Imperial College Consortium on Pore-Scale Modelling

Yearly progress report

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Executive Summary
This is the annual report of the Imperial College Consortium on Pore-Scale Modelling. At our project meeting we will highlight the progress we have made over the last year as well as presenting plans for the future.

We have now developed a suite of tools for modeling single and multiphase flow and transport, using a combination of network modelling and simulation directly on images. Our current research is presently two-fold. The first is to use our current tools, combined with X-ray imaging, to assess the waterflood recovery potential of different rock types, with a particular emphasis on carbonates. The second is to extend our ability to simulate flow and transport directly on pore-space images, and then to use these tools to study fundamental behavior.

We are working on promising new methods to model multiphase flow in pore-space images using the volume of fluid method. This approach provides unrivalled insight into pore-scale displacement processes. This work has been used to analyse snap-off and the effect of capillary number and its control on residual saturation.

We are also extending our streamline-and-diffusion pore-scale dispersion model to handle reactive transport. This is an exciting and novel area of study, with many applications in contaminant transport, enhanced oil recovery and carbon dioxide storage. We will present our latest progress at the project meeting.

As mentioned last year, complementing our modelling has been the development of a large experimental programme, principally sponsored through the Qatar Carbonates and Carbon Storage Research Centre funded by Qatar Petroleum, Shell and the Qatar Science and Technology Park. A suite of new laboratory facilities to support this research was opened in 2012. The central theme of our work is fundamentals of complex fluid flow in porous media, using a combination of experiment and modelling. First, we use a variety of imaging techniques to image the pore structure of porous media at different length scales. Then we develop multi-scale simulation methods to calculate multi-phase and reactive flow directly on pore space images. We are now able to study of fluid configurations at the pore scale – at representative reservoir conditions – that can serve as severe tests for our modelling work. The first results from our new micro-CT facility will be presented at the meeting.

There are a number of PhD projects using these new experimental facilities and developing related modelling approaches that can help support the research of the Pore-Scale Consortium. This includes micro-fluidic studies of reactive transport in micro-models, Lattice-Boltzmann studies of multi-component flow in porous media and multi-scale imaging of porous media. New projects include experimental and numerical studies of hydrodynamic dispersion and reactive flow in porous media, reactive flow and asphaltene deposition in micro-fluidic micro-models, reactive transport in CO₂-cap rock systems, and multi-scale transport in nano-porous carbon. Some of these projects will be reviewed at the meeting.

The first part of this report is a paper recently accepted in Water Resources Research that presents a pore-network study of carbonates. Different generic behaviour is studied as a function of coordination number and wettability, based on images of different rock types, including two field samples from the Middle East. The results are compared with data in the literature and implications for waterflood recovery are discussed.

The second part is a detailed analysis of dispersion in bead packs, a sandstone and a carbonate that shows very good predictive agreement with experimental measurements of propagators (essentially concentration as a function of distance and time). This work extends our previous studies presented last year and has been accepted for publication in Physical Review E.
The third part continues the theme of dispersion and presents a comprehensive study of pre-asymptotic transport in different carbonates. As for multiphase flow, we see a wide range of behavior dependent on the connectivity of the pore structure. Here the principal determinant of the transport is the voxel-by-voxel velocity distribution. This work has been submitted to *Water Resources Research*.

The current researchers in the group are:

Martin Blunt, Professor of Petroleum Engineering – overall supervision and fundamental studies of three-phase flow.

Branko Bijeljic, Research Fellow – dispersion and reactive transport in porous media.

Edo Boek, Senior Lecturer in Chemical Engineering – fundamentals of flow in porous media and wettability.

Rafi Blumenfeld, Research Fellow – statistical analysis of granular packs.

Ali Raeini – 3rd year PhD student – Multiphase flow on pore-space images.

Zaki Al-Nahari – 3rd year PhD student – Reactive transport

João Paulo Nunes – 1st year PhD student – Reactive transport and multiphase flow

Chamsi Bouhafs – 1st year PhD student – Pore-scale modelling of shale gas

All our publications, theses, reports and presentations are available on our Website: [http://www3.imperial.ac.uk/earthscienceandengineering/research/perm/porescalemodelling](http://www3.imperial.ac.uk/earthscienceandengineering/research/perm/porescalemodelling)

**Project publications in 2012**

**Journal publications**


Conference proceedings

Our current sponsors are: BG, Petrobras, JOGMEC, Shell, Statoil and Total with iRock Technologies and Lithicon (formerly Numerical Rocks before their merger with DigiCore) as service company supporters. Petrobras joined the consortium this year, while Total now supports a related research programme on pore-scale network analysis. I would like to thank you all for your continued support that allows us to fund so many students and without which this research would not be possible.

