

Pore-scale dynamics of multiphase reactive transport in water-wet carbonates under CO₂-acidified brine injection: Dissolution patterns and reaction rates

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ABSTRACT

Depleted carbonate reservoirs are promising sites for geological CO₂ storage, yet the presence of residual hydrocarbon introduces complex pore-scale interactions that influence the dynamics of solid dissolution. We combined time-resolved X-ray microtomography (micro-CT), core-flooding experiments, and pore-scale modeling to investigate how residual hydrocarbon affects dissolution patterns and effective reaction rates during CO₂-acidified brine injection into Ketton limestone under reservoir conditions. We find that the pore structure and fluid distribution control flow heterogeneity, reactive surface accessibility, dissolution patterns and the reaction rates. At low injection rate, two distinct dissolution patterns were observed: 1) a positive feedback loop of channel widening that efficiently enhanced transport properties; and 2) a suppressed regime in which heterogeneity and hydrocarbon blockage resulted in only a modest increase in permeability. At high injection rates, a more uniform dissolution occurred caused by re-mobilization of hydrocarbon that initially blocked the flow of brine. Effective reaction rates in two-phase flow were lower than in the equivalent single-phase case and up to two orders of magnitude lower than the batch rates due to persistent transport limitations. These findings provide mechanistic insights into multiphase reactive transport in carbonates and highlight the importance of accurately understanding the impact of the residual phase on reactions to improve predictions of CO₂ storage efficiency.

1. Introduction

Carbon dioxide storage in geological formations is a key strategy for mitigating atmospheric CO₂ emissions (Chai et al., 2025, 2022; Leung et al., 2014; Bui et al., 2018). Among various geological targets, depleted carbonate reservoirs have large pore volumes, existing infrastructure, and favorable mineralogy (Zhou et al., 2024). However, the long-term security of stored CO₂ remains a critical concern (D'Alessandro et al., 2010), as interactions between injected CO₂, formation brine, and carbonate minerals can lead to mineral dissolution and precipitation. Specifically, the formation of carbonic acid upon CO₂ dissolution in brine initiates geochemical reactions with the rock, altering the pore structure and potentially impacting reservoir integrity (Van Offenwert et al., 2019). These coupled fluid-rock interactions affect key properties such as porosity, permeability, and flow pathways, and must be understood to predict reactive transport behavior and ensure the stable long-term containment of CO₂ in carbonate formations.

Key insights for characterizing reactive transport include identifying dissolution regimes and quantifying reaction rates. To understand dissolution regimes, a useful framework is the Péclet (Pe) and Damköhler (Da) diagram (Golfier et al., 2002; Battiatto and Tartakovsky, 2011), where Pe is the ratio of advective to diffusive rates of transport, and Da is the ratio of reaction to advection rates. In fluid–solid systems, different regimes are commonly observed dependent on the Pe and Da numbers. First, when both Da and Pe are high, both reaction and injection rate are rapid, leading to the formation of wormholes with a sharp dissolution front. This is the wormholing regime, as exemplified by acidizing in field operations (Esteves et al., 2020; Furui et al., 2022; Soulaire et al., 2017). Next, when Pe is low and diffusion dominates, face (compact) dissolution occurs: a slowly advancing dissolution front progresses in the flow direction. Third, when Da is low and Pe is high, dissolution is uniform: flow reaches most reactive surfaces, reactions are slow, and material dissolves evenly throughout the volume. Another

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regime, channel widening, emerges when the interplay of flow heterogeneity and transport conditions is considered (Menke et al., 2016; Pereira Nunes et al., 2016; Al-Khulaifi et al., 2018; Menke et al., 2023). This pattern is particularly relevant in systems with a low Da, heterogeneous flow, and a moderate Pe, where both advection and diffusion are significant. For instance, in CO₂ storage, carbonic acid forms when supercritical CO₂ dissolves in brine. At typical reservoir conditions, its pH is about 3.1–3.5 (Menke et al., 2015), which corresponds to a low Da and might suggest a uniform dissolution regime. Instead, experiments injecting single-phase, CO₂-acidified brine into calcite (Menke et al., 2016, 2017) and dolomite (Al-Khulaifi et al., 2017, 2019, 2018) have shown that these conditions produce preferential pathways that widen over time, making channel widening the dominant dissolution mechanism. The development of flow heterogeneity by channel formation and widening has been widely reported (Fredd et al., 2000; Cooper et al., 2023), and shown to alter the conventional porosity–permeability relationship (Noiriel et al., 2004, 2005; Luquot and Gouze, 2009; Smith et al., 2013; Ott and Oedai, 2015; Luhmann et al., 2014; Yang et al., 2020). These studies collectively highlight the critical roles of transport limitations, coupled flow-dissolution dynamics, and mineral heterogeneity in shaping reactive dissolution under single-phase flow conditions.

The primary knowledge gap, and the focus of this work, emerges when considering the more realistic multiphase conditions of depleted reservoirs, which invariably contain residual hydrocarbon. The presence of a second fluid phase creates more complex local flow fields and may reduce the available reactive surface area (Akindipe et al., 2022; Zhao et al., 2025). Previous studies on multiphase flow systems have often been decoupled, failing to capture the concurrent interactions between hydrocarbon, acidic brine, and rock (Singh et al., 2018; Honarvar et al., 2017). These complexities underline a fundamental difference between single-phase and multiphase flow systems: the hydrocarbon phase introduces spatial and temporal heterogeneity in transport and reaction that has not yet been fully investigated at the pore scale. Therefore, a complete understanding of how residual hydrocarbons influence reactive transport in carbonates is still lacking. A further challenge is the accurate estimation of effective reaction rates, which are known to be scale-dependent and significantly lower in real porous media than intrinsic rates measured in batch reactors (Maher, 2010). This discrepancy is further influenced by mineral reactivity (e.g., dolomite vs. calcite), rock heterogeneity, and flow conditions including the Péclet number (Peng et al., 2015).

The present study investigates multiphase reactive transport in carbonate rocks under reservoir-relevant conditions using an integrated experimental and modeling approach. We designed the experiments to inject CO₂-saturated brine for two Pe into two Ketton limestone samples containing varying levels of remaining hydrocarbon. Time-resolved X-ray microtomography was used to capture dynamic changes in pore structure, porosity, fluid occupancy and reactive surface accessibility. Based on these 4D datasets, we performed direct numerical simulations (Bijeljic et al., 2013a,b) to quantify the evolution of permeability and velocity fields. This approach allows us to systematically evaluate how initial pore structure and hydrocarbon saturation interact to govern flow heterogeneity, dissolution patterns, reaction rates and dissolution dynamics.

2. Materials and methods

2.1. Materials

Two cylindrical samples of oolitic Ketton limestone (12 mm in length, and 6 mm in diameter) were studied. The rock was composed of 99.1% calcite and characterized by a well-connected, bimodal pore size distribution, with micro-pore and macro-pore throat radius peaks below 0.1 μm and above 10 μm, respectively, separated by almost three orders of magnitude (Patmonoaji et al., 2025). The rock had a helium porosity

of 0.239 ± 0.008 (Patmonoaji et al., 2025). The absolute permeabilities of the two samples were measured based on Darcy's law at three flow rates under single-phase (brine) flow conditions to be 2.45 ± 0.03 Darcy and 2.65 ± 0.03 Darcy.

Decane was selected as the oil phase due to its well-characterized interfacial properties and frequent use in multiphase transport studies. This choice also reduces oil–rock interactions observed with crude oil (Akindipe et al., 2022). Ketton limestone is generally regarded as strongly water-wet (Singh et al., 2016). This characterization is supported by experimental observations where Ketton samples, prior to contact with crude oil, have demonstrated strongly water-wet properties under brine and decane conditions (Singh et al., 2016). The synthetic brine consisted of 5 wt% NaCl and 1 wt% KCl dissolved in deionized water, doped with 30 wt% potassium iodide (KI) to enhance X-ray contrast during imaging (Lin et al., 2021). At the experimental conditions of 50 °C and 8 MPa, the viscosities of brine and decane were 0.82 mPa s (Patmonoaji et al., 2025) and 0.838 mPa s (provided by PubChem, open chemistry database), respectively.

2.2. Experimental methods

i. Preparation of CO₂-saturated brine. The brine was equilibrated with CO₂ in a high-pressure reactor at 8 MPa and 50 °C for one week.

ii. System assembly. The Ketton limestone sample was enclosed in a Viton sleeve and mounted into a core holder. The assembled core holder was then installed in a CT scanner (Versa XRM-500 X-ray Microscope) and connected to the fluid delivery and receiving system, pressure transducer, and other experimental components, as shown in Fig. 1.

iii. System cleaning. A confining pressure of 2 MPa was applied to ensure proper sealing and eliminate bypass flow between the sample and sleeve. The temperature was then increased to 50 °C. CO₂ was injected for 30 min (approximately 740 pore volumes (PV)) to flush residual fluids and fines, followed by 24 h of vacuuming to evacuate the remaining gases.

iv. Baseline imaging. A high-resolution dry scan was acquired to serve as a baseline for subsequent comparisons.

v. Brine saturation. The sample was saturated with brine at a constant flow rate of 0.05 mL min^{−1} for 100 pore volumes (PVs). The back pressure and confining pressure were then steadily increased to 8 MPa and 10 MPa, respectively, and the temperature was maintained at 50 °C, after which a brine saturated scan was performed. Throughout the experiment, injection occurred through the bottom inlet.

vi. Establishment of initial oil saturation (S_{oi}). Decane was injected at 0.05 mL/min for 100 PVs to establish S_{oi} , after which a corresponding micro-CT scan was obtained.

vii. Establishment of residual oil saturation (S_{or}). Brine was re-injected at 0.05 mL/min for 20 PVs to achieve S_{or} , followed by another scan. The resulting S_{or} values were 39.8% for Sample 1 and 31.1% for Sample 2.

ix. Reactive flooding with CO₂-saturated brine. (i) Injection at 0.05 mL/min for 315 min. (ii) Flow was halted for 135 min to promote diffusion-dominated transport and reaction. (iii) Resumed injection at 0.5 mL/min for an additional 225 min.

