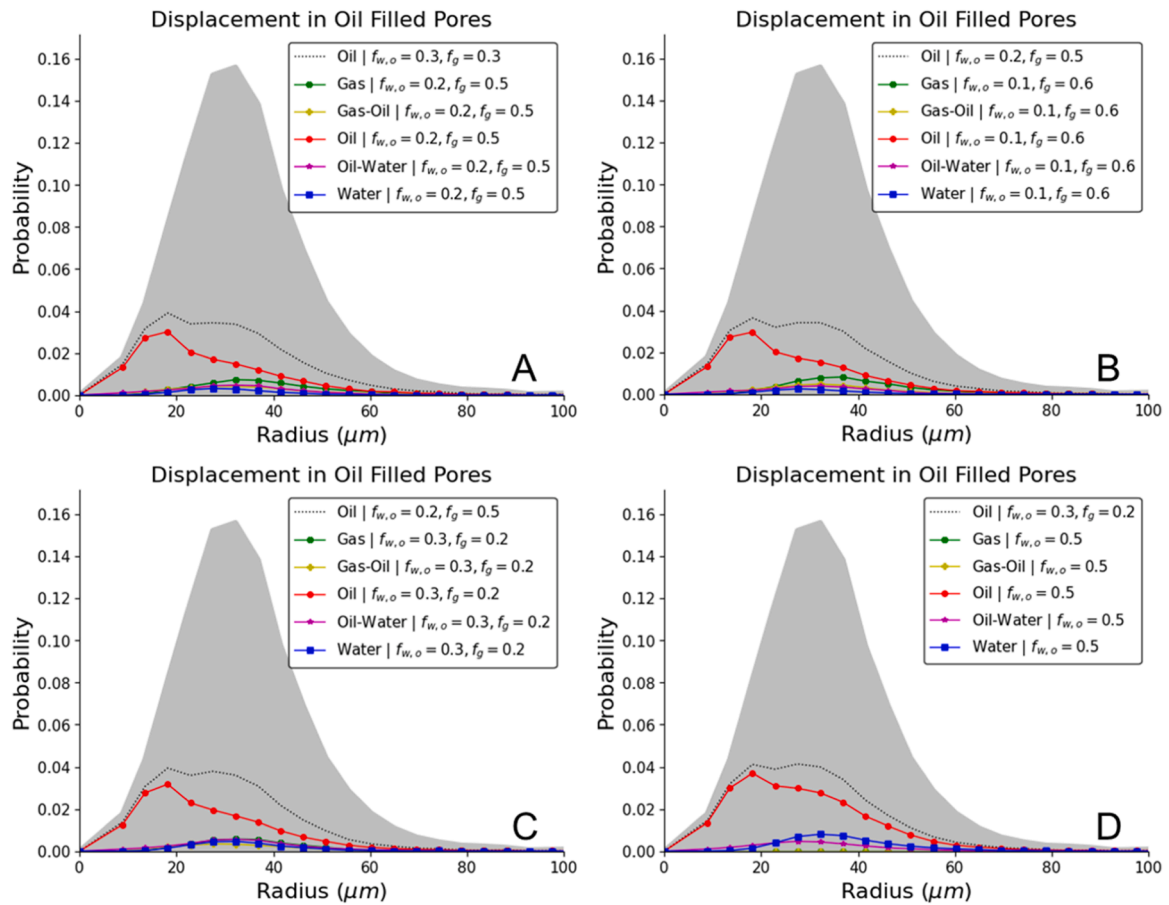
As  $f_g$  is decreased, and  $f_o$  and  $f_w$  are increased, oil is mostly displaced now by water or oil-water intermittency, see Fig. 15c and d.

On the other hand, water is mostly displaced by oil or oil-water intermittency regardless of the flow path direction as shown in Fig. S5 in the supplementary material.

To summarize this section, when  $f_g$  is increased, and  $f_o$  and  $f_w$  are decreased, oil is mostly displaced by gas, and water is displaced by oil, whereas when  $f_g$  is decreased, and  $f_o$  and  $f_w$  are increased, gas is mostly displaced oil, oil is displaced by water, and water is displaced by oil.

From this we can explain why, as  $f_g$  is increased, and  $f_o$  and  $f_w$  are decreased, the water saturation decreases considerably as the gas saturation is increased, although gas mostly displaces oil. As gas invades the pore space, it mainly displaces oil in the largest pores. The displaced oil then moves to mobilize water in smaller pores. The mobilized water then gets produced. At the next fractional flow, gas invades the newly invaded pores by oil, displacing oil out and forcing it to mobilize water in even smaller pores until the irreducible water saturation is reached at a gas fractional flow of one.

