

PORE-SCALE MODELLING OF CARBONATE DISSOLUTION

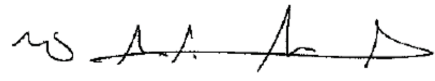
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of the requirements for the degree of
Doctor of Philosophy*

**Imperial College London
Department of Earth Science and Engineering**

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*I hereby declare that all material in this thesis which is not the result
of my own work has been properly referenced and acknowledged.*

A handwritten signature in black ink, consisting of a series of connected loops and strokes, representing the name João Paulo Pereira Nunes.

João Paulo Pereira Nunes

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To Alice & Carol

ABSTRACT

High resolution micro-CT images of porous rocks provide a very useful starting point to the development of pore-scale models of fluid flow and transport. Following a literature review covering recent results on the applicability of tomographic imaging to study reaction phenomena at the pore and core scales, this thesis presents a pore-scale streamline-based reactive transport model to simulate rock dissolution. The focus is on carbonate dissolution in CO₂-saturated fluids.

After injecting CO₂-rich fluids into carbonate reservoirs, chemical reactions between the acidic fluid and the host rock are to be expected. Such reactions may cause significant variations in the flow and transport properties of the reservoir, with possible consequences for field development and monitoring. The interplay between flow and reaction exhibits a very rich behaviour that has not yet been fully understood, especially in the case of carbonate rocks, which possess a complex pore structure.

The model is developed within a Lagrangian framework, where the advective displacement employs a novel streamline tracing method which respects the no-flow boundary condition at the pore walls. The method is implemented in the pore-space geometry reconstructed from micro-CT images of sedimentary rocks. Diffusion is incorporated with a random walk and fluid-solid reactions are defined in terms of the diffusive flux of reactants through the grain surfaces.

To validate the model, simulation results are compared against a dynamic imaging experiment where a carbonate sample was flooded with CO₂-saturated brine at reservoir conditions. The agreement is very good and a decrease of one order of magnitude in the average dissolution rate, compared to the rate measured in an ideal reactor, is explained in terms of transport limitations arising from the flow field heterogeneity.

The impact of the flow heterogeneity in the reactive transport is illustrated in a series of simulations performed in rocks with different degrees of complexity. It is shown that more heterogeneous rocks, in the sense of flow heterogeneity, may exhibit a decrease of up to two orders of magnitude in the sample-averaged reaction rates, and that the flow rate is also an important factor when studying carbonate dissolution.

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CONTENTS

Abstract	vii
Acknowledgements	viii
List of Figures	xi
List of Tables	xii
List of Symbols	xiii
1 Introduction	1
1.1 Pore-scale imaging	3
1.2 Geochemical reactions in carbonate rocks subjected to CO ₂ injection	5
1.2.1 Summary of core-scale experimental results	5
1.2.2 A field-scale example: the Weyburn project	7
1.3 Pore-scale description of flow and transport	12
1.3.1 Flow simulation in micro-CT images	12
1.3.2 Lagrangian approach for solute transport	14
1.4 Modelling mineral dissolution in porous rocks	16
1.4.1 Pore-network models	17
1.4.2 Direct simulation: Eulerian approach	18
1.4.3 Direct simulation: The particle approach	19
1.4.4 Proposed methodology: a streamline-based particle track- ing model	20
1.5 Thesis Outline	20
2 Streamline tracing in porous media	22
2.1 Introduction and definitions	22
2.2 Streamline tracing - Pollock's algorithm	24
2.3 Semi-analytical streamline tracing in pore-scale images	26
2.3.1 Transit times and exit points for voxels with one solid bound- ary	27
2.4 Flow between two parallel plates	29

2.5	Streamline tracing in images of sedimentary rocks	33
2.6	Comparison with time-stepping methods	39
2.7	Applications and concluding remarks	41
3	Pore-scale simulation of carbonate dissolution in micro-CT images	44
3.1	Heterogeneous reactions at interfaces	44
3.1.1	Transport and reaction regimes: dimensionless numbers . . .	45
3.2	Reaction rates in the laboratory and in porous rocks	48
3.3	Mineral Dissolution in the Particle Approach	50
3.4	Dissolution of a planar front	51
3.5	Calcite Dissolution in CO ₂ -saturated Fluids	53
3.5.1	Alternative physical interpretations for the particles	56
3.6	Modelling carbonate dissolution using dynamic imaging data	57
3.6.1	Experimental conditions and simulation parameters	57
3.6.2	Simulation procedure	60
3.6.3	Results and discussion	64
3.7	Average dissolution rate vs. batch rate	72
3.8	Summary of results	73
4	Flow field heterogeneity and average reaction rates	75
4.1	Sample characterization	75
4.2	Simulation method	78
4.3	Uniform dissolution and average dissolution rates	78
4.4	Initial pore-structure and dissolution regimes under variable flow rates	82
4.4.1	Channelized flow and the uniform dissolution regime	86
4.5	Discussion	87
5	Conclusions and directions for future work	89
5.1	Discussion and summary of results	89
5.2	Suggestions for future work	91
A	Summary of sample characteristics	93
B	Representative Elementary Volume	94
C	Transit times and exit coordinates for the voxels with two, three and four solid boundaries	96
C.1	Pores with two solid boundaries	96
C.1.1	Two solids in the same direction	96
C.1.2	Two adjacent solids	97
C.2	Pores with three solid boundaries	98
C.2.1	One solid in each direction	98

C.2.2	Two solids in the same direction	99
C.3	Pores with four solid boundaries	99
C.3.1	Two directions blocked	100
C.3.2	Solids in three directions	100
D	Average Flux of Particles in a Diffusion Step	101
	Bibliography	102

LIST OF FIGURES

1.1	Schematics of a typical micro-CT system. A source emits X-rays, which penetrate a rock sample. A 3D image is reconstructed from the attenuated rays.	4
1.2	Evolution of image quality during the past decades. (a) A Coconino sandstone acquired with synchrotron light [Flannery et al., 1987]; (b) The pore-space of a Fontainebleau sandstone [Spanne et al., 1994]; (c) Contact surfaces between fluid phases and a carbonate grain at reservoir conditions [Andrew et al., 2014a].	4
1.3	A slice of a raw tomography of a Silurian dolomite (a); the same slice after filtering (b) and segmentation (c). The segmented image has two phases: solids (grey) and pores (black). Courtesy of Yousef Al-Khulaifi.	5
1.4	Time-lapse, three-dimensional micro-CT image of a ramified worm-hole formed during the dissolution of a bioclastic limestone by a CO ₂ -saturated fluid. From Vialle et al. [2014].	6
1.5	Neutron radiographs illustrating the influence of the flow and reaction regime on the wormholing pattern limestone samples of 10cm in length. From Fredd and Fogler [1998].	6
1.6	Evolution of the flow field of a bioclastic limestone during the high flow rate injection of a CO ₂ -saturated brine at reservoir conditions. Modified from Menke et al. [2016].	7
1.7	Increase in fracture aperture for experiments with $Pe = 54$ and $Pe = 216$. Dissolution is more uniform for the higher Pe . Reproduced from Detwiler et al. [2003].	8
1.8	Fines migration in a oolitic limestone after reactive flow. Pre (top) and post (bottom) images from micro-CT, from Qajar et al. [2013].	9
1.9	Geochemical parameters obtained from produced fluids before injection and following 930 days of CO ₂ injection in the Weyburn field, excerpt from Wilson and Monea [2004].	10
1.10	Temporal evolution of the concentration of Ca ²⁺ in the produced fluids in the Weyburn field, Wilson and Monea [2004].	11

1.11	4D seismic anomalies for the Weyburn field. Negative differences (yellow) show regions of high CO ₂ saturation, from White [2009]. Compare with the regions of high calcite and dolomite production in figure 1.10.	12
1.12	Pictorial representation of the advection-diffusion-reaction process. A particle moves along the analytically-traced streamlines during advection (black arrows), jumps from one to another during diffusion (red arrows) and crosses the pore-solid interface during reaction. The total displacement during a time-step is the sum of the advective and diffusive displacements. White cells are pores and black are solid.	13
1.13	Dissolution structures obtained from two-dimensional Darcy-scale simulations for a range of Pe and Da numbers. (a) Face dissolution, (b) conical wormhole, (c) dominant wormhole, (d) ramified wormhole and (e) uniform dissolution. From Golfier et al. [2002].	17
1.14	Emergence of channeling in two-dimensional networks following transport-limited dissolution. Reproduced from Hoefner and Fogler [1988]. . . .	17
2.1	A voxel representing a solid and its velocity components. In a staggered grid the velocities are assigned to the faces of the voxels.	24
2.2	Schematics of the Pollock algorithm for a two dimensional staggered grid. a) A particle enters a cell with coordinates x_p and y_p , the associate exit times are calculated according to eqs. 2.3. b) The smallest time defines the exit face (the face to the right in the figure) and the exit coordinates. Modified from Thiele [2005].	25
2.3	Pore voxel limited by a solid voxel in lattice position $(i+1, j, k)$	27
2.4	The streamline tracing algorithm and its prediction of transport are validated using the analytical solution for the flow of an incompressible fluid between two infinite parallel plates shown schematically here. We study how accurately transport is simulated for different numbers of voxels used to resolve the pore space between the two plates.	30
2.5	Particle velocities with one (a), two (b) and four (c) grid cells between the plates. The analytical solution is shown in blue dots, the standard Pollock method in the solid black line and our modified approach in red dashed line. With one grid cell our modified method is an exact match to the analytical solution while the linear interpolation from the original method completely fails to reproduce the expected parabolic profile. With two and four grid cells our extended method also produces better estimates than the original method.	31

- 2.6 Breakthrough curves with one (a), two (b) and four (c) grid cells between the plates. Unit time is defined as the breakthrough time of the particles moving at the average flow speed. The analytical solution is the dotted blue line, the standard Pollock is the black solid line and our method is the red dashed line. Using one grid cell the modified method is an exact match to the analytical solution. With a constant velocity (see figure 2.5), the Pollock method assumes transport with no dispersion of the original delta-function concentration profile in the absence of molecular diffusion. With two and four grid cells our extended method also yields better results than the original method and correctly captures the late-time tail of the distribution. The Pollock method, assuming piecewise constant velocities, again fails to reproduce the wide distribution of travel times. 32
- 2.7 Increasing the number of grid cells across the plates (fifty in this example) both methods converge to the analytical solution for the breakthrough curve. The analytical solution is shown in the solid line, the standard Pollock in the green dots and our method is the dashed red line. Here, for a fair comparison, we have binned the concentration to construct a smoothed histogram. 32
- 2.8 Orthogonal slices of three-dimensional segmented micro-CT images of a Bentheimer sandstone (a) and a Ketton carbonate (b). We launch streamlines according to a flow weighted rule at the inlet and trace until the outlet face. Flow in the Bentheimer sandstone is relatively homogeneous (c), while in the Ketton carbonate it tends to be concentrated in high velocity channels (d). Color in the streamlines is indicative of advective travel time (slow paths in light blue, fast paths in red), distances in μm 34
- 2.9 Probability distributions of the horizontal velocity – Bentheimer sandstone (solid line) and Ketton limestone (dashed line). The low velocity voxels (the heavy tails of the distributions) correspond to the high transit times in fig. 2.10. 35
- 2.10 Distribution of voxel transit times against dimensionless time τ in a Bentheimer sandstone (top) and in a Ketton carbonate (bottom) obtained using both the standard Pollock algorithm (dashed line) and our modified version (solid line). Because it ignores the decay of the tangential velocities in the voxels neighbouring the solid phase, the standard Pollock method tends to underestimate the transit times in such slower voxels. 36

- 2.11 In a system with diffusion time τ_{diff} , the voxels where the time-of-flight $\tau > \tau_{diff}$ are diffusion-dominated ($Pe < 1$), and the ones where $\tau < \tau_{diff}$ are advection-dominated ($Pe > 1$). 37
- 2.12 Breakthrough curves (concentration as a function of time) in a Bentheimer sandstone (top) and in a Ketton carbonate (bottom) simulated with both the standard Pollock algorithm (dashed line) and our modified version of the algorithm (solid line). Using our method we have longer tails and smaller exponents ($\alpha = 1 + \beta$) for the power law describing the late time behaviour. Under the CTRW approach, the standard Pollock simulation predicts Fickian behaviour ($\beta > 2$) for the Bentheimer sandstone, while our approach predicts non-Fickian behaviour ($\beta < 2$). . . 38
- 2.13 Breakthrough curves for the Ketton rock. The voxel velocity is given by a linear interpolation of the face velocities and three time-stepping methods are used: streamline (Pollock - blue), the Euler method (green) and the adaptive time-step (red). 40
- 2.14 Breakthrough curves for the Ketton rock obtained with streamline tracing (blue), the Euler method (green) and with an adaptive time-step (grey). Here the velocities are given by the bi-linear expressions satisfying the no-slip condition. 40
- 2.15 In the presence of diffusion, a time-step (Δt) is needed. When $\Delta t < \tau_e$, the particle does not change voxels and the final position $x_f(t + \Delta t), y_f(t + \Delta t)$ is obtained analytically (a). When $\Delta t > \tau_e$ (b), the advective motion is divided into successive applications of the formulas derived earlier in this chapter: the particle exits the current voxel at $x^*(t + \tau_e), y^*(t + \tau_e)$ and moves inside the next one with time-step $\Delta t - \tau_e$ 42
- 3.1 Schematics of a heterogeneous surface reaction. Following the diffusion of a reactant to the surface, the reaction occurs and the product must be diffused away. The slowest of these steps (characterized by the rate constants k_d and k_s) controls the overall kinetics – $k_d \gg k_s$ for reaction-controlled kinetics and $k_s \gg k_d$ for diffusion-controlled. In general, the diffusive time of both the reactant and the product is considered to be the same. 45
- 3.2 Dissolution behaviour diagram in terms of the nondimensional numbers Pe and $PeDa$. Depending on the flow and reaction characteristics, different patterns are formed during rock dissolution, this is described qualitatively in terms of a competition between the transport time scales, both advective and diffusive, and the reaction time scale at the solid surface [Golfier et al., 2002; Daccord et al., 1993]. 47

3.3	Particle trajectories in the pore space of a porous rock. For purely advective transport ($Pe \rightarrow \infty$), the particle does not collide with the pore walls and its path line connect the inlet to the outlet (blue line). As the Péclet number decreases, the mean free path also decreases, and the dissolution is restricted to positions close to the inlet. $Pe = 1100$, red line, $Pe = 110$, orange line and $Pe = 1$, light blue line.	47
3.4	Reaction rates are scale dependent, with field scale rates being usually several orders of magnitude lower than laboratory rates. This is due to the combined effect of different physical and chemical heterogeneities that manifest themselves at different spatial scales.	48
3.5	One end of a rod of square cross-section of area l^2 is dissolved by a fluid with constant concentration of reactants. The kinetics is reaction-controlled.	52
3.6	Evolution of the position of the rod interface with non-dimensional time – analytical results (eq. 3.11, dashed red lines) and simulation (solid grey lines). Dissolution is reaction-controlled – $Da < 1$	53
3.7	Apparatus for the experiments against which we compare our results: the core holder is kept inside the micro-CT scanner, a series of pumps are used to inject the saturated brine, control the flow and maintain the pressure. The entire experiment is conducted at at 10 MPa and 50°C, from Menke et al. [2015].	58
3.8	Top, three-dimensional segmented image of a Ketton carbonate superimposed with the velocity along the flow direction. The pore space is shown in grey. Bottom, streamlines traced using a pore-scale semi-analytical method in the pore space reconstructed from the micro-CT and coloured by vertical coordinate. Solute particles move from left to right following streamlines due to advection. Diffusion and reaction are then incorporated as shown in figure 1.12.	59
3.9	A subvolume of the Ketton carbonate (a) is used to study particle concentration gradients in the pores. We compute the flow field (b), and keep the average velocity the same as in the experiment. The conditions of flow and reaction are such that $Pe \gg 1$ and $PeDa \ll 1$: the system is strongly transport-dominated and dissolution is reaction-limited. Thus, the instantaneous particle concentration, indicated by the colour scale, is approximately uniform, in both the axial (c) and radial (d) directions.	61
3.10	Slice-averaged porosity profiles along the flow direction after fifteen minutes of injection. Results are stable upon the choice of the porosity increment that controls the frequency of the flow field updates.	62

3.11	Slice-averaged porosity profiles after fifteen minutes of reaction. The dissolution kinetics is independent of the number of particles used in the simulations.	63
3.12	Outline of the advection-diffusion-reaction algorithm.	64
3.13	Time-lapse image showing the dissolved portions of the Ketton carbonate after fifty minutes of flow and reaction with a CO ₂ -saturated brine (a). Orthogonal slices showing the dissolution (in black) – experimental (b) and simulated (c) images. Conditions of flow are such that an almost uniform dissolution occurs (b) and our simulation captures this pattern when using the same experimental conditions (c).	65
3.14	Evolution of porosity and permeability following injection of CO ₂ -enriched brine in the Ketton carbonate. The dashed blue line shows the computed permeability based on the experimentally-measured images while the red line shows the predictions from our simulations.	66
3.15	Slice-averaged porosity profiles along the direction of flow before injection (solid gray) and after seventeen (solid lines), thirty three (dashed lines) and fifty minutes (dotted lines) of injection. There is good agreement between the experimental (blue lines) and simulated (red lines) results. Our simulation method is capable of capturing in detail the variation of dissolution across the whole sample. The numbers 1 and 2 mark the position of the slices shown in figures 3.17, 3.18 and 3.20.	67
3.16	Slice-averaged relative porosity difference – top figure, experimental results in blue, simulation in red – after seventeen (solid lines), thirty three (dashed lines) and fifty minutes (dotted lines) of injection. There tends to be more dissolution in the lower porosity slices; the initial porosity is shown in the bottom figure.	68
3.17	Experimental (top row) and modelled (bottom row) results showing the dissolved portions of the rock (in black are the differences relative to the image before reaction) after seventeen, thirty three and fifty minutes of reaction. Slices are taken perpendicular to flow from a low porosity portion of the sample - position 1 in figure 3.15.	68
3.18	Similar to figure 3.17, the changes in pore structure are shown in black, but with the slices taken from a high porosity region – position 2, figure 3.15.	69
3.19	Experimental (top row) and modelled (bottom row) differences relative to the initial time after seventeen, thirty three and fifteen minutes of reaction. Slices are taken parallel to the flow through the middle of the sample.	69

3.20	Slices perpendicular to flow showing the dissolution (in black) around the grains after thirty three minutes of flow and reaction. The velocity ratio to the average velocity is superimposed. The colour scale is logarithmic, in red are the high velocities, in blue the low and zero or negligible flow in white. The top image is taken from position 1 and the bottom from position 2 from figure 3.15. Dissolution is the result of a complex interaction between the flow field and diffusion, both being influenced by the geometry of the pore space.	71
4.1	Surface of the solid grains (top row), velocity fields (bottom row) and corresponding tortuosities for the Estailades limestone (a), the Ketton oolite (b) and the pack of spheres (c). The tortuosity (T , eq. 3.22) is higher in the Estailades sample, which has the most heterogeneous flow field.	76
4.2	Velocity probability distributions – Estailades limestone (red line), Ketton oolite (blue line) and beadpack (green line). Of the three, Estailades has the widest distribution, reflecting the very heterogeneous nature of its flow field. Ketton and beadpack have broadly similar and narrower distributions. This will help explain the similarity in their sample-averaged reaction rates, section 4.3	77
4.3	Ratio of the average reaction rate (eq. 3.23) over the batch reaction rate during injection of a CO_2 -saturated brine. The average rates for the more heterogeneous rock (Estailades, in red) is lower than the rate of the relatively homogeneous ones (Ketton in blue and beadpack in green). Higher flow rates yield higher average reaction rates – $Pe = 100$, solid lines. The dashed lines are for $Pe = 10$. The early time behaviour is an artefact, and it is related to the point in time where the flow field is first updated.	79
4.4	Dissolved portions (shown in red) superimposed with the original pore space (light grey) after injecting 1000 pore volumes, starting with an initial Péclet of 100. Dissolution in the Estailades sample (a) is more channelized and restricted than in the Ketton (b) and beadpack (c) samples. This is a result of the flow field heterogeneity, see figure 4.1.	80
4.5	Time-lapse images after injecting 1000 pore volumes. Dissolution varies with the flow rate, green corresponds to $Pe = 10$ and red to $Pe = 100$. In the Estailades (a), a secondary channel develops when increasing the flow rate, while in the Ketton (b) and beadpack (c), high flow rates yield a more uniform dissolution than low flow rates.	80

- 4.6 PDFs of velocities, before (dashed lines) and after injection of 1000 pore volumes at $Pe = 100$ (solid lines). Beadpack (green) is mostly unaffected, Ketton (blue) becomes narrower with a more pronounced peak. The PDFs of the Estailades (red lines) rock show the development of high velocity channels. The velocities are normalized to the corresponding average velocity before flow and reaction. 81
- 4.7 Slice-averaged relative porosity difference *versus* distance over the characteristic length (L), after injecting 10 pore volumes in Ketton (top) and in Estailades (bottom). Dissolution penetrates further for the higher flow rates, particularly in Estailades, the more channelized rock. Flow is from left to right. Ketton is 8.2L in length and Estailades 7.9L. . . . 83
- 4.8 Dissolution fronts following the injection of 10 pore volumes under four flow rates, corresponding to $Pe = 1, 2, 5$ and 10. For low flow rates ($Pe = 1, 2$), reaction is contained close to the inlet. Increasing the injection rate ($Pe = 5, 10$), the channelized nature of flow in the Estailades focuses the reaction into high flow channels, with a greater impact on permeability. 84
- 4.9 Permeability evolution for Ketton (dashed lines) and Estailades (solid lines) following the injection of 10 pore volumes with four different flow rates, corresponding to $Pe = 1, 2, 5$ and 10. Ketton permeability is largely unaffected for the range of flow rates considered: a consequence of dissolution being concentrated at the inlet. In contrast, Estailades shows a marked increase in permeability for the higher rates: a result of fast flow channels dissolving. 85
- 4.10 Slice-averaged relative porosity difference in Ketton for different Pe . A very high rate is necessary to extend the dissolution to the outlet. . . . 86
- 4.11 Dissolution transitions from compact to uniform (channelled in Estailades) when, for a fixed and low reaction rate, the flow rate increases. In the Ketton sample, this transition happens at a much higher rate than in the Estailades sample. The blue dots represent simulation points. . . 87
- 5.1 The permeability changes in field-scale simulations are usually obtained as a function of the porosity increments given by a curve derived from cores and well logs expressing some sort of representative diagenetic trend. The initial permeability (k_0) is obtained from the initial porosity (Φ_0) – step 1. The porosity is updated via successive applications of a geochemical model – step 2, causing the permeability to be updated – step 3. This process is repeated for every grid block, for the duration of the simulation. 91

B.1	Idealized scheme illustrating the scale dependency of the REV concept. Once the correlation lengths approach the size of the system, the continuum approach, on which the REV concept rests, is no longer valid. Reproduced from Nordahl and Ringrose [2008].	94
B.2	Normalized porosity (top) and velocity (bottom) variograms for the four samples (Beadpack, Bentheimer, Estailades and Ketton) versus distance over characteristic length.	95

LIST OF TABLES

2.1	Percentage of the total pore-space and to the total flux across the samples (Bentheimer and Ketton) of the voxels with different numbers of solid neighbours.	33
3.1	Species activities in the brine used in the experiment of Menke et al. [2015]. The dominant ion is H_2CO_3^* . Modified from Menke [2016]. . .	54
3.2	List of image and simulation parameters. Quantities in bold are the input to the simulations. The remaining are derived from them together with the image geometry and the flow field.	62
3.3	Time evolution of the experimental and simulated image porosities (ϕ) and permeabilities (k). By construction the experiment and simulation agree at the beginning.	66
3.4	Image-based experimental and simulated porosity increases and the inferred average dissolution rates – r^{eff} , eq. 3.23. For each time interval the rates are derived from the increase in porosity and tomographic surface area. Compared to the batch calcite dissolution rate – $8.1 \times 10^{-4} \text{mol.m}^{-2}.\text{s}^{-1}$ [Peng et al., 2015] – the effective rates are approximately one order of magnitude smaller.	73
4.1	Summary of the samples' properties. Porosity, permeability and the characteristic length (L) are image-calculated and the hydraulic tortuosity (T , eq. 3.22) is calculated from the semi-analytical streamlines. . .	76
A.1	Summary of the properties of the samples used in this work. Porosity, permeability and characteristic length (L , eq. 2.21) are image calculated and the hydraulic tortuosity (T , eq. 3.22) is calculated from the semi-analytical streamlines.	93

LIST OF SYMBOLS

$A \text{ [m}^{-2}\text{]}$	Sample cross-sectional area.
$C \text{ [m}^{-3}\text{]}$	Solute/particle concentration.
$Da \text{ [–]}$	Damköhler number, reaction rate over transport rate.
$D_m \text{ [m}^2\text{.s}^{-1}\text{]}$	Molecular diffusion coefficient.
$k \text{ [D]}$	Permeability.
$k_d \text{ [m.s}^{-1}\text{]}$	Diffusion rate constant in a heterogeneous reaction.
$k_s \text{ [m.s}^{-1}\text{]}$	Surface rate constant in a heterogeneous reaction.
$K_{eff} \text{ [s}^{-1}\text{]}$	Effective rate coefficient.
$l \text{ [}\mu\text{m]}$	Voxel size.
$L \text{ [}\mu\text{m]}$	Characteristic length.
$L_x \text{ [m]}$	Sample length.
$n \text{ [mol.m}^{-3}\text{]}$	Molar density of the rock mineral.
$N_{hits} \text{ [–]}$	Number of particle hits to dissolve a solid voxel.
$N_{mol}^{voxel} \text{ [mol]}$	Number of mineral moles per solid voxel.
$N_p \text{ [–]}$	Number of particles in the system.
$P \text{ [Pa]}$	Pressure.
$Pe \text{ [–]}$	Péclet number, advection rate over diffusion rate.
$q \text{ [m.s}^{-1}\text{]}$	Darcy velocity, the total discharge over the cross-sectional area (Q/A).
$Q \text{ [m}^3\text{.s}^{-1}\text{]}$	The total flow rate.
$r \text{ [mol.m}^{-2}\text{.s}^{-1}\text{]}$	Intrinsic reaction rate, i.e. free of mass transfer limitations.

r^{eff} [mol.m ⁻² .s ⁻¹]	Effective, sample-averaged reaction rate.
S_A [m ²]	The total surface area between solids and pores.
T [—]	Hydraulic tortuosity.
u_{avg} [m.s ⁻¹]	Average flow velocity (q/ϕ).
V [m ³]	Sample volume (pores + solids).
$\vec{V}$ [m.s ⁻¹]	Fluid velocity.
$\vec{X}_p(t)$ [m]	Position of particle p at time t .
$\Delta\phi$ [—]	Porosity threshold for the flow field updates.
Δt [s]	Simulation time-step.
ϕ [—]	Image-calculated porosity.
ϕ_{grain} [—]	Porosity of the rock grains.
ϕ_{HP} [—]	Helium porosity.
μ [Pa.s]	Fluid viscosity.
ρ [kg.m ⁻³]	Fluid density.
$\vec{\xi}$ [—]	A vector of uniformly distributed components.
τ [—]	The dimensionless time or the time-of-flight.
$\psi(t)$ [—]	Distribution of voxel transit times.

INTRODUCTION

The study of fluid flow and transport phenomena in sedimentary rocks has a wide range of scientific and engineering applications, such as water management, contaminant transport, oil & gas recovery and geological carbon storage [Sahimi, 2011; Lake, 1996; Bear, 1988; Celia et al., 2015]. Depending on the characteristics of the fluids and rocks, the flow is classified as: single- or multiphase, reactive or non-reactive and compressible or incompressible. Each one of these has a particular domain of interest and applicability. This thesis is concerned with reactive, incompressible, single-phase flows in porous rocks at the pore scale.

The subject of fluid-rock reactions in subsurface environments can be summarized as the study of the interactions between the formation fluids and the rocks through which the fluid percolates. Depending on the specific conditions of pressure, temperature, fluid and mineral compositions, we observe rock dissolution and/or precipitation [Lasaga, 1984; Wilson and Monea, 2004; Noiriel et al., 2009]. These reactions occur over time-scales that range, typically, from a few hours (e.g. acid stimulation of oil bearing reservoirs [Fredd and Fogler, 1998]) to thousands of years (diagenesis and basin evolution [Maher et al., 2006; Al-Helal et al., 2012]). Over the last few decades, a common modelling framework started being developed to address this variety of chemical and transport phenomena, which span time and spatial scales over several orders of magnitude, as well as different reservoir and fluid types (e.g. [Lasaga, 1984; Sahimi, 2011; Steefel and Maher, 2009]). The majority of this early work focused on the macro (Darcy) scale, but with the development of experimental techniques, and improvement in computational power, there has been a recent shift in the research focus to the pore (micron) scale [Molins et al., 2012; Noiriel, 2015].

Applications in geological carbon storage (CCS) [Wright et al., 2009; Mathieson et al., 2011; Wilson and Monea, 2004; Celia et al., 2015; Szulczewski et al., 2012] and enhanced oil recovery (EOR) [Christensen et al., 2001; Pizarro and

Branco, 2012; Espie, 2005; Alvarado and Manrique, 2010] have created a surge in research focused on simulating and predicting geochemical reactions between formation fluids and host rocks triggered by the injection of CO_2 . Following injection, the CO_2 combines with the reservoir fluids forming an acidic solution that gradually reacts with alkaline minerals in the rock, particularly in carbonate reservoirs, due to the high reactivity of the calcite matrix. Petrophysical and mechanical alterations resulting from such reactions may have significant implications for the management and monitoring of these reservoirs. In addition, understanding rock dissolution is also of interest when modelling diagenetic processes [Whitaker and Smart, 2011] and matrix stimulation of oil reservoirs [Nierode and Williams, 1971; Fredd and Fogler, 1998].

The dissolution of carbonate minerals is one of the most important geochemical reactions occurring in near Earth surface conditions, be it caused by natural flows or human-induced during reservoir exploitation. Calcite is by far the most abundant carbonate mineral in deep-sea sediments and, understandably, the most studied [Morse and Arvidson, 2002]. Carbonate reservoirs hold more than 60% of the world's oil reserves [Schlumberger, 2007] and are notoriously difficult to characterize. Their abrupt facies variations give rise to drastic changes in the petrophysical and mechanical properties of the reservoir [Lucia, 2007]. This heterogeneity, when further associated with variations in the rock mineralogy caused by diagenesis, results in a challenging scenario to model from the pore- to the field-scale.

It is no novelty that acidic fluids percolating through carbonate reservoirs react with the rock, potentially leading to changes in the geometry of the pore space. In fact, this has been known for several decades [Schechter and Gidley, 1969; Nierode and Williams, 1971]. However, despite being a routinely observed phenomenon (e.g. Luquot and Gouze [2009]; Noiriél et al. [2009]; Menke et al. [2015]; Lamy-Chappuis et al. [2014]; Hoefner and Fogler [1988]; Fredd and Fogler [1998]), a predictive first-principles model describing rock dissolution is still missing, and some of the basic properties of reactive flows in porous media have yet to be understood. In particular, it is of interest to investigate the role played by the pore-space geometry in reducing the average reaction rates compared to measurements in batch reactors with no mass transfer limitations.

Current academic and commercial software to simulate reactive transport at the field scale do not provide a rigorous way of relating the “macro reactivity” to laboratory reaction rates and assume that permeability variations follow an exponential law as a function of porosity initially set by the user, see Steefel et al. [2014] and references therein. This is, essentially, due to the absence of a rigorous and complete upscaling methodology that could be applied to reactive flows. Upscaling of petrophysical properties of inert flows has been a subject of intense research

activity and, compared to reactive flows, it is a well understood subject [Renard and de Marsily, 1997]. Recently, with the development of dedicated pore-scale experimental and modelling techniques, more attention has been dedicated to the problem of upscaling reaction rates, from the pore to the macro scales [Lichtner and Kang, 2007; Noiriél et al., 2012; Porta et al., 2013]. Moreover, the combined effect of all the relevant physical, chemical and geological heterogeneities is intrinsically present in reservoir scale observations. Hence, this is not the most suitable spatial scale to validate and calibrate reactive transport models, as it is currently impossible to interpret field observations in terms of the manifestations of all relevant heterogeneities across different scales. In contrast, thanks to recent advances in image acquisition and processing, real time pore-scale imaging during controlled flow and reaction experiments is now possible, e.g. Andrew et al. [2014b]; Menke et al. [2015]. Consequently, modelling reactive transport directly on micro-CT images is a clear improvement in comparison with macro-models constructed from spatially and temporally scarce field-scale observations, and this is the approach to be pursued in this work.

1.1 Pore-scale imaging

With the recent improvements in the quality of X-ray microtomographic imaging, high resolution images (here called micro-CT images) of porous materials have been made widely available. X-ray tomography is a non-destructive technique where X-rays are detected after passing through the object to be imaged. The compact size and cost of standard micro-CT systems make them available to most universities and industries. Additionally X-rays from synchrotron¹ light sources offer higher resolutions and smaller acquisition times, and can be used to image fluid phenomena occurring at very short time scales.

X-rays are sensitive to the elements forming the imaged object; different elements absorb more energy of the X-rays than others, denser materials, with a higher atomic number, generally absorbing more. Specially designed detectors are engineered to detect a range of variation in the attenuation coefficients, composing a radiograph (a 2D projection of the X-rays onto the detector) of the desired object. The imaged object is slowly rotated during acquisition and several radiographs are then obtained; these are later combined to form a three-dimensional image. Micro-CT images have voxel² sizes of a few microns and are a very convenient way of obtaining detailed descriptions of the geometry of the pores of sedimentary rocks. See Wildenschild and Sheppard [2013] for a comprehensive review.

¹Synchrotron radiation/light is emitted by charged particles following curved trajectories. When filtered to the adequate wavelength, they generate a very powerful X-ray beam.

²Voxels are the volume elements of three-dimensional images

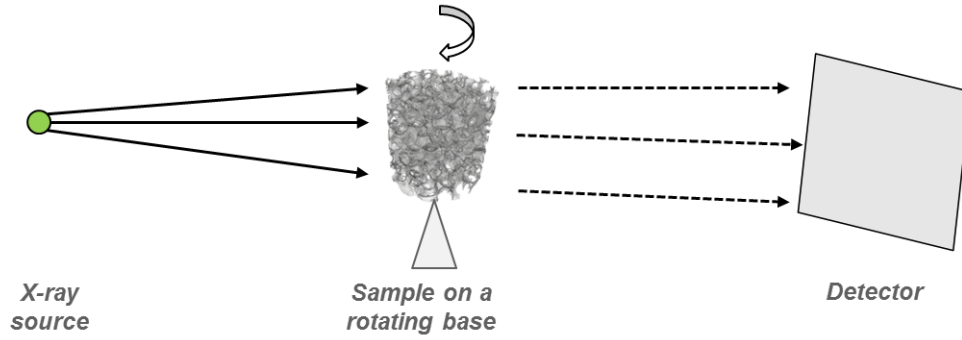


Figure 1.1: Schematics of a typical micro-CT system. A source emits X-rays, which penetrate a rock sample. A 3D image is reconstructed from the attenuated rays.

The application of X-ray tomography to the characterization of porous rocks was pioneered by Flannery et al. [1987], who used both a micro-CT and a synchrotron light source to generate three-dimensional images of coals and sandstones. Since then, both the quality of the images and the processing techniques increased considerably, to the point where it is now possible to visualize multiphase fluid distributions at reservoir conditions, figure 1.2. Three-dimensional tomographies are now routinely used to characterize and model petrophysical properties in sedimentary rocks. Image processing techniques have been developed to map the continuum values of the attenuation coefficients onto a set of discrete values (this is called "segmentation"), representing the different materials and elements forming the imaged sample, figure 1.3. Subsequently, a myriad of petrophysical properties can be simulated directly on these segmented images. Several studies of flow and transport [Blunt et al., 2013], as well as electric and elastic properties [Saenger, 2008; Arns et al., 2002], have been performed in a wide range of rocks, from relatively homogeneous sandstones to heterogeneous carbonates [Bijeljic et al., 2011]. In short, the availability of high resolution tomographic images of rock samples makes it possible to study in detail fluid and rock phenomena at the pore scale. Moreover, it creates an impetus for the development and adaptation of traditional fluid simulation techniques to this new context.

In this thesis, micro-CT images of three porous rocks (one sandstone and two limestones) and one artificial pack of spheres, appendix A, will be used to study transport and reaction phenomena. In particular, images acquired during a reactive transport experiment performed at high pressure and temperature conditions [Menke et al., 2015] are used to present and validate a pore-scale particle tracking algorithm that simulates carbonate dissolution by CO_2 -saturated fluids from first principles.

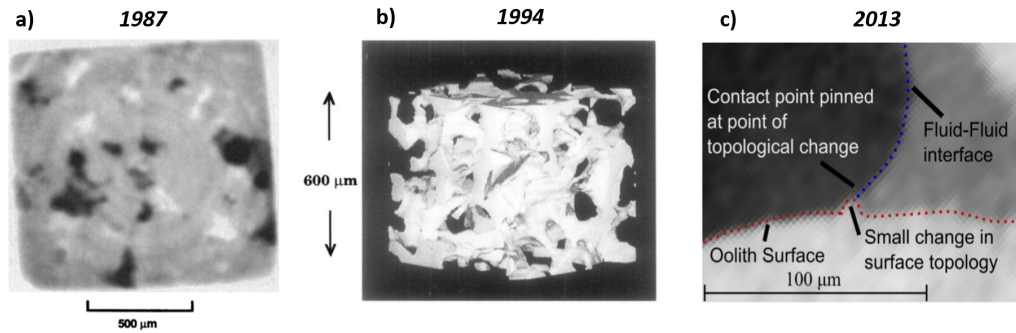


Figure 1.2: Evolution of image quality during the past decades. (a) A Coconino sandstone acquired with synchrotron light [Flannery et al., 1987]; (b) The pore-space of a Fontainebleau sandstone [Spanne et al., 1994]; (c) Contact surfaces between fluid phases and a carbonate grain at reservoir conditions [Andrew et al., 2014a].