2.3. Image acquisition

Two distinct micro-CT imaging protocols were employed: a high-spatial-resolution protocol for the detailed static characterization of the initial pore structure, and a high-temporal-resolution protocol to monitor the dynamic evolution of the pore structure during reactive transport.

To characterize the evolution of fluid occupancy and pore structure, a series of high-resolution micro-CT scans were conducted throughout the experiment. Prior to flooding, a dry scan of the sample was acquired

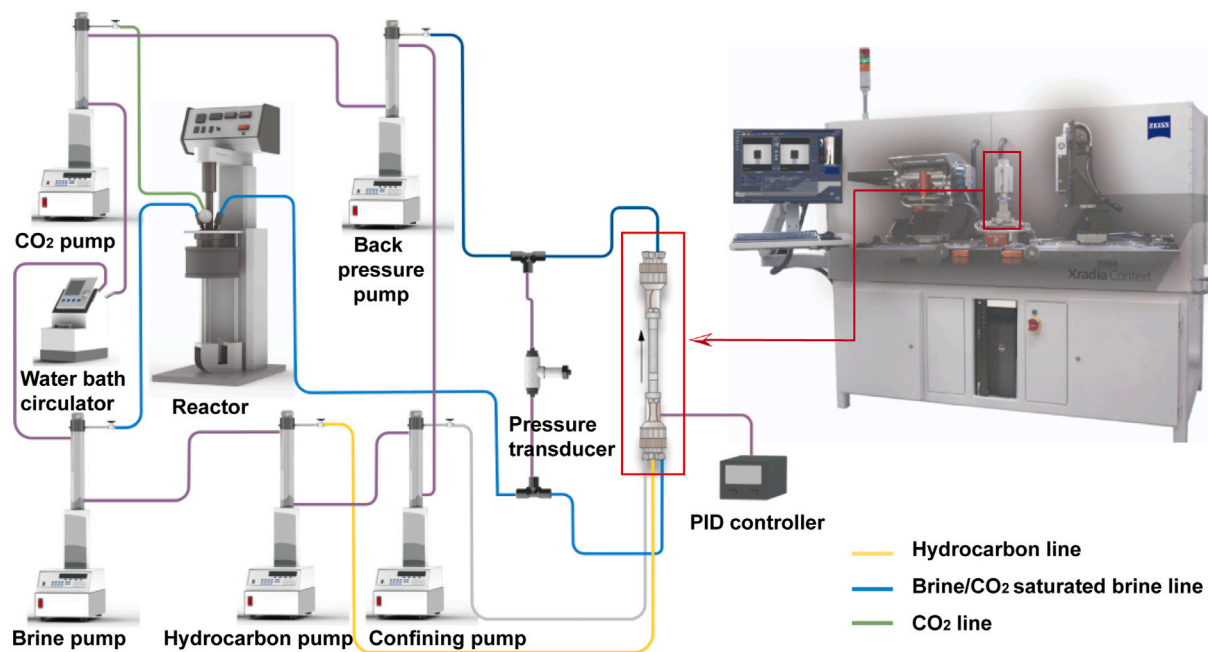


Fig. 1. The experimental apparatus including the flow loop and micro-CT scanner.

to capture the initial pore geometry. This was followed by a brine-saturated scan after full saturation and a scan after decane injection to determine the initial oil distribution. All these scans used 2601 projections with an energy of 100 keV and a power of 9 W. The scans were conducted at a voxel resolution of $3.57\ \mu\text{m}$ and required approximately 12 h each to ensure optimal image quality and accurate segmentation. This resolution resulted in a corresponding field of view (FOV) of $7.14\ \text{mm} \times 7.14\ \text{mm} \times 7.14\ \text{mm}$. To obtain a sufficiently representative image size at this high resolution, we performed two consecutive scans along the sample's axial direction and subsequently computationally stitched the resulting image data.

For the time-resolved imaging, a baseline scan was first acquired after brine re-injection to determine the residual oil saturation. The dynamic imaging sequence commenced at the onset of CO_2 -saturated brine injection ($t = 0$), during which 12 images were acquired. These dynamic scans, along with the residual oil saturation scan, were performed using 901 projections at an energy of 100 keV and a power of 9 W. Each scan required approximately 45 min and used a voxel size of $6\ \mu\text{m}$, which resulted in a $12\ \text{mm} \times 12\ \text{mm} \times 12\ \text{mm}$ FOV sufficient to capture the entire region of interest in a single acquisition. Consequently, the first scan during reaction was performed from $t = 0$ to $t = 45\ \text{min}$: this is called the 45 min scan. The second image is called 90 min and so on, as detailed in Table 1. The entire reaction experiment lasted for a total of 675 min. This imaging protocol was chosen to balance temporal resolution with image quality, enabling the accurate tracking of dissolution fronts and structural evolution without introducing significant motion artifacts or radiation damage.

2.4. Image processing and analysis

Three-dimensional tomograms were reconstructed using Zeiss Reconstructor software correcting for beam hardening and center shift. Image processing was conducted in commercial image analysis software (Avizo) using a standardized workflow to ensure cross-scan comparability. Initially, images were denoised using a combination of non-local means and anisotropic diffusion filters. This was followed by intensity normalization to standardize grayscale ranges. For the high-quality $3.57\ \mu\text{m}$ scan, two individual sections were aligned and stitched to form a single contiguous sample. Finally, all scans were co-registered

Table 1

Second imaging protocol with 45-min scans at $6\ \mu\text{m}$ voxel size and the corresponding cumulative pore volumes injected.

Scan	Time interval (Start-End) (min)	Pore volumes	
		Sample 1	Sample 2
0 min scan	Residual oil saturation scan		
<i>Low flow rate injection start</i>			
45 min scan	t = 0 to t = 45	45	40
90 min scan	t = 45 to t = 90	88	79
135 min scan	t = 90 to t = 135	128	117
180 min scan	t = 135 to t = 180	163	154
225 min scan	t = 180 to t = 225	198	191
270 min scan	t = 225 to t = 270	233	228
315 min scan	t = 270 to t = 315	268	264
<i>Stop injection (t = 315 to 450 min)</i>			
<i>High flow rate injection start</i>			
495 min scan	t = 450 to t = 495	587	627
540 min scan	t = 495 to t = 540	861	920
585 min scan	t = 540 to t = 585	1130	1178
630 min scan	t = 585 to t = 630	1351	1409
675 min scan	t = 630 to t = 675	1562	1620

to a common reference and resampled to a resolution of $6\ \mu\text{m}$. This systematic approach guaranteed consistency across all imaging stages, facilitating accurate segmentation and quantitative analysis.

Phase segmentation employed a hybrid workflow that combined differential imaging (Gao et al., 2017), interactive thresholding, and watershed-based segmentation (Lin et al., 2016), enabling robust delineation of three primary phases: rock matrix, brine, and oil.

Pre-reaction datasets. (i) The rock matrix was extracted from the dry reference scan. (ii) Oil was segmented directly from the images without differential imaging. (iii) Brine was isolated by subtracting the dry scan from the brine- or oil-saturated scans, thereby identifying the pores occupied by the aqueous phase.

Post-reaction datasets. (i) Mineral dissolution was quantified by subtracting the segmented pre-reaction rock volume from the post-reaction image, yielding the dissolved fraction. (ii) The reacted rock matrix was obtained by subtracting the dissolution volume from the original rock phase. (iii) Brine and oil were segmented using the

same protocol as for the pre-reaction datasets, ensuring methodological consistency across all time steps.

2.5. Pore-scale simulation

Following image segmentation, the lower region of the segmented micro-CT volume ($5.7 \times 5.7 \times 6 \text{ mm}^3$) was selected for pore-scale flow simulation in the brine phase. The modeling approach follows the method developed by Bijeljic et al. (2013a) and Raeini et al. (2012), implemented within the OpenFOAM framework. The solver employs the finite volume method to simultaneously solve the continuity and steady-state incompressible Navier–Stokes equations:

$$\nabla \cdot \mathbf{u} = 0 \quad (1)$$

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} \quad (2)$$

where p is the pressure (Pa), and u is the velocity (m/s), both obtained for each voxel of the image; μ is the fluid (brine) viscosity (Pa s); ρ is the fluid density (kg/m^3). The flow rate (m^3/s) is calculated as $Q = \int u_x dA_x$, where A_x is the cross-sectional area of the image (m^2) and u_x is the velocity in the direction of overall flow (m/s). The Darcy velocity (m/s) is then calculated as $q = \frac{Q}{L_y L_z}$, where L_y and L_z are the lengths of the image (m).

Permeabilities (K) were calculated at the core scale using Darcy's law:

$$K = -\mu \frac{q}{\nabla p} \quad (3)$$

where, q is the Darcy velocity (m/s), ∇p is the pressure gradient (Pa/m) across the sample and μ is the fluid viscosity (Pa s). In Section 3.1, the reported permeabilities specifically correspond to the brine phase in the presence of residual oil. These values were determined by simulating the flow field within the connected, brine-saturated pore network, where the residual oil was assumed to remain immobile. For comparison, the absolute permeability was also calculated by simulating the flow through the entire connected pore space, assuming complete saturation by the brine phase.

