

MODELLING OF MULTICOMPONENT REACTIVE TRANSPORT ON PORE SPACE IMAGES

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DECLARATION OF ORIGINALITY

I declare that this thesis is entirely my own work under the supervision of Dr Branko Bijeljic and Prof. Martin J. Blunt. The work was performed in the Department of Earth Science and Engineering at Imperial College London. All published and unpublished materials used in the thesis have been given full acknowledgement. This work has not been previously submitted, in whole or in part, to any other academic institution for a degree, diploma, or any other qualification.

Thomas David Serafini de Oliveira

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ABSTRACT

We present a new model to simulate multispecies reactive transport on pore space images. We solve the Navier-Stokes equations and the advection-diffusion equation for concentration fields on an unstructured grid using the finite volume method. We couple it with the chemical model Reaktoro, which we use to calculate the chemical equilibrium in each grid cell, considered as a completely mixed batch reactor.

We validate the model against analytical solutions and experimental data, and investigate, for a range of Péclet numbers, the interplay between transport and reaction for multispecies reactive transport in a 3D bead pack where two streams of reactants at different pH are injected in parallel. We analyse the distribution of species and the rates of formation and consumption and find that, despite the relative homogeneity of the bead pack, the concentration fields of the products can be asymmetric because of the interplay between transport and chemical equilibrium. We observe that lower Péclet numbers give rise to higher relative yields because of increased transverse mixing by diffusion. However, higher absolute yields are obtained at higher injection velocities because of larger amount of matter available for reaction. Reaction is more favoured in the faster-flowing regions. However, this effect is more marked for species for which advection is the dominant mechanism of transport to reactive sites, as opposed to diffusion-mediated reactions where the full velocity distribution is sampled before reaction occurs.

Furthermore, we study multispecies mixing and reaction in a more heterogeneous carbonate sample. We use a micro-CT image of Portland limestone containing both macroporosity resolved at the image resolution, and sub-resolution microporosity which is quantified using difference imaging. We extend our solver to accommodate transport and reaction in microporous regions. We demonstrate how the highly variable flow field in carbonate allows reactants and products to disperse more rapidly compared to the more homogeneous bead pack, resulting in a highly non-uniform reaction rate and concentration distribution. This is due to a complex interplay between advection-dominated flow and reaction in the connected fast-flowing macroporous regions, and diffusion-mediated transport and reaction in microporosity. Multispecies mixing and reaction in natural rocks are much more complex than hitherto observed, which needs to be considered in reactive transport studies at different length-scales.

Finally, we test the applicability of our code to study dissolution. We first validate our code on multispecies dissolution of a single sphere and a semi-infinite solid. Then, we study dissolution on a micro-CT image composed of dolomite and calcite in ratio 10:1. We find that fast channels are strongly associated with dissolved dolomite, high concentrations of reactants, and low concentrations of products.

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INTRODUCTION

1.1 Reactive transport in porous media

Many natural and man-made processes involve simultaneous flow and reaction in porous media, and would have significantly different outcomes if the reactions did not take place. Since the reactions can contribute to the objective of a devised process or be an obstacle to its achievement, it is important to study them to understand and possibly control their effects.

One example of such a process is groundwater remediation. Industrialization, urbanization and intensive farming techniques have led to elevated concentrations of a wide range of important contaminants in groundwater, which affect the quality of water supply of millions of people worldwide. For instance, nitrate from nitrogen fertilizer ([Babiker et al., 2004](#)), wastewater or solid waste disposal ([Wakida and Lerner, 2005](#)) can reach groundwater and render it improper to human consumption. To mitigate the effect of pollutants in aquifers, reactants such as zero-valent iron ([Fu et al., 2014](#)) can be injected in the subsurfaces of the contaminated areas to transform the contaminant into safer products.

A second example is the injection of CO_2 for enhanced oil recovery or carbon geosequestration, which has led researchers to study how the injected streams change the composition ([Xu et al., 2010](#), [Nazarian et al., 2014](#)) and distribution of fluids ([Lu et al., 2009](#), [Sigfusson et al., 2015](#)), and the structure of the rock ([Kang et al., 2010](#), [Steefel et al., 2013](#), [Ovaysi and Piri, 2014](#), [Trebotich et al., 2014](#)), and hence its hydraulic and mechanical properties ([Alam et al., 2014](#)). To increase the recovery factor, CO_2 is injected into the reservoir to reduce the oil viscosity and oil-water interfacial tension ([Lake, 1989](#)). However, along with these effects, CO_2 can dissolve in the in situ brine forming carbonic acid, which reacts with the rock.

Reactive transport modelling is also important in other fields, such as fuel cell design ([Haberman and Young, 2004](#)) and the storage of reactive gases for the chemical

industry (Hughes, 2008). However, underground reservoirs have two characteristics not present in manufactured materials that call for special techniques for their study: they have a more heterogeneous structure and composition and their exact characteristics are not known except in very limited locations.

Numerical simulation is useful to investigate the behaviour of reactive transport in porous media, assess the value of properties that cannot be measured in the laboratory or in the field, explore a variety of conditions whose replication can be expensive or time-consuming, replace destructive experiments, and forecast the probable outcome of alternative designs and operating conditions. A widespread approach for numerical simulation is to discretize the medium into cells and assign to each of them a single value for properties such as porosity, permeability, pressure and saturations, then relate each cell and its neighbour's properties by evolution equations and solve the set of equations obtained. Since calculation time increases with the number of cells used, there is a practical upper bound, which is around 10^7 to 10^9 cells in currently commonly available computers and clusters. For a subsurface reservoir, this implies grid cells that are tens or hundreds of metres long. Since the reservoir is not homogeneous at the scale of the cell, some upscaling method is required to assign to each cell an equivalent overall value for each property and/or to find out alternative evolution equations that better represent the system at the scale of the cell.

At the same time, reactive transport phenomena in porous media occur at pore scale. Although their effect can be felt at larger scales, it is to the pore scale that phenomena such as dissolution and precipitation of minerals, and changes in porosity and permeability, can be traced. It is also at this scale that continuum models can provide excellent agreement between models and observations because homogeneous extents of fluid and rock can be better identified, and the geometry of grains and the distribution of minerals can be taken into account in an explicit way. These considerations explain why reactive transport modelling has been employed at different scales, with the ultimate goal of linking the scale at which rock properties and fluid distribution vary to the scale of blocks used in whole field simulations (Scheibe et al., 2015).

Several studies have shown how to properly transfer information from the pore to field continuum scale. However, there is still no consensus on how to perform these operations (Sanchez-Vila and Fernàndez-Garcia, 2016). One reason for this is that we still lack fundamental understanding about the behaviour of pore-scale reactive transport through physically and chemically heterogeneous porous media. Lichtner and Kang (2007b) proposed a multiscale formulation to upscale reactive transport equations. They simulated reactive transport at the pore scale in an idealized geometry, and were able to reproduce the results using a larger-scale dual-continuum model. The reaction considered was a linear kinetics law and involved a single component. Li et al. (2006) used a significantly more complex kinetics model in their work for the

dissolution of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8(\text{s})$) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})$). Their starting point was a pore-network model in which each pore was described in terms of surface area and volume. Consequently, no detailed geometric description of the pore space was possible. While the approach of previous works involved first running a pore-scale simulation and then using the results to parametrise a continuum-model, [Battiato et al. \(2011\)](#) proposed the use of hybrid simulation, where pore-scale and continuum-scale simulations were performed in a coupled way, constantly exchanging data. They applied their method to an idealized fracture with reacting walls.

In spite of these contributions, the scale at which they were applied does not take into account the detailed physical structure of the pore space in the simulation. In 2015, [Pereira Nunes et al.](#) proposed a methodology that contributed to filling this gap. They showed how to simulate a reactive flow directly on an image obtained from microtomography using a streamline-based particle tracking approach. Using this methodology, [Pereira Nunes et al. \(2016a\)](#) demonstrated a large impact of initial physical (flow) heterogeneity on reaction rates in a bead pack, Ketton and Estailades limestone in numerical simulations of acidization. However they did not address multispecies reactive transport and the impact of chemical heterogeneity, which can play a significant role in the estimation of reaction rates, as [Li et al. \(2006\)](#) have demonstrated for pore-network models.

A promising approach to understanding reactive transport is to start at the pore scale, where the system is well characterized, and then, by a succession of upscaling steps, get to equivalent properties and equations at the larger scale desired ([Lichtner and Kang, 2007b](#), [Kim et al., 2011](#)). Pore-scale experiments and models have been shown to be able to provide insights into the behaviour of reactive flow in porous media ([Szymczak and Ladd, 2009](#), [Ovaysi and Piri, 2014](#), [Pereira Nunes et al., 2016b](#)), the source of the scale dependency of mineral reaction rates ([Kang et al., 2010](#), [Molins et al., 2012](#)), and have been used to compute upscaled properties — such as overall reaction rate — for use in larger-scale models ([Porta et al., 2012](#), [Noiriel et al., 2012](#), [Varloteaux et al., 2013a](#)).

Although a complete understanding of the pore-scale behaviour has not yet been achieved ([Blunt et al., 2013](#)), the advances in the last two decades are remarkable, pushed by developments in laboratory techniques ([Steefel et al., 2015b](#), [Noiriel, 2015](#)) and modelling ([Molins, 2015](#)). A previously unexplorable area was opened to modelling when the observation of rocks at the pore scale by X-ray microtomography (micro-CT) ([Wildenschild et al., 2002](#)) and magnetic resonance imaging ([Baldwin et al., 1996](#), [Sheppard et al., 2003](#)) became available. Recent progress has enabled reservoir-condition experimentation ([Andrew et al., 2013](#)), dynamic synchrotron tomography ([Berg et al., 2013](#), [Andrew et al., 2015](#), [Menke et al., 2016](#)) and the study of the impact of physical and chemical heterogeneity at the pore scale ([Al-Khulaifi et al., 2017, 2018](#)). X-ray images provide the spatially resolved geometry of the pore space and fluid distributions, which poses a new challenge for reactive transport

models — while in reservoir-scale simulation grid cells contain both fluid and solid phases modelled as volume fractions, in pore-scale simulation there can be a clear distinction between void and solid cells, which requires treatment of the interface between them.

One of the key properties of interest in reactive flow in porous media is the reaction rate, which can differ by orders of magnitude depending on the scale of the system under consideration. An early statement of this scale dependency was made by [Swoboda-Colberg and Drever \(1993\)](#), who reported a factor of 200 between mineral dissolution rates measured for $\sim 100\mu\text{m}$ soil samples and those observed on 2m^2 soil plots. This discrepancy could be due to the experiments having been conducted in conditions farther from thermodynamic equilibrium than those observed in the field, and reaction being controlled by transport, which impacts the rate of mixing of reactants (see, e.g., [White and Brantley \(2003\)](#), [Dentz et al. \(2011\)](#), [Porta et al. \(2012\)](#)).

As computational power increases, a wider range of models for direct numerical simulation of reactive transport have become available, such as those presented by [Molins et al. \(2014\)](#), [Alhashmi et al. \(2015\)](#), [Pereira Nunes et al. \(2016b\)](#), [Mostaghimi et al. \(2016\)](#), [Gray et al. \(2016\)](#), [Soulaine and Tchelepi \(2016\)](#), [Engdahl et al. \(2017\)](#), [Maes and Geiger \(2018\)](#). The accurate description of pore space geometry present in direct simulation allows incomplete mixing to be correctly modelled as shown, for example, by [Alhashmi et al. \(2015\)](#), who were able to reproduce the early incomplete mixing present in [Gramling et al. \(2002\)](#)'s experiment of bimolecular reaction in a bead pack without requiring calibration parameters. Moreover, [Alhashmi et al. \(2016\)](#) studied the impact of physical heterogeneity for bimolecular reactive transport in a bead pack and two sandstones using a characterization of physical heterogeneity by velocity distributions ([Bijeljic et al., 2013a](#)). They showed that the evolution of reaction rates depends strongly on the physical heterogeneity, manifested by the existence of fast flow channels and slow stagnant regions. However, few of these models offer a general multispecies geochemistry formulation. With the exception of the models by [Molins et al. \(2014\)](#), which incorporate the capabilities of CrunchFlow ([Steeffel et al., 2015a](#)), and the models by [Engdahl et al. \(2017\)](#) and [Maes and Geiger \(2018\)](#), which make use of Phreeqc ([Parkhurst and Wissmeier, 2015](#)), reactions are limited to a couple of species and modelled to suit a specific application. This points to a need for further development of multispecies reactive transport models on micro-CT pore space images.

Considering that an accurate description of solid geometry is now available through micro-CT imaging, the present work aims to establish a novel methodology to perform the direct simulation of multicomponent reactive transport in heterogeneous media, and so to reveal new insights into the impact of physical heterogeneity on mixing and reaction. This aims to help develop better understanding of the pore-scale phenomena which can in future be used for description of processes at larger

scales.

1.2 Unresolved problems

Current efforts in search of a better understanding of pore-scale reactive transport in heterogeneous rocks, especially when a large number of chemical species are involved, are focused on investigating the influence of the physical heterogeneity and spatial distribution of minerals on dissolution regimes and reaction rates. In this thesis, we will endeavour to answer the following questions:

1. How does multicomponent mixing impact reaction rates in porous media at different transport conditions?
2. How does physical heterogeneity impact mixing and reaction rates in multicomponent systems?
3. Which insights can we obtain at the pore scale that can be useful for upscaling?

1.3 Objectives of this work

1. To develop a new model to perform pore-scale simulation of reactive transport and so contribute for the understanding of fluid-fluid and fluid-solid reactive transport processes that happen at the pore scale. The model is able to simulate single-phase multimineral and multicomponent advective-diffusive-reactive transport through pore space images, and can be used to study the impact of physical and chemical heterogeneity on reaction rates and the impact of multicomponent reaction on mixing driven systems.

We solve the Navier-Stokes equations and the advection-diffusion equation for concentration fields using the finite volume method and, considering each grid cell as a completely mixed batch reactor, we compute homogeneous reactions in the liquid phase using a geochemical model. Part of the strength of poreReact relies on using OpenFOAM ([Ubbink, 1997](#), [Rusche, 2002](#), [OpenFOAM, 2015](#)), which is a parallel open source library for the development of numerical solvers for continuum mechanics problems. It employs the finite volume method to solve partial differential equations on unstructured grids and offers a variety of pre- and post-processing tools, discretization schemes and parallel numerical solvers, which are immediately available for poreReact. Grids can be composed of any combination of convex polyhedra, such as hexahedra, pyramids and tetrahedra. In this work, emphasis is put on regular hexahedral grids because of our interest in voxelized pore space images of consolidated rock obtained from X-ray microtomography.

The reaction step in our model is performed using Reaktoro, a general and advanced solver for chemical reaction modelling (Leal, 2015, Leal et al., 2016a). Reaktoro implements novel and fast numerical methods for chemical equilibrium and kinetics calculations that are specifically designed for applications that require thousands to millions of such calculations, such as reactive transport simulation. Each calculation assumes a completely mixed batch system, and is performed in each grid cell at every time step of the simulation to account for fluid-fluid reaction. Because Reaktoro can be used for a variety of chemical systems, poreReact is not limited to a small predefined set of chemical reactions, and is applicable for numerous problems that involve reactive transport besides the geoscience applications we focus on in this work.

2. To look into the impact of physical heterogeneity on mixing-driven fluid-fluid multicomponent chemical reaction in porous media. Exemplars of a homogeneous medium (bead pack) and a highly complex heterogeneous medium (microporous carbonate) are used to have a variety of pore-scale complexity which is reflected in different physical heterogeneity.
3. To examine the impact of transport on reaction rate during multicomponent dissolution. To explore this impact, we test the performance of our model on multicomponent dissolution of a single sphere, and multicomponent dissolution on a semi-infinite solid. Here we examine the applicability of our model to simulate dynamic changes in solid geometry caused by dissolution.

1.4 Thesis outline

In what follows, Chapter 2 provides a detailed literature review of the topics addressed in this thesis with a particular emphasis on imaging, experiments and pore-scale reactive transport. The dimensionless quantities used in the thesis are also presented as well as the geochemical reactions used for limestones.

Chapter 3 presents the numerical model developed. The flow and transport model is validated against analytical and well-established test cases.

Chapters 4 and 5 present the main body of the results on fluid-fluid multispecies reactive transport in porous media. Chapter 4 first validates the model for fluid-fluid reactive transport with comparison against micromodel experiments in the literature. Then numerical results for reaction in a bead pack under a variety of flow conditions are presented. In Chapter 5 we examine in detail how complex pore structure of a microporous carbonate impacts mixing, and in turn, the formation and consumption rates. This chapter puts an emphasis on studying complexities related to non-asymptotic reactive transport behaviour.

CHAPTER 1. INTRODUCTION

[Chapter 6](#) presents our results on dissolution, showing first numerical comparisons against analytical solutions and then some exploratory results for dissolution in a heterogeneous carbonate.

[Chapter 7](#) concludes the thesis with an overall discussion and suggestions for future work.

LITERATURE REVIEW

2.1 Mixing and reaction in heterogeneous rocks

Mixing and reaction in heterogeneous rocks have received attention from the scientific community for many decades. Recent reviews of the efforts in studying these processes by modelling (Steeffel et al., 2015b, Molins, 2015) and imaging at the pore scale (Noiriel, 2015) and at the Darcy scale (Dentz et al., 2011) provide a comprehensive view of the achievements and unresolved problems.

As mentioned in Chapter 1, one of the long-standing problems involving reactive transport in porous media is that reaction rates observed at large scales are much lower than those measured in batch reactors. Possible causes for that are the loss of reactive sites with time (Maher et al., 2006), the existence of preferential flow paths and non-uniformity of particle distribution (Malmström et al., 2000), and concentration gradients not captured by large-scale models, which can be caused by the spatial distribution of minerals (Li et al., 2007b) and transport limitations (Li et al., 2008). These causes are related to physical and chemical heterogeneity.

A heterogeneous property is one whose spatial average over a sample volume of a certain size and orientation varies if the sample volume is translated. By *physical heterogeneity*, we refer to the pore structure heterogeneity whose effects on the flow would exist even if the rocks were made of an inert material, while by *chemical heterogeneity*, we refer to the heterogeneity in the spatial distribution of minerals.

Physical heterogeneity is related to the geometric structure of the pore space. Many properties are used to physically characterize the pore space, and the medium can be heterogeneous in relation to one or more of them. Example of such properties are porosity, permeability, tortuosity, average coordination number, pore- and throat-size distribution, and distribution of the velocity magnitude of flow through it. Among those properties, one that is particularly useful when studying reactive transport is the distribution of the velocity magnitude. Bijeljic et al. (2013a) studied the

velocity distribution in some representative quarry carbonates (Indiana, Estailades, Ketton, and Mount Gambier). We can see in Fig. 2.1 some of their results. It shows the probability density functions (PDFs) of the velocities normalized by the average flow speed for the different samples and the homogeneous limit of a single circular tube (black solid line). We can observe that the normalized velocities in Mt Gambier have a narrower distribution than in Indiana, with more velocities similar to the average, which allows us to say that the former is more physically homogeneous. One of the consequences of the heterogeneity is a larger deviation from Fickian behaviour of solute dispersion through the rock.

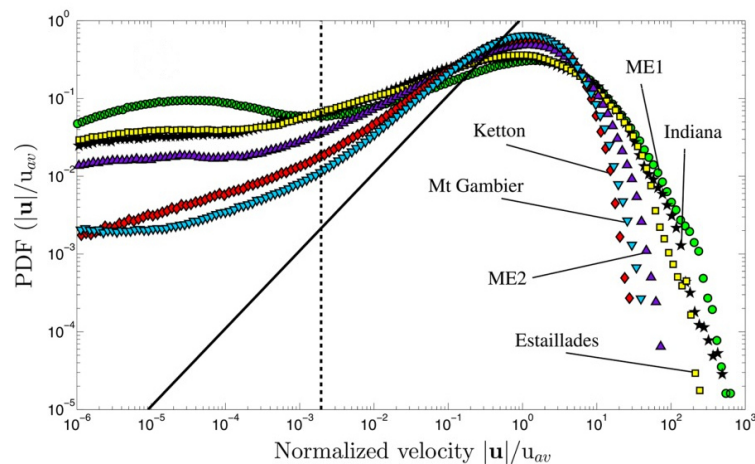


Figure 2.1: PDF of the velocity distributions for the carbonates Indiana, Estailades, Ketton, Mount Gambier, and two samples from the Middle East, ME1 and ME2. The solid line shows the homogeneous limit of velocity distribution, represented by a single circular tube. Fig. 6b from Bijeljic et al. (2013a) reprinted with permission. ©2013 American Geophysical Union.

In one of the first experimental studies on the impact of physical heterogeneity on reaction, Willingham et al. (2008) examined the impact of porous media structure on mixing and fluid-fluid reaction by building periodic 2D micromodels with different patterns: a periodic array of small cylinders; a periodic array of large cylinders; an array in which small cylinders are located between large cylinders; horizontal ellipses; and vertical ellipses. Then they injected a solution of Ca^{2+} in parallel with a solution of OG5N (a fluorescent Ca^{2+} indicator). It was observed that, even in these periodic idealized structures, the grain size alone is not sufficient to explain mixing, but that the grain orientation impacts mixing and product formation, and flow focusing enhance transverse concentration gradients that favours diffusion.

Flow focusing was also the subject of experimental study by Ye et al. (2015a). They filled a cuboid chamber with glass beads and created a high-permeability inclusion with coarser beads in the centre of it. The inlet face of the chamber contained 5×5 ports, which allowed them to vary the injection position of two tracers injected in parallel. They evaluated the overall impact of two competing effects created by

the inclusion: on the one hand, the approximation of streamlines and consequent increase in transversal concentration gradients, which increased transverse mixing; on the other hand, the time to travel a certain longitudinal distance is smaller through the inclusion, which decreased mixing. They concluded that the two effects cancel each other if the flow focusing is identical in the two transverse directions. In a similar experimental arrangement, the same authors studied flow focusing in 2D to evaluate the effect of dimensionality. The 2D arrangement also served as a limiting case for anisotropy in the two transverse direction, where the flow focusing occurs in only one direction. They observed that, while transverse mixing is more pronounced in 3D because dispersion acts in two directions, the effect of flow focusing in mixing is more pronounced in 2D, and it prevails over the effect of reduction in travel time across the inclusion.

Fluid-solid chemical reaction such as carbonate dissolution is also a process in which the impact of initial physical heterogeneity needs to be addressed. While manufactured arrangements allow a better control of pore structures, observations in natural porous media require a method to group samples to study and discern patterns of the evolution of reaction, especially when destructive fluid-solid reaction is involved. Dissolution patterns in small calcite samples were studied using micrometre-resolution imaging under different flow conditions by [Menke et al. \(2016\)](#). This work was extended by [Al-Khulaifi et al. \(2018\)](#) who used the distribution of pore-scale velocities to screen samples before studying dissolution. Firstly, using X-ray microtomography they imaged eight samples drilled from a single block of Silurian dolomite. Then, they used a Navier-Stokes flow solver to simulate the velocity field in each sample, analysed the frequency distribution (PDF) of flow velocities, and chose two pairs for experimentation based on the similarity of the PDFs. For each pair, the experiment was performed at two flow rates, and the screening allowed them to distinguish the impact of initial pore structure from that of the flow rate. A higher flow rate promoted the dissolution and widening of many channels, while the low flow rate led to the creation of few preferential flow-paths. This effect was more accentuated in the samples that were initially more heterogeneous.

Modelling to study fluid-fluid reactive transport on pore space images was first employed by [Alhashmi et al. \(2015\)](#), who developed a model to simulate flow, transport and fluid-fluid bimolecular reactions ($A + B \longrightarrow C$). We describe their model in [Section 2.5](#) but highlight here some of their findings. The first application of their model was to simulate mixing and reaction in a bead pack. Reactant A was initially present in the whole pore space and reactant B was injected at the inlet face. A good agreement between the simulations and the experimental results presented by [Gramling et al. \(2002\)](#) was obtained, while the 1D continuum scale advection-diffusion-reaction (ADRE) equation overestimated the reaction rate at early times. The key reason for the discrepancy was incomplete mixing, whose effect was not captured by the standard 1D ADRE. [Sanchez-Vila et al. \(2010\)](#) proposed a modification

to the reactive term of the ADRE that successfully captured this effect.

Using the same numerical model, [Alhashmi et al. \(2016\)](#) evaluated the impact of physical heterogeneity on fluid-fluid reaction rate in natural porous media. They simulated the reactive transport in a bead pack, a Bentheimer sandstone, and a Doddington sandstone for a range of Péclet and Damköhler numbers. They found that for intermediate Péclet numbers, the amount of reaction in the sandstones is higher than in the bead pack, and suggested that this is promoted by the higher physical heterogeneity which increases mixing. For high Péclet numbers, however, the trend is reversed because the injected reactant flows preferentially through fast channels and does not reach more stagnant zones. It is of great interest to examine the role of physical heterogeneity in multicomponent fluid reactive transport, and in particular how it affects mixing and reaction dynamics. To address this, in this study we will perform reactive transport simulations on micro-CT images of a microporous carbonate (Portland limestone) and compare it to the corresponding study on a mono-spherical bead pack.

Simulation has also been used to study the impact of physical heterogeneity on dissolution. For example, [Pereira Nunes et al. \(2016a\)](#) employed a particle approach to simulate the dissolution of three images of calcite in order of increasing complexity and heterogeneity: a bead pack, a Ketton oolite and an Estailades carbonate. They obtained rates of dissolution one or two orders of magnitude lower than the batch reactor rates due to transport limitations. This effect was more pronounced in the more heterogeneous sample, where dissolution occurs preferentially in fast flow channels, leaving stagnant zones largely undissolved. This is in agreement with the observations of [Alhashmi et al. \(2016\)](#) for fluid-fluid reaction mentioned above, and the experimental results of [Menke et al. \(2016\)](#). By simulating the dissolution in a 2D system with different degrees of heterogeneity, [Molins et al. \(2012\)](#) also concluded that more heterogeneous systems exhibited smaller reaction rates because the existence of slow velocity regions meant that reaction was more strongly limited by transport in parts of the domain.

[Meile and Tuncay \(2006\)](#) analysed the scale dependence of reaction rates on an artificial porous medium generated using the overlapping sphere method with spheres of constant radii. They employed a Galerkin finite element algorithm for the transport of the concentration field and considered a homogeneous bimolecular reaction and a heterogeneous reaction with one component in the liquid phase. They compared the simulated results at the pore scale with results obtained by a continuum model. The discrepancy between the models was only a few percent for the bimolecular reaction but one order of magnitude for the heterogeneous reaction, and they concluded that this discrepancy is higher for surface reactions because these reactions cause larger concentration gradients. We speculate that the lower concentration gradients they found for homogeneous reaction compared to heterogeneous reaction and the consequent degree of agreement between the pore-scale and the continuum

models, are the result of their choice of boundary conditions: while in the heterogeneous reactions the characteristic length for the variation of the concentration is about the distance between grains, in the homogeneous reactions this characteristic length is about the whole length of the model since maximum and minimum values for the concentration fields were fixed at the faces of the model.

It is also worth mentioning that in addition to physical heterogeneity, chemical heterogeneity can play a significant role in the estimation of reaction rates (Li et al., 2006) and interact with physical heterogeneity both in subsurface porous media (Al-Khulaifi et al., 2017) and fractures (Noiriel et al., 2007, 2013). Ellis et al. (2011) considered how a fractured carbonate caprock formed mainly by calcite and dolomite would dissolve in the presence of CO₂-acidified brine. They injected CO₂-saturated brine at $T = 27^\circ\text{C}$ and $p = 10\text{ MPa}$ on a sample core composed of around 45 % calcite, 45 % dolomite and 10 % of other minerals such as quartz, K-feldspar, clay minerals and pyrite, in which they created a fracture prior to injection. Since calcite is more reactive than dolomite, it dissolved faster and led to an uneven erosion of the fracture surface. The width of the fracture increased with dissolution. However, a localized unaltered band of silicates near one of the extremities of the fracture remained as a narrow restriction limited the increase in permeability.

Molins et al. (2017) simulated reactive transport in a 2D domain that was a conceptualization of a cross-section from the experiment of Ellis et al. (2011). They showed that as the calcite dissolves, the remaining calcite surface is further away from the fracture channel, which increases transport limitations on the rate of dissolution of calcite. At the same time, a larger area of dolomite is exposed and the concentration of Mg²⁺ in the effluent increases.

Li et al. (2007a,b) evaluated the ability of a continuum-scale model for dissolution of spatially distributed anorthite and kaolinite to reproduce the results obtained with the pore network models (PNM). The reactive minerals were spatially grouped in clusters of different size. The reaction rates per unit surface area were higher for smaller clusters. The models were in closer agreement when the reactive minerals were grouped in more and smaller clusters because in these cases the spatial distribution of concentration is more homogeneous. This adds to the body of evidence that large-scale models differ more from small-scale ones when gradients in concentration are present.

Li et al. (2008) studied the dissolution of cylindrical pores drilled through single crystals of calcite. This simple and well-controlled geometry allowed them to precisely represent the domain in the pore-scale simulation they performed on the same system. The simulation reproduced the concentration of Ca²⁺ in the effluent within 12 % of the measured value. They then used the simulator to evaluate the impact of flow velocity and rate constant on the rate of dissolution, and compared the predicted values with those that would be obtained by assuming the pore as a continuous stirred tank reactor. They found that the predictions obtained in these

two ways disagreed if concentration gradients were formed within the pore. They concluded that the concentration gradient at the scale of a single pore cannot explain the discrepancy observed between field-measured reaction rates and rates measured in the laboratory under well-mixed conditions because in practical applications flow velocities are typically lower than 10^{-5} m/s, meaning that advection is not important at the pore scale. We would like to point out, however, that for a characteristic length of $L = 100\text{ }\mu\text{m}$ and a diffusion coefficient of $D = 1 \times 10^{-9}\text{ m}^2/\text{s}$, a Péclet number of 1, indicating an equal balance of advective and diffusive transport, is obtained for flow velocities of 10^{-5} m/s. Moreover, a typical average flow velocity in an oil field is 3×10^{-6} m/s (e.g., Coats et al. (1971), Christie and Blunt (2001), Ren et al. (2015)) while groundwater flow velocities can be of the order of 10^{-4} m/s (e.g., Sugisaki (1961)). In addition, these are averages, and flow velocities near wells or in higher permeability regions of the reservoir, which are also those which contribute most to the flow, can be higher. These observations mean that advective control at the pore scale is in reality common in subsurface flows.

Salehikhoo and Li (2015) explored the role of reactive surface distribution by injecting a low-pH ($pH = 4$) solution in packed columns of magnesite and quartz grains distributed in different spatial patterns. One of the patterns was a random distribution of magnesite grains within quartz grains, and the others were 1, 2 or 3 continuous cylindrical regions of magnesite grains surrounded by quartz grains. For each pattern, by varying the size of the magnesite grains, two columns were created, with different permeability ratios between the magnesite and the quartz regions. To complete the experimental design, the experiments were repeated at different flow rates. They noticed that the rate of dissolution of magnesite was lower by one to three orders of magnitude than the rate that would be expected from well-mixed conditions. However, they found that the rate of dissolution is proportional to the area A_e of magnesite exposed to fluid where $IAP/K_{eq} < 0.1$ (IAP is the ion activity product defined as $a_{\text{Mg}^{2+}}a_{\text{CO}_3^{2-}}$ and K_{eq} is the equilibrium constant for the dissolution of magnesite). The observed rate of dissolution was 2.5 times larger than kA_e . Accordingly, the rates of dissolution are highest under conditions that maximize A_e : high-permeability in the magnesite region or uniform distribution of magnesite grains.

Detailed experiments on the impact of heterogeneity at the pore scale have been performed but most of the modelling to date has been dedicated to simple irreversible bimolecular reaction or 2D geometries. In Section 2.5, we will focus our review specifically on the current state of multispecies reactive transport modelling. In the next section, we will describe the use of X-ray microtomography to obtain pore space images which are inputs to the modelling performed in this work. Our choice is driven by the ability of X-ray tomography to provide a detailed geometrical description of pore space with $\sim$ billion voxel information.

2.2 X-ray microtomography for reactive transport

The numerical modelling presented in this work requires a detailed description of the pore space geometry. One technique to obtain this description is X-ray microtomography (XMT), which consists of taking 2D radiographs of the sample from different angles and processing them to reconstruct a 3D image, which can be further treated and analysed. A thorough review on the current use of X-ray microtomography for the study and characterization of porous media can be found in [Noiriel \(2015\)](#).

XMT is non-invasive and non-destructive, and can be used over the course of dynamic experiments at in situ pressures and temperatures. A recent development in experimental apparatus reported by [Andrew et al. \(2013\)](#), for example, allowed the imaging of flow at 10 MPa and 50 °C by employing a carbon fibre core holder to maintain pressure, while remaining largely X-ray transparent.

The radiographs are typically composed of approximately 2000×2000 pixels, and the reconstructed image has around $2000 \times 2000 \times 2000$ voxels. The typical resolutions are from $0.5 \mu\text{m}$ to $5 \mu\text{m}$, which allows imaging of objects that measure from 1 mm to 10 mm. Therefore, what limits the resolution of the images is the desired size of the field of view. [Figure 2.2](#) shows a sample core plug and typical images obtained by XMT.

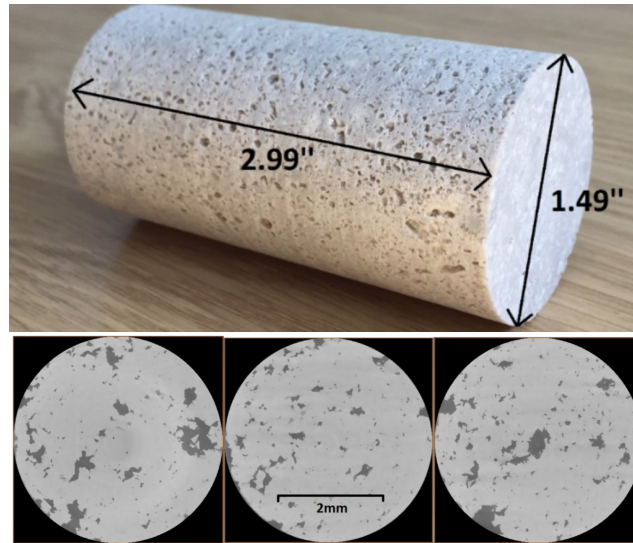


Figure 2.2: Top: a Silurian dolomite core plug. Bottom: cross-sections of a $2 \mu\text{m}$ resolution dry scan of Silurian dolomite. Courtesy of Yousef Al-Khulaifi.

Different materials absorb X-rays more or less efficiently, which generates images with different shades of grey. The greyscale data can be converted into several groups of voxels corresponding to the distinct phases (e.g., mineral, water, oil) based on their different X-ray absorption properties. This conversion is called segmentation. Laboratory-based X-ray sources provide polychromatic X-ray beams. Alternatively, synchrotron-based sources can be used. These can provide monochromatic X-ray

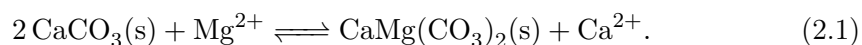
beams that result in higher signal-to-noise ratios. They also offer a higher flux of photons allowing the imaging of fast processes that can only be captured if a shorter exposure time is used.

Segmentation of the solid phase in different minerals can be done based on their attenuation properties and on their morphology, if the grains or mineral aggregates have regular shapes. Combining XMT to other microscopy observation techniques is also an alternative. [Peters \(2009\)](#) proposed methods to combine XMT to higher-resolution scanning electron microscopy (SEM) images and energy-dispersive spectroscopic (EDS) analysis to examine the mineral content of the surface in contact with the pore space. [Smith et al. \(2013\)](#) reported the use of these methods on parts of their samples of dolomite/anhydrite to calibrate the XMT greyscale and infer mineral distributions from it. More recently, these methods were used by [Lai et al. \(2015\)](#) to generate maps of minerals on the surface of Berea sandstone, and Edwards and Guelph carbonates. They were able to divide the minerals present in the Berea sandstone into four groups: feldspar, quartz, clay and other (mainly calcite). The minerals present in the Edwards carbonates were divided into quartz, dolomite+calcite and other (mainly hematite and pyrite).

Another improvement in characterization of carbonate rocks pore space was achieved by employing differential X-ray tomography ([Lin et al., 2016, 2017](#)). This method is based on subtracting the scans of carbonate rocks saturated with a 30 wt% KI brine solution and dry scans. The main advantages of this method are in that it provides spatially resolved information of porosity, including the sub-resolution pores, and, in particular, the information on pore space connectivity. In this thesis, we will use the Portland limestone image obtained in [Lin et al. \(2016\)](#) to study, for the first time, multicomponent mixing and reaction between two fluids flowing in parallel on a 3D pore space image including the effects of microporosity.

2.3 Geochemistry in carbonate rocks

Carbonates are sedimentary rocks composed primarily by carbonate minerals, the two main ones being calcite and dolomite ([Morse and Arvidson, 2002](#)). Most carbonate rocks are formed from the deposition of calcium carbonate in marine environments by marine organisms ([Miller, 1999](#)). Calcite is the most stable polymorph of calcium carbonate ($\text{CaCO}_3(\text{s})$), which can also crystallise in the form of the less stable aragonite. Rocks composed mainly of calcite and aragonite are called limestones. Magnesium ions can replace calcium ions in calcite according to the reaction: ([Chou et al., 1989](#))



The mineral product $\text{CaMg}(\text{CO}_3)_2$ is called dolomite, as are the rocks formed by this mineral. Most dolomites are secondary, formed from calcite through this process

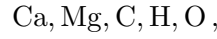
(Whitaker and Xiao, 2010).

According to Schlumberger (2007), more than 60% of the world's oil and 40% of the world's gas reserves are found in carbonate reservoirs. In Brazil, 54% of the oil and gas production (Agência Nacional do Petróleo Gás Natural e Biocombustíveis, 2018) in March 2018 came from the geological formations collectively known as the Pre-Salt layer, which are composed mainly of carbonates.

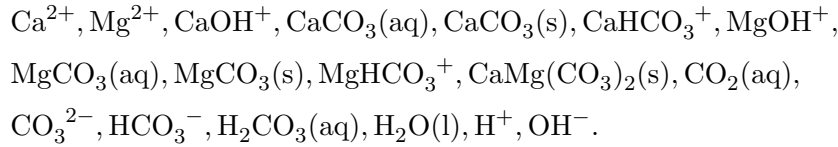
The injection of CO₂ in those rocks for carbon sequestration or enhanced oil recovery triggers chemical reactions that can alter the rock permeability and porosity.

2.3.1 Reaction equations

Applying the modelling proposed by Smith and Missen (1982) to the reaction of carbonated water with calcite and dolomite, we identify that the elements of interest are:

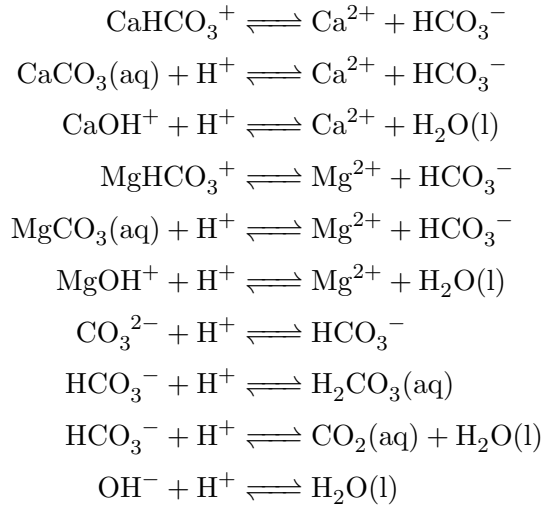


and that the chemical species of interest are:

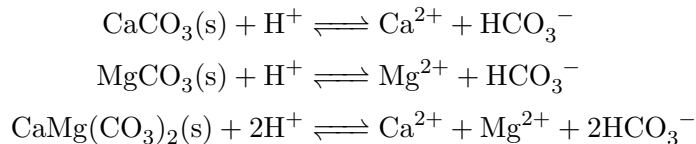


For this set of chemical species, the chemical reactions that can occur are linear combinations of the following ones:

- Homogeneous reactions:



- Heterogeneous reactions:



Under the assumption of partial equilibrium (Helgeson, 1968, Helgeson et al., 1969, 1970), we assume that homogeneous reactions reach equilibrium instantaneously, while the heterogeneous reactions are treated as kinetic reactions.

Plummer et al. (1978) measured the rate of calcite dissolution in carbonated water and noticed the existence of three regimes as a function of pH and partial pressure of CO_2 , as illustrated in Fig. 2.3. For low pH, the rate of dissolution is dependent only on pH. For intermediate pH, the rate is dependent on both pH and partial pressure of CO_2 . For high pH, they demonstrated that the back reaction (precipitation of CaCO_3) becomes important.

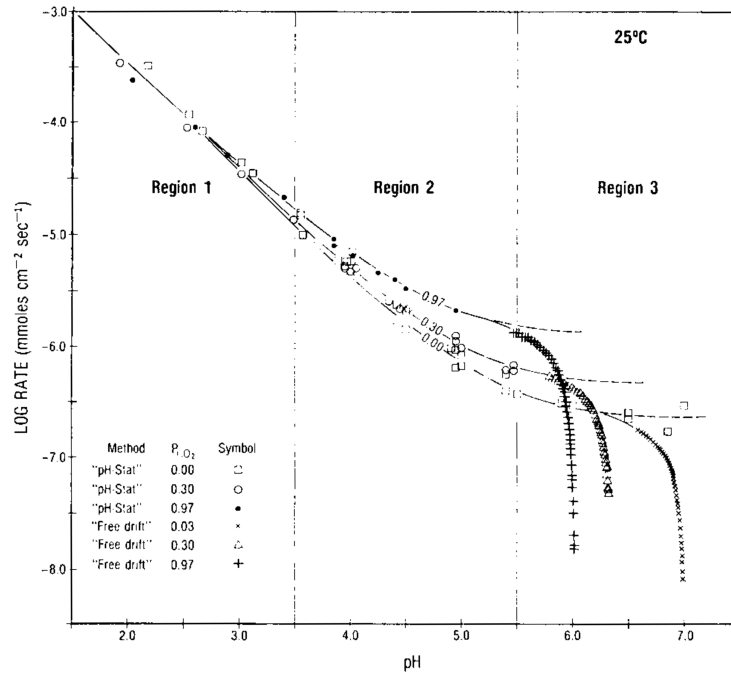
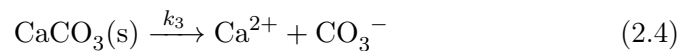
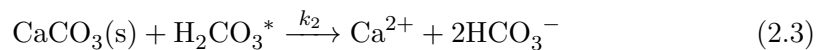
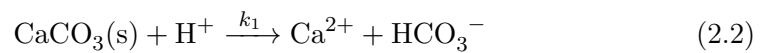


Figure 2.3: Rate of calcite dissolution as a function of pH and P_{CO_2} in stirred solutions at 25 °C. Three regimes can be observed. For low pH, the rate of dissolution. Fig. 1 of Plummer et al. (1978) reprinted with permission. ©1978 American Journal of Science.

To better comprehend these regimes and assign rate constant to which of them, Plummer et al. (1978) described the dissolution of CaCO_3 by the following parallel reactions, which can be obtained by linear combination of the chemical reactions presented above:



where H_2CO_3^* is the sum of $\text{CO}_2(\text{aq})$ and $\text{H}_2\text{CO}_3(\text{aq})$ in the aqueous system.

Far from equilibrium, the total CaCO_3 rate of dissolution can be modelled by

$$r = k_1 \alpha_{\text{H}^+}^{n_1} + k_2 \alpha_{\text{H}_2\text{CO}_3^*}^{n_2} + k_3, \quad (2.5)$$

where α_i is the activity of species i , and n_i is the reaction order.

Similar dissolution rate expressions can be written for magnesite and dolomite. Since our samples do not include magnesite and in this work we do not study precipitation, we focus our attention on calcite.

The equilibrium $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$ is greatly in favour of $\text{CO}_2(\text{aq})$, with an equilibrium constant of $K \approx 1.7 \times 10^{-3}$ (Housecroft and Sharpe, 2012, page 462), which led Peng et al. (2015) to approximate the activity of H_2CO_3^* by the activity of $\text{CO}_2(\text{aq})$. In our work, we follow them and do not consider the species $\text{H}_2\text{CO}_3(\text{aq})$.