This process is reversed when  $f_g$  is decreased, and  $f_o$  and  $f_w$  are increased. Now, oil displaces gas from the smaller pores first. This is



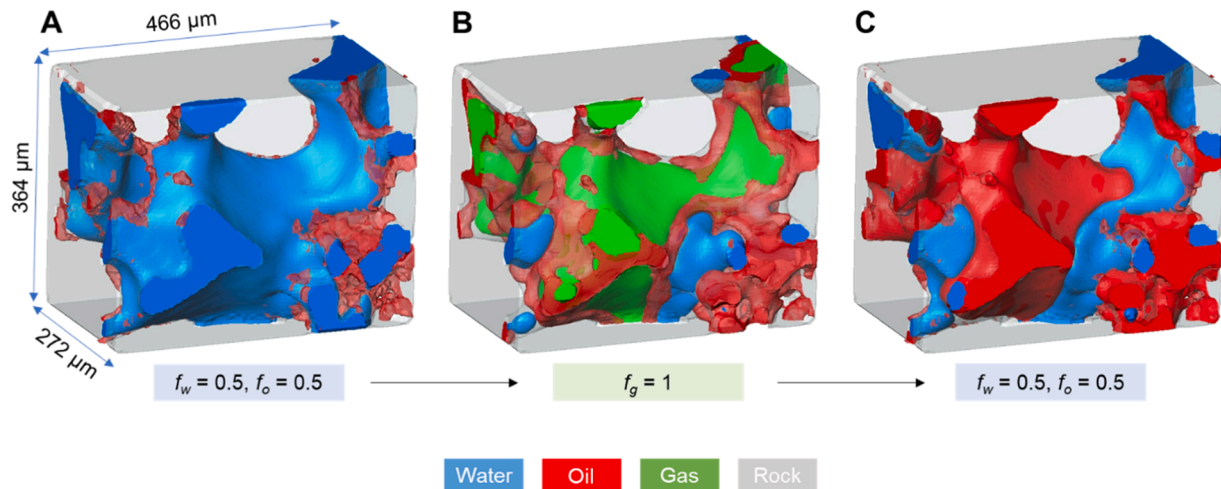
**Fig. 15.** Displacement in the oil-filled pores at different fractional flows in the mixed-wet rock during (a) and (b) increasing gas fractional flow, decreasing oil and water fractional flows, and (c) and (d) decreasing gas fractional flow, increasing oil and water fractional flows, plotted as a function of pore size. Displacement here refers to the change in volume-weighted pore occupancy from one fractional flow to another. Gas, oil and water fractional flows ( $f_g$  and  $f_{w,o}$ ) are stated.

accompanied by displacement of oil by water either in intermediate-sized pores, or large pores where oil displaced gas. The displaced gas gets produced flowing through the largest pores. This continues until there is no more gas in the pore space.