A fixed 1 Pa pressure drop was applied along the flow direction, while all solid boundaries were treated as no-slip walls. To analyze the spatial distribution of flow, the velocity field was normalized by the average pore velocity:

$$u_{av} = \frac{q}{\phi} \quad (4)$$

where ϕ is the porosity (dimensionless), and the ratio u/u_{av} was visualized to assess local deviations from the mean flow behavior.

To quantify the tortuosity of the flow field, the following definition was used:

$$\tau = \frac{\langle |\mathbf{u}| \rangle_{\text{pore}}}{\langle u_x \rangle_{\text{pore}}} \quad (5)$$

where $\langle |\mathbf{u}| \rangle_{\text{pore}}$ is the average magnitude of the velocity field within the pore space, and $\langle u_x \rangle_{\text{pore}}$ is the average velocity in the primary flow direction. This ratio accounts for the increased path length due to the tortuosity of the pore network, providing a dimensionless measure of the flow complexity.

2.6. Dimensionless numbers and reaction rates

In this study, the dimensionless number, Péclet (Pe) and Damköhler (Da), are used to characterize and quantify the reactive transport. The Péclet number quantifies the relative efficiency of solute mass transfer through advection compared to diffusion (Péclet, 1827):

$$\text{Pe} = \frac{\text{advective transport rate}}{\text{diffusive transport rate}} = \frac{u_{av} L_c}{D_m} \quad (6)$$

where D_m is molecular diffusion coefficient in brine (m^2/s), u_{av} is the average pore velocity, which is the Darcy velocity from the experiment

divided by the product of porosity and brine saturation, while L_c is characteristic length (m), calculated by Mostaghimi et al. (2012):

$$L_c = \frac{\pi}{S} \quad (7)$$

where the specific surface area S (m^{-1}), is the image surface area per unit volume at the beginning of the time period, calculated by V_B/A_s , where V_B is bulk volume, and A_s is the surface area from image analysis.

The Damköhler number quantifies the ratio between the timescales of a chemical reaction and the mass transfer (Lasaga, 1984):

$$\text{Da} = \frac{\text{reaction rate}}{\text{advective transport rate}} = \frac{L_c}{u_{av}} k \quad (8)$$

where k is the chemical reaction rate constant (s^{-1}), calculated by: $k = \frac{\pi r}{nL}$. r is the mineral reaction rate ($\text{mol m}^{-2} \text{s}^{-1}$), L is the sample length (m), and n is calculated by Menke et al. (2015):

$$n = \frac{\rho_{\text{mineral}} f_{\text{mineral}}}{M_{\text{mineral}}} \quad (9)$$

where ρ is the mineral density, M_{mineral} is their molecular mass. Therefore, Eq. (8) can be rewritten as follows (Al-Khulaifi et al., 2018):

$$\text{Da} = \frac{\pi r_{\text{mineral}}}{u_{av} n} \quad (10)$$

where r is the non-transport limited reaction rate.

The effective reaction rate (r_{eff}) of mineral is determined as (Al-Khulaifi et al., 2017):

$$r_{\text{eff}} = \frac{\rho_{\text{mineral}} (1 - \phi_{\text{unresolved}}) \Delta \phi_{\text{CT}}}{M_{\text{mineral}} S \Delta t} \quad (11)$$

where Δt is the time between scans (s), $\Delta \phi_{\text{CT}}$ is the corresponding change in porosity and S is the image surface area per unit volume (m^{-1}). We observe almost no change in grayscale values for solid voxels containing sub-resolution features, indicating no measurable change in porosity in these regions. The unresolved porosity ($\phi_{\text{unresolved}}$) is calculated based on data from a sister sample drilled from the same block (Patmonaoji et al., 2025). The specific calculation methods are provided in the supporting information.

3. Results and discussion

3.1. Pore-scale heterogeneity

The interplay between initial pore-scale structural heterogeneity and the subsequent distribution of residual oil creates a coupled dual heterogeneity, which governs the flow field and transport dynamics. Our findings reveal that although both carbonate samples originate from the same formation, their distinct pore structure leads to different distributions of residual oil and, consequently, contrasting dissolution patterns and reaction rates.

Sample 1 is characterized by a well-connected network of intergranular macro-pores, resulting in a relatively homogeneous structure (Fig. 2a, b). This architecture facilitates more uniform brine flooding, leading to a piston-like displacement and a relatively dispersed distribution of residual oil throughout the accessible pore space (Fig. 2e, f). Based on SEM and mercury intrusion data (Patmonaoji et al., 2025), Sample 2's heterogeneity stems from a dual-porosity system consisting of intergranular macro-pores and poorly-connected intermediate sized pores formed by fine interstitial particles (Fig. 2c, d), in contrast to Sample 1's more uniform macro-pore network. The porosity map (Fig. 2b and d) further reveals that Sample 2 exhibits significant intergranular packing of interstitial particles, particularly near the inlet, which appears as intermediate gray tones. During brine flooding, this structural complexity promotes capillary fingering and incomplete displacement, causing residual oil to become concentrated in localized, isolated clusters (Fig. 2f, h). The resulting oil clusters in Sample 2 act as localized flow

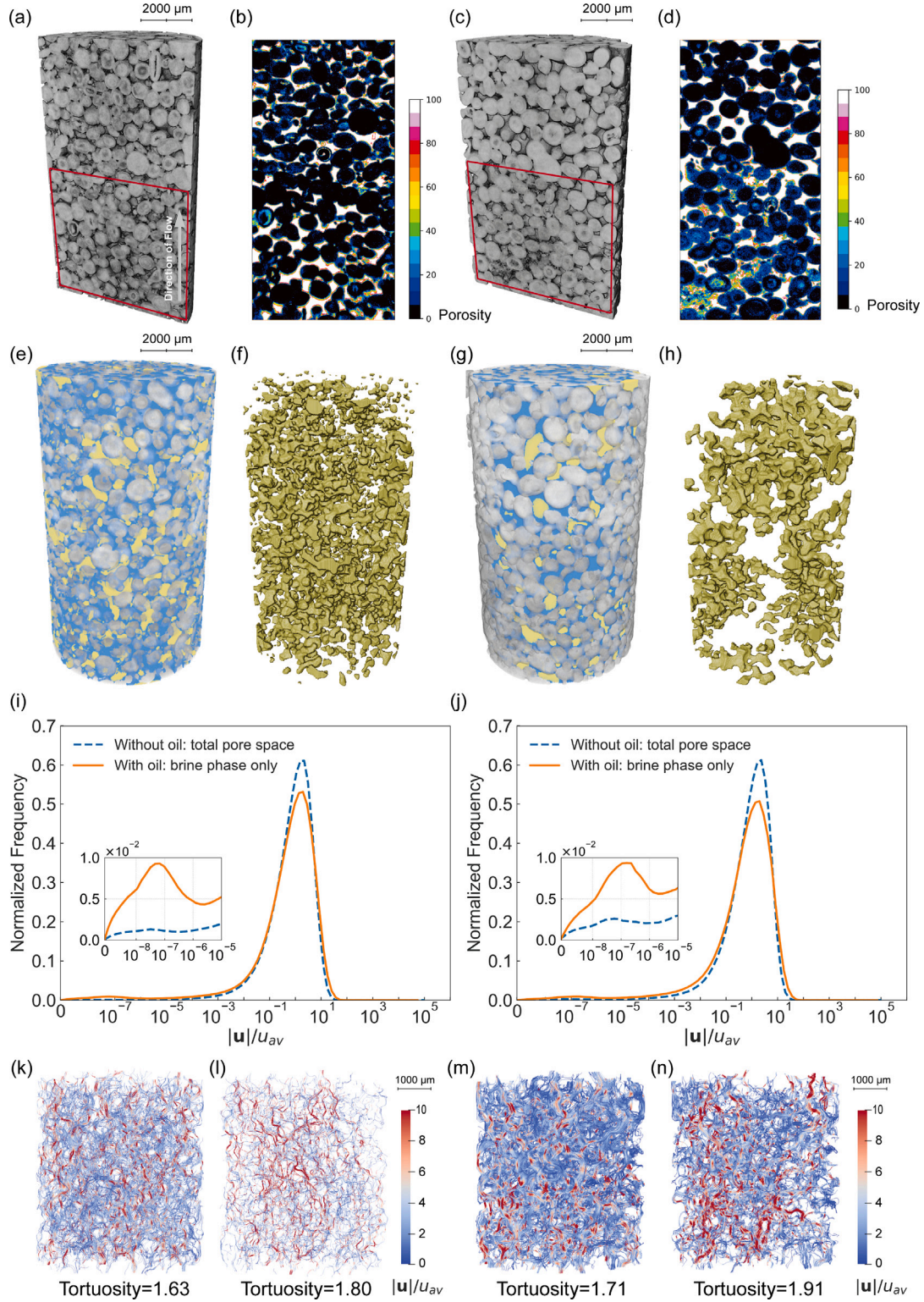


Fig. 2. 3D dry-image renderings for Sample 1 (a) and Sample 2 (c) show solids in gray, with red boxes highlighting regions corresponding to the pore-scale simulations. Porosity maps (b, d) color unresolved porosity: white = resolved macro-pores (porosity = 1), black = solid (0), intermediate shades = unresolved pores. Fluid distributions (e–h) show oil in yellow, brine in blue and solids in gray. Initial probability density functions, PDFs, of log-velocity compare with/without oil for Sample 1 (i) and Sample 2 (j); voxel velocities u are sorted into 128 bins of $\log(|u|/u_{av})$, where $|u|/u_{av}$ is the ratio of $|u|$ to the average velocity defined by Eq. (4). Streamlines show velocity fields without and with oil for Samples 1 (k–l) and 2 (m–n), with corresponding tortuosities, Eq. (5).

barriers, further amplifying the intrinsic structural heterogeneity. The sample-scale average parameters for Samples 1 and 2 are shown in Table S1.