2.3.2 Laboratory measurements of mineral reaction rates

The rate constants and reaction orders present in Eq. (2.5) must be obtained experimentally. The scarcity of data in the literature for the dissolution of carbonates at high pressure (> 6 MPa) and high temperatures (> 373 K) typical of oil reservoirs or potential CO_2 storage sites motivated Peng et al. (2015) to perform measurement of dissolution rates under such conditions. Most of the previous works were interested in lower temperatures and pressures relevant for seawater and shallow aquifers.

To separate the effect of the dissolution mechanisms from each other (Eqs. (2.2) to (2.4)), they first noted that k_3 is small compared to the rate of dissolution at the pressures and temperatures we are interested in. This is a fair assumption: they measured $r > 2 \times 10^{-4} \text{ mol}/(\text{m}^2 \text{ s})$ while Chou et al. (1989), for example, reported a value of $k_3 = 6.5 \times 10^{-7} \text{ mol}/(\text{m}^2 \text{ s})$. Then, Peng et al. (2015) performed experiments of dissolution of calcite in $\text{HCl} + \text{H}_2\text{O}$ to obtain k_1 , followed by experiments of dissolution in $\text{CO}_2 + \text{H}_2\text{O}$ to obtain k_2 . They found both reaction mechanisms to be first-order, that is, $n_1 = n_2 = 1$, so that

$$r_{\text{calcite}} = k_1 \alpha_{\text{H}^+} + k_2 \alpha_{\text{H}_2\text{CO}_3^*}. \quad (2.6)$$

The dependency of the reaction rate constant k_j on temperature is modelled via the Arrhenius equation:

$$k_j = A \exp\left(-\frac{E_j}{RT}\right), \quad (2.7)$$

where A is the pre-exponential factor, E_j is the activation energy, R is the universal gas constant and T is the absolute temperature. Often, mineral reactions databases do not provide the value of A , but the value of $k_j = k_j^\circ$ at reference temperature T° . It is straightforward to calculate k_j at another temperature:

$$k_j = k_j^\circ \exp\left(-\frac{E_j}{R} \left(\frac{1}{T} - \frac{1}{T^\circ}\right)\right). \quad (2.8)$$

The carbonate samples were cleaved from a single crystal of Iceland Spar, and the surface exposed to the aqueous solution was imaged using vertical scanning interferometry before and after the experiments to ensure that the surface remained essentially flat, with a well defined area, during the whole duration of the dissolution. The initial nearly-atomically-flat surface developed etch pits, but they were so shallow that the increase of surface area was less than 0.2 %.

The carbonate samples were mounted over a rotating-disc, and the researchers were careful to measure the dissolution rates at different angular velocities to make sure that only those measurements free of mass transfer effects were considered. As a consequence, the rates they found are higher than other works, such as [Pokrovsky et al. \(2009\)](#).

In the experiments, the measured quantities are the ion concentration in the liquid phase inside the batch reactor and the area of the sample being dissolved. From them, the rate of dissolution is calculated, as well as the species activities. Then, imposing a functional form to the rate of dissolution such as [Eq. \(2.5\)](#), the rate constants were calculated.

In the simulation, we proceed in the opposite direction. From the rate constants, species activities and surface area, we calculate the rate of dissolution. This process is only correct if the species activities calculated in the simulation are close enough to the species activities used by the experimentalists in their work. Since the species activities are usually calculated from models, it is good practice to check the consistency between the value of activities used in the simulation and those used in the experimental work. Alternatively, the modeller can recalculate the rate constants based on the activity model used in the simulation, which is what we do.

For the estimation of k_1 for calcite, we consider the rate of dissolution per unit surface area r at high angular velocities for $\text{HCl} + \text{H}_2\text{O}$ systems reported in [Peng et al. \(2015, Table 1\)](#) and calculate the activity α_{H^+} using Reaktoro ([Leal, 2015, Leal et al., 2016a](#)) with the HKF model ([Helgeson et al., 1981](#)). Then we calculate the rate constant $k_1 = r/\alpha_{\text{H}^+}$ obtaining the values shown in [Table 2.1](#).

[Figure 2.4](#) shows the values of r and k_1 for different concentrations of HCl at $T = 353.15 \text{ K}$ and illustrates the validity of the functional form $r = k_1 \alpha_{\text{H}^+}$. k_1 remains constant along the range of α_{H^+} here represented by $\text{pH} = \log_{10} \alpha_{\text{H}^+}$. This figure can be compared to [Peng et al. \(2015, Fig. 5\)](#).

In [Fig. 2.5](#), we plot $\ln k_1$ versus $1/T$ to obtain the value of the activation energy and k_1 at the reference temperature $T = 298.15 \text{ K}$. The leftmost point ($T = 353.15 \text{ K}$) was not considered in the regression. In [Peng et al. \(2015, Figure 6\)](#), the regression is within the margin of error of that point. However, it does not seem to us that the value of $\ln k_1$ they plotted is consistent with the average k_1 obtained at $T = 353.15 \text{ K}$ in the same work, which is lower and similar to our results. Since we are performing simulations at temperatures up to $T = 323.15 \text{ K}$ ($1/T = 0.0031/\text{K}$), this question does not affect our work.

Table 2.1: Calcite rates of dissolution per unit surface area r reported by Peng et al. (2015) for $\text{HCl} + \text{H}_2\text{O}$ systems, and our calculation of activity α_{H^+} and rate constant k_1 , at $p = 0.1$ MPa, concentrations of HCl C and temperatures T .

C mol/m ³	T K	r mol/(m ² s)	α_{H^+} 1	k_1 mol/(m ² s)
10	294.15	1.5×10^{-3}	9.04×10^{-3}	0.17
10	302.15	2.0×10^{-3}	9.05×10^{-3}	0.22
10	316.15	2.3×10^{-3}	9.08×10^{-3}	0.25
10	323.15	2.5×10^{-3}	9.09×10^{-3}	0.28
10	331.15	3.2×10^{-3}	9.11×10^{-3}	0.35
10	353.15	3.2×10^{-3}	9.17×10^{-3}	0.35
0.61	353.15	0.19×10^{-3}	0.61×10^{-3}	0.31
0.66	353.15	0.2×10^{-3}	0.66×10^{-3}	0.30
1.3	353.15	0.33×10^{-3}	1.28×10^{-3}	0.26
1.6	353.15	0.43×10^{-3}	1.57×10^{-3}	0.27

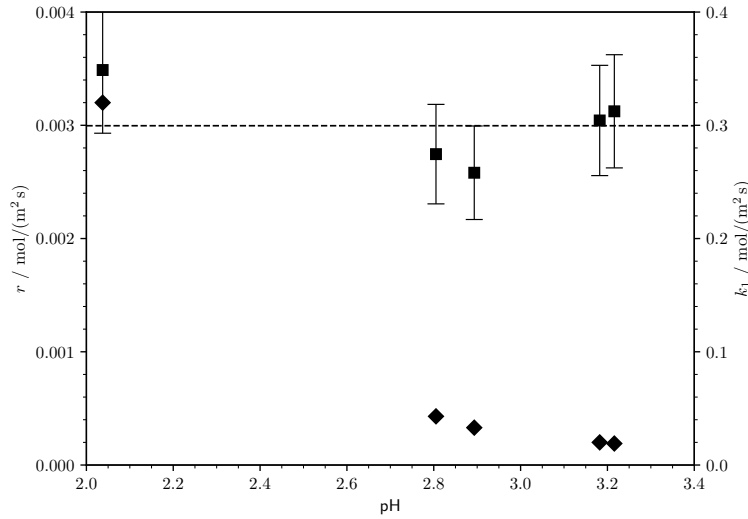


Figure 2.4: Rates of dissolution per unit surface area r (◆), rate constant k_1 (■) and average rate constant (—) for dissolution of calcite in $\text{HCl} + \text{H}_2\text{O}$ at $T = 353.15$ K as a function of pH. The rates of dissolution and error bars were taken from Peng et al. (2015).

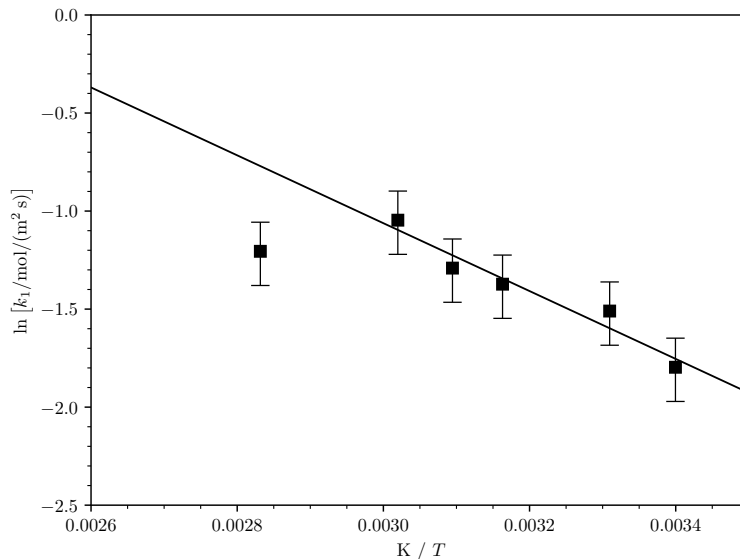


Figure 2.5: Regression of the rate constant k_1 following the Arrhenius equation (Eq. (2.7)), ignoring the leftmost data point. We calculated the rate constant from the rates of dissolution per unit surface area measured by Peng et al. (2015), who also provided the magnitude of the error bars. In their work, leftmost data point is not an outlier, but it does not seem to us that the value of $\ln k_1$ plotted is consistent with the average k_1 obtained in the same work.

In summary, the values obtained are: $k_1^\circ = 0.187 \text{ mol}/(\text{m}^2 \text{s})$ at $T^\circ = 298.15 \text{ K}$, activation energy $E = 14.4 \text{ kJ/mol}$ and pre-exponential factor $A = 62.2 \text{ mol}/(\text{m}^2 \text{s})$. Peng et al. (2015) estimates the uncertainty of k_1 and E to be of 16 % and 25 %, respectively, at 95 % confidence level.

Knowing the contribution of H^+ to the rate of dissolution in Eq. (2.5), Peng et al. (2015) turned their attention to the dissolution of calcite in H_2O saturated with CO_2 to find the contribution $\text{CO}_2(\text{aq})$ in Eq. (2.5). Using the value they obtained for the rate of dissolution, we calculate k_2 using for $\alpha_{\text{CO}_2(\text{aq})}$ the same thermodynamic model we will use in our simulations of reactive transport, and obtain the values shown in Table 2.2.

In Fig. 2.6, we plot $\ln k_2$ versus $1/T$ to obtain the value of the activation energy and k_2 at the reference temperature $T = 298.15 \text{ K}$. The functional form Eq. (2.5) with $n_1 = n_2 = 1$ does not seem to have render the values of $\ln k_2$ independent of pressure. Similar results can be observed in Peng et al. (2015, Fig. 12) and it would be interesting to analyse other datasets or study the possibility of using a fractional order rate law. The values we obtained with this regression are: $k_2^\circ = 0.324 \times 10^{-3} \text{ mol}/(\text{m}^2 \text{s})$ at $T^\circ = 298.15 \text{ K}$, activation energy $E = 18.7 \text{ kJ/mol}$ and pre-exponential factor $A = 0.624 \text{ mol}/(\text{m}^2 \text{s})$. Peng et al. (2015) estimated the uncertainty of k_2 to be 17 % at 95 % confidence level.

In another work, Peng et al. (2016a) measured the rate of dissolution of several carbonates, including dolomite, in CO_2 -saturated water or brine under conditions

Table 2.2: Calcite rates of dissolution per unit surface area r reported by Peng et al. (2015) for CO_2 -saturated H_2O , and our calculation of activities α_{H^+} and $\alpha_{\text{CO}_2(\text{aq})}$, and rate constant k_2 , at pressures p and temperatures T .

p MPa	T K	r mol/(m ² s)	α_{H^+} 1	$\alpha_{\text{CO}_2(\text{aq})}$ 1	k_2 mol/(m ² s)
6	325.15	0.56×10^{-3}	0.67×10^{-3}	0.80	0.44×10^{-3}
6	333.15	0.71×10^{-3}	0.64×10^{-3}	0.72	0.68×10^{-3}
6	353.15	0.77×10^{-3}	0.55×10^{-3}	0.58	0.89×10^{-3}
6	373.15	1.0×10^{-3}	0.47×10^{-3}	0.50	1.44×10^{-3}
10	323.15	0.81×10^{-3}	0.79×10^{-3}	1.05	0.55×10^{-3}
10	333.15	1.0×10^{-3}	0.75×10^{-3}	0.96	0.77×10^{-3}
10	353.15	1.2×10^{-3}	0.66×10^{-3}	0.81	1.10×10^{-3}
10	373.15	1.3×10^{-3}	0.57×10^{-3}	0.72	1.33×10^{-3}
13.8	323.15	1.0×10^{-3}	0.83×10^{-3}	1.13	0.67×10^{-3}
13.8	333.15	1.2×10^{-3}	0.80×10^{-3}	1.06	0.87×10^{-3}
13.8	353.15	1.6×10^{-3}	0.72×10^{-3}	0.94	1.34×10^{-3}
13.8	373.15	1.7×10^{-3}	0.63×10^{-3}	0.86	1.52×10^{-3}

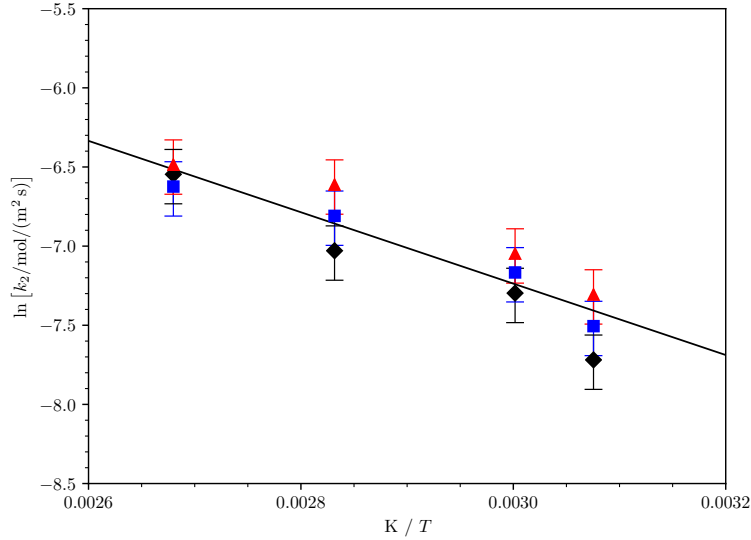


Figure 2.6: Regression of the rate constant k_2 following the Arrhenius equation (Eq. (2.7)). We calculated the rate constant from the rates of dissolution per unit surface area measured by Peng et al. (2015), who also provided the magnitude of the error bars, and from our estimate of k_1 . Pressures are $p = 6$ MPa ($\blacklozenge$), $p = 10$ MPa ($\blacksquare$), $p = 13.8$ MPa ($\blacktriangle$).

free of mass-transfer limitations and far from equilibrium, at pressures between 6 and 15 MPa, and temperatures between 325 and 373 K. It was the first study to perform these measurements at pressures and temperatures relevant for deep aquifers and oil reservoirs. While [Palandri and Kharaka \(2004\)](#) modelled the rate of dissolution of dolomite using all terms in [Eq. \(2.5\)](#) and fractional orders for the rate laws, [Peng et al. \(2016a\)](#) found that, under the conditions studied, the rate can be described by a first-order rate law as a function of α_{H^+} only, and that the terms relative to the neutral and carbonate mechanism can be neglected:

$$r_{\text{dolomite}} = k_1 \alpha_{\text{H}^+} . \quad (2.9)$$

They obtained the values shown in [Table 2.3](#), with an experimental uncertainty of about 15 %. In the same table, we show the value of α_{H^+} we calculated using Reaktoro. We adjust the pre-exponential factor A and the activation energy E of [Eq. \(2.7\)](#) to minimize the residual sum of squares between [Eq. \(2.9\)](#) and the measured values for $r(\text{Ca}^{2+})$ and $r(\text{Mg}^{2+})$, and obtain: $k_1^\circ = 0.0381 \text{ mol}/(\text{m}^2 \text{ s})$ at $T^\circ = 298.15 \text{ K}$, activation energy $E = 16.2 \text{ kJ/mol}$ and pre-exponential factor $A = 26.2 \text{ mol}/(\text{m}^2 \text{ s})$. [Peng et al. \(2015\)](#) estimated the uncertainty of k_1 and E to be less than of 15 %.

From the rate constants calculated for calcite and dolomite, we can compare their rates of dissolution at the same pressure and temperature. For example, at $p = 10 \text{ MPa}$ and $T = 323.15 \text{ K}$ exposed to CO_2 -saturated water, the rates are $r_{\text{calcite}} = 84.2 \times 10^{-5} \text{ mol}/(\text{m}^2 \text{ s})$ and $r_{\text{dolomite}} = 4.99 \times 10^{-5} \text{ mol}/(\text{m}^2 \text{ s})$, which can be compared to the experimental values $r_{\text{calcite}} = 81 \times 10^{-5} \text{ mol}/(\text{m}^2 \text{ s})$ and $r_{\text{dolomite}, \text{Mg}^{2+}} = 5.1 \times 10^{-5} \text{ mol}/(\text{m}^2 \text{ s})$. It is worth noting that at these conditions calcite is 17 times more reactive than dolomite.

2.3.3 Activity models

As seen from [Eq. \(2.5\)](#), the rate of dissolution is a function of activities, which can be calculated from thermodynamic models. The activity and fugacity coefficient models available in Reaktoro ([Leal, 2015](#), [Leal et al., 2016a](#)), besides the ideal one, are:

- for ionic species:
 - the extended Debye-Hückel model proposed by [Truesdell and Jones \(1973\)](#), also in [Langmuir \(1997, page 140\)](#),
 - HKF, an extended Debye-Hückel model proposed by [Helgeson et al. \(1981\)](#). This model is also used for $\text{H}_2\text{O}(\text{l})$,
 - the extended Debye-Hückel model described in [Oelkers and Helgeson \(1991\)](#), available if GEMS3K is used as a thermodynamic backend,
 - the Pitzer model ([Harvie et al., 1984](#)), available built in Reaktoro and via PHREEQC if it is used as a thermodynamic backend;

Table 2.3: Dolomite rates of dissolution per unit surface area r reported by [Peng et al. \(2016b\)](#) for $\text{HCl} + \text{H}_2\text{O}$ and CO_2 -saturated H_2O , and our calculation of activity α_{H^+} at pressures p and temperatures T .

Dissolution media	p MPa	T K	$r(\text{Ca}^{2+})$ mol/(m ² s)	$r(\text{Mg}^{2+})$ mol/(m ² s)	α_{H^+} 1
HCl (1 mol/m ³)	0.1	353.15	12 $\times 10^{-5}$	10 $\times 10^{-5}$	9.9 $\times 10^{-4}$
HCl (7 mol/m ³)	0.1	322.15	43 $\times 10^{-5}$	38 $\times 10^{-5}$	65 $\times 10^{-4}$
HCl (7 mol/m ³)	0.1	333.15	52 $\times 10^{-5}$	49 $\times 10^{-5}$	65 $\times 10^{-4}$
HCl (10 mol/m ³)	0.1	343.15	85 $\times 10^{-5}$	75 $\times 10^{-5}$	91 $\times 10^{-4}$
HCl (10 mol/m ³)	0.1	353.15	100 $\times 10^{-5}$	92 $\times 10^{-5}$	92 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	6	323.15	5.0 $\times 10^{-5}$	4.2 $\times 10^{-5}$	6.8 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	6	333.15	6.8 $\times 10^{-5}$	5.9 $\times 10^{-5}$	6.4 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	6	353.15	7.0 $\times 10^{-5}$	6.0 $\times 10^{-5}$	5.5 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	6	373.15	7.7 $\times 10^{-5}$	6.3 $\times 10^{-5}$	4.7 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	10	323.15	5.9 $\times 10^{-5}$	5.1 $\times 10^{-5}$	7.9 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	10	333.15	7.6 $\times 10^{-5}$	6.1 $\times 10^{-5}$	7.5 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	10	353.15	9.4 $\times 10^{-5}$	7.1 $\times 10^{-5}$	6.6 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	10	373.15	9.4 $\times 10^{-5}$	8.1 $\times 10^{-5}$	5.7 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	13.8	333.15	7.1 $\times 10^{-5}$	6.6 $\times 10^{-5}$	8.0 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	13.8	353.15	9.0 $\times 10^{-5}$	6.8 $\times 10^{-5}$	7.2 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	13.8	353.15	9.1 $\times 10^{-5}$	7.7 $\times 10^{-5}$	7.2 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	13.8	373.15	12 $\times 10^{-5}$	11 $\times 10^{-5}$	6.3 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	15	323.15	6.4 $\times 10^{-5}$	4.5 $\times 10^{-5}$	8.4 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	15	333.15	8.1 $\times 10^{-5}$	6.4 $\times 10^{-5}$	8.1 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	15	353.15	11 $\times 10^{-5}$	8.8 $\times 10^{-5}$	7.4 $\times 10^{-4}$
$\text{CO}_2 + \text{H}_2\text{O}$	15	373.15	14 $\times 10^{-5}$	11 $\times 10^{-5}$	6.5 $\times 10^{-4}$

- for $\text{CO}_2(\text{aq})$, the models of
 - [Drummond \(1981\)](#),
 - [Rumpf et al. \(1994\)](#),
 - [Duan and Sun \(2003\)](#);
- for neutral aqueous species other than $\text{CO}_2(\text{aq})$, the model of [Setschenow \(1889\)](#);
- for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, the models of
 - [Spycher and Reed \(1988\)](#),
 - [Spycher et al. \(2003\)](#);
- for the gaseous phase, the cubic equation of states by [van der Waals \(1910\)](#), [Redlich and Kwong \(1949\)](#), [Soave \(1972\)](#) and [Peng and Robinson \(1976\)](#);
- for the mineral phase, the Redlich-Kister ([Redlich and Kister, 1948](#)) for binary solid solutions.

CHAPTER 2. LITERATURE REVIEW

For the modelling of the activity of ionic species, we choose the HKF model. Peng (2015) studied how well the HKF model implemented in Reaktoro and the Pitzer model implemented in PHREEQC predicted the pH of CO₂-saturated NaCl brines, which they measured for brines with concentrations of 1000 mol/m³ and 5000 mol/m³, at pressures up to 15.4 MPa and temperatures between 308 K and 373 K. For temperatures above 323 K, both performed similarly, with difference from the experimental result of up to 0.2 pH. The largest differences were obtained at the concentration of 5000 mol/m³. At this concentration, the Pitzer model systematically overpredicted the pH, while the HKF model systematically underpredicted it.

For the calculation of activity of CO₂(aq), we use the model of Duan and Sun (2003) as it performed better than Drummond (1981) in matching experimental solubility data of CO₂ in brines in a study by Leal et al. (2013). The comparison were made using the HKF model for the activity of ionic species, the model of Duan et al. (2006) for the fugacity of CO₂(g) and experimental data of Tong et al. (2013) for NaCl, MgCl₂ and CaCl₂ brines., the one by Duan and Sun (2003) performed better for MgCl₂ and CaCl₂ brine for pressures between 1.2 MPa and 38 MPa and temperatures between 308.90 K and 424.64 K. While both models showed similar results for NaCl brines predicting molar fractions of CO₂(aq) that deviated around 7 % from the values experimentally measured, the one by Duan and Sun (2003) performed better for MgCl₂ and CaCl₂ brines, with errors of 6.7 % and 6.9 %, respectively, versus errors of 17.2 % and 15.4 % in the predictions made using Drummond (1981)'s model.

In the same work, using the measurements of solubility of CO₂ in NaCl brines at pressures between 2.6 MPa and 18.2 MPa and temperatures between 323.15 K and 423.15 K, Leal et al. (2013) compared the models of Spycher and Reed (1988), Spycher et al. (2003) and Duan et al. (2006) for the fugacity of CO₂(g). The model Duan et al. (2006) performs better, with percentage deviation of less than 8 % for pressures over 6 MPa, while Spycher and Reed (1988) and Spycher et al. (2003) have similar performance. Appelo et al. (2014) compared the fraction of H₂O in the gas phase of CO₂-H₂O systems to data compiled by Spycher et al. (2003) and found that they are in good agreement. With no data strongly supporting the use of one model over the other, we use Peng-Robinson, also used by PHREEQC (Parkhurst and Appelo, 2013) because it is more general for a variety of gases, even though we are only interested in the composition of the aqueous phase in equilibrium with CO₂.

For neutral aqueous species, we use an ideal activity since the Setschenow (1889) model is more appropriate to the study of solubility of organic compounds (e.g., Ni and Yalkowsky (2003), Jonker and Muijs (2010)). The choice of an ideal model is also made for the mineral phase.

2.3.4 Diffusion coefficients

The diffusion coefficient of a species in solution is a function of its molecular or ionic size. Assuming that (1) molecules or ions move independently from each other, (2) they have the same kinetic energy as gas molecules at the same temperature, (3) they are spherical and move through a liquid with low Reynolds number, so that the Stokes's law ([Stokes, 1851](#)) applies, (4) the solvent is composed of proportionately small particles, so that it can be assumed as a continuum, the diffusion coefficient D can be calculated as

$$D = \frac{kT}{6\pi\mu r}, \quad (2.10)$$

where k is the Boltzmann's constant, T is the absolute temperature, μ is the dynamic viscosity of the solvent and r is the effective radius of the molecule or ion. This relation is known as Stokes-Einstein equation ([Einstein, 1905](#)), although it was also independently found by [Sutherland \(1905\)](#). Extensions to the Stokes-Einstein equation have been proposed based on empirical measurements and by relaxing some of the assumptions used in its derivation (e.g., [Wilke and Chang \(1955\)](#), [Edward \(1970\)](#), [Pollack and Enyeart \(1985\)](#)).

In ionic solutions, if the different ions diffused independently from each other, a charge imbalance could be created. In reality, any charge imbalance is rapidly damped out due to Coulombic interactions, which are usually modelled using the Nernst-Planck equation ([Cussler, 2009](#)).

Recent experimental studies in porous media have shown the importance of accounting for species-specific diffusion coefficients, and consequent species-specific dispersion coefficients. [Muniruzzaman and Rolle \(2017\)](#), for example, measured the breakthrough curves for the injection of MgCl_2 in a quasi-2D flow-through system homogeneously packed with glass beads. When the system was initially filled with pure water, Mg^{2+} and Cl^- tended to travel together in order to keep the local charge balance of the system. However, when the system was initially filled with a high-concentration NaBr solution, Mg^{2+} and Cl^- travelled in accordance with their individual dispersion coefficients, since the movement of Na^+ and Br^- , ubiquitously present, contributed to keep the local charge balance.

Similar results were obtained by [Ye et al. \(2015b\)](#) who performed multi-tracer experiments using fluorescein and dissolved oxygen in quasi-2D and 3D flow-through system. Since no Coulombic interaction existed between the two tracers, they observed a compound-specific behavior of the transverse dispersion coefficient.

Despite experimental evidences of the impact of species-specific diffusion coefficients, previous modelling works were able to satisfactorily represent multispecies pore-scale reactive transport experiments using a single diffusion coefficient ([Al-hashmi et al., 2015](#)) or even a single species ([Pereira Nunes et al., 2016b](#), [Soulaine et al., 2017](#)). For simplicity, when we model systems where species-specific diffusion coefficients could lead to charge imbalance, we use a single diffusion coefficient for all

the species (Lichtner, 1985, Lichtner and Kang, 2007a, Li et al., 2007c). The incorporation of the Nernst-Planck equation, as done by Gray et al. (2018) for example, would eliminate this restriction.

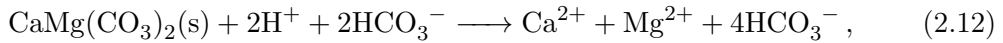
Moreover, we would argue that Coulombic interactions are not the only process that tends to equalize the effective diffusion coefficient of different species, but also the presence of chemical equilibrium (which is taken into account in our model). Consider, for example, a system with multiple species being transported in chemical equilibrium, and where the species form a single chemical system (that is, it is not possible to separate the species into two or more chemically non-interacting sets). If one of the species has a diffusion coefficient different from the remaining ones and migrated according to it, this would generate a chemical disequilibrium that would promptly be compensated by forward and reverse reactions, tending to equalize the effective diffusion coefficients of all species. This claim, however, needs to be verified in future work.

As discussed above, we use a single diffusion coefficient for all species when species-specific coefficients could lead to charge imbalance. In these cases, we need to estimate an overall diffusion coefficient from the diffusion coefficient of each species. It has been shown (Jost, 1952, van Schaik et al., 1966, cited in Yuan-Hui and Gregory (1974)) that the diffusion coefficient D of a salt in solution is given by

$$D = \frac{(|z_1| C_1 + |z_2| C_2) D_1 D_2}{|z_1| C_1 D_1 + |z_2| C_2 D_2}, \quad (2.11)$$

where D_i is the diffusion coefficient of each ion, z_i is its charge and C_i is its concentration.

When we study the dissolution of dolomite in CO_2 -saturated water, we are especially interested in the diffusion of the ions of the equation



which are among the most abundant at the conditions we study and whose diffusion may play a role in the reaction depending on the Péclet-Damköhler number. The diffusion coefficients of these ions are shown in Table 2.4.

Table 2.4: Diffusion coefficients at 298.15 K compiled by Vanyšek (2018). We calculated their values at 323.15 K using the Stokes-Einstein equation (Eq. (2.13)).

Species	D at 298.15 K m^2/s	D at 323.15 K m^2/s
Ca^{2+}	0.792×10^{-9}	1.25×10^{-9}
Mg^{2+}	0.706×10^{-9}	1.40×10^{-9}
HCO_3^-	1.185×10^{-9}	2.09×10^{-9}

From the Stokes-Einstein equation (Simpson and Carr, 1958), the diffusion coefficient D of a species at temperatures T_1 and T_2 are related by

$$\left. \frac{D\mu}{T} \right|_{T_1} = \left. \frac{D\mu}{T} \right|_{T_2}, \quad (2.13)$$

where μ is the dynamic viscosity of the solution. We took the values for water $\mu = 0.890$ mPa s at $T = 298.15$ K, and $\mu = 0.547$ mPa s at $T = 298.15$ K from Rumble (2018).

Using Eq. (2.11) and the values from Table 2.4, we estimate the overall diffusion coefficient to be $D = 1.6 \times 10^{-9}$ m²/s.

In this section, we have described geochemistry in carbonate rocks. In reactive transport in porous media, it is useful to introduce dimensionless numbers that compare the relative magnitude of flow, transport and reaction. They will be described in the next section.

2.4 Dimensionless quantities for reactive transport in porous media

Among the dimensionless numbers used in this field, three of the most useful ones are the Péclet (Pe), the Damköhler (Da) and the Péclet-Damköhler ($PeDa$) numbers. The rationale of their definition relies on characteristic times for advective transport, diffusive transport and reaction. Possible definitions for these characteristic times are:

$$\tau_{adv} = \frac{L}{u}, \quad (2.14)$$

$$\tau_{diff} = \frac{L^2}{D}, \quad (2.15)$$

$$\tau_{reac} = \frac{Ln}{r}, \quad (2.16)$$

where L (m) is a characteristic length of the system, u (m/s) is a characteristic velocity, D (m²/s) is a characteristic diffusion coefficient, r (mol/(m² s)) is a characteristic rate of a heterogeneous reaction and n (mol/m³) is a characteristic number density of the solid phases.

Using these characteristic times, the Péclet number is defined as

$$Pe = \frac{\text{advective transport rate}}{\text{diffusive transport rate}}, \quad (2.17)$$

or, equivalently,

$$Pe = \frac{\text{diffusive transport characteristic time}}{\text{advective transport characteristic time}} = \frac{\tau_{diff}}{\tau_{adv}} = \frac{uL}{D}. \quad (2.18)$$

The Damköhler number is defined as

$$Da = \frac{\text{reaction rate}}{\text{advective transport rate}}, \quad (2.19)$$

or, equivalently,

$$Da = \frac{\text{advective transport characteristic time}}{\text{reaction characteristic time}} = \frac{\tau_{adv}}{\tau_{reac}} = \frac{r}{un}. \quad (2.20)$$

The Péclet-Damköhler number is defined as

$$PeDa = Pe \times Da = \frac{\text{reaction rate}}{\text{diffusive transport rate}}, \quad (2.21)$$

or, equivalently,

$$PeDa = \frac{\text{diffusive transport characteristic time}}{\text{reaction characteristic time}} = \frac{\tau_{diff}}{\tau_{reac}} = \frac{rL}{Dn}. \quad (2.22)$$

The above nomenclature is supported by some authors (e.g., [Varloteaux et al. \(2013a\)](#)), but it is not unique. [Table 2.5](#) shows some of the possible variations.

Table 2.5: Alternative names for the Damköhler numbers.

τ_{diff}/τ_{adv}	τ_{adv}/τ_{reac}	τ_{diff}/τ_{reac}	Authors
Pe	Da	$PeDa$	Varloteaux et al. (2013a)
			This work
Pe	Da_I	Da_{II}	Salehikhoo et al. (2013)
			Steeffel et al. (2013)
Pe	—	Da	Porta et al. (2013)
Pe	—	<i>diffusive</i> <i>Damköhler</i>	Molins et al. (2012)

These dimensionless numbers require a definition of characteristic length, velocity and diffusion coefficient. Although different choices may be equally valid in a given problem, it is important to have in mind which ones are being used when comparing results reported in terms of dimensionless numbers.

In this thesis, when we study porous media in which microporosity is not present ([Chapters 4 and 6](#)), we will use the following expression for the characteristic length ([Whitaker, 1977](#), page 347):

$$L = \frac{6\phi V_T}{A_s} = \frac{6\phi}{S}, \quad (2.23)$$

where V_T is the total volume of the porous medium (grains+pores), A_s is the area of the surface between grains and pores, $S = V_T/A_s$ is the specific surface area and ϕ is the porosity of the medium. For the characteristic velocity u , we define

$$u = \frac{\int_{\Omega} |\mathbf{u}| \, d\Omega}{\int_{\Omega} d\Omega}, \quad (2.24)$$

where Ω is the pore space, $\mathbf{u}$ is the pore velocity and $d\Omega$ is a differential volume element. For the characteristic diffusion coefficient D , we consider the single value of diffusion coefficient that we use for all species in our model.

In [Chapter 5](#), when we study a medium composed of regions of microporosity and macroporosity, we consider for [Eq. \(2.23\)](#), the porosity ϕ associated only with the macropores, and the area A_s of the surface between the macropores and micropores+solid phase. Accordingly, we consider in [Eq. \(2.24\)](#) the pore space Ω of the macropores.

2.5 Reactive transport modelling at the pore scale

The subject of modelling reactive transport at the pore scale has recently received considerable attention inspired by developments in the characterization of the pore space by X-ray tomography. This is a challenging task since it involves solving for flow, transport and reaction in a complicated pore space geometry.

The approaches used to perform direct numerical simulation on pore space images can be based on Eulerian and Lagrangian methods. Recent works employing both methods include ([Bijeljic et al., 2011](#), [Mostaghimi et al., 2012](#), [Bijeljic et al., 2013b](#)), who solved the Navier-Stokes equation using the finite volume method to calculate the flow on the voxelized images, and a particle-tracking method to simulate transport along streamlines calculated from the flow field. Diffusion was taken into account by superimposing a random walk on the particle movement. Since the geometry of the pore space was well described, these modelling efforts were able to identify signatures of flow and non-Fickian transport in bead packs, sandstones and carbonates as a function of heterogeneity in pore structure. The streamline algorithm was further improved by [Pereira Nunes et al. \(2015\)](#) who demonstrated better characterization of the nature of non-Fickian transport in a sandstone and a carbonate by using a modification of [Pollock \(1988\)](#)'s algorithm that did not violate the non-slip condition at the interface between the liquid and the rock.

One of the main issues in characterizing dynamics of reactive transport is that transport and reaction are coupled. Hence, the metrics used for describing transport properties which impact reaction need to be carefully employed. Solute transport in porous media can be measured by describing its spreading and mixing. Spreading is typically measured by dispersion coefficients while mixing is characterized by dilution index and reactor ratio. There exists a large body of experimental data on dispersion coefficients in unconsolidated bead packs and sand packs and, to a less extent, on sandstones and carbonates. Recently X-ray tomography at the core scale was used to characterize the impact of physical heterogeneity on solute transverse spreading and mixing ([Boon et al., 2017](#)). Enhanced transverse spreading was shown to exist for more heterogeneous rocks, starting from Berea sandstone, and increasing in Ketton and Indiana carbonates, and for higher Pe . In more heterogeneous media, mixing occurs more rapidly, and in the most heterogeneous Indiana carbonate the mass-weighted dilution index exhibits characteristics of a non-Fickian behaviour. Another interesting experimental technique combines pulse-tracer tests with the simultaneous

imaging of the flow by Positron Emission Tomography (PET) (Pini et al., 2016). One of the most important contributions arising from this work is the application of the dispersion-echo technique, which enables decoupling the effects of spreading and mixing in heterogeneous porous media (Kurotori et al., 2018).

The longitudinal dispersion coefficient D_L is calculated as

$$D_L(t) = \frac{1}{2} \frac{d\sigma^2(t)}{dt}, \quad (2.25)$$

where σ^2 is the variance of the position of the plume along the longitudinal direction of the tube. The variance σ^2 is a function of the concentration $C(\mathbf{x}, t)$ and given by

$$\sigma^2(t) = \int_{\Omega} p(\mathbf{x}, t) x_i^2 dV - \left(\int_{\Omega} p(\mathbf{x}, t) x_i dV \right)^2, \quad (2.26)$$

$$p(\mathbf{x}, t) = \frac{C(\mathbf{x}, t)}{\int_{\Omega} C(\mathbf{x}, t) dV}, \quad (2.27)$$

where x_i is the projection of the position $\mathbf{x}$ along the longitudinal direction.

It was very early recognised that dispersion coefficient depends on velocity resulting in a range of transport regimes: restricted diffusion, transition, power-law and linear regimes (Fried and Combarous, 1971, Sahimi, 2011).

As a measure of mixing Kitanidis (1994) introduced the dilution index E . Rolle et al. (2009) adapted this concept and proposed the flux-related dilution index to take into account the distribution of flow rates. If we restrict it to a species i , the flux-related dilution index can be written for a cross-section A at $\mathbf{x} = (x, y, z)$ as

$$E_i(x) = \exp \left(- \int_A p_i(\mathbf{x}) \ln(p_i(\mathbf{x})) u_x(\mathbf{x}) dA \right), \quad (2.28)$$

$$p_i(\mathbf{x}) = \frac{C_i(\mathbf{x})}{\int_A C_i(\mathbf{x}) u_x(\mathbf{x}) dA}, \quad (2.29)$$

where u_x is the x-component of the velocity and C_i is the species concentration.

Kitanidis (1994) also proposed the reactor ratio M as the ratio between the dilution index E and the theoretical maximum value it could reach under some chosen constraints. By analogy, Rolle et al. (2009) defined the flux-related reactor ratio. The maximum value E_{max_i} of the flux-related reactor ratio is obtained when $C_i(\mathbf{x})$ is constant over the cross-section A , in which case Eq. (2.28) simplifies to the volumetric flow rate across A . Therefore, the flux-related reactor ratio is given by

$$M_i(x) = \frac{E_i(x)}{E_{max_i}} = \frac{E_i(x)}{\int_A u_x(\mathbf{x}) dA}. \quad (2.30)$$

We will use this expression to quantify the behaviour of transport and reaction later in the thesis.

2.5.1 Pore-scale models for fluid-fluid reactive transport

Different approaches have been used for the simulation of fluid-fluid reactive transport at the pore scale. [Acharya et al. \(2007\)](#) used the lattice-Boltzmann method to solve the steady state Stokes equation and the finite volume method to solve the steady-state advection-diffusion-reaction equations (ADRE) for three species that reacted according to $A + B \longrightarrow C$ and a second-order rate equation. The rate constant was set to a very high value to mimic an instantaneous reaction.

A similar model was used by [Willingham et al. \(2008\)](#) to simulate the same experiments in micromodels that were mentioned in [Section 2.1](#). Given that the thickness of the micromodel was much smaller than its length and width, they used a 2D model. They obtained a very good agreement with the experiment for the spatial distribution of concentration, while small discrepancies were explained by accidental variations in the flow rate of one of the pumps.

[Tartakovsky et al. \(2009\)](#) used smooth particle hydrodynamics (SPH) to solve the Navier-Stokes equation, the advection-diffusion equation and the bimolecular reaction $A + B \longrightarrow C$. They compared a pore-scale and a Darcy-scale simulation of a 2D domain where A and B were injected in parallel for different Péclet numbers, and used the dilution index ([Kitanidis, 1994](#)) to quantify the mixing between A and B. They found that the Darcy-scale simulation overpredicted the formation of C, and that the magnitude of the error increases with the reduction of the dilution index.

Another work comparing pore- and continuum-scale model was published by [Porta et al. \(2013\)](#). They simulated the injection of a solute A into a 2D porous medium represented by an array of disks initially containing a solute B. They reacted according to a non-instantaneous bimolecular reaction. The flow field was solved using the finite difference method, and the transient ADRE by a particle tracking method. The continuum-scale model was derived using the volume averaging method [Whitaker \(1999\)](#), which is able to take into account incomplete mixing effects. Both models agreed for large Damköhler numbers.

As mentioned in [Chapter 1](#), [Alhashmi et al. \(2015\)](#) used a streamline-based particle tracking model to simulate bimolecular reaction in a bead pack and obtained good agreement with the experimental results of [Gramling et al. \(2002\)](#), showing how, even in the relatively homogeneous 3D domain, incomplete mixing limits the overall reaction rate.

2.5.2 Pore-scale models for fluid-solid reactive transport

An early contribution to pore-scale simulation of dissolution is due to [Békri et al. \(1995\)](#). They used their model to determine the effective reaction rate and the impact of dissolution on the geometry and permeability of the pore space. They assumed that the dissolution is slow enough that the transport can be assumed to be in steady-state when compared to reaction. They first calculated the flow by solving

the Stokes equation using a finite-difference multigrid method. Then, they calculated the transport in two ways: (i) by a particle-tracking method in which particles are advected along streamlines and diffusion is modelled by a random walk; and (ii) by solving the transport equations using the finite-difference method. When the particle-tracking method was used, the dissolution was calculated from the number of particles that hit the walls by random walk: after a certain number of hits in a solid cell, the cell turned into a liquid one. When the finite difference method was used, the dissolution flux was treated as boundary condition for the solute concentration: from the flux at the boundary, they calculated the mass that a solid cell lost to the liquid phase, and turned the cell into a liquid one accordingly. They applied their method to different geometries, the most interesting one being a Menger sponge, which is a fractal pore geometry constructed from successive removal of smaller and smaller cubes from an initial solid cube. They were able to reproduce numerically on the Menger sponge the dissolution regimes that previous experiments (e.g., [Daccord et al. \(1993\)](#)) had identified.

[Molins et al. \(2012\)](#) and [Trebotich et al. \(2014\)](#) developed a simulator called Chumbo-Crunch by coupling Chumbo ([Adams et al., 2015](#)) and CrunchFlow ([Steefel and Molins, 2016](#)). Chumbo is used to solve the Navier-Stokes equation and the advection-diffusion-reaction (ADRE) equation, while CrunchFlow is a continuum-scale reactive transport whose geochemical solver was used to calculate the reaction source term in the ADRE. Chumbo-Crunch uses volume-of-fluid/embedded boundary method ([Colella et al., 2000](#)) to calculate the area and position of the fluid-solid interface. The simulator is able to address 3D multispecies dissolution problems and was used by [Molins et al. \(2014\)](#) to study reactive flow through a pack of crushed calcite crystals. The solid geometry, however, did not evolve with reaction. The simulation considered $3072 \times 256 \times 256$ cubic grid cells, 14 components and 6144 processors. In this work, they compared the pore- and continuum-scale simulations and found only minor differences between them, the reasons being that the high aspect ratio of the pack and the uniformity of the grain sizes contributed to the homogeneity of concentrations in the fluid phase. As mentioned in [Section 2.1](#), discrepancies between pore- and continuum-scale models are significant when gradients of concentration are present.