Martin Blunt, London, January 2013
Part 1

The impact of wettability and connectivity on relative permeability in carbonates: a pore network modelling analysis

*Water Resources Research* (in press, 2013)

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Abstract

We use pore network modelling to study the impact of wettability and connectivity on waterflood relative permeability for a set of six carbonate samples. Four quarry samples are studied: Indiana, Portland, Guiting and Mount Gambier; and two subsurface samples obtained from a deep saline Middle Eastern aquifer. The pore space is imaged in three dimensions using X-ray micro-tomography at a resolution of a few microns. The images are segmented into pore and void and a topologically representative network of pores and throats is extracted from these images. We then simulate quasi-static displacement in the networks. We represent mixed-wet behaviour by varying the oil-wet fraction of the pore space. The relative permeability is strongly dependent on both the wettability and the average coordination number of the network. We show that traditional measures of wettability based on the point where the relative permeability curves cross are not reliable. Good agreement is found between our calculations and measurements of relative permeability on carbonates in the literature. The work helps establish a library of benchmark samples for multiphase flow and transport computations. The implications of the results for field-scale displacement mechanisms are discussed, and the efficiency of waterflooding as an oil recovery process in carbonate reservoirs is assessed depending on the wettability and pore space connectivity.

1. Introduction

Relative permeability curves describe the averaged flow behaviour of immiscible fluids and are universally used in large-scale flow predictions for applications in improved oil recovery, carbon dioxide storage and contaminant transport. Several excellent reviews that have investigated the physics of relative permeability are available [Raza et al., 1968; Anderson, 1987; Morrow, 1990]. In these papers it is demonstrated that relative permeability depends on wettability, pore structure and connectivity.

The direct measurement of relative permeability is often expensive and, for a single field, generally limited to a single displacement sequence on a limited number of samples at one wettability condition. Digital core analysis is a complement to this activity, allowing predictions of multiphase properties to be made for different samples, displacement sequences and wettability to be made easily, once verified against good-quality measurements on benchmark samples. The recent development of high-resolution imaging capabilities has enabled different rock types to be studied that serve as the basis for predictions of flow and transport properties [Arns et al., 2004; Knackstedt et al., 2006; Blunt et al., 2012].

It is estimated that more than half of the world’s remaining recoverable reserves of conventional oil are contained in carbonate reservoirs [Ahlbrandt et al., 2005]. Several experimental investigations and field results have shown that a large number of carbonate reservoirs present a heterogeneous wettability where a fraction of the pore space is water-wet and the remaining fraction is oil-wet [Treibar et al., 1971]. Brow and Fatt [1956] proposed the term fractional wettability to define a heterogeneous wettability where the wetting preference of the surface is randomly distributed throughout the pore space. Salathiel [1973] introduced the term mixed-wettability where larger pores are oil-wet whereas the smaller pores remain water-
wet. We will use the term mixed-wettability to characterize a heterogeneous wettability where the wetting preference of the porous medium is randomly distributed through the pore space.

Pore network modelling can successfully predict multiphase flow properties for sandstones, including the effects of wettability [Dixit et al. 1999; van Dijke and Sorbie, 2002; Al-Futaisi and Patzek, 2003; Oren and Bakke, 2003; Valvatne and Blunt, 2004]. Several recent studies have discussed improving traditional network modelling techniques to study carbonates. Sok et al. [2009] presented a multi-scale imaging methodology that better accounts of pore structure and connectivity in carbonates. Pore space registration was used to combine 3D and 2D images using micro-computed tomography, and focused ion beam and backscattered scanning electron microscopy. Ioannidis and Chatzis [2000] presented a dual network model that accounts of interconnected channels in vuggy carbonates by superimposing vugs on matrix blocks. They qualitatively compared the model predictions to measurements of capillary pressures. The results showed that qualitatively similar behaviour is observed. Dong et al. [2008] compared four different network extraction and reconstruction methods (medial axis, velocity based, grain recognition and maximal ball algorithms) on 3D images of sandstones and carbonates. Waterflood relative permeability predictions for water-wet cases showed similar behaviour for carbonates. They concluded that generally, maximal ball extraction and velocity based algorithms give similar predictions of multiphase properties.

However, only a few studies have investigated the relative permeability of carbonate samples. Al-Kharusi and Blunt [2008] presented a predictive workflow for carbonate samples based on 2D scanning electron microscopy images, statistical reconstruction, network extraction and modelling that was applied to a reservoir sample. Zhao et al. [2010] used pore network modelling to assess the impact of wettability for networks extracted from different types of rock: a sand pack, a Middle Eastern sandstone, Berea and a granular carbonate. Their results showed that for mixed-wet samples, optimal recovery occurs when a small fraction of the medium is water-wet. Bauer et al [2012] developed a dual method to account, in an averaged sense, for microporosity in carbonates and presented good predictions of relative permeability.

The main objective of this study is to analyze relative permeability for a set of carbonate samples with different connectivity and pore structure. The impact of wettability and connectivity on multiphase properties is then highlighted and the generic behaviour of relative permeability in carbonates is discussed. First, we briefly present our methodology and present the results obtained from the network models for different wettability. This is followed by a comparison of the computational results with measurements in the literature. Finally, we discuss the implications for field-scale recovery and we assess waterflooding efficiency in carbonate reservoirs.