To quantify the impact of this dual heterogeneity on transport, pore-scale simulations were performed, the results of which underscore the compounding effect of structure and saturation. The flow field was computed in the pore space containing brine (with oil), and where we assumed that no oil was present, so the flow field was computed in the entire pore space (without oil). In the absence of oil, both samples show relatively narrow, unimodal velocity probability density functions (PDFs) indicative of more uniform flow, although Sample 2 already displays a slightly higher intrinsic tortuosity due to its more complex intergranular pore structure (i.e., 1.63 vs 1.71) (Fig. 2k, m). As shown in Fig. 2i and j, the PDFs of velocity in the without oil cases display narrow, unimodal distributions centered around the average pore velocity, indicating relatively uniform flow. In contrast, with oil, the PDFs are broader with reduced peak velocities and a marked increase in the fraction of low-velocity voxels, especially in Sample 2. This is visually confirmed by the 3D velocity renderings (Fig. 2k–n), which reveal that residual oil forces the flow into highly disconnected and tortuous pathways in Sample 2, while flow in Sample 1 remains better connected. Quantitatively, this translates to a higher tortuosity of 1.91 in the oil case for Sample 2 compared to tortuosity of 1.80 in Sample 1. These results provide quantitative evidence that dual heterogeneity—stemming from both intrinsic pore structure and residual oil distribution—amplifies transport heterogeneity by disrupting flow continuity and enhancing the tortuosity of the local flow paths.

In summary, our results demonstrate that flow field heterogeneity is not merely a function of the rock's static pore structure but is amplified by the distribution of the residual phase. Sample 2, with its high intrinsic structural heterogeneity, fosters a trapping mechanism that creates a higher layer of heterogeneity in the presence of residual oil. This dual system synergistically enhances flow tortuosity and reduces overall permeability, creating diffusion-limited zones that are likely to significantly influence reactive transport and mineral dissolution patterns, as explored in Section 3.2. Moreover, we will see in the next section how widening of the pore space as a consequence of displaced oil (coupling of rock dissolution and oil displacement) has a profound impact on dissolution patterns.

3.2. CO₂-acidified brine injection and dissolution

Reactive transport experiments with CO₂-saturated brine revealed two distinct dissolution patterns governed by the interplay between initial pore-scale heterogeneity and multiphase displacement dynamics. Sample 1 developed dominant, displacement-driven channels, whereas Sample 2 showed dissolution suppressed by its fine-scale intergranular packing and oil blockage.

Channel formation and widening in Sample 1 is a direct consequence of multiphase flow dynamics: the presence of oil and its displacement creates a more heterogeneous flow field and encourages channel formation compared to single-phase flow (Menke et al., 2016, 2017; Al-Khulaifi et al., 2017, 2019). The process initiates in the larger pores where the injection of brine initially causes little dissolution because the presence of oil hinders the flow of brine. As the pore space is altered by the initial dissolution, preferential pathways are progressively widened and then further expanded by displacement-induced oil re-mobilization. This pore-scale process is directly visualized in its early stages (Fig. 3b–c, yellow box), where the brine dissolved the confining carbonate pore throats allowing for trapped oil to be displaced. This action triggers a positive feedback loop: oil displacement improves acid access, which in turn accelerates dissolution and further enhances channel breakthrough and widening. This self-reinforcing process culminates in the channel breaking through the entire sample by 135 min (Fig. 3d, orange box). This event is corroborated by the sharp, concurrent increase in porosity and decrease in S_{or} at 135 min, as shown

in the profiles (Fig. 3k–j). Ultimately, this leads to the formation of a single, highly conductive dominant channel by 315 min (Fig. 3e, red box). The importance of oil re-mobilization can be seen in the residual oil saturation profiles. In Fig. 3j, at the outlet of Sample 1, the oil saturation initially increased but then decreased. This is due to an oil bank flowing through the sample but getting stuck at the outlet between 45 and 90 min, which subsequently gets released.

Conversely, the heterogeneity of the initial pore space and residual oil distribution in Sample 2 effectively suppressed this feedback loop. Here, the presence of fine intergranular particles in the region near the inlet (Fig. 2c–d) leads to high capillary entry pressures and reduced flow connectivity. Therefore, the channel formation caused by displacement is confined to a limited region. However, in this region, the blockage of flow pathways by oil hinders further channel development and breakthrough. This is reflected in the porosity and S_{or} profiles, which show only modest and localized changes at the inlet, confirming a spatially confined reaction. Comparing brine to oil occupying the blue circles A (0 min) and B (45 min) in Fig. 3d showing the grayscale images of Sample 2, we can also clearly see the small oil ganglion that blocks channel formation from 45 min (Fig. 3d, blue circle). This results in the channel formation being confined to this inlet region (Fig. 3j, red box) preventing feedback-driven channel development.

In conclusion, this analysis elucidates how initial pore-scale heterogeneity dictates dissolution patterns within a multiphase flow context. The results distinguish between two phenomena: (1) Displacement-driven channel growth and widening, with dissolution-induced further displacement to create a positive feedback loop; and (2) heterogeneity and oil blockage-suppressed dissolution, where fine-scale features in the low-permeability region limit channel formation and oil blockage prevents channel breakthrough. This demonstrates that predicting reactive transport in subsurface reservoirs requires models that account not only for static heterogeneity but also for the dynamic, pore-scale coupling between fluid displacement and mineral reaction.

3.3. Flow fields

Flow modeling provides a dynamic visualization of how the two distinct dissolution patterns, established in the previous section, manifest in the fluid flow field and govern the evolution of transport properties. Analysis of the time-resolved velocity distributions immediately quantifies the contrasting flow dynamics. In Sample 1, the velocity probability density function (PDF) progressively broadens and shifts, indicating a significant increase in flow heterogeneity as the system evolves, with more stagnant velocities and fewer velocities similar to the mean velocity (Fig. 4a). This is the statistical signature of channel formation and widening. The 3D velocity streamlines (Fig. 4c) provide a visual confirmation, showing the formation of two high-velocity preferential flow paths that monopolize the flow, leaving large surrounding regions stagnant. In contrast, Sample 2 maintains a stable, narrow velocity PDF over time (Fig. 4b), which, combined with its more spatially distributed flow field (Fig. 4d), confirms a distinct time-dependent dissolution pattern initially characterized by localized dissolution near the inlet, and the development of a localized channel that did not fully break through. It should be noted that our model uses a mesh identical to the 6 μm voxel grid, meaning sub-voxel micro-porosity is unresolved. While this may affect the prediction of initial permeability, our study focuses on the system's dynamic evolution. Once dissolution forms dominant channels, fluid flow bypasses the low-permeability micro-porous regions. Consequently, their influence on the evolution of transport properties is likely to be negligible, and the model correctly captures the system's dynamic behavior.

This profound difference in flow field evolution directly dictates the macroscopic relationship between permeability (K) and porosity (ϕ). The relationship between permeability and porosity for both samples can be described by a power-law relationship of the form:

$$\frac{K}{K_0} = \left(\frac{\phi}{\phi_0} \right)^n \quad (12)$$

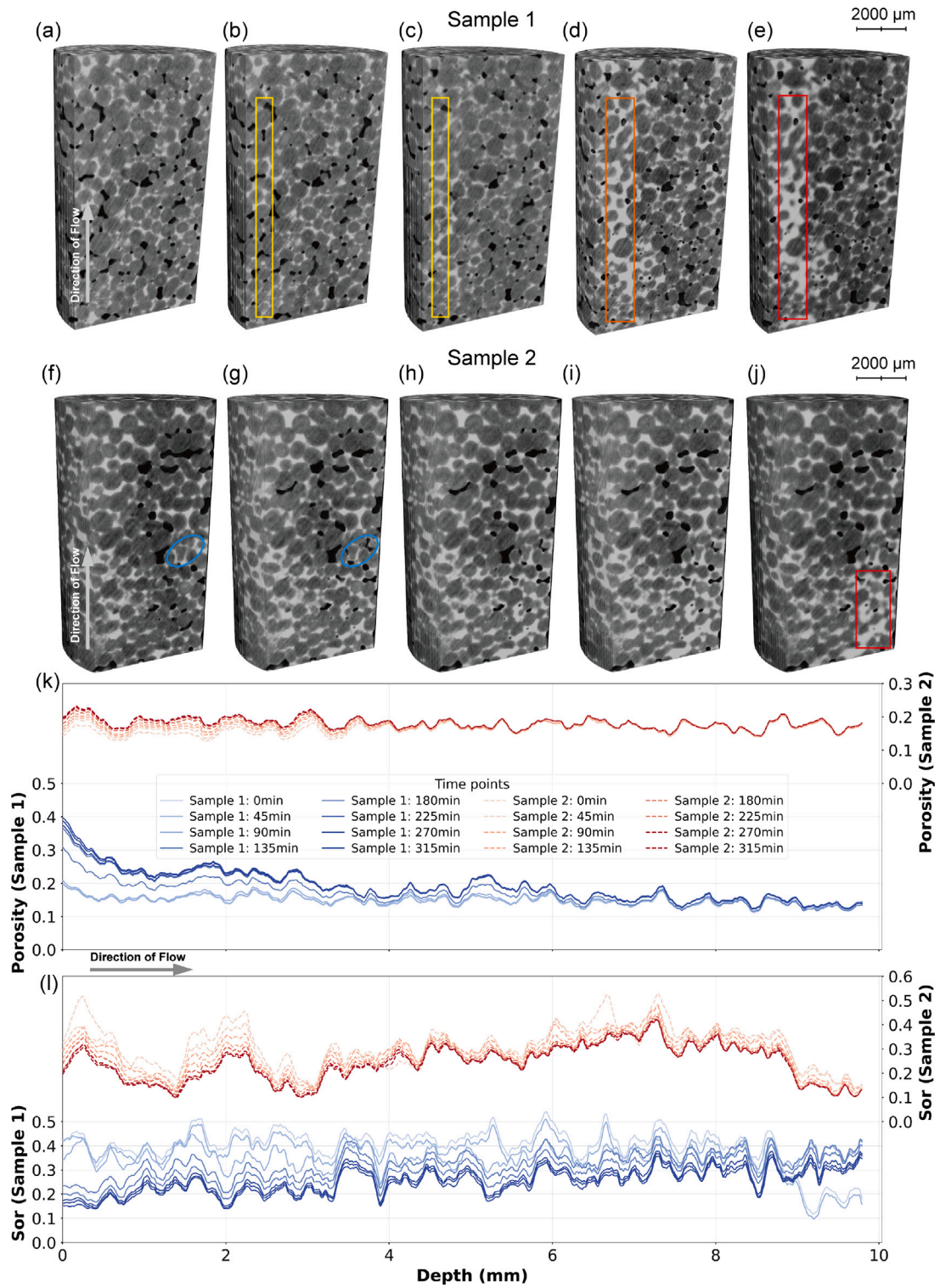


Fig. 3. Grayscale images depicting the temporal evolution of dissolution in Sample 1 (a–e) and Sample 2 (f–j) at 0 min, 45 min, 90 min, 135 min and 315 min, under a flow rate of 0.05 ml/min. In these images, gray represents solids, black represents oil, and white represents brine. Also shown is the temporal evolution of porosity and oil saturation averaged across slices perpendicular to the flow direction: (k) Porosity profiles for Samples 1 and 2; and (l) the oil saturation profiles for Samples 1 and 2. As rock dissolution proceeds, porosity increases while oil saturation decreases. Sample 1 (red) and Sample 2 (blue) in the caption for both (k) and (l). The 0 min mark corresponds to the scan before reaction. The 45 min mark corresponds to the first scan performed from $t = 0$ to $t = 45$ min, and 90 min corresponds to the second scan performed from $t = 45$ to $t = 90$ min, and so on for subsequent scans.

where K and ϕ are the permeability and porosity at a given time, K_0 and ϕ_0 are their corresponding initial values, and n is the power-law exponent characterizing the sensitivity of permeability to changes in porosity. This relationship is shown in Fig. 5.

For our experiments, two cases were considered. In the case corresponding to the brine phase in the presence of residual oil (Fig. 5a), Sample 1 yielded $n = 6.1$, while Sample 2 yielded $n = 4.5$. The absolute permeability was also calculated by simulating the flow

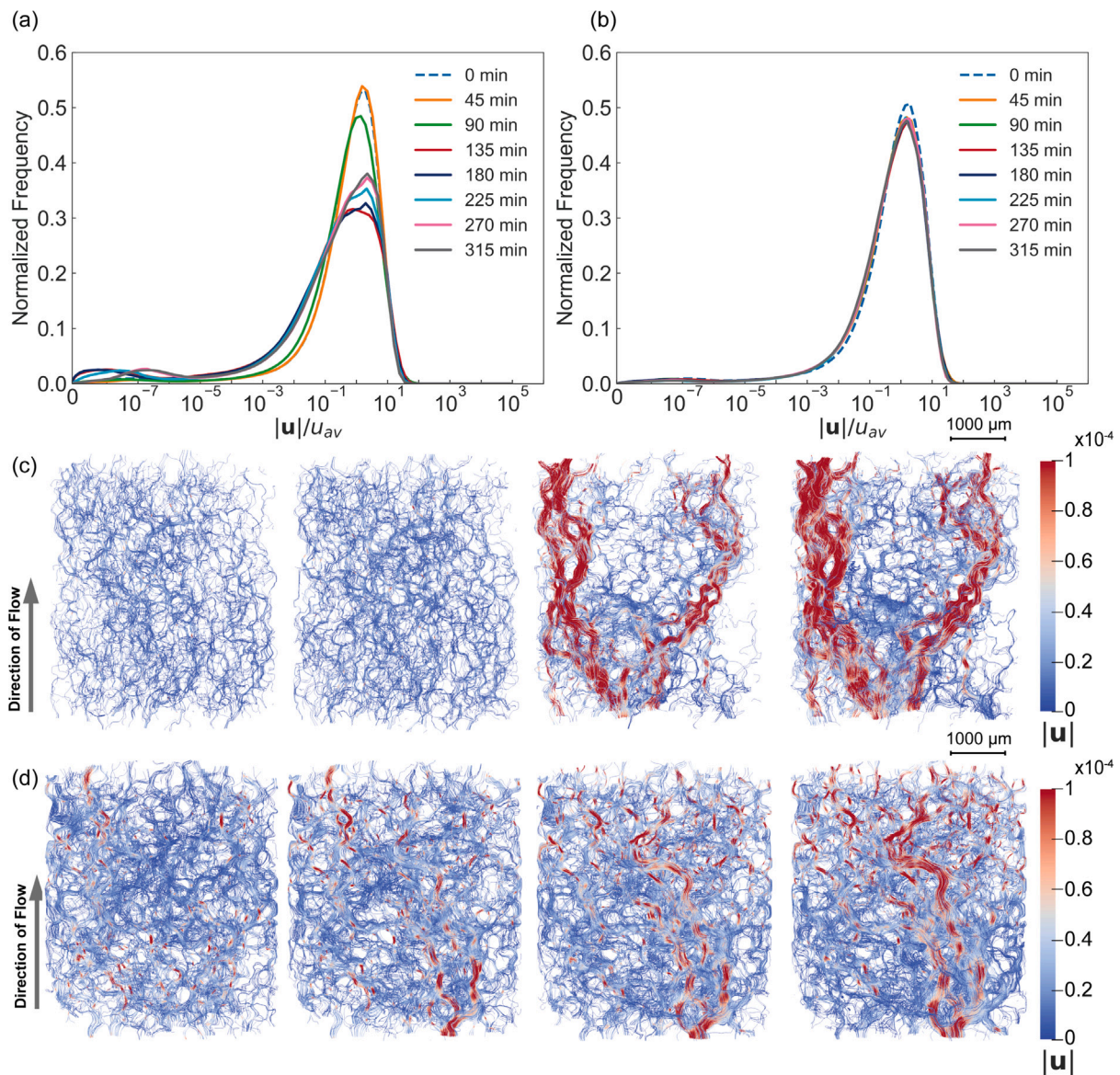


Fig. 4. Probability density functions (PDFs) of the velocity for Sample 1 (a) and Sample 2 (b), with oil over time (from 0 min to 315 min). Voxel velocities, u , were collected from the simulations and uniformly sampled into 128 bins of $\log(|u|/u_{av})$, where $|u|/u_{av}$ represents the ratio of the magnitude of u to the average velocity, u_{av} , Eq. (4). Velocity streamlines for Sample 1 (c) and Sample 2 (d) at 0 min, 45 min, 135 min and 315 min. For the cumulative PVs corresponding to these time points, see Table 1. The 0 min mark corresponds to the residual oil scan before reaction. The 45 min mark corresponds to the first scan performed from $t = 0$ to $t = 45$ min, and 90 min corresponds to the second scan performed from $t = 45$ to $t = 90$ min, and so on for subsequent scans.

through the entire connected pore space, assuming complete saturation by the brine phase (Fig. 5b). Under these conditions, Sample 1 yielded $n = 5.5$, while Sample 2 had $n = 6.0$. The high exponent in Sample 1 under brine phase only conditions confirms that the observed channel widening is a highly efficient mechanism for permeability increase, where dissolution creates a disproportionately large increase in flow conductance. The lower exponent in Sample 2 reflects a less efficient, spatially confined dissolution process due to a low permeability region. In previous work, Akindipe et al. (2022) investigated various multiphase dissolution patterns in Prairie Shell limestone samples (approximately 60 mm in length and 9 mm in diameter) and determined the changes in absolute permeability. The experiments, conducted at 10 MPa and 60 °C, yielded a range of exponents. For example, a highly conductive, sample-spanning channel formed under an injection rate of 0.5 mL/min, resulting in an exponent of $n = 12.7$, while a less stable, tapering channel formed under an injection rate of 0.1 mL/min, producing $n = 2.1$. Additionally, a more homogeneous, cylindrical-shaped

channel was formed under an injection rate of 0.5 mL/min, resulting in $n = 6.9$. Comparing these findings, Sample 1 consistently maintains high exponents ($n \approx 5.5$ – 6.1) across both conditions, mirroring the efficient transport of the cylindrical regime ($n = 6.9$) reported by Akindipe et al. (2022). Notably, under single-phase conditions, Sample 2 also aligns closely with this cylindrical mode ($n = 6.0$), indicating that the dissolution forms a hydraulically efficient pathway when oil is absent. However, the presence of residual oil in Sample 2 reduces the exponent to 4.5; this shift marks a deviation from the ideal cylindrical geometry toward a less connected pattern, highlighting how residual oil exacerbates the impact of local heterogeneities.