In [Molins et al. \(2017\)](#), a moving boundary was introduced and the dissolution of an array of cylindrical grains, modelled in 2D was studied. Chumbo-Crunch was also used by [Deng et al. \(2018\)](#) to investigate the impact of roughness on reaction rates on 2D fractures. The fracture surface was generated by the superposition of sine waves. By varying their frequency and amplitude, different roughness were obtained. The simulations considered 2500×250 square cells and 19 components. The researchers found that an increase in surface roughness causes the overall reaction rate to increase. At low flow rates, the roughness is not important in itself and its impact can be ascribed simply to the associated increase in surface area. At higher

flow velocities and higher surface roughness, immobile zones develop creating local concentration gradients and limiting the impact of the increased surface area in the reaction rate.

Pereira Nunes et al. (2016b) developed a reactive transport model and used it to study the impact of physical heterogeneity on average reaction rates (Pereira Nunes et al., 2016a), as previously mentioned. One of their main contributions was in the calculation of the streamlines along which particles are advected. While previous works integrated numerically the velocity calculated at the cell centre to obtain the particle trajectory, Pereira Nunes et al. (2015) built on a previous attempt by Mostaghimi et al. (2012) and proposed a quadratic functional form for the velocity field to interpolate the velocity based on the values calculated at the cell centre and its neighbours. This functional form honoured the no-slip condition at the walls and was integrated analytically, providing a closed-form expression for the particle trajectories that is both more precise and computationally advantageous. Using this method, they avoided overestimation of velocities near the wall that leads to erroneous transport predictions.

In their formulation, the diffusion process is modelled using a random walk method that allow particles to jump from one streamline to another. In this process, a particle can also hit a solid cell. After a certain number of hits, which is a function of the dissolution rate, the solid cell becomes a liquid cell, and the geometry and the velocity field is updated. This method is equivalent to a first order reaction. To avoid the expensive task of updating the velocity field every time a solid cell becomes a liquid one, the choice was made of updating the geometry and recalculating the velocity field when the resulting variation in porosity was larger than 0.001. This method proved to be very cost effective: simulations of dissolution of $650 \times 650 \times 650$ cubic grid cells during the injection of 1000 pore volumes took less than 7 days on 12 processors.

Soulaine and Tchelepi (2016) developed a reactive transport simulator that solves the Darcy-Brinkman equation, which allowed them to simulate the flow through a domain composed of porous cells ($\phi > 0$) and liquid cells ($\phi = 1$). To each porosity ϕ , a value of permeability was assigned using a Kozeny-Carman relation (Kozeny, 1927, Carman, 1937). They also showed results for the transport of one component. The solution of the flow and transport equations was implemented using OpenFOAM (2015). They included in their formulation a first order chemical reaction. At each time step, the amount of dissolved solid was calculated for each cell porous cell, and the porosity and permeability were updated accordingly. This approach avoids the need to define explicit boundaries between the fluid and solid regions. They simulated flow through a 2D fracture composed of two minerals characterized by different rate constants, and the formation of wormholes in a 3D domain discretized into $150 \times 150 \times 300$ cells. Due to the simplified reaction model and the transport of only one species, the simulations were fast: the formation of a main wormhole

that goes through the whole domain took less than 2 hours on 242 processors. A distinguishing feature of their model is the presence of an energy equation, which allowed them to simulate oil shale pyrolysis. In this case, the reaction is not only a source of mass to the liquid phase but also of energy, which heats the system.

Soulaine et al. (2017) studied dissolution regimes by performing 2D simulations based on an experiment by Song et al. (2014). For this experiment, the researchers created a micromodel by directly etching a large calcite crystal and then injected acid. Soulaine et al. (2017) obtained five flow regimes by varying Péclet and Damköhler numbers: conical, compact and uniform dissolution, and dominant and ramified wormholes. In the same work, they compared their method to a variation of it in which the fluid-solid interface evolved according to the arbitrary-Lagrangian-Eulerian (ALE) method (Hirt et al., 1974). Using ALE, the Navier-Stokes equation were solved only in the liquid phase, the boundary between fluid and solid was explicitly defined and moved with a receding velocity proportional to the rate of dissolution. In Soulaine et al. (2018), they extended their model to account for production of $\text{CO}_2(\text{g})$ during dissolution of calcite, the presence of two fluid phases and the surface tension between them.

Gray et al. (2016) developed a dissolution model, also described by Gray and Boek (2016). They used the lattice Boltzmann method instead of the finite volume method (FVM) to calculate the flow field because its parallelization is more efficient. However, they used the FVM to solve for the transport of one reactant. The dissolution kinetics was modelled by a first-order rate law far from chemical equilibrium, so that the products of the reaction were neglected. The domain was discretized in a Cartesian grid. They proposed a method they called surface rescaling to counteract the staircase effect of the grid. According to this method, the reactive surface is not taken directly from the face area of the solid cells exposed to the fluid. Instead those faces are projected into a parabolic surface that interpolates the fluid-solid interface, and the area of this projected is considered as the reactive surface. Each solid cell has an associated solid fraction that is reduced as dissolution progresses, and the solid cell is turned into a liquid cell when the solid fraction reaches 0.

Another distinguishing feature of Gray et al. (2016)'s model is that it was implemented to be run on graphic processing units (GPUs). Using this model, they simulated the dissolution of 3D Ketton limestone sample by an HCl solution, and found different dissolution patterns as a function of the Péclet number in accordance with experimental observations. The grid was composed of $200 \times 200 \times 200$ cells. To reduce the number of time steps required in the simulation, they rescaled the acid concentration and the simulation time. Gray et al. (2018) extended their model to take into account multispecies transport and reaction, and also the effect of charge-coupling on ion diffusion. They considered four chemical species (H^+ , H_2CO_3 , Ca^{2+} and HCO_3^-) and wrote a chemical solver to calculate the equilibrium among them. They simulated 14 hours of dissolution of a Ketton limestone sample discretized in

630 × 625 × 1415 cells in around 2 days using 8 Tesla P100 GPUs.

We have focused our discussion on direct numerical simulation (DNS). However, it is worth mentioning another approach: pore-network modelling (PNM). These models are situated between DNS and continuum-scale models both in terms of scale and details of the geometry of the pore space. PNM is more efficient than DNS in terms of computation time. However, this comes at the cost of simplifying the geometry of the pore space. The geometry used in PNM can more closely represent a real pore space if it is extracted from an experimentally imaged sample (Silin and Patzek, 2006, Al-Kharusi and Blunt, 2007, Raeini et al., 2017). We do not see DNS, PNM and continuum-scale models as competing approaches but complementary, addressing different levels of detail and model sizes, as exemplified by Varloteaux et al. (2013b) and Varloteaux et al. (2013a). For reactive models, the change in geometry by dissolution when neighbouring pores in the network grow and overlap is particularly challenging. This issue was addressed by Tansey and Balhoff (2016), who proposed a pore-merging criterion.

Steefel et al. (2013) remarked that there was (and there still is) a need to be able to model multicomponent systems at the pore scale resolving gradients of velocity, concentration and reaction rates.

2.5.3 Coupling of transport and reaction

The commonly used approaches to couple reaction and transport equations are the global implicit approach, the sequential non-iterative approach (SNIA) and the sequential iterative approach (SIA) (Steefel and Macquarrie, 1996). The global implicit approach involves solving simultaneously all the transport and reaction equations. It is the most computationally demanding as it involves the construction and solution of linear systems whose dimensions are much bigger than they would be if transport and reaction were treated separately, and it does not allow the coupling of two transport and reaction codes that exist independently.

The sequential non-iterative approach (SNIA) involves solving the transport and the reaction problems separately. For each time step, the transport problem is solved for concentration fields as if no chemical reaction took place. Then, the reaction problem is solved and the concentration fields are updated. It is a good approximation provided that the characteristic time for reaction is much longer than the characteristic time for transport.

To reduce the error associated with this assumption, Strang (1968) proposed a variation to it in which the transport equation is solved for half of a time step, the resulting composition is used to solve the reaction problem for the whole time step, and finally, the transport equation is solved for the other time step. This method can also be adapted to include multiple reaction steps separated by transport steps.

The SIA can be a good compromise between the global implicit approach and

the SNIA method. It avoids the construction of linear systems of large dimensions at the same time that a fully coupled solution is obtained at the end of the time step (Steeff and Macquarrie, 1996). It consists of iterating between the reaction and the transport equations until convergence is obtained.

Both SNIA and SIA are used in many well-known codes (Saaltink et al., 2004). The difference between the numerical behaviour of the SIA and SNIA has been studied previously. In general, SNIA is numerically more efficient but less accurate than SIA (Xu et al., 1999), and SNIA is well adapted for advection-dominated problems but not for diffusion-dominated problems (de Dieuleveult et al., 2009, Carrayrou et al., 2010). When SNIA and Strang splitting are compared, the latter gives more accurate results for a similar CPU time (Steeff and Macquarrie, 1996).

If the simulation is run with small time steps, the error associated to the use of the SNIA is reduced, but the computational cost may become greater than running SIA with a larger time step (Steeff and Macquarrie, 1996). In this work, we choose the SNIA method to couple the transport solver to the geochemical solver because of its numerical efficiency.

2.5.4 Discussion

Although the methodology for reaction processes proposed by Pereira Nunes et al. (2015) yields excellent results for chemically homogeneous rocks, extending it to model reaction in chemically heterogeneous rocks and complex reactions is not straightforward. As seen in Section 2.3.1, the number of species and reactions increases significantly with the addition of each single mineral — e.g., the addition of dolomite to the system increased the number of species from 12 to 18 and the number of reactions from 8 to 13. Extending the particle tracking approach to this situation would require computing the distance between particles of different types at every time step. Moreover, this approach does not take advantage of the partial equilibrium hypothesis (Barton Jr. et al., 1963, Helgeson, 1968, Helgeson et al., 1969, 1970), discussed in Section 3.1.5, according to which some reactions are fast enough to be considered permanently in equilibrium, and it may face difficulties in capturing the non-ideality of the mixture.

Therefore, it is of interest the existence of a model that can be applied to multi-component systems elegantly.

MODELLING OF FLOW, TRANSPORT AND REACTIONS

In this thesis, we have developed a numerical model to simulate reactive transport on pore space images. The model solves either the Stokes or Navier-Stokes equation for the steady state velocity and pressure fields on an unstructured grid representative of the pore space geometry using the finite volume method (FVM). On the same grid and also using the FVM, it solves the advection-diffusion equation for the transient concentration field of each species. Then, for each grid cell, it calculates chemical equilibrium and kinetics using a geochemical solver specifically designed for sequential equilibrium problems such as the ones that arise from the perturbation of the concentration fields by advection and diffusion. The advection-diffusion and the geochemical solvers are coupled using a sequential non-iterative approach.

In the next section, we describe the governing equations, their numerical implementation and how the solvers are coupled.

3.1 Model description

3.1.1 Flow equations

To simulate the velocity and pressure fields on the pore space image, we assume that the body forces can be neglected, the flow is incompressible and any transient behaviour due to changes in the geometry of the pore space is damped out before any significant transport or reaction happen. Therefore, we do not consider the time dependency of velocity and pressure. The flow is modelled by the single-phase steady-state Navier-Stokes equation subject to the incompressibility condition ([White, 1999](#), [Fox et al., 2004](#)):

$$\rho \nabla \cdot (\mathbf{u}\mathbf{u}) = \nabla \cdot (\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) - \nabla p, \quad (3.1)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (3.2)$$

where ρ is the density of the fluid phase and uniform in the domain, $\mathbf{u}$ is the velocity field, μ is the dynamic viscosity of the fluid, which we assume constant in this thesis, and p is the pressure field.

For systems in which $\mathbf{u} \rightarrow 0$, we have $\rho \mathbf{u} \cdot \nabla \mathbf{u} \ll \mu \nabla^2 \mathbf{u}$, and the advective term $\nabla \cdot (\mathbf{u}\mathbf{u})$ can be neglected. Eq. (3.1) can then be simplified to the Stokes equation

$$\mu \nabla^2 \mathbf{u} = \nabla p. \quad (3.3)$$

This equation describes a creeping flow, characterized by a Reynolds number $Re = \rho |\mathbf{u}| L / \mu \ll 1$, where L is a characteristic length of the system. Both the steady-state Navier-Stokes and Stokes equations are implemented in poreReact, the name of the code developed. We assume that the flow is laminar so no turbulence modelling is required.

The solution of these equations requires the imposition of boundary conditions for $\mathbf{u}$ and p . On the grain walls, these conditions are

$$\mathbf{u} = \mathbf{0}, \quad (3.4)$$

$$\frac{\partial p}{\partial \mathbf{n}} = \mathbf{0}, \quad (3.5)$$

where $\mathbf{n}$ is the unit normal vector to the boundary.

On the inlet and outlet faces, we impose $\partial \mathbf{u} / \partial \mathbf{n} = \mathbf{0}$, $p = p_{face}$ on both faces, or $\partial \mathbf{u} / \partial \mathbf{n} = \mathbf{0}$, $p = p_{face}$ on one face and $\mathbf{u} = \mathbf{u}_0$, $\partial p / \partial \mathbf{n} = 0$ on the other. On the sides of the model, we impose either the same condition as for the grain walls, or symmetry boundary conditions, i.e., $\partial \mathbf{u} / \partial \mathbf{n} = \mathbf{0}$, $\partial p / \partial \mathbf{n} = 0$.

In Chapter 5, we will study a pore space image where microporosity is present. To obtain the velocity field, we use the model of Bijeljic et al. (2018), who implemented the Darcy-Brinkman equation (Brinkman, 1949) subject to the incompressibility condition:

$$\frac{\mu}{\phi} \nabla^2 \mathbf{u}_D = \nabla p + \frac{\mu \mathbf{u}_D}{k}. \quad (3.6)$$

$$\nabla \cdot \mathbf{u}_D = 0, \quad (3.7)$$

where $\mathbf{u}_D$ is the Darcy velocity, ϕ is the porosity, and k is the permeability obtained using the method proposed by Bijeljic et al. (2018), which is outlined in Section 5.2. In the cells that represent free fluid, i.e., with no microporosity, $\phi = 1$, $k \rightarrow \infty$, therefore $\mathbf{u}_D \rightarrow \mathbf{u}$.

In Eqs. (3.1) and (3.2), we assumed that the fluid density is uniform and that body forces can be neglected. However, given that the fluid density depends on salinity, which can be modified by mixing and reaction, this assumption is not always

valid (e.g., (Holzbecher, 1998, Dentz et al., 2006)). Since the geochemical library we use (Section 3.1.5) also calculates fluid density, our model can be extended in future work to include density-driven flow. The most direct extension involves using the Boussinesq approximation (Boussinesq, 1897, Tritton, 1977), according to which density variations are important only in the body force term of the Navier-Stokes equation, so that the fluid can still be considered incompressible. In Eq. (3.1), we also assumed that any transient behaviour of the velocity field, caused only by changes in geometry, would be damped out before any significant transport or reaction happened. However, in density-driven flow, the evolution of density variations happens in the same timescale of transport, and a transient-state Navier-Stokes equation must be considered. Under these new assumptions, the flow equations for density-driven would become:

$$\rho_0 \left(\frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (\mathbf{u}\mathbf{u}) \right) = \nabla \cdot (\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) - \nabla p + (\rho_0 + \Delta\rho) \mathbf{g}, \quad (3.8)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (3.9)$$

where ρ_0 is a characteristic density of the fluid, $\Delta\rho = \rho - \rho_0$ is a small density variation around ρ_0 , and $\mathbf{g}$ is the gravity acceleration. For a more efficient numerical solution (Ferziger and Perić, 2002), it is convenient to replace the term $-\nabla p + (\rho_0 + \Delta\rho) \mathbf{g}$ with $-\nabla P + \Delta\rho \mathbf{g}$, where $P = p + \rho_0 g h$, g is the magnitude of the gravity acceleration and h is the elevation.

The Boussinesq approximation is adequate provided that $\Delta\rho/\rho_0 \ll 1$. This is the case for many fluids typically encountered in experiments and applications. For example, in Chapter 4 and Chapter 5, we use a solution of Na_2CO_3 and a solution of CaCl_2 with densities of 999.62 kg/m^3 and 999.13 kg/m^3 , respectively ($\Delta\rho = 0.02 \%$), while in Chapter 6, we simulate the dissolution of a carbonate sample by injecting a solution with density 1036.5 kg/m^3 , which increases to 1041.4 kg/m^3 if the solution is saturated with calcite ($\Delta\rho = 0.2 \%$).

3.1.2 Transport equations

For the transport of species, some previous works on direct numerical simulation of reactive transport opted for an Eulerian approach (e.g., Molins et al. (2012)), while others used a Lagrangian particle-tracking approach (e.g., Pereira Nunes et al. (2016b)). While the latter has the advantage of not introducing numerical diffusion and dispersion in the model, the former makes the coupling to a geochemical solver and incorporation of other physical-chemical phenomena, such as electrochemical migration and different diffusion coefficients, more straightforward. Therefore, we opt for the Eulerian approach.

Using the velocity field $\mathbf{u}$ calculated from Eqs. (3.1) and (3.2), or Eqs. (3.2) and (3.3), the transport of each species is modelled by the advection-diffusion equa-

tion

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (D_{m_i} \nabla C_i) - \nabla \cdot (C_i \mathbf{u}), \quad (3.10)$$

where C_i is the concentration field of species i , and D_{m_i} is its molecular diffusion coefficient. To prevent the violation of charge balance (Lichtner, 1985, Lichtner and Kang, 2007a, Li et al., 2007c), we use the same diffusion coefficient for all species when modelling systems where species-specific diffusion coefficients could lead to charge imbalance. The incorporation of the Nernst-Planck equation (Cussler, 2009) would eliminate this restriction (see discussion in Section 2.3.4).

The solution of these equations requires the imposition of boundary conditions for C_i . On the inlet face, we impose $C_i = C_{i_0}$. On the grain walls, outlet and side boundaries of the model, we impose $\partial C_i / \partial \mathbf{n} = 0$. Note that this condition prevents the species leaving the domain by diffusion, but not by advection.

Note that Eq. (3.10) does not contain source terms for chemical reaction. The coupling between transport and reaction is performed using a sequential non-iterative approach, as detailed in Section 3.1.7.

If microporosity is present, we use the velocity field $\mathbf{u}_D$ calculated from Eqs. (3.6) and (3.7), and model the transport of each species by the advection-diffusion equation

$$\phi \frac{\partial C_i}{\partial t} = -\nabla \cdot (\mathbf{u}_D C_i) + \nabla \cdot (D_{eff} \nabla C_i), \quad (3.11)$$

where D_{eff} is an effective diffusion coefficient. A derivation of this can be found in Appendix B. It is worth emphasizing that C_i is the amount of species i per volume of fluid, as opposed to the amount of species per volume of the continuum domain.

According to Boving and Grathwohl (2001), D_{eff} is related to the diffusion coefficient D measured in a liquid not surrounded by a porous medium by

$$D_{eff} = \frac{\phi D \delta}{\tau^2}, \quad (3.12)$$

where τ is the tortuosity (dimensionless) and δ is the constrictivity (dimensionless), which is only appreciably different from 1 when the pore size is comparable to the size of the solute (Grathwohl, 1998). The tortuosity used in Eq. (3.12) is defined by

$$\tau = \frac{l_e}{l}, \quad (3.13)$$

where l_e is the shortest distance through the pore space between two points A and B, and l is the straight-line distance between those two points. As noted by Epstein (1989), some authors define $\tau = (l_e/l)^2$, in which case Eq. (3.12) should be adapted accordingly.

Shen and Chen (2007) review some empirical relations between tortuosity and porosity. One class of those relations, which is a consequence of Archie's law (Archie, 1942), has the form

$$\tau^2 = (A\phi^{(1-m)})^n, \quad (3.14)$$

where A , m and n are parameter experimentally determined. Substituting Eq. (3.14) into Eq. (3.12) leads to the following empirical relation

$$D_{eff} = \frac{\phi D \delta}{(A \phi^{(1-m)})^n}. \quad (3.15)$$

Boving and Grathwohl (2001) measured the porosity and effective diffusion coefficient in 15 samples of limestone and 14 samples of sandstone. They considered an empirical relation of the form $D_{eff} = \phi^m D$, which is Eq. (3.15) with $\delta = 1$, $A = 1$, $n = 1$, and found that the value of m that best fitted their data was approximately 2.2, which is the one we adopt in this thesis.

3.1.3 Numerical solution of flow and transport

We solve the flow and transport equations using the finite volume method (Patankar, 1980, Versteeg and Malalasekera, 1995, Ferziger and Perić, 2002) implemented in OpenFOAM (Ubbink, 1997, Weller et al., 1998, Rusche, 2002, OpenFOAM, 2015), a parallel open source library for the solution of solve partial differential equations on unstructured grids, available at <http://openfoam.org>. OpenFOAM offers a variety of pre- and post-processing tools, discretization schemes and parallel numerical solvers, which are immediately available for poreReact. It has been previously used to perform direct numerical simulation on pore space images. Raeini et al. (2014), for example, used it to implement their non-reactive non-diffusive two-phase flow model.

In the applications studied in this thesis, the grids are composed of regular hexahedral cells (Fig. 3.1), which could give the impression that they are structured grids. In fact, the grids are unstructured and their cells could be composed of any collection of convex polyhedra, such as hexahedra, pyramids and tetrahedra. The regular hexahedral cells shapes are used for convenience because the grids have been obtained from voxelized micro-CT images of the pore space.

As mentioned in Section 2.2, micro-CT tomography generates greyscale images such as the one illustrated at the top left of Fig. 3.1. The segmentation of the greyscale voxels into solid and liquid voxels is not univocal. It is affected by noise in the image acquisition and by the presence of subresolution features (Noiriel, 2015), such as microporosity and fluid-solid interfaces that are not aligned with the voxel faces. For example, a voxel that is crossed by a fluid-solid interface has a intermediate grey value between the values for solid and liquid phases. However, after segmentation, it will represent just one of the phases, which has the effect of moving the representation of the interface to the position of the voxel faces. Therefore, a good approximation is obtained only if the resolution of the image is high enough to resolve the geometry of the solid and liquid phases. A possible extension of our model would involve using the volume-of-fluid/embedded boundary method (Colella et al., 2000), as done by Molins et al. (2014). In this method, the description of

the interface is improved by estimating the position of the interface from the partial volumes occupied by both fluid and solid and for the interfacial area between fluid and solid in each voxel.

Another condition to obtaining a good approximation of the pore space from a segmented image is that microporosity is absent or negligible. When microporosity is present, intermediate grey values occur not only in voxels that are crossed by a pore-scale interface. In this case, it is necessary to increase the complexity of the model by assigning a value of porosity for each voxel, as done in [Chapter 5](#). These considerations about segmenting an image in solid and liquid voxels also apply when we need to segment an image in different solid phases to model multiminerall fluid-solid reaction. In [Section 6.2](#), for example, we assigned a single mineral (calcite or dolomite) to each voxel, which is a good approximation provided that the image resolution is high enough to resolve the mineral spatial distribution, i.e., provided that the extent of each mineral phase is large compared to the voxel size.

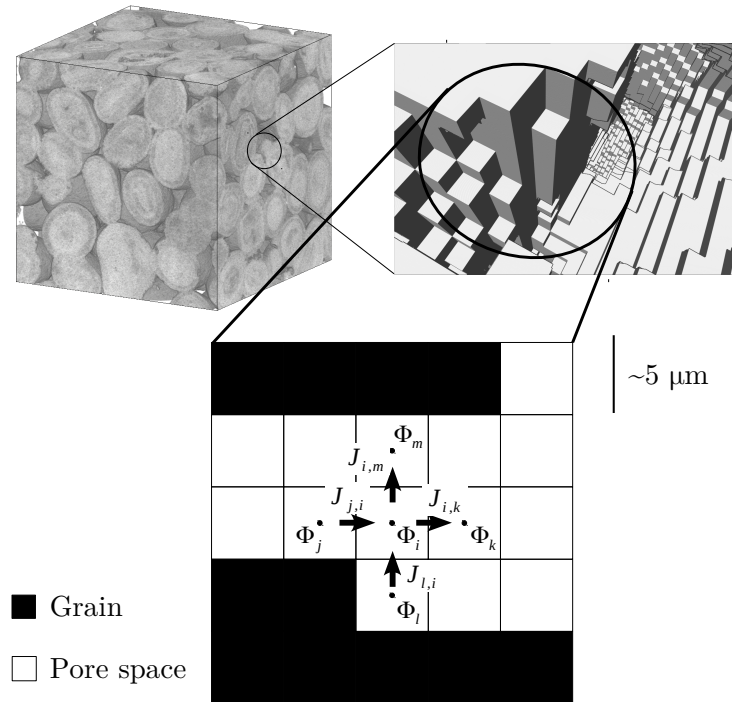


Figure 3.1: A greyscale image of the porous medium (top left) is obtained by microtomography. The image is segmented into solid and pore space and a voxelized representation of pore space is obtained (top right). The pore space is discretized into cells (bottom) which form a grid on which transport and reaction are calculated. The property Φ — which represents velocity, pressure or concentration — is stored in the centre of the cell. Its evolution is calculated taking into account the momentum or mass fluxes J between neighbouring cells. The scale shows a typical cell size for a grid used in pore-scale simulation of reactive transport through rocks. Each grain cell can be associated to a different mineral, with different reaction mechanism and rate laws. From [Oliveira et al. \(2019\)](#).

The algorithm for the solution of the flow equation is taken from simpleFoam, one of OpenFOAM standard solvers. It implements SIMPLE (Patankar and Spalding, 1972, Patankar, 1980), a segregated velocity-pressure procedure to decouple the solutions of pressure and velocity, which are coupled in Eq. (3.1). OpenFOAM uses a collocated grid (as opposed to a staggered grid), meaning that the value of both pressure and velocity are calculated at the centre of the grid cell. To eliminate non-physical checkerboard pressure solutions, simpleFoam employs a pressure interpolation proposed by Jasak (1996) which follows the Rhie and Chow (1983) interpolation.

Since we consider a uniform dynamic viscosity μ , the term $\nabla \cdot (\mu(\nabla \mathbf{u})^T)$ in Eq. (3.1) equals 0 because $\nabla \cdot \mathbf{u} = 0$. Nevertheless, it was kept in the equation because it improved the numerical stability in some simulations we performed. For completeness, it is worth mentioning that $\nabla \cdot (\mu(\nabla \mathbf{u})^T)$ is implemented as $\nabla \cdot (\mu \text{dev}((\nabla \mathbf{u})^T))$ (Holzmann, 2017), where $\text{dev}(\cdot)$ is the deviatoric operator.

We discretize the time derivative of Eq. (3.10) using the first-order implicit Euler method (Ferziger and Perić, 2002). This method is unconditionally stable, allowing arbitrarily large time steps to be taken without loss of stability. Nonetheless, reasonably small time steps are needed to ensure the accuracy of results. In the explicit Euler method for an uniform grid it is required that the time step is chosen so that the Courant–Friedrichs–Lewy (CFL) (Courant et al., 1928) number is less than 1. The CFL number is calculated as

$$\text{CFL} = \frac{u \Delta x}{\Delta t}. \quad (3.16)$$

Here, u is the magnitude of the velocity in the cell and Δx is the grid spacing.

However, the range of velocity spans many orders of magnitude in natural rocks, as illustrated by the probability density functions (PDF) of the logarithm of normalized velocities in Figs. 2.1 and 5.2. Therefore, a time step that satisfied $\text{CFL} < 1$ in every cell would be prohibitively small for the applications we are interested. On the other hand, there are few cells where the velocity is larger than the average. This is better seen by the PDFs of normalized velocities plotted in linear scale in Fig. 3.2, from which it is clear that the fraction of cells where $u > u_{avg}$ is small, especially for more physically heterogeneous rocks, such as Portland (for a definition and discussion of PDFs of normalized velocities and PDFs of their logarithms, see Section 3.2.2). Based on this discussion, we choose the implicit Euler method for the discretization of time derivative and commonly use a time step such that the CFL number calculated based on the average velocity equals 1. In the validation case examined in Section 3.3.2, for example, a value of $\text{CFL} = 1.2$ was used and allowed a good agreement between the simulations and results found in the literature.

Among the discretization schemes for the advection term of Eq. (3.10) available in poreReact, there are upwind (Courant et al., 1952) and flux-limiter schemes such as SFCD (Ziman, 1990), superbee (Roe and Baines, 1982) and van Leer (van Leer,

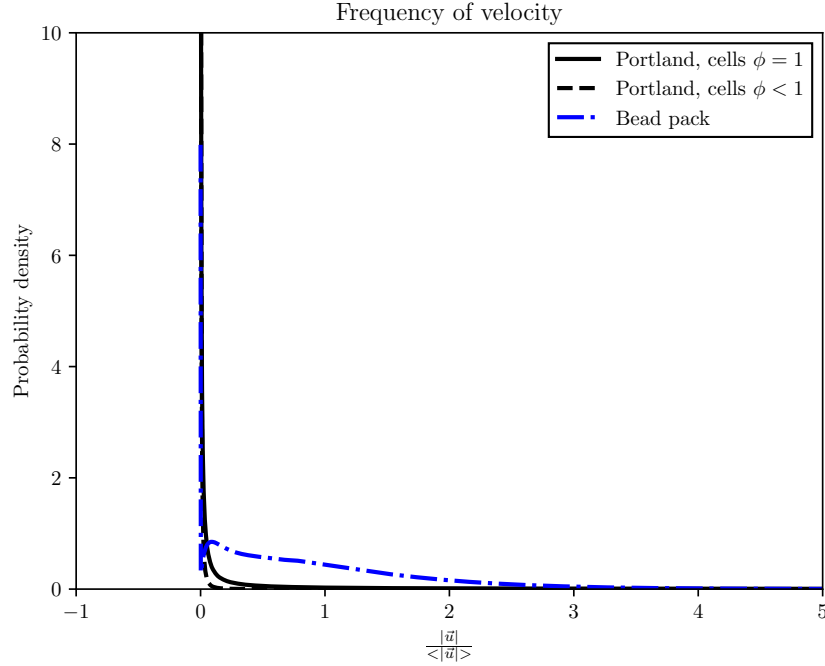


Figure 3.2: PDF of velocity for bead pack (Eq. (3.43)) and partial PDFs of velocity for Portland (Eq. (3.46)) in linear scale. The macro- and microporosity contributions for the PDF for Portland have been separated in two partial PDFs to highlight the different characteristic of these regions.

1974). While flux limiter schemes would have the advantage of reducing numerical diffusion, we choose the upwind scheme in this study to ensure the boundedness of the solution in 3D and non-structured grids.

The convergence of the solution of the flow and transport equations is achieved when the residual of the discretized equations is smaller than a user-defined tolerance. For a discretized equation of the form $A_{n \times n} x_{n \times 1} = b_{n \times 1}$ for the values of a quantity in n cells, the residual r is calculated as

$$r = \frac{|Ax - b|_1}{|Ax - t|_1 + |b - t|_1}, \quad (3.17)$$

where

$$t_i = \left(\sum_{j=1}^n A_{ij} \right) \cdot \left(\frac{1}{n} \sum_{i=1}^n x_i \right), \quad (3.18)$$

and $|\cdot|_1$ is the L1-norm. In this work, we have considered a tolerance of 10^{-9} .

3.1.4 Irreversible instantaneous bimolecular reaction

One of the chemical reaction models implemented in poreReact is the irreversible instantaneous reaction



In the reaction step, the concentrations C_A, C_B, C_C of species A, B, C in each grid cell are updated as follows:

Algorithm 1 Irreversible bimolecular reaction.

- 1: $\Delta \leftarrow \max(\min(C_A, C_B), 0)$ $\triangleright \max(\cdot, 0)$ avoids reaction of negative concentrations
 - 2: $C_A \leftarrow C_A - \Delta$
 - 3: $C_B \leftarrow C_B - \Delta$
 - 4: $C_C \leftarrow C_C + \Delta$
-

The use of $\max(\cdot, 0)$ in [Line 1](#) of [Algorithm 1](#) avoids the reaction of negative concentrations that may appear if a non-bounded numerical scheme is used to discretize the advection term of the transport equation ([Eq. \(3.10\)](#)).

3.1.5 Chemical equilibrium modelling

For the solution of geochemical reactions, poreReact leverages on Reaktoro ([Leal, 2015](#), [Leal et al., 2016a](#)), an open source C++ library for the solution of multispecies multiphase chemical equilibrium and kinetics problems in a completely mixed batch reactor, available at <http://reaktoro.org>.

The simulation of chemical equilibrium can account for a significant portion of the total computational cost of a reactive transport simulation. The reasons are that (i) each equilibrium calculation can involve the iterative solution of a nonlinear system of equations, (ii) each iteration can require the evaluation of thermodynamic properties such as activities and chemical potentials that depend on temperature, pressure and chemical composition, (iii) stability tests may be required to check phase appearance and disappearance, and (iv) all the equilibrium calculations may need to be performed at every time step for every grid cell of the model. For example, in a model with a million grid cells and ten thousand time steps, ten billion equilibrium calculations will have been performed by the end of the simulation.

Considering these requirements, [Leal et al. \(2015\)](#) proposed novel numerical methods for the solution of multiphase chemical equilibrium and kinetics problems in a well-stirred batch model. They abstracted the underlying mathematics from multiphase chemical equilibrium and kinetics problems and implemented modern and efficient methods from the mathematical literature for solving them. In accordance with the partial equilibrium ([Barton Jr. et al., 1963](#), [Helgeson, 1968](#), [Helgeson et al., 1969, 1970](#)), [Leal et al. \(2015\)](#) classified the reactions in two groups: slow reactions, which are controlled by kinetics, and fast reactions, which are assumed to be in equilibrium. Due to its time-dependence, chemical kinetics consists of solving a system of ordinary differential equations, whereas chemical equilibrium requires only the solution of algebraic equations. Therefore, the consideration of partial equilibrium considerably simplifies the problem by replacing stiff differential equations by algebraic ones.

Reaktoro was designed for applications that require sequential equilibrium calculations such as reactive transport problems. Efficiency was achieved by modelling the chemical equilibrium using a Gibbs energy minimization (GEM) approach, casting it in a nonlinear optimization problem, and using modern techniques borrowed from the literature in optimization for its solution. In this section, we discuss some of these ideas and refer the reader to the relevant literature.

The chemical equilibrium problem can be formulated in two ways: by the use of reaction equilibrium constants and by the minimization of the Gibbs energy (Smith and Missen, 1982, Bethke, 2007). Both formulations are mathematically equivalent as shown by Zeleznik and Gordon (1968) and van Zeggeren and Storey (1970). The formulation that uses reaction equilibrium constants is also known as the stoichiometric formulation or law of mass action (LMA), first proposed by Guldberg and Waage (1864). Its detailed description can be found in, e.g., Reed (1982), van der Lee (1998), Parkhurst and Appelo (1999) and Leal (2014), and it is summarized below.

We use the same notation used by Leal (2014), following Smith and Missen (1982):

$\mathbf{e} = (e_1, \dots, e_E)$ is a tuple of elements, e.g., (C, O, H, Ca, Mg).

$\alpha = (\alpha_1, \dots, \alpha_N)$ is a tuple of chemical species, e.g., (H₂O, CaCO₃, CO₂(aq), CO₂(g)).

Note that if the same chemical compound is present in more than one phase, it is represented by a different species for each phase in which it occurs, e.g., CO₂(aq) and CO₂(g) are two different species.

$\mathbf{W} \in \mathbb{R}^{E \times N}$ is the formula matrix. The position w_{ij} indicates the number of atoms of elements e_j in species α_i .

K_{eq_j} the equilibrium constant of the j -th reaction.

ν_{ij} is the stoichiometric coefficient of the i -th species in the j -th the reaction. It is positive for products and negative for reactants.

n_i is the amount of molecules of species α_i in the system. Therefore $\mathbf{n} \in \mathbb{R}^N$ is a vector that represents not only the composition but also the size of the system.

b_k is the amount of atoms of element e_k in the system.

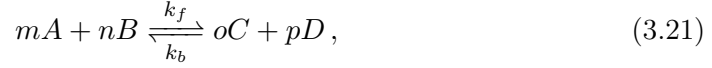
a_i is the activity of species α_i in the system at T and P.

With this notation, the conservation of mass and charge in a reaction can be written as

$$\mathbf{W}\mathbf{n} = \mathbf{b}, \quad (3.20)$$

where $\mathbf{b}$ is given. An extra row can be added to matrix $\mathbf{W}$, and an extra position to the vector $\mathbf{b}$ to represent the charge of each species, in which case this equation for conservation of mass also takes into account the conservation of charge.

The law of mass action states that the rate of a reaction is proportional to the product of the activities of the reactants, so that for the chemical equation



the rate of the forward reaction is $k_f a(A)^m a(B)^n$ and the rate of the backward reaction is $k_b a(C)^o a(D)^p$. At equilibrium, both rates are equal

$$k_f a(A)^m a(B)^n = k_b a(C)^o a(D)^p. \quad (3.22)$$

The ratio between the rate constants k_f and k_b is the equilibrium constant K_{eq} :

$$K_{eq} = \frac{k_f}{k_b} = \frac{a(C)^o a(D)^p}{a(A)^m a(B)^n}. \quad (3.23)$$

More generally, an equilibrium reaction

$$\sum_i \nu_i \alpha_i \rightleftharpoons 0, \quad (3.24)$$

has an equilibrium constant

$$K_{eq}(T, P) = \prod_i a_i(\mathbf{n}, T, P)^{\nu_i}, \quad (3.25)$$

which is a function of temperature T and pressure p , and can be calculated from empirical relations or interpolated from tables.

Taking the logarithm of both sides, we have:

$$\ln K_{eq}(T, P) = \sum_i \nu_i \ln a_i(\mathbf{n}, T, P). \quad (3.26)$$

For each equilibrium reaction, an equation in the form of [Eq. \(3.26\)](#) can be written and, together with conservation of chemical elements and electrical charge, they form the nonlinear system

$$\begin{bmatrix} W\mathbf{n} - \mathbf{b} \\ \ln K_{eq}(T, P) - \sum_i \nu_i \ln a_i(\mathbf{n}, T, P) \end{bmatrix} = 0. \quad (3.27)$$

Given thermodynamic models for the species activities, this nonlinear equation is solved for $\mathbf{n}$.

[Leal et al. \(2016a\)](#) noted that most geochemical codes, as well as all reactive transport simulators reviewed in [Steeff et al. \(2015a\)](#), use this formulation (LMA). As reasons for that, they mention historical ones, such as the availability of thermodynamic data described in the form of equilibrium constants, and some advantages

it offers. The LMA formulation requires less thermodynamic data (that is, equilibrium constants for every reaction instead of chemical potentials for every species), and fewer unknowns than the GEM formulation, which has its number of unknowns increased by the use of Lagrange multipliers. The total number of implicit variables solved at every iteration in a GEM calculation can, however, be reduced to that of LMA algorithms, with the other variables being computed explicitly.

Despite the popularity of the LMA formulation, it has some disadvantages. Most importantly, it requires the determination of which phases are present in the chemical system before building the nonlinear system of equation that needs to be solved. When looking for a solution of Eq. (3.27), another set of constraints that should be obeyed is $n_i > 0$. Note that if $n = 0$, then $a = 0$ and $\ln a(\mathbf{n}) \rightarrow \infty$. Therefore the mass-action equations in which the species participate become undefined. In reality, n_i can be zero just if all the other species in its phase are also absent, that is, if the phase vanishes altogether (Smith and Missen, 1982). In this case, the mass-action equations related to this phase must be removed from the model. Algorithmically, it translates into the necessity of determining which phases are present before building the system equation at each iteration of the solving procedure of the nonlinear system. Most geochemical solvers do this by a trial-and-error approach, using heuristic techniques to verify whether a phase is stable. If, during the iterative solution of the nonlinear system, the solution progresses to a state in which a phase becomes stable or unstable, the system of equations needs to be reassembled. The recurring stability tests and reassemblies may slow down the solution.

The second formulation for the chemical equilibrium problem is the non-stoichiometric formulation or Gibbs energy minimization (GEM) (White et al., 1958, Karpov et al., 1997, Kulik et al., 2013, Leal et al., 2016a). While LMA is very popular in aquatic chemistry (Leal et al., 2016b), the GEM formulation is widely used in petrology, hydrothermal geochemistry and metallurgy because it is naturally capable of detecting which phases are stable at equilibrium (Karpov et al., 1997, Kulik et al., 2013, Leal et al., 2016a). This formulation is based on the thermodynamic fact that the equilibrium composition of a reactive system at constant temperature and pressure is the one that minimizes the Gibbs energy, which is given by

$$G(\mathbf{n}, T, P) = \sum_i n_i \mu_i(\mathbf{n}, T, P), \quad (3.28)$$

where n_i and μ_i are the amount and the chemical potential of species α_i , respectively. The chemical potentials are calculated by

$$\mu_i(\mathbf{n}, T, P) = \mu_i^o(T, P) + RT \ln a_i(\mathbf{n}, T, P), \quad (3.29)$$

where μ_i^o are the standard chemical potentials and R is the gas constant. The minimization of G with respect to $\mathbf{n}$, together with thermodynamic models for the species activities and constraints on the conservation of elements amounts and non-negativity of the species amounts, form a nonlinear optimization problem.

An important advantage of the GEM approach is that it does not require the verification of the stability of the phases during the solution process, which is computationally expensive (Kulik et al., 2013, Leal et al., 2016a).

The definition in Eq. (3.28) considers all species, even those belonging to unstable phases. If a phase and its species vanishes, then the respective $n_i\mu_i$ term tends automatically to zero. After convergence is reached, one can check for the stability of the phase if needed. Since the check is performed only when the solution is obtained, one can afford to do it using a rigorous phase stability test instead of ad hoc less expensive techniques that are dependent on the type of phases and species. In addition, the GEM approach lends itself to a general and elegant formulation as a nonlinear optimization problem that can more easily take advantage of developments in optimization theory. By considering all species, the linear system solved at each Newton iteration could become larger and slow down the solution. However, Leal et al. (2016a, Sections 3.2 and 3.3) present strategies that reduce the dimension of the linear system from $2N + C$ to C , where N is the number of species and C is the number of elements in the chemical system.

Since it is our objective to develop a model that can be extended in future work to complex chemical systems with many non-ideal multispecies solution and fluid-solid reactions, while being computationally efficient, we opted for the GEM approach and its implementation in Reaktoro.

The thermodynamic database we use is SUPCRT92 (Johnson et al., 1992), which contains parameters for the revised Helgeson-Kirkham-Flowers equation of state, presented by Helgeson et al. (1981) and revised by Tanger and Helgeson (1988) and (Shock et al., 1992), for over 450 organic and inorganic aqueous species. It is worth noting that the choice for the GEM approach does not prevent the use of LMA thermodynamic databases. Leal et al. (2016b) presented how to convert these to GEM thermodynamic databases, and exemplified this by making PHREEQC (Parkhurst and Appelo, 2013) databases available in Reaktoro. As a consequence, they are available for use with poreReact as well.

3.1.6 Chemical kinetics modelling

For reactions between the liquid and solid phases, three choices are available to the modeller in poreReact. Reactions that are fast compared to transport can be modelled as being in equilibrium, which is calculated by the geochemical solver Reaktoro as described in Section 3.1.5. For reactions that promotes small changes in the composition of the fluid phase during a time step, we obtain the rate of reaction from the geochemical solver and, assuming it constant, integrate it over the time step. For a general reaction that cannot be simplified in one of the two previous groups, we rely on the geochemical solver to perform the integration over the time step.

The rate of the reaction

$$0 \rightleftharpoons \sum_i \nu_i \alpha_i \quad (3.30)$$

is defined as

$$r = \frac{1}{\nu_i} \frac{dn_i}{dt}. \quad (3.31)$$

Therefore the amount of each species follows the evolution law

$$\frac{dn_i}{dt} = \nu_i r(\mathbf{n}, T, P). \quad (3.32)$$

If more than one reaction takes place at the same time, the production or consumption of the species at each reaction is taken into account by

$$\frac{dn_i}{dt} = \sum_{j=1}^M \nu_{ij} r_j(\mathbf{n}, T, P). \quad (3.33)$$

The rates $r_j(\mathbf{n}, T, P)$ are calculated using mineral rate laws. [Leal et al. \(2015\)](#) adapted the mineral rate laws presented by [Lasaga \(1981, 1995, 1998\)](#), [Lasaga et al. \(1994\)](#), [Aagaard and Helgeson \(1982\)](#), [Steefel and Van Cappellen \(1990\)](#), [Steefel and Lasaga \(1994\)](#), [Oelkers et al. \(1994\)](#), [Perkins et al. \(1997\)](#), [Palandri and Kharaka \(2004\)](#), and adopted the following general rate law for mineral precipitation and dissolution:

$$r_m(T, p, \mathbf{n}) = \mathcal{A}_m(\mathbf{n}) \sum_i \mathcal{M}_{m,i}(T, p, \mathbf{n}), \quad (3.34)$$

where T is the temperature (K), p is the pressure, n_j is the amount of each species j in the fluid phase (mol), r_m is the rate of precipitation (if $r_m > 0$) or dissolution (if $r_m < 0$) of mineral m (in amount per unit time, mol/s), $\mathcal{A}_m(\mathbf{n})$ is the surface of the mineral (in distance squared, m^2) which can be a function of n , and $\mathcal{M}_{m,i}$ is the kinetic mechanism function i for mineral m (in amount per unit mineral surface area per unit time, $\text{mol}/(\text{m}^2 \text{s})$).

