

4D multi-scale imaging of reactive flow in carbonates: Assessing the impact of heterogeneity on dissolution regimes using streamlines at multiple length scales

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ABSTRACT

We have experimentally investigated the impact of heterogeneity on the dissolution of two limestones, characterised by distinct degrees of flow heterogeneity at both the pore and core scales. The two rocks were reacted with reservoir-condition CO₂-saturated brine at both scales and scanned dynamically during dissolution. First, 1 cm long 4 mm diameter cores were scanned during reactive flow with a 4 μm voxel size between 10 and 71 times using 4D X-ray micro-tomography (μ-CT) over the course of 90 min. Second, 3.8 cm diameter, 8 cm long cores were reacted at the same conditions inside a reservoir-condition flow apparatus and imaged using a medical-grade X-ray computed tomography scanner (XCT). Each sample was imaged ~13 times over the course of 90 min at a 250 × 250 × 500 μm resolution. These larger cores were then scanned inside a μ-CT at a 27 μm voxel size to assess the alteration pore-space heterogeneity after reaction. Both rock types exhibited channel widening at the *mm* scale and progressive high porosity pathway dissolution at the *cm* scale. In the more heterogeneous rock, dissolution was more focussed and progressed along the direction of flow. Additionally, the dissolution pathways contained a distinct microstructure captured with the μ-CT that was not visible at the resolution of the XCT, where the reactive fluid had not completely dissolved the internal pore-structure. This microstructure was further analyzed by performing a direct simulation of the flow field and streamline tracing on the image voxels.

We found that at the larger scales the interplay between flow and reaction significantly affects flow in the unreacted regions of the core. When flow is focussed in large reacted channels, this focusing is carried through to the unreacted parts of the rock where flow continues to be confined to preferential pathways after passing the reaction front. This focussing effect is greater with increasing pore space heterogeneity indicating that the representative elementary volume (REV) for dissolution is far greater than the dissolution front itself. This study of scale dependence using *in situ* 4D tomography provides insight into the mechanisms that control local reaction rates at the *mm* and *cm* scales. Furthermore, this work suggests that under these conditions at larger scales it is likely to be structural heterogeneity that dominates the pattern of dissolution and therefore the evolution of high permeability pathways.

1. Introduction

A major concern in the implementation of carbon capture and storage (CCS) is long-term storage security (Herzog et al., 2003; Metz et al., 2005). Carbon dioxide (CO₂) injected into the subsurface will dissolve in the resident brine and form carbonic acid (Langmuir et al., 1997; Morse and Mackenzie, 1990; Peng et al., 2013). Carbonate host rocks have the potential to react with and be dissolved by CO₂ acidified brine (Peng et al., 2015). Dissolution of the host rock is commonly

associated with changes in fluid flow patterns and can weaken carbonate cements and damage the formation around injection wells (Birkholzer et al., 2011). Therefore, it is important to have a holistic understanding of dissolution in the brine-rock system to predict the distribution and the rate of fluid movement, as well as the amount and impact of dissolution in reservoir rocks (Daccord et al., 1993a, 1993b; Maheshwari et al., 2013).

However, the nature and rate of dissolution in carbonates is dependent on both the chemical properties of the brine (El-Maghraby

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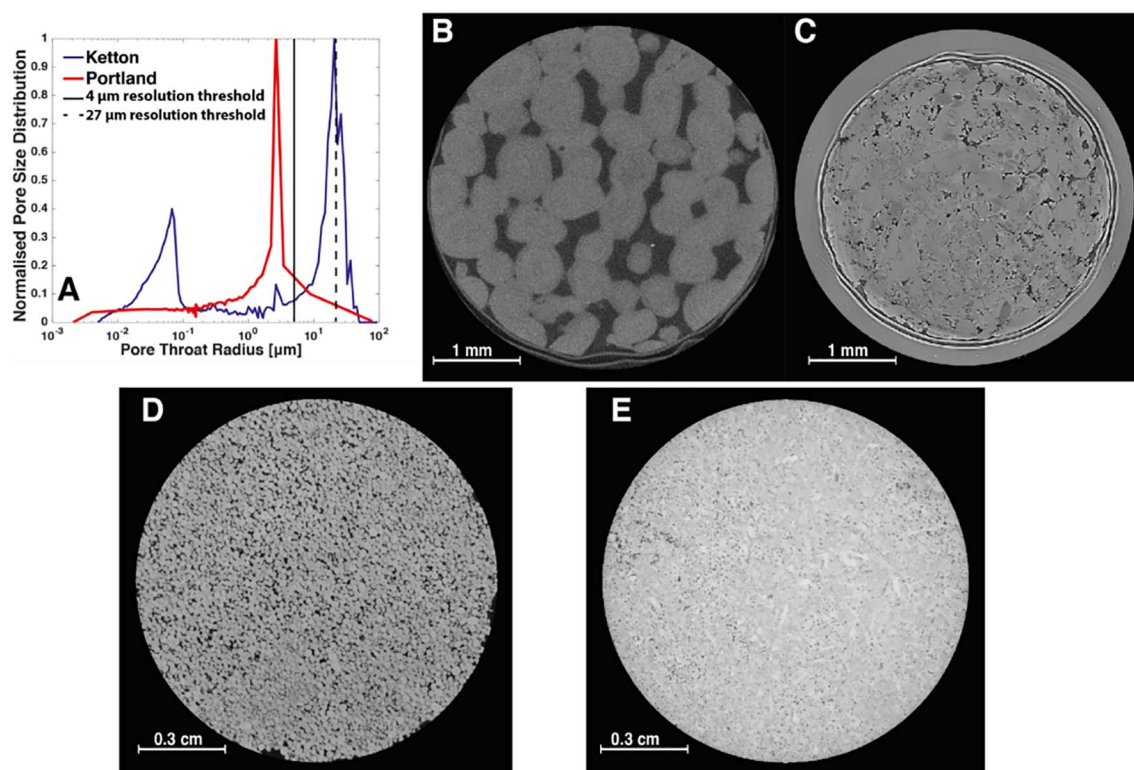


Fig. 1. The pore throat size distribution of Ketton and Portland (A) derived from mercury injection tests by Weatherford labs, UK. 2-D slices of 3D μ -CT images of Ketton (B), Portland (C) at 4 μ m resolution, and Ketton (D), and Portland (E) at 27 μ m resolution.

et al., 2012; Fredd and Fogler, 1998; Luquot and Gouze, 2009) and the geometrical properties of the pore-space of the host rock (Li et al., 2006; Rötting et al., 2015). Carbonate dissolution rates are also strongly dependent on brine temperature and pressure (Peng et al., 2015), making it necessary to develop experimental techniques to measure complex time-dependent processes at representative reservoir conditions. All combined, physical and chemical heterogeneities have been shown to be the cause of different dissolution regimes (Fredd and Fogler, 1999, 1998) including wormholing, channelling, uniform, and face dissolution.

Reactive transport in porous media is commonly investigated using core-flooding techniques coupled with three-dimensional imaging to track the reaction at the fluid/solid boundary. One accepted imaging technique is medical-grade computed tomography scanners (XCT), which can operate at different scales. XCT scanners (Mettler Jr et al., 2000) are commonly paired with core-flooding to image rocks at the core ($\sim$ cm) scale. Core-scale imaging is valuable because it is three-dimensional, and depending on the experimental conditions, can be temporally resolved. However, it has a maximum resolution of $\sim$ 100 μ m and thus can only resolve the fluid/solid boundary of large features, such as fractures and vugs. The greater portion of the pore space is only resolved as an average greyscale value because several pores or parts of pores will be contained in a single voxel, thus making segmentation and analysis of local changes in connectivity and reaction rate very difficult. X-ray microtomography (μ -CT) (Ritman, 2004) provides higher resolution, and although it is possible to image cm-scale samples, the time required for imaging increases with increasing sample size. Thus, μ -CT is ideal for mm-scale samples when studying dynamic μ m-scale processes on short time-scales ($\sim$ 1 h). However, due to the small sample size μ -CT does not always capture the full range of physical heterogeneities seen at the core scale and may not capture the representative elementary volume (REV) for heterogeneous dissolution processes.