Overall, Sample 1 exhibits a large increase in permeability. This increase is not smooth but occurs in distinct steps. These steps are the macroscopic signature of the channel breakthrough events visualized in the flow fields (Fig. 4c). Once a dominant channel connects the inlet and outlet, the permeability increases significantly. Conversely, Sample 2 shows a modest and continuous permeability increase, reflecting the

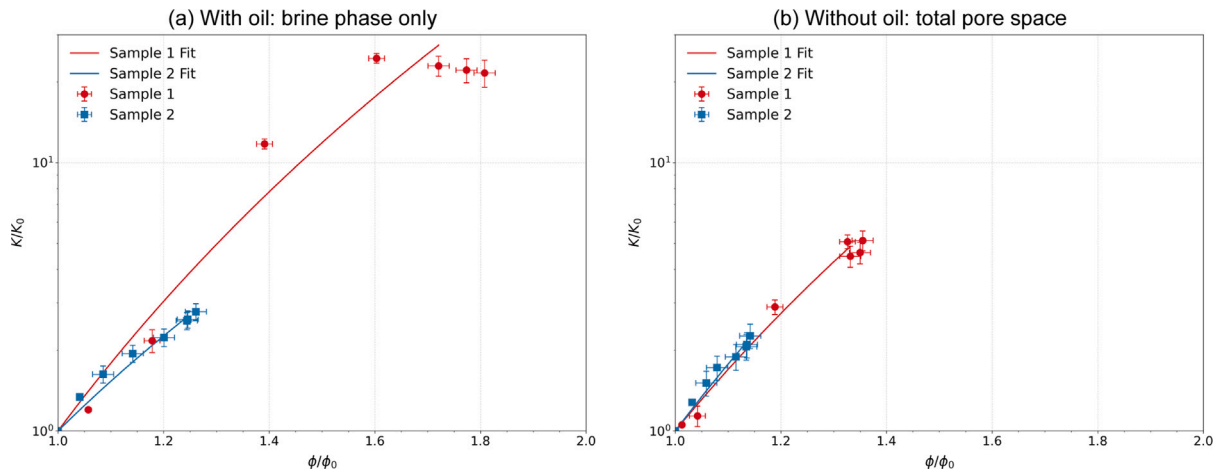


Fig. 5. Permeability-porosity relationships. (a) Permeability of the brine phase in the presence of residual oil. These values were determined by simulating the flow field within the connected, brine-saturated pore network, assuming the residual oil remains immobile. For comparison, (b) the absolute permeability was also calculated by simulating the flow through the entire connected pore space, assuming complete saturation by the brine phase.

Table 2

Comparison of reaction rates in our multiphase flow experiments with single-phase flow experimental results in the literature and the batch reaction rate with Pe number before the reaction starts.

Condition	Reaction rate ($\text{mol m}^{-2} \text{s}^{-1}$)	
Ketton limestone multiphase	Sample 1	Sample 2
Low flow rate	8.6×10^{-6} (Pe = 217)	3.9×10^{-6} (Pe = 187)
High flow rate	3.0×10^{-5} (Pe = 1154)	4.2×10^{-5} (Pe = 1615)
Silurian dolomite single-phase (Al-Khulaifi et al., 2018)	Heterogeneity A	Heterogeneity B
Low flow rate	3.15×10^{-6} (Pe = 421)	1.35×10^{-6} (Pe = 369)
High flow rate	5.47×10^{-6} (Pe = 1632)	10.6×10^{-6} (Pe=2653)
Ketton limestone single-phase (Menke et al., 2015)	5.0×10^{-5} (Pe = 933)	
Batch reaction rate (Peng et al., 2015)	6.9×10^{-4}	

gradual, uniform enlargement of many small pores rather than the creation of a single dominant channel.

In summary, the flow simulations provide a link between pore-scale dissolution patterns and their macroscopic consequences. In Sample 1 channel widening creates preferential flow paths, leading to a large increase in permeability. In Sample 2, inlet heterogeneity and oil blockage-suppressed dissolution resulted in a lower increase in porosity and permeability. This highlights that for reactive transport, knowing the change in average porosity alone is insufficient to predict the change in permeability; the spatial pattern of that change is important.

3.4. Effective reaction rates

The influence of dissolution patterns on reaction kinetics was investigated by comparing the two samples at two flow rates (Fig. 6). At low flow rates, the samples exhibited distinct behaviors due to differences in their structures and oil distributions. Sample 1 exhibited channel formation and widening as the injected acid displaced oil, resulting in a sharp initial increase in the surface-normalized reaction rate, followed by a decline (Fig. 6a). This trend suggests that while channel formation initially enhances acid transport to new surfaces, their stabilization ultimately leads to inefficient mass transfer as a significant portion of the acid bypasses the bulk of the reactive matrix. In contrast, Sample 2, characterized by the presence of interstitial particles in the region near the inlet, showed a lower and more stable reaction rate (Fig. 6b). Its low connectivity caused rapid acid consumption only near the inlet (Fig. 3j, red box), initially confining the reaction to a dispersed pattern of isolated zones and preventing the formation of a continuous, effective channel (Fig. 3j).

The difference in dissolution patterns directly translated to differing overall reaction rates. As summarized in Table 2, the average reaction

rate in Sample 1 ($8.6 \times 10^{-6} \text{ mol/m}^2 \text{ s}$) was 2.2 times higher than in Sample 2 ($3.9 \times 10^{-6} \text{ mol/m}^2 \text{ s}$), which experienced heterogeneity and oil blockage that suppressed dissolution. Our finding that channel widening, leading to the new channel breakthrough in Sample 1 is characterized by a higher average reaction rate is conceptually consistent with the single-phase reactive flow experiments of Al-Khulaifi et al. (2018). In their experiment, Silurian dolomite (4.8 mm in length and 4.8 mm in diameter) was used during reaction experiments involving the injection of CO_2 -saturated brine at 10 MPa and 50 °C. In this single-phase study, the dominant channel(s) formation was linked to the initial physical heterogeneity and the lower Pe studied, where a more homogeneous rock structure led to a higher effective reaction rate (Table 2). However, the channel widening in our study is also a direct consequence of multiphase displacement dynamics. As established in Section 3.2, the dominant channel in Sample 1 is not only a feature of the pore space structure but is dynamically carved out by a positive feedback loop involving dissolution-induced oil displacement. While the channels in single-phase flow are a feature of the rock's initial physical heterogeneity, in multiphase flow they also depend on the residual oil distribution and the fluid-fluid displacement process. Nevertheless, both rates are substantially lower than those from single-phase flow (Menke et al., 2015) (5.0×10^{-5}) or batch experiments (Peng et al., 2015) (6.9×10^{-4}), highlighting the critical role of multiphase flow and pore-scale transport limitations.

A quantitative analysis of the transport regime during the low flow rate injection further reveals the origin of transport limitations. As dissolution progressed, both samples exhibited a decreasing Péclet (Pe) number and an increasing Damköhler (Da) number (Fig. 7). The decrease in Pe, caused by the relative slowing of fluid flow as pore channels widen, indicates a shift from a more advection-dominated to a more diffusion-influenced transport. Concurrently, the rise in Da