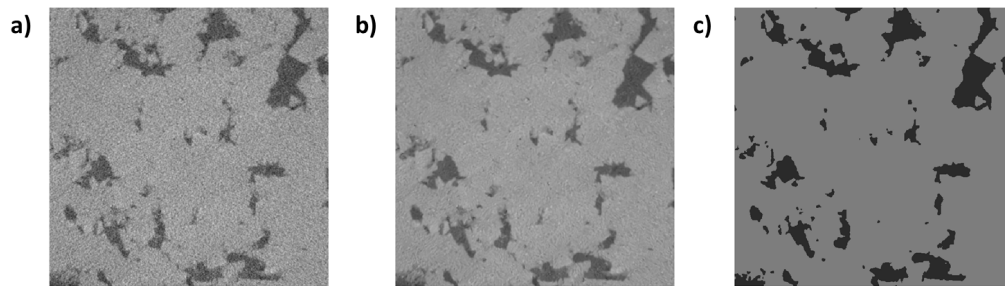


Figure 1.3: A slice of a raw tomography of a Silurian dolomite (a); the same slice after filtering (b) and segmentation (c). The segmented image has two phases: solids (grey) and pores (black). Courtesy of Yousef Al-Khulaifi.

1.2 Geochemical reactions in carbonate rocks subjected to CO₂ injection

1.2.1 Summary of core-scale experimental results

A number of experimental studies have investigated the variation of petrophysical properties caused by the flow of CO₂-saturated fluids in carbonate rocks. Luquot and Gouze [2009] studied porosity and permeability changes under different flow rates in calcitic limestone reservoir samples and found that the magnitude and distribution of the petrophysical changes are strongly dependent on the transport and reaction regimes. Vialle et al. [2014] described how hydraulic, electrical and structural properties of a carbonate sample evolve under slow flow conditions and used X-ray tomography to characterize the changes in rock structure after the flow experiment. By subtracting images acquired at different times, they were able to image wormhole formation in the Estailades carbonate (figure 1.4), which is a heterogen-

eous bioclastic limestone, see also chapter 4 and appendix A. In another example of the use of X-ray tomography, Gharbi et al. [2013] observed wormhole formation and increases in pore connectivity following the injection of CO_2 -saturated brine in heterogeneous carbonate samples at *in situ* conditions. Noiriél et al. [2009] addressed the relationship between reactive surface area, measured from micro-CT images, and porosity following limestone dissolution. Studying dissolution in a calcareous sandstone, Lamy-Chappuis et al. [2014] reported evidence that relatively small increases in porosity could precipitate steep changes in permeability.

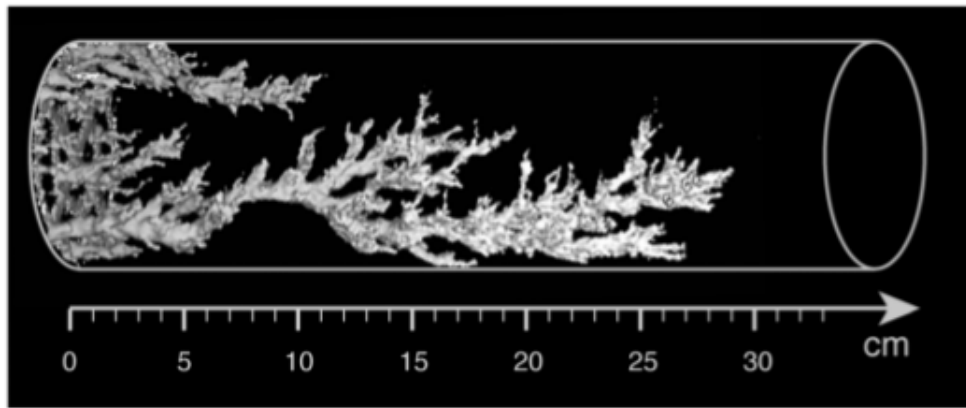


Figure 1.4: Time-lapse, three-dimensional micro-CT image of a ramified wormhole formed during the dissolution of a bioclastic limestone by a CO_2 -saturated fluid. From Vialle et al. [2014].

Even in homogeneous rocks the reaction-induced increase in porosity can be non-uniform and different dissolution patterns (e.g. wormholes, face and uniform dissolution) may emerge according to the specifics of the flow and reaction regimes, as discussed in Daccord et al. [1993], Golfier et al. [2002] and Luquot and Gouze [2009], for example. An early example of this phenomenon was shown by Fredd and Fogler [1998], who studied wormhole formation in limestones during acidic stimulation, figure 1.5.

In a recent application of synchrotron tomography, Menke et al. [2016] explored the effect of the initial pore geometry on the dissolution patterns and average reaction rates in millimetre-scale rocks. They showed that, under specific conditions of high flow and slow reactions, the pore structure of heterogeneous rocks may develop into a channelized pattern, distinct from wormholes, figure 1.6.

The influence of the flow rate on the dissolution of fractures in limestones was investigated by Garcia-Rios et al. [2015]. The sample-averaged reaction rate increases following the increase of the flow rate and this is interpreted as the kinetics being transport-controlled at the sample scale. Also, the dissolution pattern transitions from face (compact) to wormhole to uniform as the flow rate increases and

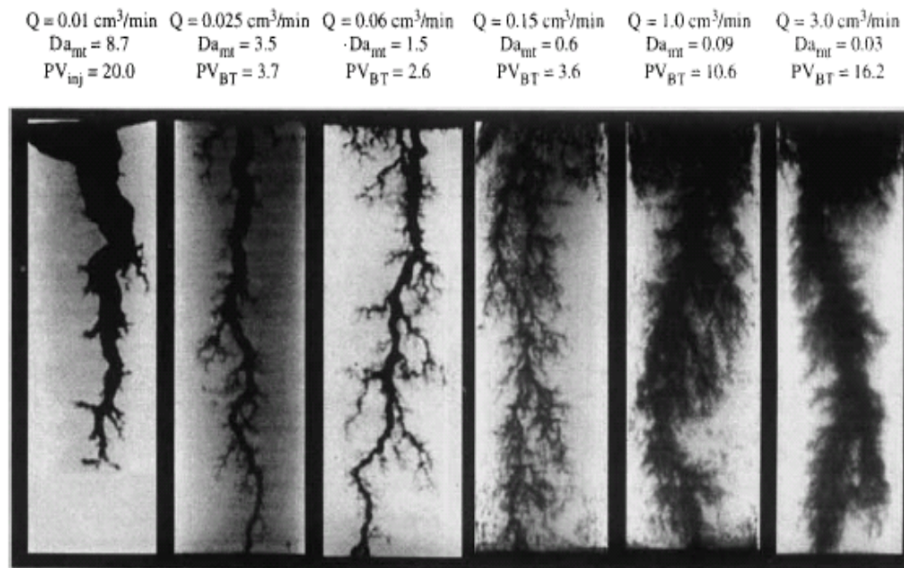


Figure 1.5: Neutron radiographs illustrating the influence of the flow and reaction regime on the wormholing pattern limestone samples of 10 cm in length. From Fredd and Fogler [1998].

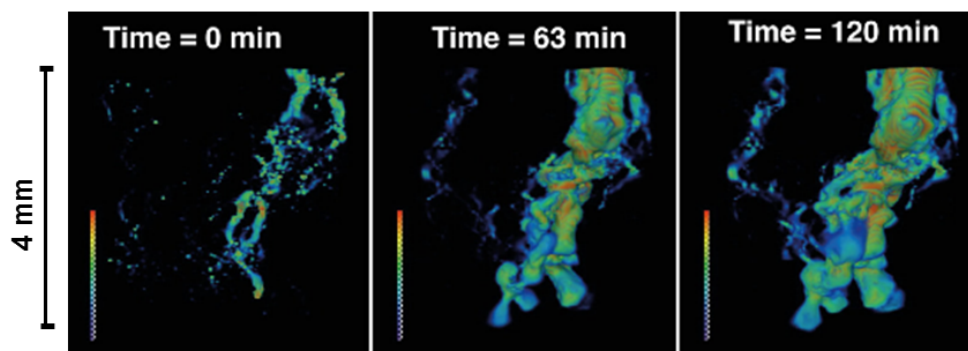


Figure 1.6: Evolution of the flow field of a bioclastic limestone during the high flow rate injection of a CO_2 -saturated brine at reservoir conditions. Modified from Menke et al. [2016].

the permeability behaviour is highly dependent on it. These results are consistent with those of Detwiler et al. [2003], measuring fracture the evolution of the aperture with light transmission techniques, figure 1.7

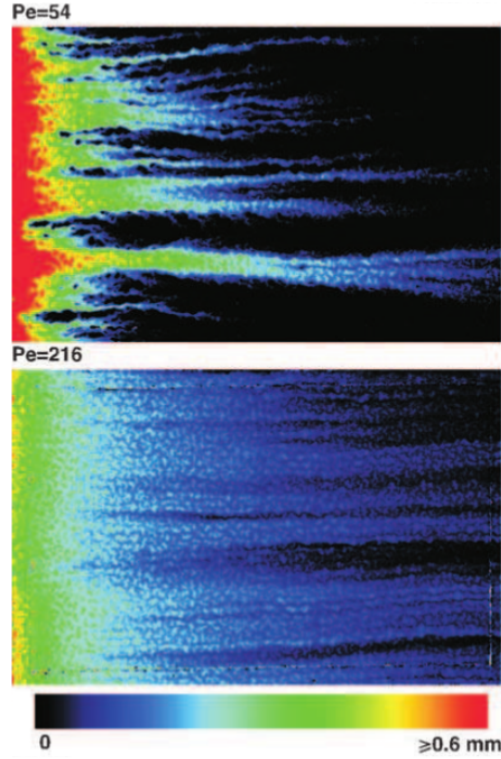


Figure 1.7: Increase in fracture aperture for experiments with $Pe = 54$ and $Pe = 216$. Dissolution is more uniform for the higher Pe . Reproduced from Detwiler et al. [2003].

Dissolution of the rock matrix is not the only by-product of acidic flows in a porous rock. Important structural changes, involving solid movement and loss of mechanical integrity, may also occur. Some examples are shown by Qajar et al. [2013], who reported fines migration following carbonate dissolution (figure 1.8) and by Vialle et al. [2014], who discussed how seismic velocities are impacted by matrix dissolution. Such phenomena are extremely complex to model and may have significant impacts for field management.

1.2.2 A field-scale example: the Weyburn project

As a direct consequence of the increase in CO_2 -rich gas injection for both CCS and EOR, the oil industry and academia have started to explore the possible implications of rock-fluid interactions for reservoir-scale development projects.

Rock-fluid reactions are phenomena occurring inherently at the pore scale. However, they may have macro (m or km) scale manifestations, which have considerable repercussions for reservoir monitoring and modelling. To exemplify this point we

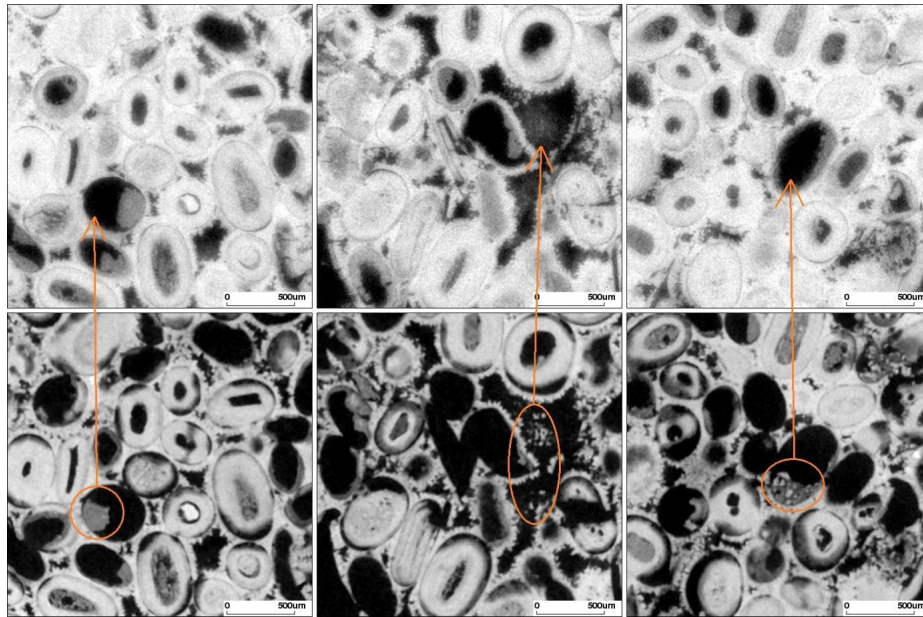


Figure 1.8: Fines migration in a oolitic limestone after reactive flow. Pre (top) and post (bottom) images from micro-CT, from Qajar et al. [2013].

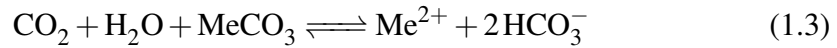
present a brief description of the Weyburn project, which is perhaps the most widely studied field-scale carbonate CO_2 injection project to date.

Together with Statoil's Sleipner (Norway) and BP's In Salah (Algeria), the Weyburn project (EnCana, Canada) is one of the largest and most successful field-scale CO_2 -injection operations in the world [Wright et al., 2009; Mathieson et al., 2011; Wilson and Monea, 2004]. These pioneering projects, operated by major oil companies and researched in close cooperation with the academia, are intended to test and develop best practices for future application in commercial projects. The Weyburn field is a particularly relevant example because it is the longest-running and biggest field-scale project injecting CO_2 into a carbonate reservoir.

Full scale CO_2 flooding in the Weyburn field was initiated in the year 2000 by EnCana. After eight years, the total cumulative amount of CO_2 stored was over 12 million tonnes. Injection was done in two main carbonate units, a lower limestone layer, the Vuggy, and an upper dolostone layer, the Marly. Injection was monitored using a suite of geochemical and geophysical technologies, the most important being the geochemical analysis of the produced fluids and time-lapse seismic. Particularly interesting and informative is the joint comparison of both techniques.

Neglecting the presence of impurities (non-carbonate minerals), the key chemical reactions occurring between a carbonate rock (typically comprised of a mixture of calcite and dolomite) and the reservoir brine following the injection of CO_2 can

be summarized as:



where Me = Ca, Mg. The geochemical monitoring consisted of regular sampling and analysis of the produced fluids. Examining figure 1.9 it is straightforward to notice that these three main geochemical processes took place in the first three years of injection [Wilson and Monea, 2004]: 1) CO₂ dissolution within the reservoir brine (eq. 1.1), causing a decrease in pH; 2) The resultant acidic fluid reacts with the carbonate matrix, inducing mineral dissolution (eq. 1.2) and an increase in alkalinity; 3) The mineral dissolution causes an increase in the amount of dissolved solids in the produced reservoir brine (e.g. the change in Ca²⁺ and Mg²⁺ concentrations). A map of the change in Ca²⁺ production was generated interpolating the sampling data points, figure 1.10.

	Pre-injection		930 days of Injection		
	Mean	Standard Deviation	Mean	Standard Deviation	%Change
pH	6.7	0.2	6.7	0.3	-1
Total Alkalinity (mg/L)	429	104	1094	375	155
Ca (mg/L)	1372	186	1913	298	39
Mg (mg/L)	374	27	597	69	60
Resistivity (ohm m)	0.149	0.023	0.104	0.014	-43
δ ¹³ C _{HCO3}	-2.8	2.7	-5.7	4.7	N/A
Cl (mg/L)	38440	7930	39530	7410	3
SO ₄ (mg/L)	3465	207	3596	252	4

Figure 1.9: Geochemical parameters obtained from produced fluids before injection and following 930 days of CO₂ injection in the Weyburn field, excerpt from Wilson and Monea [2004].

Time-lapse seismic monitoring (also known as 4D Seismic) is based on the comparison of repeated seismic acquisitions over the same area of interest. Given that field production induces changes in the reservoir rocks (e.g. saturations, pressures) and/or in the caprock (mainly geomechanical effects) and that these changes usually produce variations in the seismic wave velocities, the subtraction of the seismic surveys gives an estimate of the spatial distribution of these production related changes. More specifically, the injection of a low (high) density fluid in the reservoir causes a decrease (increase) in the compressional seismic velocity and an associated change in the top of reservoir reflectivity. This change in reflectivity can then be mapped and enhanced using specially designed seismic processing tools. Figure 1.11 shows a very clear example of the 4D seismic signatures obtained in the Weyburn field

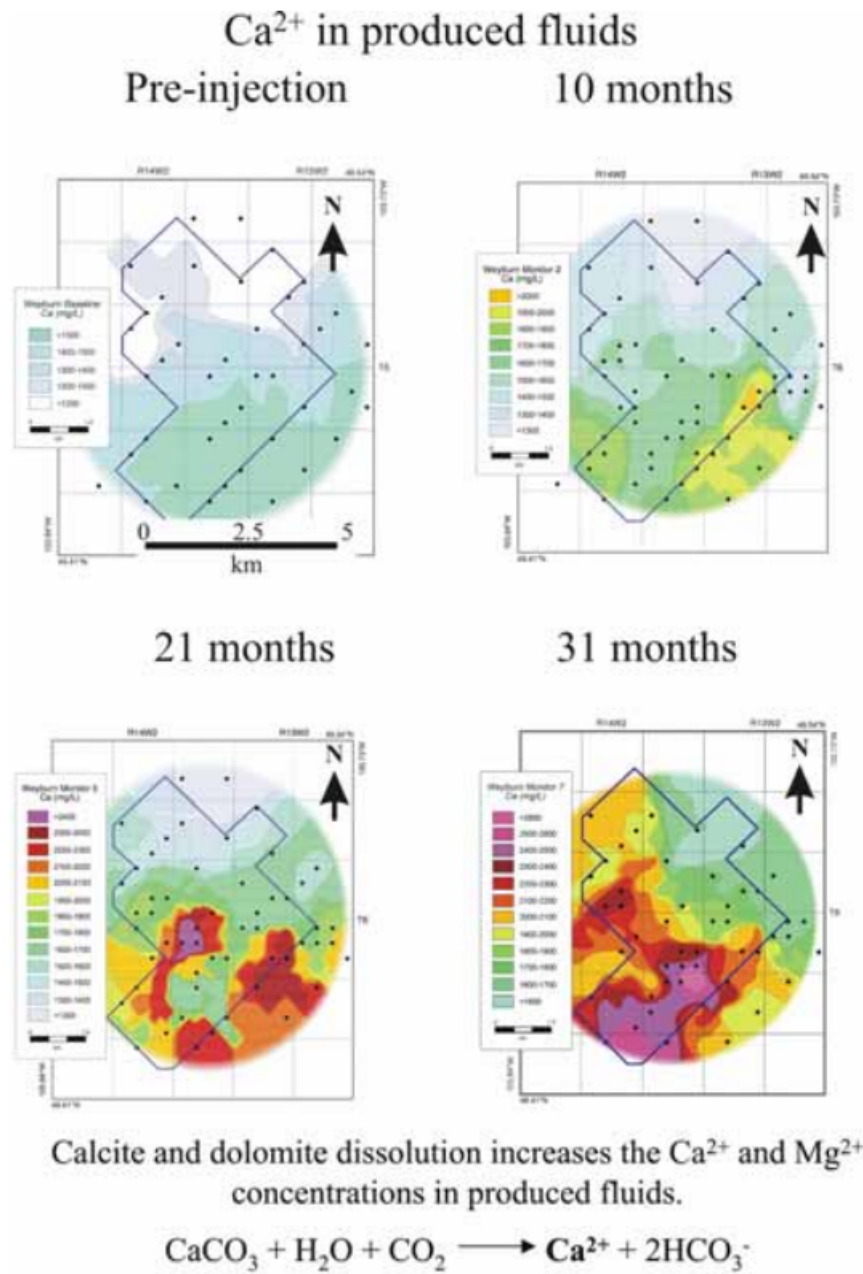


Figure 1.10: Temporal evolution of the concentration of Ca²⁺ in the produced fluids in the Weyburn field, Wilson and Monea [2004].

after CO₂ injection. It is interesting to note that regions where the seismic anomalies are higher coincide with the regions where the amount of produced Ca²⁺ is maximum. Knowing that carbonate reservoirs are not particularly prone to seismic monitoring due to its low rock compressibility (calcite and dolomite are very stiff minerals), can lead us to the speculation that the increase in CO₂ saturation is not the sole factor causing these huge seismic anomalies. Perhaps they could be amplified by the rock dissolution observed in the geochemical monitoring.

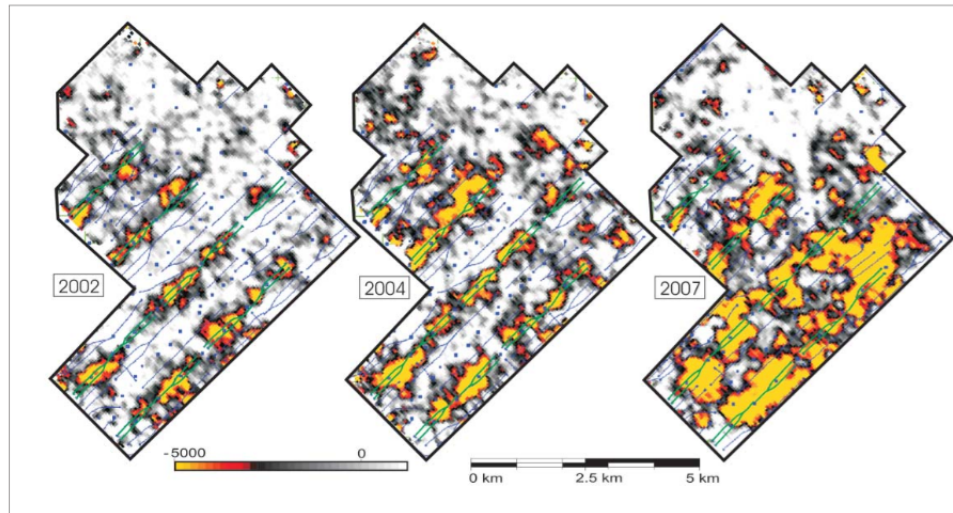


Figure 1.11: 4D seismic anomalies for the Weyburn field. Negative differences (yellow) show regions of high CO₂ saturation, from White [2009]. Compare with the regions of high calcite and dolomite production in figure 1.10.

1.3 Pore-scale description of flow and transport

The numerical solution for the transport of (inert or reactive) solute in porous media at the pore scale involves two steps: 1) computing the velocity field in the pores by solving the Navier-Stokes equation and 2) transporting the solute concentration in this field. Solute transport is, in turn, divided into two contributions: advection and diffusion. In the Lagrangian approach, particles move along streamlines during advection and diffusion is modelled as a random motion where particles jump across streamlines, eventually crossing the pore-solid interface. Inert particles are bounced back into the pores, while reactive particles will stick in the solids. This process is shown in schematic form in figure 1.12. The reaction rate is controlled by the local flux of particles at the interfaces, as detailed later in chapter 3.

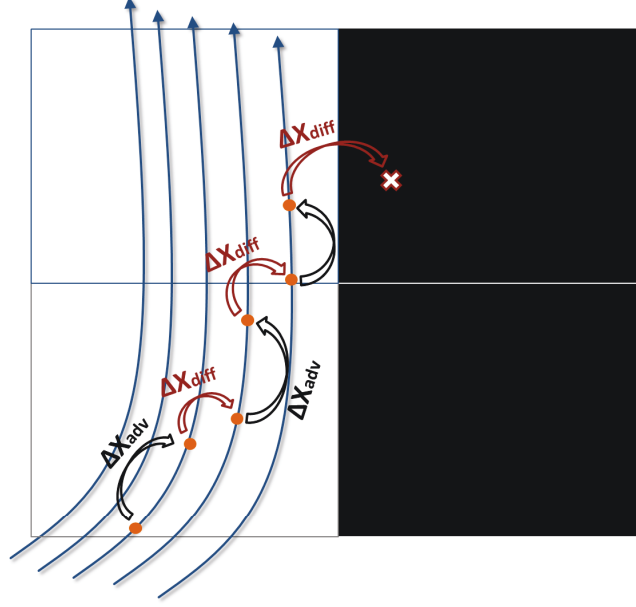


Figure 1.12: Pictorial representation of the advection-diffusion-reaction process. A particle moves along the analytically-traced streamlines during advection (black arrows), jumps from one to another during diffusion (red arrows) and crosses the pore-solid interface during reaction. The total displacement during a time-step is the sum of the advective and diffusive displacements. White cells are pores and black are solid.

1.3.1 Flow simulation in micro-CT images

Incompressible flow in a porous medium is governed by the Navier-Stokes equation:

$$\rho \left(\frac{\partial \vec{V}}{\partial t} + \vec{V} \cdot \nabla \vec{V} \right) = -\nabla P + \mu \nabla^2 \vec{V} \quad (1.4)$$

subject to the incompressibility condition $\nabla \cdot \vec{V} = 0$, where μ is the fluid viscosity, ρ the fluid density, $\vec{V}$ the velocity and P the pressure. Throughout the simulations we consider $\mu = 0.001$ Pa.s and $\rho = 1000$ kg/m³, the values for water. Finite-difference (volume) and lattice-Boltzmann are the most common methods to solve for incompressible flow at the pore scale [Manwart et al., 2002]. All the simulations done in this thesis employed the finite volume method implemented in OpenFoam (an open source library [OpenFoam, 2013]) and described by Raeini et al. [2012] and Bijeljic et al. [2013b] to solve the Navier-Stokes equation with constant pressure boundary conditions at inlet and outlet. The simulations are done directly in the pore-space of segmented micro-CT images, the simulation gridblocks are the image voxels. No-flow ($\vec{V} = 0$) at the pore-solid interfaces is imposed. The resulting velocity field is used as input to the streamline tracing algorithms (chapter 2) and to the reactive transport code, chapter 3.

The permeability (k) of a sample of length L_x and cross-sectional area A is read-

ily determined from Darcy's law:

$$k = \frac{L_x \mu Q}{A \Delta P} \quad (1.5)$$

where Q is the total flow rate calculated from the velocity field at the sample outlet and ΔP is the imposed pressure drop.

Porosity and permeability are the most common properties used to describe rocks at the core (centimetre) scale. However, to acquire pore-scale images with the current available micro-CT equipment, the samples must be of the order of a few millimetres. Thus, it is important to check that their volume is larger than the representative elementary volume (REV). This is discussed in appendix B.

1.3.2 Lagrangian approach for solute transport

In a broad sense, there are two approaches to describe flow and transport in fluids: the Eulerian and the Lagrangian. In the Eulerian approach the flow field and concentrations are specified at fixed positions in space, while in the Lagrangian approach, the fluid and concentrations are followed while moving through space and time. This thesis makes use of a hybrid scheme, where particles (representing inert tracers or reacting chemical species) have their movement described in Lagrangian terms within an Eulerian background, namely the flow field obtained by solving the Navier-Stokes equations.

In the Eulerian approach, the evolution of the solute concentration (C) in a time-independent and incompressible velocity field is governed by the advection-diffusion equation, which is typically solved in a fixed grid using a finite-difference (volume) approach [Datta-Gupta and King, 2007; Lasaga, 1998; Sahimi, 2011]:

$$\frac{\partial C}{\partial t} + \vec{V} \cdot \nabla C = D_m \nabla^2 C \quad (1.6)$$

In this way, concentrations are intrinsically associated with the spatial grid elements. The main difficulty encountered when employing an Eulerian approach is the numerical solution of advection-dominated flows.

The relative strength of advection over diffusion is conveniently represented by the Péclet number:

$$Pe = \frac{t_{diff}}{t_{adv}} \quad (1.7)$$

where t_{diff} and t_{adv} are the timescales of advection and diffusion defined over the same characteristic length. Most finite-difference/volume methods suffer from numerical dispersion when the Péclet number is high. The stability requirement for explicit methods is $Pe_{grid} < 2$ [Versteeg and Malalasekera, 2007], where:

$$Pe_{grid} = \frac{V_{max} \Delta x}{D_m} \quad (1.8)$$

is the grid Péclet number, V_{max} is the maximum flow velocity and Δx the grid spacing. As the ratio V_{max}/D_m increases, smaller grid sizes are needed to stabilize the solution. Depending on the size of the problem at hand this may come at very high computational costs.

In the Lagrangian approach, instead of solving the transport equation for the concentration (eq. 1.6), stochastic particle trajectories are tracked³. The proposal of explaining an observed macroscopic behaviour (described by some sort of PDE) in terms of an underlying particle-based stochastic model goes back to, at least, Einstein, who derived the diffusion equation from a model of molecular random motion [Einstein, 1906]. Since then, this route has been validated and extended to treat a multitude of physical and chemical phenomena, see, for instance, Gardiner [2004], Van Kampen [2011] and references therein. The solute concentration is recovered by calculating the average number of particles in a reference volume at a given time. Unlike Eulerian methods, Lagrangian methods do not suffer from numerical dispersion, are easily parallelizable, and, for advection-dominated problems, deliver a far superior computational performance [Batycky et al., 1997; Datta-Gupta and King, 2007].

Each particle follows a Brownian motion where its displacements, after a time-step (Δt), are given by the sum of two terms, an advective displacement and a (random) diffusive displacement:

$$\Delta \vec{X}_p = \Delta \vec{X}_p^{adv}(\vec{V}, \Delta t) + \Delta \vec{X}_p^{diff} \quad (1.9)$$

where $\Delta \vec{X}_p = \vec{X}_p(t + \Delta t) - \vec{X}_p(t)$ and $\vec{X}_p(t)$ is the position of a particle p at a time t . A convenient way of writing the displacements is given by the Ito-Taylor scheme:

$$\vec{X}_p(t + \Delta t) = \vec{X}_p(t) + \vec{V}(\vec{X}_p(t))\Delta t + \sqrt{2D_m\Delta t}\vec{Z}(t) \quad (1.10)$$

where $\vec{Z}(t)$ is a vector of normally distributed variables with zero mean and unit variance. The formal connection between both approaches is well known. In the limit of a very large number of particles, solving eq. 1.10 is equivalent to solving a Fokker-Planck equation for the probability distribution of the particle positions, which is then interpreted as the concentration. This is discussed in detail in Gardiner [2004], Kinzelbach [1988] or Tompson and Gelhar [1990], for example.

Advection

The advective term depends on the local velocity and the time-step and is sometimes calculated with an Euler approximation: $\Delta \vec{X}_p^{adv} = \vec{V}(\vec{X})\Delta t$, which requires that

³Lagrangian simulation methods are commonly referred to as "particle tracking methods" and we use both terms interchangeably.

the time-step is made very small, particularly in regions of high velocity [Tompson and Gelhar, 1990; Sàlles et al., 1993; Békri et al., 1995]. This limitation can be overcome using semi-analytical tracing methods, such as the Pollock algorithm.

A modified Pollock method to trace streamlines is presented in chapter 2. This is a semi-analytical approach that imposes the non-slip boundary condition at the pore-solid walls and avoids numerical stability issues inherent in conventional time-stepping methods, thus allowing the time-step to be constrained by diffusion only. Once the solution for the velocity field is obtained (eq. 1.4), streamlines are traced through the image voxels and solute particles are transported along them.

Diffusion

The diffusive term in eq. 1.9 is responsible for simulating particle jumps across streamlines and it is modelled with a random walk method. At every time-step the diffusive displacement is calculated using the transformed random variable of mean zero and variance $2D_m\Delta t$ [Benson and Meerschaert, 2008]:

$$\Delta\vec{X}_p^{diff} = \lambda \left(\vec{\xi} - \frac{\vec{1}}{2} \right) \quad (1.11)$$

where

$$\lambda = \sqrt{24D_m\Delta t} \quad (1.12)$$

and $\vec{\xi}$ is a random vector whose components are uniformly distributed between 0 and 1. The resulting random process has a three-dimensional mean-free path of $\sqrt{6D_m\Delta t}$, where D_m is the diffusion coefficient and Δt is the simulation time-step. For the simulations (chapters 3 and 4), the time-step is fixed such that the maximum diffusive jump in each direction is equal to half of the voxel size.

1.4 Modelling mineral dissolution in porous rocks

From the modelling perspective, dissolution dynamics has been studied on a range of spatial scales using several different approaches. These include: the numerical solution of the advection-dispersion-reaction (ADR) equation using finite difference/volume methods [Panga et al., 2005; Molins et al., 2012; Maheshwari et al., 2013]; the lattice-Boltzmann method [Kang et al., 2007]; the smoothed particle hydrodynamics (SPH) approach [Tartakovsky et al., 2007]; or pore-network modelling [Hoefner and Fogler, 1988; Budek and Szymczak, 2012; Algive et al., 2010].

In realistic porous media, the transitions from one particular dissolution pattern to another are difficult to predict on a purely theoretical basis [Daccord et al., 1993] and are commonly investigated by numerical means. Special attention has been devoted to the problem of reproducing computationally the dissolution patterns arising

during dissolution under different flow and reaction regimes, section 1.2.1. This has been achieved successfully at the Darcy-scale by solving numerically the ADR equation with a continuum model [Maheshwari et al., 2013; Golfier et al., 2002], figure 1.13, and in random networks representing core-scale experiments of channel formation, figure 1.14. Similar results using a particle approach combined with lattice-Boltzmann were shown by Szymczak and Ladd [2004], studying dissolution in millimetre-scale fractures. Despite the appealing empirical qualitative match, most of these methods suffer from the lack of a solid link between laboratory measured reaction rates and sample-averaged rates. Also, their quantitative predictions are difficult to evaluate.

Fundamentally, there are two modelling approaches for simulating reactions at the pore scale in image-based models: direct simulation, *i.e.*, the image voxels are the simulation domain, and pore-network models, when the simulations are performed on a network extracted from the segmented images.

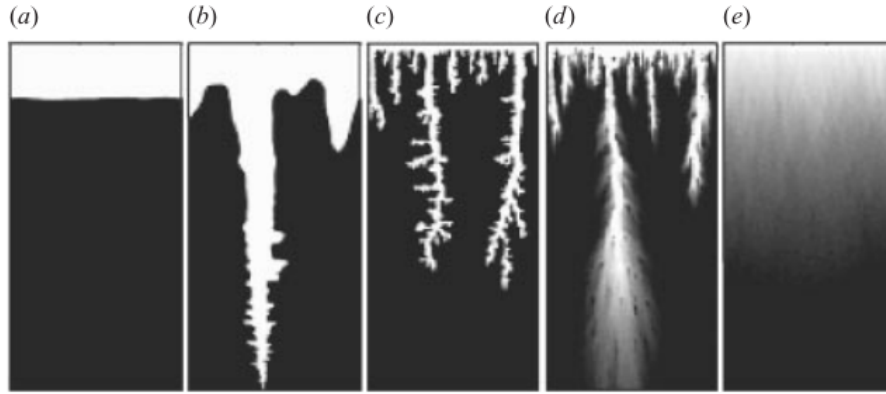


Figure 1.13: Dissolution structures obtained from two-dimensional Darcy-scale simulations for a range of Pe and Da numbers. (a) Face dissolution, (b) conical wormhole, (c) dominant wormhole, (d) ramified wormhole and (e) uniform dissolution. From Golfier et al. [2002].

1.4.1 Pore-network models

In the network approach, the pore-space is described in terms of two elements: nodes and bonds. The connectivity is regulated by the resistance to flow associated with the bonds. Earlier implementations employed random networks with a fixed coordination number and bond diameters drawn from an arbitrary probability distribution that matched empirical data [Hoefner and Fogler, 1988]. With the advent of high-resolution imaging, topologically equivalent networks can now be extracted directly from micro-CT images to simulate flow and transport [Blunt et al., 2013]. Again, the pore-space is represented by two classes of elements: pores and throats, which are described by basic shapes (cylindrical, triangular etc.). In the context of

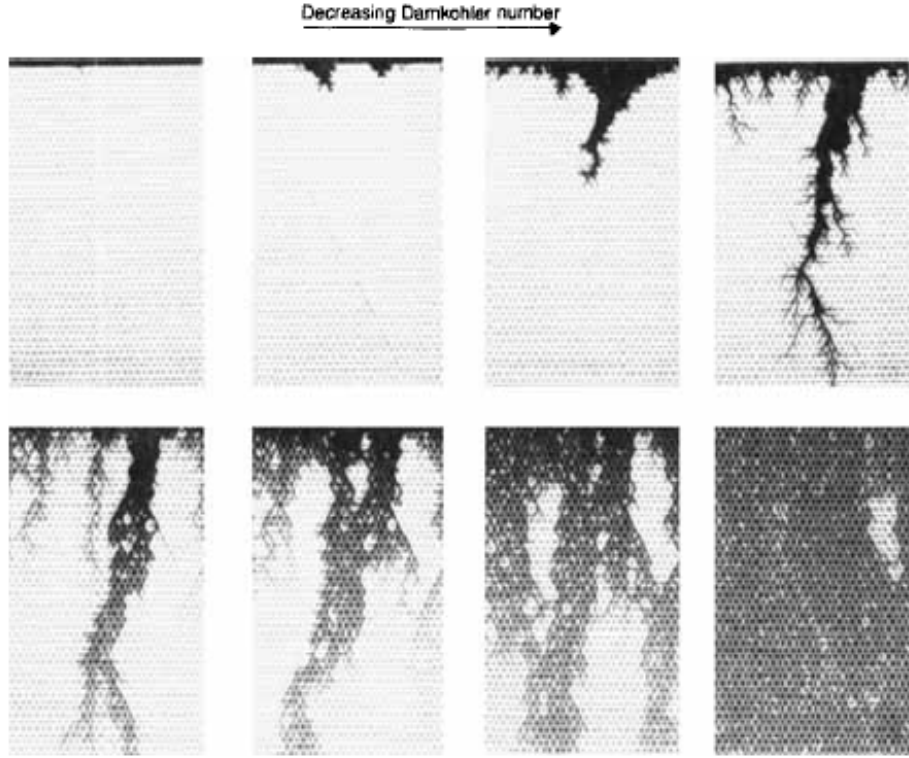


Figure 1.14: Emergence of channeling in two-dimensional networks following transport-limited dissolution. Reproduced from Hoefner and Fogler [1988].

reactive flows, fluid mixing occurs at the pores, while dissolution occurs at the throat walls, increasing the radius, and hence the conductivity. The simplified geometry of the pores and throats reduces the complexity of the problem and allows the reactive transport in such idealized geometries to be tackled analytically [Varloteaux et al., 2013].