In their original work, [Leal et al. \(2015\)](#) considered a functional form for $\mathcal{A}_m(\mathbf{n})$ that made it dependent on the amount of the solid phase. In our model, we consider that the area of the fluid-solid interface of each cell, which is obtained from the geometry of the model, remains constant until the whole cell is dissolved. To allow for that, we suggested a modification to Reaktoro. We thank Dr Allan Leal, the main developer of the geochemical solver, for kindly improving and incorporating our suggestion into his code.

The functional form available in Reaktoro for the kinetic mechanism function $\mathcal{M}_{m,i}$ is given by

$$\mathcal{M}_{m,i}(T, P, \mathbf{n}) = \text{sgn}(1 - \Omega_m) k_{m,i} |1 - \Omega_m^{p_{m,i}}|^{q_{m,i}} \mathcal{C}_{m,i}, \quad (3.35)$$

where Ω is the saturation index of the mineral, $k_{m,i}$ is the rate constant (in amount per unit mineral surface area per unit time, $\text{mol}/(\text{m}^2 \text{s})$), $p_{m,i}$ and $q_{m,i}$ are empirical

parameters obtained by fitting experimental data, and $\mathcal{C}_{m,i}$ is a function to model the effect of catalysts and inhibitors.

The saturation index Ω_m is defined as

$$\Omega_m = \frac{Q_m}{K_m}. \quad (3.36)$$

For a chemical reaction

$$\sum_j \nu_j \alpha_j \rightleftharpoons 0, \quad (3.37)$$

Q_m is the ion activity product

$$Q_m = \prod_i a_j(\mathbf{n}, T, P)^{\nu_j}, \quad (3.38)$$

and the equilibrium constant K_m , already defined in Eq. (3.25) is the value of Q_m at equilibrium. To avoid confusion, it should be noted that other authors, e.g., Allaby (2008), use the term saturation index to refer to $\log \Omega_m$ instead of Ω_m .

As mentioned in Section 2.3.1, the dependency of the reaction rate constant $k_{m,i}$ on temperature is modelled via the Arrhenius equation:

$$k_{m,i} = A \exp\left(-\frac{E_{m,i}}{RT}\right), \quad (3.39)$$

or

$$k_{m,i} = k_{m,i}^\circ \exp\left(-\frac{E_{m,i}}{R} \left(\frac{1}{T} - \frac{1}{T^\circ}\right)\right), \quad (3.40)$$

where A is the pre-exponential factor, $E_{m,i}$ is the activation energy, R is the universal gas constant and T is the absolute temperature, T° is a reference temperature and $k_{m,i}^\circ = k_{m,i}$ at the reference temperature.

The function that models the effect of catalysts and inhibitors is given by

$$\mathcal{C}_{m,i} = \prod_j a_j^{\xi_j} \prod_g P_g^{\eta_g}, \quad (3.41)$$

where a_j is the activity of aqueous species j and P_g is the partial pressure of the gaseous species g . The empirical exponents ξ_j and η_g are positive for catalyst, negative for inhibitors and zero otherwise.

The evolution of the composition in a time interval is obtained by successively integrating Eq. (3.33) over a small time step and calculating the equilibrium of the homogeneous equations. As mentioned, the modeller can rely on poreReact to integrate the rate of reaction over a time step, during which the rate is assumed constant, or on Reaktoro, which divides the time step in smaller ones in which a constant rate can be assumed.

3.1.7 Coupling of flow, transport and reaction

In this section, we describe how the coupling between the previously presented flow, transport and geochemical solvers is performed. We outline the model algorithm, how the mesh is updated as dissolution happens, and options available to the user of the model. A summary view of the model is presented in [Algorithm 2](#). As discussed in [Section 2.5.3](#), we choose the sequential non-iterative approach (SNIA) to couple transport and reaction. We will concentrate our discussion on the most complete usage of the model, which involves the solution of flow, transport, fluid-solid reaction and changes in geometry. Depending on the problem studied, some of these steps can be skipped. By setting the options `solveFlowField`, `solveTransport`, `fluidSolidReaction` and `dissolution` to false, the user can skip the solution of the flow field, the transport equation, the geochemical reaction and the change in geometry, respectively.

The model makes use of two meshes: one for the whole domain, called the background mesh, and one for the liquid phase, called the liquid mesh. The field `mineralType` is defined on the background mesh and indicates which phase is present in the cell. If it is a solid cell, it also indicates which mineral is associated with it, which has a corresponding reaction mechanism and reaction rate constants.

Note that we attribute only one mineral to each cell. It is a fair assumption provided that the image resolution is high enough to resolve the mineral spatial distribution, which is the case if the extent of each mineral phase is large compared to the cell size. If more than one mineral were assigned to each cell and one mineral was more reactive than the others, a question would arise as to how to model the evolution of the geometry. For example, if calcite completely dissolved in a cell containing calcite and a non-reactive mineral, how should the non-reactive mineral be modelled? In a real rock, the non-reactive mineral could stay in its original location, giving rise to a cell with microporosity, or be carried by the flow, giving rise to fines migration. In [Chapter 5](#), we consider images with initial microporosity, and extending our model to cases in which microporosity is created by mineral dissolution is straightforward. The fines migration would require further development to include modelling of the particles motion (e.g., using a Lagrangian approach) and the clogging (e.g., implementing the model proposed by [Natsui et al. \(2012\)](#)).

From the background mesh, we extract the liquid mesh, on which we solve the Stokes or Navier-Stokes equation (see [Section 3.1.1](#)) to obtain the steady-state solution for the pressure and velocity fields. Using the resulting velocity field, we solve the advection-diffusion equation (see [Section 3.1.2](#)) for the concentration of each species, followed by the calculation of new chemical equilibrium on each cell using the solver described in [Section 3.1.5](#).

For the cells that are in contact with minerals, we use the chemical kinetic model described in [Section 3.1.6](#). Alternatively, if it is known that the time required for

Algorithm 2 Multicomponent reactive transport solver.

Input: solveFlowField, solveTransport, fluidSolidReaction, dissolution

```

1: if solveTransport and not solveFlowField then
2:   Read user provided velocity field
3: end if
4: updateMesh  $\leftarrow$  false
5: while  $t \leq t_{\text{final}}$  do
6:   if updateMesh then
7:     Find liquid mesh as a subset from the background mesh using mineralType
8:     Map fields from old liquid mesh to the new liquid mesh
9:     updateMesh  $\leftarrow$  false
10:    solveFlowField  $\leftarrow$  true
11:   end if
12:   if solveFlowField then
13:     Solve Stokes or Navier-Stokes equation
14:   end if
15:   if solveTransport then
16:     Solve advection-diffusion equation for each species
17:     Calculate equilibrium of liquid phase for every cell in the liquid mesh
18:     if fluidSolidReaction then
19:       for every cell in the liquid mesh do
20:         Calculate fluid-solid reactions
21:         if dissolution then
22:           Update solidFraction accordingly
23:         end if
24:       end for
25:       if dissolution then
26:         for every cell in the background mesh do
27:           if solidFraction  $\leq$  solidFractionTriggerUpdate then
28:             updateMesh  $\leftarrow$  true
29:           end if
30:         end for
31:         if updateMesh then
32:           for every cell in the background mesh do
33:             if solidFraction  $\leq$  solidFractionThresholdUpdate then
34:               Change mineralType
35:             end if
36:           end for
37:         end if
38:       end if
39:     end if
40:   end if
41:    $t \leftarrow t + \Delta t$ 
42: end while

```

the equilibrium between liquid and solid to be reached is much smaller than the characteristic time for transport, we can opt to solve for the chemical equilibrium between the two phases. In any case, we calculate the amount of each species that is removed from the solid and added to the liquid phase. A new chemical equilibrium is then calculated for the liquid taking into account the species that were added to it by dissolution.

For the cells that are not in contact with minerals, chemical equilibrium is calculated as well. Since transport during a time step does not profoundly change the liquid composition, the chemical equilibrium obtained for a cell in one time step is used as the initial guess for the calculation of the next chemical equilibrium for that cell. This provides a significant reduction of the number of iterations needed for convergence. In regions away from the injection front or fluid-solid interfaces, the change of the concentration fields between two time steps may be so small that the computational effort required by the reaction step is not justified. To save computation time, our model allows the definition by the user of thresholds for each species so that the reaction step in a cell is run only if the variation of at least one species concentration since the last chemical equilibrium calculation in that cell is larger than the provided threshold.

It should be emphasised that each liquid cell is considered as a well-mixed batch, with an added solid phase if the cell is in contact with a solid one. Since each cell is considered independently, the reaction step scales linearly with the number of processors and is well-suited for parallelization on high-performance computing infrastructures.

The removal of species from a solid cell is taken into account by changing the field `solidFraction`, which is defined on the background mesh. The amount of mineral in a solid cell is proportional to the cell volume and the `solidFraction`, and inversely proportional to the molar volume of the mineral. In systems where it is assumed that advection and diffusion reach a steady state before a significant change in geometry takes place, we can multiply the change in `solidFraction` in a time step by a factor we call `solidFractionChangeAccelerator`. This factor applies only for the amount of species removed from the solid phase, and does not impact the amount of species transfer to the fluid. Unless stated otherwise, we use a value of 1 to `solidFractionChangeAccelerator`.

Note that we remove a solid cell only once it is completely dissolved, and no update of the flow field is done prior to that. Other authors have made this same modelling choice and obtained good agreement between simulations and experiments (e.g., [Pereira Nunes et al. \(2016b\)](#)). However, this choice is not a good approximation to model channels that are initially few cells wide, where even a change in width of a fraction of the cell size would result in a large change in flow rate. This is even more evident when we remember that the permeability of a cylindrical tube varies with the fourth power of its diameter. A possible extension of our model would involve

using a level set method to capture the evolution of the interface, as described by [Li et al. \(2010\)](#) and applied to 2D pore-scale models by [Molins et al. \(2017\)](#).

At the end of each time step, we verify if an update in geometry is needed. This is done by comparing the value of `solidFraction` to the user-provided values `solidFractionTriggerUpdate` and `solidFractionThresholdUpdate`. The geometry is updated if the value of `solidFraction` in any cell is less than `solidFractionTriggerUpdate`. Then, all cells where `solidFraction` is less than `solidFractionThresholdUpdate` have their value of `mineralType` changed to the one corresponding to a liquid phase. Most accurate simulations are obtained when `solidFractionThresholdUpdate` and `solidFractionTriggerUpdate` are set to 0. However, by choosing values of `solidFractionTriggerUpdate` < 0 and `solidFractionThresholdUpdate` > 0 , the user can avoid too frequent mesh updates and make a compromise between accuracy and practical run time based on their knowledge and assumptions about the system being modelled. Unless stated otherwise, we use a value of 0 for these two variables.

If a mesh update is required, a new liquid mesh is found as a subset from the background mesh using the most recent values of `mineralType`. The pressure, velocity and species concentrations of the old mesh are mapped to the new mesh. The initial guess for pressure and velocity in new cells is based on the average of the pre-existing neighbouring cells. The initial value for the composition of the liquid in new cells is input by the user at the beginning of the simulation. The process is repeated until the end of the simulation.

The proposed methodology is validated against sample cases in [Chapters 3, 4 and 6](#), and enables the simulation of multispecies reactive flow through pore space images obtained from micro-tomography.

3.2 Transport and reaction quantities for analysis

3.2.1 Rate of formation and consumption

Although we consider fluid-fluid reactions instantaneous, the rate of formation is finite because it is limited by transport. We calculate a rate of formation for each species i as

$$r_i(\mathbf{x}, t) = \frac{\partial}{\partial t} C_i(\mathbf{x}, t), \quad (3.42)$$

where $\mathbf{x}$ is a position in the pore space, t is time, and C_i is the concentration. If $r_i < 0$, we may call $|r_i|$ the rate of consumption.

3.2.2 Probability density function of velocity weighted by rates of formation and consumption

Multispecies reactive transport simulations can generate large amounts of data, so much that turning that data into insights can be challenging. We propose a transform that can be useful to assess the velocity of the sites where reactions take place, which we call the probability density function (PDF) of velocity weighted by rates of formation (or consumption). It is inspired by the PDF of velocity proposed by [Bijeljic et al. \(2013b\)](#) to characterize the physical heterogeneity of a porous medium, and on [Alhashmi et al. \(2016\)](#)'s adaption of it to fluid-fluid reactions.

We start by recalling that the PDF of velocity can be defined as

$$p(u) = \frac{d}{du} \left(\frac{\int_{\Omega} [U(\mathbf{x}) < u] d\Omega}{\int_{\Omega} d\Omega} \right), \quad (3.43)$$

where Ω is the pore space, $\mathbf{x}$ a position in it, $U(\mathbf{x}) = |\mathbf{U}(\mathbf{x})|$ the magnitude of the flow velocity, $d\Omega$ a differential volume element and $[\cdot]$ is the Iverson bracket (it equals 1 if the proposition inside it is true, 0 otherwise). In words, the expression in the numerator is the volume of the region where the flow velocity is less than u .

We define the PDF of velocity weighted by the rate of formation of species i as

$$p_i(u) = \frac{d}{du} \left(\frac{\int_{\Omega} r_i(\mathbf{x}) [U(\mathbf{x}) < u, r_i(\mathbf{x}) > 0] d\Omega}{\int_{\Omega} r_i(\mathbf{x}) [r_i(\mathbf{x}) > 0] d\Omega} \right), \quad (3.44)$$

where $r_i(\mathbf{x})$ is the rate of formation of species i at $\mathbf{x}$. Similarly, the PDF of velocity weighted by the rate of consumption is defined by replacing the condition $r_i(\mathbf{x}) > 0$ with $r_i(\mathbf{x}) < 0$. We choose to define the PDF of velocity weighted by the rate of formation and consumption separately to avoid formation and consumption masking each other. Note that in the particular case where $r_i(\mathbf{x})$ is positive and uniform throughout the domain, [Eq. \(3.44\)](#) degenerates to [Eq. \(3.43\)](#).

Since we are usually interested in comparing different injection conditions or different porous media, it is more convenient to consider a normalized velocity. Furthermore, since the flow velocity in a porous medium can vary by many orders of magnitude, we consider the logarithm

$$\tilde{U} = \log_{10} \left(\frac{U}{\langle U \rangle} \right), \quad (3.45)$$

where $\langle \cdot \rangle$ is the average in the domain, and use $\tilde{U}$ instead of U in [Eqs. \(3.44\)](#) and [\(3.45\)](#).

If microporosity is present in the domain, we will use an adaptation of the PDFs to study how the regions with microporosity differ from the regions with macroporosity. Using the Darcy velocity field $\mathbf{U}_D$ calculated by the Darcy-Brinkman equation

(Eqs. (3.6) and (3.7)) and the porosity field ϕ , we define two functions similar to Eq. (3.43), one for macroporosity and another for microporosity, by

$$p_j(u) = \frac{d}{du} \left(\frac{\int_{\Omega_{Dj}} \left[\frac{|\mathbf{U}_D|}{\phi} < u \right] \phi d\Omega_{Dj}}{\int_{\Omega_D} \phi d\Omega_D} \right), \quad (3.46)$$

where j refers to the macro- or microporous region, and Ω_{Dj} is the region of Ω_D with macro- or microporosity. The quantity $|\mathbf{U}_D|/\phi$ is an approximation of the pore velocity $\mathbf{U}$ and differs from $\mathbf{U}$ by the tortuosity factor, which we are ignoring in these expressions. Note that the sum of these two curves is a PDF, but not each one independently, and we will refer to each of them as a partial PDF.

Likewise, we define two functions similar to Eq. (3.44), one for macroporosity and another for microporosity, by

$$p_{i,j}(u) = \frac{d}{du} \left(\frac{\int_{\Omega_{Dj}} r_i(\mathbf{x}) \left[\frac{|\mathbf{U}_D|}{\phi} < u, r_i(\mathbf{x}) > 0 \right] \phi d\Omega_{Dj}}{\int_{\Omega_D} r_i(\mathbf{x}) [r_i(\mathbf{x}) > 0] \phi d\Omega_D} \right), \quad (3.47)$$

and we shall refer to each them as partial PDFs of velocity weighted by the rate of formation of species i . Similarly, the partial PDFs of velocity weighted by the rate of consumption is defined by replacing the condition $r_i(\mathbf{x}) > 0$ with $r_i(\mathbf{x}) < 0$.

Also for microporous domains, it is often more insightful to use the logarithm of the normalized velocity instead of $|\mathbf{U}_D|/\phi$ in expressions Eqs. (3.46) and (3.47). This logarithm $\tilde{U}$ is given by

$$\tilde{U} = \log_{10} \left(\frac{|\mathbf{U}_D|}{\phi} \middle/ \langle U \rangle \right), \quad (3.48)$$

where

$$\langle U \rangle = \frac{\int_{\Omega_D} \frac{|\mathbf{U}_D|}{\phi} \phi d\Omega_D}{\int_{\Omega_D} \phi d\Omega_D} = \frac{\int_{\Omega_D} |\mathbf{U}_D| d\Omega_D}{\int_{\Omega_D} \phi d\Omega_D}. \quad (3.49)$$

3.3 Validation

We assess the convergence of the flow solver with grid refinement. Furthermore, we validate the flow and transport model on a tube with a constant square cross-section and in a bead pack whose bead centres locations were measured by Finney (1968) and are available in Finney and Prodanovic (2016). We compare the simulated permeability with the value predicted by the Kozeny-Carman equation (Kozeny, 1927, Carman, 1937) and the one obtained by Alhashmi et al. (2015), and the longitudinal dispersion coefficients with data found in the literature.

3.3.1 Convergence of the flow solver

To assess the convergence of the flow solver, we simulated the flow of water across a tube of square cross-section and verified how the calculated velocity field converged to the analytical solution as the grid spacing was reduced. The pressure drop is $\Delta P = 1$ Pa, the dynamic viscosity of the water is $\mu = 1 \times 10^{-3}$ kg/(ms), the length of the tube is $L = 5000$ μm and the side of the square cross-section is $2a = 205$ μm , as illustrated in Fig. 3.3

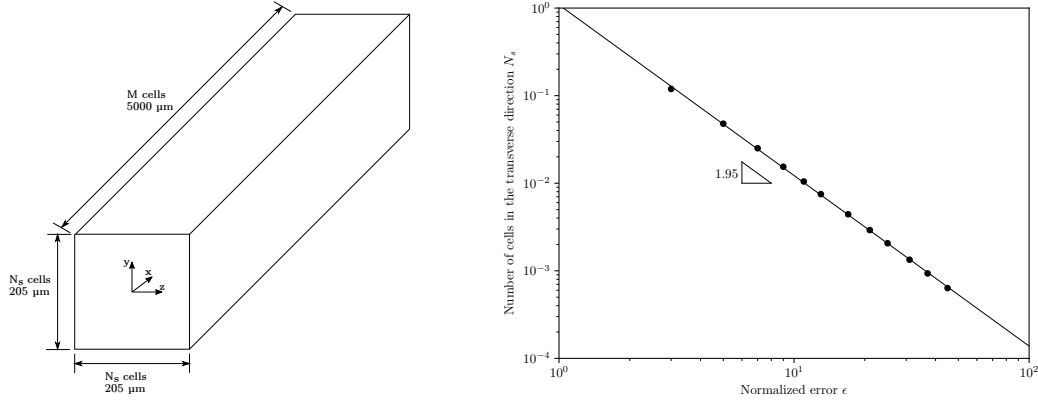


Figure 3.3: Left: Geometry of tube of square cross-section used in simulation to assess the convergence of the flow solver. The channel is discretized in M cells along its length and N_s cells along its width. The error ϵ between the numerical and analytical solutions is not dependent on M . Right: The error ϵ as a function of the number N_s of cells along the width of the channel. We observe an approximately quadratic convergence with grid refinement.

An analytical solution for the velocity $u(y, z)$ as a function of the flow rate Q of a laminar flow through a tube of square cross-section defined by a plane yz is (White, 1991)

$$u(y, z) = \frac{12}{\pi^3} \frac{Q}{a^2} \frac{\sum_{i=1,3,5}^{\infty} (-1)^{\frac{i-1}{2}} \left[1 - \frac{\cosh\left(\frac{i\pi z}{2a}\right)}{\cosh\left(\frac{i\pi}{2}\right)} \right] \frac{\cos\left(\frac{i\pi y}{2a}\right)}{i^3}}{1 - \frac{192}{\pi^5} \sum_{i=1,3,5}^{\infty} \frac{\tanh\left(\frac{i\pi}{2}\right)}{i^5}}. \quad (3.50)$$

Shah and London (1971) give the solution as a function of ΔP :

$$u(y, z) = \frac{16a^2}{\pi^3} \frac{\Delta P/L}{\mu} \sum_{i=1,3,5}^{\infty} (-1)^{\frac{i-1}{2}} \left[1 - \frac{\cosh\left(\frac{i\pi z}{2a}\right)}{\cosh\left(\frac{i\pi}{2}\right)} \right] \frac{\cos\left(\frac{i\pi y}{2a}\right)}{i^3}. \quad (3.51)$$

Combining Eqs. (3.50) and (3.51), we obtain

$$Q = \frac{4a^4}{3} \frac{\Delta P/L}{\mu} \left[1 - \frac{192}{\pi^5} \sum_{i=1,3,5}^{\infty} \frac{\tanh\left(\frac{i\pi}{2}\right)}{i^5} \right] \approx 0.562308 \times a^4 \frac{\Delta P/L}{\mu}. \quad (3.52)$$

We compare the numerical solution to the analytical solution by calculating the following normalized L_2 norm:

$$\epsilon = \frac{\sqrt{\sum_i^N (\tilde{u}_i - u_i)^2}}{\sqrt{N} \max(u_i)}, \quad (3.53)$$

where i is the cell index, N is the total number of cells of the model, u_i is the analytical solution for velocity at the cell center and $\tilde{u}_i$ is the corresponding numerically calculated value.

The velocity boundary conditions are $\mathbf{u} = 0$ at the sides of the tube and $\partial \mathbf{u} / \partial \mathbf{n} = 0$ at the inlet and outlet. The pressure boundary conditions are $p = 1$ Pa at the inlet, $p = 0$ Pa at the outlet and $\partial p / \partial \mathbf{n} = 0$ at the sides of the tube.

The relation between the error ϵ and the level of refinement characterized by the number N_S of cells used to discretize in the transverse direction is shown in Fig. 3.3. The error is proportional to $h^{1.95}$, where h is the grid spacing in the transverse direction, which is an almost quadratic convergence to the analytical solution.

3.3.2 Transport along a tube of square cross-section

The tube measures $25\,000\,\mu\text{m} \times 150\,\mu\text{m} \times 150\,\mu\text{m}$ and is discretized into $5000 \times 30 \times 30$ cubic cells, giving a cell side length $\Delta x = 5\,\mu\text{m}$. We run simulations for $Pe=1, 10, 25, 50, 65, 80, 90$ and 100 , with a molecular diffusion coefficient $D_m = 9 \times 10^{-10}\,\text{m}^2/\text{s}$. The time step Δt is chosen so that the Courant–Friedrichs–Lewy (CFL) number, calculated as $CFL = \bar{u}\Delta x / \Delta t$, equals 1.2. The characteristic length calculated using Eq. (2.23) equals $225\,\mu\text{m}$, that is, 1.5 times the tube side length. A tracer is initially placed as a $100\,\mu\text{m}$ -long pulse sufficiently away from the inlet face so as not to reach it by diffusing upstream.

We calculate the longitudinal dispersion coefficient from Eq. (2.25). The asymptotic regime is deemed reached when $dD_L/dt < \epsilon D_L$, with $\epsilon = 10^{-5}/\text{s}$. The asymptotic values for D_L/D_m as a function of Pe^2 are shown in Fig. 3.4. A function of the form

$$\frac{D_L}{D_m} = 1 + \xi Pe^2, \quad (3.54)$$

where ξ is a shape factor (Aris, 1956), was fitted to them using ordinary least square regression, giving $\xi = 0.00396 \pm 0.00002$, which is within the range $0.00337 < \xi < 0.00400$ obtained by Bruderer and Bernabé (2001) and close to the value $\xi = 0.00380$ obtained by Bijeljic et al. (2004).

3.3.3 Flow and transport through a bead pack

We validate the flow and transport model on a bead pack by comparing the simulated permeability and longitudinal dispersion coefficients with data found in the literature.

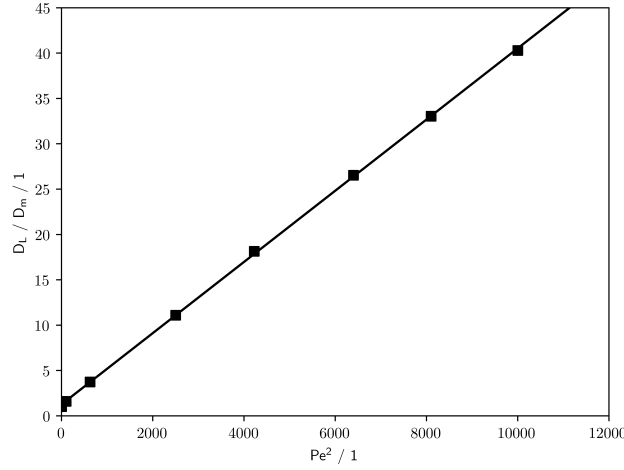


Figure 3.4: Ratio of simulated asymptotic longitudinal dispersion coefficient (D_L) to molecular diffusion coefficient (D_m) against the square of Péclet number for transport along a tube of square cross-section. The adjusted fit is $D_L/D_m = 1 + \xi Pe^2$, $\xi = 0.00396 \pm 0.00002$, which is within the range $0.00337 < \xi < 0.00400$ obtained by [Bruderer and Bernabé \(2001\)](#) and close to the value $\xi = 0.00380$ obtained by [Bijeljic et al. \(2004\)](#). From [Oliveira et al. \(2019\)](#).

[Finney \(1968\)](#) manufactured a bead pack, measured the coordinates of the centre of each bead and made this dataset is available in [Finney and Prodanovic \(2016\)](#). We rescaled the beads to the arbitrary diameter of $325.9 \mu\text{m}$. The envelope of the beads in the original dataset is spherical itself. From it, the largest inscribed cubic volume was extracted. The resulting image is a cubic volume with side length of 3.259 mm . It was discretized into $500 \times 500 \times 500$ cubic cells with a resolution of $6.518 \mu\text{m}$. It has a porosity of 0.3624 and its characteristic length from [Eq. \(2.23\)](#) is $190.62 \mu\text{m}$.

Our simulation predicts an absolute permeability of $6.5 \times 10^{-11} \text{ m}^2$ for the packing, which is just outside the value $(6.9 \pm 0.2) \times 10^{-11} \text{ m}^2$ predicted by the Kozeny-Carman equation ([Kozeny, 1927](#), [Carman, 1937](#)) and the value $6.8 \times 10^{-11} \text{ m}^2$ predicted by [Alhashmi et al. \(2015\)](#) on the same geometry once a correction is made for the different bead size used.

Since the $500 \times 500 \times 500$ image is not long enough for the asymptotic regime of the longitudinal dispersion to be achieved, we extend it by successively reflecting the image through the plane in which the outlet face is contained until a $10\,000 \times 500 \times 500$ cell image is obtained. We run simulations for $Pe=0.02, 0.1, 1, 7.29, 22.3, 37.1$ and 74.2 , with a molecular diffusion coefficient $D_m = 1 \times 10^{-9} \text{ m}^2/\text{s}$. The time step is chosen so that the CFL number equals 0.05 . A tracer is initially placed as a one-cell-long pulse sufficiently away from the inlet face so as not to reach it by diffusing upstream. We calculate longitudinal dispersion coefficients $D_L(t)$ for the different Péclet numbers using [Eqs. \(2.25\) to \(2.27\)](#). The asymptotic regime is deemed reached when $dD_L/dt < \epsilon D_L$, with $\epsilon = 10^{-5}/\text{s}$. In [Fig. 3.5](#), we compare the asymptotic

values of D_L with experimental results obtained on bead packs and other unconsolidated media. The agreement between them is good over the whole range of Péclet numbers studied.

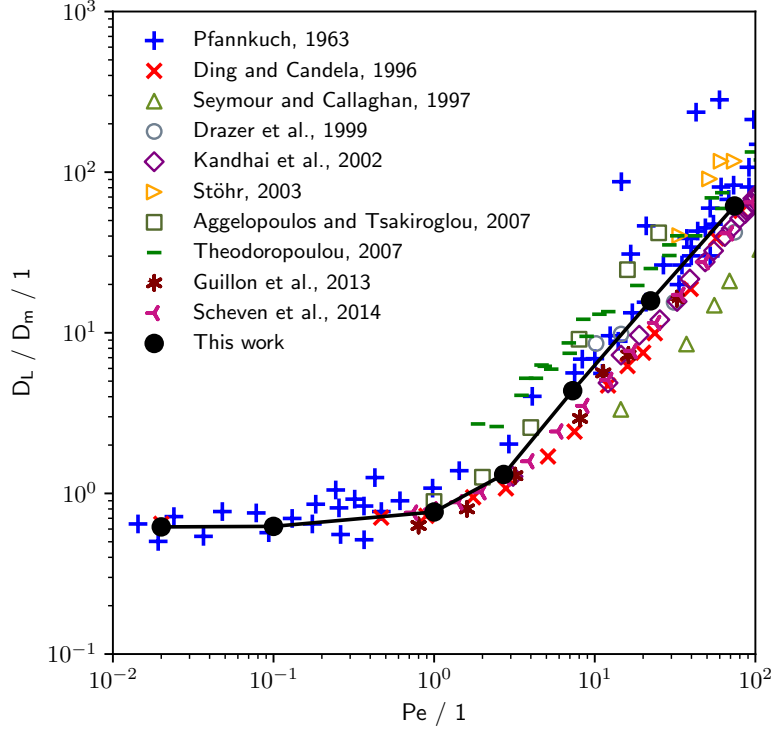


Figure 3.5: Ratio of simulated asymptotic longitudinal dispersion coefficient (D_L) to molecular diffusion coefficient (D_m) against Péclet number for transport through bead packs (black dots) compared with experiments on bead packs and other unconsolidated media found in the literature. Original data from Pfannkuch (1963), Ding and Candela (1996), Seymour and Callaghan (1997), Drazer et al. (1999), Kandhai et al. (2002), Stöhr (2003), Aggelopoulos and Tsakiroglou (2007), Theodoropoulou (2007) (compiled by Mostaghimi et al. (2012)) and from Guillon et al. (2013), Scheven et al. (2014). From Oliveira et al. (2019).

These tests give us some confidence in the validity of our transport solver. In the next chapter we will validate our model for reactive transport for a fluid-fluid system with comparison against experimental results. We will then consider reactive transport in a bead pack. Further tests for fluid-solid reaction will be presented in Chapter 6.

TRANSPORT AND FLUID-FLUID REACTION ON PORE SPACE IMAGES

4.1 Bimolecular reaction in a micromodel

We validate the coupling between transport and reaction models using a micromodel experiment performed by [Willingham et al. \(2008\)](#). They fabricated micromodels of various pore structures by photolithography on a photoresist polymer, injected the reactants Invitrogen’s Oregon Green 488 Bapta-5N (OG5N) and a solution of Ca^{2+} by two parallel inlet ports, and recorded the light intensity of the domain. OG5N and Ca^{2+} react to form OG5N·Ca, which is fluorescent. From that study, we selected the structure called “small cylinders” to simulate.

The simulation domain can be seen at the top of [Fig. 4.1](#). It consists of a periodic staggered array of cylinders, which measure $300\text{ }\mu\text{m}$ in diameter and are spaced by $40\text{ }\mu\text{m}$ pore throats. The array contains 41.5×8 unit cells of the repeating pattern and measures $19955\text{ }\mu\text{m} \times 3846.7\text{ }\mu\text{m}$ in total. In the experiment, its depth is $28\text{ }\mu\text{m}$, thin enough to allow us to model it as a 2D system. We discretize the domain into square cells with a side length of $2.0035\text{ }\mu\text{m}$.

On the top and bottom faces of the model, symmetry boundary conditions (BC) are applied for pressure, velocity and concentrations. On the inlet face, the pressure is fixed at a uniform arbitrary value, and a zero gradient BC is used for velocity. OG5N and Ca^{2+} are injected at uniform concentration of $30 \times 10^{-3}\text{ mol/m}^3$ at the top and bottom halves of the inlet face, respectively. On the outlet face, a zero gradient BC is used for pressure and concentrations, and the velocity is fixed at a uniform value of $1055.6\text{ }\mu\text{m/s}$, giving the Darcy velocity of $39.7\text{ }\mu\text{m/s}$ reported for the experiment. We use a time step of $2.799 \times 10^{-5}\text{ s}$. We model the production of OG5N·Ca as a bimolecular reaction, following [Section 3.1.4](#). The molecular diffusion coefficients for OG5N, Ca^{2+} and OG5N·Ca are $3.6 \times 10^{-10}\text{ m}^2/\text{s}$, $7.9 \times 10^{-10}\text{ m}^2/\text{s}$

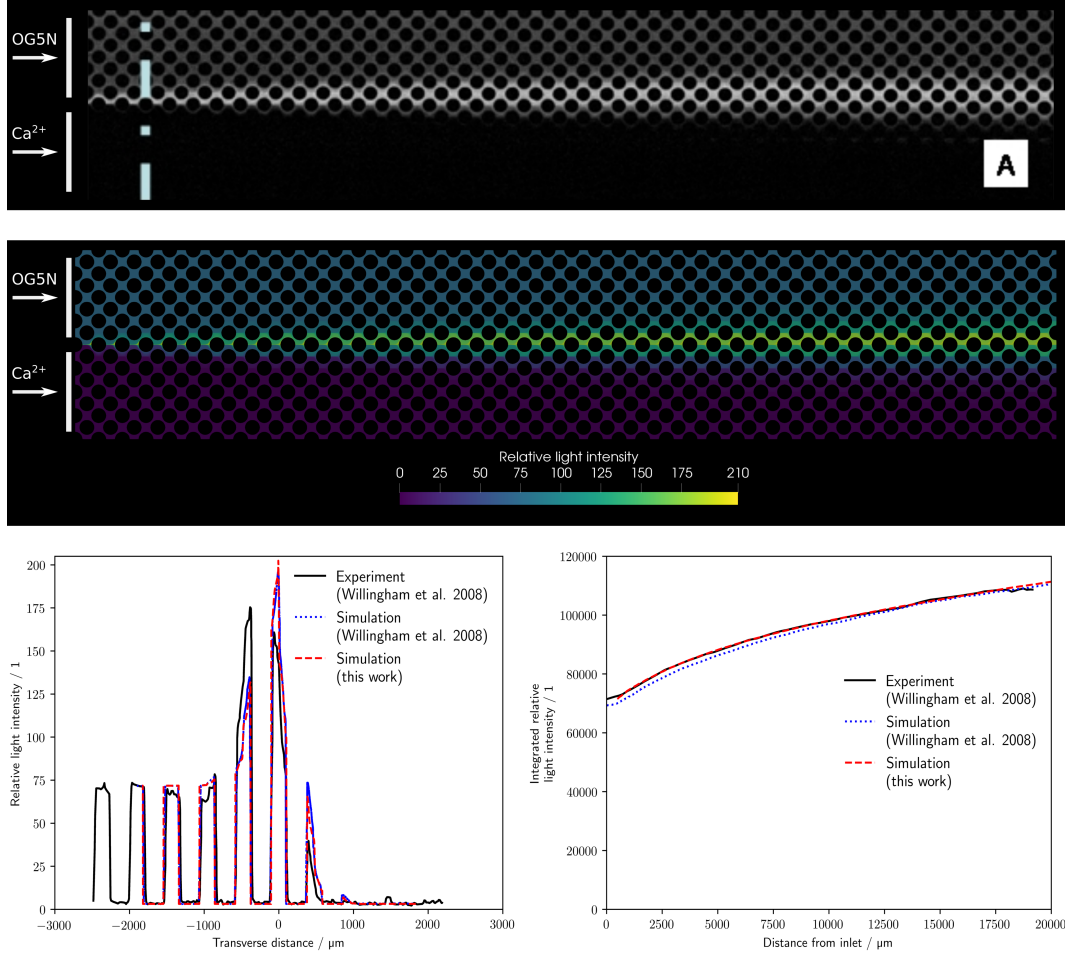


Figure 4.1: Top: image of the micromodel experiment. (Adapted with permission from Fig. S5 in [Willingham et al. \(2008\)](#). ©2008 American Chemical Society.) Over the top half of the left face, they injected Invitrogen’s Oregon Green 488 Bapta-5N (OG5N). Over the bottom half, a solution of Ca^{2+} . These species react to form OG5N-Ca, which is fluorescent. Middle: relative light intensity calculated from our simulation of the same experiment. In the experiment, the solid cylinders are as bright as pure Ca^{2+} ; here, they are in black to make the geometry of the model more visible. Bottom left: relative light intensity along a cross-section 16 530 μm from the inlet. The black line is the result from the experiment. The blue dash-dot line is their simulation result. The red dashed line is our simulation result. Bottom right: Relative light intensity integrated along the transverse direction and averaged over a moving window of a unit cell of the lattice. From [Oliveira et al. \(2019\)](#).

and $3.6 \times 10^{-10} \text{ m}^2/\text{s}$, respectively.

We ran the simulation until steady state was reached and converted the concentration of reactants and products to relative light intensity following Willingham et al. (2008) (Fig. 4.1, middle). We compare our result for the relative light intensity along a cross-section $16\,530 \mu\text{m}$ from the inlet with the experimental result and the simulation performed by Willingham et al. (2008). They used the lattice-Boltzmann method to solve for the velocity and the finite volume method for the advection-diffusion-reaction equation. Our results are in very close agreement with their simulations, and the agreement between both simulations and the experiment is generally good. The difference between the experimental and simulation results is, according to Willingham et al. (2008), “most likely due to small variations in the flow rate between the two syringe pumps” that injected OG5N and Ca^{2+} .

We further make a similar comparison with the experimental result and the simulation performed by Willingham et al. (2008), this time considering relative light intensity integrated along the transverse direction. To eliminate the periodicity introduced by the geometry, we apply a moving average with a window length of a unit cell of the lattice, as did the authors of the experiment. Once again, our results are in very close agreement with their simulated and experimental results (see Fig. 4.1, bottom right).

4.2 Multispecies reactive transport in a bead pack

To demonstrate the capabilities of our model to provide new insights into multispecies reactive transport in 3D pore structures, we simulate the parallel injection of two aqueous solutions on the bead pack image described in Section 3.3.3. In this section, we describe the simulation case and analyse the results by examining concentration fields, rates of formation and consumption, relative yields, flux-related reactor ratios and probability density functions of velocity.

4.2.1 Simulation description

We simulate the parallel injection of two aqueous solutions on the bead pack image described in Section 3.3.3. We place the origin of a Cartesian coordinate system at the centre of the inlet face, with the x-axis pointing to the outlet face, and the y- and z-axes aligned to the sides of the image. Over the top half of the inlet face ($x = 0$, $y > 0$), we inject a solution of Na_2CO_3 at 25 mol/m^3 . Over the bottom half ($x = 0$, $y < 0$), a solution of CaCl_2 at 25 mol/m^3 . The reaction between sodium carbonate and calcium chloride is a common choice for laboratory studies of the formation of calcium carbonate (Ogino et al., 1987, Barrett and Parsons, 1998, Zhang et al., 2010). The chemical species considered and the composition of the inlet streams are shown in Table 4.1. The next reaction step is run in a cell when the variation of at least

one species concentration since the last reaction step in that cell is larger than 10^{-3} times the range of concentrations expected for that species. This range considers the composition of the inlet streams and the composition, shown in Table 4.2, that would be obtained if the inlet streams were mixed in an ideal continuous stirred tank reactor.

Table 4.1: Composition of the injected fluids.

Species	Top half (mol/m ³)	Bottom half (mol/m ³)
Na ⁺	4.997×10^1	0
CO ₃ ²⁻	2.319×10^1	0
HCO ₃ ⁻	1.811	0
CO ₂ (aq)	2.250×10^{-5}	0
NaOH(aq)	3.472×10^{-2}	0
Ca ²⁺	0	2.474×10^1
Cl ⁻	0	4.974×10^1
CaCl ⁺	0	2.545×10^{-1}
CaCl ₂ (aq)	0	3.568×10^{-3}
CaOH ⁺	0	1.718×10^{-5}
HCl(aq)	0	8.270×10^{-7}
NaCl(aq)	0	0
CaCO ₃ (aq)	0	0
CaHCO ₃ ⁺	0	0
H ⁺	8.877×10^{-9}	1.341×10^{-4}
OH ⁻	1.776	1.178×10^{-4}
H ₂ O(l)	5.534×10^4	5.531×10^4

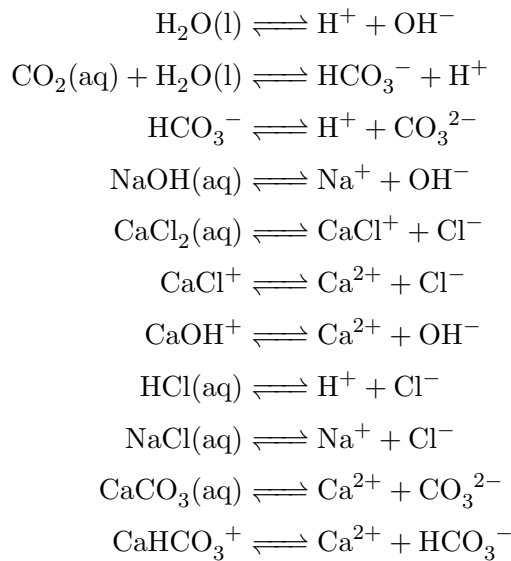
We apply symmetry boundary conditions on the four side faces of the domain for pressure, velocity and species concentration; a uniform velocity on each half of the inlet face; an arbitrary uniform pressure on the outlet; and zero gradient boundary condition for pressure, velocity and concentration fields are imposed on the inlet, outlet and outlet faces, respectively. To ensure that the inflow rate is the same in each half despite of their different pore area, velocities were adjusted accordingly. For the geochemical reactions, we impose a uniform temperature $T = 298.15$ K and pressure $p = 1 \times 10^5$ Pa. In case the fluid becomes supersaturated with respect to some species, the supersaturated concentration is transported as such since we do not consider precipitation of a solid phase. The molecular diffusion coefficient $D_m = 9 \times 10^{-10}$ m²/s is the same for all species.

We ran simulations for Péclet numbers of 1, 10 and 100, corresponding to characteristic velocities (as defined by Eq. (2.24)) of 4.721×10^{-6} m/s, 4.721×10^{-5} m/s and 4.721×10^{-4} m/s, and Darcy velocities of 1.334×10^{-6} m/s, 1.334×10^{-5} m/s and 1.334×10^{-4} m/s. The time step is chosen so that the CFL number equals 1. We ran the simulation until 2.7 pore volumes were injected and verified that steady state was reached after 2.25 pore volumes.

Table 4.2: Average concentration at the outlet. The columns correspond to the concentration obtained if no reaction took place in the system (No reaction), if the system were an ideal continuous stirred tank reactor (Fully mixed), and for the simulated system with $Pe = 1, 10$ and 100 .