Imaging of dissolution in limestone rock has been performed at the

core ($\sim$ cm) scale using XCT. Ott et al. (2012) investigated dissolution using core flooding and XCT where, for several rock types and flow regimes, it was found that reaction of the dissolved CO₂ with the rock matrix increased physical heterogeneity. Ellis et al. (2011) used imaging to show that exposure to CO₂ progressively reduced the sealing capacity of fractured claystone caprocks. Smith et al. (2012) imaged dissolution of a dolomitic core before and after reaction with CO₂ acidified brine and found dissolution rates $17\times$ slower than in calcite. Lamy-Chappuis et al. (2014) used CT scanning to measure calcite dissolution in calcareous gritstone and found that the permeability increase with porosity did not agree with classical models (e.g. Kozeny-Carman) and that the dissolution rate was impacted largely by the acid supply. Tutolo et al. (2014) examined dolomite dissolution in the presence of CO₂ saturated brine and found evidence of dissolution at low temperatures followed by exsolution and precipitation as the temperature increased. Ott and Oedai (2015) examined carbonate dissolution in the presence of two-phase flow and found large differences in dissolution regimes depending on the CO₂ saturation.

There are relatively few experiments that investigate the impact of coupled dissolution and flow phenomena at the micron scale ($\sim$ μ m) – the observation scale that is necessary for pore-scale analysis and numerical simulations of both flow and transport. Noiriél et al. (2013) used μ -CT to measure changes in a limestone fracture at several locations during acid dissolution at ambient conditions. Additionally, Noiriél et al. (2004) reported a power law relationship between porosity and permeability during limestone dissolution by scanning the rock periodically *ex situ*. Menke et al. (2015) imaged the dissolution dynamics of a relatively homogeneous carbonate at *in situ* reservoir conditions in the advective flow regime and low brine acidity (pH 3.1) while Menke et al. (2016) used fast synchrotron tomography to image dissolution in two heterogeneous carbonates at two flow rates and identical brine conditions. They found that the porosity can either increase uniformly through time along the length of the samples, or may exhibit a spatially and temporally varying increase that is attributed to

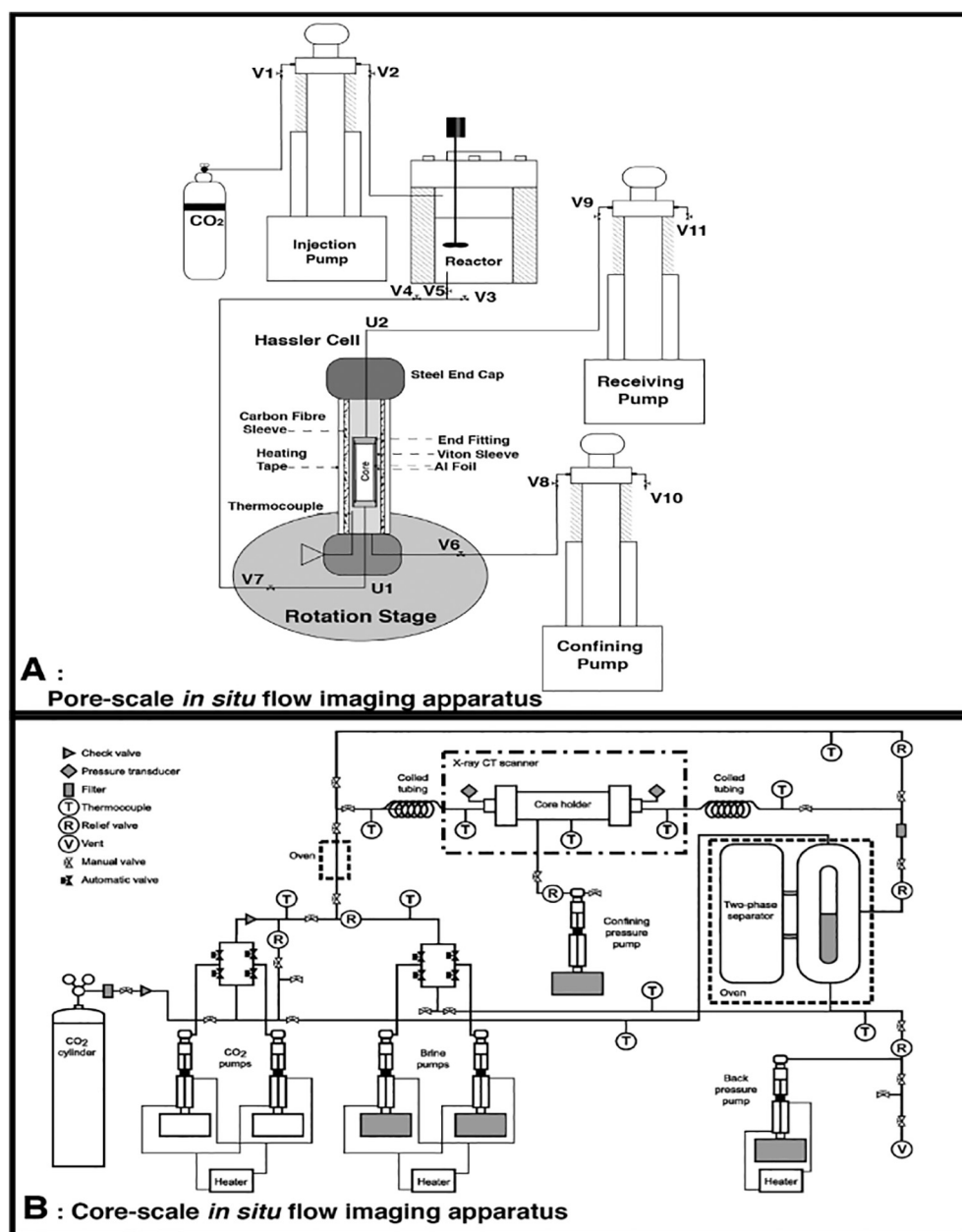


Fig. 2. The pore (A) and core (B) scale flow and imaging apparatus which show how high pressure syringe pumps were connected to the flow cells to assemble the *in situ* experiments. In (A) CO₂ is pressurized by the injection pump and used to equilibrate brine in the reactor. Reactive brine is pulled through core assembly by the receiving pump. The cell is confined by deionized water in the confining pump and heated using heating tape controlled by a thermocouple in the confining fluid. The experimental system is connected using tubing and fluid flow is directed using Valves (V) and Unions (U). In the core-scale apparatus (B) CO₂ and brine are circulated using the bypass loop and two-phase separator to equilibrate the brine. Reactive brine is then pushed through the core assembly by the brine pumps. Pressure is measured by the pressure transducers on either side of the core and the cell is confined by deionized water in the confining pump. The entire system is heated using PID controlled heaters and thermocouples.

Table 1
Experimental parameters.