Network models predict qualitatively correct dissolution patterns [Budek and Szymczak, 2012; Hoefner and Fogler, 1988] and are an efficient alternative for simulating large systems. They have the advantage of capturing the critical pore-space characteristics (e.g. connectivity, tortuosity) while keeping the geometric features simple. However, this may lead to oversimplification and misrepresentation of the reactive surface areas, of the flow paths, and of the general physics of the problem. There is also an inherent ambiguity in the construction of the network; the same original image may be represented by distinct networks, depending on the algorithm used [Bondino et al., 2013]. Moreover, dissolution causes a change in the network connectivity and its components, hence in the overall network topology. A key weakness of the pore-network approach is its incapacity of consistently updating the network upon dissolution.

1.4.2 Direct simulation: Eulerian approach

Pore-scale direct simulations are performed on grids directly constructed from segmented images of porous rocks, so as to reproduce the geometric details of the pore-space geometry in the best possible way. The flow field is computed by solving the Navier-Stokes equations according to the imposed boundary conditions (no-flow at the pore walls, fixed pressure drop etc.). This is usually done with a finite volume or difference method. Next, the ADR equation is solved in conjunction with a geochemical model that describes the reactions occurring between the mineral and fluid species [Molins et al., 2012, 2014]. From the implementation perspective, this approach has the advantage of using pre-existent multi-purpose computational libraries developed in the past decades for computational fluid dynamics. Another advantage of the direct method is the ability to account for changes in the pore-structure naturally; once the geometry changes, the flow field is updated. Furthermore, this approach is also the most suitable to treat systems described by multicomponent kinetics with complex speciation, in which case, one transport equation must be solved for each species. This scenario is very difficult to tackle in the particle approach, both from the conceptual and the practical point of view. However, there are two points that should be taken into consideration when using the Eulerian approach. The first is the stability issues arising from the numerical solution of the ADR equation in strongly advective flows [Versteeg and Malalasekera, 2007], and the second is the numerical efficiency when modelling systems with complex kinetics in large pore-systems with complicated boundary conditions.

1.4.3 Direct simulation: The particle approach

At the pore scale, another alternative to model rock-fluid interactions is to work within a Lagrangian framework adopting a hybrid continuum-particle approach, in which reactants are represented by particles moving in an Eulerian flow field. The advantages are an improved computational performance, the absence of numerical instabilities associated with solving the ADR equation directly, and straightforward coding. The main drawbacks are the numerical difficulty in dealing with multispecies reactions and the need to map particles to concentrations before applying available geochemical solvers. This last step requires a large number of particles to be tracked, thus sharply decreasing the efficiency of the codes.

Some of the earliest results were obtained by Sallès et al. [1993] and Békri et al. [1995], who used a finite-difference method to solve for Stokes flow combined with a random walk method to move particles, simulating dissolution and deposition in three-dimensional synthetic rocks. Békri et al. [1995] distinguished the three main flow and reaction regimes: reaction-, diffusion- and advection-controlled. They

also noticed that dissolution was concentrated along the main flow paths in the advection-controlled regime. However, they did not compute an average effective reaction rate. Sadhukhan et al. [2012] solved the Navier-Stokes equation with a finite-difference method in a two-dimensional stochastically generated medium. They related the solute concentration to the porosity increase and showed qualitative agreement with experimental results. In the framework of continuous time random walks (CTRW), Edery et al. [2011] applied a particle tracking method to simulate dedolomitization and carbonate precipitation in synthetic two-dimensional systems.

Particle-tracking methods have also been widely used to simulate homogeneous reactions in porous media, illustrating the effect of pore-space heterogeneity on the mixing of reactants and how it affects the average reaction rate, e.g. Benson and Meerschaert [2008], Edery et al. [2009], Paster et al. [2013], Ding et al. [2013], Hansen et al. [2014] and Alhashmi et al. [2015]. Paster et al. [2013] demonstrated that the particle method introduced earlier by Benson and Meerschaert [2008] recovers the diffusion-reaction equation when the time steps are infinitesimally small. Using the same method, Ding et al. [2013] reported a decrease of up to 40% in the overall rate of homogeneous reactions in idealized column experiments, attributed to incomplete solute mixing at the pore-scale. Also studying the effect of incomplete mixing on average rates, Alhashmi et al. [2015] developed a first-principles model in which particles within a diffusive distance may with a probability of reaction that is explicitly written in terms of the batch rate. An application of CTRW theory to the same kind of systems was introduced by Edery et al. [2009], while Hansen et al. [2014] expanded this treatment to relate an effective radius, within which reaction occurs, to the intrinsic reaction rate. The implementation of particle methods to systems governed by multispecies reactions and/or high-order kinetics is not straightforward and could, potentially, inhibit the application of the method to more complex systems. However, it is worth noting that there are examples applying particle methods to study both multispecies coupled reactions obeying first-order kinetics [Henri and Fernández-García, 2014] and also homogeneous reactions described by non-linear kinetics [Tompson and Dougherty, 1992].

1.4.4 Proposed methodology: a streamline-based particle tracking model

This thesis combines and extends the modelling approaches described above into a particle-based method to simulate carbonate dissolution at the pore scale. The Navier-Stokes equation for the flow field in the pore space is solved with a finite-volume method. A streamline tracing method describes advective transport semi-analytically, while diffusion is accommodated using a random particle motion.

Mineral reaction is governed by the local particle flux at the solid surface, and this flux is analytically related to the batch reaction rate when the kinetics is reaction-controlled. In the case of calcite dissolution under CO₂-saturated brine, chemical reactions are described by the concentration of a single species, representing the deviation from the calcium equilibrium concentration. As porosity evolves, the velocity field is updated and the petrophysical properties recalculated. The simulations are done directly on the voxels of three-dimensional micro-CT images. Such approach does not require the geometric simplifications inherent in the pore network model and avoids most of the numerical stability issues that emerge when solving directly the advection-diffusion-reaction using conventional finite-differences methods.

Reactive transport will be studied under a range of flow and transport conditions, corresponding to different values of the Péclet number (eq. 1.7). The modelling results will be validated against the analytical solution for the dissolution of a planar front and using dynamic imaging data from the injection of brine-dissolved supercritical CO₂ in a carbonate sample.

1.5 Thesis Outline

This thesis is concerned with the development of a Lagrangian method to simulate mineral dissolution at the pore scale. The advective-transport of reactants uses a semi-analytical streamline tracing method designed to be used in grids extracted from micro-CT images. Dissolution is simulated with a first principles article approach. Special attention will be devoted to understand the relationship between the initial pore structure and the reduction of the sample-averaged reaction rates in comparison with intrinsic reaction rates.

Chapter 2 presents a streamline tracing algorithm based on a substantial development of the most widely used method (the Pollock algorithm) employed for macroscale (Darcy) flow, making it consistent with the pore-scale boundary conditions: no-flow at pore-solid walls. This new algorithm is used to calculate breakthrough curves and time-of-flight distributions for advection-dominated transport in two three-dimensional images of sedimentary rocks containing up to 10⁹ voxels: a sandstone and a carbonate. This approach provides a more accurate description of flow, particularly when only a few image voxels span each pore. Therefore, it is better suited to capture anomalous (non-Fickian) transport behaviour than the standard Pollock method. This method is suitable to simulate advection in a range of situations, from purely advective to reactive-diffusive transport problems.

Chapter 3 reviews the basics of heterogeneous reactions (with a focus on mineral dissolution) and presents a particle-based method to simulate carbonate dissolution

at the pore scale directly on the voxels of three-dimensional micro-CT images. The flow field is computed on the images by solving the incompressible Navier-Stokes equations and rock-fluid interaction is modelled using a three step approach – solute advection, diffusion and reaction. Advection is simulated with the streamline tracing method discussed in Chapter 2. The method is validated against a dynamic imaging experiment where a Ketton oolite is imaged during CO₂-saturated brine injection at reservoir conditions.

Chapter 4 applies the method introduced in Chapter 3 to the study of the impact of the pore-space heterogeneity and of the injection rate on the average reaction rates of heterogeneous rocks. Three rocks with an increasing degree of complexity are studied: a beadpack, an oolitic limestone and a bioclastic limestone. It is shown that the average rates decrease as the flow field heterogeneity increases and that even while maintaining the regime of quasi-uniform dissolution, the flow rate has an influence on the average dissolution rate.

Chapter 5 summarizes the results and discuss the limitations and possible extensions of the methods presented in chapters 2 and 3.

STREAMLINE TRACING IN POROUS MEDIA

This chapter presents an extension of the standard field-scale streamline tracing algorithm, the Pollock method, to the pore scale. This is necessary to make it consistent with the appropriate pore-scale boundary conditions: no flow at the pore-solid interfaces.

2.1 Introduction and definitions

Streamline tracing is a Lagrangian method where solute particles are followed along streamlines traced in the simulation domain. A streamline is a line whose tangential vector is instantaneously parallel to the velocity field at every point of the flow domain. In a steady flow field, streamlines are the solutions of:

$$\frac{d\vec{x}}{d\tau} = \vec{V}(\vec{x}) \quad (2.1)$$

where $\vec{V}(\vec{x})$ is the velocity field previously calculated on a computational grid and τ is the time-of-flight (*tof*); the time that a particle following the streamline needs to travel a given distance. The solution of the Navier-Stokes equations is a necessary input for all streamline tracing algorithms at the pore scale. At the field scale the prerequisite is the solution of the pressure equation with the assumption of a Darcy regime between adjacent grid cells, from which the velocity field is then recovered.

The Pollock algorithm [Pollock, 1988] is widely used to trace streamlines in field-scale models, where the average flow is described by Darcy's law, in both hydrocarbon reservoirs [Batycky et al., 1997; Datta-Gupta and King, 2007] and aquifers [Obi and Blunt, 2004]. It calculates the particle velocities through a linear interpolation of the (staggered) grid velocities in each coordinate direction independently. In doing so, eq. 2.1 has an analytical solution for each grid element,

these solutions are then concatenated to trace the streamlines for the entire domain. While originally developed for rectangular grids, Pollock's algorithm was later adapted for unstructured grids [Prevost et al., 2002; Matringe et al., 2006].

However, despite its broad range of applications, the Pollock method cannot be immediately applied at the pore scale. It does not obey the more strict no-slip boundary conditions – $\vec{V} = 0$ at the interfaces – necessary when simulating fluid flow and transport on segmented micro-CT images consisting of void and solid voxels. Pore-space images inevitably have to make a trade-off between resolution (having many image voxels to describe each pore) and the overall size of the system, to capture the connectivity and heterogeneity of the sample. As a result, generally only a few voxels span the smallest pores in the image. As we show later in section 2.4, the application of the Pollock algorithm, with the wrong boundary condition at the solid interface, leads to significant errors, particularly when the distance between solid boundaries is a small number of voxels.

In this chapter we propose an extension of the Pollock method where both the normal and tangential components of the interpolated velocity field are zero at the pore-solid walls, thus respecting the no-flow boundary condition. The main result is a semi-analytical streamline tracing algorithm capable of simulating transport properties directly in three-dimensional pore-space images. Mostaghimi et al. [2012] attempted to solve the same problem, but for transport simulations only calculated the velocity at a point in the pore space and then took a small time-step with this fixed velocity. Here streamlines are traced semi-analytically, allowing a very rapid and accurate prediction of advection-dominated transport.

The chapter is organised as follows: we start with a brief description of the Pollock algorithm, then we proceed explaining why and how it has to be adapted for use at the pore scale and present our methodology. We explore the differences between the original method and our improved version for flow between parallel plates, whose analytical solution is known. Next we exemplify the application of the new transport method using the geometry and velocity fields of two micro-CT images of rock samples: a carbonate and a sandstone. We show how the results of time-of-flight distributions and breakthrough curves (BTCs, concentration of solute particles *versus* time) calculated with our method differ qualitatively from the ones obtained using the standard Pollock algorithm. In particular, the BTCs have the long tails and power law like behaviour characteristic of non-Fickian transport [Haggerty et al., 2000]. The conclusion highlights the most important steps of the method and presents a comparison with more the more traditional Euler and adaptive step methods.

2.2 Streamline tracing - Pollock's algorithm

Pollock's algorithm [Pollock, 1988] is a semi-analytical approach that calculates the voxel time-of-flight (the amount of time a tracer particle takes to cross the voxel) as well as particle entry and exit positions assuming that the velocity in any point inside a grid cell is a linear interpolation of the face velocities. This method was developed for large-scale flows governed by Darcy's law. Here the focus is on a different problem: pore-scale dynamics described by the Navier-Stokes equation. Hence, we will need to adapt and extend the methodology to account for the different boundary conditions encountered.

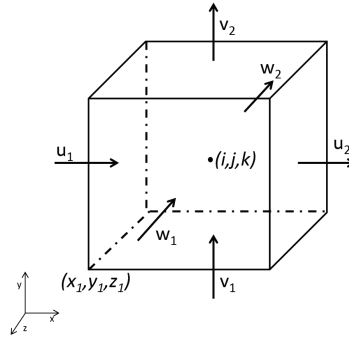


Figure 2.1: A voxel representing a solid and its velocity components. In a staggered grid the velocities are assigned to the faces of the voxels.

The computational domain is a cubic lattice where voxels assume binary values, representing a pore or a solid. The velocity field is represented in a staggered grid so that its components are located at each face of the voxel and denoted by u_1 , u_2 (faces perpendicular to the x -direction), v_1 , v_2 (perpendicular to the y -direction) and w_1 and w_2 (perpendicular to the z -direction), see figure 2.1. The velocity field at a point with coordinates (x, y, z) inside a grid block is obtained through a linear interpolation of the face velocities:

$$V_x(x, y, z) = u_1 + \frac{\Delta u}{\Delta x}(x - x_1) \quad (2.2a)$$

$$V_y(x, y, z) = v_1 + \frac{\Delta v}{\Delta y}(y - y_1) \quad (2.2b)$$

$$V_z(x, y, z) = w_1 + \frac{\Delta w}{\Delta z}(z - z_1) \quad (2.2c)$$

where x_1 , y_1 and z_1 are the coordinates of the corner voxel marked in figure 2.1, and Δx , Δy and Δz are the linear dimensions of the grid block and $\Delta u = u_2 - u_1$, $\Delta v = v_2 - v_1$ and $\Delta w = w_2 - w_1$. For a particle with initial position (x_p, y_p, z_p) and using the interpolated velocity it is possible to calculate the time required to leave

the voxel through either one of its faces:

$$\tau_x = \frac{\Delta x}{\Delta u} \ln \left[\frac{u_2 \Delta x}{u_1 \Delta x + \Delta u (x_p - x_1)} \right] \quad (2.3a)$$

$$\tau_y = \frac{\Delta y}{\Delta v} \ln \left[\frac{v_2 \Delta y}{v_1 \Delta y + \Delta v (y_p - y_1)} \right] \quad (2.3b)$$

$$\tau_z = \frac{\Delta z}{\Delta w} \ln \left[\frac{w_2 \Delta z}{w_1 \Delta z + \Delta w (z_p - z_1)} \right] \quad (2.3c)$$

and the particle will leave through the face with the smallest travel time:

$$\tau_e = \min(\tau_x, \tau_y, \tau_z) \quad (2.4)$$

The exit coordinates are obtained inverting equations 2.3:

$$x_e = x_1 - \frac{u_1 \Delta x}{\Delta u} + \left[\frac{u_1 \Delta x}{\Delta u} + (x_p - x_1) \right] \exp \left(\frac{\Delta u \tau_e}{\Delta x} \right) \quad (2.5a)$$

$$y_e = y_1 - \frac{v_1 \Delta y}{\Delta v} + \left[\frac{v_1 \Delta y}{\Delta v} + (y_p - y_1) \right] \exp \left(\frac{\Delta v \tau_e}{\Delta y} \right) \quad (2.5b)$$

$$z_e = z_1 - \frac{w_1 \Delta z}{\Delta w} + \left[\frac{w_1 \Delta z}{\Delta w} + (z_p - z_1) \right] \exp \left(\frac{\Delta w \tau_e}{\Delta z} \right) \quad (2.5c)$$

A summary of the algorithm is: 1) Calculate the *tofs* given the entry coordinates; 2) Select the minimum and 3) Calculate the exit point, figure 2.2. Streamlines are then traced concatenating a series of line segments crossing the voxels inside the pore space: the point where a segment leaves a voxel is the entrance point for the next one.

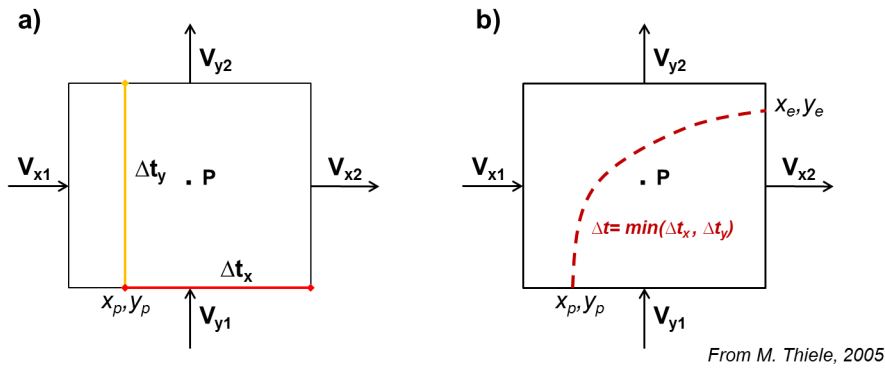


Figure 2.2: Schematics of the Pollock algorithm for a two dimensional staggered grid. a) A particle enters a cell with coordinates x_p and y_p , the associate exit times are calculated according to eqs. 2.3. b) The smallest time defines the exit face (the face to the right in the figure) and the exit coordinates. Modified from Thiele [2005].

2.3 Semi-analytical streamline tracing in pore-scale images

Pore-scale images segregate pores and solids; each voxel is either one or the other, while in field-scale models the grid cells are assigned a porosity (fraction of void space) and permeability. The assumption that velocities can be calculated via linear interpolations inside the voxels does not apply to pore-scale models. These velocities do not obey the strict no-flow condition at the solid walls, since their tangential component is not zero. To address this problem we modify the original Pollock algorithm postulating analytical expressions for the velocities where both the normal and tangential components are zero at the pore-solid walls. These new velocities are then integrated to obtain the particle trajectories and the streamlines are traced in the usual way: adding streamline increments through each voxel. A complication is that now the pore space geometry is the crucial factor, requiring that each pore geometry must be treated separately. In a cubic lattice, there are sixty three possible configurations for a voxel with solid boundaries - six for one solid, fifteen for two solids, twenty for three solids and fifteen for four solids, plus the degenerate cases (the velocity is everywhere zero) with five solid boundaries and the case of an isolated pore (six boundaries). Each of the non-degenerate geometries will have a particular choice of velocity that has to be integrated and solved for the exit times and positions, just as in the original Pollock method.

There are fifty six cases of potential interest plus the case without any solid boundary – treated with the standard Pollock algorithm. We note that the number of cases of interest can be reduced by analysing the velocity field of the rock under study. In the images of real rocks that we study (see examples in section 2.5) the voxels with three and four solid boundaries contribute less than 5% of the pore space and 0.3% of the flux, having negligible impact on the total flow across the sample, see table 2.1. Although we derived the full semi-analytical expressions for the time-of-flight and exit coordinates for these blocks, in the results presented later we use the standard Pollock method in these cases for simplicity.

Our approach is an extension of the Pollock method, where the components of the velocity vector vary linearly with coordinate direction between average values at each voxel face. We adapt this to allow the components of the velocity to vary linearly or quadratically with each direction, subject to the following three constraints. Firstly, that the velocity field everywhere is divergence free (incompressible flow). Secondly, that the no-flow boundary conditions at the solid are strictly obeyed. Thirdly, that the average velocity normal to a face is the same as computed from the numerical solution of the Navier-Stokes equations. This ensures conservation of volume. In principle there is also a pressure field within each grid block

that is consistent with this velocity and the Navier-Stokes equations. However, as this pressure is not used in the simulations we do not need to compute it. These constraints are sufficient to define the velocity field uniquely for every arrangement of solid boundaries. The time-of-flights can then be computed analytically from the known velocity field.

To demonstrate our method we show the derivation of the analytical expressions for the case of voxels with one solid neighbour. The velocities, transit times and exit points for the cases with two, three and four solid boundaries are shown in Appendix C.

2.3.1 Transit times and exit points for voxels with one solid boundary

Given a pore voxel in lattice location (i, j, k) there are six possible positions for the neighbouring solid: $(i + 1, j, k)$, $(i - 1, j, k)$, $(i, j + 1, k)$, $(i, j - 1, k)$, $(i, j, k + 1)$ or $(i, j, k - 1)$. We show the derivation of the case where the limiting solid voxel is in the position $(i + 1, j, k)$, figure 2.3. The other five cases with one solid boundary can be derived in the same way.

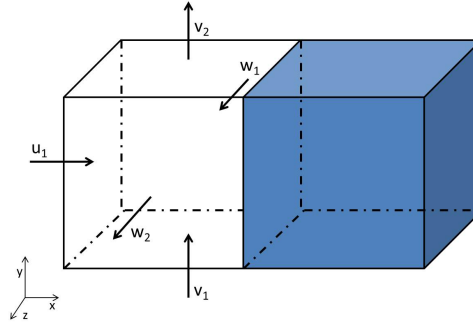


Figure 2.3: Pore voxel limited by a solid voxel in lattice position $(i + 1, j, k)$.

As in the original Pollock method the time-of-flight must be calculated in each direction according to the velocity distribution inside the pore. It is necessary to define a velocity field satisfying the no-slip boundary condition at the pore-solid wall and the conservation of flux.

Assuming that the tangential component y varies linearly with the distance from the solid wall and requiring that it takes its average values v_1 and v_2 at the cell faces we can write:

$$V_y = \frac{\alpha}{\Delta x}(x_2 - x) \left[v_1 + \frac{\Delta v}{\Delta y}(y - y_1) \right] \quad (2.6)$$

then, the average velocity at $y = y_1$ is:

$$\overline{V}_y = \frac{1}{\Delta x \Delta z} \int_{z_1}^{z_2} \int_{x_1}^{x_2} \alpha v_1 \frac{x_2 - x}{\Delta x} dx dz = \frac{\alpha v_1}{2} \quad (2.7)$$

From the condition $\overline{V}_y = v_1$, we have $\alpha = 2$. V_z can be calculated in an analogous way. The component x of the velocity is obtained applying the condition $\nabla \cdot \vec{V} = 0$:

$$\frac{\partial V_x}{\partial x} = -\frac{2\Delta v(x_2 - x)}{\Delta x \Delta y} - \frac{2\Delta w(x_2 - x)}{\Delta x \Delta z} \quad (2.8)$$

together with the conservation of flux (note that $u_2 = 0$, so $\Delta u = -u_1$)

$$\frac{-u_1}{\Delta x} + \frac{\Delta v}{\Delta y} + \frac{\Delta w}{\Delta z} = 0 \quad (2.9)$$

which results in:

$$\frac{\partial V_x}{\partial x} = \frac{-2u_1}{\Delta x^2} (x_2 - x) \quad (2.10)$$

Finally, the velocity field is:

$$V_x = \frac{u_1}{\Delta x^2} (x_2 - x)^2 \quad (2.11a)$$

$$V_y = \frac{2v_1}{\Delta x} (x_2 - x) + \frac{2\Delta v}{\Delta x \Delta y} (x_2 - x)(y - y_1) \quad (2.11b)$$

$$V_z = \frac{2w_1}{\Delta x} (x_2 - x) + \frac{2\Delta w}{\Delta x \Delta z} (x_2 - x)(z - z_1) \quad (2.11c)$$

The *tof* in the x -direction (τ_x) is defined by the integral:

$$\tau_x = \int_{x_p}^{x_1} \frac{dx}{V_x} = \frac{\Delta x^2}{u_1} \left[\frac{1}{\Delta x} - \frac{1}{x_2 - x_p} \right] \quad (2.12)$$

The *tof* in the y direction is the time spent to travel to a point with vertical coordinate y_2 along a streamline passing through (x_p, y_p) :

$$\tau_y = \int_{y_p}^{y_2} \frac{dy}{V_y(x, y)} \quad (2.13)$$

To eliminate the dependency on x in eq. 2.13 we make use of the fact that the slope of the streamline is given by the ratio of the velocity components and write:

$$\frac{dy}{dx} = \frac{V_y(x, y, z)}{V_x(x, y, z)} \quad (2.14)$$

Using equations 2.11a and 2.11b and integrating eq. 2.14 from (x_p, y_p) to (x, y) yields:

$$\left[\frac{x_2 - x_p}{x_2 - x} \right]^{\frac{2\Delta v \Delta x}{u_1 \Delta y}} = \frac{v_1 \Delta y + \Delta v(y - y_1)}{v_1 \Delta y + \Delta v(y_p - y_1)} \quad (2.15)$$

$$(x_2 - x) = (x_2 - x_p) \left[\frac{v_1 \Delta y + \Delta v (y_p - y_1)}{v_1 \Delta y + \Delta v (y - y_1)} \right]^{\frac{u_1 \Delta y}{2 \Delta v \Delta x}} \quad (2.16)$$

Substituting eq. 2.16 into eq. 2.11b and solving the integral in equation 2.13, we have the time-of-flight:

$$\tau_y = \frac{\Delta x^2}{(x_2 - x_p) u_1} \left\{ \left[\frac{v_2 \Delta y}{v_1 \Delta y + \Delta v (y_p - y_1)} \right]^{\frac{u_1 \Delta y}{2 \Delta v \Delta x}} - 1 \right\} \quad (2.17)$$

Following the derivation outlined above τ_z is readily calculated:

$$\tau_z = \frac{\Delta x^2}{(x_2 - x_p) u_1} \left\{ \left[\frac{w_2 \Delta z}{w_1 \Delta z + \Delta w (z_p - z_1)} \right]^{\frac{u_1 \Delta z}{2 \Delta w \Delta x}} - 1 \right\} \quad (2.18)$$

Now using equations 2.12, 2.17 and 2.18 and remembering that the exit time is defined as $\tau_e = \min(\tau_x, \tau_y, \tau_z)$ the exit locations are calculated:

$$x_e = x_2 - \left[\frac{u_1 \tau_e}{\Delta x^2} + \frac{1}{\Delta x_{2p}} \right]^{-1} \quad (2.19a)$$

$$y_e = y_1 - \frac{v_1 \Delta y}{\Delta v} + \frac{v_1 \Delta y + \Delta v \Delta y_{p1}}{\Delta v} \left[\frac{\tau_e u_1 \Delta x_{2p}}{\Delta x^2} + 1 \right]^{\frac{2 \Delta x \Delta v}{u_1 \Delta y}} \quad (2.19b)$$

$$z_e = z_1 - \frac{w_1 \Delta z}{\Delta w} + \frac{w_1 \Delta z + \Delta w \Delta z_{p1}}{\Delta w} \left[\frac{\tau_e u_1 \Delta x_{2p}}{\Delta x^2} + 1 \right]^{\frac{2 \Delta x \Delta w}{u_1 \Delta z}} \quad (2.19c)$$

where we define $\Delta x_{2p} = x_2 - x_p$, $\Delta y_{p1} = y_p - y_1$ and $\Delta z_{p1} = z_p - z_1$.

2.4 Flow between two parallel plates

To validate the method and stress the differences between the original and the extended versions of the Pollock algorithm we consider the flow of an incompressible fluid between two infinite parallel plates separated by a distance L_y , figure 2.4. The analytical solution with no-slip boundary conditions predicts a parabolic velocity profile in the axial direction [Pozrikidis, 2011]:

$$V_x = -\frac{\nabla P}{2\mu} y(L_y - y) \quad (2.20)$$

We place 10^3 particles uniformly along the y -direction and trace streamlines assuming that the velocity is previously solved in a square grid with an error free numerical method that finds the average fluxes at the faces of the grid blocks. In figure 2.5 we plot the particle velocities calculated with our method and the standard Pollock approach for one, two and four grid cells across the plates. In this case,

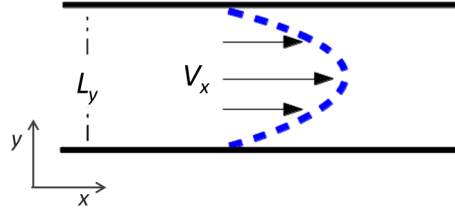


Figure 2.4: The streamline tracing algorithm and its prediction of transport are validated using the analytical solution for the flow of an incompressible fluid between two infinite parallel plates shown schematically here. We study how accurately transport is simulated for different numbers of voxels used to resolve the pore space between the two plates.

the velocity is in the x -direction only and varies with y , figure 2.4. The Pollock interpolation therefore assumes a fixed velocity in each voxel. Our new method reduces to the same approximation when there are no solid boundaries, but allows a linear and a quadratic variation of velocity away from a solid boundary for voxels with one or two solid boundaries respectively. This captures more accurately the smallest flow speeds next to the solids. The case of one grid cell corresponds to the two-dimensional version of the case discussed in the appendix C.1.1 – a voxel with two opposing solid boundaries – and the interpolated velocity using our method is an exact match to the analytical solution. With two cells, our method now assumes a piece-wise linear velocity profile, for voxels with one solid boundary, as described above (equation 2.11b where the second term on the right-hand-side is zero). While this is a poorer representation of the analytical solution, it is still far superior to the Pollock approach which assumes that the velocity is constant within each cell. As the number of cells increases, both our approach and that of Pollock converge to the correct solution; however, the Pollock method always over-states the velocity in the cell closest to the solid boundary.

Figure 2.6 shows the breakthrough curves (BTC) corresponding to the cases depicted in figure 2.5. We assume an initial delta-function pulse concentration and by definition a particle moving at the average velocity breaks through at unit normalized time. We ignore molecular diffusion and study transport by advection only. As expected, with only one grid cell our method reproduces exactly the analytical curve, which the original Pollock completely fails to reproduce: with a constant velocity, there is no dispersion of concentration and the BTC is a delta-function. With two and four grid cells, even if our proposed method is not able to reproduce exactly the results, it converges to the true solution for late time arrivals, determined by the particles close to the walls, while the original method fails to capture the characteristics of the analytical solution. When the number of grid cells is high enough both methods match the exact solution, figure 2.7. However, this requires

a large number of voxels across each pore, which is rarely - if ever - achieved in pore-scale images and numerical models.

As the preceding results suggest, our method is suitable to simulate transport in the relatively coarse grids typical of pore-scale imaging applications - where individual pores are resolved with only a few voxels. Real sedimentary rocks have a typical pore throat size of few microns [Nelson, 2009]. Since the tomographic images have resolutions of the same order of magnitude, this means the pore throats must be represented with just a few grid cells. Computing flow on a refined grid, to remove this restriction, rapidly leads to prohibitive simulation times [Blunt et al., 2013]. Inevitably, the trade-off between system size and resolution means that for realistic systems some pores will be only one or two voxels across; it is necessary that a numerical model represents transport through these pores with reasonable accuracy. The Pollock method fails to reproduce the slow flows near the solid, while our modified method gives a much better representation of the long-time tail of the transport.

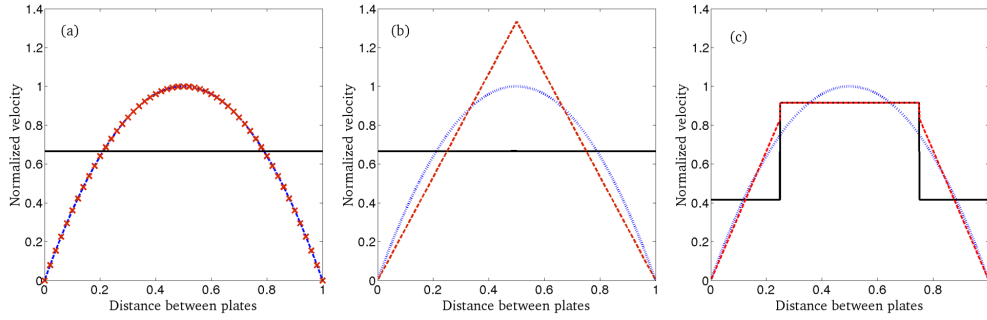


Figure 2.5: Particle velocities with one (a), two (b) and four (c) grid cells between the plates. The analytical solution is shown in blue dots, the standard Pollock method in the solid black line and our modified approach in red dashed line. With one grid cell our modified method is an exact match to the analytical solution while the linear interpolation from the original method completely fails to reproduce the expected parabolic profile. With two and four grid cells our extended method also produces better estimates than the original method.

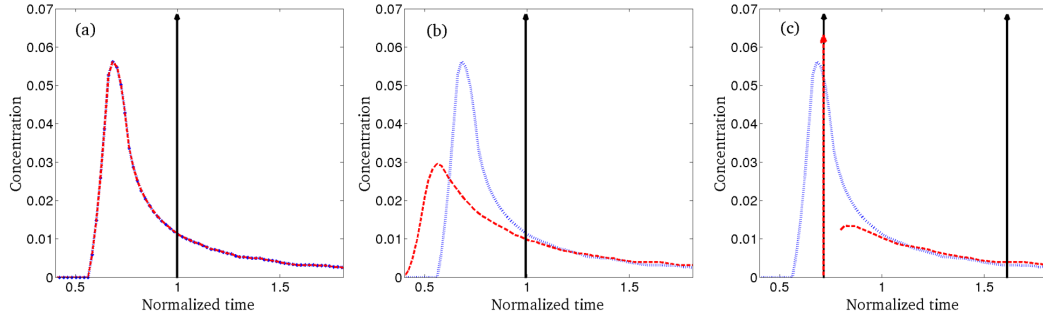


Figure 2.6: Breakthrough curves with one (a), two (b) and four (c) grid cells between the plates. Unit time is defined as the breakthrough time of the particles moving at the average flow speed. The analytical solution is the dotted blue line, the standard Pollock is the black solid line and our method is the red dashed line. Using one grid cell the modified method is an exact match to the analytical solution. With a constant velocity (see figure 2.5), the Pollock method assumes transport with no dispersion of the original delta-function concentration profile in the absence of molecular diffusion. With two and four grid cells our extended method also yields better results than the original method and correctly captures the late-time tail of the distribution. The Pollock method, assuming piece-wise constant velocities, again fails to reproduce the wide distribution of travel times.

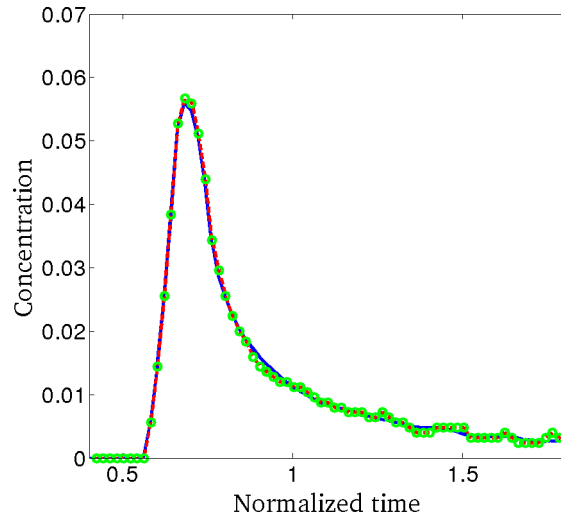


Figure 2.7: Increasing the number of grid cells across the plates (fifty in this example) both methods converge to the analytical solution for the breakthrough curve. The analytical solution is shown in the solid line, the standard Pollock in the green dots and our method is the dashed red line. Here, for a fair comparison, we have binned the concentration to construct a smoothed histogram.

2.5 Streamline tracing in images of sedimentary rocks

Next we show how streamline tracing can be used to study transport properties in real rocks, a sandstone and a carbonate, see appendix A for a thorough description. The sandstone is a Bentheimer with image size of 1000^3 voxels, voxel size (l) of $3.0\mu\text{m}$, 21.6% porosity and the image-calculated permeability is $3 \times 10^{-12}\text{m}^2$. The carbonate is a Ketton oolite with dimensions $911 \times 902 \times 922$, voxel size of $3.8\mu\text{m}$, 13.5% porosity and image-calculated permeability of $13 \times 10^{-12}\text{m}^2$, figure 2.8. A convenient choice for the characteristic length is to define it as the diameter of an inscribed sphere in a cube of side L :

$$L = \pi \frac{V}{S_A} \quad (2.21)$$

where V is the volume of the porous medium and S_A is the area of the pore-solid interface [Mostaghimi et al., 2012]. This results in $L = 558\mu\text{m}$ for the Bentheimer and $L = 420\mu\text{m}$ for the Ketton. The Reynolds number is defined as:

$$Re = \frac{\rho q L}{\phi \mu} \quad (2.22)$$

where q is the Darcy velocity. Establishing a pressure gradient of $\Delta P = 1\text{Pa}$, results in $Re = 10^{-3}$ and $Re = 10^{-2}$ for the sandstone and the carbonate, respectively. The flow is in the low Reynolds number limit – Stokes flow.

The flow field is calculated using a finite-volume method, as explained in section 1.3.1. Tracer particles are injected using a flow weighted rule at the inlet and tracked until they reach the outlet. In both images we inject 5×10^4 particles and impose constant pressure at the inlet and outlet faces (perpendicular to the x -direction) and no-flux in the lateral (y and z) boundaries. In addition to the voxels with no-solid boundaries, the ones with four and five boundaries are also treated with the standard Pollock method, as they have negligible impact on the total flux across the sample, as shown in table 2.1.

Distributions of the time-of-flight can be used to characterize the degree of heterogeneity of the rock [Bijeljic et al., 2011]. In addition, BTCs also provide useful

	Bentheimer		Ketton	
# of solid boundaries	% of pore space	% of the total flux	% of pore space	% of total flux
0	82.5	97.3	90.1	99.06
1	7.5	1.74	4.2	0.61
2	5.2	0.7	3.1	0.23
3	3.9	0.242	2.5	0.09
4	0.8	0.018	0.055	0.01
5	0.1	-	0.005	-

Table 2.1: Percentage of the total pore-space and to the total flux across the samples (Bentheimer and Ketton) of the voxels with different numbers of solid neighbours.