Species	No reaction (mol/m ³)	Fully mixed (mol/m ³)	$Pe = 1$ (mol/m ³)	$Pe = 10$ (mol/m ³)	$Pe = 100$ (mol/m ³)
Na ⁺	25.0	24.9	24.9	25.0	25.0
CO ₃ ²⁻	11.6	3.71	6.84	9.25	9.98
HCO ₃ ⁻	906×10^{-3}	752×10^{-3}	854×10^{-3}	891×10^{-3}	896×10^{-3}
CO ₂ (aq)	11.2×10^{-6}	22.5×10^{-6}	22.6×10^{-6}	22.6×10^{-6}	22.3×10^{-6}
NaOH(aq)	17.4×10^{-3}	7.84×10^{-3}	11.5×10^{-3}	14.5×10^{-3}	15.4×10^{-3}
Ca ²⁺	12.4	4.41	7.75	10.0	10.8
Cl ⁻	24.9	24.9	24.9	24.9	24.9
CaCl ⁺	127×10^{-3}	26.9×10^{-3}	66.0×10^{-3}	96.6×10^{-3}	106×10^{-3}
CaCl ₂ (aq)	1.78×10^{-3}	0.206×10^{-3}	0.768×10^{-3}	1.28×10^{-3}	1.44×10^{-3}
CaOH ⁺	0.01×10^{-3}	22.7×10^{-3}	18.0×10^{-3}	10.3×10^{-3}	6.87×10^{-3}
HCl(aq)	414×10^{-9}	0.066×10^{-9}	0.144×10^{-9}	0.754×10^{-9}	18.5×10^{-9}
NaCl(aq)	0	71.4×10^{-3}	46.7×10^{-3}	23.4×10^{-3}	16.0×10^{-3}
CaCO ₃ (aq)	0	8.02	4.72	2.34	1.61
CaHCO ₃ ⁺	0	17.8×10^{-3}	14.4×10^{-3}	8.10×10^{-3}	5.39×10^{-3}
H ⁺	67.1×10^{-6}	0.02×10^{-6}	0.03×10^{-6}	0.13×10^{-6}	3.00×10^{-6}
OH ⁻	888×10^{-3}	740×10^{-3}	826×10^{-3}	872×10^{-3}	879×10^{-3}

When calculating the chemical equilibrium by minimising the Gibbs energy (see [Section 3.1.5](#)), one does not explicitly prescribe which reactions can take place. However, they can be inferred from the chemical species that exist in the system. For the set of chemical species in [Table 4.1](#), the chemical reactions that can occur are linear combinations of the following:



Note that the number of reactions $M = 11$, the number of chemical species $N = 17$ and the number of components $C = 6$ (Ca, C, O, H, Na, Cl) satisfy

$M + C = N$, showing that an equivalent LMA formulation that used the chemical reactions above would have number of constraints equal to the number of unknowns. Admittedly, we could have been more parsimonious in the choice of the primary species considered in the transport. In this particular simulation case where all species have the same diffusion coefficient, we could have gone as far as to consider the components Ca, C, O, H, Na, Cl themselves as primary species, solve only the transport equation skipping the reaction step, and obtain the concentration of the species of interest by post-processing the simulation results (see, e.g., [Lichtner \(1985\)](#)). Since our focus is in developing a framework that can be easily extended to more general cases, we have accepted to incur the extra computational cost associated with including reaction and transport together.

4.2.2 Results and discussion

In this subsection, we examine the interplay between multispecies transport and reaction in the 3D pore space of a bead pack and highlight complexities that are not present in models that rely on bimolecular reactions or homogenized descriptions of the medium. For brevity, we concentrate our discussion on six species that represent a wide range of behaviour in terms of spatial distribution of concentration and reaction.

[Figure 4.2](#) shows the concentration of selected species averaged along a direction perpendicular to the flow, at steady state for different Péclet numbers. Among the reactions that take place, the one with biggest impact on the concentration field is $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{aq})$. Most of the $\text{CaCO}_3(\text{aq})$ is formed close to the median plane that divides the inlet face in the two halves where $\text{Na}_2\text{CO}_3(\text{aq})$ and $\text{CaCl}_2(\text{aq})$ are injected, and disperses to the rest of the image volume. The behaviour of Ca^{2+} and CO_3^{2-} is consistent in that they are kept mostly in one half of the image. As the Péclet number increases, the plume of $\text{CaCO}_3(\text{aq})$ becomes narrower because the advection along the main flow direction dominates diffusion away from the median plane. The overall symmetry around the median plane is broken by the impact of pH on the chemical equilibrium. This impact can be seen clearly in the distribution of CaOH^+ , whose plume disperses mostly on the bottom half of the image because it dissociates in the presence of high pH over the top half.

The impact of Péclet number and reaction on the mixing of species is better quantified by the variation of the flux-related reactor ratio along the image ([Fig. 4.3](#)). We observe that lower Péclet number results in more mixing, due to a greater influence of transverse dispersion. This behaviour is altered by reaction. As Ca^{2+} and CO_3^{2-} disperse into the top and bottom halves of the image, respectively, most of them react; as a result, their reactor ratio is kept close to the value at the inlet face. The behaviour of the flux-related reactor ratio for H^+ at $Pe = 10$ is noteworthy. It first decreases near the inlet because it is consumed on regions close to the median plane. Closer to the outlet, as the consumption progresses in regions away from the me-

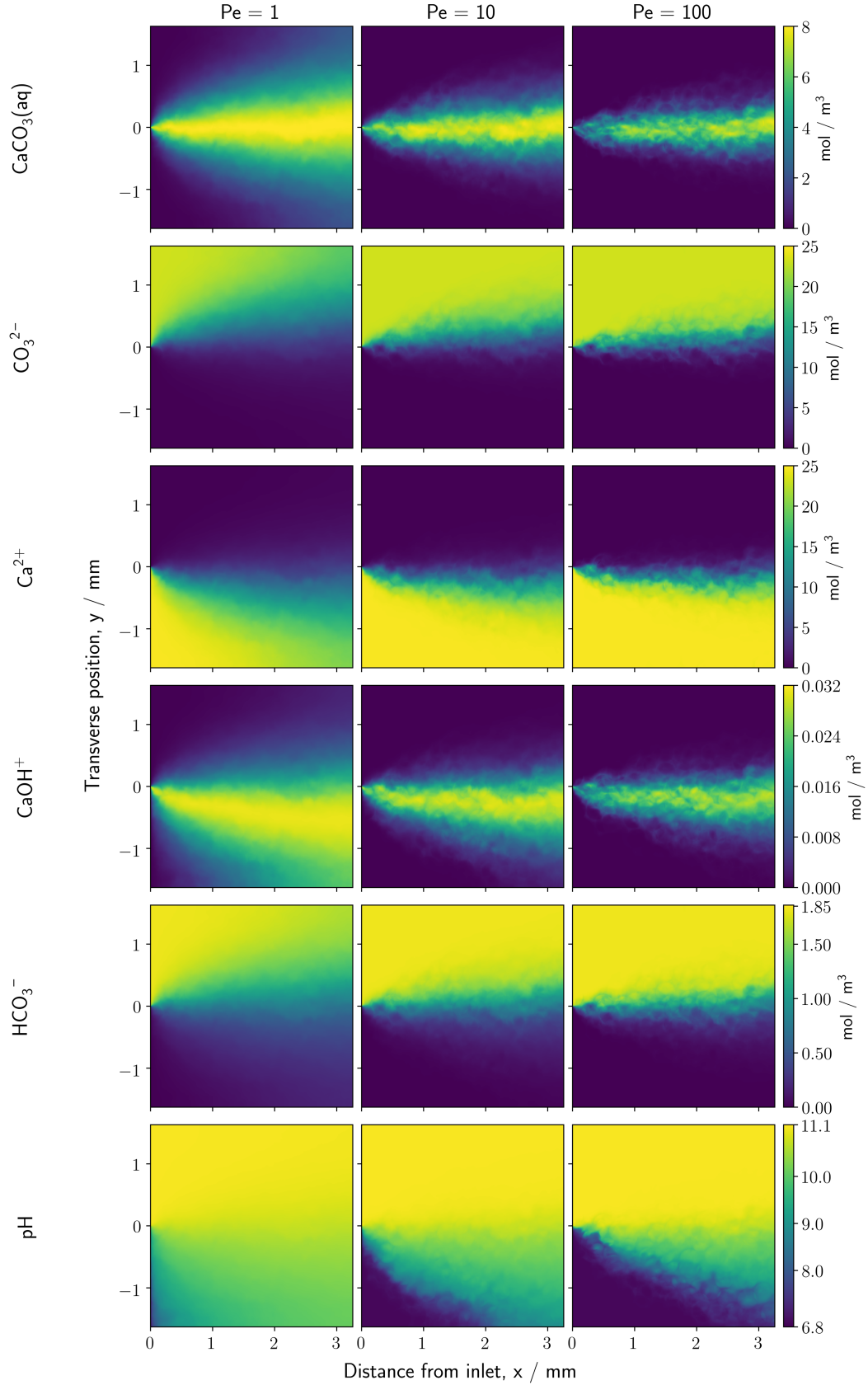


Figure 4.2: Concentration in the pore space averaged in a direction perpendicular to the flow, for different Péclet (Pe) numbers at steady state. Flow is from left to right. A solution of Na_2CO_3 is injected over the top half of the left face; a solution of CaCl_2 is injected over the bottom half. The bottom figure shows the pH corresponding to the average concentration of H^+ . From Oliveira et al. (2019).

dian plane, its concentration become more homogeneous again, with a consequent increase in the flux-related reactor ratio.

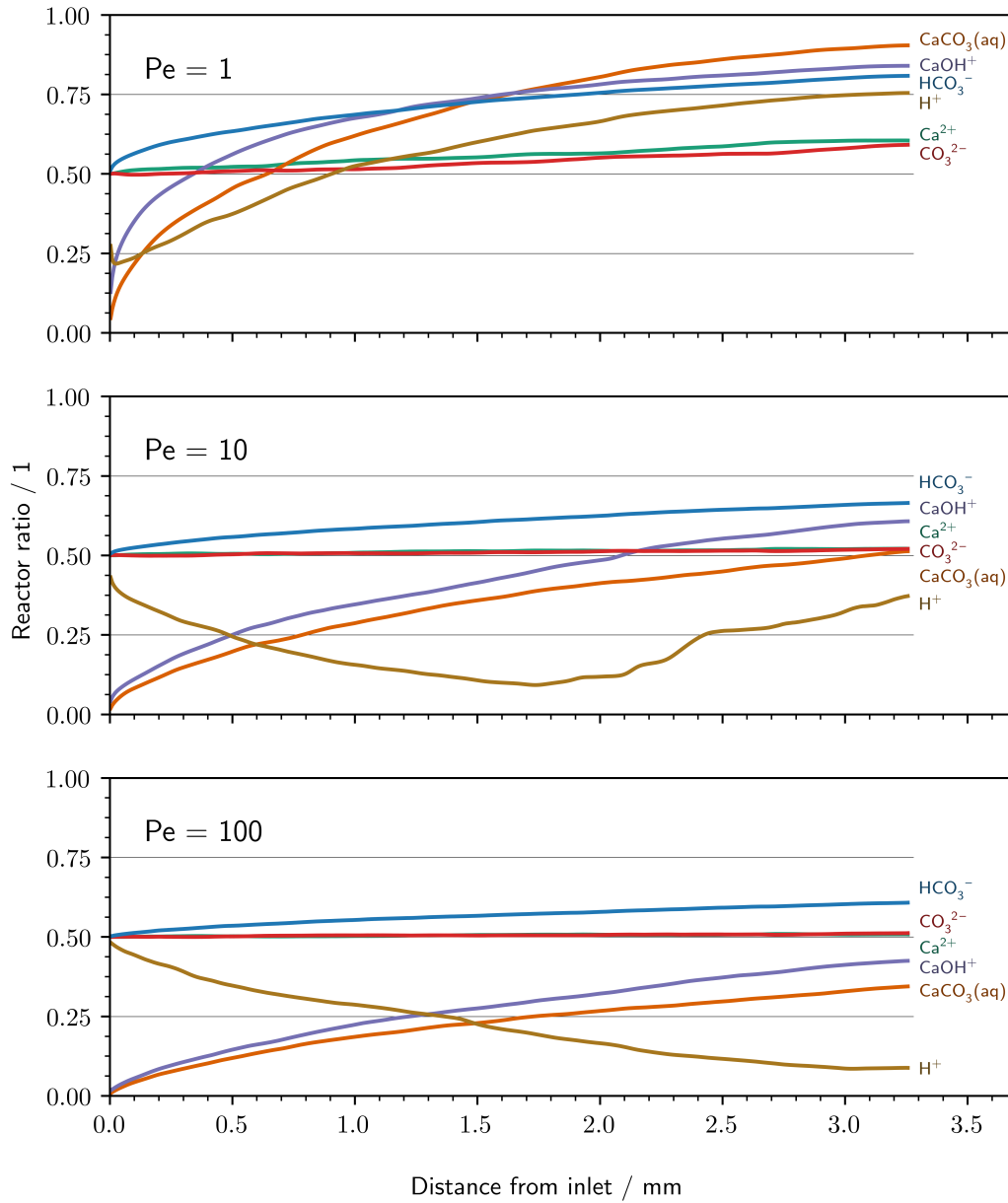


Figure 4.3: Flux-related reactor ratio, defined by Eq. (2.30), of selected species for $Pe = 1$, 10 and 100 as a function of distance from the inlet face. From Oliveira et al. (2019).

The spatial distribution of rates of formation/consumption for each species is examined in Fig. 4.4. As the Péclet number increases, the rate of formation/consumption increases as well. We observe that a small fraction of $\text{CaCO}_3(\text{aq})$ is formed away from the median plane. At the top of the bead pack image, for example, we observe a small but perceptible rate of formation for $\text{CaCO}_3(\text{aq})$ coinciding with

a similar rate of consumption of Ca^{2+} . This is possible because as Ca^{2+} disperses to the top of the image, it encounters regions with a larger excess of CO_3^{2-} , causing the equilibrium reaction $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{aq})$ to be driven to the right-hand side.

We remark that our model also captures reverse reactions. The consumption of $\text{CaCO}_3(\text{aq})$ in the bottom part of the domain is explained by the pH of the injected fluids. The solutions injected over the top and bottom halves of the left face have pH values of 11.1 and 6.87, respectively. As $\text{CaCO}_3(\text{aq})$ is formed near the median plane of the domain, it disperses to the top and bottom of the domain. At the bottom, the more acidic conditions favours its dissociation into Ca^{2+} and CO_3^{2-} , which reacts with H^+ to form HCO_3^- . In this figure, it is possible to confirm that the overall symmetry around the median plane observed in the concentration fields of some species is broken by the complex chemical interaction between them. For example, CaOH^+ , formed by mixing of the two injected streams, dissociates for higher values of pH, which explains why its concentration is low in the upper half of the image. For most species, the overall rate of formation is about two orders of magnitude higher or smaller than its rate of consumption. HCO_3^- is an exception and exhibits rate of formation and consumption of the same order of magnitude.

Besides studying how reactions are distributed in space, it is interesting to assess how they are distributed as a function of velocity, which can be done by calculating PDFs of velocity weighted by the rate of formation/consumption (Eq. (3.44)). As the Péclet number increases, the reactions tend to occur on sites where the velocity is higher. This can be verified from the PDF of velocity weighted by the rate of formation of $\text{CaCO}_3(\text{aq})$ (Fig. 4.5). For low Péclet numbers, this PDF is similar to the intrinsic PDF of velocity (not weighted by the rate of formation, in black). As the Péclet number increases, the PDF shifts to the right, indicating that reaction is favoured in faster-flowing regions. This behaviour agrees with the findings of Alhashmi (2015), who modelled a bimolecular reaction taking place on the same image for similar injection conditions. In another work, Alhashmi et al. (2015) found that this behaviour is less pronounced if one of the reactants is initially placed on the image and the other one is injected over the whole inlet face.

This tendency, however, depends on the main mechanism that transports species to the sites where reaction takes place. Consider the PDFs of velocity weighted by rates of formation and consumption of HCO_3^- shown in Fig. 4.5. The consumption of HCO_3^- , which takes place mostly in the same locations as the formation of $\text{CaCO}_3(\text{aq})$ (see Fig. 4.4), is more affected by a change in Péclet number than the formation of HCO_3^- . As the Péclet number increases, the PDF for consumption of HCO_3^- shifts to the right, while the PDF for formation of HCO_3^- stays close to the intrinsic velocity distribution.

Reactions happen because of changes in geochemical conditions produced by the transport of species, hence a likely explanation for the difference between the PDFs

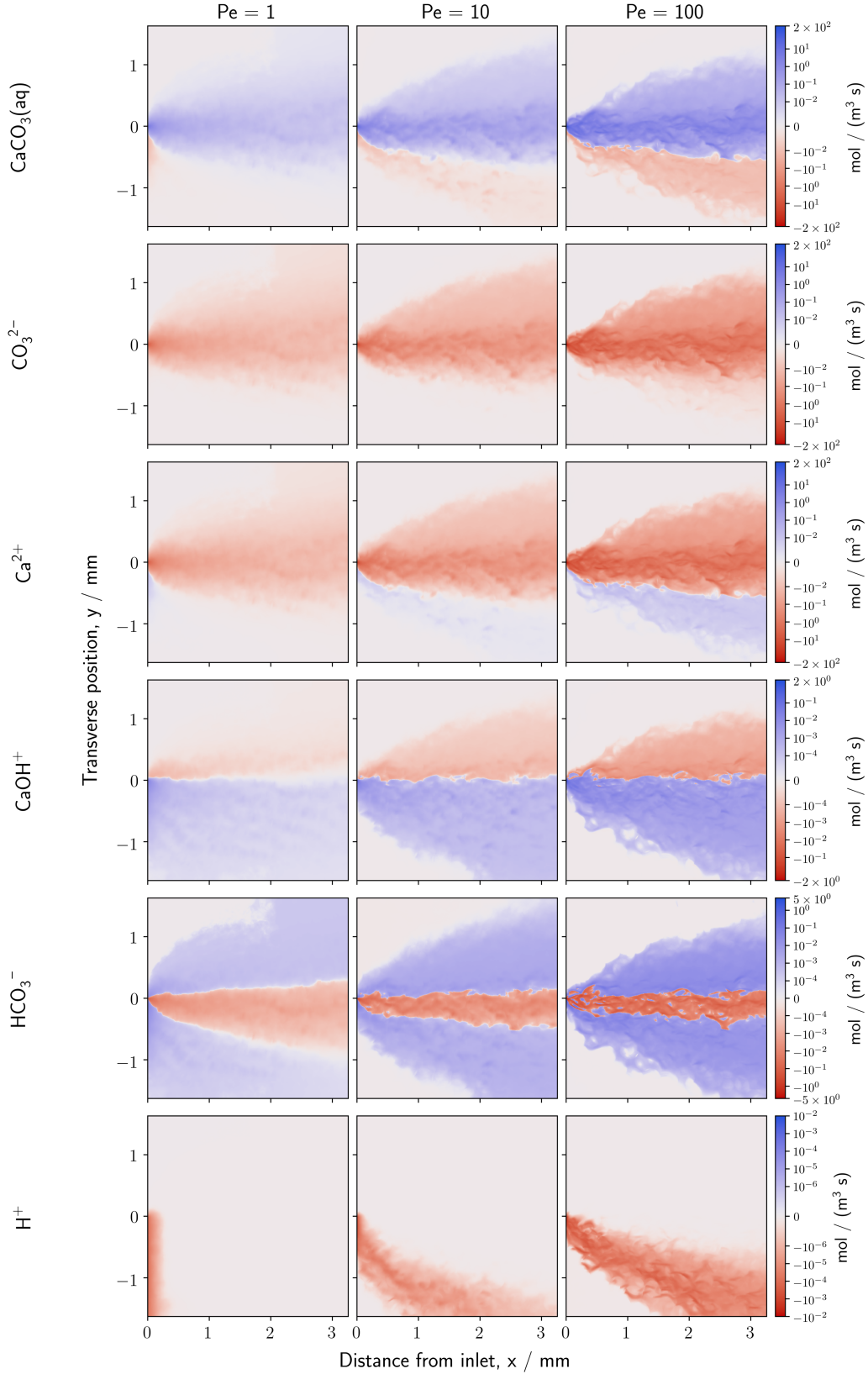


Figure 4.4: Rate of formation, defined by Eq. (3.42), in the pore space averaged in a direction perpendicular to the flow, for different Péclet (Pe) numbers at steady state. Blue indicates formation of the product, while negative rates of formation, i.e., consumption, are shown in red. As the velocity increases, the rate of formation/consumption increases as well. Flow is from left to right. A solution of Na_2CO_3 is inject over the top half of the left face; a solution of CaCl_2 is injected over the bottom half. From Oliveira et al. (2019).

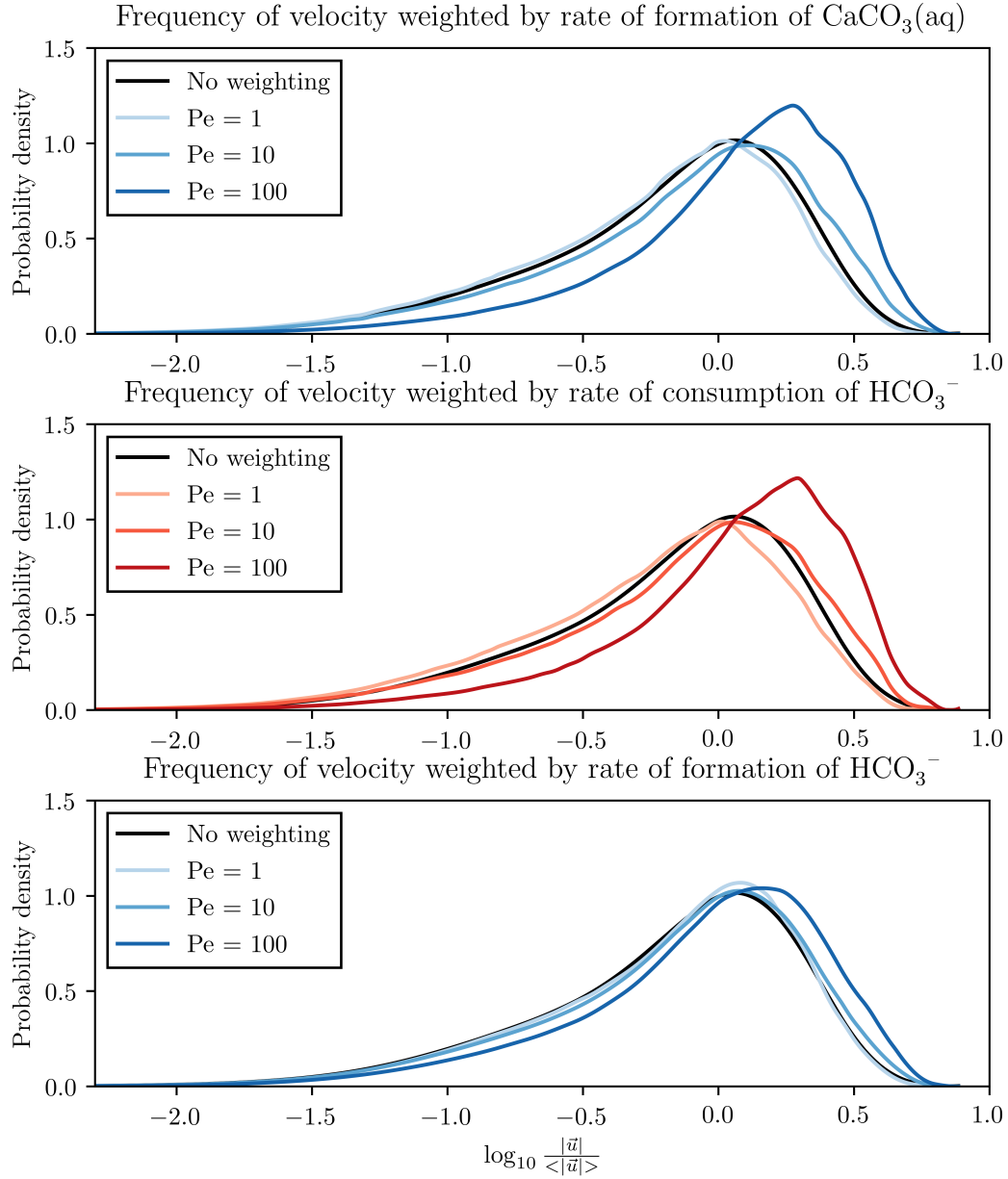


Figure 4.5: PDFs of velocity weighted by rates of formation and consumption of different species, for different Péclet numbers. These PDFs are defined by Eq. (3.44). The black line ('No weighting') denotes the intrinsic frequency of velocities, that is, the frequency of velocities in the domain irrespective of the chemical reactions. As Péclet number increases, reactions tend to happen at sites where the velocity is higher. However, this tendency depends on the main transport mechanism that takes the reactants to the sites where the reaction takes place. From Oliveira et al. (2019).

for formation and consumption of HCO_3^- is the different contribution of advection and diffusion to the transport involved in each reaction for high Péclet numbers. The impact of the Péclet number on the PDF for the consumption of HCO_3^- is an indication of the importance of advection for changes in geochemical conditions that shift the chemical equilibrium towards the consumption of HCO_3^- . To corroborate this interpretation, we observe in Fig. 4.4, at $Pe = 100$, that the consumption happens mostly near the median plane of the image, before the species injected over each half of the inlet face have had enough time to diffuse in the transverse direction. In the same figure, we note the existence of meandering patterns where HCO_3^- is consumed (in red) around blue pockets where HCO_3^- is produced (in blue), indicating that the effect of diffusion, which promotes the smoothing of the geochemical conditions, is small compared to advection, which delivers reactants through fast-flowing channels.

In contrast, the smaller impact of the Péclet number on the PDF for the formation of HCO_3^- observed in Fig. 4.5 indicates that diffusion plays a larger role for the formation than it does for the consumption of HCO_3^- . We note in Fig. 4.4 that the formation of HCO_3^- happens mostly in regions away from the median plane. Before reaching these regions and reacting to form HCO_3^- , there was sufficient time for species to sample the entire velocity distribution, and be distributed in slow and fast flowing regions in a way that more closely matches the intrinsic velocity distribution.

An important result of direct simulations of reactive transport is the quantification of the impact of incomplete mixing on the conversion of reactants. This result can be used as input for larger scale models and inform expected reaction rates in laboratory experiments and field applications. Table 4.2 shows the steady-state average concentration at the outlet for each species if no reaction took place in the bead pack, if the bead pack behaved like an ideal continuous stirred tank reactor, and in the simulations for the three Péclet numbers studied. From Table 4.2, the relative yield presented in Table 4.3 was calculated as the ratio of the difference of the average concentration at the outlet between the respective simulation and “No reaction” to the difference of the average concentration at the outlet between “Fully mixed” and “No reaction”.

It is interesting to note that the relative yield is different for each species, which means that the departure from a fully mixed system is species dependent. Furthermore, the relative yield decreases as Péclet increases because a relative reduction in diffusion hinders mixing, which is required for reaction to occur. Figure 4.6 shows the relative yield not only at the outlet face but for each cross-section parallel to the inlet face. We note that the relative yields of all species increase after the first 0.1 mm. However, the influence of the Péclet number on their increase is also species dependent.

This chapter has shown how to simulate multispecies reactive transport in relatively simple pore geometries. Our predictions match experiments, and show the

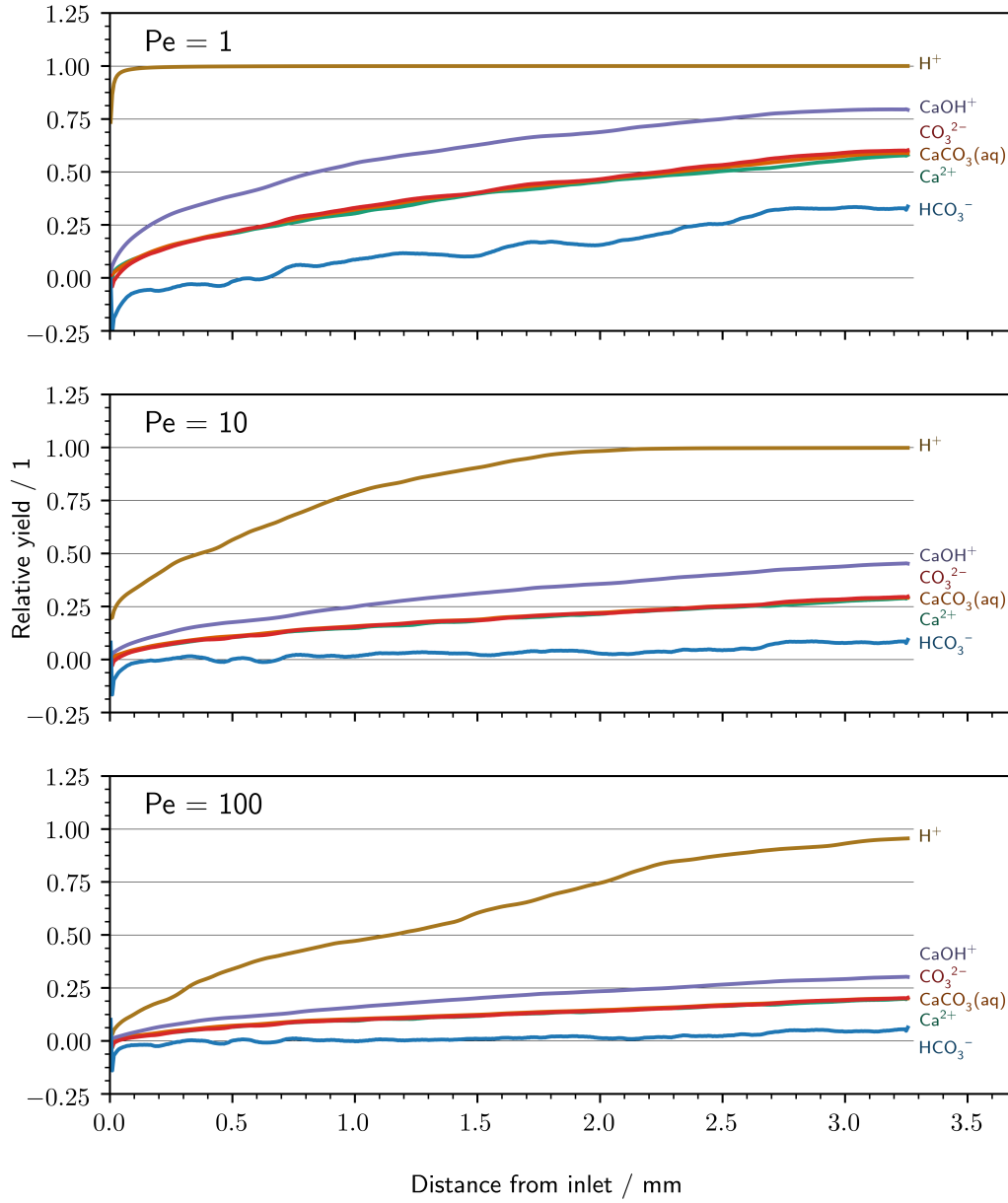
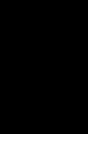


Figure 4.6: Relative yield of selected species for $Pe = 1$, 10 and 100 as a function of distance from inlet face. The value at the outlet is shown in [Table 4.3](#). From [Oliveira et al. \(2019\)](#).

Table 4.3: Relative yield at the outlet face for $Pe = 1, 10$ and 100 .

Species	$Pe = 1$	$Pe = 10$	$Pe = 100$
Na^+	0.67	0.33	0.23
CO_3^{2-}	0.60	0.30	0.20
HCO_3^-	0.34	0.09	0.06
$\text{CO}_2(\text{aq})$	1.00	1.00	0.98
$\text{NaOH}(\text{aq})$	0.62	0.30	0.21
Ca^{2+}	0.58	0.29	0.20
Cl^-	0.54	0.26	0.18
CaCl^+	0.61	0.31	0.21
$\text{CaCl}_2(\text{aq})$	0.64	0.32	0.22
CaOH^+	0.79	0.45	0.30
$\text{HCl}(\text{aq})$	1.00	1.00	0.96
$\text{NaCl}(\text{aq})$	0.65	0.33	0.22
$\text{CaCO}_3(\text{aq})$	0.59	0.29	0.20
CaHCO_3^+	0.81	0.46	0.30
H^+	1.00	1.00	0.96
OH^-	0.42	0.11	0.06

complex species-dependent dynamics that emerge from transport and reaction, even in a regular medium. We now extend the work to consider reaction and transport through a complex microporous carbonate.



TRANSPORT AND FLUID-FLUID REACTION IN MICROPOROUS CARBONATE

In this chapter we focus on studying the dynamics of mixing-driven multispecies reaction in a microporous limestone. We study the impact of physical heterogeneity and pay special attention to the fact that in this case the 3D pore space is a complex structure containing not only solid cells and macroscopic void cells where porosity $\phi = 1$, but also microporous cells where $0 < \phi < 1$ grouped in a number of categories of porosities (see [Table 5.1](#)). This is in contrast to the bead pack studied in the previous chapter which had only macroscopic pore space and no microporosity, and for which we put an emphasis on investigating different transport conditions on multispecies reactive transport.

5.1 Portland limestone image

In this study, we examine multispecies fluid-fluid reactive transport on a micro-CT image of Portland limestone. This sample was selected because of its low permeability (we calculated a value of $k = 11$ mD), which is typical of many carbonate reservoirs. X-ray imaging was performed on a Portland limestone cylindrical mini-core of 4.81 mm in diameter and 10.0 mm in length obtaining an image size of 1000^3 voxels. The voxel size was 5 μm . A cropped subvolume of 650^3 voxels was then used for numerical simulation of flow and reactive transport.

A novel X-ray differential image method ([Lin et al., 2016](#)) was used here to discriminate between macropores (where the pore space is explicitly resolved on the image), solid grains and classes of microporosity sub, and to assign values of porosities to them. This method is based on obtaining difference in greyscale values

Table 5.1: Some key values of the simulation in Portland for $Pe = 100$.

Property	Value
Total number of cells	650 ³
Fraction of cells with $\phi = 0$	0.541
Fraction of cells with $\phi = 0.227$	0.142
Fraction of cells with $\phi = 0.333$	0.103
Fraction of cells with $\phi = 0.437$	0.066
Fraction of cells with $\phi = 0.539$	0.040
Fraction of cells with $\phi = 0.637$	0.025
Fraction of cells with $\phi = 1$	0.084
Average porosity	0.216
Height top part inlet face	390 cells
Height bottom part inlet face	260 cells
Flow rate top part inlet face	$3.67 \times 10^{-10} \text{ m}^3/\text{s}$
Flow rate bottom part inlet face	$3.82 \times 10^{-10} \text{ m}^3/\text{s}$
Pore cells top part inlet face	130×10^3
Pore cells bottom part inlet face	100×10^3
Permeability	$1.06 \times 10^{-14} \text{ m}^2$
Cell size (cubic cells)	$5 \times 10^{-6} \text{ m}$
Characteristic length L	$38.7 \times 10^{-6} \text{ m}$
Characteristic velocity u	$2.33 \times 10^{-3} \text{ m/s}$
Image length L_x	$3250 \times 10^{-6} \text{ m}$
Darcy velocity U_D	$7.09 \times 10^{-5} \text{ m/s}$
Molecular diffusion coefficient	$9 \times 10^{-10} \text{ m}^2/\text{s}$
Characteristic advection time (based on L and u)	0.017 s
Characteristic diffusion time (based on L)	1.660 s
Characteristic advection time (based L_x and U_D)	46 s
Characteristic diffusion time (based L_x)	11 736 s

between a dry scan and a scan with the sample saturated with a solution of KI. After applying a non-local means edge preserving filter to the differential image, a global thresholding method was firstly used to segment the image into three phases which — as mentioned above — were solid grains, macroporosity and microporosity. Then, the histogram of the greyscale values in microporosity was divided into five equally spaced intervals along the greyscale value axis, defining five categories of cell, called microporosity subphases. For each microporosity subphase, the frequency distribution of greyscale values was calculated, and the greyscale value corresponding to its mode was considered as representative of the whole subphase. Using this value, the porosity ϕ of the subphase was calculated by linear interpolation between the values for solid grains and macropores. [Lin et al. \(2016\)](#) found that the total porosity of the sample was in good agreement with Helium porosity measurements.

The permeability of each subphase was estimated using the methodology presented in [Bijeljic et al. \(2018\)](#). First, they obtained a capillary pressure curve of the sample from mercury injection capillary pressure (MICP) measurements. By assum-

ing that subphases with larger porosity correspond to larger radii, they associated lower and upper bounds of mercury saturation in the capillary pressure curve to each microporosity subphase so that the range of saturation between these bounds corresponded to the fraction of the total pore space each subphase contributed to. Finally, they calculated an average pore radius R between the corresponding lower and upper bounds for each subphase, and assigned a permeability using the Kozeny-Carman equation (Kozeny, 1927, Carman, 1937) assuming that the average grain diameter of the subphase is given by $d = 2R(1 - \phi)/\phi$. They validated this method by calculating the absolute permeability from direct numerical simulation on the whole image, which agreed well with the permeability measured on Portland limestone mini-core. More details on imaging procedure, image filtering and analysis can be found in the original studies by Lin et al. (2016) and Bijeljic et al. (2018).

5.2 Simulation description

Flow through the Portland image is simulated using the Darcy-Brinkman equation (Eq. (3.6)) implemented by Bijeljic et al. (2018). The Darcy-Brinkman equation combines the Stokes equation for flow in macropore space (Eq. (3.3)) with a Darcy term $\mu \mathbf{u}_D/k$ representing flow in microporosity.

On the inlet and outlet faces, we impose constant and uniform values of pressure and a zero gradient boundary condition for velocity. On the remaining external boundaries of the domain, which are the other sides of the image and the interfaces between solid cells and cells with macro- or microporosity, we impose zero gradient boundary condition for pressure and zero velocity.

Using the velocity field thereby obtained, we simulate the parallel injection of two aqueous solutions transported according to Eq. (3.11). We place the origin of a Cartesian coordinate system at one of the corner of the image on the inlet face, with the x-axis pointing to the outlet face, and the y- and z-axes aligned to the sides of the image. Over the top part of the inlet face ($x = 0, 1300 \mu\text{m} < z < 3250 \mu\text{m}$), we inject a solution of Na_2CO_3 at 25 mol/m^3 . Over the bottom part ($x = 0, 0 \mu\text{m} < z < 1300 \mu\text{m}$), a solution of CaCl_2 at 25 mol/m^3 . The boundary between the two parts ($z = 1300 \mu\text{m}$) was chosen to result in the most even distribution of the total flow rate among the two parts: 49% of the flow rate is injected at the top part, 51% at the bottom. Initially, the domain contains pure water. On the inlet face we impose the concentrations of the inlet streams shown in Table 4.1, which are the same ones used for the study of reactive transport in a bead pack in Chapter 4. On the outlet face, remaining side faces of the image boundaries and interfaces between solid cells and cells with macro- or microporosity, we impose a zero gradient boundary condition for concentrations. For the geochemical reactions, we impose a uniform temperature $T = 298.15 \text{ K}$ and pressure $p = 1 \times 10^5 \text{ Pa}$. In case the fluid becomes supersaturated with respect to some species, the supersaturated concentration is transported as

such since we do not consider precipitation of a solid phase. The molecular diffusion coefficient $D_m = 9 \times 10^{-10} \text{ m}^2/\text{s}$ is the same for all species, and the effective diffusion coefficient D_{eff} in microporous cells is a function of the porosity ϕ : $D_{\text{eff}} = \phi^{2.2} D_m$ (see Eq. (3.15)).

As mentioned in Chapter 4, when calculating the chemical equilibrium by minimising the Gibbs energy (see Section 3.1.5), one does not explicitly prescribe which reactions can take place. However, they can be inferred from the chemical species that exist in the system. For the set of chemical species in Table 4.1, the chemical reactions that can occur are shown in Section 4.2.1.

To define a characteristic length and velocity (Eqs. (2.23) and (2.24)), we consider only the values in the macropores and the area of the surface between macropores and micropores+solid. The reason for this choice is that the surface area in the micropores is not known. The time step $\Delta t = 2.15 \times 10^{-3} \text{ s}$ is chosen so that the CFL number calculated based on the characteristic velocity equals 1. We ran the simulation for 29.7345 s, until 3 pore volumes were injected, for the Péclet number of 100. This corresponds to a characteristic velocity of $2.33 \times 10^{-3} \text{ m/s}$, and a Darcy velocity of $7.09 \times 10^{-5} \text{ m/s}$, which were obtained by fixing the corresponding pressure drop across the image.

5.3 Results

Our main goal in this chapter is to examine the impact of mixing on multispecies reaction during parallel injection of two reactant streams described in the bead pack study in Chapter 4. However, we are now interested in investigating the role of the profoundly different flow field in carbonate rock and, in particular, the impact of microporosity on mixing, and in turn on the dynamic of multispecies reaction.

Visualisation of 3D flow fields of Portland carbonate and the bead pack can help us understand the large differences between them, as illustrated in Fig. 5.1. Moreover, an analysis of their respective velocity distributions clearly identifies their distinctive nature of physical (flow) heterogeneity. This is observed by the comparison of their probability and partial probability density functions of velocities (Eqs. (3.43), (3.45), (3.46) and (3.48)) in Fig. 5.2. The bead pack velocity distribution is unimodal with most of the cell velocities similar to the average speed which reflects its homogeneous velocity field. In contrast, Portland carbonate is characterized by the velocities that are much higher than the average speed, which are present in fast flow channels, and, at the same time, by a large number of low velocities, especially in the microporous regions.

In Fig. 5.3, the spatial distribution of concentration of six selected species weighted by porosity and averaged along a direction perpendicular to the flow in the full image, macroporosity, and microscopic pore space are presented. For brevity, we concentrate our discussion on six species that represent a wide range of behaviour in terms

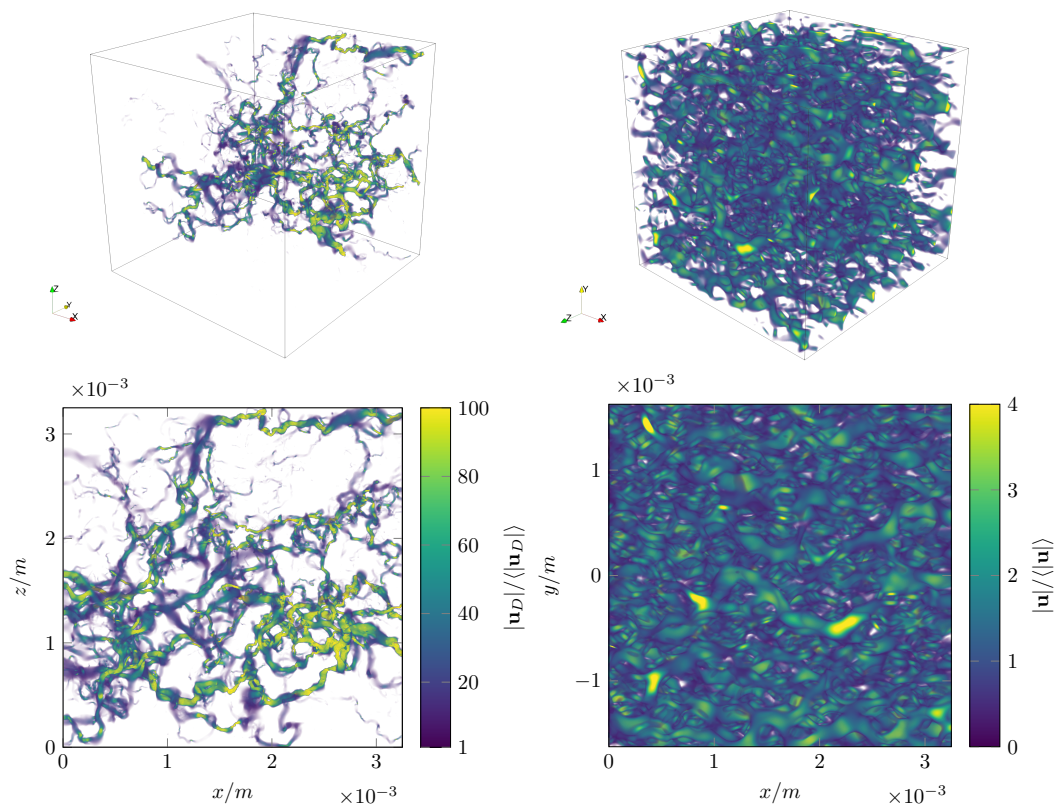


Figure 5.1: Left: Perspective and side view in a direction perpendicular to the flow of the magnitude of the velocity field normalized by the average velocity for Portland. Right: The same for the bead pack image, studied in [Chapter 4](#). We observe that in the bead pack the flow channels are more evenly distributed throughout the image and are approximately parallel to the main flow direction, while in the Portland image many of the main flow paths are oblique to the flow direction and separated by areas of slow velocity.

of spatial distribution of concentration and reaction. The steady state has not been achieved after 3 pore volumes (PV) of the reactants were injected at $Pe = 100$ as will be clear when we analyse [Fig. 5.10](#).