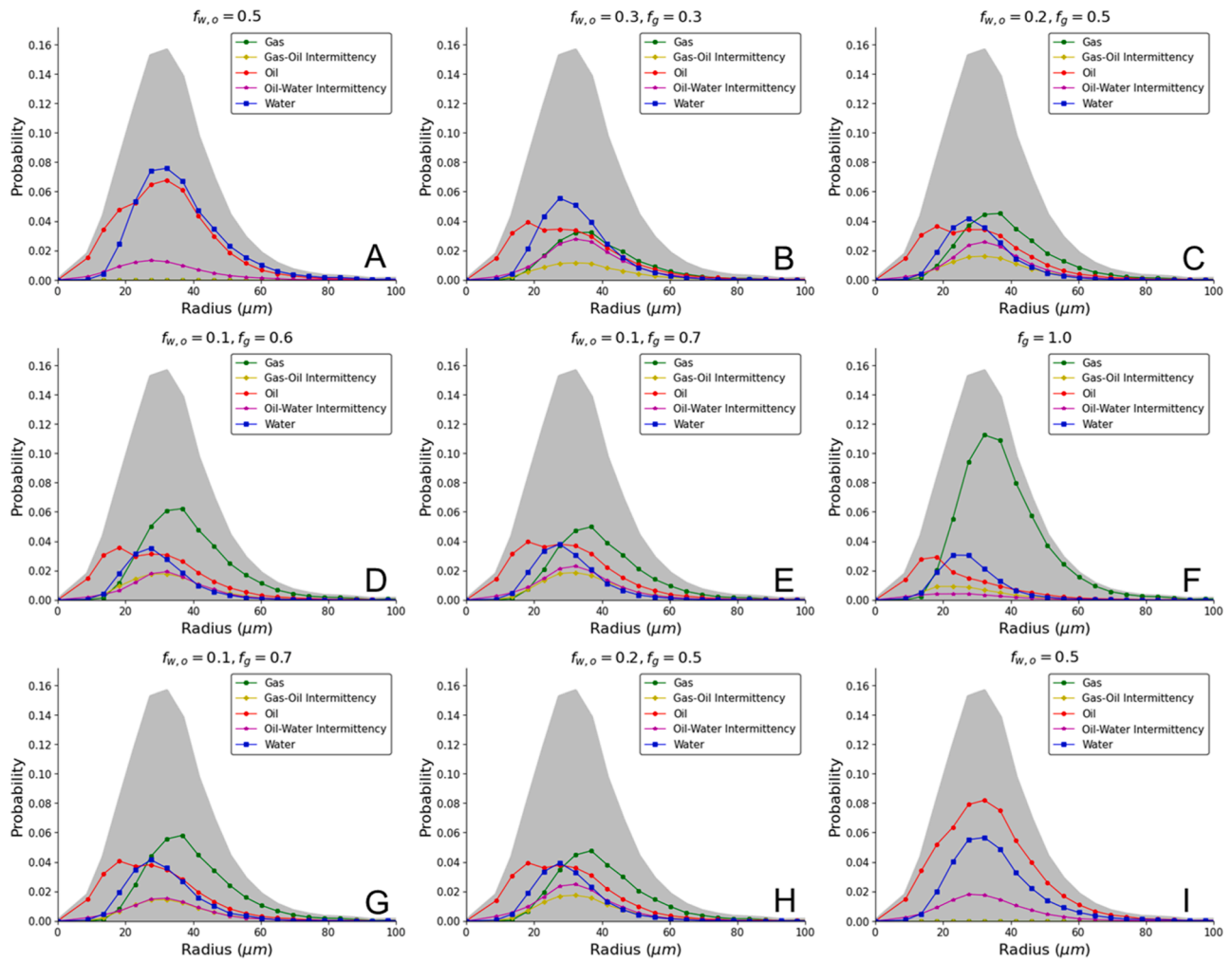
While gas can directly displace oil and vice versa, water and gas can only displace each other in a double displacement process mediated by oil, i.e., gas-oil-water and water-oil gas double displacement processes.

#### 4.10. Trapping and implications for $\text{CO}_2$ storage

Fig. 16 shows the fluid arrangements in a single pore before, during, and after gas injection in the mixed-wet rock. Before gas injection, oil existed in thin wetting layers in the corners of the pores, as expected for mixed-wet media, see Fig. 16a. Once gas was injected, Fig. 16b, the oil connectivity significantly improved as seen in Section 3.4; the thickness



**Fig. 16.** Three-dimensional representation of the fluids arrangement in a single pore (a) before, (b) during and (c) after gas injection in the mixed-wet rock. Oil is shown in red, water in blue, gas in green, while the rock is rendered semi-transparent (grey).  $f_g, f_w$ , and  $f_o$  refer to gas, water, and oil fractional flows, respectively.



**Fig. 6.** Probability histograms showing the volume-weighted pore occupancy in the mixed-wet rock in three-phase steady-state conditions at different fractional flows. Gas, oil, and water fractional flows ( $f_g$ ,  $f_o$ , and  $f_w$ ) are stated in the respective images. The fractional flows add up to 1 but the quoted values have been rounded to one decimal point; refer to Table 1 for exact numbers. The grey-shaded area represents the size distribution of all the pores.

of oil layers increased as it spread between gas and water. Once gas injection was stopped, at  $f_w = 0.5$  and  $f_o = 0.5$ , oil and water completely displaced gas from the pore centre; there is no gas trapping, except, possibly, in smaller pores, below the resolution of the images. We attribute this behaviour to the mixed-wet nature of the surface where neither oil nor water can completely surround the gas phase, preventing snap-off and capillary trapping.

This work illustrates the impact that pore-scale displacement can have on field-scale carbon dioxide storage. While this observation needs to be confirmed for other samples, the absence of gas trapping in macropores does have significant implications on the design of CO<sub>2</sub> storage in depleted oil reservoirs with a mixed wettability state. It shows that the widely implemented water-alternating-gas (WAG) injection strategy in oil reservoirs may not be ideal for secure CO<sub>2</sub> storage. While the strategy is well known for increasing the oil recovery, this work shows that it can lead to recycling of the injected CO<sub>2</sub> as it continuously gets produced.

We suggest that an injection strategy of continuous CO<sub>2</sub> injection is in fact better for secure storage in mixed-wet reservoirs. This is for two reasons: (i) CO<sub>2</sub> naturally gets disconnected when injected as we have shown in Section 3.4; this restricts its flow conductance in the reservoir; and (ii) the injection of large amounts of water, after CO<sub>2</sub> injection, mobilizes CO<sub>2</sub> in the reservoir, producing significant quantities of the stored CO<sub>2</sub>.