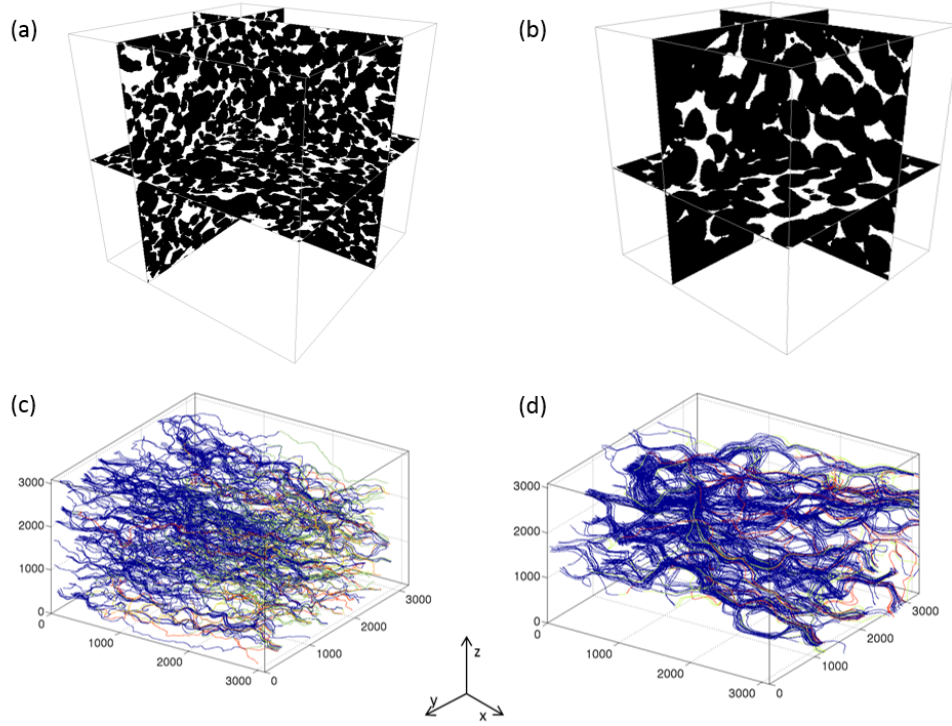


Figure 2.8: Orthogonal slices of three-dimensional segmented micro-CT images of a Bentheimer sandstone (a) and a Ketton carbonate (b). We launch streamlines according to a flow weighted rule at the inlet and trace until the outlet face. Flow in the Bentheimer sandstone is relatively homogeneous (c), while in the Ketton carbonate it tends to be concentrated in high velocity channels (d). Color in the streamlines is indicative of advective travel time (slow paths in light blue, fast paths in red), distances in μm .

insights about the nature of the transport in porous media, the presence of a heavy tail being indicative of anomalous (non-Fickian) transport that cannot be adequately described by the classical advection-diffusion equation, e.g. Berkowitz et al. [2000].

Heterogeneous porous media are characterized by wide probability distribution functions (PDF) of their corresponding velocity fields. These distributions are, typically, long-tailed, indicating the presence of slow velocity zones [Bijeljic et al., 2013a]. Figure 2.9 shows the PDFs of the voxelized horizontal component of the velocity field for Bentheimer and Estailades. There is a significant number of voxels with a low velocity. These voxels have a long time-of-flight, and correspond to the heavy tails in the transit time distributions shown in figure 2.10.

In each image we trace streamlines using both the standard Pollock method for every voxel and our modified version (in the voxels with two and three solid neighbours). We compute the distribution of voxel transit times - $\psi(\tau)$ - as a function of the dimensionless time $\tau = t/\tau_{avg}$, where $\tau_{avg} = \Delta x/u_{avg}$ and u_{avg} is the aver-

age flow velocity, see figure 2.10. The standard Pollock method gives lower voxel transit times in the slow regions, typically the ones close to the solid interface, compared to our new tracing method. Based on the results of the section 2.4, we suggest that ignoring the no-slip boundary conditions at the solid walls tends to overestimate the speed of the slowest particles and truncate $\psi(\tau)$ for long τ . We also note that both distributions are almost identical for short times, as it would be expected since the “free” pores, which tend to have the fastest advective travel times, are treated the in same way.

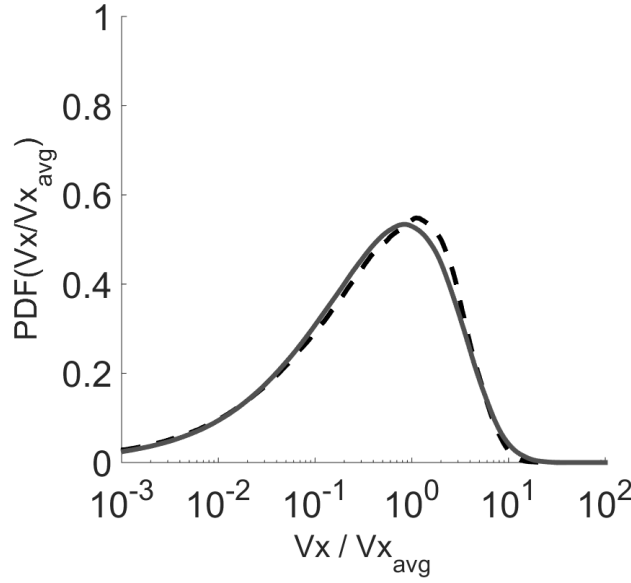


Figure 2.9: Probability distributions of the horizontal velocity – Bentheimer sandstone (solid line) and Ketton limestone (dashed line). The low velocity voxels (the heavy tails of the distributions) correspond to the high transit times in fig. 2.10.

The transit times depicted in fig. 2.10 were obtained for a system without diffusion, where transport is purely advective. However, for modelling purposes, they can be used to estimate the importance of correctly addressing the no-flow condition in the presence of diffusion. Consider the Péclet number (eq. 1.7), which compares the advection time to the diffusion time. In a system characterized by a diffusive time-scale τ_{diff} , voxels with transit time $\tau > \tau_{diff}$ have a local Péclet number $Pe < 1$, i.e. they are diffusion-dominated. While the voxels where $\tau < \tau_{diff}$ are advection-dominated $Pe > 1$. This is shown in schematic form in figure 2.11. Now, analysing fig. 2.10, we can estimate a lower bound for the diffusion time-scale above which the distributions do not coincied – $\tau_{diff} \approx 10$. This corresponds, in a first approximation, to $Pe \approx 10$. This means that, for both Ketton and Bentheimer, whenever $Pe > 10$, transport simulations will benefit from properly addressing the no-flow boundary condition.

One of the analytical frameworks to describe anomalous transport in porous

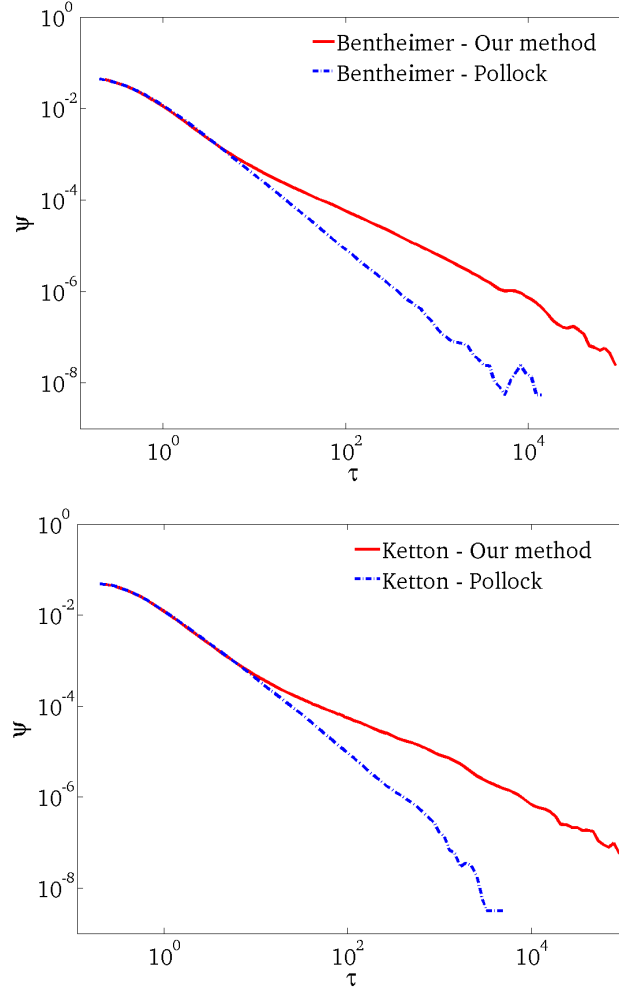


Figure 2.10: Distribution of voxel transit times against dimensionless time τ in a Bentheimer sandstone (top) and in a Ketton carbonate (bottom) obtained using both the standard Pollock algorithm (dashed line) and our modified version (solid line). Because it ignores the decay of the tangential velocities in the voxels neighbouring the solid phase, the standard Pollock method tends to underestimate the transit times in such slower voxels.

media is the continuous time random walk (CTRW) approach, see Berkowitz et al. [2006] and references therein. Under its assumptions it can be shown that asymptotically when $\psi(t) \sim t^{-1-\beta}$, then the breakthrough concentration scales as $C(t) \sim t^{-1-\beta}$. The exponent β is related to the degree of heterogeneity of the system and controls the nature of dispersion (e.g. Fickian or non-Fickian). When $\beta > 2$ the first and second moments of the transit time distribution are finite and the system displays asymptotic Fickian behaviour. To calculate β from the breakthrough curves, we first define $\alpha = 1 + \beta$, meaning that $C(t) \sim t^{-\alpha}$.

BTCs are computed as histograms of the total particle travel times. The sampling is uniform in the logarithmic space and the number of bins is 200. Next, using a maximum-likelihood method [Clauset et al., 2009], we compute α in the tails of

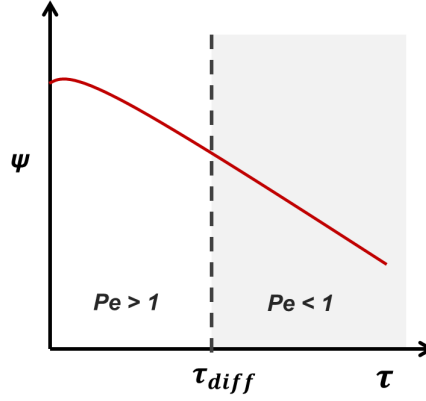


Figure 2.11: In a system with diffusion time τ_{diff} , the voxels where the time-of-flight $\tau > \tau_{diff}$ are diffusion-dominated ($Pe < 1$), and the ones where $\tau < \tau_{diff}$ are advection-dominated ($Pe > 1$).

the breakthrough curves obtained by both the standard Pollock method and by our modified version, figure 2.12. Simulating BTCs with the Pollock method gives us values of β of 2.6 and 1.9 for Bentheimer and Ketton, respectively, which would lead us to infer Fickian (or almost-Fickian) behaviour, contradicting several earlier experimental and modelling results on transport in natural porous media, see, for instance, Sahimi [2011], Bijeljic et al. [2011], Berkowitz et al. [2000], Becker and Shapiro [2000], Silliman and Simpson [1987] and Bijeljic et al. [2013b]. However, using our new method we obtain $\beta = 1.2$ and $\beta = 0.9$, respectively, indicating the expected non-Fickian transport behaviour.

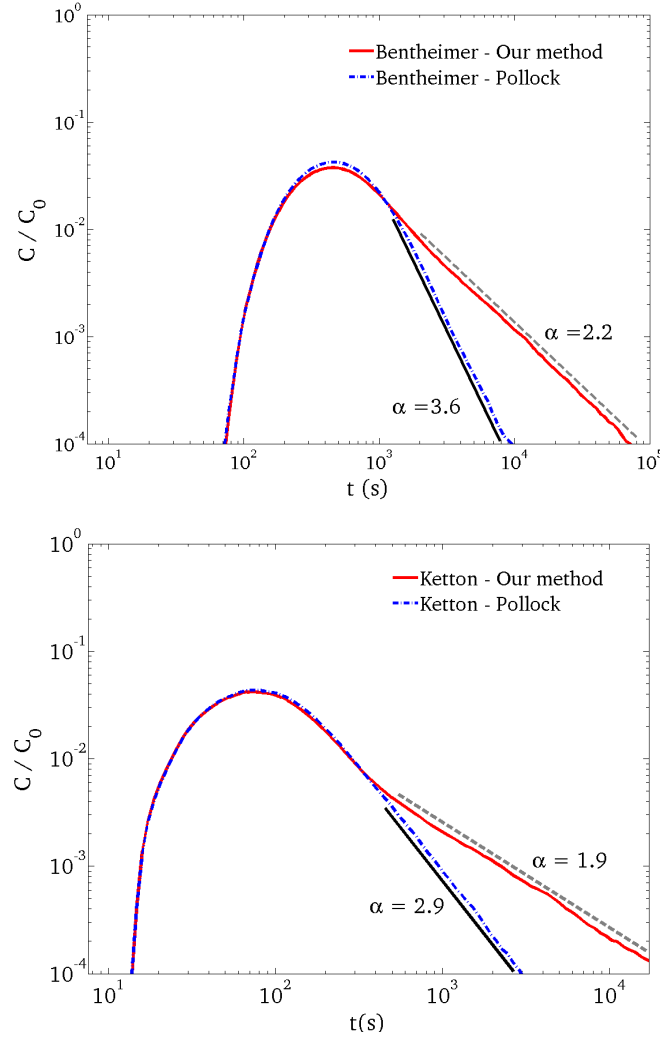


Figure 2.12: Breakthrough curves (concentration as a function of time) in a Bentheimer sandstone (top) and in a Ketton carbonate (bottom) simulated with both the standard Pollock algorithm (dashed line) and our modified version of the algorithm (solid line). Using our method we have longer tails and smaller exponents ($\alpha = 1 + \beta$) for the power law describing the late time behaviour. Under the CTRW approach, the standard Pollock simulation predicts Fickian behaviour ($\beta > 2$) for the Bentheimer sandstone, while our approach predicts non-Fickian behaviour ($\beta < 2$).

2.6 Comparison with time-stepping methods

Time-stepping methods are a common choice for modelling advection [Tompson and Gelhar, 1990; Bensabat et al., 2000]. In comparison with semi-analytical methods they are easily implemented and their conceptual framework is straightforward, section 1.3.2. However, they are prone to numerical instabilities and computational performance can be poor. In this section we compare the results obtained with Pollock's method with a standard Euler integrator and an adaptive time-step (ATS) scheme. More refined methods, e.g. Runge-Kutta, could potentially overcome numerical instabilities at the expense of longer running times and will not be discussed here. Our objective is to illustrate the efficiency of the (modified) Pollock's approach in comparison with time-stepping methods.

Euler's method integrates eq. 2.1 by approximating the derivative with a forward finite-difference expression. The particle position is then updated according to:

$$\vec{X}_p(t + \Delta t) = \vec{X}_p(t) + \vec{V}(\vec{X}_p)\Delta t \quad (2.23)$$

The geometric interpretation is a series of small steps along the tangent line of the streamline, requiring that the time-step is made very small, particularly in regions of high velocity [Tompson and Gelhar, 1990; Békri et al., 1995]. The time-step is limited by fixing the maximum displacement (δ):

$$\Delta t = \frac{\delta}{V_{max}} \quad (2.24)$$

When the velocity distribution is very wide, as is the case in heterogeneous rocks, Δt is constrained by the highest velocity, even if it corresponds only to a minor portion of the pore space. This is, of course, extremely inefficient.

An alternative is to employ an adaptive time-step, where the time-step is recalculated locally as a function of the velocity. This has the advantage of not requiring many steps in the slow regions, in contrast with the Euler method. For a jump of size δ , the time-step is:

$$\Delta t_\delta = \frac{\delta}{|\vec{V}(\vec{X}_p)|} \quad (2.25)$$

and the particle moves to a new position:

$$\vec{X}_p(t + \Delta t_\delta) = \vec{X}_p(t) + \vec{V}(\vec{X}_p)\Delta t_\delta \quad (2.26)$$

In the simulations presented below, $\delta = l/50$.

When the velocity inside the voxels is given by a linear interpolation of the face velocities, both methods should recover Pollock's results for a sufficiently small time-step. This is shown in figure 2.13, where we plot the BTCs for the Ketton carbonate discussed in the previous section.

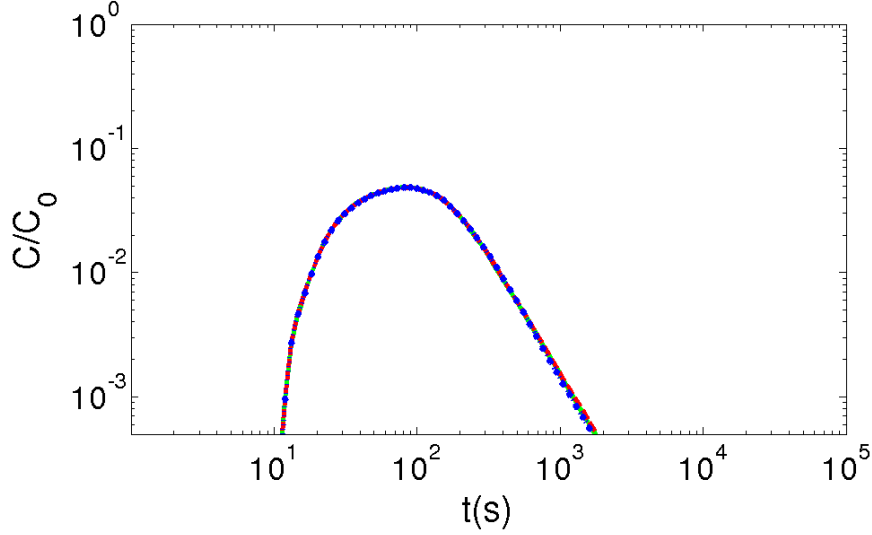


Figure 2.13: Breakthrough curves for the Ketton rock. The voxel velocity is given by a linear interpolation of the face velocities and three time-stepping methods are used: streamline (Pollock - blue), the Euler method (green) and the adaptive time-step (red).

Alternatively, we could consider the velocity interpolations derived earlier (eqs. 2.11, C.1, C.4d, C.10, C.13, C.18 and C.19) and use them in conjunction with both methods, Euler and ATS. This is a reasonable approximation of the "true" solution obtained with the semi-analytical approach, figure 2.14. The running times using a single core in a Intel XEON 2.2GHz were 470 s, 445 s and 75 s, for the Euler, ATS and our streamline method, respectively. The streamline method has a lower run time, as expected.

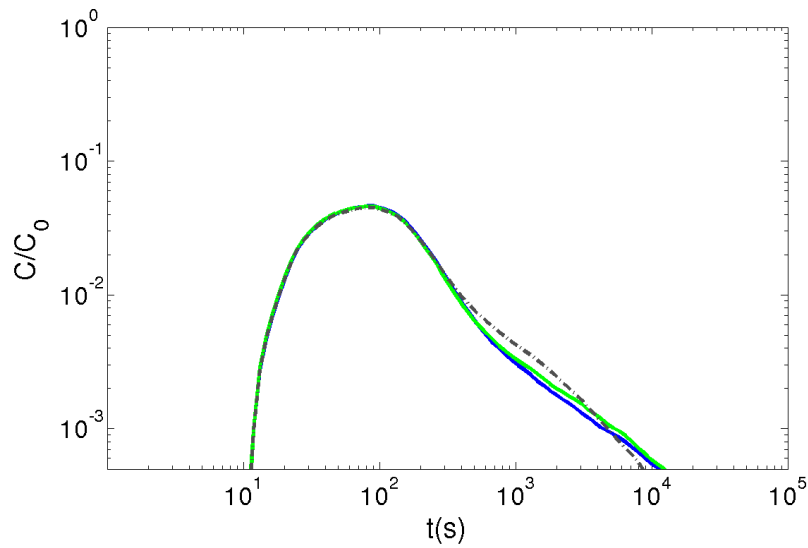


Figure 2.14: Breakthrough curves for the Ketton rock obtained with streamline tracing (blue), the Euler method (green) and with an adaptive time-step (grey). Here the velocities are given by the bi-linear expressions satisfying the no-slip condition.

2.7 Applications and concluding remarks

This chapter presented a semi-analytical streamline tracing method to simulate pore-scale transport in heterogeneous porous media. The method is a development of the Pollock method, a well established algorithm that has been in use for field-scale (Darcy flow) simulations for many years. The new methodology is applied to flow controlled by the Navier-Stokes equation at the pore scale and is a very efficient way of obtaining transport properties in advection-dominated flows. The use of analytically traced streamlines eliminates the numerical stability constraints associated with the size of the time step, an obvious advantage over standard particle tracking methods.

As examples of the proposed approach, we presented the time-of-flight distributions and breakthrough curves calculated directly in voxelised micro-CT images of two sedimentary rocks, a Bentheimer sandstone and a Ketton carbonate, and compared them to the ones obtained with the original Pollock method. The tails of the distributions are significantly different, which may give misleading indications about the nature of the transport (Fickian or non-Fickian) in the rocks. In particular, depending on the choice of the tracing method, the transport in the Bentheimer sandstone would be characterized as Fickian (using the standard Pollock) or non-Fickian (using the modified version), figures 2.10 and 2.12. The simulation time was only a few minutes using a standard desktop computer, even for billion-cell models.

In the context of purely advective transport, the method can also be used to study the pore-scale origin of anomalous transport. Using semi-analytical streamlines in a Berea sandstone, Kang et al. [2014] showed that the non-Fickian nature of transport in real porous rocks is related to the intermittent structure of the Lagrangian velocities. Moreover, the presence of long range correlations in both time and space in the Lagrangian velocities plays a significant role in determining the anomalous scaling characteristic of the particle spreading.

In another application of the method, Siena et al. [2014] described the power law scaling behaviour of the Lagrangian velocities in two rocks: Estailades (a heterogeneous carbonate, see chapter 4) and the Bentheimer. Analysing sample structure functions, they showed that the Bentheimer sandstone obeys a single power law regime over a wide range of spatial lags, while the Estailades limestone follows two power law trends. This is assumed to be a manifestation of an underlying correlated structure in space.

Diffusion can be readily handled by superimposing a random walk in the particle tracers following the advective motion [Tompson and Gelhar, 1990; Sàlles et al., 1993]. In the presence of diffusion, a time-step (Δt) is needed. The analytical

formulas derived early in this chapter calculate the time needed to exit the current voxel (τ_e). If $\Delta t > \tau_e$, the particle first exits the voxel and then the appropriate voxel-type dependent expression is applied again to move the particle, this time with a time-step $\Delta t - \tau_e$, figure 2.15. This guarantees that the particle follows the streamline during advection. An application of this, including reactions, will be presented in the next chapter. Also of interest is the work of Alhashmi et al. [2015], who applied the streamline tracing method to the modelling of homogeneous (fluid-fluid) reactions in a moving fluid in which the reaction rate was defined in terms of diffusion and distance between reactants.

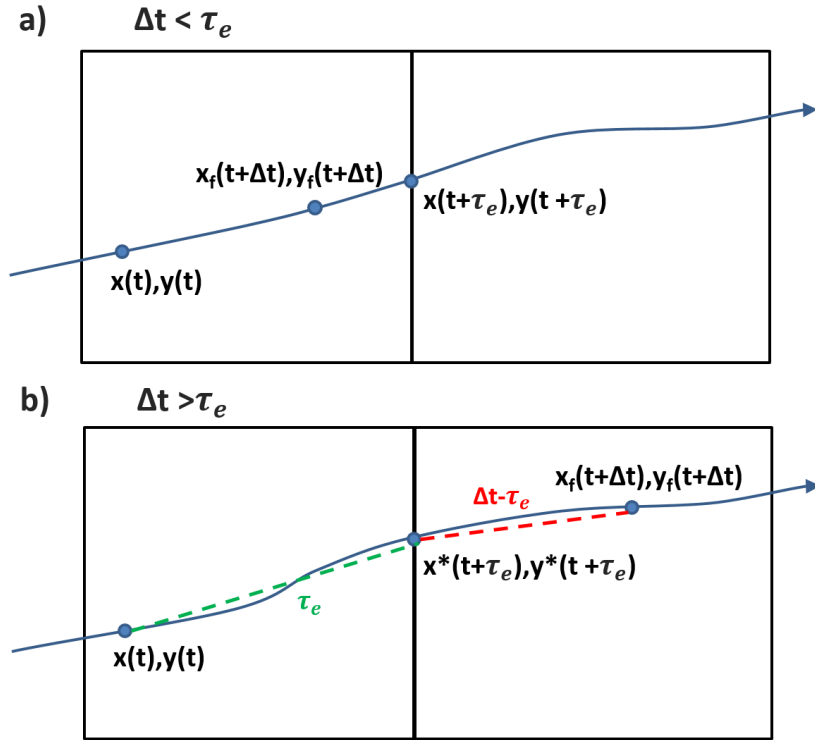


Figure 2.15: In the presence of diffusion, a time-step (Δt) is needed. When $\Delta t < \tau_e$, the particle does not change voxels and the final position $x_f(t + \Delta t), y_f(t + \Delta t)$ is obtained analytically (a). When $\Delta t > \tau_e$ (b), the advective motion is divided into successive applications of the formulas derived earlier in this chapter: the particle exits the current voxel at $x^*(t + \tau_e), y^*(t + \tau_e)$ and moves inside the next one with time-step $\Delta t - \tau_e$.

In practical implementations of a particle-based advection-diffusion process, the time-step is constrained by the maximum diffusive jump (eqs. 1.11 and 1.12) and by the maximum grid velocity:

$$\delta_{max} = |v_{max}| \Delta t + \sqrt{6D_m \Delta t} \quad (2.27)$$

where δ_{max} is the maximum displacement per time-step, which is usually defined in terms of the grid size l : $\delta_{max} \ll l$ [Tompson and Gelhar, 1990; Sàlles et al., 1993;

Verberg and Ladd, 2002]. The advantage of using the modified Pollock algorithm instead of standard particle tracking approaches, lies in the fact that the time-step is constrained by the diffusive step only, allowing for larger time steps and a consequent saving in computational time.

PORE-SCALE SIMULATION OF CARBONATE DISSOLUTION IN MICRO-CT IMAGES

This chapter starts by reviewing the basics about heterogeneous¹ reactions in porous rocks, in particular dissolution. Next, a particle-based model to describe mineral dissolution under reaction-controlled kinetics is proposed and then applied to study the CO₂-induced dissolution of a carbonate rock at the pore scale under reservoir conditions.

3.1 Heterogeneous reactions at interfaces

In the context of flow through sedimentary rocks, surface reactions between the flowing fluids and the minerals comprising the rock are the most relevant heterogeneous chemical reactions. Common examples are dissolution of the rock grains or solute precipitation, as exemplified in section 1.2.1. The kinetics of heterogeneous reactions can be roughly divided into three steps: 1) the transport of reactants to the solid surfaces, 2) the reaction at the surface² and 3) the transport of the products away from the surface. The slowest of these is the limiting factor in the overall kinetics, figure 3.1. There are two limiting cases of interest. The first is when the characteristic time of reaction is much smaller than the transport characteristic time, meaning that the reaction is transport-controlled. The second is when the transport time is much smaller than the reactive time, the reaction is limited

¹Heterogeneous reactions are the ones in which the reactants are in different phases, e.g. solid-fluid, gas-liquid etc.

²Of course, the reaction at surface itself is composed of several elementary steps, most of them occurring at the quantum scale.

by the reaction rate at the surface and dissolution is reaction-controlled, also called surface-controlled or surface reaction-controlled.

In the context of dissolution reactions, the laboratory techniques are focused on the measurement of the so-called intrinsic rate, *i.e.*, free of mass transport limitations, k_s in figure 3.1. These include stirred and flow through reactors. When the stirred reactor is closed to mass transfer, it is called a batch reactor. In stirred reactors, the fluid is constantly agitated, so as to carry fresh reactants to the surface and remove the reaction products, thus eliminating mass transport restrictions. This is usually performed with the rotating disk apparatus, in which a flat, pure crystal is mounted on a spinning disk. When the rotation velocity is high enough, concentration gradients within the fluid are eliminated and the surface rates are accessed [Pokrovsky et al., 2005; Peng et al., 2015]. In the absence of catalytic effects, these surface rates are then upper bounds to the overall rates. In geologic settings, depending on the temperature, dissolution can be either transport- or reaction-controlled: with increasing temperature, transport controls become more important. In aqueous solutions, minerals with low solubility tend to be dissolved via a reaction-controlled process, this is the case of calcite in pure water [Berner, 1978; Lasaga, 1998].

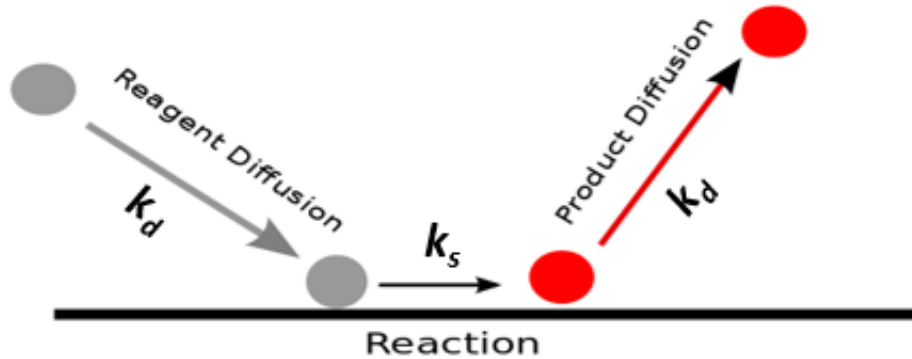


Figure 3.1: Schematics of a heterogeneous surface reaction. Following the diffusion of a reactant to the surface, the reaction occurs and the product must be diffused away. The slowest of these steps (characterized by the rate constants k_d and k_s) controls the overall kinetics – $k_d \gg k_s$ for reaction-controlled kinetics and $k_s \gg k_d$ for diffusion-controlled. In general, the diffusive time of both the reactant and the product is considered to be the same.

3.1.1 Transport and reaction regimes: dimensionless numbers

Transport and chemical phenomena in fluid flow are conveniently described by dimensionless numbers. The Péclet number (Pe , section 1.3.2) compares the rate of

advection to the rate of diffusion over a specified characteristic length L [Lasaga, 1998]:

$$Pe = \frac{qL}{\phi D_m} \quad (3.1)$$

where q is the Darcy velocity (the total discharge over the sample cross-sectional area). The specification of L is arbitrary, and it has to be chosen carefully to correctly represent the characteristics of the system. For a porous rock, we adopt the definition introduced early (eq. 2.21): $L = \pi V / S_A$, where V is the volume of the sample and S_A is the area of the pore-solid interface [Mostaghimi et al., 2012]. This is a good approximation for the diameter of the rock grains and for the REV, appendix B. When $Pe > 1$, transport is advection-dominated.

The (advective) Damköhler number (Da) is defined as the ratio of the advective time and the reaction time, both, again, calculated over the same characteristic length. The reaction time to dissolve a volume V of a porous rock with molar density n [mol.m⁻³] and surface area S_A is:

$$t_{react} = \frac{Vn(1 - \phi)}{rS_A} \quad (3.2)$$

where r [mol.m⁻².s⁻¹] is the intrinsic dissolution rate. Now, considering the advective time ($t_{adv} = L\phi/q$), and the definition of L from above:

$$Da = \frac{\pi r \phi}{qn(1 - \phi)} \quad (3.3)$$

Since the no-slip condition imposes $\vec{V} = 0$ at the surfaces, the transport of reactants close to the solids is diffusion-dominated. Therefore, the product $PeDa^3$, which compares the reaction rate to the diffusion rate, provides a more useful characterization of the dissolution dynamics and it is used in conjunction with the Pe number to draw a behaviour diagram describing the most common dissolution regimes in porous rocks, figure 3.2. A similar diagram was firstly proposed by Daccord et al. [1993], and later expanded and modified by a number of authors (e.g. Budek and Szymczak [2012]; Golfier et al. [2002]).

In a reaction-controlled kinetics, the reaction is slow compared to the rate of transport – $PeDa < 1$. Two distinct patterns emerge, compact (or face) dissolution when the flow rate is low ($Pe \approx 1$) and uniform dissolution when the rate is high ($Pe \gg 1$). The exact meaning of "high" and "low" is still open for discussion, and it will be shown later (chapter 4) that these cut-offs are rock dependent. Also, uniform dissolution does not mean that the entire pore space is equally accessible to the

³The advective and diffusive Damköhler numbers are also denoted by Da_I and Da_{II} , respectively [Steeffel and Maher, 2009]. In this case, $PeDa = Da_{II}$

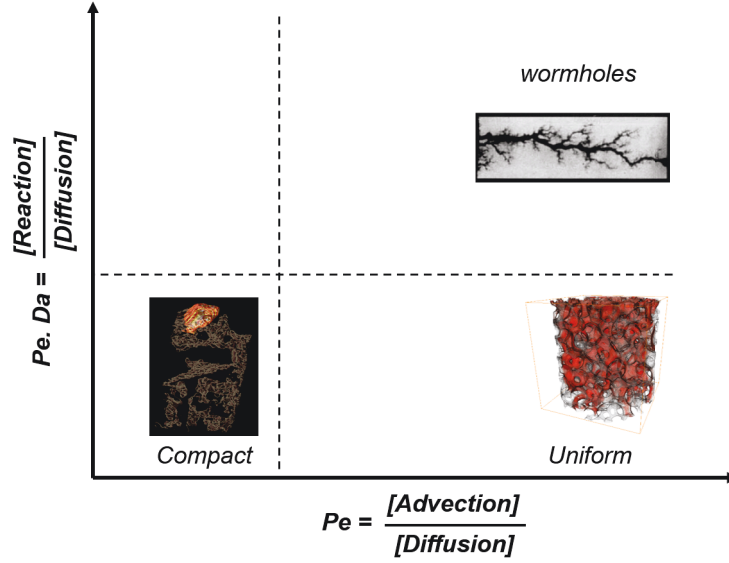


Figure 3.2: Dissolution behaviour diagram in terms of the nondimensional numbers Pe and $PeDa$. Depending on the flow and reaction characteristics, different patterns are formed during rock dissolution, this is described qualitatively in terms of a competition between the transport time scales, both advective and diffusive, and the reaction time scale at the solid surface [Golfier et al., 2002; Daccord et al., 1993].

reactants. It means that the mean free path of the reactants is at least the length of the sample, thus fresh solute is carried to the outlet face, figure 3.3. In contrast, in a non-uniform regime, the solute reacts before it leaves the rock. It should be kept in mind this classification had its origin in core (cm) scale studies, and it does not consider the influence of the underlying pore geometry. As a matter of fact, in the uniform regime, very different dissolution patterns may develop depending on the initial pore structure. This will be discussed in chapter 4.

Finally, when the reaction is fast ($PeDa \gg 1$), the reactants are consumed almost immediately where injected, typically in high permeability channels. This creates a positive feedback that forms wormholes, highly conductive channels where all the reaction occurs. Wormholes are of interest in acid stimulation jobs, where strong acids are pumped into the formation at high rates. The objective is to create conductive channels to improve well performance [Nierode and Williams, 1971].

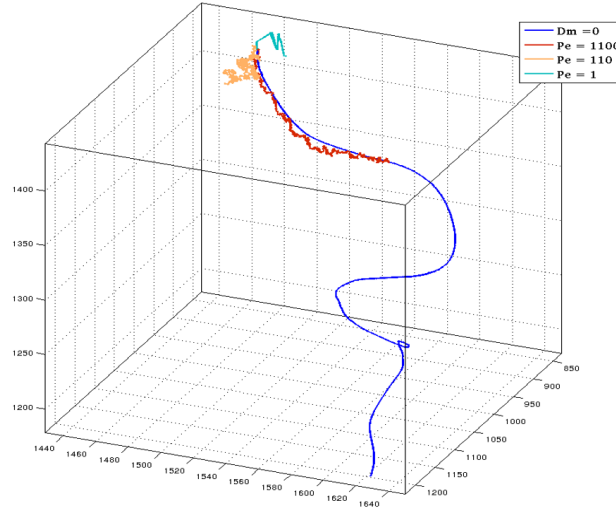


Figure 3.3: Particle trajectories in the pore space of a porous rock. For purely advective transport ($Pe \rightarrow \infty$), the particle does not collide with the pore walls and its path line connect the inlet to the outlet (blue line). As the Péclet number decreases, the mean free path also decreases, and the dissolution is restricted to positions close to the inlet. $Pe = 1100$, red line, $Pe = 110$, orange line and $Pe = 1$, light blue line.

3.2 Reaction rates in the laboratory and in porous rocks

As discussed previously, intrinsic reaction rates for well-mixed fluids flowing through pure mineral suspensions or next to a pure, flat sample can be measured in the laboratory [Lasaga, 1998]. In this thesis the intrinsic rates (i.e. those not affected by transport limitations) will be referred to as batch rates and the average rate (also called effective rate) is the rate at which a sample of porous rock reacts with solute dissolved in the fluid flowing through its pores. The direct application of batch rates to geological reservoirs is questionable, figure 3.4. Batch reaction rates are known to be often several orders of magnitude higher than the ones reported in field studies and core measurements, e.g. Swoboda-Colberg and Drever [1993], Salehikhoo et al. [2013], Steefel et al. [2005]. This could be the result of: differences between reactive surface areas in fresh and weathered minerals and the fact that natural systems are closer to equilibrium than laboratory systems [White and Brantley, 2003]; incomplete mixing of solute reactants [Li et al., 2008]; or the presence of physical and chemical heterogeneities in the field [Steefel et al., 2005; Li et al., 2006]. Another important factor contributing to the decrease of field-scale rates is their dependence on fluid residence times, since apparent reaction rates decrease with residence time [Maher, 2010]. Studying silica dissolution rates in HCl irrigated plots, Swoboda-Colberg and Drever [1993] reported a difference of two orders of magnitude between laboratory and field rates.