We first focus on the concentrations of the dominant product $\text{CaCO}_3(\text{aq})$, for which we observe a broad dispersion in the lateral direction in both macroscopic and microscopic pore space. This indicates a strikingly different behaviour to that observed in spatially periodic 2D porous media made up of different geometries ([Willingham et al. \(2008\)](#), one of the geometries was presented in [Fig. 4.1](#)) and a 3D bead pack ([Fig. 4.2](#)) for which the $\text{CaCO}_3(\text{aq})$ product was confined in a narrower, symmetrically expanding mixing zone. Interestingly, the microporous cells further from the injection face contain more $\text{CaCO}_3(\text{aq})$, which could be due to the mass transfer of either product $\text{CaCO}_3(\text{aq})$ or reactants Ca^{2+} and CO_3^{2-} which were all advected through the preceding fast channels. As the mixing zone expands, there are more fast channels in contact with slow microporous regions resulting in an enhanced

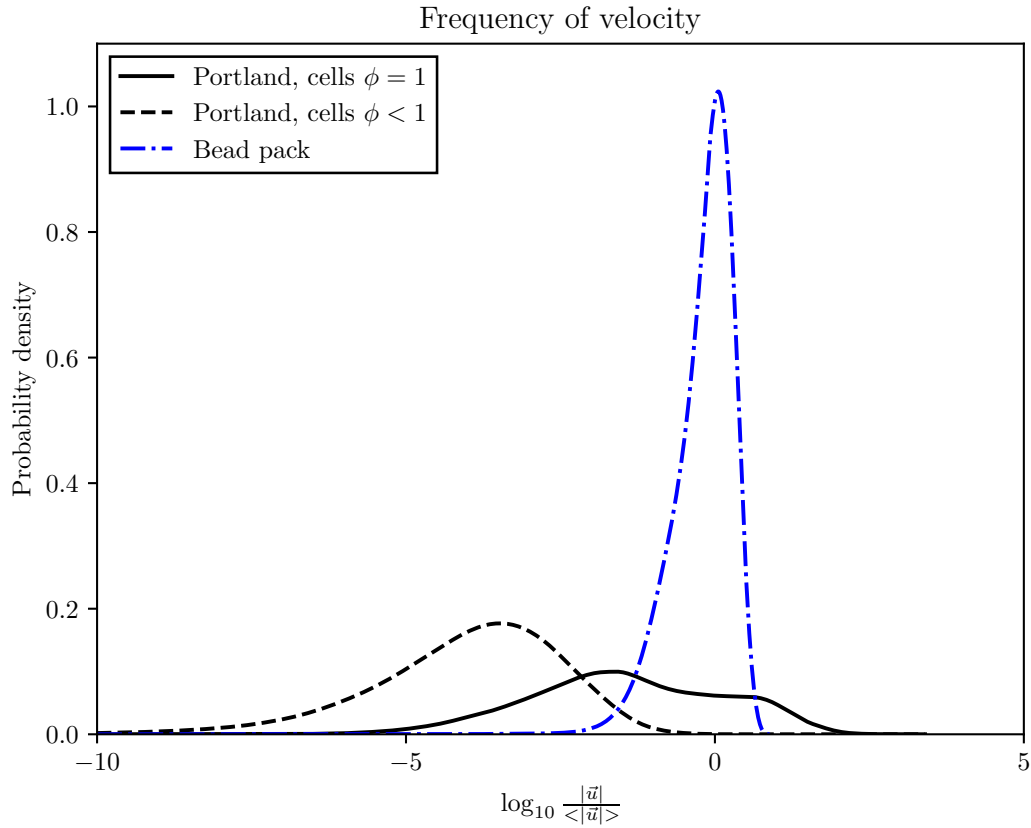


Figure 5.2: PDF of velocity for bead pack (Eqs. (3.43) and (3.45)) and partial PDFs of velocity for Portland (Eqs. (3.46) and (3.48)). The macro- and microporosity contributions for the PDF for Portland have been separated in two curves to highlight the different characteristic of these regions.

mass transfer exchange. This is also shown in Fig. 5.4 showing that the microporous cells further from the injection face contain much less $\text{CaCO}_3(\text{aq})$ after injection of 1 PV than after injection of 3 PV. This behaviour will be explained when we analyse the spatial distribution of rates of formation/consumption for these three species shown in Fig. 5.5.

Patterns in concentrations of reactants Ca^{2+} and CO_3^{2-} in Portland carbonate are more dispersed than in the bead pack pore space presented in Fig. 4.2. The nature of flow field in the carbonate is such that the streamlines intertwine and cross the cross-sectional area which separates the two streams of injected reactants. This promotes advective mixing which results in a more non-uniform distribution of these reactants. Another noteworthy observation from Fig. 5.3 is that pH is higher in the macroscopic pore space in comparison to microporosity.

The variation of the flux-related reactor ratio (Eq. (2.30)) along the image for the six selected species is shown in Fig. 5.6. For the products $\text{CaCO}_3(\text{aq})$ and CaOH^+ we observe a two-stage mixing behaviour. In the region that is up to 0.5 mm from the injection face, we observe a slow increase in the reactor ratios, in contrast to

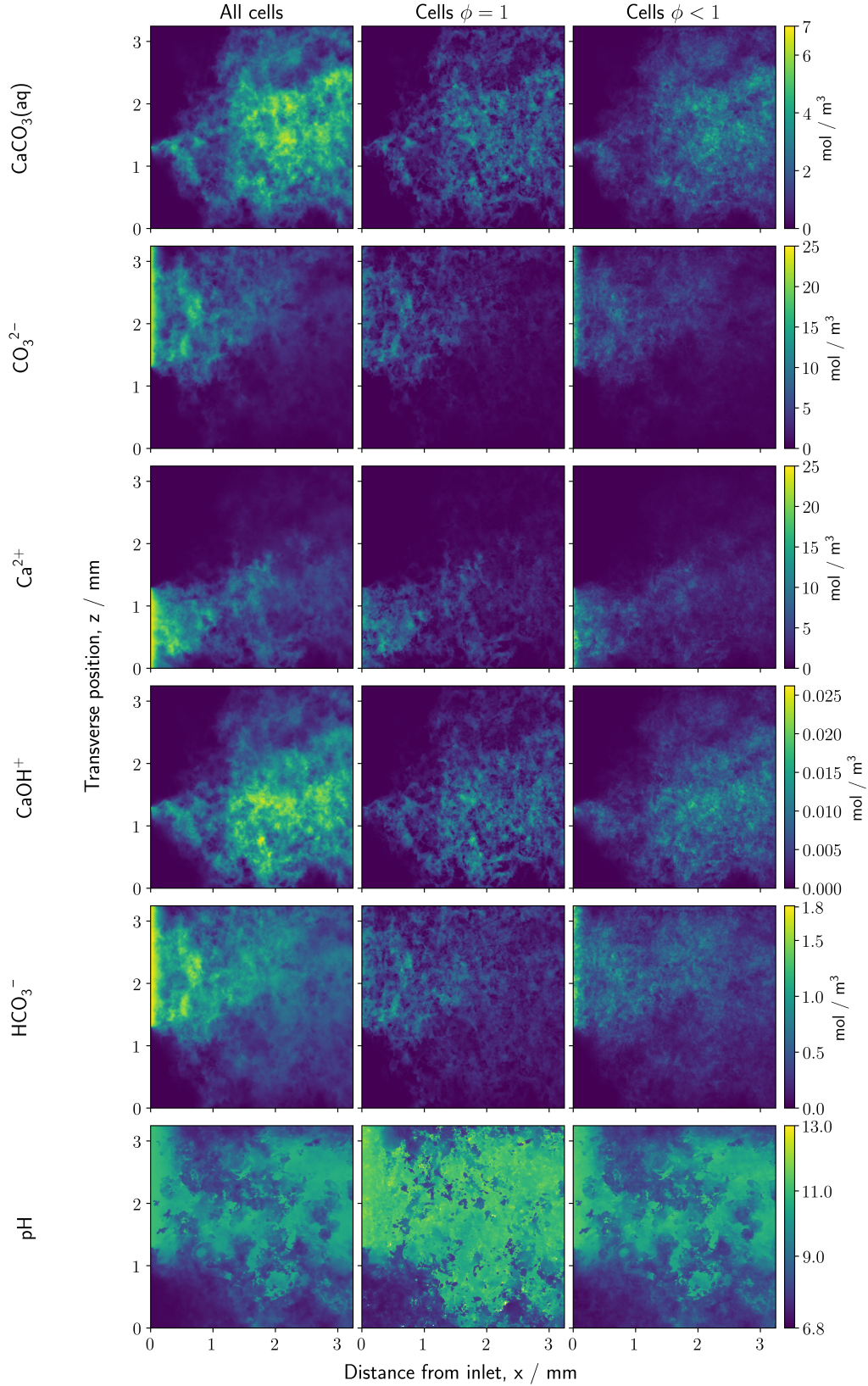


Figure 5.3: Concentration in the pore space weighted by porosity and averaged in a direction perpendicular to the flow, for the whole image (left), only for cells where porosity $\phi = 1$ (middle), and only for cells where $0 < \phi < 1$ (right) at 3 pore volumes injected. Flow is from left to right. A solution of Na_2CO_3 is injected over the top part of the left face; a solution of CaCl_2 is injected over the bottom part. The bottom figure shows the pH corresponding to the average concentration of H^+ .

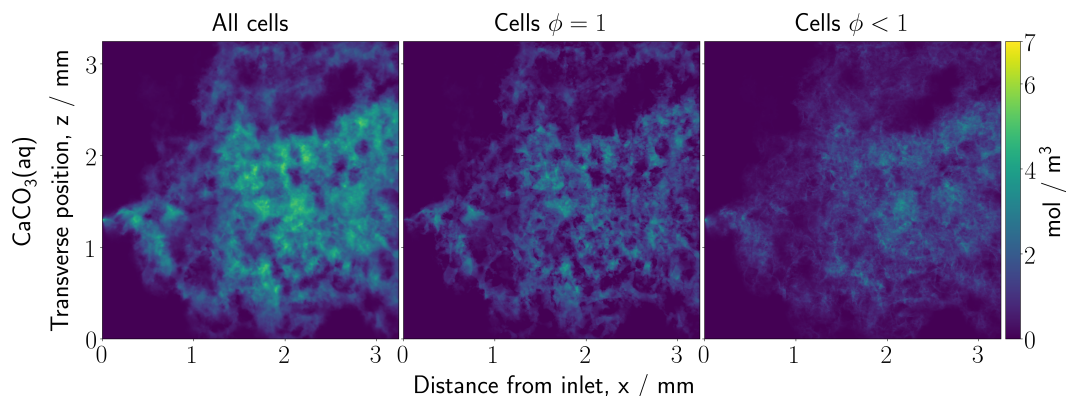


Figure 5.4: Concentration in the pore space weighted by porosity and averaged in a direction perpendicular to the flow, for the whole image (left), only for cells where porosity $\phi = 1$ (middle), and only for cells where $0 < \phi < 1$ (right) at 1 pore volume injected. Flow is from left to right. A solution of Na_2CO_3 is injected over the top part of the left face; a solution of CaCl_2 is injected over the bottom part.

the region between 0.5 mm to 1 mm. For the latter distances, we see a much steeper increase in the reactor ratios which can be attributed to a more efficient spreading by advection through a dominant channel that is not aligned with the flow direction. This is clearly seen in Fig. 5.5 showing the spatial distribution of rates of formation for $\text{CaCO}_3(\text{aq})$ and CaOH^+ in which the dominant channel exists in the bottom half of the image.

This provides evidence for how the reactants Ca^{2+} and CO_3^{2-} disperse into the top and bottom halves of the image, respectively, by enhanced mixing by advection for which the streamline orientation deviates from the main flow direction. This happens in Portland limestone to a much greater extent than in the bead pack where the streamlines are very much aligned to the main flow.

Moreover, due to presence of microporosity not all of the Ca^{2+} and CO_3^{2-} react; as a consequence, their reactor ratios increase in value along the image length. This is in stark contrast to the reactor ratio values for the same reactants in the bead pack in Fig. 4.3, which maintain the similar values from the inlet face along the image length.

The behaviour of the flux-related reactor ratio for H^+ fluctuates along the image, reaching a maximum after 3 mm from the inlet when H^+ is more mixed.

The spatial distribution of rates of formation/consumption for each species is examined in Fig. 5.5. Since our model captures reverse reactions, each species reaction rate has a net value dependent on the formation and consumption, which is represented by the colour bars.

We observe that a large fraction of $\text{CaCO}_3(\text{aq})$ is formed in fast channels which are away from the median plane and with an orientation deviating from the flow direction. This is a highly important observation which distinguishes multispecies re-

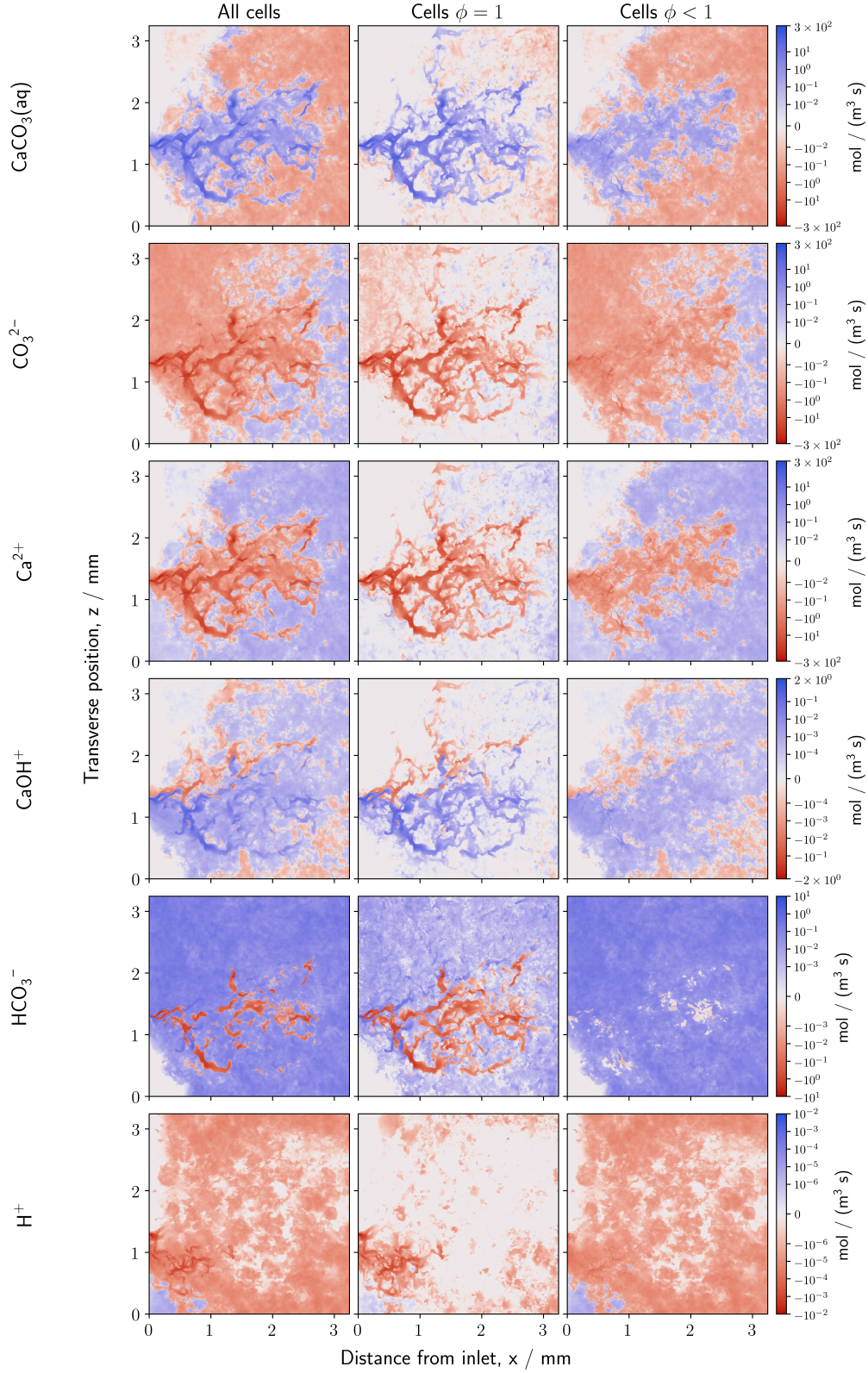


Figure 5.5: Rate of formation, defined by Eq. (3.42), in the pore space weighted by porosity and averaged in a direction perpendicular to the flow, for the whole image (left), only for cells where porosity $\phi = 1$ (middle), and only for cells where $0 < \phi < 1$ (right), at 3 pore volumes injected. Blue indicates formation of the product, while negative rates of formation, i.e., consumption, are shown in red. Flow is from left to right. A solution of Na_2CO_3 is inject over the top part of the left face; a solution of CaCl_2 is injected over the bottom part.

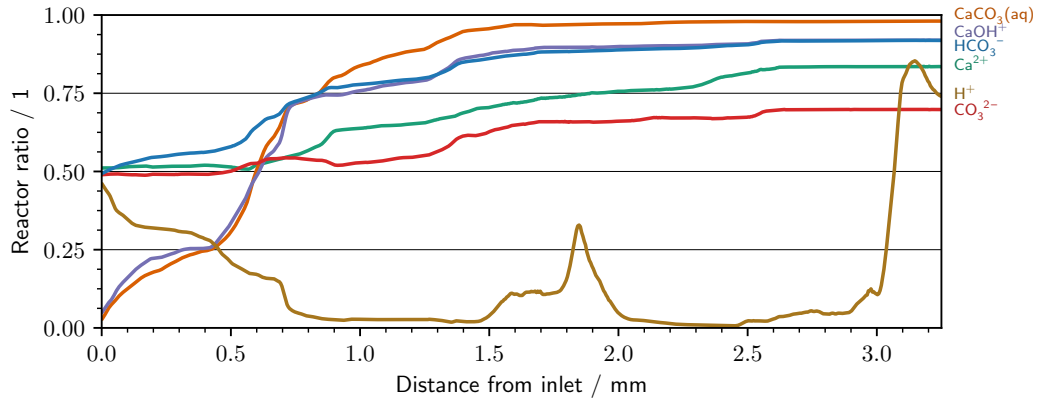


Figure 5.6: Flux-related reactor ratio, defined by Eq. (2.30), of selected species as a function of distance from the inlet face at 3 pore volumes injected.

active transport behaviour in heterogeneous flow fields found in carbonate rocks from those in more homogeneous bead packs. This heterogeneity is not observable from a porosity map alone: while it is possible to associate the regions where $\text{CaCO}_3(\text{aq})$ is formed to fast channels (Fig. 5.1, left), it is not possible to find the general shape of these regions from the averaged porosity map alone (Fig. 5.7).

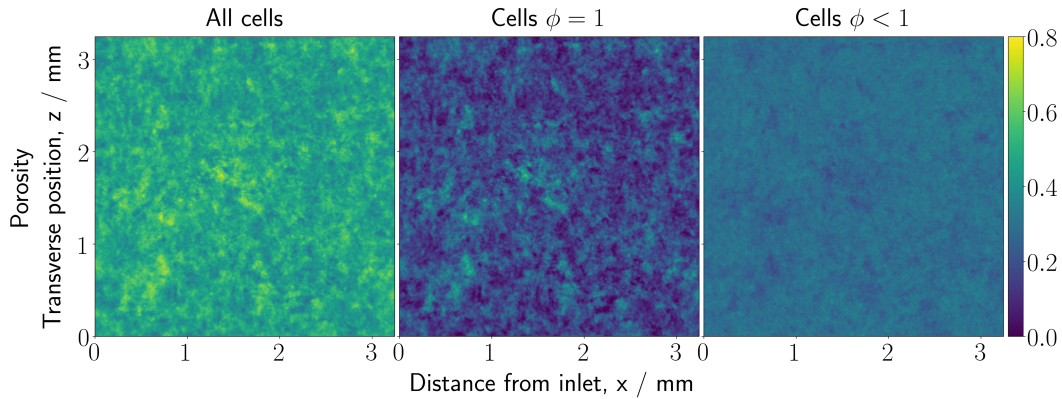


Figure 5.7: Porosity averaged in a direction perpendicular to the flow, for the whole image (left), only for cells where porosity $\phi = 1$ (middle), and only for cells where $0 < \phi < 1$ (right).

The second important observation concerning carbonate rocks is associated with the impact of microporosity, resulting in a non-uniform spatial distribution of reaction rates. The formation reaction rate of $\text{CaCO}_3(\text{aq})$ is much higher in the macroscopic pore space in comparison to the rate of formation in microporosity. Mixing by advection in fast channels enhances the rate of consumption of Ca^{2+} and CO_3^{2-} , and in turn the rate of formation of $\text{CaCO}_3(\text{aq})$. This is most clear when comparing Ca^{2+} and $\text{CaCO}_3(\text{aq})$, which show similar patterns in both the macroscopic pore space and microporosity. An interesting observation for the rate of consumption of

CO_3^{2-} can be inferred from the top left part of the Portland image. Here the rate of consumption of CO_3^{2-} is additionally affected by the rate of formation of HCO_3^- , which can also be seen in the respective subfigure for HCO_3^- .

For the Portland image we do not observe a net average consumption of HCO_3^- in microporosity. On the other hand, H^+ is consumed throughout the microporosity in Portland, in contrast to the reaction in the bead pack (see Fig. 4.4) in which it was only consumed in the bottom half. Again this is because in a more heterogeneous rock reactants are more rapidly and extensively dispersed throughout the porous domain. Due to the consumption of H^+ in Portland we observed an increase in pH, as previously shown in Fig. 5.3.

We have hitherto noted in Chapter 4 for the bead pack that the overall symmetry around the median plane observed in the concentration fields of some species was broken by the complex chemical interaction between them. Furthermore, in Portland limestone this symmetry is additionally broken by the heterogeneous flow field generating additional mixing by advection, and by the presence of microporosity generating a non-uniform diffusion-driven mixing.

It is vital to emphasize that the overall reactive transport behaviour is a consequence of complex dynamics impacted by mixing due to advection, mixing due to diffusion, and multispecies reaction which can be either formation or consumption.

It is of interest to evaluate the difference between the formation and consumption rates that may exist at different times as a function of the number of pore volumes injected. To evaluate this, we plot these rates after 1 PV injected, as shown in Fig. 5.8, and compare it to the results where 3 PV were injected (Fig. 5.5). It can be immediately recognised that the rates of formation and consumption for all six species are similar in the macroscopic space. This is because forward and reverse reactions occur continuously under the supply of fresh reactants at a high flow rate in fast velocity channels. However, the same reactions occur in microporosity after longer times which are associated with mass transfer exchange between macroscopic pore space and microporous regions by diffusion. The amount of fresh reactants Ca^{2+} and CO_3^{2-} which diffused into microporosity after 1 PV injected is significantly less than after 3 PV. The consequence of this is that less product $\text{CaCO}_3(\text{aq})$ is being formed after 1 PV than after 3 PV injected, which can be seen by comparing the $\text{CaCO}_3(\text{aq})$ formation rates (and at the same time the Ca^{2+} and CO_3^{2-} consumption rates) in Fig. 5.8 and Fig. 5.5. This further confirms our observation in Fig. 5.3 that the microporous cells further from the injection face contain more $\text{CaCO}_3(\text{aq})$, which is due to the slow mass transfer of reactants Ca^{2+} and CO_3^{2-} supplied from the preceding fast channels. Similar behaviour can be observed for the second product CaOH^+ , which, as previously mentioned, also exhibits similar mixing behaviour.

Furthermore, we now examine how the formation/consumption rates are impacted in the velocity space. In Chapter 4 we have used this method for the bead pack by calculating PDFs of velocity weighted by the rate of formation/consumption.

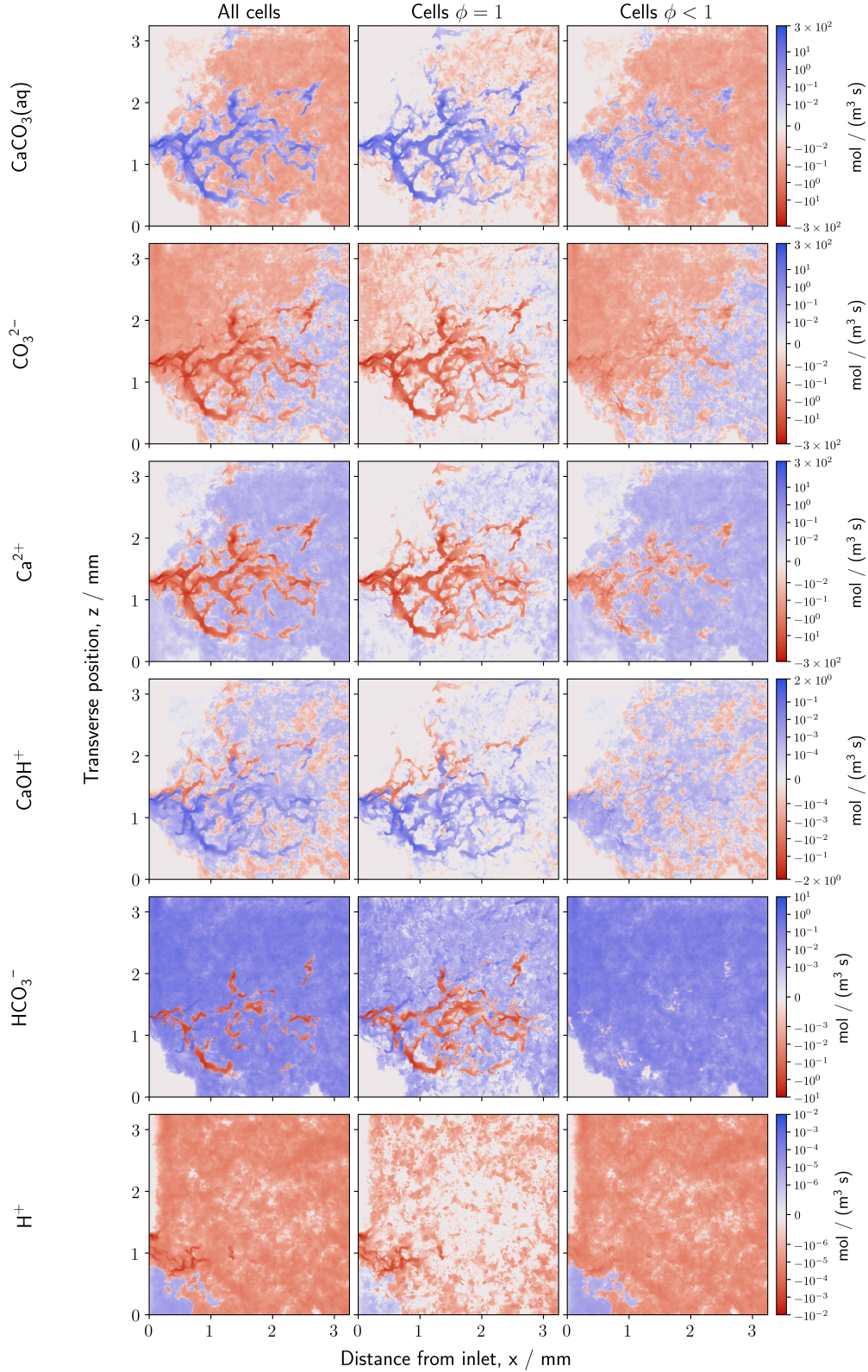


Figure 5.8: Rate of formation, defined by Eq. (3.42), in the pore space weighted by porosity and averaged in a direction perpendicular to the flow, for the whole image (left), only for cells where porosity $\phi = 1$ (middle), and only for cells where $0 < \phi < 1$ (right), at 1 pore volume injected. Blue indicates formation of the product, while negative rates of formation, i.e., consumption, are shown in red. Flow is from left to right. A solution of Na_2CO_3 is inject over the top part of the left face; a solution of CaCl_2 is injected over the bottom part.

Figure 5.9 presents the frequency of image cell velocities in which reaction occurs after 3 PV injected weighted by the rate of formation and the rate of consumption (Eq. (3.47)) for the six selected species studied. The normalization is performed so that the sum of the two areas under the curves for microporous and macroscopic regions equals 1. The product $\text{CaCO}_3(\text{aq})$ is predominantly formed in faster velocity cells associated with macroscopic pore space, while a small amount is formed in microporosity. This is almost exactly mirrored by the partial PDFs of velocity associated with the rate of consumption of CO_3^{2-} . Similarly, the cell velocities in which $\text{CaCO}_3(\text{aq})$ is consumed largely corresponds to the velocities in which Ca^{2+} and CO_3^{2-} are formed. This symmetry does not apply to the frequency of slow velocities in microporosity in which CO_3^{2-} is consumed — this is seen as a larger peak of slow velocities. This is because additional CO_3^{2-} is consumed for the formation of HCO_3^- in microporosity. The partial PDFs of velocity reveal the significant differences between the two products $\text{CaCO}_3(\text{aq})$ and CaOH^+ indicating that consumption of the latter species is much higher in the macroscopic pore space characterized by faster velocities. Both HCO_3^- and H^+ are predominantly formed in microporosity while they are preferentially consumed in the macroscopic pore space.

A methodology using the PDF velocity of cells in which reactions occur was introduced in the work by Alhashmi et al. (2016) who characterized the dynamics of reactive transport behaviour in a homogeneous bead pack and two sandstones for an irreversible bimolecular reaction. In their work, the overall behaviour was shown to depend on transport condition, reactive conditions, and heterogeneity of the pore structure. We have now applied this concept for multispecies reversible reaction in a bead pack (Chapter 4) and in a complex microporous carbonate, demonstrating that this metric can reveal subtle time-dependent impacts of transport on both formation and consumption rates of species. The transport dynamics is impacted by the physical (flow) heterogeneity, which is profoundly different in a microporous carbonate compared to the bead pack. Carbonates are characterized by faster advection in the channels which promotes more rapid mixing, and a larger number of slow microporous regions, which favour slow mixing. This, accompanied by reaction reversibility creates much more complex dynamics which can be better characterized by this methodology.

The evolution of reaction rates as a function of the number of PV injected is presented in Fig. 5.10. The rates of formation of two products $\text{CaCO}_3(\text{aq})$ and CaOH^+ in the macroscopic pore space increase over time, and after 3 PV injected they appear to reach asymptotic values. This behaviour is mirrored in the rates of consumption of two reactants Ca^{2+} and CO_3^{2-} in the macroscopic pore space. However, the corresponding rates of formation and consumption in microporosity for these four species are still increasing after 3 PV injected. We also note that the rate of consumption of $\text{CaCO}_3(\text{aq})$ decreases over time in the macroscopic pore space but increases in microporosity. This is mirrored by the corresponding decrease

CHAPTER 5. FLUID-FLUID REACTION IN MICROPOROUS CARBONATE

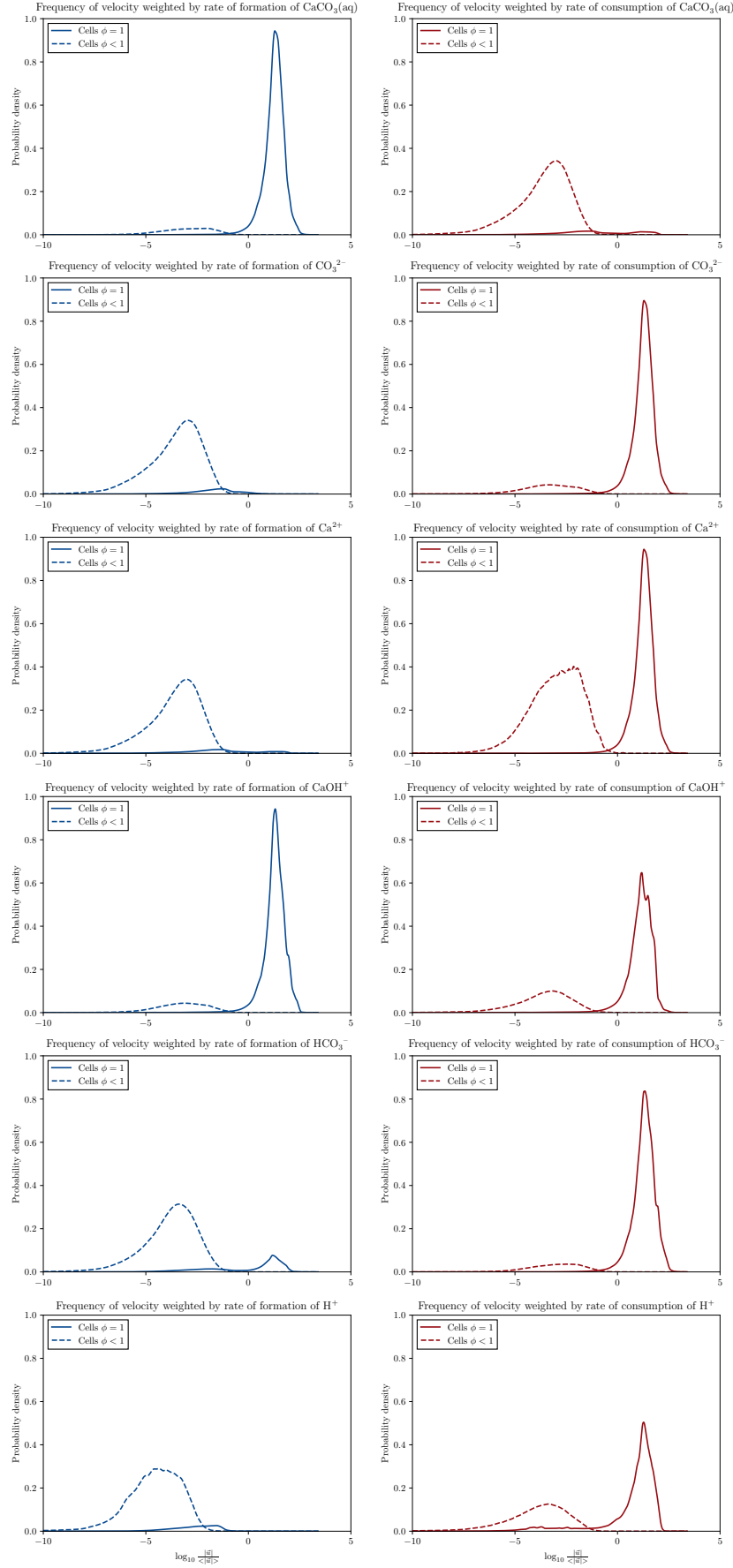


Figure 5.9: Partial PDFs of velocity weighted by rates of formation and consumption of different species, on macro- and microporous regions. These functions are defined by Eq. (3.47).

in the formation rate of Ca^{2+} in the macroscopic pore space and an increase in microporosity. The rates of formation of H^+ are much smaller than the rates of consumption in both macro- and microporosity. Moreover, both rates of consumption decrease over time.

This analysis opens up a question on whether the reaction rates of multiple species in microporous carbonates have a “true” asymptotic value for the timescale of practical applications. A good example is the rate of formation of HCO_3^- in microporosity which exhibits a non-monotonic behaviour: it increases at first until 1 PV injected, and then decreases. If we recall, before reactants were injected there was only water as resident fluid in the pore space including microporosity. Initially, the injected reactants mix with the resident water in microporosity and the rate of formation of HCO_3^- increases until 1 PV is injected. However, as time passes resident water is displaced as larger amounts of injected reactants can diffuse into microporosity. Moreover, they mix and react themselves therefore altering equilibrium conditions.

The relative yield as a function of distance from the inlet is presented in [Fig. 5.11](#) for each cross-section parallel to the inlet face. Recalling from the previous chapter, the relative yield was calculated as the ratio of the difference between the respective simulation and “No reaction” to the difference between “Fully mixed” and “No reaction”, using the values obtained for the simulation in Portland ([Table 5.2](#)).

Table 5.2: Average concentration at the outlet. The columns correspond to the concentration obtained if no reaction took place in the system (No reaction), if the system were an ideal continuous stirred tank reactor (Fully mixed), and for the simulated system with $Pe = 100$.

Species	No reaction (mol/m ³)	Fully mixed (mol/m ³)	$Pe = 100$ (mol/m ³)
Na^+	24.5	24.4	24.4
CO_3^{2-}	11.4	3.49	4.56
HCO_3^-	887×10^{-3}	730×10^{-3}	782×10^{-3}
$\text{CO}_2(\text{aq})$	11.0×10^{-6}	22.5×10^{-6}	22.6×10^{-6}
$\text{NaOH}(\text{aq})$	17.0×10^{-3}	7.44×10^{-3}	8.41×10^{-3}
Ca^{2+}	12.6	4.68	5.92
Cl^-	25.4	25.4	25.4
CaCl^+	130×10^{-3}	29.1×10^{-3}	40.6×10^{-3}
$\text{CaCl}_2(\text{aq})$	1.82×10^{-3}	0.227×10^{-3}	0.360×10^{-3}
CaOH^+	0.01×10^{-3}	23.4×10^{-3}	23.2×10^{-3}
$\text{HCl}(\text{aq})$	422×10^{-9}	0.082×10^{-9}	0.0862×10^{-9}
$\text{NaCl}(\text{aq})$	0	71.4×10^{-3}	61.6×10^{-3}
$\text{CaCO}_3(\text{aq})$	0	8.01	6.82
CaHCO_3^+	0	18.3×10^{-3}	18.3×10^{-3}
H^+	68.4×10^{-6}	0.02×10^{-6}	0.0247×10^{-6}
OH^-	870×10^{-3}	717×10^{-3}	723×10^{-3}

As for the bead pack, we observe that the relative yield has different values for

CHAPTER 5. FLUID-FLUID REACTION IN MICROPOROUS CARBONATE

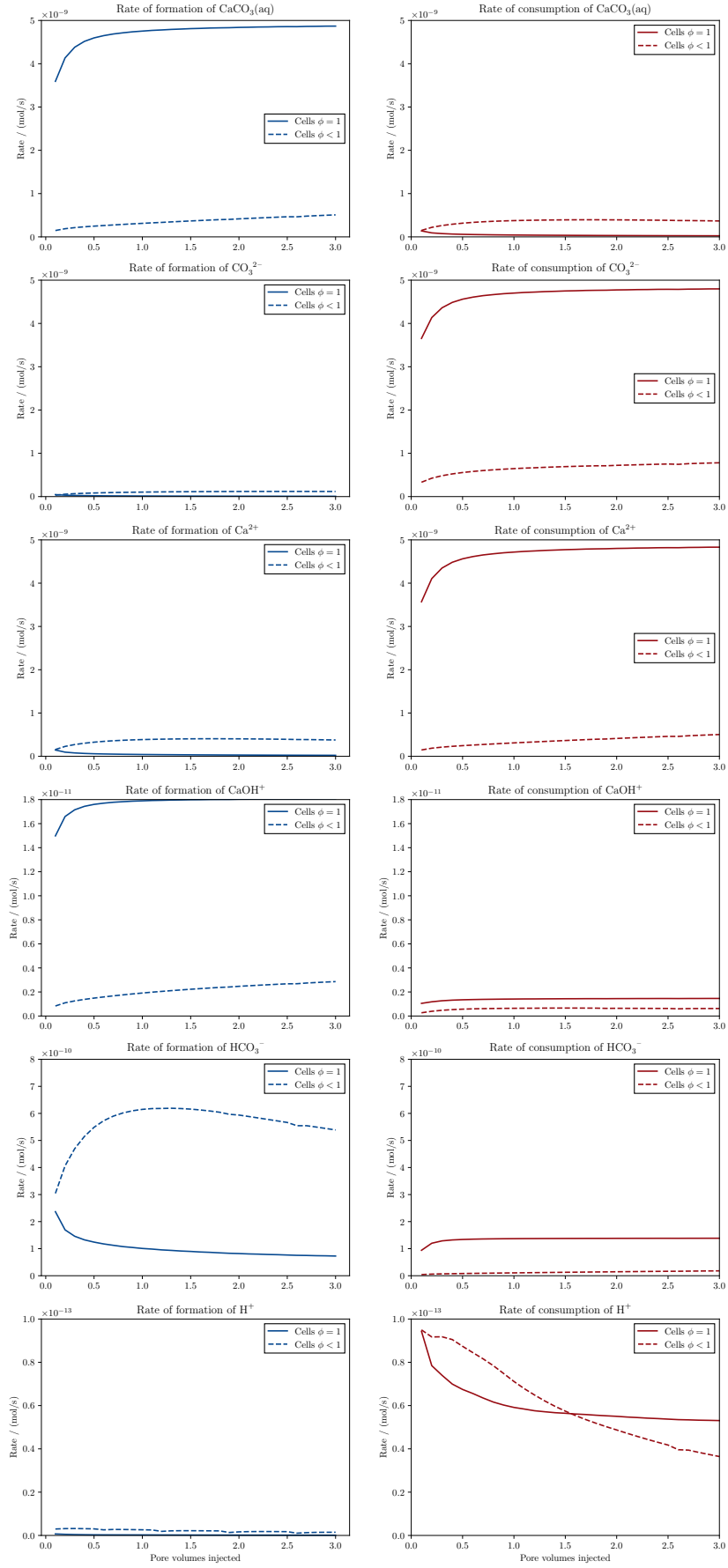


Figure 5.10: Rates of formation and consumption on macro- and microporous cells as a function of pore volumes injected for selected species.

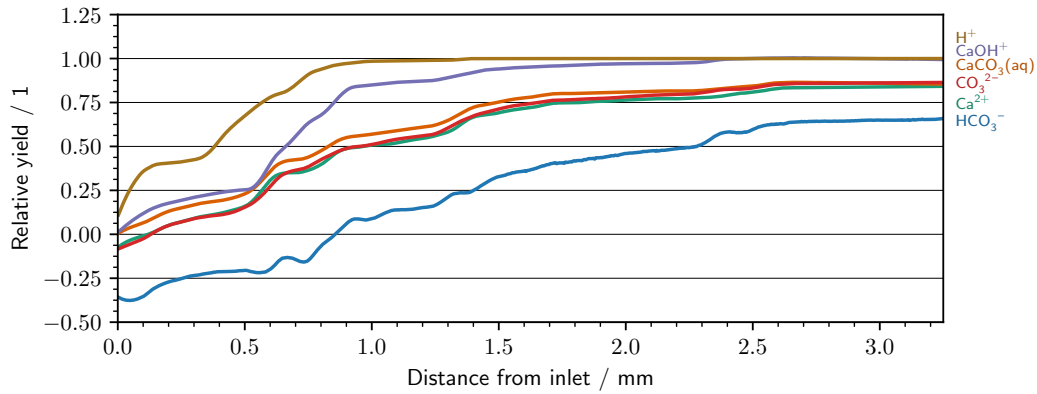


Figure 5.11: Relative yield of selected species as a function of distance from inlet face.

each species, implying that the difference from the fully mixed system is species dependent. Moreover, due to different nature of mixing in the carbonate, we observe a much more fluctuating behaviour for each curve in comparison to the bead pack, which for the main product $\text{CaCO}_3(\text{aq})$ is most pronounced from 0.5 mm to 1 mm.

It is important to recognise that the relative yields in Fig. 5.11 correlate well to the reactor ratios, given by Eq. (2.30) and shown in Fig. 5.6 — a good exemplar for this is $\text{CaCO}_3(\text{aq})$. This helps us better understand the impact of mixing on reaction. The higher the amount of mixing (reactor ratio), the higher is relative yield.

More spreading leads to more mixing, which in turn results in higher reaction rates and relative yield. Hence, the relative yields of the species in the complex pore space of Portland limestone are much higher than in the bead pack. This is confirmed in Fig. 5.11, from which we see that relative yields of all the species reach the maximum values at distances closer to the inlet than in the bead pack case Fig. 4.6.

Overall, these results demonstrate the complex reaction dynamics that emerges from multispecies reversible reaction in a complex pore space. In Portland, we see a combination of advection-dominated flow in the macroporosity, and diffusion-mediated transport in microporosity. Combined with reaction, this leads to a much more rapid and disperse mixing of reactants and products, and a complex and often non-monotonic time dependence of reaction rates. This first study has uncovered an interesting reaction dynamics, and further work could focus on finding appropriate upscaled reactions rates for use in field-scale models for different chemical processes and rocks.