Experiment number	1	2	3	4
Rock type	Ketton Limestone	Ketton Limestone	Portland Basebed	Portland Basebed
Flow rate [L·min ⁻¹]	0.0001	0.009	0.0001	0.009
Brine pH	3.1	3.1	3.1	3.1
Temperature [°C]	50	50	50	50
Pressure [MPa]	10	10	10	10
Number of Scans	10	13	71	14
Resolution [μm]	4.1	250/27	4.76	250/27
Projections	800	1000	1000	1000
Core diameter [cm]	0.4	3.8	0.4	3.8
Core Length [cm]	1.2	80	1.2	80

channel widening, a broadening of fast flow pathways through the rock in a flow regime where the injected acid penetrates throughout the rock. This is distinct from wormholing, seen at faster reaction rates,

where the injected acid etches a hole through the sample, and the injected acid is confined to this hole. Menke et al. (2017) examined reaction at the pore scale for multiple brine pH and found that in heterogeneous samples, channelling was faster with increasing heterogeneity and decreasing pH of the injected brine. However, to date no studies have investigated the scale dependence of reaction-induced changes in pore structure.

The main goal of this study is to investigate how different transport and reaction conditions alter complex pore structures at the pore and core scales by comparing dynamic reaction-induced changes in pore-space geometry, and flow in subsurface rock systems at reservoir temperatures and pressures.

2. Sample characterisation

Two carbonate rocks were chosen for these experiments, Ketton and Portland basebed. Both are oolitic limestones of Jurassic age made of > 97.1% calcite with a minor quartz component. Ketton is quarried in Ketton, Rutland, UK. It is an almost pure calcite medium-grained

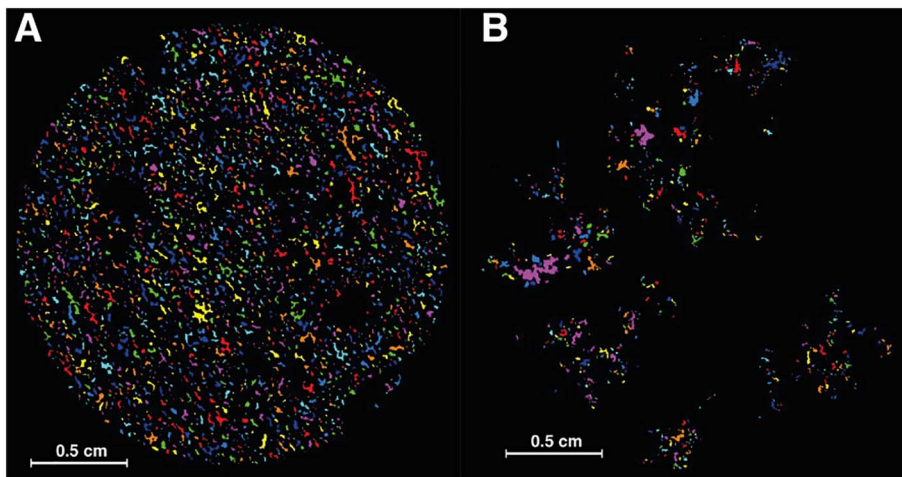


Fig. 3. Post-reaction core-scale Ketton (A) and Portland (B) are sliced perpendicular to the axis of flow and each individual channel is labelled.

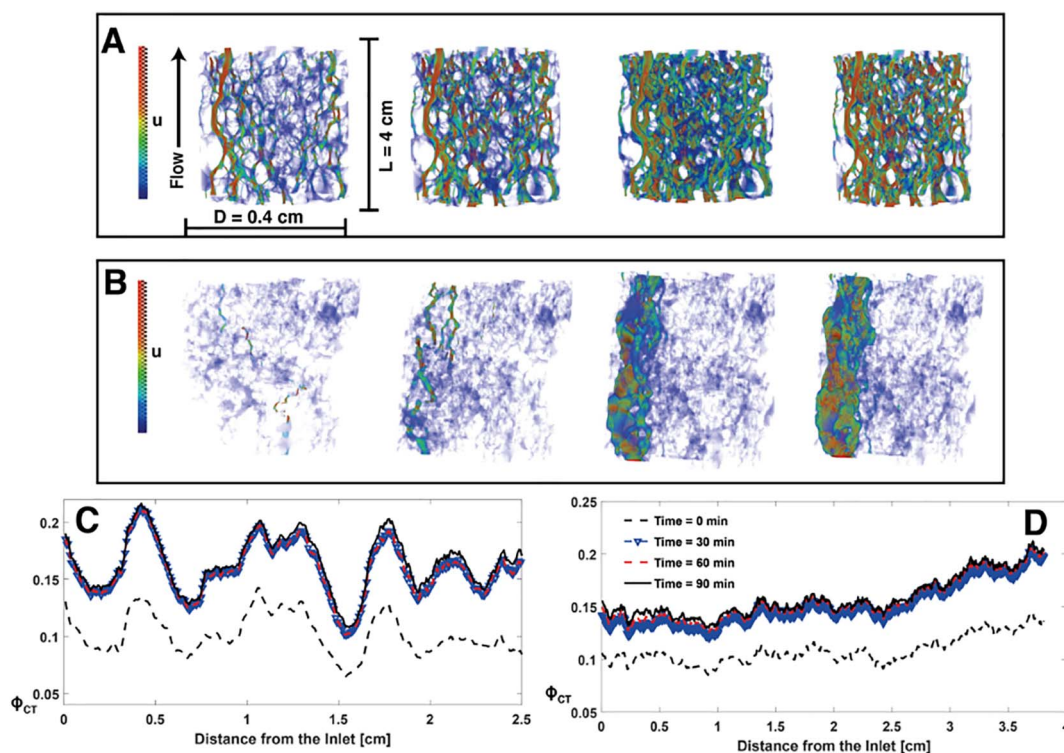


Fig. 4. Pore scale porosity, permeability, and velocity evolution with time for Ketton (A) and Portland (B). Average porosity profiles for Ketton (C) and Portland (D) along the direction of flow and connected porosity with high velocity regions are visualised for 0, 30, 60, and 90 min. High velocity regions are red. Connected porosity is blue. Data from (Menke et al., 2017, 2016). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oolite with microporous cement with a standard micritic texture. Portland Baseded is quarried in Portland, UK. It is a fine-grained grainstone containing tightly packed ooids with interparticular porosity and microporous cement. Fig. 1 shows the normalised pore size distributions for Ketton and Portland derived from mercury injection capillary pressure (MICP) tests. The image resolution limits for $4\ \mu\text{m}$ (solid line) and $27\ \mu\text{m}$ (dashed line) show that our imaging is likely to capture the largest pore throats for segmentation, but are unlikely to capture the smallest flow pathways, especially in Portland which has much narrower pore throats than Ketton. At the resolution of XCT ($250\ \mu\text{m}$), no segmentable initial pore structures are likely to be captured. Menke et al. (2015, 2016) performed network extractions at the pore scale for Ketton and Portland and found that Ketton is well connected with a homogenous pore structure while Portland is poorly connected with a highly heterogeneous pore structure. Additionally, Menke et al. (2015,

2016) looked at the PDFs of velocity and found that the distribution of velocities was narrow for Ketton indicating flow homogeneity and broad and irregular for Portland indicating a heterogeneous flow field.

3. Experimental methods

Two experimental apparatus were used to image the dynamics of dissolution in our samples. Fig. 2A depicts the apparatus used for the mm-scale experiments and Fig. 2B depicts the apparatus used for the cm-scale experiments. The Zeiss Versa XRM-500 $\mu\text{-CT}$ scanner for Ketton and the Diamond Lightsource pink beam for Portland were used to image reaction between calcite and CO_2 -saturated brine at reservoir conditions (50°C and $10\ \text{MPa}$). $\sim 1\ \text{cm}$ length and $4\ \text{mm}$ diameter samples were reacted by injecting supercritical (sc) CO_2 saturated brine (pH 3.1) at a flow rate of $0.1\ \text{mL}\cdot\text{min}^{-1}$. These cores were imaged over

Table 2

The porosity, permeability, Péclet, and Péclet-Damköhler numbers for all experiments. ϕ_{total} is calculated using $\phi_{total} = \phi_{grain} (1 - \phi_{CT}) + \phi_{CT}$ where the grain porosity ϕ_{grain} is estimated using the helium porosity for the first image and assumed constant for the duration of the experiments. Pe and $PeDa$ are calculated according to the method presented in Menke et al. (2015) using ϕ_{total} and characteristic length L . PV represents the number of pore volumes of brine to pass through the sample.