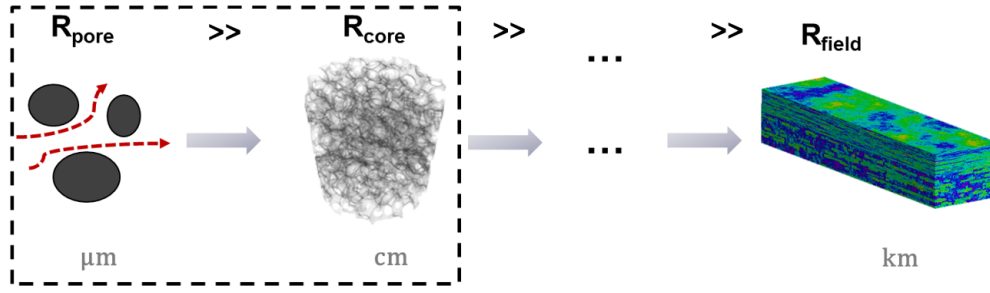


Figure 3.4: Reaction rates are scale dependent, with field scale rates being usually several orders of magnitude lower than laboratory rates. This is due to the combined effect of different physical and chemical heterogeneities that manifest themselves at different spatial scales.

It is reasonable to expect that some of the same constraints (incomplete mixing of solutes, physical and chemical heterogeneities) are also present at the pore (micron) and core (millimetre/centimetre) scales, thus diminishing the observed reaction rates in comparison with the batch rates. This has been explored computationally in artificial media. Meile and Tuncay [2006] investigated the impact of pore-scale heterogeneity in diffusion-reaction processes using computer generated porous media. For the case of calcite dissolution, they reported a wide range of mismatch (up to two orders of magnitude) between true rates and upscaled rates, when arbitrarily changing the effective reactive surface. A decrease in the effective reaction rate was also predicted by Molins et al. [2012], who employed a continuum approach to study the impact of pore space heterogeneity in a synthetic two-dimensional porous medium, but the effect - a decrease of only 20% - was much smaller than expected from the laboratory and field results quoted above. A pore-network approach was employed by Li et al. [2007] to illustrate the possible impacts of variations in the distribution of minerals in reaction rates of sandstone reservoirs subjected to CO_2 injection. They found that the size of the clusters of reactive minerals and their position relative to the flow direction may have major effects on the upscaling of the reaction rates. Experiments by Salehikhoo et al. [2013] and Li et al. [2014] studied the influence of the spatial distribution of minerals and flow velocity on magnesite dissolution. They found that the flow rate directly influences the centimetre-scale dissolution rate. Menke et al. [2015] performed a dynamic imaging experiment in which a relatively homogeneous carbonate slowly dissolved during the flow of CO_2 -saturated brine. They reported an average reaction rate approximately 14 times smaller than the batch calcite dissolution rate. A similar dynamic imaging experiment was later performed by Menke et al. [2016], this time in a set of more heterogenous carbonates. They reported a decrease of up to two orders of magnitude in the average rates, which was attributed to transport limitations

due to the heterogeneous nature of the flow field.

It is still not evident whether the average reaction rate can be lower in porous rocks exclusively due to a heterogeneous flow field. Later, in section 3.6, we will simulate flow and reaction in a realistic three-dimensional system and show that one order of magnitude decrease in the reaction rate can be caused entirely by the limited transport of reactants in the pore space, a consequence of flow heterogeneity. These results are in accord with experimental measurements. Previous work focused on simulating fluid-rock reactions in relatively simple synthetic porous media and there is still a need to develop predictive pore-scale models capable of reproducing reactive flow experiments in realistic rock samples and explaining the emergence of dissolution patterns and effective reaction rates from first principles. This thesis is a contribution in this direction, as will be discussed further in this chapter.

An important outcome that will follow from the simulations is that, since chemical heterogeneities are not considered in the model, physical heterogeneities alone are responsible for the observed average dissolution rate. This will lead to the conclusion that the restrictions imposed by the characteristics of flow – a reduction of both the amount of solute in contact with the solids and the local residence time – have a major impact in the dissolution dynamics, even for fast flows where the reactants are distributed throughout the pore space. The net effect is a reduction of at least one order of magnitude in the observed dissolution rate in millimetre-scale rock samples.

3.3 Mineral Dissolution in the Particle Approach

To translate the reaction rate into the particle framework, we have to establish a relationship between the particle flux and the batch dissolution rate. We propose a model that is applicable under first-order, reaction-controlled kinetics at the solid surface. Under these assumptions, it is possible to derive analytically an expression relating the flux of particles to the laboratory measured rate in terms of *a priori* characteristics of the system, as shown below.

The model assumes first-order kinetics, meaning that the reactive flux (J_R) at the mineral surface is proportional to the particle concentration, and reaction-controlled dissolution, implying that no significant concentration gradients develop in the vicinity of the surface. Once a stationary state is reached, the diffusive flux equals the reactive flux.

The reactive flux is determined by the intrinsic reaction rate r [$\text{mol.m}^{-2}.\text{s}^{-1}$]. Given a fluid with reactant concentration C [n. of particles. m^{-3}], the diffusive flux is determined by the average number of particles crossing the interface in a time-

step (p). Taking a small volume containing a single plane surface it can be shown (see appendix D) that:

$$p = Cl^2 \frac{\lambda}{8} \quad (3.4)$$

where l^2 is the area of the voxel face. Then, the diffusive flux in terms of number of particles per area, per time, is written as:

$$J_{diff} = \frac{C \lambda}{\Delta t 8} \quad (3.5)$$

The mass balance at the interface requires that $J_R = J_{diff}$ and the relation between moles and number of particles is established imposing that N_{mol} moles of the mineral are dissolved by a flux of N_{diff} particles and equate this with the reaction rate:

$$r = J_{diff} \frac{N_{mol}}{N_{diff}} \quad (3.6)$$

The model does not account for sub-resolution dissolution; a solid voxel is suddenly dissolved once the number of particles hitting it reaches N_{hits} , which is related to the number of mineral moles in the voxel N_{mol}^{voxel} and the reaction rate as follows:

$$r = J_{diff} \frac{N_{mol}^{voxel}}{N_{hits}} \quad (3.7)$$

N_{hits} is the total number of particles that is necessary to dissolve one voxel comprised of N_{mol}^{voxel} moles of the dissolving mineral. Equation 3.7 establishes a direct relationship between the batch dissolution rate and the flux of particles necessary to dissolve the solid voxels. Using the definition of λ (eq. 1.12) we finally write:

$$N_{hits} = \frac{\sqrt{6}}{4} \sqrt{\frac{D_m C N_{mol}^{voxel}}{\Delta t r}} \quad (3.8)$$

Thus, N_{hits} is explicitly written in terms of physically meaningful variables: diffusion coefficient, time-step, particle concentration, moles of calcite per voxel and, crucially, the batch reaction rate. It represents the total number of particles necessary to dissolve a given amount of calcite. In realistic 3D geometries, solids with more than one face exposed dissolve faster than the ones with only one exposed face, since they receive particle hits through any of its free faces.

In summary, in a first-order surface reaction, dissolution is proportional to the local flux of particles at the pore-solid walls, which in turn is determined by diffusion. The flux is calculated by counting the number of particles that cross from the surrounding pore voxels to a specific solid voxel. The goal is to represent conditions under which the fluid is constantly undersaturated⁴, thus implying that the

⁴If the rock is a carbonate, the saturation refers to the concentration of Ca^{2+} , produced during calcite dissolution

flux of particles is from the pore to the solid. Once a particle crosses the solid-fluid interface it reacts (it is removed from the simulation) and the number of hits which that particular solid voxel has received is updated. After a given number of hits (emulating the reaction rate), the solid voxel is dissolved into a pore voxel.

3.4 Dissolution of a planar front

This section applies the particle-based model developed in the preceding section to the reaction-controlled dissolution of a rod of square cross-sectional area.

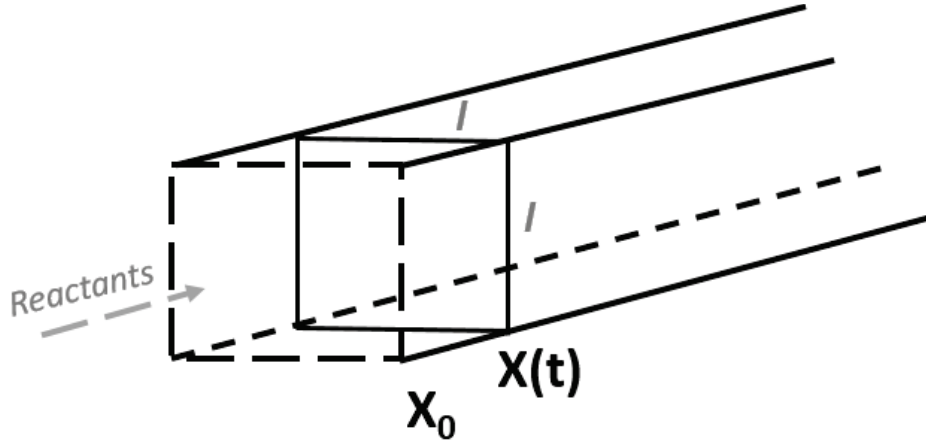


Figure 3.5: One end of a rod of square cross-section of area l^2 is dissolved by a fluid with constant concentration of reactants. The kinetics is reaction-controlled.

The rod is discretized in voxels of side length l , the cross-section has one voxel. One end is put into contact with a stagnant solution with constant concentration of reactants (C), which dissolves the solid phase with a given surface rate r [$\text{mol.m}^{-2}.\text{s}^{-1}$]. There is no dissolution on the sides, figure 3.5. When the diffusive transport is much faster than the reaction kinetics, then the interface concentration is equal to the bulk concentration – there are no concentration gradients. The dissolution is reaction-controlled and the dissolution flux is fully described by the reaction flux. Assuming that the material has a molar density n [mol.m^{-3}], the volume variation of the rod is readily obtained:

$$\frac{dV}{dt} = l^2 \frac{r}{n} \quad (3.9)$$

If the cross sectional area stays constant:

$$\frac{dX}{dt} = \frac{r}{n} \quad (3.10)$$

where X is the position of the rod extremity. The position of the solid-liquid interface as a function of time is then written as:

$$X(t) = X_0 + \frac{r}{n}t \quad (3.11)$$

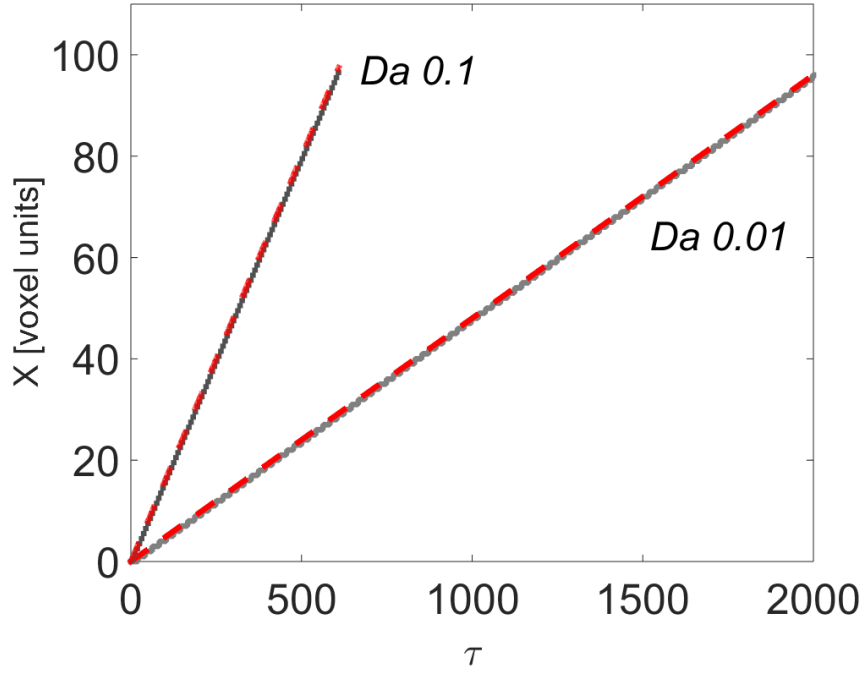


Figure 3.6: Evolution of the position of the rod interface with non-dimensional time – analytical results (eq. 3.11, dashed red lines) and simulation (solid grey lines). Dissolution is reaction-controlled – $Da < 1$.

For this system, the diffusive Damköhler number⁵ is defined as:

$$Da_{II} = \frac{rl}{nD_m} \quad (3.12)$$

Figure 3.6 shows a comparison between the predicted position of the interface according to eq. 3.11 and the simulated positions according to the model described in the previous section, both plotted against the non-dimensional time $\tau = tD_m/l^2$. The simulations were performed with $N_p = 100$ particles and the time step was determined as $\Delta t = l^2/24D_m$, thus limiting the displacement to $l/2$. When a particle hits the rod, it reacts and is removed from the simulation, simultaneously, another particle is placed at random in the voxel adjacent to the rod end, thereby keeping the concentration constant and avoiding the development of a concentration gradient. This is consistent with a reaction-controlled kinetics. The agreement between the simulation and the analytical solution is excellent. The staircase-like aspect of the simulated curve is due to the interface being displaced in discrete jumps.

⁵Not to be confused with the *advective* Damköhler number, introduced previously and used to characterize reactions in the presence of a moving fluid.

3.5 Calcite Dissolution in CO₂-saturated Fluids

This section describes the kinetics of calcite dissolution in CO₂-acidified brines and a possible physical interpretation about the nature of the particles for the case of calcite dissolution.

In the experiment of Menke et al. [2015], which will be used later in this chapter to validate our model, a CO₂-equilibrated brine of deionized water in which 1% wt.KCl and 5% wt.NaCl are dissolved is injected into a carbonate core. This section summarizes the main reactions occurring in the CO₂-brine-calcite system.

The kinetics of calcite dissolution is largely determined by the acidity of the brine, which is described in terms of the pH, defined as the logarithm of the H⁺ activity: $\text{pH} = -\log[\text{H}^+]$. Using the method by Leal et al. [2014] results in $\text{pH}=3.1$ for the injected brine, which indicates that the brine is very acidic. Salinity is not expected to have a major influence on the dissolution kinetics. In particular, Wolf-Gladrow et al. [2007] showed that, even for seawater – which has a much higher salinity ($\sim 30000\text{ppm}$) than the brine we use ($\sim 400\text{ppm}$) – the dominant carbonate species is $\text{H}_2\text{CO}_3^* \leftrightarrow \text{CO}_{2(sc)} + \text{H}_2\text{O}$ for $\text{pH} \leq 5.9$. This scenario (kinetics dominated by the CO₂species) was confirmed by Menke [2016], who calculated the activities of the dissolved species at the experimental conditions, table 3.1. The activity of the dissolved species deriving from halite (NaCl) and sylvite (KCl) are, at least, one order of magnitude lower than that of H_2CO_3^* . Thus, establishing that, at the low pH conditions of interest for this work, the dominant ion in the system is H_2CO_3^* . This allow us to ignore the salinity effects on the dissolution of calcite in the CO₂-acidified brine.

Species	Activity
H ⁺	8.7×10^{-4}
H ₂ O _(l)	9.5×10^{-1}
Cl ⁻	6.2×10^{-1}
K ⁺	8.2×10^{-2}
Na ⁺	6.6×10^{-1}
H ₂ CO ₃ [*]	1.0×10^0

Table 3.1: Species activities in the brine used in the experiment of Menke et al. [2015]. The dominant ion is H_2CO_3^* . Modified from Menke [2016].

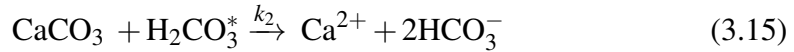
Dissolution or precipitation of a mineral dissolved in water is controlled by the saturation index [Lasaga, 1998]:

$$SI = \log \left[\frac{Q}{K_{eq}} \right] \quad (3.13)$$

where K_{eq} is the equilibrium constant and Q is the ion activity product. For example, in the case of halite dissolving into water: $\text{NaCl} \leftrightarrow \text{Na}^+ + \text{Cl}^-$, and $K_{eq} =$

$[\text{Na}^+]_{eq}[\text{Cl}^-]_{eq}$, and $Q = [\text{Na}^+][\text{Cl}^-]$. When $SI = 0$, the system is at equilibrium and neither dissolution nor precipitation occurs. Menke [2016] calculated $SI = -1.99$ for NaCl, and $SI = -2.32$ for KCl. Both salts are under-saturated: no precipitation will occur.

In the presence of CO_2 -saturated water, the kinetics of calcite dissolution is described by the following chemical reactions, occurring in parallel at the solid surface [Peng et al., 2015; Pokrovsky et al., 2005; Chou et al., 1989]:



where k_1 , k_2 and k_3 are the rate constants. In the context of the transition state theory, the overall intrinsic dissolution rate (r [$\text{mol.m}^{-2}.\text{s}^{-1}$]) at far from equilibrium conditions is then written as a function of the rate constants and the activity of the aqueous species ($\alpha_{\text{H}^+}; \alpha_{\text{H}_2\text{CO}_3}$): $r = k_1 \alpha_{\text{H}^+} + k_2 \alpha_{\text{H}_2\text{CO}_3} + k_3$. Under the conditions of flow and reaction of interest for this work, the concentration of the aqueous species is nearly constant. This will allow us to simplify the reaction behaviour and describe it in terms of a single species, as described below.

The solute concentration (with units of number of particles per volume) of a reactive tracer in a system controlled by one single chemical species and described by first-order kinetics satisfies the advection-diffusion-reaction equation [Lasaga, 1998]:

$$\frac{\partial C}{\partial t} + \vec{V} \cdot \nabla C = D_m \nabla^2 C + K_{eff} (C_{eq} - C) \quad (3.17)$$

where C_{eq} is the equilibrium concentration of the solute in the liquid phase and $K_{eff} = \frac{S_A}{V} \frac{r N_A}{C_{eq}}$ is the effective rate coefficient (in [s^{-1}]), expressed as a function of $\frac{S_A}{V}$, the interfacial area per unit of rock volume and N_A , Avogadro's constant. Dissolution occurs when $C < C_{eq}$, and precipitation when $C > C_{eq}$. The term $(C_{eq} - C)$ represents a deviation from equilibrium and we rewrite eq. 3.17 in terms of a new variable $C^* = C_{eq} - C$:

$$\frac{\partial C^*}{\partial t} + \vec{V} \cdot \nabla C^* = D_m \nabla^2 C^* - K_{eff} C^* \quad (3.18)$$

Note the change of the sign of the last term, implying that C^* decreases during dissolution. From eq. 3.18 it is evident that the equilibrium concentration in terms of the new variable is $C_{eq}^* = 0$. A Lagrangian approach to the problem of reactive transport replaces eq. 3.18, governing the evolution of the solute concentration, with equations for the particle trajectories (eq. 1.9), as discussed in section 1.3.2. The

reaction term of eq. 3.18 is defined by the flux of particles through the interface, as explained in section 3.3.

Under slow reactions (i.e. low Damköhler number), pH gradients in the pore space are insignificant (see section 3.1.1) and we describe the kinetics of calcite dissolution solely as a function of the Ca^{2+} concentration in the liquid phase, which is conveniently written in terms of particles using the variable C^* introduced above. Hence, the particle concentration represents the Ca^{2+} undersaturation, or the deviation from the equilibrium concentration in the liquid phase. As stated before, the fluid is in equilibrium with respect to the solid when $C^* = 0$ and no dissolution occurs, as expected, since the net flux of particles to the solids is zero. When simulating the injection of a fluid out of equilibrium with the rock, it is more natural to describe the reactions in terms of C^* rather than C : particles are injected at the inlet, representing the absence of calcium ions and hence the fluid moves from equilibrium and the reaction starts; the density of particles represents the value of C^* . The higher the particle concentration, the further from equilibrium the fluid is. Furthermore, associating the particles with the absence of Ca^{2+} rather than with Ca^{2+} itself requires fewer particles to be tracked, which is more efficient computationally.

In more general terms, eq. 3.17 describes instantaneous reactions, where the rate coefficient describes the kinetics in the limit $\Delta t \rightarrow 0$. Considering a reaction of the form $A + B \rightarrow C$, then K_{eff} is the slope of the product concentration: $K_{eff} = -d[C]/dt$ and it is assumed constant in eq. 3.17. In reality, K_{eff} is a function of the concentration (and of time), and when considering transport and reactions occurring over long periods of time, it has to be adjusted to account for changes in the reactivity of the system as a function of time [Lasaga, 1998]. Extending this kind of description to reactions occurring at longer time-scales requires accounting for changes in K_{eff} over time. In the context of naturally occurring reservoirs and soils, this is not straightforward. The estimation of weathering rates requires the collection and analysis of detailed rock and fluid data and it is still an area of active research [Maher, 2010; Steefel and Maher, 2009; Maher et al., 2004]. In the particle approach, non-instantaneous reactions could be addressed by introducing a reaction probability (P), which decreases the rate of reaction once two particles (or a particle and a solid) come into contact, subjected to $P = 1$ when $K_{eff} \rightarrow \infty$. In numerical implementations, this constrains the time-step.

3.5.1 Alternative physical interpretations for the particles

The preceding section discussed the possibility of interpreting the solute particles as a measure of the Ca^{2+} undersaturation relative to equilibrium, when describing calcite dissolution. However, this is not the only interpretation. In the most common conditions of pressure and temperature in subsurface reservoirs, the rate constants

(k_1, k_2, k_3) are very dissimilar: $k_1 \gg k_2 \gg k_3$ and the system of reactions described by eqs. 3.14 – 3.16 can be simplified, yielding $r \approx k_1 \alpha_{H^+}$ [Chou et al., 1989; Peng et al., 2015]. In this case, the particles could be interpreted as H^+ ions colliding with the solids, and their concentration would be related to pH of the solution. Albeit tempting, this alternative has two drawbacks. Firstly, it is limited to systems where $k_1 \gg k_2 \gg k_3$ and secondly, it would require more particles in the system to represent the neutral pH, which cannot be associated with a zero concentration⁶. Hence the interpretation in terms of a "disequilibrium concentration" is preferred and was adopted in this work.

3.6 Modelling carbonate dissolution using dynamic imaging data

To validate and assess the predictive power of the method we test it against the results of the dynamic imaging experiment conducted at reservoir conditions by Menke et al. [2015]. The experiment was performed on a sample of Ketton carbonate, a relatively homogeneous, oolitic limestone. Figure 3.8 shows the pore space superimposed with the corresponding horizontal flow velocity calculated directly on the segmented image and semi-analytical streamlines traced from inlet to outlet. A core of 4mm diameter was flooded with a CO_2 -saturated brine at 10MPa and $50^\circ C$, pH = 3.1, figure 3.7. Micro-CT images were acquired after seventeen, thirty three and fifty minutes of flow and reaction, then segmented and compared to the simulations.

3.6.1 Experimental conditions and simulation parameters

The simulation is performed on a cubic lattice – dimensions $455 \times 451 \times 461$, with voxel size of $7.6 \mu m$ – obtained from an upscaled, segmented micro-CT image acquired prior to flow and reaction. While originally registered with a $3.8 \mu m$ voxel size, we run the model on a coarser grid to save computational time. The initial surface area – the product of the number of voxel faces separating grains from pores and the cross sectional area of the voxels – is $S_A = 2.5 \times 10^{-4} m^2$ and the image-computed porosity (ϕ) and permeability (k) are 0.163 and 13.4D, respectively. These values are different from those obtained on the finer-resolution images, where the average porosity was 0.172 and the surface area was $3.4 \times 10^{-4} m^2$. Increasing the resolution of the scan allows more of the small-scale porosity and surface area to be resolved.

⁶From the definition of pH: $pH = -\log [H^+]$. Of course when the concentration is zero, the pH is not 7 (neutral).

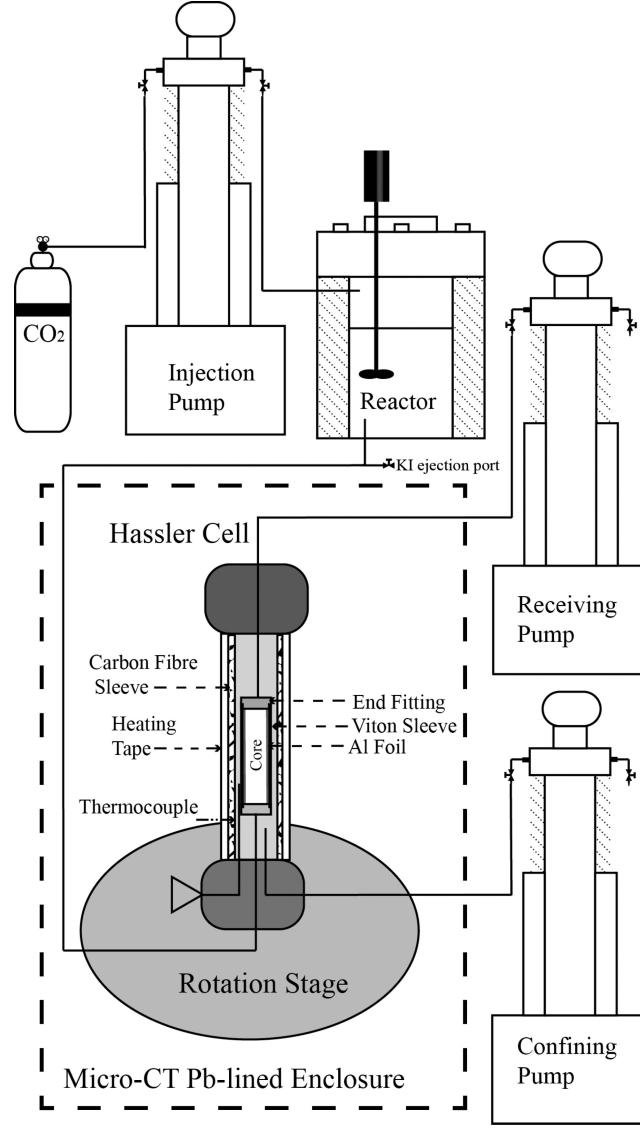


Figure 3.7: Apparatus for the experiments against which we compare our results: the core holder is kept inside the micro-CT scanner, a series of pumps are used to inject the saturated brine, control the flow and maintain the pressure. The entire experiment is conducted at at 10 MPa and 50°C, from Menke et al. [2015].

To establish the number of hits to dissolve (eq. 3.8), we take the independently measured intrinsic rate of calcite dissolution at the experimental pressure and temperature conditions using a rotating disc apparatus with a single calcite crystal – $r = 8.1 \times 10^{-4} \text{ mol.m}^{-2}.\text{s}^{-1}$ [Peng et al., 2015], and the molecular diffusion coefficient of Ca^{2+} , $D_m = 7.5 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$ [Luquot and Gouze, 2009]. The solid voxels are assumed to be pure calcite, a very good approximation for the Ketton oolite, composed of 99% calcite [Andrew et al., 2014b]. Micro and intragranular porosity may constitute a relevant portion of the pore space in carbonate rocks, Lucia [2007]. Together with surface rugosity, they are usually below the resolution of the micro-CT scanners. However, such sub-resolution rock attributes can be taken into account in the model by introducing the grain porosity (ϕ_{grain}), which corrects

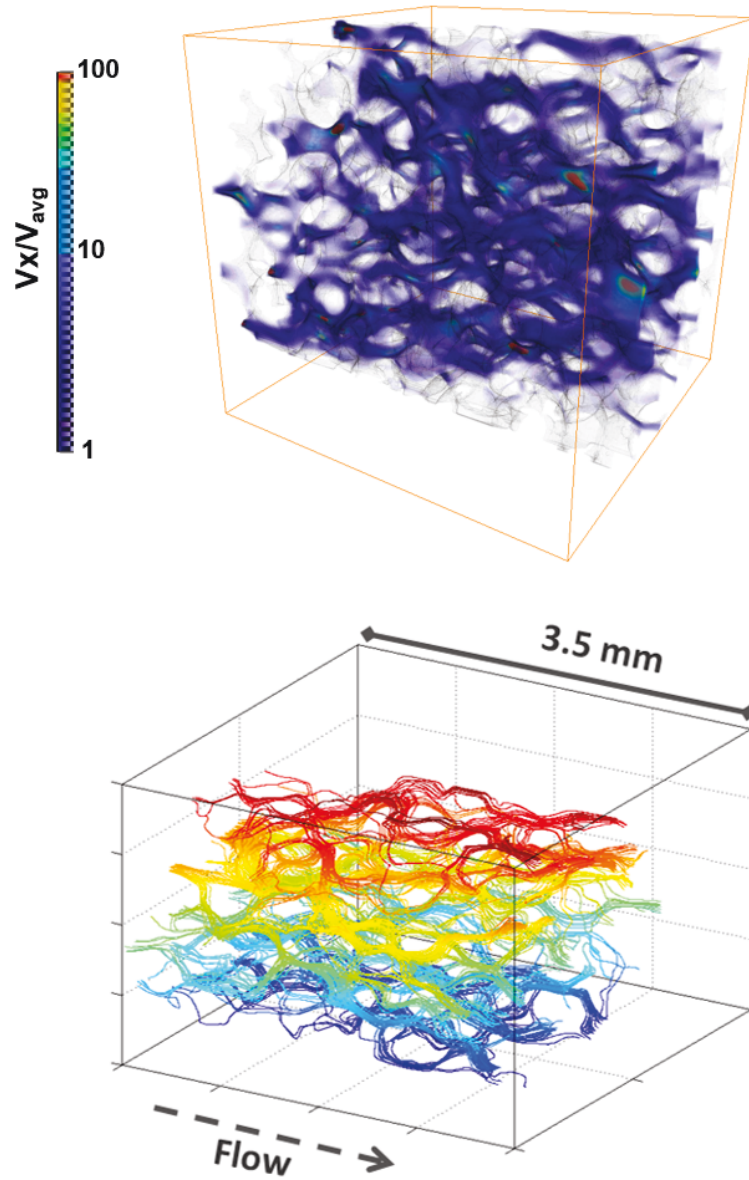


Figure 3.8: Top, three-dimensional segmented image of a Ketton carbonate superimposed with the velocity along the flow direction. The pore space is shown in grey. Bottom, streamlines traced using a pore-scale semi-analytical method in the pore space reconstructed from the micro-CT and coloured by vertical coordinate. Solute particles move from left to right following streamlines due to advection. Diffusion and reaction are then incorporated as shown in figure 1.12.

the number of calcite moles present in the solid phase. Grain porosity is calculated by comparing the helium porosity (ϕ_{HP}) with the micro-CT porosity (ϕ), the difference between both being attributed to sub-resolution porosity located in the grains

$$\phi_{grain} = \frac{\phi_{HP} - \phi}{1 - \phi} \quad (3.19)$$

Using the data from Andrew et al. [2014b] we have $\phi_{grain} = 0.12$ in the Ketton carbonate and the effective number of calcite moles in the solid voxels is:

$$N_{mol}^{voxel} = nl^3(1 - \phi_{grain}) \quad (3.20)$$

where l^3 is the voxel volume and $n = 2.71 \times 10^4 \text{ mol.m}^{-3}$ is the calcite molar density [Wenk and Bulakh, 2004]. Finally, the number of calcite moles in each solid voxel is obtained according to eq. 3.20, resulting in $N_{mol}^{voxel} = 10.56 \times 10^{-12} \text{ mol}$.

Péclet and Damköhler numbers

The experiment was conducted at a fixed flow rate of 0.5 mL/min, corresponding to $q = 660 \mu\text{m/s}$; the same was also imposed during the simulations. Under these conditions, the Péclet number (eq. 3.1) at the beginning of the experiment is $Pe = 2300$. After fifty minutes it decreases to 1500 due to the increase in porosity.

To estimate the Damköhler number (eq. 3.3) we take $n = n_g = 2.39 \times 10^4 \text{ mol.m}^{-3}$ as the number of moles of calcite per cubic metre in the Ketton grains: $n_g = n(1 - \phi_{grain})$. At the experimental conditions Da increases from 3.2×10^{-5} when starting the flow to 5.0×10^{-5} after fifty minutes, the same is valid for the simulations. $PeDa$ stays approximately constant during the entire experiment (and simulation) – $PeDa = 7 \times 10^{-2}$. A summary of the image, flow and reaction parameters is presented in table 3.2.

Under the experimental conditions, while advection dominates over diffusion, $Pe \gg 1$, diffusion is faster than reaction in the vicinity of the grain surfaces, $PeDa \ll 1$. When Pe is large and $PeDa$ small, as in our particular case, the solute renewal rate is high (conversely, the residence time is short) and the fluid is constantly out of equilibrium with respect to the solid. Hence, there is not enough time for the development of pH and concentration gradients within the pore space. To illustrate this, we perform a simulation in a subsample of the Ketton carbonate, injecting 1.2×10^6 particles while keeping the average flow velocity the same as in the experiment. The results are shown in figure 3.9, which is consistent with the two-dimensional results of Li et al. [2008]. Furthermore, advection-dominated transport and reaction-limited reaction favour the development of a mostly uniform dissolution and the experimental data – section 3.6.3 – show that dissolution spreads across the sample.

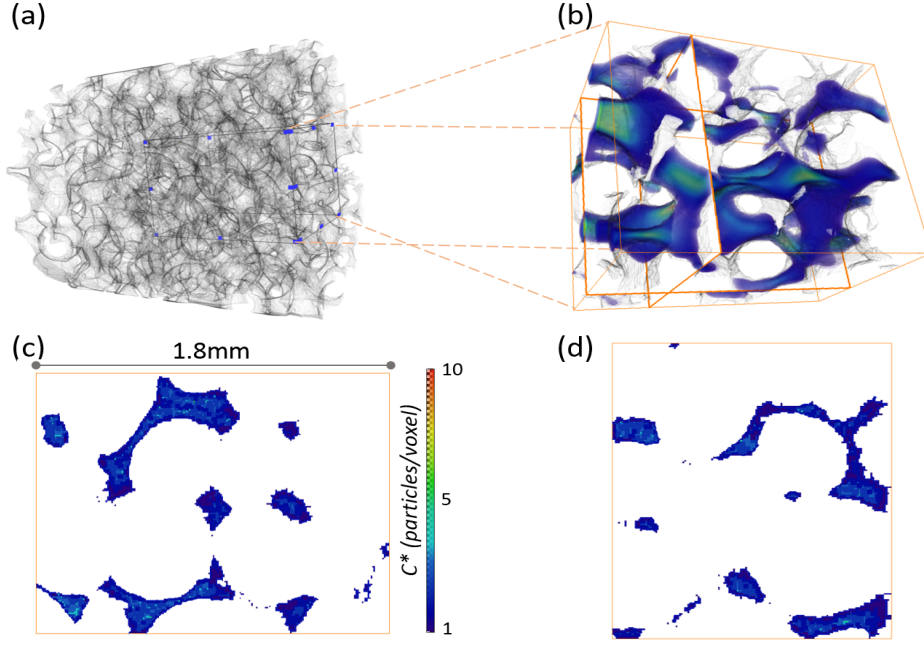


Figure 3.9: A subvolume of the Ketton carbonate (a) is used to study particle concentration gradients in the pores. We compute the flow field (b), and keep the average velocity the same as in the experiment. The conditions of flow and reaction are such that $Pe \gg 1$ and $PeDa \ll 1$: the system is strongly transport-dominated and dissolution is reaction-limited. Thus, the instantaneous particle concentration, indicated by the colour scale, is approximately uniform, in both the axial (c) and radial (d) directions.

This is in agreement with previous results in the literature, e.g. Golfier et al. [2002] or Luquot and Gouze [2009].

3.6.2 Simulation procedure

To initialize the simulation, 2.0×10^4 particles are injected with a flow weighted rule at the inlet and the flow rate is kept constant at 0.5 mL/min. When a particle exits the domain either by diffusion or advection, or crosses the pore-solid interface, a new particle is injected at the inlet, keeping the number of particles constant and representing constant sample-averaged pH conditions. This is consistent with a high velocity flow where there is a constant replenishing of solute. It should be noted that, in our specific case, the rock dissolution is not limited by the amount of solute injected, but by the specifics of flow controlling the contact of the particles with the solid phase.

Due to the evolving pore space geometry caused by the reactive flow, the velocity field must be updated. Since dissolution is distributed throughout the sample, we assume a quasi-steady regime where small local increases in porosity do not lead

to large variations in the global pressure field. The velocity field is updated only after the porosity increment ($\Delta\phi$) is above a certain threshold, thus saving computational time. We established that $\Delta\phi \geq 0.001$ is a good compromise between performance and accuracy; choosing a smaller $\Delta\phi$ did not affect our results, figure 3.10. We also studied the sensitivity of the results to the number of particles and the size of the time-step. The time-step is fixed such as the maximum diffusive displacement is equal to half of the voxel size. This is sufficiently small for the results to be independent of its exact value; similar findings have been reported by S  lles et al. [1993]. The number of hits to dissolve is proportional to the particle concentration, this imposes a lower bound on the number of particles, since we demand $N_{hits} > 1$ throughout the sample. However, once this condition is met, there is no need for a large number of particles, figure 3.11. The kinetics is independent of it; an increase in the number of particles leads to an increase in N_{hits} , which is counterbalanced by an increase in J_{diff} . In fact, this is one advantage of the method: it does not require a large number of particles to obtain meaningful results.