MULTICOMPONENT FLUID-SOLID REACTION

We extend the multicomponent model presented in the previous chapters to include fluid-solid reactions. [Section 3.1.7](#) detailed how dissolution and changes of geometry are taken into account. In this chapter, we validate the fluid-solid reaction model comparing simulations to analytical solutions, and give an example of application for pore space images obtained by microtomography.

This is an exploratory study; further work is required to validate the model in a broader range of problems, and to study dissolution processes systematically in a fuller series of pore space geometries.

6.1 Validation

We validate the model by comparing simulations and analytical solutions for the dissolution of two systems under diffusion-controlled conditions. The first system is a semi-infinite solid, whose discretized geometry closely matches the continuous one. The second system is a sphere, where we can study the effects produced by discretizing a curved geometry with cubic cells.

6.1.1 Dissolution of a semi-infinite solid

We consider a semi-infinite solid composed of calcite in contact with a semi-infinite liquid phase. The solid is assumed to be in equilibrium with the fluid at the interface and the dissolved species are transported away from the fluid-solid interface by diffusion. The derivation of the analytical solution for this system can be found in [Appendix A.1](#), and shows that, although the reaction rate constant is infinite (the solid is always in equilibrium with the liquid), the dissolution is limited by diffusion, resulting in a finite rate of dissolution.

Since the reaction and transport happen solely in the direction normal to the fluid-solid interface, the system can be accurately described by a 1D model. The semi-infinite solid and liquid phases are represented in the simulation by finite domains. This entails no approximation for the solid phase, as we consider the dissolution of the outermost section of the semi-infinite solid. Regarding the liquid phase, a finite domain behaves differently from a semi-infinite one. In [Appendix A.1.2](#) we compare the analytical solution for systems with a finite and infinite liquid phase. It suffices to point out here that the simulated cases are such that the discrepancy between the rates of dissolution for a bounded and an unbounded domain are less than 0.01 %, allowing us to use the analytical solution for an unbounded domain in the remainder of this section.

6.1.1.1 Case description

The system is kept at constant temperature $T = 298.15$ K and pressure $p = 0.1$ MPa. The solid phase measures $L_s = 100$ μm and is discretized into 20 cells of $\Delta x = 5$ μm . The length of the liquid phase is shown in [Table 6.1](#); it is also discretized into cells of $\Delta x = 5$ μm . The time step is $\Delta t = 10$ ms. These values were chosen to ensure that any discrepancy between the simulation and analytical results are not attributable to the time step or spatial discretization. The sensitivity to these parameters was tested using $\Delta x = 2.5$ μm and $\Delta t = 5$ ms. As observed in [Fig. 6.1](#), the numerical solution does not significantly change when these values for discretization are used.

Table 6.1: Composition of the liquid phase ($T = 25$ °C, $p = 0.1$ MPa) used in the validation cases and lengths L_l of the liquid phase for the dissolution of a semi-infinite solid.

Species	$L_l = 7600$ μm $S = 0.00916$		$L_l = 3800$ μm $S = 0.0733$		$L_l = 3800$ μm $S = 0.1466$	
	Initial (mol/m ³)	Equilibrium (mol/m ³)	Initial (mol/m ³)	Equilibrium (mol/m ³)	Initial (mol/m ³)	Equilibrium (mol/m ³)
CO ₃ ²⁻	0	341×10^{-6}	0	33.0×10^{-6}	0	12.5×10^{-6}
HCO ₃ ⁻	0	19.2	0	22.0	0	21.6
CO ₂ (aq)	0	219	0	1882	0	3814
Ca ²⁺	0	226	0	1002	0	1007
CaCl ⁺	0	11.0	0	527	0	1272
CaCl ₂ (aq)	0	998×10^{-3}	0	374	0	1556
CaOH ⁺	0	1200×10^{-9}	0	730×10^{-9}	0	494×10^{-9}
CaCO ₃ (aq)	0	6.91×10^{-3}	0	6.17×10^{-3}	0	5.30×10^{-3}
CaHCO ₃ ⁺	0	9.98	0	81.6	0	135
HCl(aq)	18.5	0.503×10^{-3}	919	32.2×10^{-3}	3820	91.8×10^{-3}
Cl ⁻	453	454	3339	2591	6182	3400
H ⁺	453	12.8×10^{-3}	3339	131×10^{-3}	6182	245×10^{-3}
OH ⁻	45.5×10^{-12}	1.64×10^{-6}	4.15×10^{-12}	84.4×10^{-9}	1.05×10^{-12}	25.6×10^{-9}
H ₂ O(l)	54.8×10^3	54.6×10^3	51.6×10^3	48.7×10^3	48.8×10^3	41.8×10^3
pH	0.51	5.1	-0.26	4.1	-0.46	3.8

The solid phase is composed of pure calcite (molar volume $V_s = 3.7 \times 10^{-5} \text{ m}^3/\text{mol}$) and is assumed to be permanently in equilibrium with the liquid at the interface. The liquid is initially a solution of HCl in water and does not contain any dissolved calcite. The initial composition of the liquid, the composition of the liquid in equilibrium at the interface with the solid, and the 14 components we consider in the simulation are shown in Table 6.1. In this model all components have a diffusion coefficient of $D = 7.5 \times 10^{-10} \text{ m}^2/\text{s}$ (value for Ca^{2+} at 25°C (Luquot and Gouze, 2009)).

To assess the quality of the numerical solution, we compare the evolution of the position of the interface and the rate of dissolution over time with the analytical results. These quantities are dependent on the diffusion coefficient D and on the solubility factor

$$S = (C^* - C_0)V_s, \quad (6.1)$$

where V_s is the molar volume of the solid phase, C_0 is the molar concentration of the dissolved solid in the bulk of the liquid phase at t_0 (it equals 0 in our simulations), and C^* is the molar concentration of the dissolved solid in the liquid in equilibrium at the interface. Therefore, a unit volume of the saturated liquid contains an amount of solid in solution that equals S times the amount contained in a unit volume of the solid phase.

To reduce the total simulation time required to observe a significant amount of dissolution, we choose high values for S (0.0092, 0.0733 and 0.1466), which are obtained for an initial liquid composition of very low pH (0.51, -0.26 and -0.46 , respectively). While these values are not realistic for subsurface oil and water reservoir, they are valid for a test case, and proved to be a fortuitous choice that allowed us to observe a behaviour of our model that would otherwise remain unnoticed.

6.1.1.2 Results

As detailed in Section 3.1.7, the mesh is updated when the solid fraction α in a solid cell is reduced under a threshold value, which is 0 in the case in study. To better assess the evolution of the discretized model when comparing it to the analytical solution, instead of considering the constant position of interface between two updates obtained directly from the mesh, we consider a position that is proportional to α . For example, if $\alpha = 0.2$, we consider in the comparison below that interface position has already moved $0.8\Delta x$ from the cell face away from the liquid.

For each value of the solubility factor S , we analyse the evolution of the position of the fluid-solid interface, the rate of dissolution per unit surface area, and the ratio between rate of dissolution per unit surface area for the simulated and the analytical solutions.

We note in Figs. 6.1, 6.4 and 6.7 that the numerical model overpredicts the dissolution of the solid phase. In Fig. 6.1 we observe that the use of a finer mesh or

smaller time step has little impact on the results, which indicates that the reason for the difference from the analytical solution is not due to a coarse mesh or time step.

In Figs. 6.2, 6.5 and 6.8, we compare the rate of dissolution per unit surface area obtained from the numerical simulation with the analytical solution. The oscillations observed are a consequence of the addition of a cell to the liquid domain when a whole solid cell is dissolved. We smoothed the rate of dissolution using a spline, taking care to preserve the area under the curve, which represents the total amount dissolved.

Figures 6.3, 6.6 and 6.9 shows the ratio between the simulated rate of dissolution and the expected analytical result. The simulation overpredicts the rate of dissolution but the discrepancy is smaller for smaller solubility factors S . The overprediction ϵ is summarized in Table 6.2.

S	Overprediction ϵ
0.1466	14.41 %
0.0733	4.72 %
0.0092	0.36 %

Table 6.2: The simulation of the dissolution of a semi-infinite solid with a plane surface in a stagnant liquid overpredicts the dissolution rate. The overprediction is larger for a larger solubility factor S . By adjusting a function $\epsilon = aS^2 + bS$ and extrapolating to solubility factors of the systems under study, which are around $S = 1.7 \times 10^{-3}$, the overprediction is around 0.06 %.

Given that the accuracy of the results depend on the solubility factor, it is important to assess how accurate the model is on realistic scenarios of application of the simulator. Table 6.3 shows the composition of a fluid that is closer to brines found in subsurface reservoirs. It was used by Menke et al. (2016) to study reactive transport in carbonates. In the same table, the composition of the solution after it is saturated with calcite is shown. The solubility factor for that system is $S = 1.7 \times 10^{-3}$. By adjusting a function $\epsilon = aS^2 + bS$, we estimate an error $\epsilon = 0.06\%$ for this fluid reacting with calcite. This gives us some confidence in the validity of result in the scenarios of practical application: our test cases were designed to be challenging but did have rather unphysically large amount of dissolution.

6.1.2 Dissolution of a sphere

In the previous section, we considered the dissolution of a semi-infinite solid. Since its fluid-solid interface was aligned to the grid, the surface area considered in the numerical model coincided with the surface area of the analytical solution. For real porous media, it is possible to use unstructured meshes to have cell aligned with fluid-solid interfaces. More often, however, the pore space image is obtained by micro-CT in a voxelized format. Post-processing the image can be difficult, require further approximations, or be incompatible with other techniques that one may need

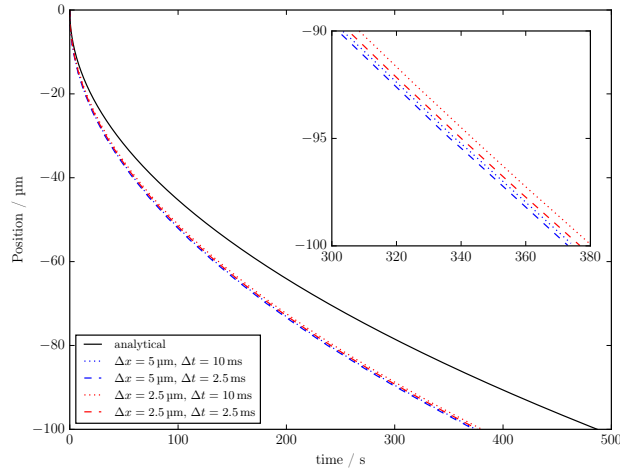


Figure 6.1: Position of the fluid-solid interface as a function of time for a semi-infinite solid when $S = 0.1466$.

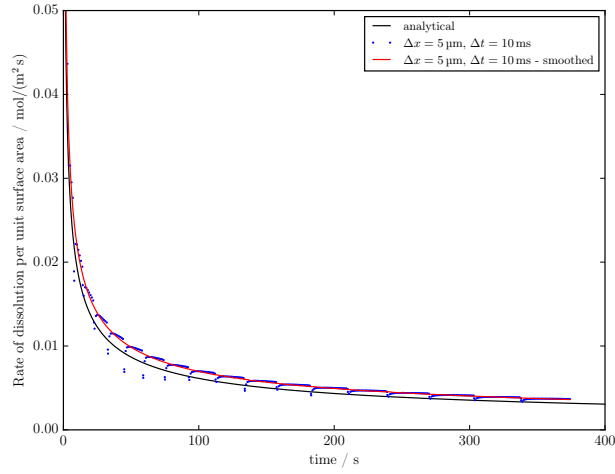


Figure 6.2: Rate of dissolution per unit surface area as a function of time for a semi-infinite solid when $S = 0.1466$.

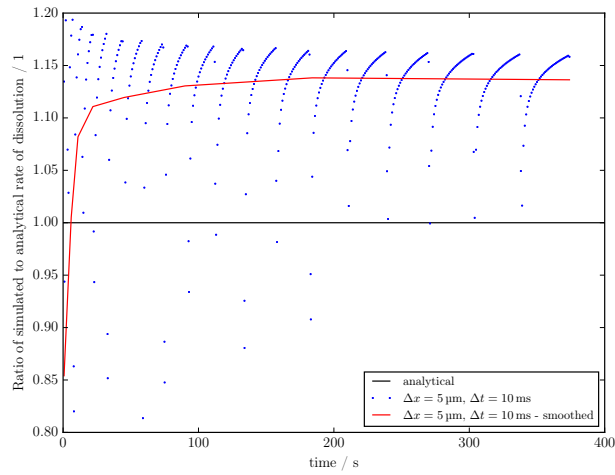


Figure 6.3: Ratio between the rate of dissolution per unit surface area obtained from the numerical solution and the analytical solution for a semi-infinite solid when $S = 0.1466$.

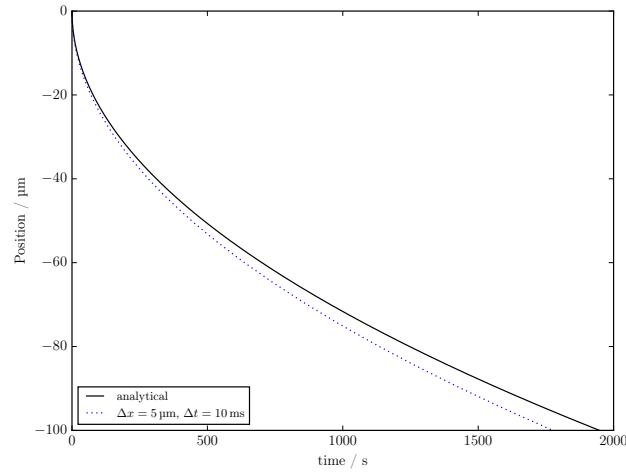


Figure 6.4: Position of the fluid-solid interface as a function of time for a semi-infinite solid when $S = 0.0733$.

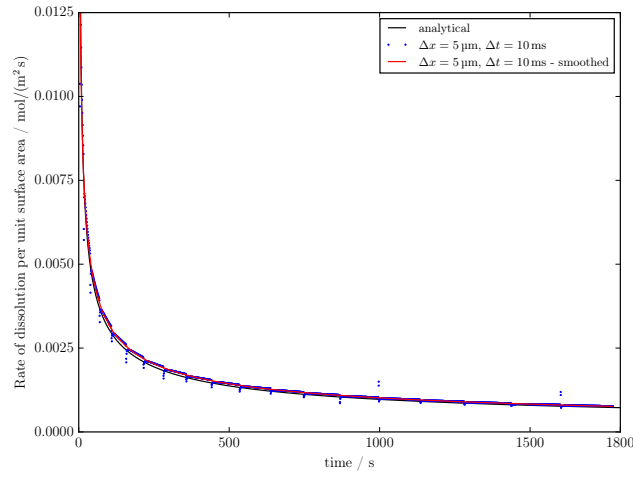


Figure 6.5: Rate of dissolution per unit surface area as a function of time for a semi-infinite solid when $S = 0.0733$.

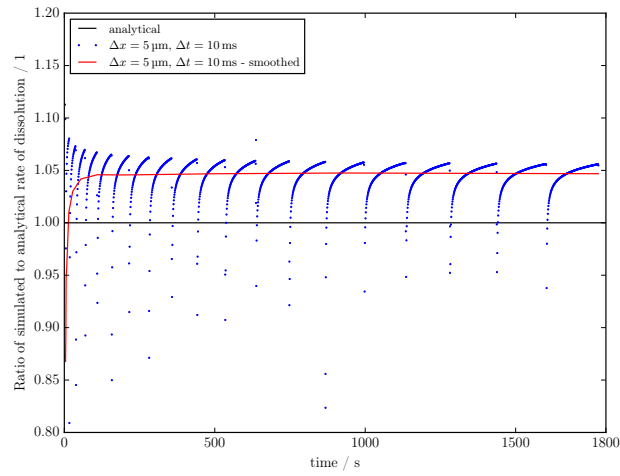


Figure 6.6: Rate of dissolution per unit surface area as a function of time for a semi-infinite solid when $S = 0.0733$.

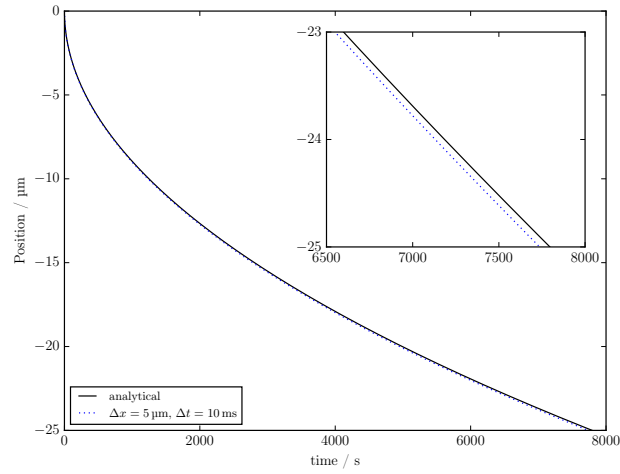


Figure 6.7: Position of the fluid-solid interface as a function of time for a semi-infinite solid when $S = 0.0092$.

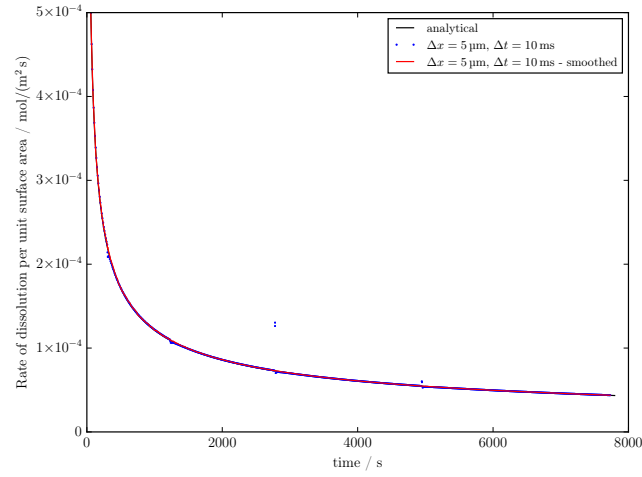


Figure 6.8: Rate of dissolution per unit surface area as a function of time for a semi-infinite solid when $S = 0.0092$.

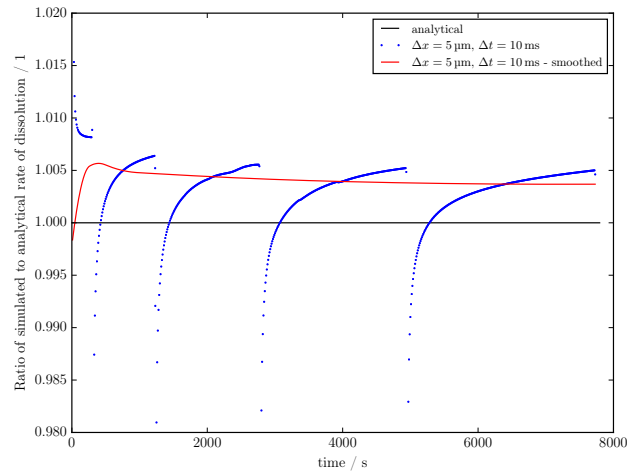


Figure 6.9: Rate of dissolution per unit surface area as a function of time for a semi-infinite solid when $S = 0.0092$.

Table 6.3: Composition of the injected fluid ($T = 50^\circ\text{C}$, $p = 10\text{ MPa}$) used in the simulation of dissolution of a carbonate sample.

Species	C_0 (mol/m ³)	C^* (mol/m ³)
CO_3^{2-}	479×10^{-9}	2.59×10^{-3}
HCO_3^-	1.19	84.7
$\text{CO}_2(\text{aq})$	797	753
Ca^{2+}	0	35.0
CaCl^+	0	3.74
$\text{CaCl}_2(\text{aq})$	0	468×10^{-3}
CaOH^+	0	1.31×10^{-6}
$\text{CaCO}_3(\text{aq})$	0	8.68×10^{-3}
CaHCO_3^+	0	6.25
K^+	134	134
$\text{KCl}(\text{aq})$	297×10^{-3}	298×10^{-3}
$\text{KOH}(\text{aq})$	2.91×10^{-9}	217×10^{-9}
Na^+	793	793
$\text{NaCl}(\text{aq})$	65.9	66.2
$\text{NaOH}(\text{aq})$	24.2×10^{-9}	1.80×10^{-6}
$\text{HCl}(\text{aq})$	78.2×10^{-3}	1.05×10^{-3}
Cl^-	927	923
H^+	1.11	15.0×10^{-3}
OH^-	103×10^{-9}	7.52×10^{-6}
$\text{H}_2\text{O}(\text{l})$	52.2×10^3	52.2×10^3
pH	3.1	5.0

to apply on the image together with a reactive transport simulator. In any case, even if the initial mesh is aligned with the pore geometry, this alignment would not be preserved in our model as dissolution happens. Therefore, it is important to study the effects produced by discretizing a curved geometry with cubic cells, especially the effect of an increased surface area between solid cells and fluid cells when compared to the real geometry. It should be noted that this increase in surface area cannot be avoided even with infinitely small cells: the surface area of a sphere with radius R discretized by cubic cells converges to $6\pi R^2$ in the limit of infinitesimal cubes, which is 50 % in excess of the area of the sphere.

In this section, we examine the performance of our model in predicting the rate of dissolution of a discretized sphere in a stagnant liquid. The derivation of the analytical solution for this system can be found in [Appendix A.2](#), and shows that, although the reaction rate constant is infinite (the solid is always in equilibrium with the liquid), dissolution is limited by diffusion, resulting in a finite rate of dissolution.

The sphere is assumed to be in equilibrium with the fluid at the interface and the dissolved species are transported away from the fluid-solid interface by diffusion.

In the numerical model, the liquid phase is finite. However, for the system described below, we can compare the numerical results to the analytical solution for an infinite domain as shown in [Appendix A.2](#)

6.1.2.1 Case description

The system is composed of a sphere of calcite in a stagnant liquid, kept at constant temperature $T = 298.15\text{ K}$ and pressure $p = 0.1\text{ MPa}$. The sphere has an initial radius $R_0 = 65\text{ }\mu\text{m}$ and is immersed in a concentric spherical liquid domain of radius $R_e = 1300\text{ }\mu\text{m}$. The solid and the liquid phases are discretized into cells of $\Delta x = 5\text{ }\mu\text{m}$, so that the sphere and the whole domain are discretized in 26 and 520 cells along their diameter, respectively. The time step is $\Delta t = 10\text{ ms}$.

As in [Section 6.1.1](#), the solid phase is composed of pure calcite (molar volume $V_s = 3.693 \times 10^{-5}\text{ m}^3/\text{mol}$) which is assumed to be permanently in equilibrium with the liquid at the interface. The liquid is initially a solution of HCl in water and does not contain any dissolved calcite. The initial composition of the liquid, the composition of the liquid in equilibrium at the interface with the solid, and the 14 components we consider in the simulation are shown in the column corresponding to $S = 0.0092$ in [Table 6.1](#). In this model all components have a diffusion coefficient of $D = 7.5 \times 10^{-10}\text{ m}^2/\text{s}$ (value for Ca^{2+} at $25\text{ }^\circ\text{C}$ ([Luquot and Gouze, 2009](#))).

6.1.2.2 Results

To examine the quality of the numerical solution, we compare the evolution of the radius of the sphere and the rate of dissolution over time with the analytical results. An average radius of the discretized sphere is calculated from the volume of solid cells. As detailed in [Section 3.1.7](#), the mesh is updated when the solid fraction α in a solid cell is reduced under a threshold value, which is 0 in the case in study. To better assess the evolution of the discretized model when comparing it to the analytical solution, instead of considering the whole volume of each solid cell, which is constant between two updates obtained directly from the mesh, we consider volumes that are proportional to the solid fraction α , as discussed previously. For example, if $\alpha = 0.2$, we consider in the comparison below that cell has already lost $0.8\Delta x$ of its volume.

We note in [Fig. 6.10](#) that the numerical model only slightly overpredicts the dissolution of the solid phase. In [Fig. 6.11](#), we compare the rate of dissolution per unit surface area obtained from the numerical simulation with the analytical solution. The oscillations observed are a consequence of the addition of a cell to the liquid domain when a whole solid cell gets dissolved. As in the previous section, we smoothed the rate of dissolution using a spline, taking care to preserve the area under the curve, which represents the total amount dissolved. [Figure 6.12](#) shows the ratio between the simulated rate of dissolution and the expected analytical result. The simulation overpredicts the rate of dissolution by an average of 2.5 %.

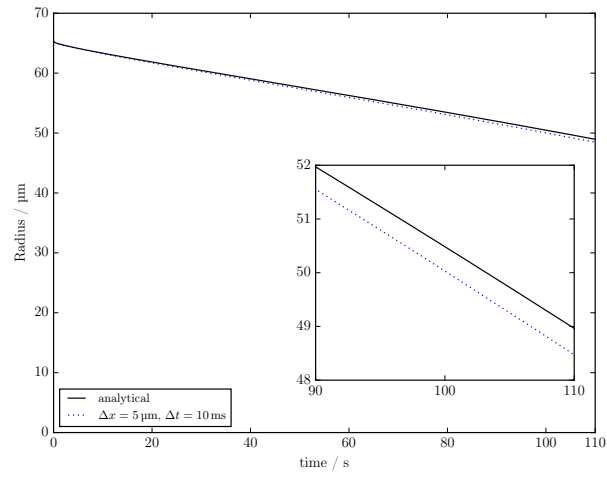


Figure 6.10: Sphere radius as a function of time.

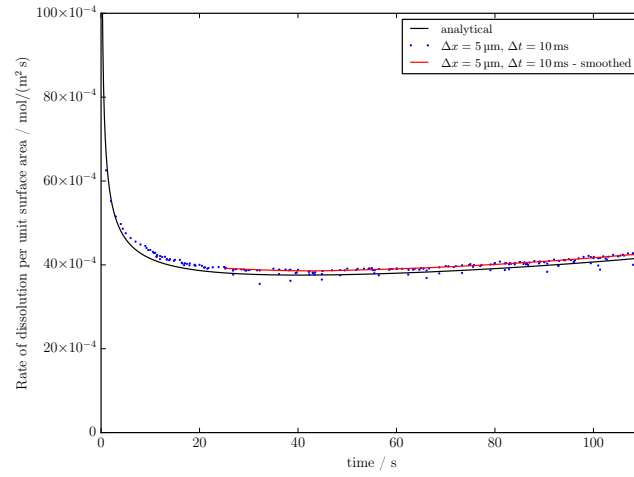


Figure 6.11: Rate of dissolution per unit surface area for a sphere as a function of time.

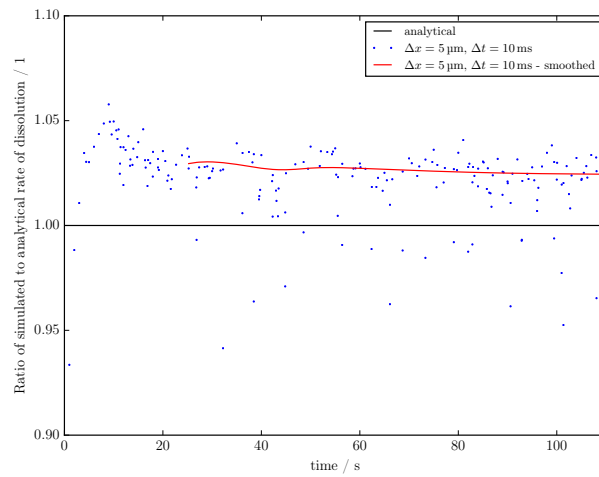


Figure 6.12: Ratio between the rate of dissolution per unit surface area obtained from the numerical solution and the analytical solution for a sphere, as a function of time.

Recalling the rate law for mineral dissolution (Eqs. (3.34) and (3.35)), we observe that the artificial increase in surface area around a liquid cell is partially compensated by an artificial increase of the saturation index in that cell caused by further transport limitations introduced by the staircase geometry. This limitation is not related exclusively to diffusion, but also to advection if the staircase geometry reduces the velocity in the vicinity of the fluid-solid interface.

This section has shown that our code can accurately model dissolution when compared to analytical solutions, even when we have a staircase style geometry to represent a smooth interface. In the next section we apply it to the dissolution on a pore space image.

6.2 Application to micro-CT image

In this section we test our model capabilities to study mineral dissolution by simulating multicomponent transport and reaction on a micro-CT image of a rock taken from the experimental study of Al-Khulaifi (2018) in which supercritical CO₂-equilibrated brine was continuously injected into the rock core at reservoir conditions ($T = 50^\circ\text{C}$ and $p = 10\text{ MPa}$). The rock was a non-uniformly distributed mixture of dolomite and calcite in an approximate ratio of 8:1, and therefore chemically heterogeneous. As discussed previously, dissolution process is associated with changes in solid geometry which requires frequent updates in the calculations of velocity field. This, together with reaction calculations to attain chemical equilibrium is often a time-prohibiting part, especially in studies of multicomponent reactive transport in which each species needs to be transported and reacted simultaneously. Hence, in this preliminary study we focus on a relatively smaller image size, and we try to have similar chemical heterogeneity as in the original image. On the other hand, due to the small sample size, no attempt was made to preserve the physical (flow) heterogeneity but the permeabilities were similar.

6.2.1 Description of micro-CT image and simulation

The image used by Al-Khulaifi (2018) measured $926 \times 925 \times 854$ voxels with a resolution of $5.2\text{ }\mu\text{m}$. For this simulation, we selected a $200 \times 200 \times 200$ voxels region of the original image where a fast flowing channel was present and dissolution happened in the experiment. The ratio of dolomite to calcite in the cropped image was approximately 10:1. It had an initial porosity $\phi = 6.8\%$ and permeability $k = 8.4 \times 10^{-15}\text{ m}^2$. We simulated the flow field on the original image to estimate the average pressure gradient across the sample that was used in the experiment. Then, we applied this same pressure gradient of by imposing a pressure drop of 58.8 kPa between the inlet and outlet faces of the cropped image. The chemical equilibrium

and kinetics is calculated at temperature $T = 50^\circ\text{C}$ and pressure $p = 10\text{ MPa}$. The composition of the injected fluid is shown at the left hand side of [Table 6.3](#).

To speed up the simulation, we use a value of `solidFractionChangeAccelerator` = 1000, which is explained in [Section 3.1.7](#) and a time step of $2.5 \times 10^{-4}\text{ s}$.

6.2.2 Results

In [Fig. 6.13](#) and [Fig. 6.14](#) we visualize cross sectional areas of the 3D reservoir rock image at $t = 0\text{ s}$ and $t = 2200\text{ s}$ from two different angles. Black is the initial pore space; red and magenta represent dissolved dolomite and calcite, respectively, over the course of the simulation ($0\text{ s} < t < 2200\text{ s}$), grey and white represent dolomite and calcite, respectively, that did not dissolve during this time range. Superimposed to the cross sectional areas, we visualize the velocity field in fast channels. In all figures, velocities have been normalized by the average velocity at $t = 0\text{ s}$. We observe that some of the fast channels are located in the proximity of the dissolved dolomite indicating that dissolution is enhanced along these preferential flow pathways. Overall, we see very a heterogeneous distribution of dissolved dolomite in pore space which happened to a much greater extent than dissolution of calcite.

These observations are supported from calculated values for the average reaction rates. The average rate of dissolution per unit surface area of dolomite $r_{dol} = 1.52 \times 10^{-5}\text{ mol}/(\text{m}^2\text{ s})$. The average rate of dissolution per unit surface area of calcite is $r_{cal} = 58.3 \times 10^{-5}\text{ mol}/(\text{m}^2\text{ s})$. These values can be compared to $r_{dol} = 5.1 \times 10^{-5}\text{ mol}/(\text{m}^2\text{ s})$ and $r_{cal} = 81 \times 10^{-5}\text{ mol}/(\text{m}^2\text{ s})$ obtained by [Peng et al. \(2015, 2016a\)](#) indicating lower effective rates values due to mass transfer limitations.

Furthermore, it is of interest to examine both reactants supply and products removal in these fast channels. For this purpose, it is instructive to compare the end of dissolution the velocity field ([Fig. 6.13](#), bottom) with the concentrations of reactants H^+ and $\text{CO}_2(\text{aq})$ ([Figs. 6.15](#) and [6.16](#) respectively) and the concentrations of products Ca^{2+} and Mg^{2+} ([Figs. 6.17](#) and [6.18](#) respectively) in the fast channels. We observe that fastest velocities in flow channels are associated with the highest concentration of H^+ and the lowest concentrations of Ca^{2+} and Mg^{2+} . This means that in the regions of pore space with the fastest flow, rapid supply of fresh reactants leads to fastest dolomite dissolution. The dissolution reaction then results in release of aqueous products Ca^{2+} and Mg^{2+} which are then rapidly swept away by the fast flow. We do not observe this relation with $\text{CO}_2(\text{aq})$ because at this pH of 3.1 the driving mechanism for dissolution is associated with H^+ .

As dissolution progresses, the field `mineralType`, which indicates if a cell is solid or liquid (see [Section 3.1.7](#)) on the background mesh, is updated. Consequently, the geometry of the liquid mesh, which is extracted from the background mesh and is where the flow equations are solved for, changes. Since the pressure drop between the inlet and outlet faces of the domain is kept constant, we observe an increase in the

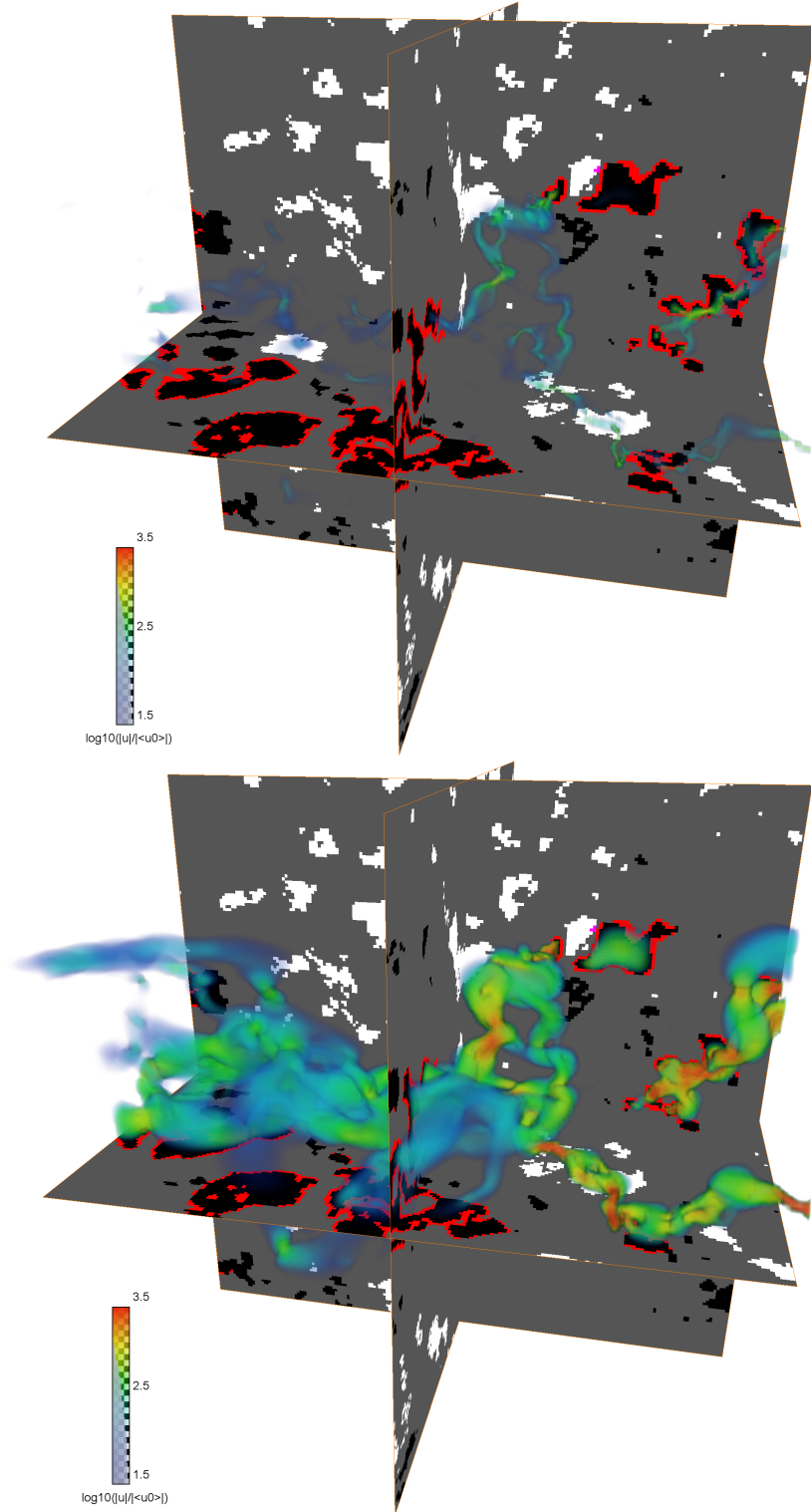


Figure 6.13: Logarithm of the magnitude of the velocity field at $t = 0$ s (Top) and $t = 2200$ s (Bottom) normalized by the initial average velocity. On the cross sections, black is the initial pore space; in grey and white, dolomite and calcite, respectively, still present at the end of the simulation ($t = 2200$ s); in red and magenta, dolomite and calcite, respectively, dissolved between $t = 0$ s and $t = 2200$ s. Flow is from left to right.

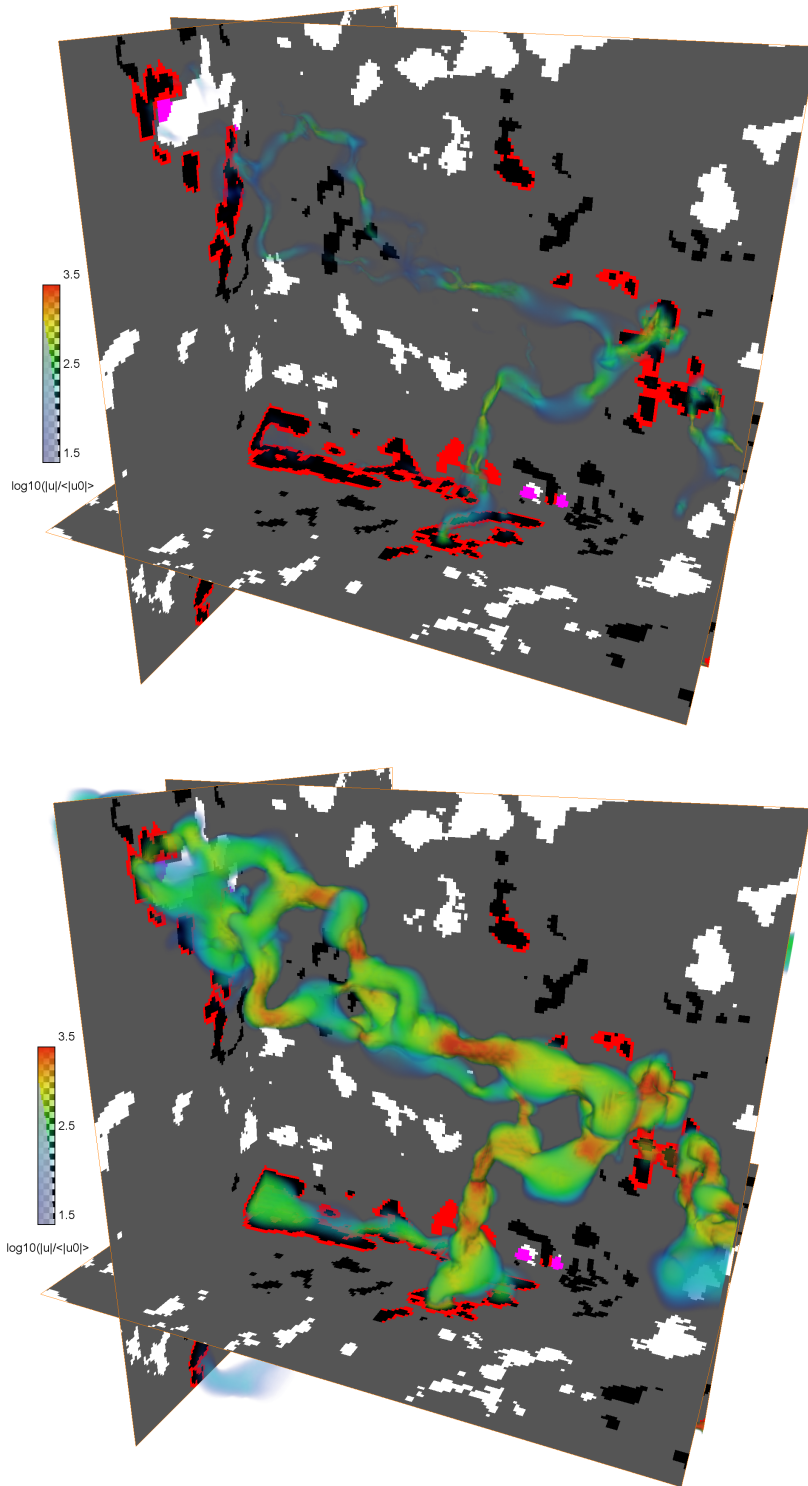


Figure 6.14: Logarithm of the magnitude of the velocity field at $t = 0$ s (Top) and $t = 2200$ s (Bottom) normalized by the initial average velocity. On the cross sections, black is the initial pore space; in grey and white, dolomite and calcite, respectively, still present at the end of the simulation ($t = 2200$ s); in red and magenta, dolomite and calcite, respectively, dissolved between $t = 0$ s and $t = 2200$ s. Flow is from left to right.

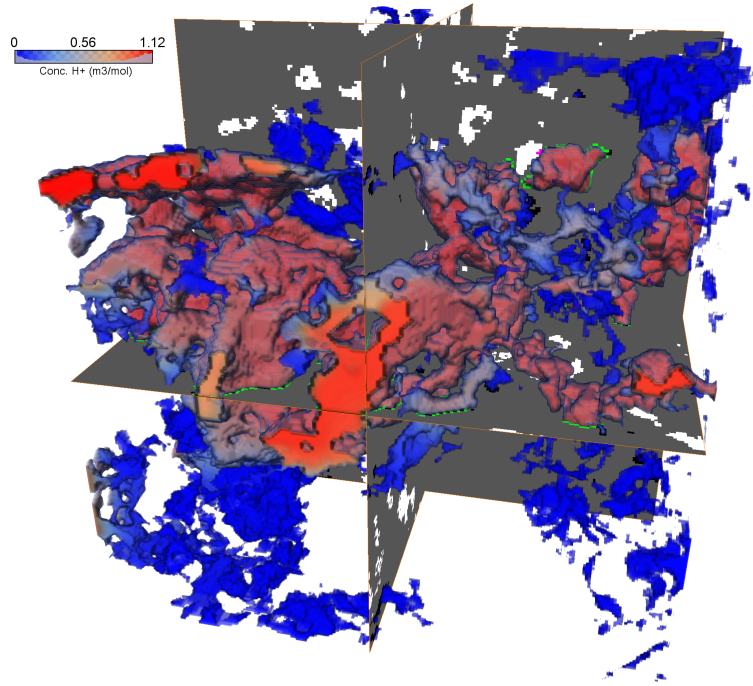


Figure 6.15: Concentration of H^+ at 2200 s. On the cross sections, black is the initial pore space; in grey and white, dolomite and calcite, respectively, still present at the end of the simulation ($t = 2200$ s); in green and magenta, dolomite and calcite, respectively, dissolved between $t = 0$ s and $t = 2200$ s. Flow is from left to right.