Time [min]	Property	Core-scale Ketton	Core-scale Portland	Pore-scale Ketton	Pore-scale Portland
0	Absolute permeability k [m ²]	4×10^{-13}	1×10^{-15}	5×10^{-13}	1×10^{-16}
	Segmented porosity ϕ_{CT} []	–	–	0.11	0.11
	Total porosity ϕ_{total} []	0.23	0.21	0.23	0.23
	Calculated Pe []	407	383	326	281
	Fluid pore volumes []	0	0	0	0
	Calculated $PeDa$ []	7×10^{-2}	6×10^{-2}	7×10^{-2}	6×10^{-2}
30	Absolute permeability k [m ²]	4×10^{-13}	6×10^{-15}	2×10^{-12}	3×10^{-14}
	Segmented porosity ϕ_{CT} []	–	–	0.13	0.15
	Total porosity ϕ_{total} []	0.24	0.22	0.25	0.27
	Calculated Pe [] [Eq. (3)]	390	366	300	239
	Fluid pore volumes []	16	18	260	260
	Calculated $PeDa$ []	7×10^{-2}	6×10^{-2}	7×10^{-2}	6×10^{-2}
60	Absolute permeability k [m ²]	4×10^{-13}	6×10^{-15}	4×10^{-12}	2×10^{-11}
	Segmented porosity ϕ_{CT} []	–	–	0.16	0.16
	Total porosity ϕ_{total} []	0.26	0.22	0.28	0.28
	Calculated Pe [] [Eq. (3)]	360	335	268	231
	Fluid pore volumes []	32	35	500	480
	Calculated $PeDa$ []	7×10^{-2}	6×10^{-2}	7×10^{-2}	6×10^{-2}
90	Absolute permeability k [m ²]	4×10^{-13}	1×10^{-13}	6×10^{-12}	5×10^{-11}
	Segmented porosity ϕ_{CT} []	–	–	0.16	0.16
	Total porosity ϕ_{total} []	0.27	0.25	0.28	0.28
	Calculated Pe [] [Eq. (3)]	346	322	268	231
	Fluid pore volumes []	50	50	710	693
	Calculated $PeDa$ []	7×10^{-2}	6×10^{-2}	7×10^{-2}	6×10^{-2}

the course of 1.5 h at a voxel size of 4 μ m. The precise details of the experimental apparatus and method are described in Menke et al. (2016) for the Portland experiment and Menke et al. (2017) for the Ketton experiment. The experimental parameters for all experiments are detailed in Table 1.

These experiments were then repeated at the core scale using samples that were drilled from the same 0.04 m³ blocks as in the previous experiments. Cores of Ketton and Portland, ~8 cm long and 3.8 cm in diameter, were reacted with CO₂ saturated brine using the core-scale experimental apparatus [Fig. 2B] by injecting pH 3.1 brine at a flow rate of 9 mL·min^{−1}. This flow rate was chosen to keep conditions identical by having the same amount of fluids injected per cross-sectional area of core [mL·m^{−2}] at both experimental scales. The core-scale samples were imaged using XCT ~13 times over the course of 1.5 h with a 250 × 250 × 500 μ m voxel size. The experimental apparatus is the same as detailed in Reynolds and Krevor (2015). Furthermore, the entirety of each core-scale sample was imaged post-reaction by Zeiss in Pleasanton, CA in an XRM-510 using automated stitching of a sequence images acquired along the axis of the core employing a flat panel detector at 27 μ m to create a high-resolution volume of 1400 × 1400 × 3000 voxels where the internal pore structure is both visible and able to be segmented for quantitative analysis.

All images were then post-processed using the image processing modules in Avizo 9.1 (www.vsg.com). The high-resolution micron-scale images were filtered using the non-local means filter and segmented using the watershed segmentation algorithm. The porosity was measured directly on the images and the permeability for the smaller cores was assessed using a Navier-Stokes solver (Bijeljic et al., 2013; Menke et al., 2016; Raeini et al., 2012). The low-resolution dynamic core-scale images acquired using XCT were analyzed for porosity by the method presented in Krevor et al. (2011) while the permeability was measured experimentally using the pressure drop across the core (Reynolds and Krevor, 2015). Furthermore, the high-resolution images acquired by μ -CT were segmented and the velocities were calculated using the LIR

Stokes solver in Math2Market GeoDict (Linden et al., 2015). Finally, the velocity fields were all used as input into the semi-analytical streamline tracing method introduced by Pereira Nunes et al. (2015); Pereira Nunes et al. (2016). The consolidated streamline density was output and the pore space of each image was then analyzed for connected paths along the direction of flow for both the core-scale and pore-scale scale images. Moreover, the total flow contribution per channel was calculated by labelling the individual channels in each slice perpendicular to the axis of flow [Fig. 3] and summing the number of streamlines passing through each label.

4. Pore-scale dynamics

Fig. 4 depicts the evolution of porosity, permeability and velocity for Ketton (A) and Portland (B) pore-scale cores over the course of 90 min of dissolution. Both cores exhibit channel widening where there is no discernable difference in dissolution rate along the direction of flow, but show a large initial increase in porosity as the high permeability channels expand followed by a smaller increase at later times after the channels are established. Ketton has many channels initially and shows a relatively small increase in permeability (computed using the flow simulator) of one order of magnitude during the experiment, while Portland has a few initial channels and has a permeability increase of over five orders of magnitude with the largest increase at early times during the channel widening stage. During the later stage of both experiments the permeability increases during a small widening of the flow pathways, but the corresponding porosity increase is nearly imperceptible.

The number of pore volumes of fluid and the Péclet (Pe) and Péclet-Damköhler ($PeDa$) were calculated for each rock [Table 2]. As expected the Pe number decreased as porosity increased during each experiment since the total flow rate is kept constant and so the average flow speed decreases. However, the $PeDa$ remained relatively constant and $\ll 1$ and thus the experimental conditions are reaction-limited. The number