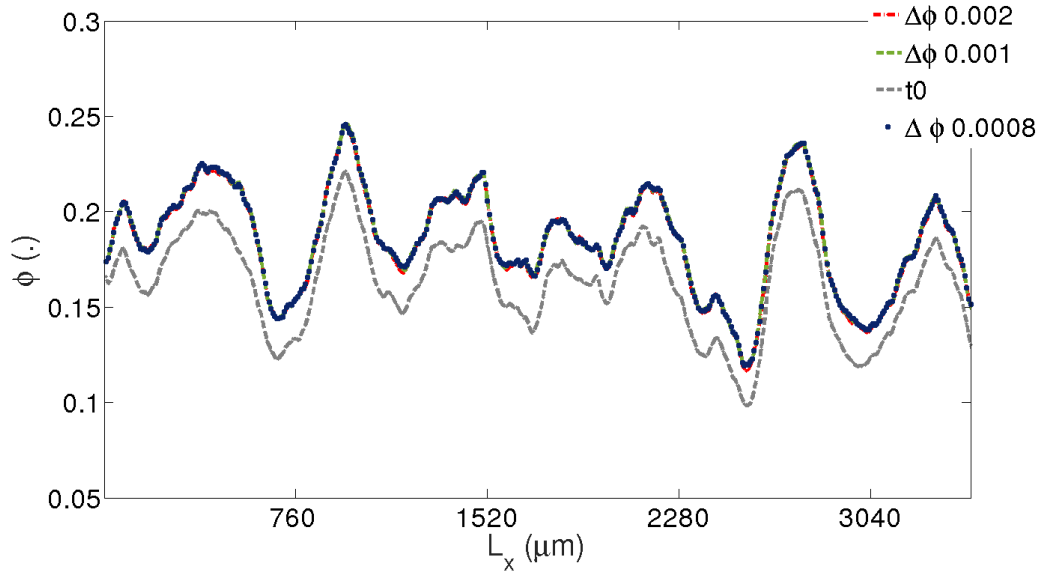


Figure 3.10: Slice-averaged porosity profiles along the flow direction after fifteen minutes of injection. Results are stable upon the choice of the porosity increment that controls the frequency of the flow field updates.

Number of hits and concentration profile

Given that the flow field is steady between updates and that reacting particles are killed and reinjected at the inlet, the particle concentration profile along the direction of flow is also (quasi-) steady. The particle concentration is higher at the inlet than at the outlet. To make the reaction rate uniform throughout the sample, as suggested by the low value of Da and the experimental results, and to eliminate

Parameter	Symbol	Value	SI units
Number of voxels	-	$455 \times 451 \times 461$	-
Voxel size	l	7.6×10^{-6}	m
Number of injected particles	N_p	2.0×10^4	-
Initial micro-CT porosity	ϕ	0.163	-
Initial micro-CT permeability	k	13×10^{-12}	m^2
Initial surface area	S_A	2.5×10^{-4}	m^2
Initial characteristic length	L	4.2×10^{-4}	m
Darcy velocity	q	660×10^{-6}	m.s^{-1}
Diffusion coefficient	D_m	7.5×10^{-10}	$\text{m}^2.\text{s}^{-1}$
Péclet number (eq. 3.1)	Pe	2300 – 1500	-
Damköhler number (eq. 3.3)	Da	$(3.2 - 5.0) \times 10^{-5}$	-
Péclet times Damköhler number	$PeDa$	7×10^{-2}	-
Ketton grains calcite moles per unit volume	n	2.39×10^4	mol.m^{-3}
Batch calcite dissolution rate	r	8.1×10^{-4}	$\text{mol.m}^{-2}.\text{s}^{-1}$

Table 3.2: List of image and simulation parameters. Quantities in bold are the input to the simulations. The remaining are derived from them together with the image geometry and the flow field.

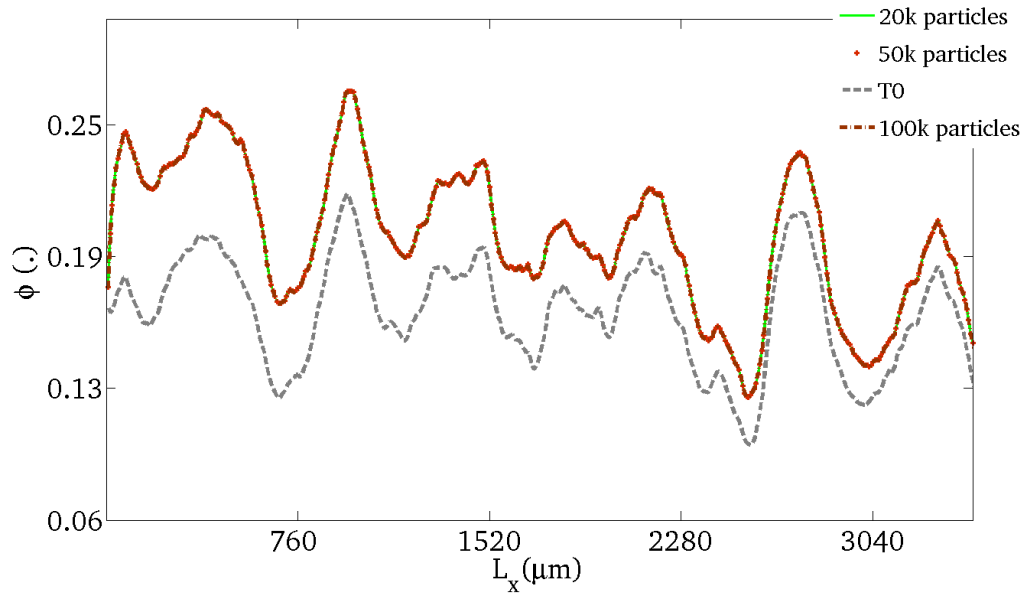


Figure 3.11: Slice-averaged porosity profiles after fifteen minutes of reaction. The dissolution kinetics is independent of the number of particles used in the simulations.

spurious boundary effects, we introduce a correction in the number of hits to dissolve. Equation 3.8 is modified replacing the volumetric particle concentration (C) with $\bar{C}(s_x)$, the slice-averaged concentration of solute,

$$N_{hits}^{eff}(s_x) = \frac{\sqrt{6}}{4} \sqrt{\frac{D_m}{\Delta t}} \frac{\bar{C}(s_x) N_{mol}^{voxel}}{r} \quad (3.21)$$

where s_x stands for the tomographic slice number in the flow direction. This is fundamentally a way of keeping the ratio N_{hits}/C (and hence the reaction rate) constant throughout the sample. The drawback of using eq. 3.21, is that the number of hits to dissolve becomes a function of the position along the sample axis. Thus, the particles do not have a straightforward stoichiometric interpretation: the amount of mineral moles being dissolved by one particle hit varies along the axis of flow. Of course, if the particle concentration is somehow uniform (e.g. by randomly placing particles in the volume), then eq. 3.21 reduces to eq. 3.8. For the Ketton rock under the experimental conditions, N_{hits}^{eff} ranges, on average, from 20 at the inlet to 11 at the outlet.

An outline of the algorithm is shown in figure 3.12, and its main steps are summarized below:

1. Inject particles at the inlet using a flow weighted rule.
2. Advance particles along streamlines traced with the modified Pollock algorithm.
3. Perform diffusion by a random walk; if a particle hits a solid, reinject a new one at the inlet.
4. When the number of hits on a particular solid voxel is equal to N_{hits}^{eff} (eq. 3.21) dissolve solid (change the solid to void) and update the porosity.
5. Repeat steps 2 - 4 for every particle and time step.
6. Update the flow field when $\Delta\phi \geq 0.001$ and update the number of hits to dissolve (eq. 3.21) to reflect the new particle concentration profile.
7. Repeat steps 2 - 6 until the end of the simulation.

3.6.3 Results and discussion

We compare our predicted reaction-altered pore space geometries to the ones obtained experimentally after seventeen, thirty three and fifty minutes of flow and reaction. Figure 3.13 shows the three-dimensional distribution of the dissolution front in the experimental and simulated images. A summary of image-calculated

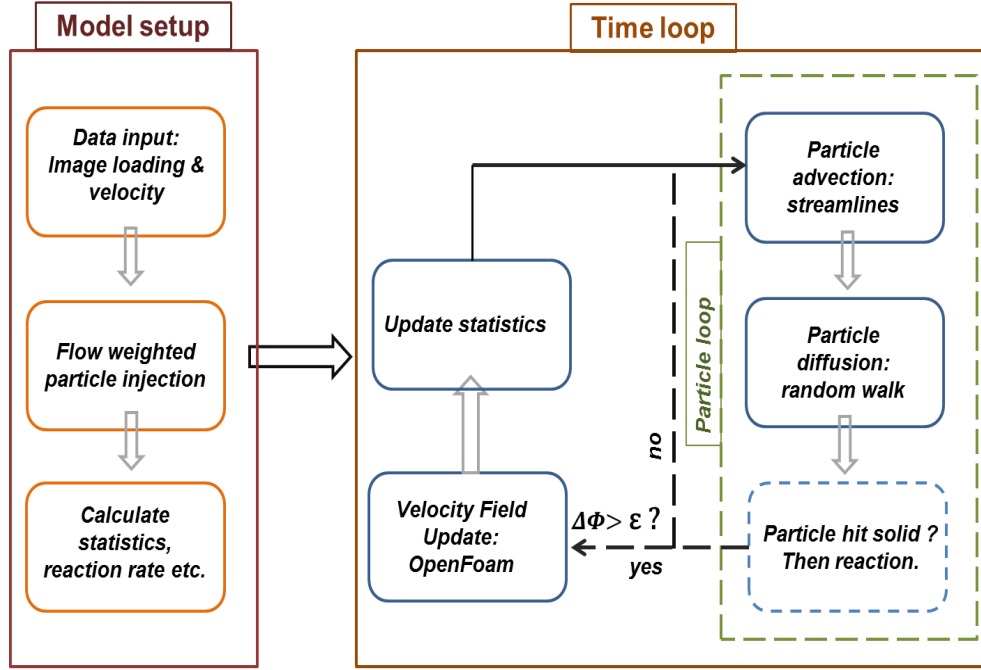


Figure 3.12: Outline of the advection-diffusion-reaction algorithm.

porosities and permeabilities is presented in table 3.3 and in figure 3.14; the agreement between simulation and experiment is very good. As we show later, we find preferential dissolution in some of the narrower pores and tighter portions of the rock that are initially constraining the flow - as a result the permeability increases sharply with a relatively small increase in overall porosity. After fifty minutes the experimental and simulated porosities increased approximately 50%, while the corresponding increase in the computed permeability was much higher, $\approx 500\%$ in the experiment and $\approx 550\%$ in the simulation. We attribute this overestimation in the simulated permeability to small, localized overpredictions in porosity that are amplified in the permeability calculation. Fitting a power law, we find that permeability scales as $k \propto \phi^{4.5}$ in the experimental images and as $k \propto \phi^{4.4}$ in the simulated images. Predominantly, the increase in permeability is the result of pore throats being enlarged throughout the whole sample, as will be discussed later. Marked increases in permeability following homogeneous rock dissolution have also been reported by Lamy-Chappuis et al. [2014] and Vialle et al. [2014].

Not only the increase in the bulk porosity is matched, but also its variation across the sample, as seen in figure 3.15, which compares the experimental and predicted slice-averaged micro-CT porosities along the flow axis and their changes in relation to the porosity prior to flow. Figure 3.16 shows the relative changes in porosity – the change in porosity divided by the initial porosity – and we note a tendency for dissolution to be higher in the tighter regions of the rock, which correspond to the troughs in the slice-averaged porosity curve. This could be an effect of the

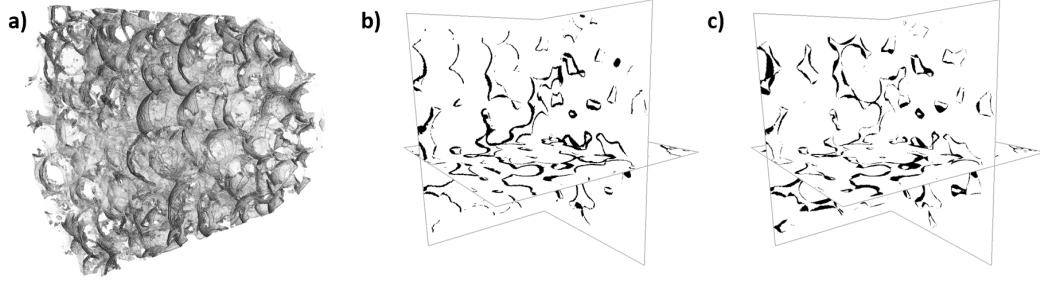


Figure 3.13: Time-lapse image showing the dissolved portions of the Ketton carbonate after fifty minutes of flow and reaction with a CO_2 -saturated brine (a). Orthogonal slices showing the dissolution (in black) – experimental (b) and simulated (c) images. Conditions of flow are such that an almost uniform dissolution occurs (b) and our simulation captures this pattern when using the same experimental conditions (c).

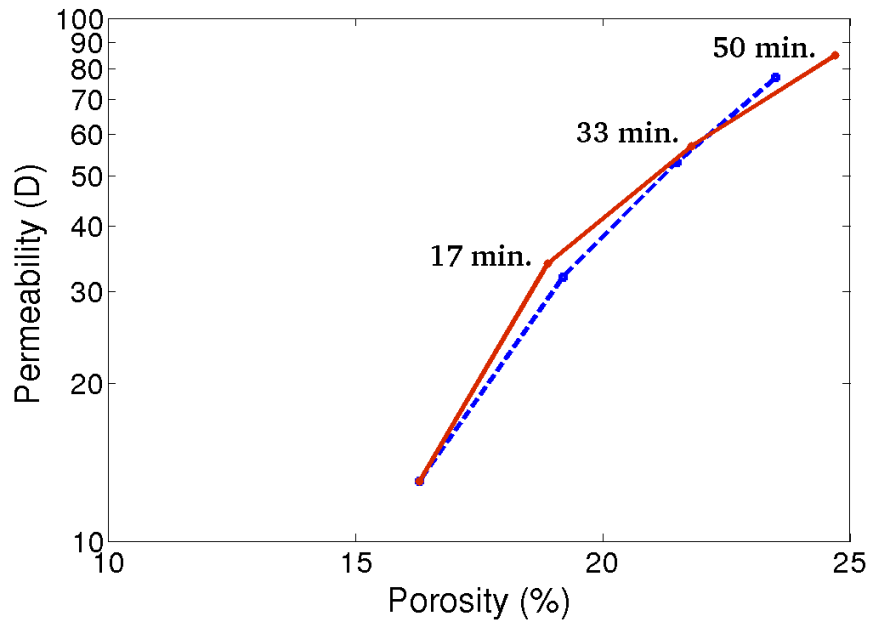


Figure 3.14: Evolution of porosity and permeability following injection of CO_2 -enriched brine in the Ketton carbonate. The dashed blue line shows the computed permeability based on the experimentally-measured images while the red line shows the predictions from our simulations.

increase in solute flux in the pore-throats. Our simulation captures this aspect of the reactive flow and we point out that the positions of the peaks in the experimental and simulated curves coincide, despite some slight disagreement in the amplitude of the change. As discussed in the previous paragraph, the preferential dissolution of tight channels manifests itself as a steep increase in permeability.

In figures 3.17, 3.18 and 3.19 we compare slices – parallel and perpendicular to the core axis – taken from both the experimental and predicted 3D images after

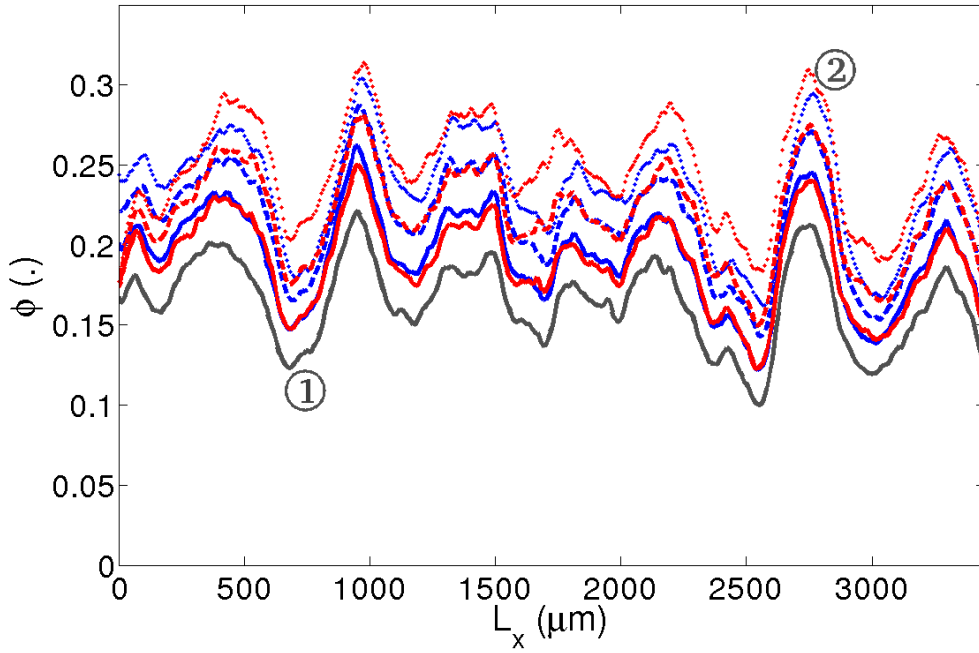


Figure 3.15: Slice-averaged porosity profiles along the direction of flow before injection (solid gray) and after seventeen (solid lines), thirty three (dashed lines) and fifty minutes (dotted lines) of injection. There is good agreement between the experimental (blue lines) and simulated (red lines) results. Our simulation method is capable of capturing in detail the variation of dissolution across the whole sample. The numbers 1 and 2 mark the position of the slices shown in figures 3.17, 3.18 and 3.20.

reactive flow. They depict the shrinking of the calcite grains and demonstrate an excellent agreement between model and experiment, as our model reproduces the measured dissolution patterns in both the radial and axial directions. It is also worth noticing that, as mentioned earlier, in high velocity flows such as this, the dissolution front is expected to reach the whole of the pore space, which is confirmed by the experimental results and reproduced in our simulations. The increase in porosity is attributed to the calcite cement and grains being continuously dissolved and no evidence of wormhole formation is seen.

To illustrate the relationship between the flow field and dissolution, we plot the predicted change in pore structure after thirty three minutes and superimpose the local magnitude of the flow field, figure 3.20. The local dissolution rate is controlled by a subtle balance between advection, diffusion and reaction in the pore space. It appears that we see generally most dissolution in portions of the pore space with the greatest gradient in flow speed perpendicular to the solid surface. Diffusion allows solute to reach the solid, while a nearby fast, or even moderate, flow provides fresh solute for reaction. As discussed above, there tends to be more dissolution in regions of higher flux, where solute is forced through narrower restrictions, allowing greater

<i>time (min.)</i>	Experimental		Simulation	
	ϕ (.)	$k(D)$	ϕ (.)	$k(D)$
0	0.163	13	0.163	13
17	0.192	32	0.189	34
33	0.215	53	0.218	57
50	0.235	77	0.247	85

Table 3.3: Time evolution of the experimental and simulated image porosities (ϕ) and permeabilities (k). By construction the experiment and simulation agree at the beginning.

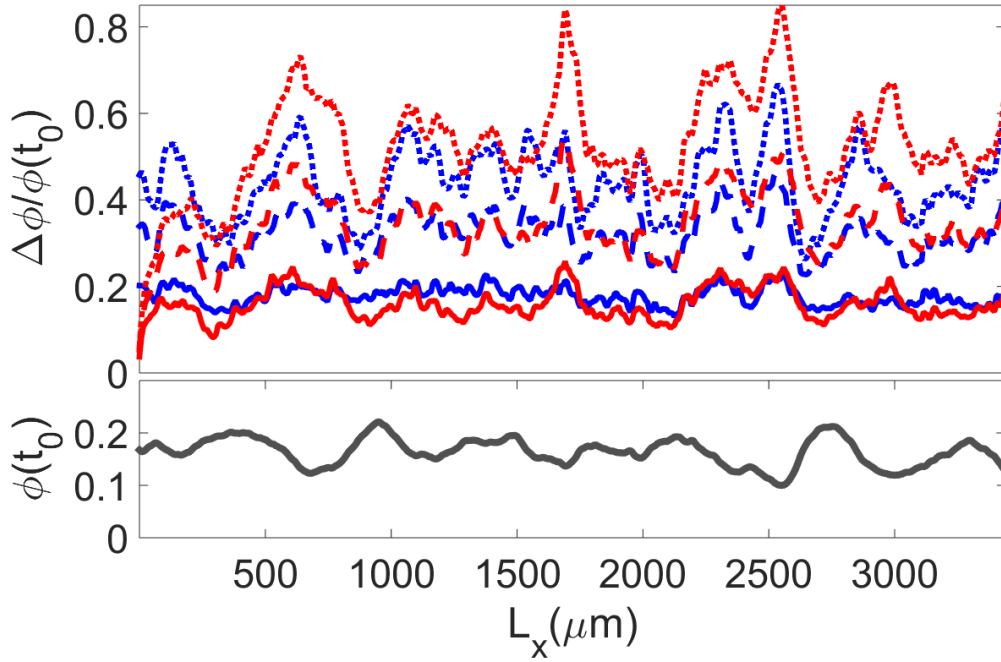


Figure 3.16: Slice-averaged relative porosity difference – top figure, experimental results in blue, simulation in red – after seventeen (solid lines), thirty three (dashed lines) and fifty minutes (dotted lines) of injection. There tends to be more dissolution in the lower porosity slices; the initial porosity is shown in the bottom figure.

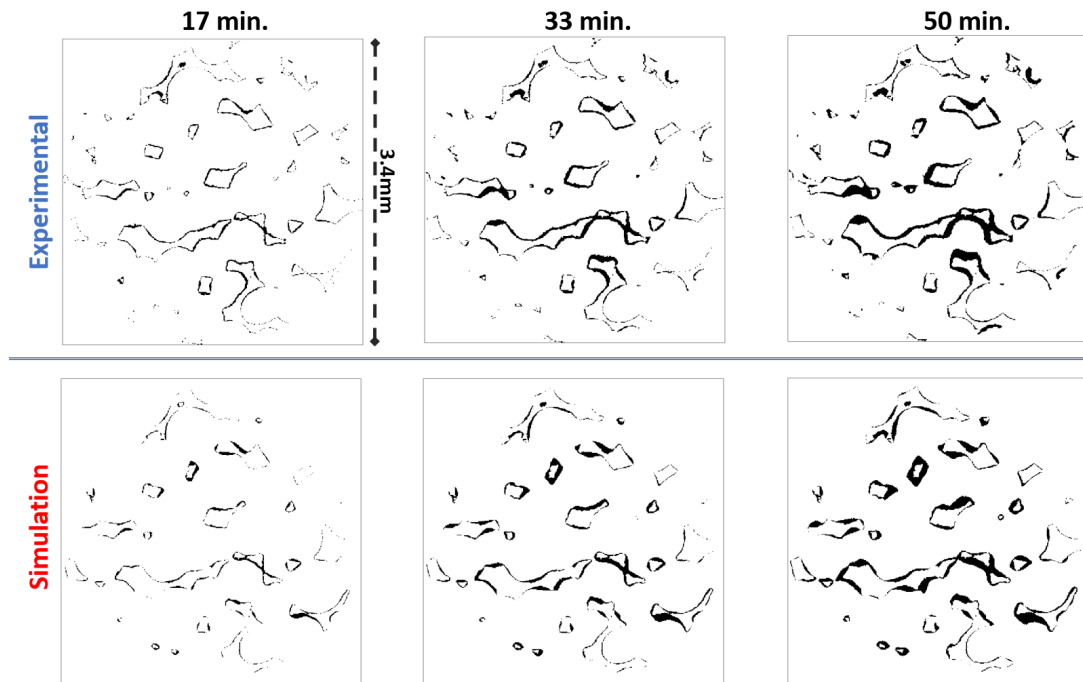


Figure 3.17: Experimental (top row) and modelled (bottom row) results showing the dissolved portions of the rock (in black are the differences relative to the image before reaction) after seventeen, thirty three and fifty minutes of reaction. Slices are taken perpendicular to flow from a low porosity portion of the sample - position 1 in figure 3.15.

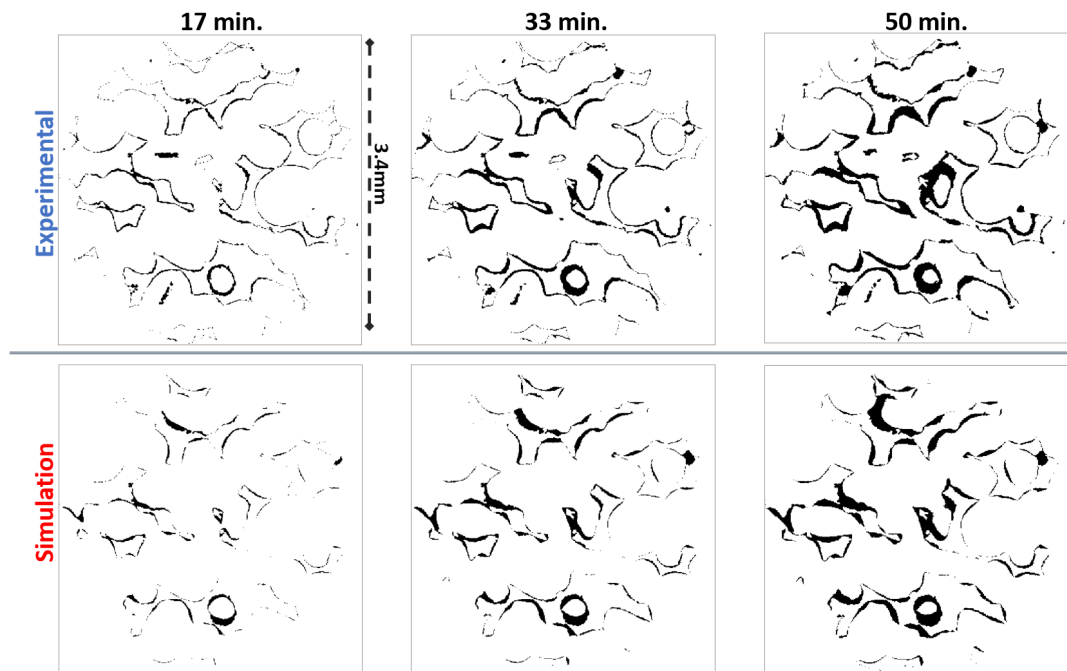


Figure 3.18: Similar to figure 3.17, the changes in pore structure are shown in black, but with the slices taken from a high porosity region – position 2, figure 3.15.

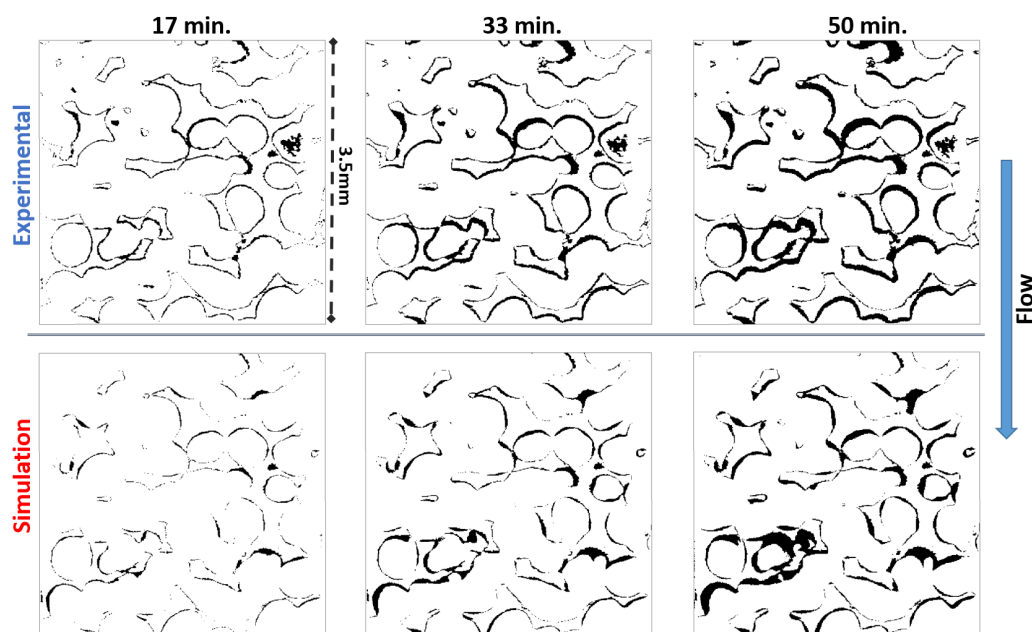


Figure 3.19: Experimental (top row) and modelled (bottom row) differences relative to the initial time after seventeen, thirty three and fifteen minutes of reaction. Slices are taken parallel to the flow through the middle of the sample.

contact with the solid surface. There is little dissolution in essentially stagnant regions of the pore space - those shown in white - since reactants can only access the solid through diffusion, a much slower process. However, in some portions of the flow domain, there is no obvious relationship between pore velocity and degree of dissolution, with little change seen in some high-speed pathways (in red) and more dissolution in pores with slower-moving flow (blue). This could be an effect of the coupled nature of dissolution and flow, as a narrow throat is dissolved and widened, its flow velocity must drop, since the flow is mass conservative. The cumulative dissolution is the result of the availability of particles in a particular portion of the sample during a time interval. However, since the geometry, and consequently, the flow field are constantly changing, the instantaneous velocity may not be a good approximation for the velocity at previous times. A more quantitative analysis of this phenomenon is a possible subject for future work.

Overall, the agreement between the simulations and experiment indicates that the reaction is indeed controlled by the transport of solute to and from the solid. Our simulations have no adjustable parameters: our inputs are the initial pore geometry, as imaged using micro-CT scanning, the experimentally-imposed flow rate, the diffusion coefficient, the calcite volume in the carbonate grains and the independently-measured batch reaction rate. Also note that we have assigned an average porosity to the grains - in reality the degree of micro-porosity may vary from grain to grain - and we do not resolve small-scale roughness in the pore space. As a consequence,

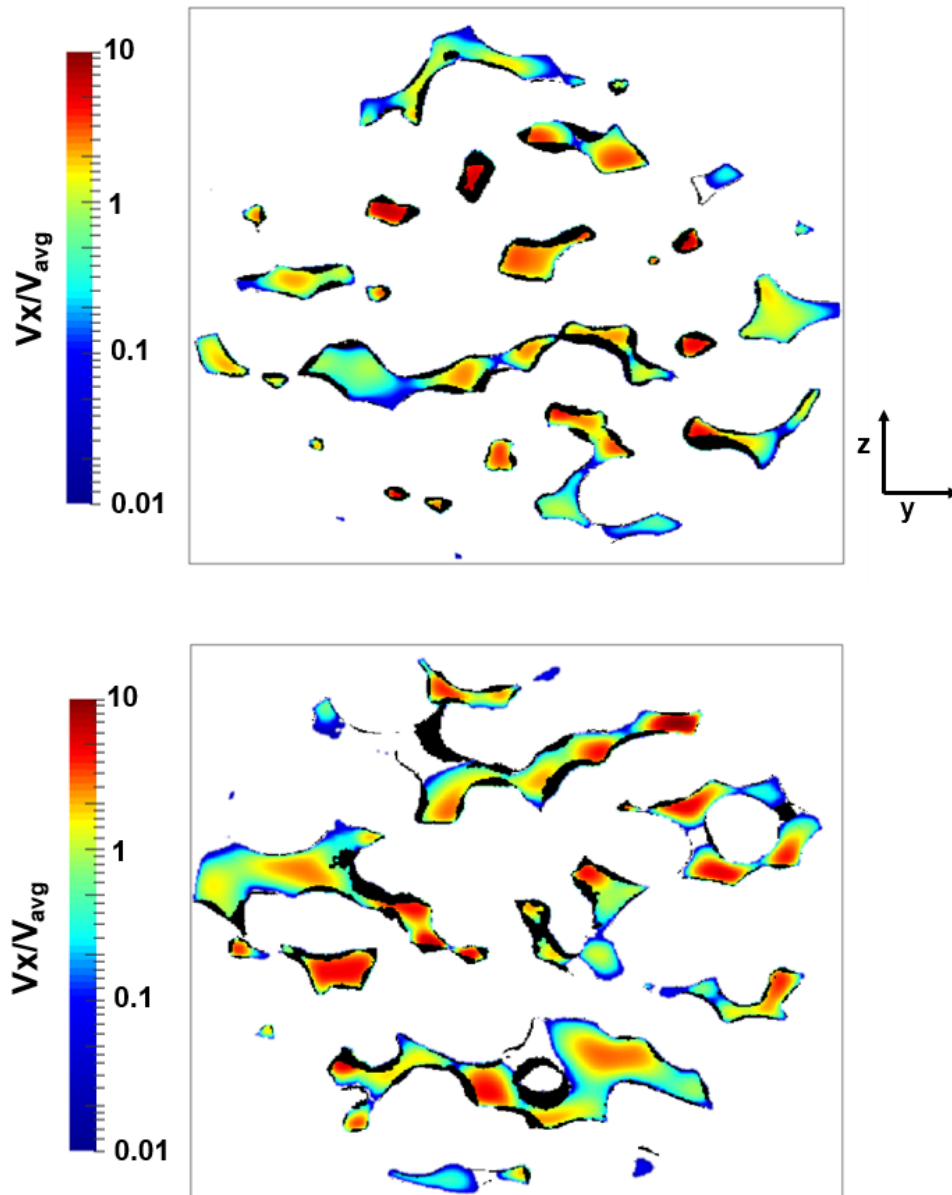


Figure 3.20: Slices perpendicular to flow showing the dissolution (in black) around the grains after thirty three minutes of flow and reaction. The velocity ratio to the average velocity is superimposed. The colour scale is logarithmic, in red are the high velocities, in blue the low and zero or negligible flow in white. The top image is taken from position 1 and the bottom from position 2 from figure 3.15. Dissolution is the result of a complex interaction between the flow field and diffusion, both being influenced by the geometry of the pore space.

the ability to predict local changes in porosity – on a pore-by-pore basis – also indicates that the reaction is controlled by the availability of reactants, rather than by the local sub-resolution properties of the solid interface.

In addition to porosity and permeability, another property influenced by changes in the porous structure is the tortuosity, a measure of the complexity and connectivity of the pore space geometry, with higher values indicating more complex geometries. Making use of the semi-analytical method described in chapter 2, and momentarily ignoring diffusion, we trace streamlines from the inlet to the outlet of the sample and calculate the hydraulic tortuosity (T), defined as [Duda et al., 2011]:

$$T = \frac{\langle L_{sl} \rangle}{L_x} \quad (3.22)$$

where $\langle L_{sl} \rangle$ is the average length of the streamlines and L_x is the length of the sample (3.5mm). Tortuosity was found to decrease from 1.54 prior to injection to 1.25 in the experimental image and to 1.22 in the simulated image after fifty minutes of flow and reaction. Such decrease reinforces the scenario of a permeability increase caused by the expansion of pore-throats – figures 3.17, 3.18 and 3.19 – and is consistent with the expected decrease in complexity of a rock experiencing an almost uniform dissolution. As the porosity increases, more pores become connected and the length of the fluid paths from inlet to outlet decrease. Of course, in the extreme case of complete dissolution, the tortuosity would decrease to unity.

3.7 Average dissolution rate vs. batch rate

The average effective reaction rate in the sample can be computed from the measured surface area and the change in porosity, which is directly proportional to the number of moles of calcite that have dissolved. Between times t and t' , we write the effective dissolution rate as:

$$r^{eff} = \frac{\Delta\phi' V n}{(t' - t) S_A(t)} \quad (3.23)$$

where $\Delta\phi' = \phi(t') - \phi(t)$ and $S_A(t)$ is the surface area at time t , which is assumed to be slowly changing, so that $S_A(t) \approx S_A(t')$. V and n have been defined in section 3.6 and are the volume of the sample and the number of moles of calcite per cubic metre in the Ketton carbonate grains, respectively. Table 3.4 shows the measured and predicted increments in porosity and the corresponding reaction rates. We see that the effective reaction rate, calculated from the experimental images, is approximately 10 times slower than the batch rate. Analysing the predicted rates, calculated from the simulated images, we would be drawn to the same conclusion. This is in a system with negligible chemical heterogeneity and where the agreement between

experiment and prediction implies that all the solid surface that comes into contact with the solute is available for reaction. This demonstrates that the heterogeneity of the flow field itself acts as a significant limitation on the transport of solute to the surface, even in a regime where diffusion dominates over reaction at the pore scale ($PeDa \ll 1$).

<i>time (min.)</i>	Experimental		Simulation	
	$\Delta\phi[.]$	$r^{eff} [\times 10^{-4} \text{mol.m}^{-2}.\text{s}^{-1}]$	$\Delta\phi[.]$	$r^{eff} [\times 10^{-4} \text{mol.m}^{-2}.\text{s}^{-1}]$
0-17	0.029	0.87	0.023	0.78
17-33	0.023	0.76	0.027	0.97
33-50	0.020	0.62	0.026	0.90

Table 3.4: Image-based experimental and simulated porosity increases and the inferred average dissolution rates – r^{eff} , eq. 3.23. For each time interval the rates are derived from the increase in porosity and tomographic surface area. Compared to the batch calcite dissolution rate – $8.1 \times 10^{-4} \text{mol.m}^{-2}.\text{s}^{-1}$ [Peng et al., 2015] – the effective rates are approximately one order of magnitude smaller.

The Ketton limestone studied is, by comparison with most reservoir rocks, or indeed other quarry carbonates, relatively homogeneous [Bijeljic et al., 2013a], yet we see transport-limited reaction which is one order of magnitude slower than its batch value when averaged over a sample only a few millimetres across, even when the effects of chemical heterogeneity and effective reactive surface area are ignored. We conjecture that the origin of this effect is the extremely wide variation in local flow speeds, as illustrated in figure 3.20. Diffusion and reaction locally depletes the particle concentration near the solid; replenishment of particles is controlled by both advection and diffusion occurring over a large range of time scales through a tortuous pore space geometry. The overall effect is a substantial decrease in mixing (here understood as the amount of solute in contact with the solids) and reaction compared to a well-mixed system. At larger scales the effective reaction rate may be several orders of magnitude lower still. This is the combined effect of several kinds of heterogeneity, both physical and chemical, at different spatial and time scales. The results indicate that, when transitioning from the micron to the millimetre scale, flow field heterogeneity plays a significant role in decreasing the average rate. However, to upscale this effect and help explain the observed discrepancy between batch and field-averaged rates referred to in the Introduction, further work in larger systems needs to be done.

3.8 Summary of results

This chapter presented a pore-scale reactive transport modelling method capable of predicting the evolution of petrophysical properties in carbonate rocks subjected to CO₂-saturated brine injection at reservoir conditions. The model was developed in the context of a Lagrangian approach where particle advection is performed using a semi-analytical streamline tracing algorithm that obeys the no-flux condition at pore-solid walls with diffusion incorporated using a random walk method. The fact that streamlines are traced semi-analytically greatly improves the computational efficiency of the code and eliminates numerical stability issues. In contrast with previous results in the literature, we have approached the problem of modelling dissolution in porous media using an image of a real, three-dimensional carbonate rock and have validated our results against an experiment performed at *in situ* conditions.