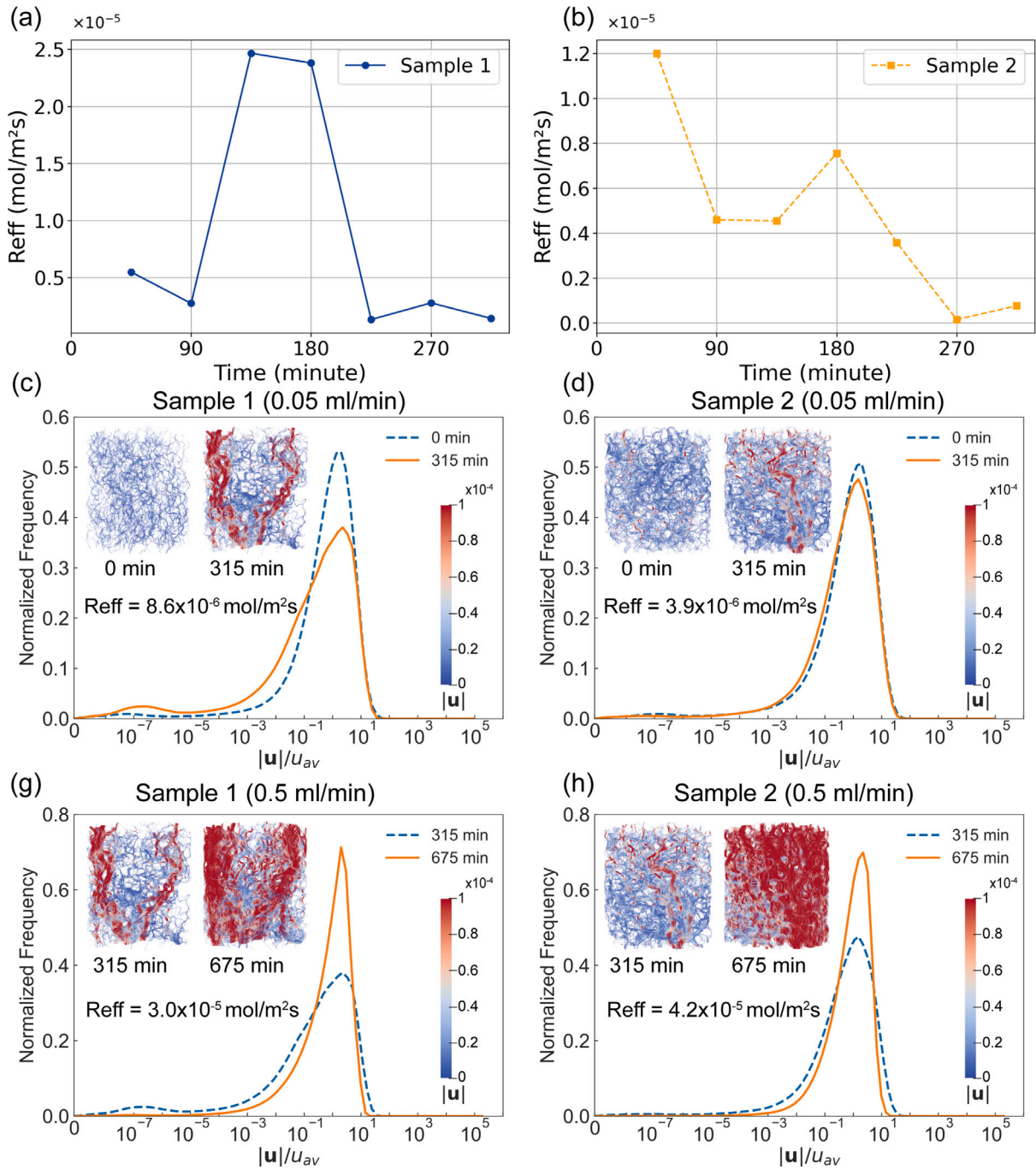


Fig. 6. (a)–(b): Effective reaction rate as a function of experimental time for Samples 1 and 2 (45–315 min). (c)–(f): Probability density functions (PDFs) of velocity for Sample 1 and Sample 2 at 0 min, 315 min, and 675 min and corresponding 3D renderings of voxel velocity normalized by average velocity. For the cumulative PVs corresponding to these time points, see Table 1. The effective reaction rate at 45 min corresponds to the first scan performed from $t = 0$ to $t = 45$ min, which represent the average state at 22.5 min ($\Delta t = 22.5$ min), and 90 min corresponds to the second scan performed from $t = 45$ to $t = 90$ min, which represents the average state at 67.5 min ($\Delta t = 45$ min), and so on for subsequent time steps.

– whose non-monotonic trend reflects the complex evolution of local porosity and surface area – is attributed to the growth of available reactive surfaces. The main finding, however, is that the combined PeDa increased only slightly for both samples. This confirms that under these low-flow conditions, the rate-limiting step for the overall dissolution process was consistently pore-scale diffusive mass transport.

Increasing the injection rate ten-fold further revealed the underlying rate-limiting mechanisms. Sample 1 exhibited a sub-linear, three-fold increase in effective reaction rate (to 3.0×10^{-5} mol/m² s), indicating that the reaction was constrained by the established channel

network; higher velocity primarily accelerated flow through existing high-permeability paths rather than engaging new reactive surfaces. Conversely, Sample 2 demonstrated a near-linear increase (to 4.2×10^{-5} mol/m² s), surpassing Sample 1's rate (Table 2). This suggests that at higher flowrate the initial diffusion limitations are successfully overcome, as acidic brine is forced into previously inaccessible pore spaces (including those blocked by oil) promoting more uniform, globally effective dissolution. This behavior is consistent with the findings of Al-Khulaifi et al. (2018) in dolomite rock and with studies showing that

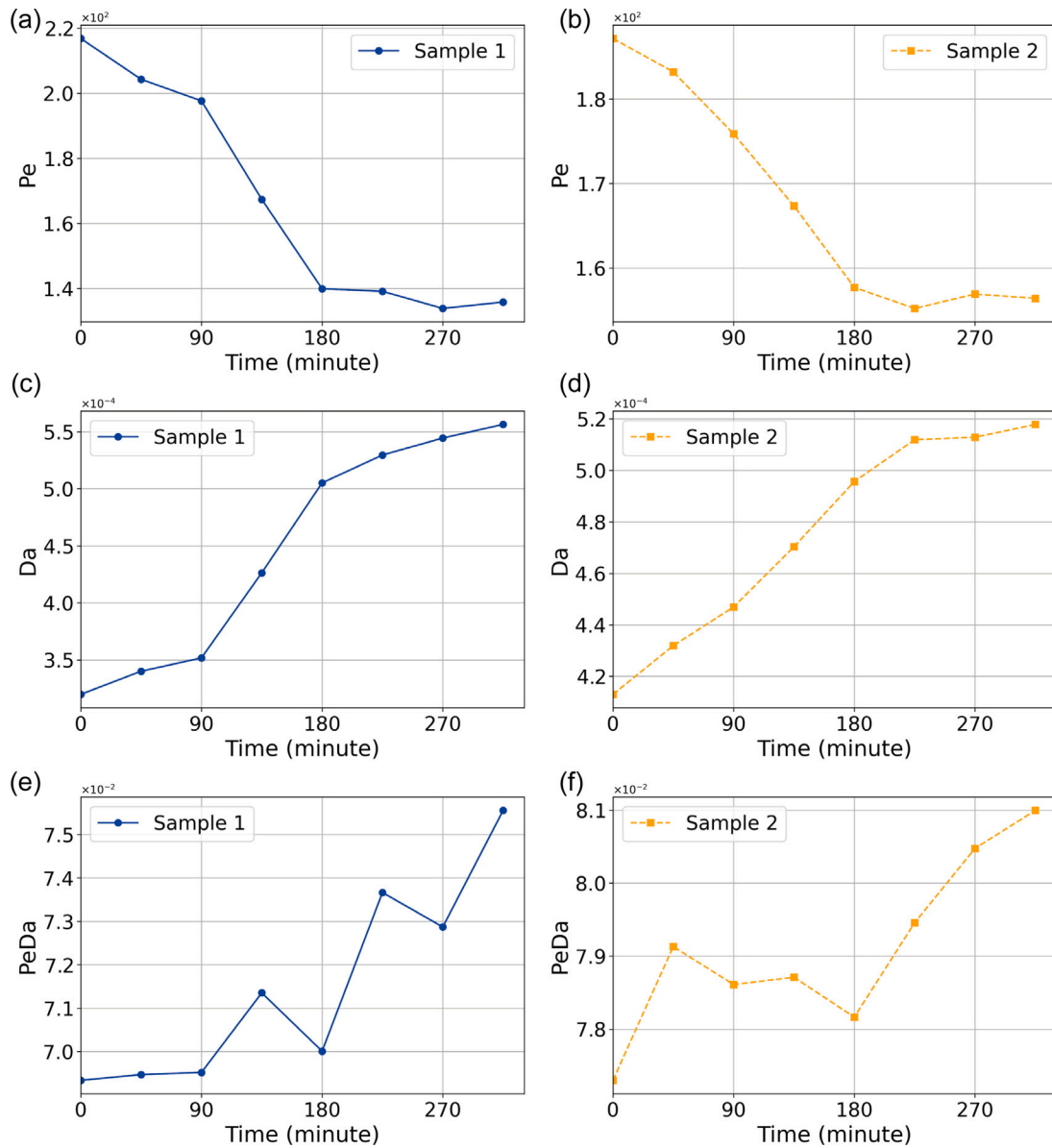


Fig. 7. (a)–(f): Dimensionless numbers (Pe, Da, and PeDa) as a function of experimental time for Samples 1 and 2 (0–315 min). For the cumulative PVs corresponding to these time points, see Table 1.

increased flow can enhance permeability and redistribute flow, overcoming local limitations on reactant consumption (Al-Khulaifi et al., 2018).

These mechanisms are supported by the evolution of the flow field (Fig. 6). At higher injection rates, the velocity distribution narrows, with a marked reduction in stagnant voxels and the velocity streamlines become more symmetric. This homogenization of the flow field signifies more uniform reactant delivery and efficient dissolution. This enhanced dissolution is further illustrated in Fig. 8, which shows the grayscale images of Sample 1 and Sample 2 after low and high flow rates (Fig. 8a–d), as well as the corresponding porosity and oil saturation profiles (Fig. 8e–f). The high flow rate promotes a rapid increase in porosity and more effective oil displacement resulting in a decrease in oil saturation in both samples. In Sample 1, due to the formation of preferential flow paths, the oil from downstream is more easily transported to the highly conductive channels, forming large oil ganglia. In Sample 2, higher injection rates re-mobilize the oil which was blocking further channel development 3 mm from the inlet at the low injection rate (recall Fig.

3l). This is seen as a decrease in oil saturation throughout the whole sample in Fig. 3.

This study further demonstrates the existence of the non-uniform dissolution regime (also termed channeling) characterized by moderate Pe, where both diffusion and advection contribute to transport, and low Da, as encountered in CO_2 storage. It reveals that the interplay between pore space heterogeneity, oil distribution, displacement and flow rate dictate the dissolution pattern, which in turn governs the overall reaction rate by controlling the efficiency of mass transport. We acknowledge limitations in the treatment of unresolved porosity. In calculating effective reaction rates, this porosity was incorporated as a static correction, as grayscale values remained nearly unchanged during the experiment, suggesting minimal reaction effects in intergranular micro-pores. Future work could leverage advanced segmentation methods (Xu et al., 2025) and super-resolution imaging methods (Ma et al., 2025a) to explicitly resolve micro-porosity and refine reactive transport assessments.