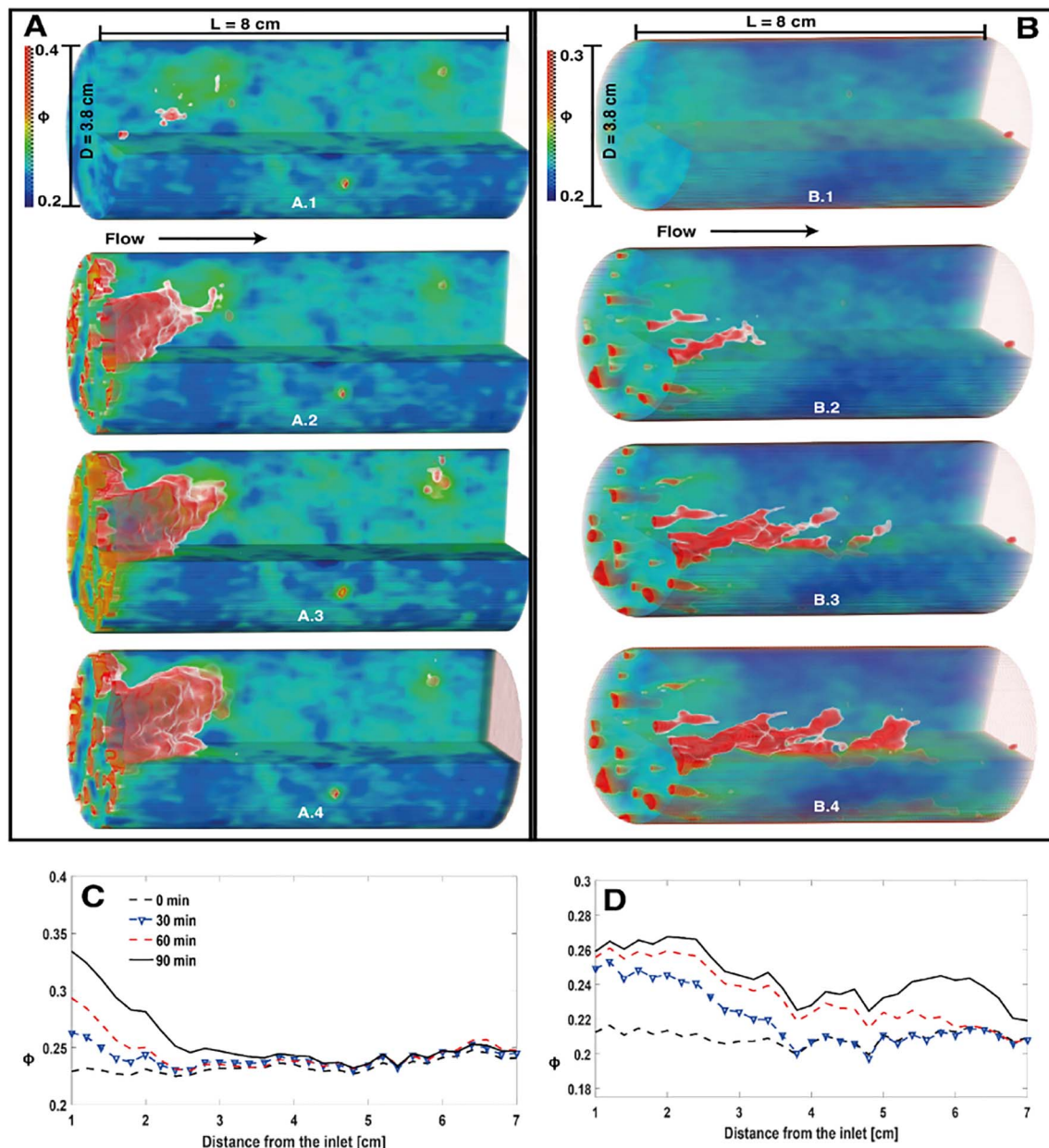


Fig. 5. Core-scale porosity and permeability evolution with time for Ketton (A) and Portland (B) for 0, 30, 60, and 90 min. High porosity regions are red and low porosity regions are blue. Porosity profiles along the direction of flow and porosity are visualised for 0, 30, 60, and 90 min for Ketton (C) and Portland (D). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of pore volumes (PV) approached 700 for each experiment suggesting that the reactions are not fluid limited.

5. Core-scale dynamics

Fig. 5 depicts the evolution of porosity and permeability for Ketton (A) and Portland (B) core-scale samples over the course of 90 min of dissolution. Both cores exhibit large increases in porosity near the sample inlet which progress along the length of the cores during the experiment. The high porosity region is narrower for Portland and extends more quickly, while Ketton has a wider high porosity region that extends more slowly. Both cores show the largest increase in porosity in the regions with the highest initial porosity and the progression of dissolution tends to extend sequentially through time into the higher porosity regions further along the core. The increase in total porosity is similar (~ 0.04) in both cases. The permeability of the Ketton core, calculated using the pressure drop across the core, shows no change

while the permeability of the Portland core increases by two orders of magnitude. The spatial distribution of porosity increase suggests that the Portland core experienced some breakthrough of the widening channels to the outlet while the Ketton channel widening terminated before the end of the core.

The Pe , $PeDa$, and PV were calculated for each experiment [Table 2]. The Pe number decreased as porosity increased was similar to the pore scale experiments. The $PeDa$ remained approximately constant, was in good agreement with the pore scale experiments and was $\ll 1$. The number of pore volumes (PV) approached 50 for each experiment, which is smaller than the pore scale experimental value of 700 PV (due to the core-scale samples being $\sim 20\times$ longer than the pore scale samples), but still suggests that the reactions are still not fluid limited.