The deviation from equilibrium saturation of calcium is represented by the particle concentration and the local flux of particles is the mechanism controlling calcite dissolution. The cumulative flux of particles required to dissolve one solid voxel is directly related to the batch dissolution rate of calcite in acidic brine at reservoir conditions through an analytical expression.

The method was validated against experimental data from a dynamic imaging dissolution experiment performed at high temperature and pressure without any adjustable parameters. The predicted increases in average porosity were matched with a high degree of accuracy and the simulated porosity-permeability trend closely follows the experimental one. The dissolution front is reproduced throughout the sample in directions parallel and perpendicular to the flow axis. The rapid increase in permeability is explained by the preferential dissolution of tighter portions of the rock. Such alterations in pore space geometry are also reflected in the decrease of the hydraulic tortuosity. We argue that the overall dissolution effect not only increases porosity and permeability but also reduces the pore space complexity.

The simulations demonstrated a decrease of one order of magnitude in the effective dissolution rate of a porous carbonate sample compared to the batch dissolution rate. There is no diffusive limitation on the reaction at the grain surfaces, suggesting that any eventual transport limitation manifests itself not at the pore scale, but rather at the sample scale. This millimetre-scale transport limitation controls the local availability and residence time of the solute particles, and its overall result is a decrease in the sample-averaged reaction rate. This occurs even with all the surface available to reaction and in a relatively homogeneous and chemically uniform sample. These results indicate that the very large differences observed between batch and core-scale reaction rates could, in large part, be explained by the inhomogeneity in the flow field and the consequent transport-limited flux of reactants at the solid surface. The local variations in dissolution are the result of a

complex interplay between the velocity field, that carries the solute from the inlet, diffusion, responsible for the flux across the pore-solid interface, and the pore space geometry, that may influence the local concentration of solute and controls the effective reactive surface area.

FLOW FIELD HETEROGENEITY AND AVERAGE REACTION RATES

This chapter presents carbonate dissolution simulations performed in images of rocks with different degrees of pore-space complexity. The impact of the initial pore geometry and the associated heterogeneous velocity field on the sample-averaged reaction rates is explored for a range of flow rates and the transition between compact and uniform dissolution is discussed.

4.1 Sample characterization

The dynamics of carbonate dissolution is studied in micro-CT images of three rock samples: an artificial packing of identical spheres, an Estailades carbonate (a bioclastic limestone) and a Ketton oolite: see appendix A for a complete description. Both Estailades and Ketton are mostly monomineralic rocks, composed of more than 95% calcite [Andrew et al., 2014b].

Figure 4.1 compares the pore space geometry and the corresponding computed velocity fields for the three samples. The Ketton sample and the beadpack have similar geometries: the grains in the Ketton carbonate are roughly spherical and the pores are well connected. There is a significant velocity throughout almost the entire pore space in both samples. In comparison, Estailades has a less connected pore space and the flow field is highly channelized. This is reflected in its tortuosity, the highest of the three samples. Table 4.1 summarizes image-calculated sample properties: porosity, permeability, tortuosity and characteristic length.

The similarity between the Ketton and beadpack flow fields is captured by the probability density function (PDF) of the horizontal velocity component. Both have a relatively narrow distribution when compared to the much wider distribution exhibited by the Estailades sample, figure 4.2. Wide velocity distributions are mani-

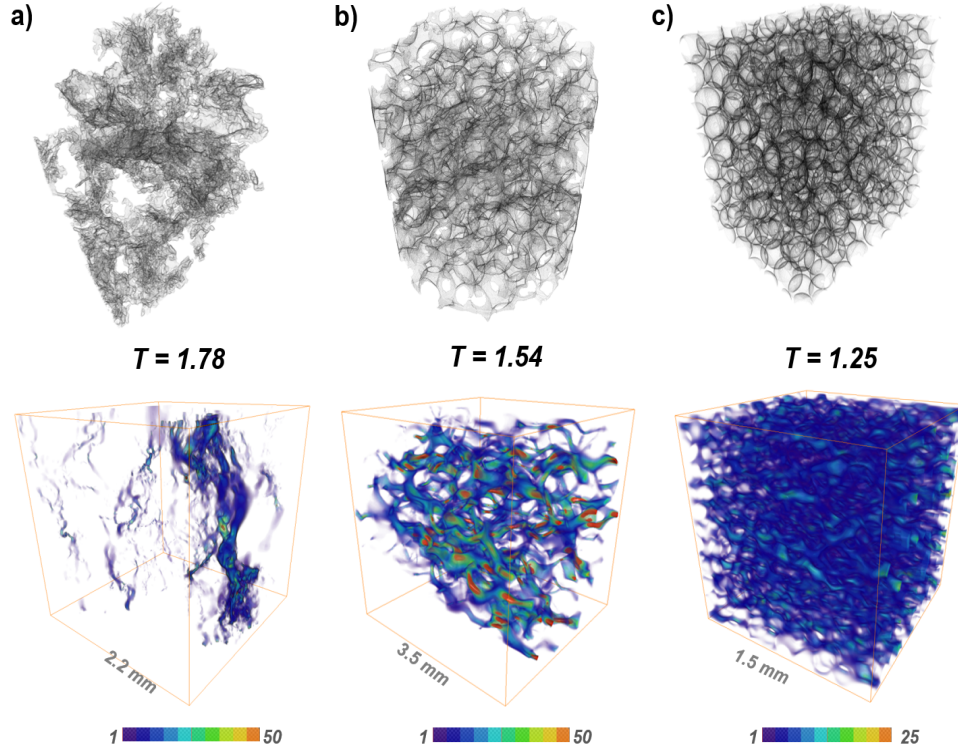


Figure 4.1: Surface of the solid grains (top row), velocity fields (bottom row) and corresponding tortuosities for the Estailades limestone (a), the Ketton oolite (b) and the pack of spheres (c). The tortuosity (T , eq. 3.22) is higher in the Estailades sample, which has the most heterogeneous flow field.

Sample	Lithology	ϕ (.)	$k(D)$	T	$L(\mu m)$	Dimensions	Voxel size (μm)
Beadpack	Artificial	0.362	13.9	1.25	84	$500 \times 500 \times 500$	3.0
Estailades	Limestone	0.119	0.5	1.75	269	$650 \times 650 \times 650$	3.3
Ketton	Limestone	0.163	13.3	1.54	420	$455 \times 451 \times 461$	7.6

Table 4.1: Summary of the samples' properties. Porosity, permeability and the characteristic length (L) are image-calculated and the hydraulic tortuosity (T , eq. 3.22) is calculated from the semi-analytical streamlines.

festations of the presence of significant stagnant zones, regions of slow flow, with restricted solute access in advection-controlled flows [Bijeljic et al., 2013a]. Ultimately, this flow characteristic is responsible for the divergence between average rates and batch rates, as discussed in section 4.3. Furthermore, the qualitative similarity between their corresponding PDFs explains why Ketton and beadpack have essentially the same behaviour upon dissolution, as will be discussed later in this chapter. From the geological perspective, the Ketton rock is an oolite¹ that has

¹ An oolitic limestone is formed by roughly spherical grains (ooids) of calcite. It is a high energy facies deposited in shallow, supersaturated environments.

undergone a mild diagenetic process, with a limited degree of consolidation. This means that it retained some of its original features as a spherical pack.

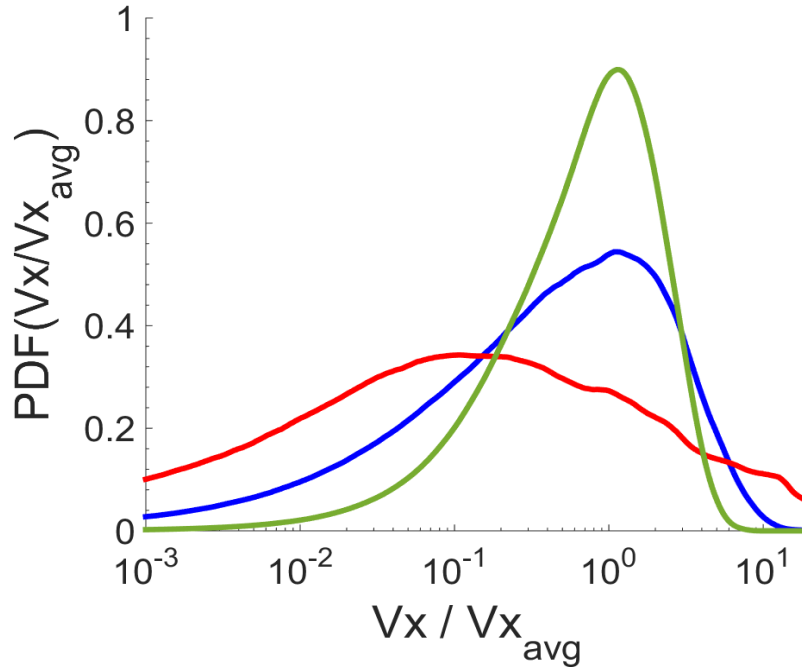


Figure 4.2: Velocity probability distributions – Estailades limestone (red line), Ketton oolite (blue line) and beadpack (green line). Of the three, Estailades has the widest distribution, reflecting the very heterogeneous nature of its flow field. Ketton and beadpack have broadly similar and narrower distributions. This will help explain the similarity in their sample-averaged reaction rates, section 4.3

Sub-resolution porosity is accounted for in the way explained in the previous chapter: by means of a factor that corrects the number of mineral moles in the solid voxels according to standard helium porosimetry measurements. Intragranular, non-connected porosity, is not considered in the model. The grain porosity (ϕ_{grain}), the porosity of the solid phase, is estimated by comparing the helium porosity (ϕ_{HP}) and the micro-CT porosity (ϕ), eqs. 3.19 and 3.20:

$$\phi_{grain} = \frac{\phi_{HP} - \phi}{1 - \phi} \quad (4.1)$$

Based on Andrew et al. [2014b], we calculate $\phi_{grain} = 0.12$ for Ketton and $\phi_{grain} = 0.22$ for Estailades. The grain porosity is then used to calculate the effective number of calcite moles in the solid voxels, eq. 3.20:

$$N_{mol}^{voxel} = nl^3(1 - \phi_{grain}) \quad (4.2)$$

where l^3 is the voxel volume and n is the calcite molar volume - $2.71 \times 10^4 \text{ mol.m}^{-3}$ [Wenk and Bulakh, 2004]. This results in $N_{mol}^{voxel} = 10.6 \times 10^{-12} \text{ mol}$ for the Ketton sample and $N_{mol}^{voxel} = 7.7 \times 10^{-13} \text{ mol}$ for Estailades. In the beadpack, $\phi_{grain} = 0$ and $N_{mol}^{voxel} = 7.3 \times 10^{-13} \text{ mol}$.

4.2 Simulation method

All the dissolution simulations in this chapter are performed using the approach developed in sections 3.3 and 3.6.2. The number of reactive particles is kept constant during the simulation time – $N_p = 2.0 \times 10^4$. Once a particle reacts with a solid, another one is injected at the inlet with a flow weighted rule. The change in porous geometry requires updates in the flow field, which are done at porosity increments of $\Delta\phi \geq 0.001$.

As detailed in section 3.6.2, the reacted particles are reinjected at the inlet, creating an imbalance in the concentration profile. The reaction rate is equalized by adjusting dynamically the number of hits to dissolve as a function of the slice-averaged concentration. As pointed out previously, this is necessary to keep the ratio N_{hits}/C constant. N_{hits}^{eff} (eq. 3.8) is updated with the same frequency as the flow field.

The flow rate is kept high enough, so as to guarantee that $Pe > 1$, while maintaining $PeDa \leq 1$. Dissolution is in the reaction-controlled regime: fast transport and slow reaction. The intrinsic reaction rate corresponds to that of calcite in the presence of CO_2 -saturated brine at $P = 10\text{MPa}$ and $T = 50^\circ\text{C}$ – $r = 8.1 \times 10^{-4}\text{mol.m}^{-2}.\text{s}^{-1}$ [Peng et al., 2015]. This results in: $PeDa = 1.8 \times 10^{-2}$ for the beadpack, $PeDa = 7.0 \times 10^{-2}$ for Ketton and $PeDa = 4.0 \times 10^{-2}$ for Estailades.

4.3 Uniform dissolution and average dissolution rates

This section studies the asymptotic average dissolution rates in the uniform dissolution regime for Estailades, Ketton and the beadpack.

In the context of this thesis, a uniform dissolution regime is associated with conditions under which the average particle displacement is large enough to propagate the reaction throughout the sample, from inlet to outlet. This is a characteristic of high Péclet flows, figure 3.3. Once this regime is established, we can compute the average dissolution rate between times t and t' from the micro-CT surface and the change in porosity, eq. 3.23:

$$r^{eff} = \frac{\Delta\phi' V n}{(t' - t) S_A(t)} \quad (4.3)$$

The average rate as a function of the number of injected pore volumes is investigated for the three samples while varying the flow rate.

Figure 4.3 shows the ratio of the averaged rates over the intrinsic calcite dissolution rate at 10 MPa and 50°C [Peng et al., 2015] for the three samples under

two initial flow rates, corresponding to $Pe = 10$ and $Pe = 100$. The Ketton and the beadpack samples (blue and green lines, respectively) have comparable average rates, a consequence of their similar velocity fields (figure 4.2), while the Estailades sample has a lower rate. We contend that this is a manifestation of its heterogeneous velocity field, which causes a very inefficient sampling of the pore space. Large portions of the Estailades pore space remain virtually unaffected by reactive transport, even after injecting 1000 pore volumes, figure 4.4. In contrast, practically all of the pore space of the Ketton and beadpack is modified after injection of the reactive particles. The channelized nature of the Estailades velocity confines the flux of solute to very localized regions, thus limiting the spread of the dissolution front. The other two, more homogeneous rocks, exhibit a much more uniform dissolution pattern, figure 4.4. As previously remarked in section 3.6.3, the tortuosity (eq. 3.22 [Duda et al., 2011]) should decrease in response to a reaction-induced increase in the pore-space connectivity. In fact, this is observed in the three samples. In the beadpack it decreases from $T = 1.25$ to 1.16, from $T = 1.54$ to 1.31 in Ketton and from $T = 1.75$ to 1.32 in Estailades.

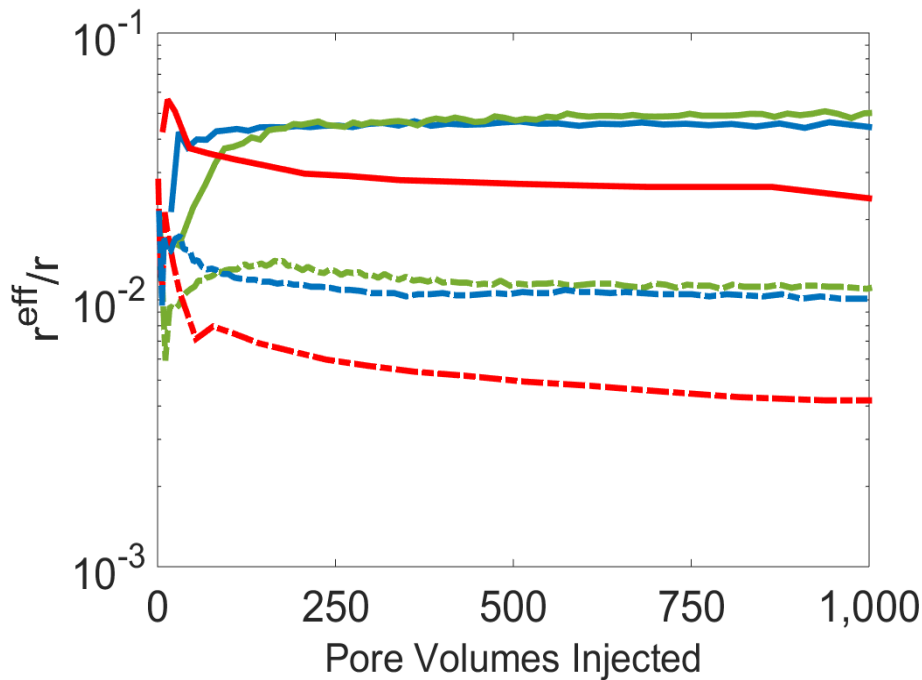


Figure 4.3: Ratio of the average reaction rate (eq. 3.23) over the batch reaction rate during injection of a CO_2 -saturated brine. The average rates for the more heterogeneous rock (Estailades, in red) is lower than the rate of the relatively homogeneous ones (Ketton in blue and beadpack in green). Higher flow rates yield higher average reaction rates – $Pe = 100$, solid lines. The dashed lines are for $Pe = 10$. The early time behaviour is an artefact, and it is related to the point in time where the flow field is first updated.

Transport is advection-dominated and the presence of stagnant zones inhibits

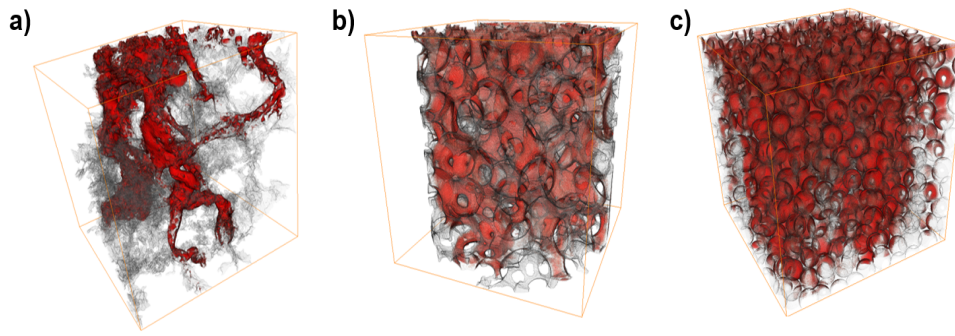


Figure 4.4: Dissolved portions (shown in red) superimposed with the original pore space (light grey) after injecting 1000 pore volumes, starting with an initial Péclet of 100. Dissolution in the Estailades sample (a) is more channelized and restricted than in the Ketton (b) and beadpack (c) samples. This is a result of the flow field heterogeneity, see figure 4.1.

the access of the reactants to a significant part of the reactive surface. Moreover, high flow rates (fig. 4.3, solid lines, $Pe = 100$) result in higher average reaction rates in comparison with the lower flow rates (fig. 4.3, dashed lines, $Pe = 10$). The increase from $Pe = 10$ to $Pe = 100$ results in an increase of almost one order of magnitude in the reaction rate for the three samples. Zones that have low velocity when $Pe = 10$ become accessible to the particles when the velocity rises, causing a more even spread of the dissolution front, figure 4.5.

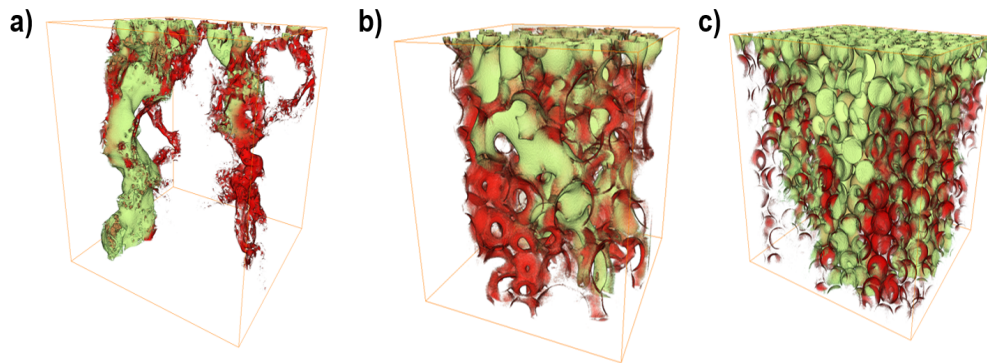


Figure 4.5: Time-lapse images after injecting 1000 pore volumes. Dissolution varies with the flow rate, green corresponds to $Pe = 10$ and red to $Pe = 100$. In the Estailades (a), a secondary channel develops when increasing the flow rate, while in the Ketton (b) and beadpack (c), high flow rates yield a more uniform dissolution than low flow rates.

The understanding of the reaction dynamics can be further strengthened by analysing the evolution of the velocity field distribution. As shown in figure 4.4, while the long term dissolution of Ketton and beadpack alters most of the original pore space, significant parts of Estailades remain largely unchanged. Figure 4.6 shows

the corresponding PDFs of velocities before and after the injection of 1000 pore volumes for the three samples for $Pe = 100$. Estailades evolves into a bimodal distribution, where the stagnant zones are mostly preserved by the reactions, while the high flow regions become more pronounced. This is a markedly different behaviour from the one exhibited by the Ketton and beadpack samples, in which the broad characteristics of the distributions remain. The beadpack PDF is virtually unchanged, and the Ketton PDF becomes narrower with a more pronounced peak (the same was also observed with the conditions of the dynamic imaging experiment of chapter 3, figure 4.6). This narrowing of the distribution, in the case of Ketton, indicates that the pore space is becoming less complex and more well connected as a result of dissolution: more pores have velocities close to the average. The opposite is happening in Estailades; dissolution preferentially enlarges pre-existing fast flow channels, while keeping the stagnant zones unchanged. The resulting flow field is more heterogeneous and its distribution is bimodal. Overall, these results are in qualitative agreement with Menke et al. [2016], who also showed that dissolution-induced changes in the velocity field depend on the initial pore structure – in channelized rocks, dissolution is stronger in the channels (regions of fast flow) leaving stagnant zones largely unaffected. The description of pore-scale heterogeneity in terms of velocity PDFs, as proposed by Bijeljic et al. [2013a], can be expanded to the context of reactive transport, and it provides a quantitative measure of reaction-induced changes in the pore space. The same approach has also been applied to wormhole formation [Gharbi et al., 2013] and calcite precipitation [Noiriel et al., 2015].

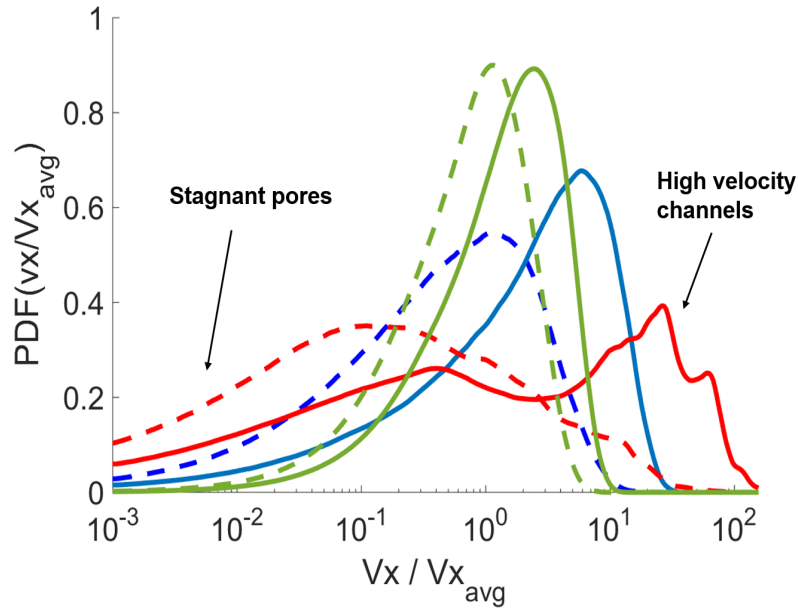


Figure 4.6: PDFs of velocities, before (dashed lines) and after injection of 1000 pore volumes at $Pe = 100$ (solid lines). Beadpack (green) is mostly unaffected, Ketton (blue) becomes narrower with a more pronounced peak. The PDFs of the Estailades (red lines) rock show the development of high velocity channels. The velocities are normalized to the corresponding average velocity before flow and reaction.

4.4 Initial pore-structure and dissolution regimes under variable flow rates

While the previous section focused on the asymptotic behaviour of the average dissolution rates in the uniform regime, this section concentrates on the early time behaviour and the influence of the initial pore geometry on the dissolution patterns.

The penetration length of a reactive particle inside a sample is highly dependent on the Péclet number, figure 3.3. When Pe is small, it is expected that the dissolution will be confined to regions close to the inlet, as explained in section 3.1.1. This means that, for a given number of injected pore volumes, if the injection rate is low enough, the dissolution front will not propagate throughout the sample, figure 3.2. The resulting pattern is termed compact. Since the dissolution is confined, the permeability (a sample-scale property) will not be strongly affected, at least until the whole sample is almost completely dissolved. In contrast, if the injection rate is high, the reactants can reach the outlet, in what is called the uniform regime. However, as already discussed in chapter 3 and section 4.3, this nomenclature is misleading. A uniform regime does not imply that the average rates are the same as the intrinsic rates or that the rock is dissolving homogeneously, as evident from the results presented in the previous section.

Figure 4.7 shows the slice-averaged relative porosity difference in Ketton and in Estailades along the direction of flow for four initial injection rates, corresponding to $Pe = 1, 2, 5$ and 10 . In both samples the difference is concentrated close to the inlet for the lowest rates ($Pe = 1, 2$), and moves towards the outlet as the rate increases, *i.e.*, the transport of reactants in the pore space is more effective and dissolution spreads throughout the rock, approaching the (quasi) uniform regime. Note, however, that the penetration length is higher in the Estailades sample than in the Ketton. This is due to the channelized characteristic of the Estailades flow field, which favours the development of a localized dissolution around a pre-existent channel, an effect that is more pronounced for higher Pe , figure 4.8.

The sample-dependent difference in the range of the dissolution (figures 4.7 and 4.8) should have an obvious impact on the permeability behaviour. This is illustrated in figure 4.9, which compares the evolution of the permeability as a function of porosity for both rocks. The alterations in Ketton are concentrated at the inlet, and do not connect across the sample, even for $Pe = 10$. Consequently, despite the increase in porosity, the permeability remains essentially unaffected for the flow rates considered. The opposite happens in Estailades, where we observe the widening of a channel extending from inlet to outlet. This occurs at the lower flow rate corresponding to $Pe = 5$. This localized enlargement of a highly conductive channel connecting inlet and outlet is responsible for a marked increase in permeability. Furthermore, the non-uniqueness of the permeability vs. porosity curve evidenced by fig. 4.9 has potential impacts for the modelling of dissolution in reservoir-scale models. These are currently constructed based on the assumption that the entire permeability field is a well-defined function of the porosity; this is further discussed in section 5.1. However, figure 4.9 shows that such assumption does not hold. Instead, the permeability behaviour upon dissolution is a function not only of porosity, but also of the pore-space morphology and the flow rate. A possible methodology to incorporate this phenomenon in macro-scale models would be to define facies-dependent permeability vs. porosity curves and adjust them dynamically to the flow rate in each simulation cell.

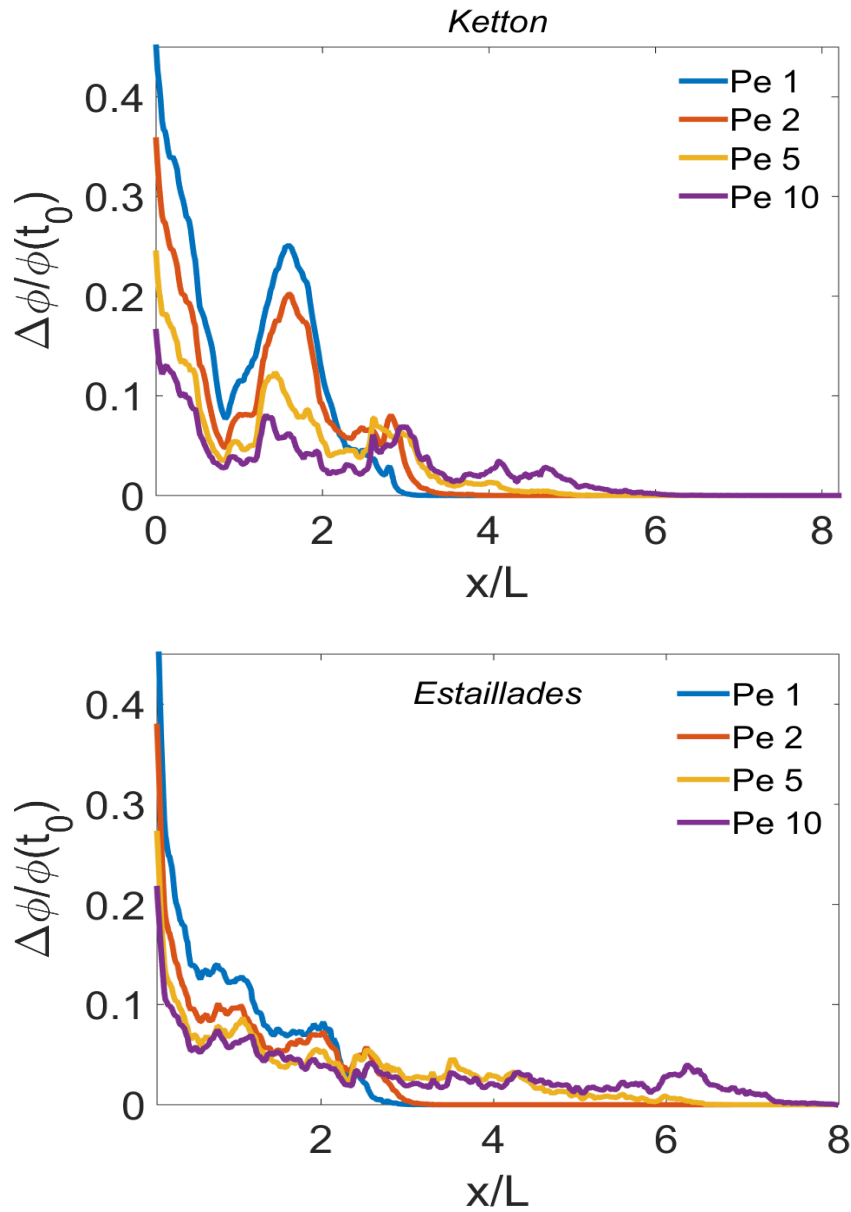


Figure 4.7: Slice-averaged relative porosity difference *versus* distance over the characteristic length (L), after injecting 10 pore volumes in Ketton (top) and in Estailades (bottom). Dissolution penetrates further for the higher flow rates, particularly in Estailades, the more channelized rock. Flow is from left to right. Ketton is $8.2L$ in length and Estailades $7.9L$.

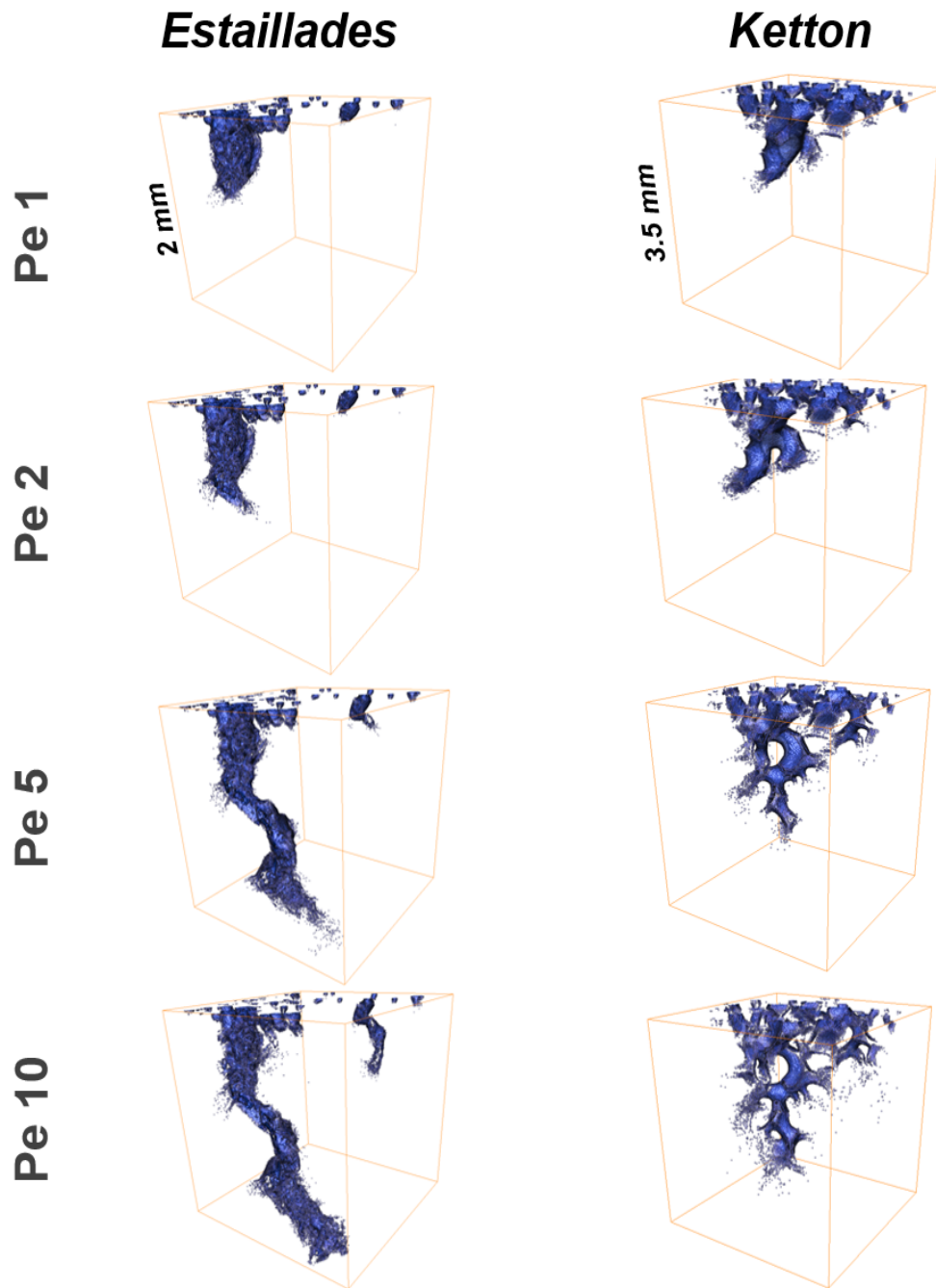


Figure 4.8: Dissolution fronts following the injection of 10 pore volumes under four flow rates, corresponding to $Pe = 1, 2, 5$ and 10 . For low flow rates ($Pe = 1, 2$), reaction is contained close to the inlet. Increasing the injection rate ($Pe = 5, 10$), the channelized nature of flow in the Estailades focuses the reaction into high flow channels, with a greater impact on permeability.

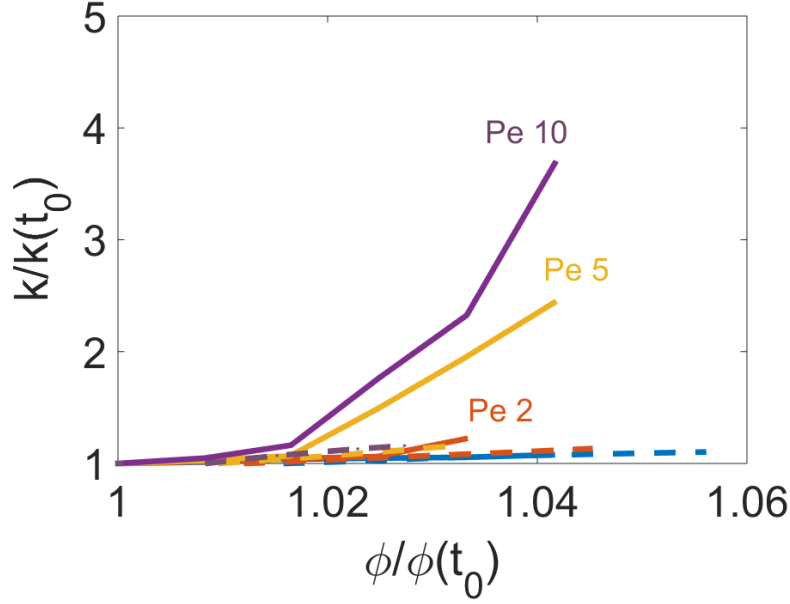


Figure 4.9: Permeability evolution for Ketton (dashed lines) and Estailades (solid lines) following the injection of 10 pore volumes with four different flow rates, corresponding to $Pe = 1, 2, 5$ and 10 . Ketton permeability is largely unaffected for the range of flow rates considered: a consequence of dissolution being concentrated at the inlet. In contrast, Estailades shows a marked increase in permeability for the higher rates: a result of fast flow channels dissolving.

4.4.1 Channelized flow and the uniform dissolution regime

As evidenced by figure 4.7, the extension of the dissolution front is structure dependent. For a given Pe , a rock will exhibit compact or uniform dissolution, depending on the geometric characteristic of its pore space. In Estailades, the transition to the uniform regime is achieved for $Pe \approx 10$, while in Ketton, this happens for much higher flow rates ($Pe \approx 50$), figure 4.10.