The interpretation of our results needs to consider the sample size relative to the Representative Elementary Volume (REV), which, for

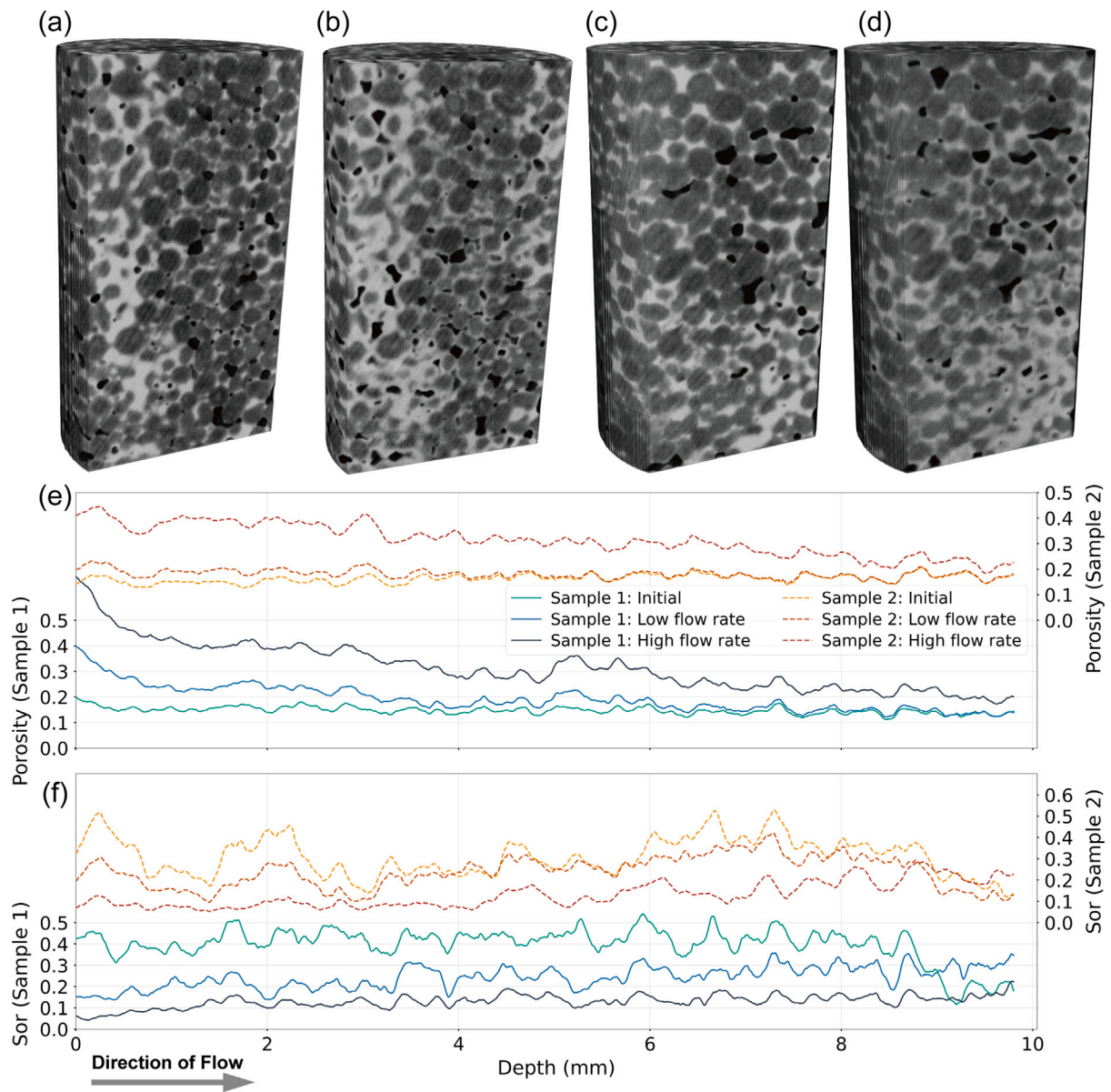


Fig. 8. Grayscale images depicting the temporal evolution of dissolution in Sample 1 (a–b) and Sample 2 (c–d) for low flow rate (0.05 ml/min) and for high flow rate (0.5 ml/min) injection. (e) and (f): Porosity and oil saturation profiles for Sample 1 at initial conditions, after low flow rate injection, and after high flow rate injection.

the porosity-based REV of Ketton limestone, is estimated to be around 1 mm (Singh et al., 2020; Shah et al., 2017). While our samples satisfy the REV condition, larger volumes may exhibit distinct flow fields and bypass mechanisms due to macro-scale heterogeneity. Existing core-scale studies support this distinction. For instance, Kurotori et al. (2019, 2020) investigated solute transport in 5 cm diameter Ketton samples. Their work revealed that larger sample volumes are essential to fully capture the significant non-Fickian tailing caused by mass transfer between mobile and immobile regions (accounting for 38% of the pore volume). Such long-term tailing behavior is often truncated or difficult to fully characterize in smaller samples due to limited residence times and boundary effects. Menke et al. (2018) demonstrated that upscaling from pore-scale (4 mm) to core-scale (3.8 cm) samples reveals differences in dissolution channeling and flow redistribution. Consequently, while our study accurately defines the pore-scale reaction mechanisms, these findings imply that transport regimes are scale-dependent, and our observations should be viewed as the fundamental building blocks for larger-scale behavior.

4. Conclusions

This study systematically demonstrates how the initial physical heterogeneity of rock and the distribution of a residual hydrocarbon phase synergistically govern pore-scale dissolution patterns, the evolution of macroscopic transport properties, and effective reaction kinetics under multiphase flow conditions in CO₂ storage. Our results show that flow field heterogeneity is not merely a function of the rock pore structure but is significantly amplified by the trapping mechanisms of the residual phase. This “dual heterogeneity” system, comprising both rock structure and residual hydrocarbon, gives rise to two distinct dissolution phenomena: (1) a positive feedback loop in which displacement-driven channel growth and widening is further enhanced by dissolution, which in turn facilitates additional hydrocarbon displacement; and (2) a suppressed dissolution regime where strong initial heterogeneity and hydrocarbon blockage prevent the formation and breakthrough of effective flow channels.

These pore-scale dissolution patterns lead to different macroscopic consequences for CO₂ injection and storage. The channel-widening

phenomenon creates preferential flow paths that result in a large increase in permeability, which favors injectivity but may pose risks to storage security by forming potential leakage pathways. In contrast, the suppressed dissolution regime leads to less change in permeability and porosity, suggesting a situation where the reservoir matrix remains relatively intact but the improvement in injectivity is limited. These observations highlight that accurate prediction of CO₂ injectivity and long-term security relies heavily on resolving these complex fluid-rock interactions at the micro-scale, rather than relying solely on averaged macroscopic parameters.

Furthermore, the observed distinct dissolution patterns directly control the overall reaction kinetics. At low flow rates, the sample in which channelized dissolution dominated exhibited a higher average reaction rate, compared to the sample with heterogeneity suppressed dissolution. However, the higher flow rate injection helped acidic brine successfully overcome initial diffusion limitations and hydrocarbon blockage in the more heterogeneous sample, forcing the reactive fluid into previously inaccessible pore spaces and promoting a more globally effective dissolution. This implies that injection strategies (e.g., flow rate control) can be optimized to manipulate pore-scale fluid distribution, thereby increasing the contact area between CO₂-saturated brine and the rock matrix.

In summary, our findings underscore the necessity of incorporating the dynamic, pore-scale coupling between fluid displacement, mineral reaction, and structural heterogeneity in models intended to predict reactive transport in subsurface reservoirs. The significantly lower reaction rates observed in our multiphase reactive flow experiments, compared to the single-phase or batch experiments, confirm that ignoring pore-scale transport limitations leads to substantial overestimation of reaction rates and mineral trapping capacity. These insights are crucial for optimizing carbon capture and storage (CCS) strategies and predicting the behavior of carbonate reservoirs (Spycher and Pruess, 2005) and groundwater remediation (Steeffel et al., 2003), as well as critical global challenges including ocean acidification (Tribollet et al., 2009) and nuclear waste disposal (Soler and Mäder, 2005), where the interplay between fluid-rock interaction and multiphase flow dynamics is a determining factor for success.

List of parameters

See Table 3.

CRedit authorship contribution statement

Qianqian Ma: Writing – original draft, Visualization, Investigation, Formal analysis. **Rukuan Chai:** Writing – review & editing, Investigation. **Sajjad Foroughi:** Writing – review & editing, Software. **Yanghua Wang:** Writing – review & editing, Resources. **Martin J. Blunt:** Writing – review & editing, Supervision, Conceptualization. **Branko Bijeljic:** Writing – review & editing, Supervision, Conceptualization.

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.

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Table 3

List of parameters, symbols, and units used in simulations and calculations.

Parameter	Symbol	Unit
Geometry and grid		
Sample lengths	L_y, L_z	m
Cross-sectional area	A_x	m ²
Porosity	ϕ	–
Unresolved porosity	$\phi_{\text{unresolved}}$	–
Specific surface area	S	m ^{–1}
Characteristic length	L_c	m
Fluid properties and flow		
Fluid density	ρ	kg/m ³
Fluid viscosity	μ	Pa s
Pressure	p	Pa
Pressure gradient	∇p	Pa/m
Velocity vector	$\mathbf{u}$	m/s
Flow rate	Q	m ³ /s
Darcy velocity	q	m/s
Average pore velocity	u_{av}	m/s
Permeability	K	m ²
Tortuosity	τ	–
Reactive transport		
Péclet number	Pe	–
Damköhler number	Da	–
Molecular diffusion coefficient	D_m	m ² /s
Reaction rate constant	k	s ^{–1}
Mineral reaction rate	r	mol m ^{–2} s ^{–1}
Effective reaction rate	r_{eff}	mol m ^{–2} s ^{–1}
Mineral density	ρ_{mineral}	kg/m ³
Molecular mass	M_{mineral}	kg/mol
Time interval	Δt	s
Porosity change	$\Delta\phi_{\text{CT}}$	–

Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.advwatres.2025.105202>.

Data availability

The dataset is made available on Zenodo with the DOI: <https://doi.org/10.5281/zenodo.17856861>. The code is available via GitHub at <https://github.com/ImperialCollegeLondon/porescale/>.

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