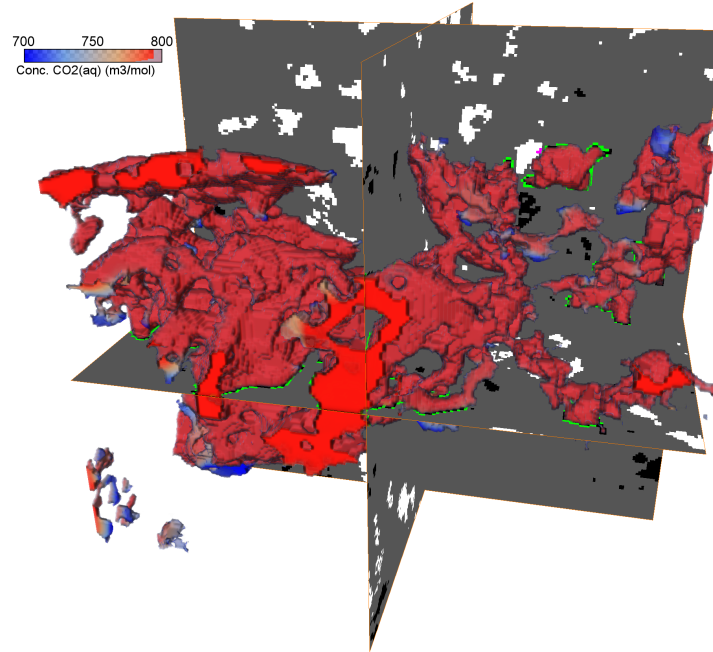


Figure 6.16: Concentration of $CO_2(aq)$ at 2200 s. On the cross sections, black is the initial pore space; in grey and white, dolomite and calcite, respectively, still present at the end of the simulation ($t = 2200$ s); in green and magenta, dolomite and calcite, respectively, dissolved between $t = 0$ s and $t = 2200$ s. Flow is from left to right.

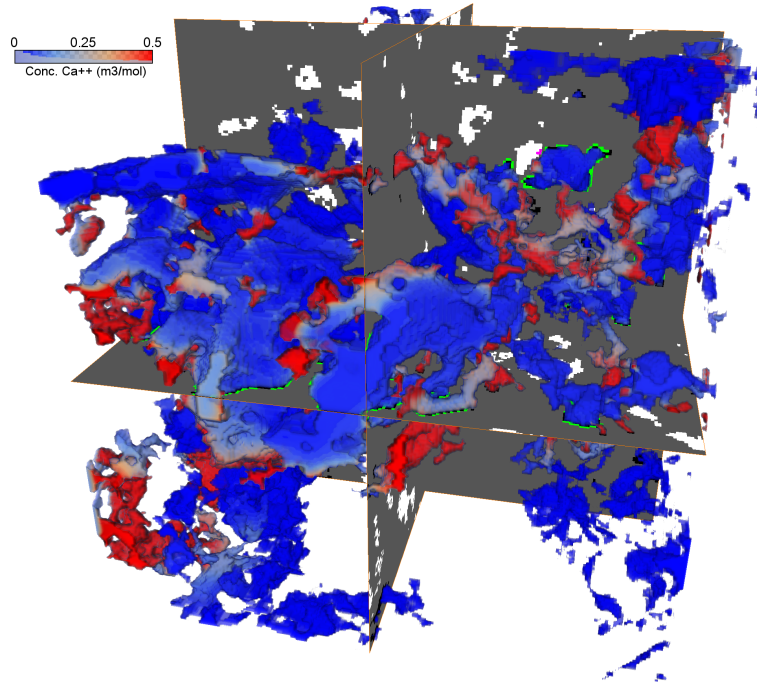


Figure 6.17: Concentration of Ca^{2+} at 2200 s. On the cross sections, black is the initial pore space; in grey and white, dolomite and calcite, respectively, still present at the end of the simulation ($t = 2200$ s); in green and magenta, dolomite and calcite, respectively, dissolved between $t = 0$ s and $t = 2200$ s. Flow is from left to right.

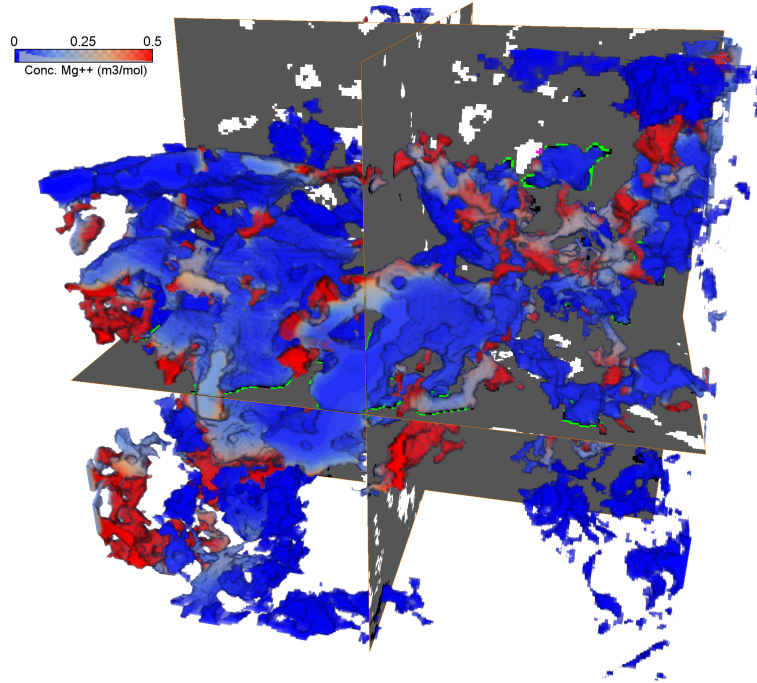


Figure 6.18: Concentration of Mg^{2+} at 2200 s. On the cross sections, black is the initial pore space; in grey and white, dolomite and calcite, respectively, still present at the end of the simulation ($t = 2200$ s); in green and magenta, dolomite and calcite, respectively, dissolved between $t = 0$ s and $t = 2200$ s. Flow is from left to right.

calculated flow rate through the image. From the pressure drop and flow rate, we calculate a new value of permeability at every mesh update. We plot the evolution of permeability versus porosity in Fig. 6.19. We observe a power-law increase in permeability with porosity with an exponent of 10.7. This value is in the mid range of what is observed in the experiments (Al-Khulaifi et al., 2018).

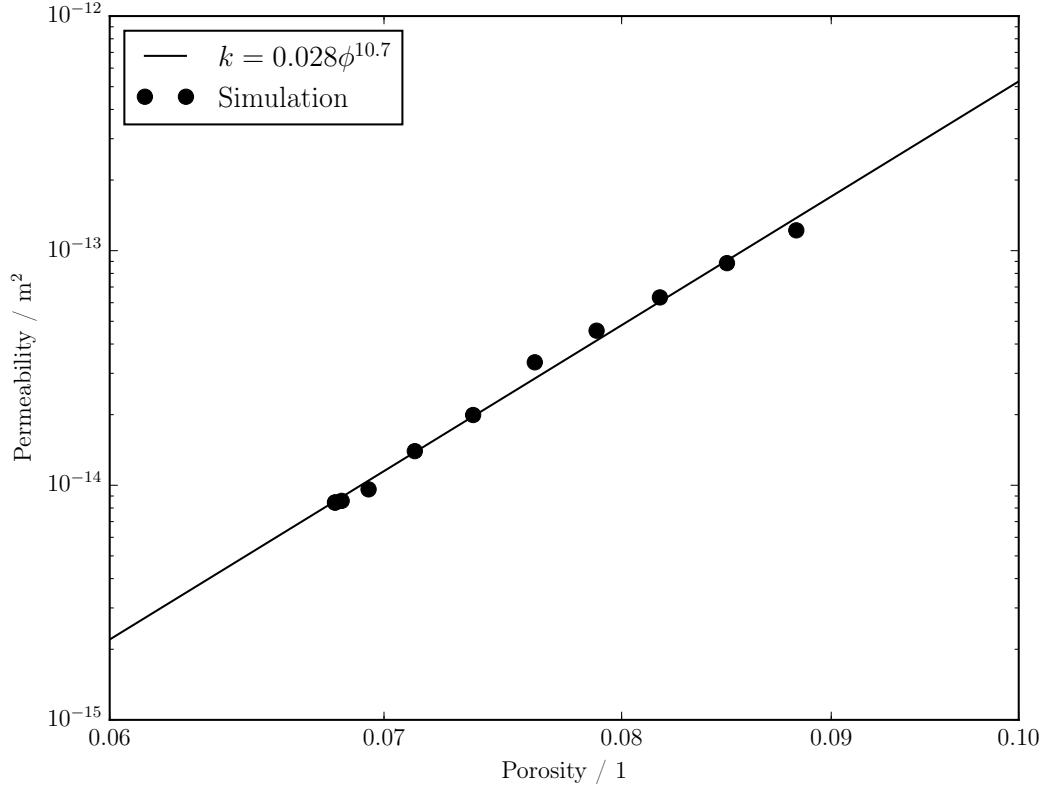


Figure 6.19: Simulated permeability as function of porosity for the dissolution from $t = 0$ s to $t = 2200$ s. The permeability data is interpolated by a power-law function.

Overall, this exploratory study is demonstrating the value of multicomponent reactive transport model when applied on micro-CT images. In particular, it is interesting to examine the coupling between the flow field and reaction in an accurately described geometry of an image. This will be the subject of future work.

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

In this study, we first developed a multispecies reactive transport simulator to perform direct numerical simulation of flow, transport and geochemical reactions on pore space images. We built on OpenFOAM, an established library to solve partial differential equations using the finite volume method solver, and Reaktoro, a recently developed geochemical solver. We validated the solution for transport against an analytical solution for dispersion in a tube with a constant square cross-section and experimental data for dispersion in unconsolidated porous media. Furthermore, we validated the coupling between transport and chemical solvers by comparing our simulation results to experimental data of fluid-fluid reaction in a 2D micromodel ([Willingham et al., 2008](#)).

A key determinant impacting mixing and reaction in subsurface media is heterogeneity of pore space. We use our simulator to examine the impact of physical heterogeneity on mixing-driven fluid–fluid reversible multispecies chemical reaction in porous media. Exemplars of a homogeneous medium (bead pack) and a highly complex heterogeneous medium (microporous Portland limestone) are employed to have a variety of pore-scale complexity which is reflected in different physical heterogeneity.

Direct numerical simulation of multispecies reactive transport is performed in a 3D bead pack where two streams of reactants of different pH are injected in parallel for a range of Péclet numbers. We examined how mixing impacts multispecies reactions and vice versa, therefore generating the distribution of species and rates of formation observed in the pore space. Analysing species concentration fields and reactor ratios, we observed that the extent to which injected species spread in the transverse direction not only depends on Péclet number but also on rates of formation and consumption. Moreover, we observed that products plumes are narrower for

high Péclet numbers. Interestingly, in spite of a relatively homogeneous bead pack structure and symmetry in injection conditions, the concentration fields of products can be asymmetric around the median plane of the domain. This is principally due to the impact of pH on the chemical equilibrium. More generally, it can be a consequence of the complex contribution of each species to the Gibbs energy of the solution.

We verified that rates of formation and consumption, and thus absolute yield, increase with an increase of injection velocities because of a larger amount of matter becoming available for reaction in a unit of time. On the other hand, an increase of injection velocity gives rise to lower relative yields because the transverse mixing by diffusion becomes smaller in comparison to advection.

Furthermore, we studied how reactions are distributed as a function of local velocity by calculating PDFs of velocities weighted by rates of formation and consumption. There is a tendency for reactions to occur in the faster flowing portions of the pore space. The magnitude of this effect is dependent on the relative contribution of advection and diffusion to the transport of species to the sites where each reaction takes place.

We then extended the work to study transport and reaction in a heterogeneous microporous carbonate. The main novelty here was the combination of largely diffusion-controlled transport in microporosity combined with advection-dominated transport in the connected macroporosity. Flow through the Portland limestone image was simulated using a methodology which consists of direct numerical simulation in the complex macro- and micropore space resolved by differential X-ray imaging, and anchoring porosity measurements to the pore size obtained from mercury injection porosimetry [Bijeljic et al. \(2018\)](#). Flow in dual porosity media is simulated using Stokes equation in macropore space and combined with Darcy term representing flow in microporosity.

We quantified the effect of heterogeneity on mixing by analysing spatially resolved maps of concentration of species and their reactor ratio. In contrast to the bead pack study, the heterogeneous flow field in the carbonate led to much more transverse mixing, with reactants provided throughout the simulation domain.

The impact of heterogeneity on reaction dynamics in the carbonate was observed from the comparison of the spatially resolved maps of the rates of formation and consumption of species after different numbers of pore volumes injected. In addition, we observed a highly non-uniform spatial distribution of reaction rates.

The evolution of the species reaction rates revealed new insights on the reaction dynamics: while some of the species reached an asymptotic rate, others were still showing transient non-monotonic behavior. This implies that in multispecies reversible reactive transport in complex porous media reaction rates exhibit much more complex behaviour in comparison to bimolecular irreversible reaction, which needs to be considered in analysis.

We demonstrated that PDFs of velocity in voxels in which reactions occur reveal different impacts of transport in macroscopic pore space and microporosity on both formation and consumption rates of species. These PDFs were impacted by the physical (flow) heterogeneity, which is profoundly different in a microporous carbonate compared to the bead pack. This is due to two main reasons: (a) carbonates are characterized by faster advection promoting more rapid mixing, especially in the channels perpendicular to the flow direction, and (b) they have a larger number of stagnant regions in microporosity, which favour slow mixing. Overall, this results a wider mixing zone in carbonate compared to the bead pack.

It is important to bear in mind that reversibility of reactions makes an additional impact on mixing, as in the bead pack case. In our study, we quantified the complex species and time-dependent reaction kinetics.

For both bead pack and carbonate, we observe different relative yield values for each species, implying that the difference from the fully mixed system is species dependent. However, due to different nature of mixing in the carbonate, we observe a much more fluctuating behaviour in comparison to the bead pack. The relative yields correlate well to the reactor ratios. More spreading leads to more mixing, which in turn results in a higher reaction rates and relative yields. Therefore, the relative yields of the species in the complex pore space of Portland limestone are much higher than in the bead pack.

An important implication arising from this study is that multispecies mixing and reaction in a realistic pore structure such as that of carbonate rock is much more complex than hitherto observed, which needs to be considered in reactive transport studies at multiple length scales.

The final stage of the work was to extend our simulator to consider fluid-solid reaction and specifically the dissolution of a solid. We tested the simulator against analytical results for multicomponent dissolution of a single sphere and multicomponent dissolution on a semi-infinite solid, which showed a good agreement.

Finally, we studied dissolution on a micro-CT image composed of a dolomite and calcite in ratio 10:1. We observed channel widening dissolution, as opposed to uniform dissolution. Due to heterogeneous composition and distribution of minerals, dolomite was predominantly dissolved. We find that fast channels were associated with dissolved dolomite, high concentrations of supplied reactant H^+ , and low concentration of removed products Ca^{2+} and Mg^{2+} . Further performance optimization on high-performance computing is required before the simulator can be applied to study dissolution in a wider range of complex systems.

7.2 Suggestions for future work

This thesis has provided a flexible computational framework for the simulation of multispecies reaction with specific application to pore space images with both macro-

and microporosity.

The examples we have shown are a first study of the rich coupled transport and reaction behaviour in heterogeneous porous media at the small (mm) scales. In particular, the work provides a quantification of effective reaction rates which could be used in larger-scale continuum reactive transport models. Future work could focus on the consideration of different reactions in a variety of rock types to create a deeper understanding of the interplay between flow, transport and reaction kinetics.

The work on fluid-solid reaction and dissolution was preliminary. Here more testing and validation of the code is required before definitive results on dissolution on larger micro-CT images can be analysed. Again, it would be interesting to explore the emergence of dissolution patterns as a function of rock structure, flow rate and reaction rate, as it has been probed experimentally. Furthermore, precipitation reactions could also be studied, with particular relevance for long-term carbon dioxide storage and injection of $\text{CO}_2(\text{aq})$ in oil reservoirs.

As discussed in [Section 3.1.3](#) and [Section 3.1.7](#), the accurate representation of the geometry of the fluid-solid interface is limited by the spatial resolution of the model. While keeping the same resolution, a more accurate representation of the interface position and evolution could be obtained by extending our model using a volume-of-fluid/embedded boundary ([Colella et al., 2000](#)) or level set ([Li et al., 2010](#)) method. As also discussed in [Section 3.1.7](#), this extension could be accompanied by the implementation of a model like the one proposed by [Natsui et al. \(2012\)](#) for particles motion and clogging to enable the simulator to model fines migration.

Lastly, for rigorous validation and testing of the codes, it would be valuable to compare directly the results with 4D imaging datasets of reaction in realistically heterogeneous rocks. This would help provide a robust and tested computational framework for the study of reactive processes in small porous media samples.

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ANALYTICAL SOLUTIONS FOR DISSOLUTION IN A STAGNANT LIQUID

The analytical solutions for the dissolution of a semi-infinite solid and of a sphere in a stagnant unbounded liquid were used to validate the fluid-solid reactive transport model in [Chapter 6](#). We present below how they were obtained and analyse their applicability for a finite domain.

A.1 Dissolution of a semi-infinite solid in a stagnant liquid

We consider a system composed of a mineral and a liquid phase, initially occupying the half-spaces $x < 0$ and $x \geq 0$ respectively. To keep the notation simpler and more intuitive, we restrict attention to the portion of the solid in $-L_s \leq x < 0$.

The position $X(t)$ of the fluid-solid interface can be derived from the mass balance for the solid phase, which is given by

$$\frac{d}{dt} \left(\frac{1}{V_s} A (X - L_s) \right) = -A N_s, \quad (\text{A.1})$$

where A is a unit area, V_s is the molar volume of the solid phase (volume of solid per unit amount of solid, m^3/mol) and N_s is the rate of dissolution per unit surface area (amount of solid per unit surface area and unit time, $\text{mol}/(\text{m}^2 \text{s})$).

The rate of dissolution per unit surface area N_s is related to the diffusion flux by

$$N_s = -D \left. \frac{\partial C}{\partial x} \right|_{x=X}, \quad (\text{A.2})$$

where D is the diffusion coefficient (m^2/s), assumed to be the same for all aqueous species into which the solid dissolves, and C is the total amount concentration of the dissolved solid in the liquid phase (mol/m^3).

From Eqs. (A.1) and (A.2), we have the relation between the velocity of the interface and the gradient of the concentration:

$$\frac{dX}{dt} = V_s D \left. \frac{\partial C}{\partial x} \right|_{x=X}. \quad (\text{A.3})$$

A.1.1 Semi-infinite liquid phase

In the liquid phase, the concentration $C(x, t)$ satisfies

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}, \quad X \leq x < \infty, \quad (\text{A.4})$$

subject to the initial and boundary conditions

$$C(x, 0) = C_0, \quad x > X, \quad (\text{A.5})$$

$$C(X, t) = C^*, \quad t > 0, \quad (\text{A.6})$$

$$C(x, t) \rightarrow C_0, \quad x \rightarrow \infty, \quad t > 0, \quad (\text{A.7})$$

where C_0 is the initial concentration in the liquid phase and C^* is the solubility of the solid.

Let us consider X constant in time and find a solution for C . As shown by Crank (1975, page 20), the solution for Eq. (A.4) subject to Eqs. (A.5) to (A.7) is

$$\frac{C - C_0}{C^* - C_0} = \text{erfc} \left(\frac{x - X}{\sqrt{4Dt}} \right), \quad (\text{A.8})$$

where $\text{erfc}(\cdot)$ is the complementary error function.

Using Eq. (A.8) in Eq. (A.2) gives

$$N_s = (C^* - C_0) \sqrt{\frac{D}{\pi t}}. \quad (\text{A.9})$$

If we now consider that X is a function of time and use Eq. (A.9) in Eq. (A.1), we obtain the equation for the evolution of the position of the fluid-solid interface

$$\frac{dX}{dt} = -S \sqrt{\frac{D}{\pi t}}, \quad (\text{A.10})$$

where $S = (C^* - C_0)V_s$ is the solubility factor. Finally, the position of the fluid-solid interface is

$$X(t) = -2S \sqrt{\frac{Dt}{\pi}}, \quad (\text{A.11})$$

and the time to complete dissolution of the region $-L_s < x < 0$ is

$$t_s = \frac{\pi L_s^2}{4DS^2}. \quad (\text{A.12})$$

In the derivation above, we first considered X as a constant to then drop this consideration. This may seem arbitrary and not consistent. However, it can be verified that the expressions Eq. (A.8) and Eq. (A.11) for $C(x, t)$ and $X(t)$ obtained satisfy the more formally posed problem Eqs. (A.13) to (A.18).

As the solid dissolves and the interface moves, the liquid phase moves as well to fill in the space that was occupied by the solid. Therefore, the dissolution entails a velocity $u = \frac{dX}{dt}$ in the liquid phase. The concentration in the liquid phase must then satisfy

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} - u \frac{\partial C}{\partial x}, \quad X(t) \leq x < \infty, \quad (\text{A.13})$$

with

$$u = \frac{dX}{dt} = V_s D \left. \frac{\partial C}{\partial x} \right|_{x=X(t)}, \quad (\text{A.14})$$

subject to the initial and boundary conditions

$$C(x, 0) = C_0, \quad x > X(t), \quad (\text{A.15})$$

$$C(X(t), t) = C^*, \quad t > 0, \quad (\text{A.16})$$

$$C(x, t) \rightarrow C_0, \quad x \rightarrow \infty, \quad t > 0, \quad (\text{A.17})$$

$$X(0) = 0. \quad (\text{A.18})$$

Problems such as Eqs. (A.13) to (A.18) which involve the solution of a diffusion equation in a moving-boundary domain are known as Stefan problems. A rich discussion on Stefan problems, including historical developments, solution techniques and solutions to archetypical problems can be found on Carslaw and Jaeger (1959, Chapter XI), Rubinshteĭn (1971), Crank (1984), Hill (1987). They are formulated in the context of heat conduction and phase change, but the application to diffusion of species and dissolution is normally straightforward.

A.1.2 Finite liquid phase

It is convenient to derive similar expressions for a domain where the liquid phase exists only on $x \leq L_l$, with a fixed concentration at $x = L_l$, and verify under which conditions the simulation of a bounded domain can be analyzed using the expressions obtained for a semi-infinite liquid phase, which are generally simpler.

For a bounded domain, the concentration $C(x, t)$ satisfies

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}, \quad X \leq x \leq L_l, \quad (\text{A.19})$$

subject to the initial and boundary conditions

$$C(x, 0) = C_0, \quad X < x \leq L_l, \quad (\text{A.20})$$

$$C(X, t) = C^*, \quad t > 0, \quad (\text{A.21})$$

$$C(L_l, t) = C_0, \quad t > 0, \quad (\text{A.22})$$

As shown by Crank (1975, page 50), the solution for Eq. (A.19) subject to Eqs. (A.20) to (A.22) is

$$\frac{C - C_0}{C^* - C_0} = - \left[\frac{x - X}{L_l - X} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left(n\pi \frac{x - X}{L_l - X} \right) \exp \left(- \frac{Dn^2\pi^2 t}{(L_l - X)^2} \right) \right]. \quad (\text{A.23})$$

Using Eq. (A.23) in Eq. (A.2) gives

$$\begin{aligned} N_s &= D \frac{C^* - C_0}{L_l - X} \left[1 + 2 \sum_{n=1}^{\infty} \exp \left(- \frac{Dn^2\pi^2 t}{(L_l - X)^2} \right) \right] = \\ &= D \frac{C^* - C_0}{L_l - X} \vartheta_3 \left(0, \exp \left(- \frac{D\pi^2 t}{(L_l - X)^2} \right) \right), \end{aligned} \quad (\text{A.24})$$

where $\vartheta_3(\cdot, \cdot)$ is one of the Jacobi theta functions (Abramowitz and Stegun, 1964, page 576).

Using Eq. (A.24) in Eq. (A.1) gives the equation for the evolution of the position of the fluid-solid interface

$$\frac{dX}{dt} = -S \frac{D}{L_l - X} \vartheta_3 \left(0, \exp \left(- \frac{D\pi^2 t}{(L_l - X)^2} \right) \right), \quad (\text{A.25})$$

where $S = (C^* - C_0)V_s$ is the solubility factor. The position of the fluid-solid interface can be obtained by integrating Eq. (A.25) numerically.

A.1.3 Approximating a semi-infinite liquid phase by a finite one

The ratio between the rates of dissolution per unit surface area for the bounded and the unbounded domains (ratio of Eq. (A.24) to Eq. (A.9)) is

$$\sqrt{\frac{D\pi t}{(L_l - X_b)^2}} \vartheta_3 \left(0, \exp \left(- \frac{D\pi^2 t}{(L_l - X_b)^2} \right) \right), \quad (\text{A.26})$$

where X_b is the position of the interface in the bounded domain case. This is the same as the ratio between the retreating velocity of the fluid-solid interface (ratio of Eq. (A.25) to Eq. (A.10)). By calling

$$\tau = \frac{Dt}{(L_l - X_b)^2}, \quad (\text{A.27})$$

this ratio can be written as

$$\sqrt{\pi\tau} \vartheta_3 \left(0, \exp \left(- \pi^2 \tau \right) \right). \quad (\text{A.28})$$

Some values of Eq. (A.28) as a function of τ are in Table A.1. For small value of τ , the evolution of the fluid-solid interface in the bounded domain is approximately the same as in the unbounded domain, in which case X_b can be approximated by Eq. (A.11), giving

$$\tau \approx \frac{1}{\left(\frac{L_l}{\sqrt{Dt}} + \frac{2S}{\sqrt{\pi}} \right)^2}, \quad (\text{A.29})$$

which is an increasing function of t . This is not surprising, since the concentrations in the liquid phase near the interface are the same for the bounded and unbounded system at $t = 0$, and differ more and more as time advances.

For a chosen maximum value for the ratio Eq. (A.28), there is a corresponding maximum value of τ so that we require $\tau < \tau^*$ for $t < t_s$, where t_s is the time for complete dissolution of the solid in the region $-L_s < x < 0$. Using the expression for t_s Eq. (A.12) in Eq. (A.29), we find a relation between L_s and L_l than gives a bounded system large enough to be well approximated by an unbounded system:

$$L_l > L_s \left(\frac{1}{2S} \sqrt{\frac{\pi}{\tau^*}} - 1 \right). \quad (\text{A.30})$$

Table A.1: Ratio between the rates of dissolution per unit surface area of a semi-infinite solid in a bounded and an unbounded domains.

τ	<i>ratio</i>
0	1
0.0689	$1 + 10^{-6}$
0.0819	$1 + 10^{-5}$
0.1010	$1 + 10^{-4}$
0.1316	$1 + 10^{-3}$
0.1887	$1 + 10^{-2}$

A.2 Dissolution of a solid sphere in a stagnant liquid

The derivations in this appendix are based on those of Rice and Do (2006), the difference being that we consider amount concentrations instead of mass concentration and neglect bulk flow effects in Fick's law (Bird et al., 1960, pg. 502) since the we also take the opportunity to estimate the error committed when using in a bounded domain their solution for the dissolution of a solid sphere in an unbounded liquid, and show that it is small.

For the slow dissolution of a sphere with time-dependent radius $R(t)$ in a stagnant liquid, the balance for the solid phase is given by

$$\frac{d}{dt} \left(\frac{1}{V_s} \frac{4\pi}{3} R^3 \right) = -4\pi R^2 N_s, \quad (\text{A.31})$$

where V_s is the molar volume of the solid phase (solid volume per unit amount of solid) and N_s is the rate of dissolution per unit surface area (amount of solid per unit surface area and unit time).

The rate of dissolution per unit surface area N_s is related to the diffusion flux by

$$N_s = -D \left. \frac{\partial C}{\partial r} \right|_{r=R}, \quad (\text{A.32})$$

where D is the diffusion coefficient, assumed to be the same for all aqueous species into which the solid dissolves, and C is the total amount concentration of the dissolved solid in the liquid phase.

In the liquid phase, the evolution of the concentration C is given by

$$D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t}, \quad R \leq r < \infty, \quad (\text{A.33})$$

subject to the boundary and initial conditions

$$C(R, t) = C^*, \quad t > 0, \quad (\text{A.34})$$

$$C(x, t) \rightarrow C_0, \quad r \rightarrow \infty, \quad t > 0, \quad (\text{A.35})$$

$$C(x, 0) = C_0, \quad r > R, \quad (\text{A.36})$$

where C_0 is the initial homogeneous concentration in the liquid phase and C^* is the solubility of the solid. As shown by [Rice and Do \(2006\)](#), the exact solution for this diffusion equation is

$$\frac{C^* - C}{C^* - C_0} = 1 - \frac{R}{r} + \frac{2}{\sqrt{\pi}} \frac{R}{r} \int_0^{\frac{r-R}{\sqrt{4Dt}}} e^{-z^2} dz = 1 - \frac{R}{r} \operatorname{erfc} \left(\frac{r-R}{\sqrt{4Dt}} \right), \quad (\text{A.37})$$

where $\operatorname{erfc}(\cdot)$ is the complementary error function. Using [Eq. \(A.37\)](#) in [Eq. \(A.32\)](#) gives

$$N_s = D \frac{C^* - C_0}{R} \left(1 + \frac{R}{\sqrt{\pi Dt}} \right). \quad (\text{A.38})$$

Using this in [Eq. \(A.31\)](#) gives the equation for the evolution of the sphere radius

$$\frac{dR}{dt} = -DS \left(\frac{1}{R} + \frac{1}{\sqrt{\pi Dt}} \right), \quad (\text{A.39})$$

where $S = (C^* - C_0)V_s$ is the solubility factor.

[Equations \(A.38\) and \(A.39\)](#), and the solubility factor differ from those presented by [Rice and Do \(2006\)](#) only in its units (amount concentration instead of mass concentration) and by not including bulk flow effects. Therefore, their analytical result for $R(t)$ and for the time to complete dissolution t_f are immediately applicable to our case and quoted here:

$$\ln \left[2S\tau + 2S \frac{R}{R_0} \sqrt{\frac{\tau}{\pi}} + \left(\frac{R}{R_0} \right)^2 \right] = \frac{2S}{\sqrt{2\pi S - S^2}} \left[\tan^{-1} \left(\frac{S + \frac{R}{R_0} \sqrt{\frac{\pi}{\tau}}}{\sqrt{2\pi S - S^2}} \right) - \frac{\pi}{2} \right], \quad (\text{A.40})$$

$$\tau_f = \frac{1}{2S} \exp \left\{ -\frac{2S}{\sqrt{2\pi S - S^2}} \left[\frac{\pi}{2} - \tan^{-1} \left(\frac{S}{\sqrt{2\pi S - S^2}} \right) \right] \right\}, \quad (\text{A.41})$$

where $\tau = tD/R_0^2$.

At a fixed position $r = R_e$, the minimum value for C is the initial value C_0 . From [Eqs. \(A.37\) and \(A.40\)](#) and given S , it is possible to calculate the maximum value

of $C(r = R_e, t)$, $0 < t < t_f$. If this maximum value is close to C_0 , we can replace the boundary condition $(C \rightarrow C_0, r \rightarrow \infty)$ by $(C = C_0, r = R_e)$ without departing much from the analytical solution derived above.

Table A.2 shows the maximum value of $\frac{C-C_0}{C^*-C_0} \times 10^2$ for some selected S and R_e/R_0 . For example, the table informs that for $S = 0.24$ the maximum concentration attained at $R_e/R_0 = 3.0$ equals $C_0 + 0.0074(C^* - C_0)$, so that setting a fixed value boundary condition $C = C_0$ at $R_e/R_0 = 3.0$ would introduce an error of at most $0.0074(C^* - C_0)$ on the concentration field of the liquid phase. Although this result does not offer a direct assessment of the impact of such boundary condition on the radius of the dissolving sphere, it gives a semiquantitative idea of the approximation made.

Table A.2: Maximum value of $\frac{C-C_0}{C^*-C_0} \times 10^2$.

S	R_e/R_0					
	3.00	3.20	3.40	3.60	3.80	4.00
0.10	4.33	3.41	2.69	2.12	1.67	1.32
0.12	3.35	2.57	1.97	1.51	1.16	0.88
0.14	2.60	1.94	1.45	1.08	0.80	0.59
0.16	2.02	1.47	1.07	0.77	0.56	0.40
0.18	1.58	1.11	0.79	0.55	0.39	0.27
0.20	1.23	0.84	0.58	0.39	0.27	0.18
0.22	0.96	0.64	0.43	0.28	0.18	0.12
0.24	0.74	0.48	0.31	0.20	0.13	0.08
0.26	0.58	0.36	0.23	0.14	0.09	0.05
0.28	0.45	0.27	0.17	0.10	0.06	0.03
0.30	0.35	0.21	0.12	0.07	0.04	0.02

DERIVATION OF THE ADVECTION-DIFFUSION EQUATION IN A POROUS DOMAIN

Consider a 3D Cartesian coordinate system and a lattice of cubes with faces perpendicular to the coordinate axes. The length of the side of the cube measures δx , each face has area A , and the point $P = (0, 0, 0)$ is the centre of the cube we consider as our control volume (CV). The points $E = (\delta x, 0, 0)$ and $W = (-\delta x, 0, 0)$ are the centre of neighbouring cubes to the “east” and “west” of the CV. The points $e = (\delta x/2, 0, 0)$ and $w = (-\delta x/2, 0, 0)$ are the centre of the faces separating the CV from the neighbouring cubes.

We derive the advection-diffusion equation for a porosity field $\phi(x, y, z, t) = \phi(x, t)$, an amount concentration field $C(x, y, z, t) = C(x, t)$ (measured in mol/m³), a Darcy velocity field $\mathbf{u}(x, y, z, t) = u(x, t)\mathbf{i}$ and an effective diffusion coefficient in the liquid phase $D^*(x, y, z, t) = D^*(x, t)$, which is in general different from the diffusion coefficient D measured in the liquid phase when it is not surrounded by a porous medium. It is worth emphasizing that C is the amount of species per volume of fluid, as opposed to amount of species per volume of the continuum domain.

The rate of change of the amount of a certain species in the CV equals the net inflow by advection and diffusion of the species into the control volume:

$$\frac{\partial}{\partial t}(A\delta x\bar{\phi}\bar{C}) = J_a + J_d, \quad (\text{B.1})$$

where J_a is the inflow rate by advection (in mol/s) into the CV, J_d is the inflow rate by diffusion (in mol/s) into the CV, and the overline ($\bar{\cdot}$) represents the average in the CV.

The inflow by advection is given by:

$$J_a = -u_e C_e A + u_w C_w A, \quad (\text{B.2})$$

where u_e and u_w are the Darcy velocities at points e and w . Since it is not the interstitial velocity, the porosity does not play a role in this expression.

By replacing u_e , u_w , C_e and C_w by their first-order Taylor expansion around P , we have

$$\begin{aligned}
 J_a &= A \left[- \left(u + \frac{\partial u}{\partial x} \frac{\delta x}{2} \right) \left(C + \frac{\partial C}{\partial x} \frac{\delta x}{2} \right) + \left(u - \frac{\partial u}{\partial x} \frac{\delta x}{2} \right) \left(C - \frac{\partial C}{\partial x} \frac{\delta x}{2} \right) \right]_P = \\
 &= -2A \left(u \frac{\partial C}{\partial x} \frac{\delta x}{2} + C \frac{\partial u}{\partial x} \frac{\delta x}{2} \right) = \\
 &= -A \delta x \left(u \frac{\partial C}{\partial x} + C \frac{\partial u}{\partial x} \right) = \\
 &= -A \delta x \frac{\partial(uC)}{\partial x}.
 \end{aligned} \tag{B.3}$$

The inflow by diffusion is given by

$$\begin{aligned}
 J_d &= \frac{\partial C}{\partial x} \Big|_e D_e^* A \phi_e - \frac{\partial C}{\partial x} \Big|_w D_w^* A \phi_w \approx \\
 &\approx \frac{C_E - C_P}{\delta x} D_e^* A \phi_e - \frac{C_P - C_W}{\delta x} D_w^* A \phi_w.
 \end{aligned} \tag{B.4}$$

In this expression, the porosity is needed because the area open to diffusive flow is the face pore area $A\phi$.

By replacing D_e^* , D_w^* , ϕ_e and ϕ_w by their first-order Taylor expansion around P , and C_E and C_W by their second-order Taylor expansion, we have

$$\begin{aligned}
 J_d &\approx A \left[\left(\frac{C + \frac{\partial C}{\partial x} \delta x + \frac{\partial^2 C}{\partial x^2} \frac{(\delta x)^2}{2} - C}{\delta x} \right) \left(D^* + \frac{\partial D^*}{\partial x} \frac{\delta x}{2} \right) \left(\phi + \frac{\partial \phi}{\partial x} \frac{\delta x}{2} \right) - \right. \\
 &\quad \left. - \left(\frac{C - \left(C - \frac{\partial C}{\partial x} \delta x + \frac{\partial^2 C}{\partial x^2} \frac{(\delta x)^2}{2} \right)}{\delta x} \right) \left(D^* - \frac{\partial D^*}{\partial x} \frac{\delta x}{2} \right) \left(\phi + \frac{\partial \phi}{\partial x} \frac{\delta x}{2} \right) \right]_P = \\
 &= A \left[\left(\frac{\partial C}{\partial x} + \frac{\partial^2 C}{\partial x^2} \frac{\delta x}{2} \right) \left(D^* + \frac{\partial D^*}{\partial x} \frac{\delta x}{2} \right) \left(\phi + \frac{\partial \phi}{\partial x} \frac{\delta x}{2} \right) - \right. \\
 &\quad \left. - \left(\frac{\partial C}{\partial x} - \frac{\partial^2 C}{\partial x^2} \frac{\delta x}{2} \right) \left(D^* - \frac{\partial D^*}{\partial x} \frac{\delta x}{2} \right) \left(\phi + \frac{\partial \phi}{\partial x} \frac{\delta x}{2} \right) \right]_P = \\
 &= 2A \left[\frac{\partial C}{\partial x} D^* \frac{\partial \phi}{\partial x} \frac{\delta x}{2} + \frac{\partial C}{\partial x} \frac{\partial D^*}{\partial x} \frac{\delta x}{2} \phi + \frac{\partial^2 C}{\partial x^2} \frac{\delta x}{2} D^* \phi + \frac{\partial^2 C}{\partial x^2} \frac{\delta x}{2} \frac{\partial D^*}{\partial x} \frac{\delta x}{2} \frac{\partial \phi}{\partial x} \frac{\delta x}{2} \right]_P = \\
 &= A \delta x \left[\frac{\partial C}{\partial x} D^* \frac{\partial \phi}{\partial x} + \frac{\partial C}{\partial x} \frac{\partial D^*}{\partial x} \phi + \frac{\partial^2 C}{\partial x^2} D^* \phi + \frac{(\delta x)^2}{4} \frac{\partial^2 C}{\partial x^2} \frac{\partial D^*}{\partial x} \frac{\partial \phi}{\partial x} \right]_P = \\
 &= A \delta x \left[\frac{\partial C}{\partial x} \frac{\partial(D^* \phi)}{\partial x} + \frac{\partial^2 C}{\partial x^2} D^* \phi + \frac{(\delta x)^2}{4} \frac{\partial^2 C}{\partial x^2} \frac{\partial D^*}{\partial x} \frac{\partial \phi}{\partial x} \right]_P \\
 &= A \delta x \left[\frac{\partial}{\partial x} \left(D^* \phi \frac{\partial C}{\partial x} \right) + \frac{(\delta x)^2}{4} \frac{\partial^2 C}{\partial x^2} \frac{\partial D^*}{\partial x} \frac{\partial \phi}{\partial x} \right]_P.
 \end{aligned} \tag{B.5}$$

Note that the second-order Taylor expansion of C_E and C_W is needed to keep $\frac{\partial C}{\partial x}$ approximated to the first order.

APPENDIX B. DERIVATION OF THE ADE IN A POROUS DOMAIN

By replacing Eq. (B.3) and Eq. (B.5) in Eq. (B.1), dividing both side by $A\delta x$, and taking the limit $\delta x \rightarrow 0$, we have

$$\frac{\partial}{\partial t}(\phi C) = -\frac{\partial(uC)}{\partial x} + \frac{\partial}{\partial x} \left(\phi D^* \frac{\partial C}{\partial x} \right). \quad (\text{B.6})$$

A similar derivation for three dimensions leads to

$$\frac{\partial}{\partial t}(\phi C) = -\nabla \cdot (\mathbf{u}C) + \nabla \cdot (\phi D^* \nabla C). \quad (\text{B.7})$$

Using an time integration procedure, Eq. (B.7) gives the change of ϕC between two time steps. Another relation would be required to find out how to distribute this change between ϕ and C . By assuming that ϕ is constant, we have

$$\phi \frac{\partial C}{\partial t} = -\nabla \cdot (\mathbf{u}C) + \nabla \cdot (\phi D^* \nabla C). \quad (\text{B.8})$$

It is customary to define an effective diffusion coefficient $D_{eff} = \phi D^*$ and write Eq. (B.8) as

$$\phi \frac{\partial C}{\partial t} = -\nabla \cdot (\mathbf{u}C) + \nabla \cdot (D_{eff} \nabla C). \quad (\text{B.9})$$

MEMORY REQUIREMENTS

To estimate the memory requirement, we used the simulation of the dissolution of a semi-infinite solid described in [Appendix A.1](#). We varied the number of liquid cells (L), solid cells (S) and species (N), and recorded the peak memory usage (M) reported in the field “Active” of `/proc/meminfo` in a Linux system when running version 52351a7 of the simulator. [Table C.1](#) shows the values of L , S , N and M for the different runs.

Table C.1: Peak memory usage of the simulator.

Liquid cells	Solid cells	Species	Peak memory usage KiB
760	5	9	23124
1520	5	9	37172
515	250	9	18628
265	500	9	14124
1025	500	9	28804
525	1000	9	19544
760	5	14	28848
1520	5	14	48324
515	250	14	22720
265	500	14	16616
1025	500	14	35844
525	1000	14	23148

We then adjust a surface of the form

$$M = c_L L + c_{LN} LN + c_S S + c_N N + c_I \quad (\text{C.1})$$

and obtain $c_L = 6.2$ KiB, $c_{LN} = 1.4$ KiB, $c_S = 0.66$ KiB, $c_N = 73$ KiB, $c_I = 8296$ KiB, with a fraction of variance unexplained by the regression of 0.031 %. This estimate was made for a 1D model. For a 3D model, the coefficients that depend solely on the number of cells may be lower because a larger fraction of points and faces will be

APPENDIX C. MEMORY REQUIREMENT

shared between the cells. In simulations that do not involve dissolution, the memory requirement is reduced because there is no need to map the fields before dissolution into the mesh after dissolution.

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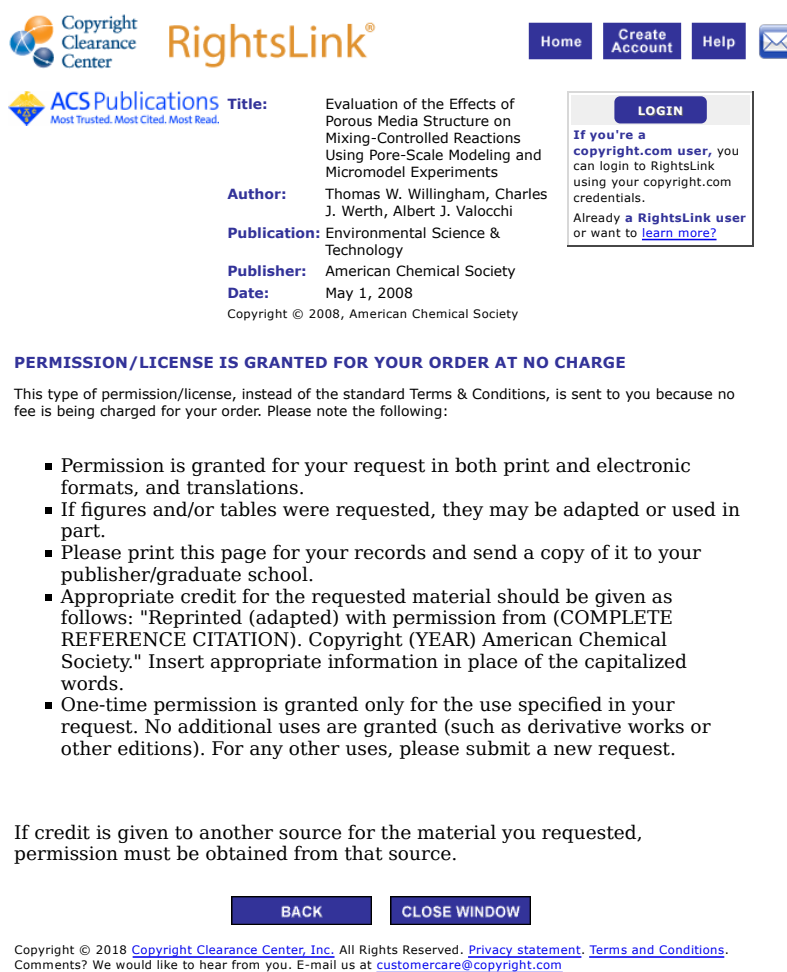
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