## 5. Conclusions

We have presented steady-state measurements of three-phase relative permeability combined with high-resolution pore-scale X-ray imaging, 5.36 μm per voxel, for a carbonate reservoir rock with a mixed wettability state. The experiment was performed under capillary-dominated, immiscible gas-oil conditions. We investigated the impact of a saturation history, where the gas fractional flow is first increased and then decreased on flow properties; oil and water fractional flows were kept the same and changed in the opposite direction to gas. The use of pore-scale imaging allowed us to characterize simultaneously, with relative permeability, the *in situ* contact angles, pore occupancy, connectivity, interfacial areas, capillary pressures, saturations, displacement processes, and trapping.

The mixed-wet nature of the rock surfaces – achieved through contact with crude oil at conditions of high temperature and pressure – was confirmed by calculating the two-phase geometric oil-water contact angle which had a value of  $82^\circ \pm 42^\circ$ . Post gas injection, the gas-oil, oil-water and gas-water contact angles were  $66^\circ \pm 41^\circ$ ,  $80^\circ \pm 41^\circ$ , and  $78^\circ \pm 40^\circ$ , respectively. While it was not possible to determine a clear wettability order from the contact angle measurements, the averaged pore occupancy results demonstrated that, at different fractional flows, oil occupied the smallest pores, water intermediate pores, and gas the largest pores, suggesting an oil-water-gas wettability order, from most to least wetting.

This wettability order was further supported by the negative oil-water and positive gas-oil local capillary pressures. A negative oil-water pressure illustrates that there are more oil-wet regions compared to water-wet regions in the pore space. No gas-water capillary was calculated since oil spread in layers between gas and water preventing their direct contact.

We observed intermittent flow regions between gas and oil, and oil and water at three-phase steady-state flow despite having capillary-dominated conditions. The pores that were intermittently occupied were filled with the phase with the increasing fractional flow at the next steady-state condition. While intermittent flow at capillary-conditions was previously observed in a three-phase water-wet system (Alhosani et al., 2021), here, it is more frequent and occupies a larger fraction of the pore space; in particular, the oil-water intermittency is significant. Both oil-water and gas-oil intermittently occupied pores of similar size, i.e., intermediate-sized pores.

We identify a distinct gas flow pattern, where gas advances in the form of disconnected ganglia mediated by double and multiple displacement processes. Oil was the only connected phase since it forms connected wetting and spreading layers; water existed in disconnected clusters. The oil relative permeability was the highest in the pore space followed by water, then gas. The high oil relative permeability is associated with its improved connectivity. In contrast, gas has a low relative permeability given that it is disconnected and its flow in the larger pores is blocked by water. The impact of saturation history on gas and water relative permeabilities was larger than its impact on the oil relative permeability.

As the gas fractional flow was increased – oil and water flows decreased – gas mainly displaced oil, and oil displaced water. When the flow path was reversed oil replaced gas in the larger pores and water displaced oil in the medium-sized pores. Oil was shifted to larger pores after gas injection. While gas can directly displace oil and vice versa, water and gas can only displace each other in a double displacement process mediated by oil, i.e., gas-oil-water and water-oil gas double displacement processes.

Surprisingly, to within the resolution of the images, there appeared to be no gas trapped when gas injection was stopped. We attributed this behaviour to the mixed-wet nature of the surface which prevents both oil and water from completely surrounding gas and capillary trapping it in the pore centres. These outcomes suggest that the subsequent water injection, after gas, is not ideal for gas storage applications. Instead, a continuous injection of gas only can ensure safe trapping as gas is naturally disconnected upon injection in the reservoir.

Future work should focus on quantifying the steady-state three-phase relative permeability, combined with imaging, in a wider range of samples, and for strongly oil-wet rocks to examine the impact of an oil-gas-water, from most to least wetting, wettability order on relative permeability. This will also provide insights into intermittency showing whether intermittent flow is as frequent as it is in a mixed-wet system. Future experiments should consider investigating the impact of different flow paths to have a comprehensive understanding of the relationship between saturation history and relative permeability. The impact of reaching near-miscible gas-oil conditions could be investigated. Furthermore, the outcomes of this study indicate that an intermittent flow behaviour must be incorporated when modeling steady-state three-phase flow experiments. Moreover, the limited gas relative permeability is a feature that needs to be incorporated in current three-phase relative permeability models.

#### Author statement

A.A. led the experimental work alongside A.S. under the supervision of M.J.B. and B.B. S.F. performed the occupancy and displacement analysis. A.A., A.S., S.F., B.B. and M.J.B. were involved in the design of the study, acquiring and analysing data, and writing the manuscript.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

The data that has been used is confidential.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.advwatres.2023.104382](https://doi.org/10.1016/j.advwatres.2023.104382).

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