6. Post-reaction high resolution core-scale imaging

The entirety of each larger core was imaged post-reaction at high

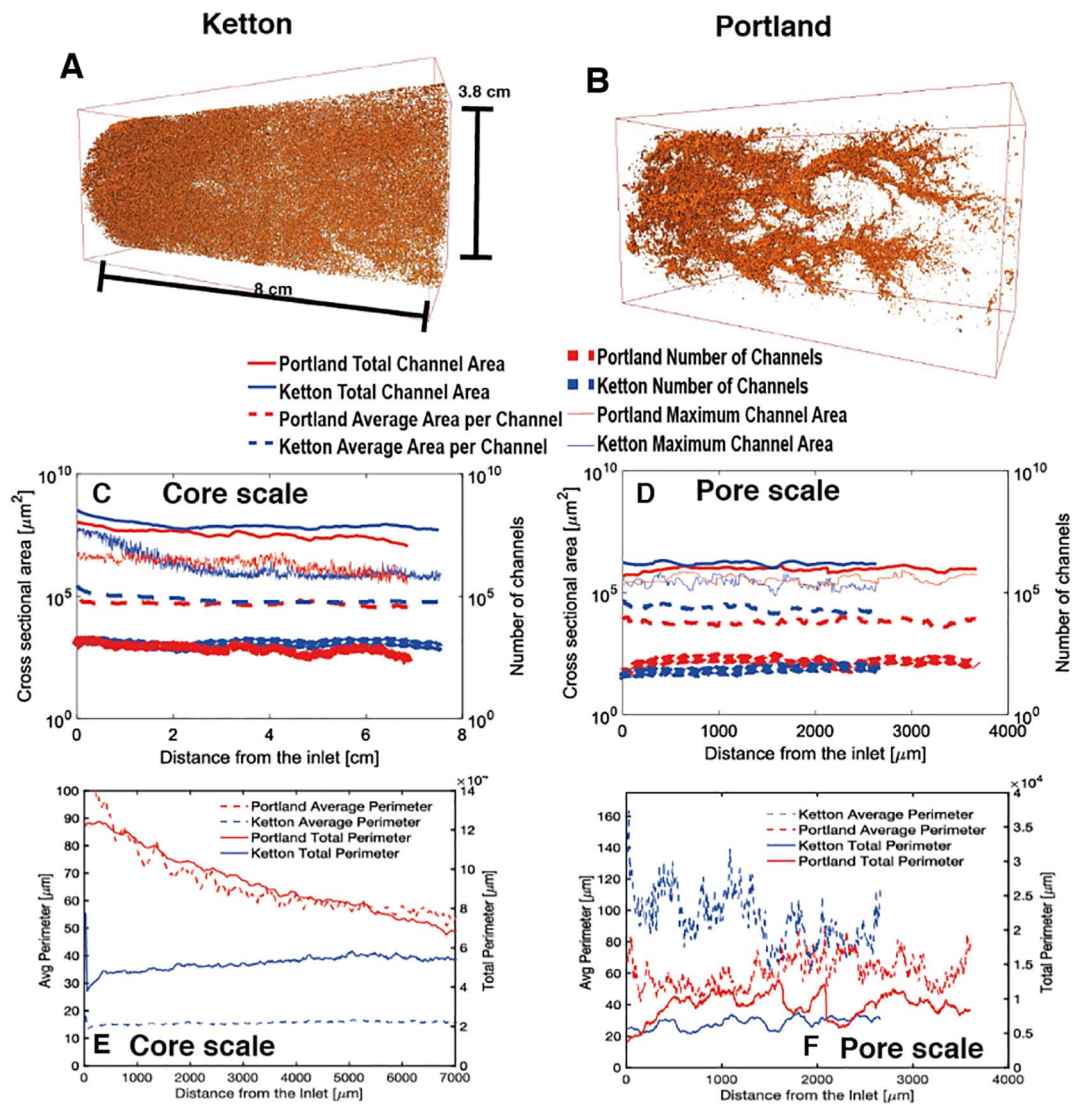


Fig. 6. Pore space renderings of Ketton (A) and Portland (B) cores at a 27 μm voxel size. The total cross-sectional area, average cross-sectional area, maximum cross-sectional area and number of channels per slice along the axis of flow for the core-scale (C) and pore-scale (D) experiments. The average perimeter per label per slice and the total perimeter per slice along the direction of flow for the core scale (E) and pore scale (F) experiments.

resolution using automated stitching of a sequence of images acquired along the axis of the core using a flat panel detector at 27 μm , to create a volume of $1400 \times 1400 \times 3000$ voxels. The images were then processed and segmented and the pore structure was extracted [Fig. 6A–B]. Ketton showed an even distribution of pore space throughout while Portland had distinct channels.

The pore space of all μm -resolution images were then analyzed for connected paths along the direction of flow. The number of paths in each individual slice perpendicular to the flow axis [Fig. 3] were counted and the cross-sectional area was measured [Fig. 6C–D]. In the core-scale images [Fig. 6C] the total number of channels remained almost constant in Ketton while Portland had fewer, wispier channels. The frequency of these channels, measured in each slice, decreased towards the outlet of the core. The total channel area was higher overall for Ketton than Portland, corresponding to the higher overall porosity. Ketton had a larger void area near the inlet and then a constant area along the rest of the length of the core while Portland showed a steady, but slow decline with distance from the sample inlet. However, the average cross-sectional area per channel remained relatively constant along the length of each core with Ketton showing a small uptick near the sample inlet. The maximum channel width was highest for Ketton near the inlet, which then stabilised at later time, while the Portland

had a steady width for the length of the channels. The higher maximum channel area in Ketton may be due to channels merging where large amounts of dissolution had occurred near the inlet. Both the total and average perimeters [Fig. 6E] were higher in Portland near the inlet and decreased towards the outlet in conjunction with the dissolution front, while Ketton had a sharp jump near the inlet where there were large amounts of dissolution but remained steady throughout the unreacted regions of the core. The increase in perimeter in the reacted regions of the core indicates that the resolution of the scans is enough to capture changes in structure but is not sufficient to capture changes in surface roughness that would be expected during dissolution.

In the pore-scale images [Fig. 6D] Portland had a greater number of channels than Ketton, but the channels were smaller on average. However, Ketton had a larger total channel cross-sectional area due to a larger proportion of the pore space contributing to the connected porosity. There was no discernable spatial variation of maximum channel area along the axis of flow for either rock type. The average perimeter was higher in Ketton [Fig. 6F] than in Portland due to larger pores overall, but there was very little difference in total perimeter between the samples.

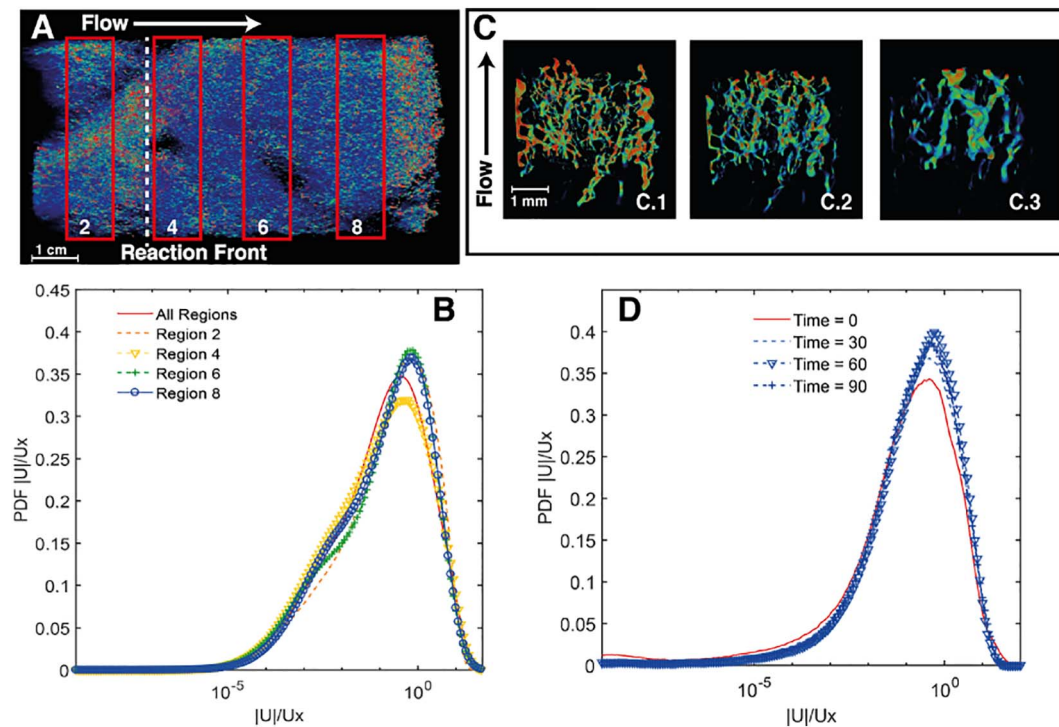


Fig. 7. The core scale velocity field of Ketton (A) perpendicular to the axis of flow with Sections 2, 4, 6, and 8 outlined in red. The probability density functions (PDFs) of the sections and for the whole sample are plotted in B. The velocity fields of the corresponding pore scale experiments are shown in C for times 0, 30 and 90 mins (C.1–3). The PDFs are plotted in D for times 0, 30, 60 and 90 mins. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