Figure 4.11 summarizes the transition between the dissolution regimes for Ketton and Estailades as the flow rate increases while keeping the same reaction rate – $PeDa \approx 10^{-2}$. While the exact value of Pe for which the transition occurs depends on the particular choice of $PeDa$ (i.e. of the reaction rate), it must be noted that the reaction rate values adopted here are representative of the behaviour of the calcite dissolution rate in subsurface conditions. Even considering deeper, hotter aquifers, $PeDa \approx 10^{-1}$ for the highest available calcite reaction rate in CO_2 -saturated brines [Peng et al., 2015]. In comparison with similar dissolution diagrams (e.g. [Daccord et al., 1993; Golfier et al., 2002]), figure 4.11 highlights differences in the uniform dissolution regime for homogeneous and heterogeneous rocks. Because it is constructed from direct pore-scale simulations, it makes explicit the impact of the pore structure on the dissolution patterns. It shows that, in comparison with the early onset of uniform dissolution in a heterogeneous rock, the uniform regime is only

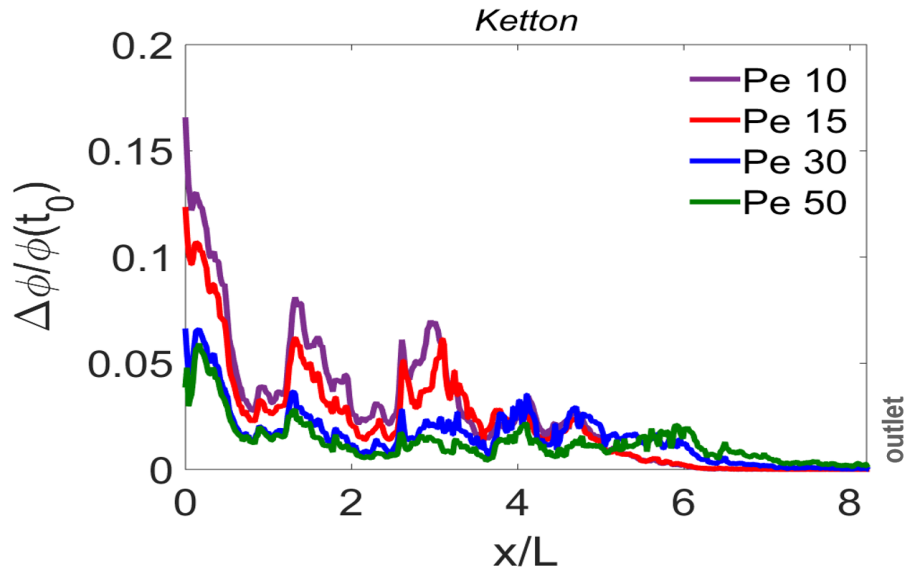


Figure 4.10: Slice-averaged relative porosity difference in Ketton for different Pe . A very high rate is necessary to extend the dissolution to the outlet.

achieved for high flow rates in a relatively homogeneous medium. It also indicates that the uniform regime in a heterogeneous rock is actually comprised of fast flow channels being enlarged.

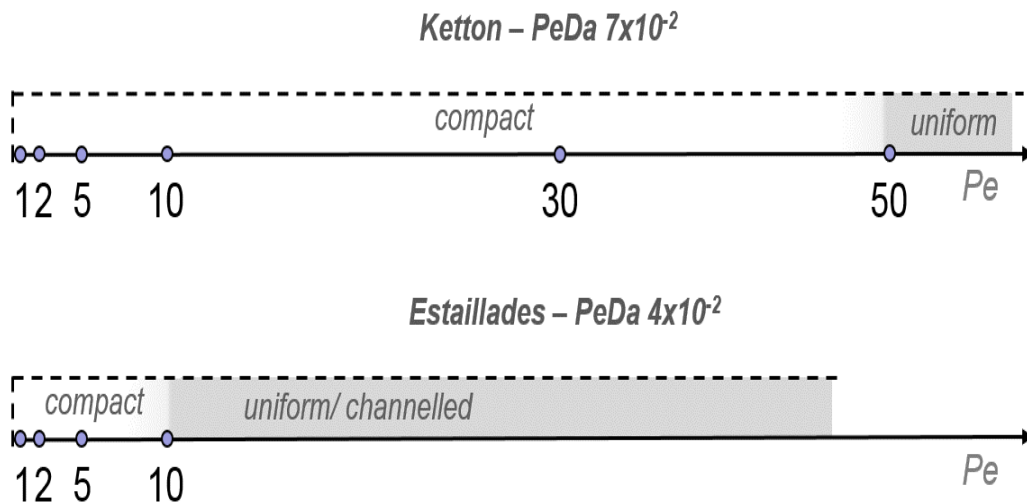


Figure 4.11: Dissolution transitions from compact to uniform (channelled in Estailades) when, for a fixed and low reaction rate, the flow rate increases. In the Ketton sample, this transition happens at a much higher rate than in the Estailades sample. The blue dots represent simulation points.

4.5 Discussion

This chapter used simulations to illustrate the influence of the initial pore structure on the transport of reactive particles in porous rocks and its associated impact on the sample-averaged fluid-solid reaction rates. A more complex pore space gives rise to a more heterogeneous flow field, which imposes limitations on the transport of reactive solute in millimetre scale rocks. These pore-scale constraints manifest themselves collectively as a sample-scale discrepancy of, at least, one order of magnitude between average reaction rates and batch reaction rates, even in relatively homogeneous rocks. Another indication of the transport-controlled kinetics at the sample scale is the dependency of the average rates on the flow rates – higher flow rates yield higher average reaction rates.

As illustrated in section 4.3, the underlying complexity of the pore geometry (and of its corresponding flow field) defines the average reaction rate in asymptotic times, even in the so-called uniform dissolution regime – $Pe \gg 1$, $PeDa \ll 1$. Despite being useful in several circumstances, this commonplace definition (“uniform”) does not fully describe what is happening at the pore scale. Specifically, in heterogeneous channelized rocks, we observe the preferential dissolution of fast-flow channels, and the flow and dissolution regime is more accurately described as channelled, rather than uniform. This was also reported in an imaging experiment tracking the pore-space evolution during reactive transport [Menke et al., 2016].

The distinct evolution of the velocity PDFs of rocks with different pore characteristics is a strong indication that a description of dissolution patterns solely based on the non-dimensional numbers Pe and $PeDa$ misses important features of the reaction dynamics in real rocks. Previous work focused on reproducing core experiments and adopted a Darcy-scale continuum representation of the porous medium. This approach fails to account for pore-scale heterogeneities and do not fully describe the dynamics of dissolution in terms of the pore structure [Daccord et al., 1993; Golfier et al., 2002; Maheshwari et al., 2013]. This chapter is a contribution in this direction: through computational modelling we investigated the interdependency between the dissolution process and the initial geometry of the pores.

Fluid-solid reactions are broadly characterized as either surface or transport-controlled. This a useful description in batch reactors, closed systems in which the reactants are readily available in the solution in contact with the mineral surface. We argue that such description is incomplete when considering reactive transport in porous media. There is one extra factor to be taken into account: the geometry of the pore space, which may limit the transport of solute to the solid surface at the sample scale. This means that a reaction can be surface-controlled at the pore scale (a rough analogy would be to consider every pore as a batch reactor) but transport-controlled at the sample scale. This was the case exemplified here.

CONCLUSIONS AND DIRECTIONS FOR FUTURE WORK

5.1 Discussion and summary of results

The main objectives of this thesis were twofold. Firstly, to develop and implement a semi-analytical streamline tracing method suitable to be used in micro-CT images of porous rocks. Secondly, to develop a first principles, particle-based approach to simulate mineral dissolution at the pore scale.

The route taken was to adopt a streamline-based method to simulate reactive transport in the reconstructed pore-space from micro-CT images of porous rocks. The Lagrangian approach is an alternative to Eulerian approaches when transport is advection-dominated and the reaction kinetics can be described by a small number of species. It is numerically stable and offers superior computational performance, while keeping the implementation straightforward.

Chapter 2 presented an extension of the Pollock method (the standard Darcy-scale streamline tracing method) that obeys the pore-scale boundary conditions – no-flow at the pore walls. The method was implemented in the pore-space geometry reconstructed from micro-CT images and used to calculate breakthrough curves and time-of-flight distributions for a carbonate and a sandstone. When compared to the predictions of the original method, the tails of the distributions (an indicative of the nature of the transport, anomalous or not) were significantly different, thus illustrating the importance of correctly representing the no-flow condition in pore-scale transport simulations. From the numerical perspective, the use of analytically traced streamlines eliminates the stability constraints of the standard time-stepping particle tracking methods.

Chapter 3 presented a particle-based model to simulate mineral dissolution under reaction-controlled conditions. The reactive flux is related to the diffusive flux

of solute through the pore walls. The number of particles necessary to dissolve a solid voxel comprised of a given mineral is related to the batch reaction rate. There are no adjustable parameters. The predictions of the method are compared against the data of a dynamic imaging experiment. The agreement is excellent and a decrease of one order of magnitude in the average reaction rate is explained in terms of transport limitations caused by the heterogeneity of the flow field alone.

Chapter 4 explored the impact of the initial pore-space geometry, of the associated flow field heterogeneity and of the flow rate on the sample-averaged dissolution rates of carbonate rocks. In comparison with more homogeneous samples (an oolite and a pack of spheres), the most heterogeneous rock (a bioclastic limestone) exhibited the lowest average rate. The reaction rate is about one order of magnitude lower for a range of flow rates. The flow is very channelized, even in the so-called “uniform” dissolution regime, and the access of the reactants to the grain surface is limited. Increasing the flow rate, the average rate rises. This is due to a more effective sampling of the pore-space. Even in chemically homogeneous rocks, transport limitations add-up to cause a decrease of up to two orders of magnitude in comparison with batch rates.

Modelling reactive transport at the pore scale provides useful insights into processes that can not be taken into account when adopting an effective medium approach, e.g. simulating flow in the Darcy regime. Field-scale simulators are built upon a macro (Darcy) representation of the reservoir. They typically work on an Eulerian framework and couple geochemical models into standard pressure and saturation solvers, figure 5.1. Implicit to it is the assumption that the mineral phases are equally accessible to the fluid phases within every simulation element. They also assume that the system is well mixed. In addition, the relationship between porosity and permeability is often the same for every simulation block and kept fixed for the entire simulation time. This relationship, obtained from well logs and core analysis, is more likely to represent a diagenetic trend within the formation than a dissolution trend that should vary according to the facies and local flow regime. However, as several results at the pore and core scale suggest, these assumptions are far from the truth. The analysis presented in chapters 3 and 4 indicate that pore-scale flow heterogeneities control the coupling of physical and chemical processes.

We suggest that our pore-scale results give valuable insights into the mechanisms governing carbonate dissolution and may provide a starting point for the refinement of upscaling techniques for reactive flows. As the results clearly show, flow field heterogeneities are a significant potential source for the discrepancy between millimetre- and centimetre-scale dissolution rates and intrinsic rates. Moreover, our methodology can be readily employed to simulate a range of dissolution patterns in a variety of carbonate rocks caused by different flow regimes and investigate fur-

ther the mechanism by which the complexity of the flow field affects the average reaction rate in heterogeneous porous media.

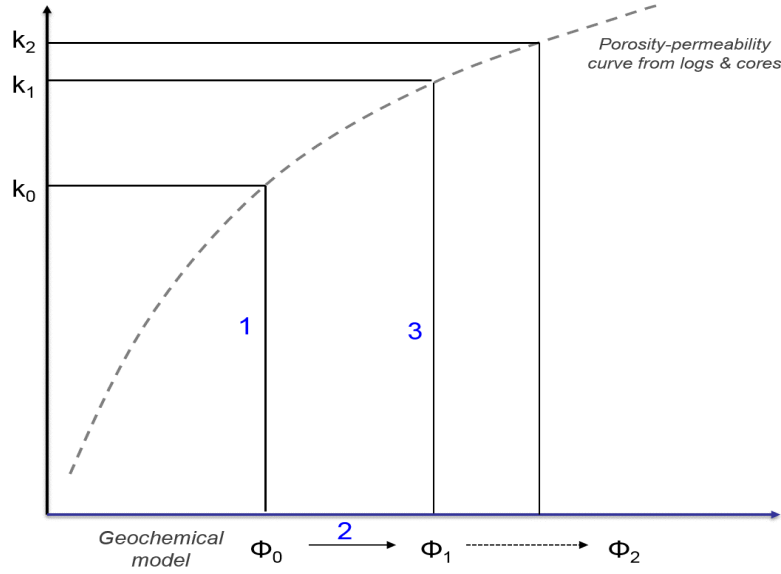


Figure 5.1: The permeability changes in field-scale simulations are usually obtained as a function of the porosity increments given by a curve derived from cores and well logs expressing some sort of representative diagenetic trend. The initial permeability (k_0) is obtained from the initial porosity (Φ_0) – step 1. The porosity is updated via successive applications of a geochemical model – step 2, causing the permeability to be updated – step 3. This process is repeated for every grid block, for the duration of the simulation.

5.2 Suggestions for future work

The streamline tracing method presented in chapter 2 considers only cubic lattices. However, more advanced representations of curved surfaces are available to properly describe the pore-rock interface. A natural extension would then be to adapt the method to work on irregular grids, similar to what has already been achieved for the standard Pollock method [Prevost et al., 2002; Matringe et al., 2006]. Furthermore, streamline tracing is a powerful tool to study the nature of the heterogeneous velocity field in sedimentary rocks and its implications for advection-dominated processes. Some examples are the relationship between intermittency in the Lagrangian velocities and anomalous transport [Kang et al., 2014], or the description of heterogeneity in terms of streamline-calculated properties [Pereira Nunes et al., 2015; Siena et al., 2014].

Chapter 3 introduced a particle tracking method that relates the particle flux to laboratory-measured dissolution rates. In the case of a reaction-limited kinetics ($Da \ll 1$), the concentration gradients close to the surface are negligible and a

simple analytical expression relates the cumulative particle flux to the batch rate. If the kinetics is transport-limited, concentration gradients will develop and this expression does not describe the kinetics correctly. Deriving an equivalence between the particle flux and the batch dissolution rate in this case would be an useful extension of the method. This would allow the study of fast reactions ($Da \gg 1$) and its related applications, such as wellbore stimulation and wormholing phenomena.

Chapter 4 described the behaviour of sample averaged rates as a function of both the initial pore geometry and the flow rate of a reactive fluid. It discussed how the behaviour diagram commonly used to characterize dissolution patterns at the core scale (figure 3.2) does not account for pore-scale flow heterogeneity. The simulation model introduced in chapter 3 can be used to complement and enhance this behaviour diagram, incorporating the effect of the initial pore-space geometry on dissolution. Once this is achieved, the model could provide guidelines to design CCS projects, finding the flow conditions under which a preferred regime can be found.

This work was focused on the modelling of calcitic carbonates. However, several carbonate reservoirs of commercial interest are formed by a combination of calcite and dolomite (other minerals may also be present in smaller concentrations). Consequently, it would be of interest to investigate the combined effect of physical and chemical heterogeneities on the average reaction rates. This could be readily achieved using a 3-phase segmentation (e.g. pores + calcite + dolomite). The dolomite voxels would dissolve with a different number of particle hits than the calcite voxels. The main difficulty involved is to have good segmented images with the adequate separation between the two minerals.

Finally, diagenesis modelling is a topic of large importance during the exploration and production stages of hydrocarbon reservoirs [Lucia, 2007; Whitaker and Smart, 2011]. It controls the reservoir quality, and is a substantial factor for the reservoir productivity. Two competing processes define the diagenetic history of a rock: dissolution and precipitation. The model discussed in this thesis is directly applicable to the low dissolution rates typical of diagenesis. To account for precipitation would involve interpreting the particle concentration as the saturation of the precipitating mineral, and grow solids from the particle collision positions. This could be achieved with minor changes to the algorithm already developed.

SUMMARY OF SAMPLE CHARACTERISTICS

Micro-CT images of four different rock samples were used in this work: 1) Beadpack is a random packing of spheres for which segmentation was performed by Prodanovic and Bryant [2006]; 2) Bentheimer is a well sorted sandstone composed of 95% quartz, quarried in Bad Bentheim, Germany; 3) Estailades is a mostly calcitic bioclastic limestone, moderately sorted, quarried in Oppede, France and 4) Ketton which is an oolite, made of 99% calcite, quarried in Ketton, UK. For further details see Andrew [2015]. The Ketton image used in the reactive simulations is a coarsened version of the one used in the transport simulation. Table A.1 summarizes the main characteristics of the samples used in chapters 2, 3 and 4. The Ketton and Estailades samples were imaged at the Imperial College rock physics laboratory. The Bentheimer sandstone was imaged by iRocks Technologies, Beijing, China, which is gratefully acknowledged.

Sample	Lithology	ϕ (%)	$k(D)$	Tortuosity	$L(\mu m)$	Dimensions	Voxel size (μm)
Beadpack	Artificial	36.2	13.9	1.25	84	$500 \times 500 \times 500$	3.0
Bentheimer	Sandstone	21.6	3.0	1.64	558	$1000 \times 1000 \times 1000$	3.0
Estailades	Limestone	11.9	0.5	1.7	269	$650 \times 650 \times 650$	3.3
Ketton 1	Limestone	17.8	13.4	1.5	420	$911 \times 902 \times 922$	3.8
Ketton 2	Limestone	16.3	13.4	1.5	420	$455 \times 451 \times 461$	7.6

Table A.1: Summary of the properties of the samples used in this work. Porosity, permeability and characteristic length (L , eq. 2.21) are image calculated and the hydraulic tortuosity (T , eq. 3.22) is calculated from the semi-analytical streamlines.

REPRESENTATIVE ELEMENTARY VOLUME

The representative elementary volume (REV) is defined as the minimum sample volume above which statistical variations of a given property become negligible [Bear, 1988]. Its value is property dependent, i.e. the permeability REV is not necessarily the same as the porosity REV, the former being normally larger due to long-range correlations in the flow field. Image-calculated properties are meaningful only when obtained from volumes larger than the REV. Moreover, the REV is related to the spatial scale. A hierarchical system may exhibit several REVs, each one associated with a specific length scale, figure B.1.

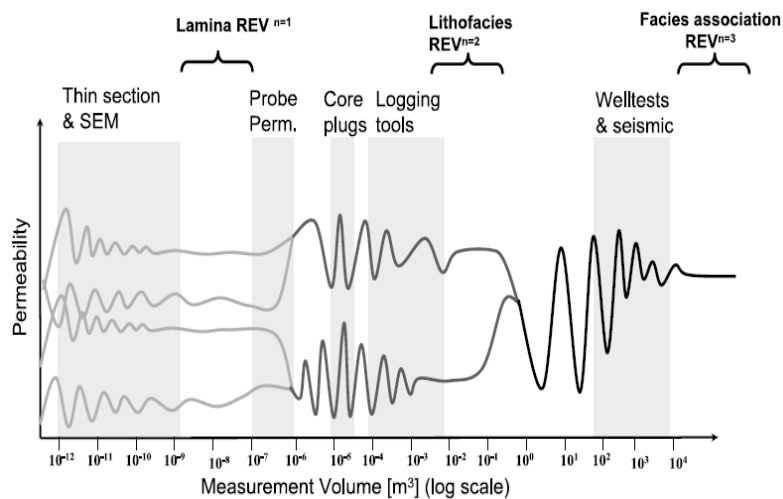


Figure B.1: Idealized scheme illustrating the scale dependency of the REV concept. Once the correlation lengths approach the size of the system, the continuum approach, on which the REV concept rests, is no longer valid. Reproduced from Nordahl and Ringrose [2008].

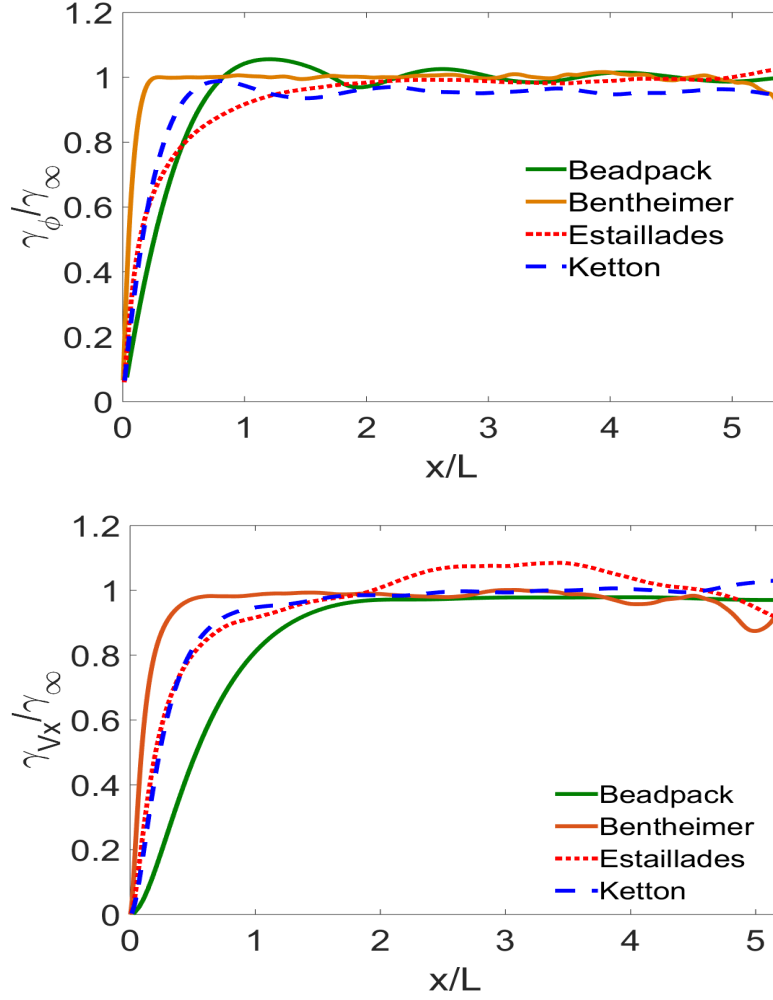


Figure B.2: Normalized porosity (top) and velocity (bottom) variograms for the four samples (Beadpack, Bentheimer, Estailades and Ketton) versus distance over characteristic length.

The empirical (semi-)variogram describes the data correlation with distance. For a given property p , it is defined as:

$$\gamma_p(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [p(x_{i+h}) - p(x_i)]^2 \quad (\text{B.1})$$

where h is the distance between two observations and $N(h)$ is the number of observations such that $|p(x_{i+h}) - p(x_i)| = h$ [Doyen, 2007]. It measures the dissimilarity between data separated by a distance h , and it is a convenient way of estimating the REV. Once the variogram reaches a plateau, the data is uncorrelated. Figure B.2 shows the porosity and velocity variograms as a function of the horizontal distance (distance measured from inlet) divided by the characteristic length for the four samples used in this work. The image volumes are above the REV and the characteristic length, $L = \frac{\pi V}{S_A}$ (eq. 2.21, table A.1), is a good approximation for it.

TRANSIT TIMES AND EXIT COORDINATES FOR THE VOXELS WITH TWO, THREE AND FOUR SOLID BOUNDARIES

C.1 Pores with two solid boundaries

There are fifteen ways of arranging two solid voxels around a pore voxel, three with the solids along the same direction and twelve with the solids in adjacent positions.

C.1.1 Two solids in the same direction

Below the case of a pore surrounded by two solids in lattice locations $(i+1, j, k)$ and $(i-1, j, k)$. The velocity field is:

$$V_x = 0 \tag{C.1a}$$

$$V_y = \frac{6v_1}{\Delta x^2}(x_2 - x)(x - x_1) + \frac{6\Delta v}{\Delta x^2 \Delta y}(x_2 - x)(x - x_1)(y - y_1) \tag{C.1b}$$

$$V_z = \frac{6w_1}{\Delta x^2}(x_2 - x)(x - x_1) + \frac{6\Delta w}{\Delta x^2 \Delta z}(x_2 - x)(x - x_1)(z - z_1) \tag{C.1c}$$

In Section 2.4, where we consider an incompressible two-dimensional flow the second term on the right-hand-side of C.1b is identically zero and we recover the parabolic velocity profile characteristic of flow between two parallel plates.

The x -direction being blocked, τ_x is undefined. For a particle starting in a point (x_p, y_p, z_p) inside the pore voxel we have the following time-of-flights in the y and

z directions:

$$\tau_y = \frac{\Delta x^2 \Delta y}{6\Delta v \Delta x_{2p} \Delta x_{p1}} \ln \left[\frac{v_2 \Delta y}{v_1 \Delta y + \Delta v (y_p - y_1)} \right] \quad (\text{C.2a})$$

$$\tau_z = \frac{\Delta x^2 \Delta z}{6\Delta w \Delta x_{2p} \Delta x_{p1}} \ln \left[\frac{w_2 \Delta z}{w_1 \Delta z + \Delta w (z_p - z_1)} \right] \quad (\text{C.2b})$$

and the exit position is calculated when $\tau_e = \min(\tau_y, \tau_z)$:

$$x_e = x_p \quad (\text{C.3a})$$

$$y_e = y_1 - \frac{v_1 \Delta y}{\Delta v} + \frac{v_1 \Delta y + \Delta v (y_p - y_1)}{\Delta v} \exp \left[\frac{6\Delta v \Delta x_{p1} (x_2 - x_p) \tau_e}{\Delta x^2 \Delta y} \right] \quad (\text{C.3b})$$

$$z_e = z_1 - \frac{w_1 \Delta z}{\Delta w} + \frac{w_1 \Delta z + \Delta w (z_p - z_1)}{\Delta w} \exp \left[\frac{6\Delta w \Delta x_{p1} (x_2 - x_p) \tau_e}{\Delta x^2 \Delta z} \right] \quad (\text{C.3c})$$

C.1.2 Two adjacent solids

The case of a pore voxel with coordinates (i, j, k) surrounded by two solids in lattice locations $(i-1, j, k)$ and $(i, j-1, k)$ is derived below. Analytical expressions for all other eleven cases can be obtained in a similar manner. The velocity field is:

$$V_x = \frac{2u_2}{\Delta x^2 \Delta y} (x - x_1)^2 (y - y_1) \quad (\text{C.4a})$$

$$V_y = \frac{2v_2}{\Delta x \Delta y^2} (x - x_1) (y - y_1)^2 \quad (\text{C.4b})$$

$$V_z = \frac{4w_1}{\Delta x \Delta y} (x - x_1) (y - y_1) + \frac{4\Delta w}{\Delta x \Delta y \Delta z} (x - x_1) (y - y_1) (z - z_1) \quad (\text{C.4c})$$

$$(\text{C.4d})$$

To calculate the *tof* in x and y -directions it is useful to note that V_x and V_y are functions of x and y only, the flow is essentially two dimensional. The time to travel to a point with x -coordinate x' along a streamline passing through (x_p, y_p) is:

$$\tau_x = \int_{x_p}^{x'} \frac{dx}{V_x(x, y)} \quad (\text{C.5})$$

but along the streamline passing through (x_p, y_p) we have:

$$(y - y_1) = (y_p - y_1) \left[\frac{x - x_1}{x_p - x_1} \right]^{\frac{v_2 \Delta x}{u_2 \Delta y}}$$

then it can be shown that C.5 yields:

$$\tau_x = \frac{\Delta x^2 \Delta y}{2u_2 (y_p - y_1)} \frac{u_2 \Delta y}{u_2 \Delta y + v_2 \Delta x} \left[\frac{1}{x_p - x_1} - \frac{1}{\Delta x} \left[\frac{x_p - x_1}{\Delta x} \right]^{\frac{v_2 \Delta x}{u_2 \Delta y}} \right] \quad (\text{C.6})$$

for the *tof* in y -direction we have:

$$\tau_y = \frac{\Delta x \Delta y^2}{2v_2 (x_p - x_1)} \frac{v_2 \Delta x}{v_2 \Delta x + u_2 \Delta y} \left[\frac{1}{y_p - y_1} - \frac{1}{\Delta y} \left[\frac{y_p - y_1}{\Delta y} \right]^{\frac{u_2 \Delta y}{v_2 \Delta x}} \right] \quad (\text{C.7})$$

and solving for the *tof* in *z*-direction we have:

$$\tau_z = \frac{\Delta x \Delta y \Delta z}{2(x_p - x_1)(y_p - y_1)\Delta w} \left[\frac{\sqrt{w_2}}{\sqrt{w_1 + \frac{\Delta w}{\Delta z}(z_p - z_1)}} - 1 \right] \quad (\text{C.8})$$

and again the exit position is calculated when $\tau_e = \min(\tau_x, \tau_y, \tau_z)$:

$$x_e = x_1 + (x_p - x_1)^{\frac{v_2 \Delta x}{v_2 \Delta x + u_2 \Delta y}} \left[\frac{1}{x_p - x_1} - \frac{2u_2(y_p - y_1)}{\Delta x^2 \Delta y} \frac{u_2 \Delta y + v_2 \Delta x}{u_2 \Delta y} \tau_e \right]^{\frac{-u_2 \Delta y}{v_2 \Delta x + u_2 \Delta y}} \quad (\text{C.9a})$$

$$y_e = y_1 + (y_p - y_1)^{\frac{u_2 \Delta y}{v_2 \Delta x + u_2 \Delta y}} \left[\frac{1}{y_p - y_1} - \frac{2v_2(x_p - x_1)}{\Delta x \Delta y^2} \frac{v_2 \Delta x + u_2 \Delta y}{v_2 \Delta x} \tau_e \right]^{\frac{-v_2 \Delta x}{v_2 \Delta x + u_2 \Delta y}} \quad (\text{C.9b})$$

$$z_e = z_1 - \frac{w_1 \Delta z}{\Delta w} + \left[\frac{w_1 \Delta z}{\Delta w} + (z_p - z_1) \right] \left[1 + \frac{2(x_p - x_1)(y_p - y_1)\Delta w}{\Delta x \Delta y \Delta z} \tau_e \right]^2 \quad (\text{C.9c})$$

C.2 Pores with three solid boundaries

There are twenty ways of arranging three solid voxels around a pore. In eight cases the solids are distributed in all three directions (one solid in *x*, one in *y* and one in *z*). The remainder twelve cases have two voxels in one direction and one in another direction (e.g. two voxels in *x* and one in *y*).

C.2.1 One solid in each direction

We show the case of a pore voxel with coordinates (i, j, k) blocked by three solids in lattice locations $(i + 1, j, k)$, $(i, j + 1, k)$ and $(i, j, k - 1)$.

The velocity field is:

$$V_x = \frac{4u_1}{\Delta x^2 \Delta y \Delta z} (x_2 - x)^2 (y_2 - y) (z - z_1) \quad (\text{C.10a})$$

$$V_y = \frac{4v_1}{\Delta x \Delta y^2 \Delta z} (x_2 - x) (y_2 - y)^2 (z - z_1) \quad (\text{C.10b})$$

$$V_z = \frac{4w_2}{\Delta x \Delta y \Delta z^2} (x_2 - x) (y_2 - y) (z - z_1)^2 \quad (\text{C.10c})$$

and the time-of-flight increment in each direction:

$$\tau_x = \frac{\Delta x^2 \Delta y \Delta z}{4u_1 \Delta x_{2p} \Delta y_{2p} \Delta z_{p1}} \ln \left(\frac{\Delta x_{2p}}{\Delta x} \right) \quad (\text{C.11a})$$

$$\tau_y = \frac{\Delta x \Delta y^2 \Delta z}{4v_1 \Delta x_{2p} \Delta y_{2p} \Delta z_{p1}} \ln \left(\frac{\Delta y_{2p}}{\Delta y} \right) \quad (\text{C.11b})$$

$$\tau_z = \frac{\Delta x \Delta y \Delta z^2}{4w_2 \Delta x_{2p} \Delta y_{2p} \Delta z_{p1}} \ln \left(\frac{\Delta z}{\Delta z_{p1}} \right) \quad (\text{C.11c})$$

when $\tau_e = \min(\tau_x, \tau_y, \tau_z)$ we have the exit point:

$$x_e = x_2 - (x_2 - x_p) \exp \left[\frac{-4u_1 \Delta x_{2p} \Delta y_{2p} \Delta z_{p1} \tau_e}{\Delta x^2 \Delta y \Delta z} \right] \quad (\text{C.12a})$$

$$y_e = y_2 - (y_2 - y_p) \exp \left[\frac{-4v_1 \Delta x_{2p} \Delta y_{2p} \Delta z_{p1} \tau_e}{\Delta x \Delta y^2 \Delta z} \right] \quad (\text{C.12b})$$

$$z_e = z_1 + (z_p - z_1) \exp \left[\frac{4w_2 \Delta x_{2p} \Delta y_{2p} \Delta z_{p1} \tau_e}{\Delta x \Delta y \Delta z^2} \right] \quad (\text{C.12c})$$

C.2.2 Two solids in the same direction

There are twelve cases with three solid boundaries and two of the solids lie in the same direction. Below we show the case in which the x -direction and the w_1 face are blocked. We have the following velocity field:

$$V_x = 0 \quad (\text{C.13a})$$

$$V_y = \frac{12v_1}{\Delta x^2 \Delta z} (x_2 - x)(x - x_1)(z - z_1) + \frac{12\Delta v}{\Delta x^2 \Delta y \Delta z} (x_2 - x)(x - x_1)(z - z_1)(y - y_1) \quad (\text{C.13b})$$

$$V_z = \frac{6w_2}{\Delta x^2 \Delta z^2} (x_2 - x)(x - x_1)(z - z_1)^2 \quad (\text{C.13c})$$

The transit times in the y and z directions are:

$$\tau_y = \frac{\Delta x^2 \Delta z^2}{6w_2 \Delta x_{2p} \Delta x_{p1} \Delta z_{p1}} \left[1 - \sqrt{\frac{v_2 \Delta y}{v_1 \Delta y + \Delta v \Delta y_{p1}}} \right] \quad (\text{C.14a})$$

$$\tau_z = \frac{\Delta x^2 \Delta z^2}{6w_2 \Delta x_{2p} \Delta x_{p1}} \frac{z_2 - z_p}{\Delta z_{p1} \Delta z} \quad (\text{C.14b})$$

and taking $\tau_e = \min(\tau_y, \tau_z)$ we have the exit point:

$$x_e = x_p \quad (\text{C.15a})$$

$$y_e = y_1 - \frac{v_1 \Delta y}{\Delta v} + \left[\frac{v_1 \Delta y + \Delta v \Delta y_{p1}}{\Delta v} \right] \left[1 - \frac{6w_2 \Delta x_{2p} \Delta x_{p1} \Delta z_{p1} \tau_e}{\Delta x^2 \Delta z^2} \right]^2 \quad (\text{C.15b})$$

$$z_e = z_1 + \frac{\Delta x^2 \Delta z^2 \Delta z_{p1}}{\Delta x^2 \Delta z^2 - w_2 \Delta x_{2p} \Delta x_{p1} \Delta z_{p1} \tau_e} \quad (\text{C.15c})$$

where $\Delta x_{2p} = x_2 - x_p$, $\Delta x_{p1} = x_p - x_1$, $\Delta y_{p1} = y_p - y_1$ and $\Delta z_{p1} = z_p - z_1$.

C.3 Pores with four solid boundaries

There are fifteen cases with a pore voxel and four solid neighbours. In three of them two directions are blocked. The other twelve have the four solids arranged in three directions (e.g. two solids in x , one in y and one in z).

C.3.1 Two directions blocked

Below the case where directions x and y are blocked, the cases with x and z or y and z blocked follow immediately.

Only the z component of the velocity field is non-zero:

$$V_z = \frac{36w_1}{\Delta x^2 \Delta y^2} (x_2 - x)(x - x_1)(y_2 - y)(y - y_1) \quad (\text{C.16})$$

integrating along the streamlines we have the time-of-flight:

$$\tau_e = \tau_z = \frac{\Delta x^2 \Delta y^2 (z_2 - z_p)}{36w_1 \Delta x_{2p} \Delta x_{p1} \Delta y_{2p} \Delta y_{p1}} \quad (\text{C.17})$$

and the exit point comes straightforwardly:

$$x_e = x_p \quad (\text{C.18a})$$

$$y_e = y_p \quad (\text{C.18b})$$

$$z_e = z_p + \frac{36w_1 \Delta x_{2p} \Delta x_{p1} \Delta y_{2p} \Delta y_{p1} \tau_e}{\Delta x^2 \Delta y^2} = z_2 \quad (\text{C.18c})$$

C.3.2 Solids in three directions

Below the case with solids in $(i+1, j, k)$, $(i-1, j, k)$, $(i, j+1, k)$ and $(i, j, k-1)$. The velocity field is:

$$V_x = 0 \quad (\text{C.19a})$$

$$V_y = \frac{12v_1}{\Delta x^2 \Delta y^2 \Delta z} (x_2 - x)(x - x_1)(y_2 - y)^2(z - z_1) \quad (\text{C.19b})$$

$$V_z = \frac{12w_2}{\Delta x^2 \Delta y \Delta z^2} (x_2 - x)(x - x_1)(y_2 - y)(z - z_1)^2 \quad (\text{C.19c})$$

the time-of-flight in y and z directions:

$$\tau_y = \frac{\Delta x^2 \Delta y^2 \Delta z}{12v_1 \Delta x_{2p} \Delta x_{p1} (y_2 - y_p)(z_p - z_1)} \ln \left(\frac{y_2 - y_p}{\Delta y} \right) \quad (\text{C.20a})$$

$$\tau_z = \frac{\Delta x^2 \Delta y \Delta z^2}{12w_2 \Delta x_{2p} \Delta x_{p1} (y_2 - y_p)(z_p - z_1)} \ln \left(\frac{\Delta z}{z_p - z_1} \right) \quad (\text{C.20b})$$

and the exit point is:

$$x_e = x_p \quad (\text{C.21a})$$

$$y_e = y_2 - \Delta y_{2p} \exp \left(\frac{-12v_1 \Delta x_{2p} \Delta x_{p1} \Delta y_{2p} \Delta z_{p1} \tau_e}{\Delta x^2 \Delta y^2 \Delta z} \right) \quad (\text{C.21b})$$

$$z_e = z_1 + \Delta z_{p1} \exp \left(\frac{12w_2 \Delta x_{2p} \Delta x_{p1} \Delta y_{2p} \Delta z_{p1} \tau_e}{\Delta x^2 \Delta y \Delta z^2} \right) \quad (\text{C.21c})$$

AVERAGE FLUX OF PARTICLES IN A DIFFUSION STEP

Here is derived the expression for the average number of particles crossing the solid-fluid interface during diffusion, eq. 1.11. A particle located at a distance s from a solid voxel face crosses it when:

$$\frac{s}{\lambda} + \frac{1}{2} \leq \xi < 1 \quad (\text{D.1})$$

which implies that $s \leq \Delta X_i^{diff} \leq \lambda/2$ and that $s \leq \lambda/2$. Since ξ is a random number, uniformly distributed over 0 and 1, the probability of crossing is:

$$P(s) = \frac{1}{2} - \frac{s}{\lambda} \quad (\text{D.2})$$

If the local concentration of particles is C and the cross-sectional area of the voxels is l^2 , the number of particles that cross this particular interface during the diffusive step is:

$$p = Cl^2 \int_0^{\lambda/2} P(s) ds = Cl^2 \frac{\lambda}{8} \quad (\text{D.3})$$

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