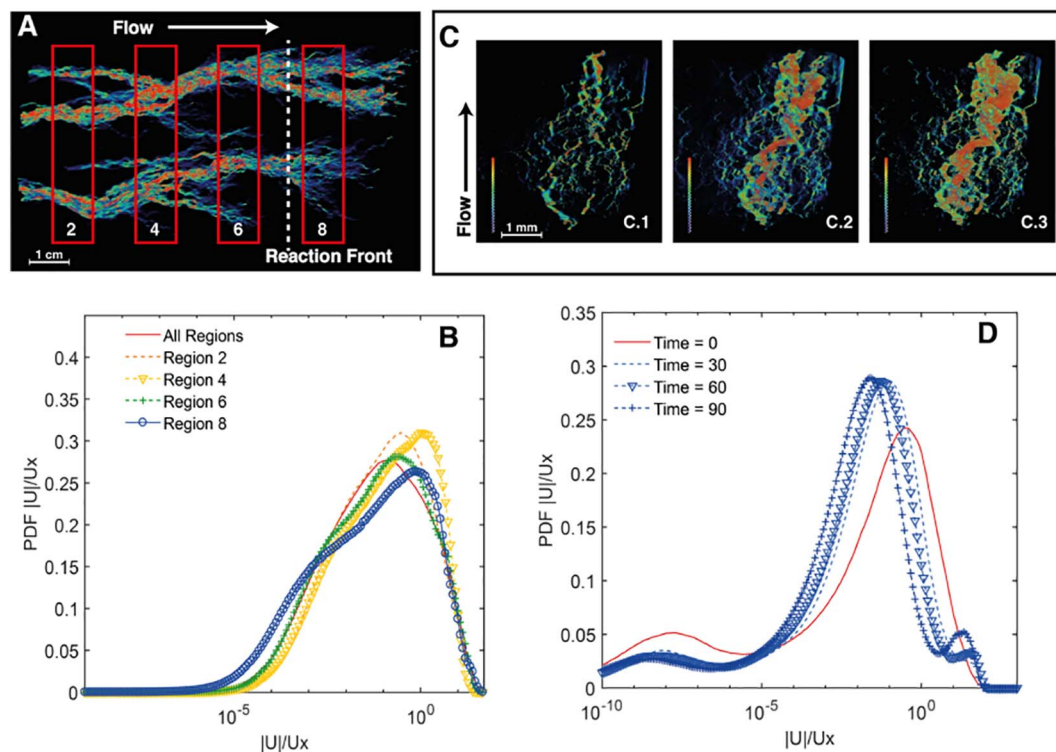


Fig. 8. The core scale velocity field of Portland (A) perpendicular to the axis of flow with Sections 2, 4, 6, and 8 outlined in red. The probability density function of the velocity, PDF, is shown for each section and for the whole system in the sections along with all regions (B). The velocity fields of the corresponding pore scale experiments are shown in C for times 0, 30 and 90 mins (C.1–3). The PDFs are plotted in D for times 0, 30, 60 and 90 mins. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

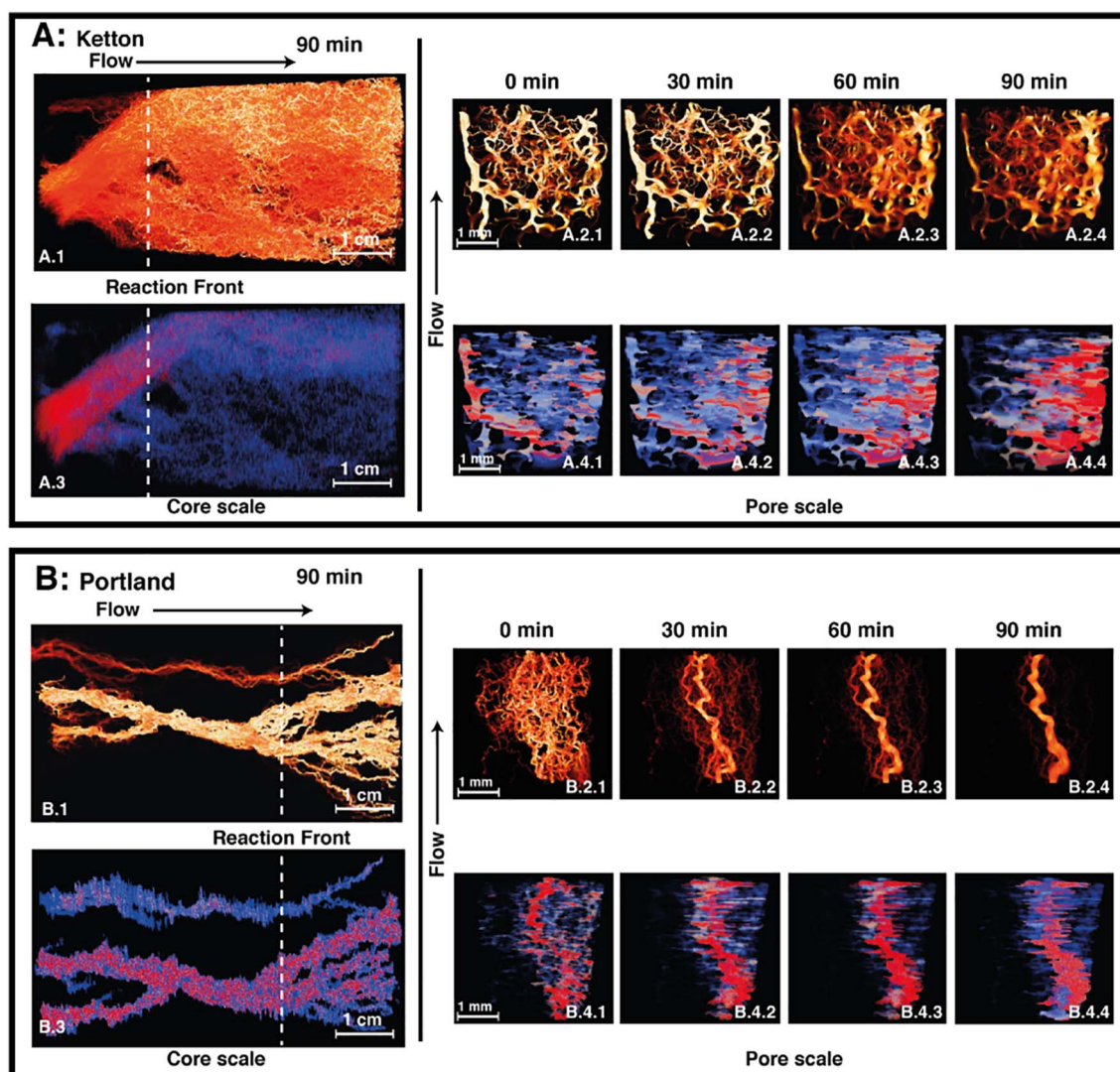


Fig. 9. The streamline density in a sample of Ketton (A) and Portland (B). The streamline densities A.1–2, B.1–2 is visualised where yellow is high density and orange is low density. The channel flow A.1–2, B.1–2 are visualised where red is high density and blue is low density. The core-scale experiments are A.1, A.3, B.1, B.3 with flow moving from left to right. The pore-scale experiments are A.2.1–4, A.4.1–4, B.2.1–4, B.4.1–4 with flow moving from bottom to top. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

7. Core-scale velocity fields

To quantify the differences in the core and pore-scale images we compared the velocity distributions. The segmented images were input into the LIR Stokes solver coded in GeoDict (www.geodict.com). The LIR solver was used because it is computationally more efficient than the finite-volume solver used in previous studies (Menke et al., 2017, 2015, 2016) while yielding equivalent results (Linden et al., 2015). This allowed us to solve for flow on very large images without high performance computing. When analyzed as a whole, Ketton showed an even distribution of velocities while Portland was less uniform [Figs. 7, 8].

The probability density functions of the logarithm of velocity, PDFs, were then plotted in sections along the axis of flow and compared to the PDFs of the corresponding pore-scale experiments at identical *in situ* conditions. At the pore scale, we see two distinct behaviours on dissolution (Menke et al., 2017, 2015, 2016). For Ketton, with the initially more homogeneous distribution of velocity, dissolution is uniform, leading to a slightly narrower PDF with a more pronounced peak and fewer stagnant regions of pore space at later times (Fig. 7). For Portland with a more heterogeneous distribution of velocities dissolution results

in the widening of preferential flow channels, leading to a wider spread of velocities, with many regions experiencing relatively slow flow (Fig. 8). Additionally, a small secondary peak with very high velocities emerges at later time representing some of the faster channels.

At the core scale we are only able to resolve flow in void spaces at least 27 μm across. Here we see qualitatively the opposite behaviour to the pore scale. For Ketton where dissolution has occurred (region 2) and just ahead of the dissolution front, which we define as the maximum distance from the inlet with dissolution detectable by XCT, (region 4) we see a lower peak in the PDF and a slightly wider spread of velocities indicating the widening of more large channels. Note that we see a different distribution in region 4 just ahead of the reaction front than in region 8 a long way away. This indicates the impact of the widening of dissolution channels in the flow field downstream. For Portland instead we see a narrowing of the PDF where reaction has occurred (Sections 2, 4 and 6) compared to Section 8 ahead of the front suggesting the focussing of flow in a few dominant channels.

Overall, while at both the mm and cm scales we see channel widening with the emergence of a few dominant flow paths in Portland, the details of the velocity fields are different. At the core scale and only resolving the larger pores, we see a focussing of the flow in the more

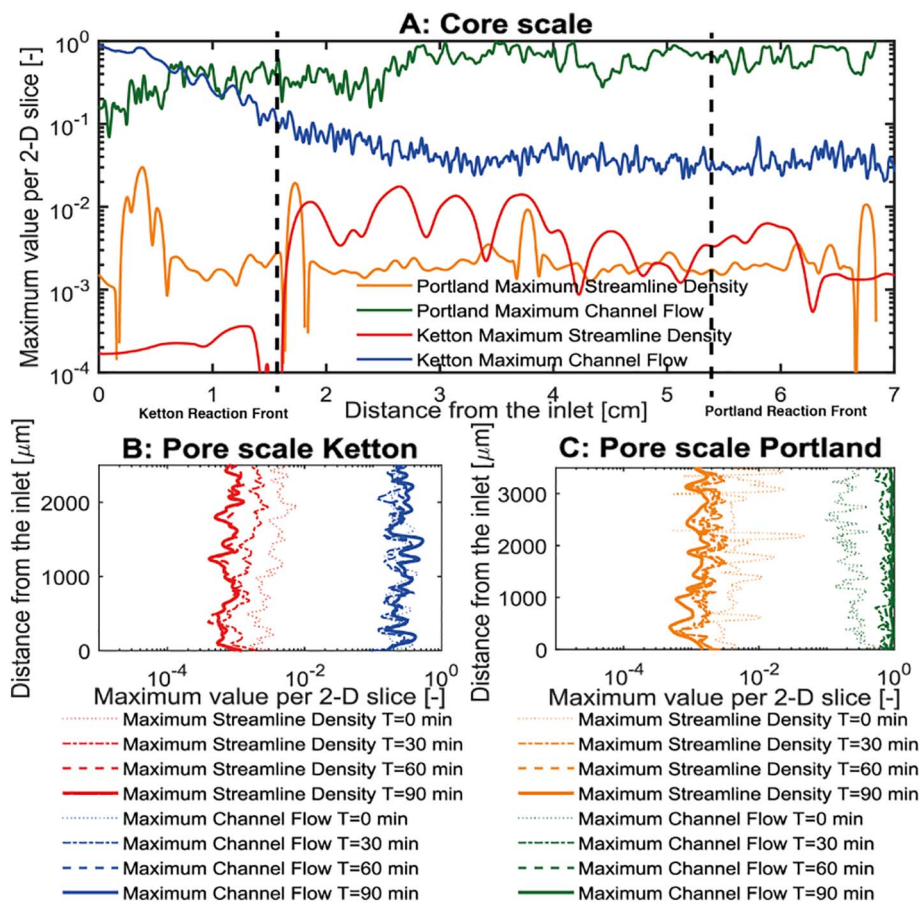


Fig. 10. The maximum normalised streamline density and maximum normalised channel flow in each slice perpendicular to the direction of flow for the core-scale (A) experiments at 90 min, and for the pore-scale experiments (B–C) at 0, 30, 60, and 90 min.

heterogeneous system, Portland, with a different distribution than computed at the pore scale. For Ketton in contrast, the PDFs at the cm and mm scales are approximately similar: here the most significant finding is the alteration in the flow field, compared to the rest of the core, just ahead of the reaction front. For Ketton where dissolution has occurred (region 2) and just ahead of the dissolution front (region 4) we see a lower peak in the PDF and a slightly wider spread of velocities, indicating the widening of more large channels. As mentioned above, we see a very different distribution in region 4 just ahead of the reaction front than in region 8 a long way away. This indicates the widening of dissolution channels impacts the flow field downstream. For Portland instead we see a narrowing of the PDF where reaction has occurred (Sections 2, 4 and 6) compared to Section 8 ahead of the front suggesting the focussing of flow in a few dominant channels.

8. Streamline density

The velocity fields were then used in combination with a semi-analytical streamline tracing method that obeys a no-flow condition at the pore walls (Pereira Nunes et al. (2016)), to further investigate the distribution of flow on a pore-by-pore basis. To represent advection with no diffusion, 100,000 particles were injected following a flow-weighted rule at the inlet that followed streamlines through the velocity field. The number of streamlines passing through each voxel was recorded and the number of streamlines was then normalised to the total number of particles [Fig. 9] – hereafter called *streamline density*. Streamline density was then summed for each individual channel in each slice to assess the contribution of each channel to total flow [Fig. 3] – this will hereafter be called the *channel flow*.

Fig. 10 shows the maximum streamline density and maximum channel flow plotted along the axis of flow. In the core-scale experiments [Fig. 10], the maximum streamline density is low for Ketton at

the inlet face of the core. This corresponds to a large amount of dissolution, meaning flow is carried across a larger area. However, the maximum channel flow is very high due to the merging of multiple channels as they are widened by dissolution (shown in Fig. 6), but as the distance from the inlet increases, this effect is lessened. It is worth noting that the maximum channel flow in Ketton never exceeds 0.1 after the reaction front. This signifies that the flow spreads out after exiting the group of enlarged channels, but is still concentrated in a few preferential pathways rather than spread uniformly over the many existing channels.

In Portland the maximum streamline density remains relatively steady throughout the core with no discernible trend. The maximum channel flow is ~ 0.1 at the front of the core. At later times, however, flow is consolidated within a single channel containing 80–90% of the total flow. This can be seen in Fig. 8, where there is one channel that connects across the system at late time.

At the pore scale [Fig. 10] there is no discernable change in either the maximum streamline density or maximum channel flow in the flow direction. However, through time both Ketton and Portland show a decrease in streamline density, as would be expected from a porosity increase during dissolution. Additionally, Portland showed an increase in maximum channel flow from 90% in the unreacted core to almost 100% at 90 min, with most of the change happening within the first 30 min. This indicates that almost all flow is initially directed through a single channel, creating a large amount of positive reaction feedback at later times. This change in maximum flow density is not seen in Ketton, implying that in the more homogenous pore structure, flow consolidation is less and thus there is less focusing of reaction as is also evident in Figs. 6–8.

9. Conclusions

We have imaged the dissolution of Portland and Ketton carbonates at the same flow and reactive conditions at the pore and core-scales. We find that evolution of porosity is structure dependent and that porosity evolution perpendicular to the axis of flow behaves similarly across scales. However, along the axis of flow the pore-scale behaviour does not capture the heterogeneous porosity propagation visible at the core-scale. Furthermore, we do not see etching of ‘wormholes’ at either scale, and instead see channels and collections of channels widening in regions of initially fast flow. Additionally, we find that at the larger scales the interplay between flow and reaction significantly affects flow in the unreacted regions of the core. When flow is focussed in large reacted channels, this focusing is carried through to the unreacted parts of the channel and most flow continues down preferential pathways well after passing the reaction front. The REV for reaction infiltration instability problems may be larger than the extent of the dissolution front itself.

This work represents the first study of scale dependence using *in situ* 4D tomography and provides insight into the mechanisms that control local reaction rates at the *mm* and *cm* scales. Furthermore, this work implies that at larger scales under these conditions it is likely to be structural heterogeneities, as proposed in simulation studies at the field scale (Buijse and Glasbergen, 2005), rather than fluid limitations that dominate dissolution and therefore the evolution of high permeability pathways.

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