2. Materials and methods

Six carbonate limestone samples are studied, four of which are quarry samples that were obtained from different locations: Portland limestone, an oolitic limestone of Jurassic age, containing peloids with inter-particular porosity, which is a standard building material; Indiana limestone, a Mississippian-age grainstone, that contains bivalve shell and peloids; Guiting carbonate, a Jurassic limestone, composed of 80% calcite and 17% quartz, where the pore space shows evidence of dissolution; and Mount Gambier limestone from the Oligocene age from Australia, composed of fragments of coral with some calcite. In addition two subsurface samples obtained from a high salinity aquifer in the Middle East are investigated: Middle Eastern Carbonate 1 (ME1) and Middle Eastern Carbonate 2 (ME2).

Small cylindrical cores (5 mm diameter and 25 mm in length) were drilled from larger cores at the native state. Upon the wet drilling, the samples were dried at an oven for approximately 1 hour at 30°C to ensure that no liquid was trapped inside the pore space. Dry scans of selected carbonate samples were made at the SYRMEP (Synchrotron Radiation for Medical Physics) beamline at the Elettra synchrotron in Trieste, Italy. The images were obtained using energies between 27-30 keV [Kaiser et al., 2010]. Two detectors were employed, with different effective pixel sizes 4.5µm (for Portland and Mount Gambier) and 3.85 µm for the rest of the samples. Images were recorded with a CCD camera located at a distance of 50 cm from the sample. The CCD camera binned the results, giving a final resolution of 9µm (for Portland and Mount Gambier) and 7.7 µm for the rest of the samples. For each topographic scan 1200 projections of the sample were acquired for equally spaced rotation angles over a total rotation.
of 180°; the scan lasted approximately 4 hours. In-house software at the SYRMEP beamline was used to reconstruct the 3D images and to eliminate noise and ring artefacts. The reconstructed images were composed of around 600³ voxels. Figure 1 shows 2D sections through the 3D images obtained.

3D images were first cropped into 3D cubic images of around 350³ voxels. The exact image dimensions are summarized Table 1. The 3D images were subsequently segmented into binary images based on a histogram analysis using Otsu’s thresholding algorithm in ImageJ software [Sahoo et al., 1988]. Based on the binary images, networks of pores and throats were extracted using the maximal ball algorithm [Dong and Blunt, 2009]. 3D visualizations of the extracted networks are shown in Figure 2.
A detailed description of the extracted networks is provided Table 1. The samples cover a wide range of average coordination numbers: ME1 and Portland are poorly connected with coordination numbers of approximately 2.5 whereas Guiting and Mount Gambier are highly connected with average coordination numbers of 5.1 and 7.4 respectively. As we show later, the average coordination number (average number of throats connected to a single pore) is a
key determinant of relative permeability and residual saturation. It is derived from the network extraction analysis and is an indicator of the connectivity of the void space.

The pore and throat distributions of the networks are presented in Figures 3 and 4.

<table>
<thead>
<tr>
<th></th>
<th>ME1</th>
<th>Portland</th>
<th>Indiana</th>
<th>ME2</th>
<th>Guiting</th>
<th>Mount Gambier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voxel resolution (µm)</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
<td>9</td>
</tr>
<tr>
<td>Number of voxels (mm³)</td>
<td>380³</td>
<td>320³</td>
<td>330³</td>
<td>320³</td>
<td>350³</td>
<td>350³</td>
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<tr>
<td>Physical Volume (mm³)</td>
<td>25.05</td>
<td>23.89</td>
<td>16.41</td>
<td>14.96</td>
<td>19.57</td>
<td>31.26</td>
</tr>
<tr>
<td>Number of pores</td>
<td>55828</td>
<td>6129</td>
<td>5653</td>
<td>10855</td>
<td>25707</td>
<td>22665</td>
</tr>
<tr>
<td>Number of throats</td>
<td>70612</td>
<td>7939</td>
<td>8539</td>
<td>20071</td>
<td>66279</td>
<td>84593</td>
</tr>
<tr>
<td>Total number of elements</td>
<td>126440</td>
<td>14068</td>
<td>14192</td>
<td>30926</td>
<td>91986</td>
<td>107258</td>
</tr>
<tr>
<td>Average coordination number</td>
<td>2.50</td>
<td>2.53</td>
<td>2.97</td>
<td>3.64</td>
<td>5.11</td>
<td>7.41</td>
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<td>Min pore radius (µm)</td>
<td>7.7</td>
<td>9</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
<td>9</td>
</tr>
<tr>
<td>Max pore radius (µm)</td>
<td>51.52</td>
<td>93.51</td>
<td>99.48</td>
<td>107.82</td>
<td>74.09</td>
<td>119.88</td>
</tr>
<tr>
<td>Average pore radius (µm)</td>
<td>8.44</td>
<td>14.89</td>
<td>10.17</td>
<td>10.90</td>
<td>11.16</td>
<td>18.17</td>
</tr>
<tr>
<td>Average aspect ratio</td>
<td>1.87</td>
<td>2.28</td>
<td>1.88</td>
<td>2.08</td>
<td>2.00</td>
<td>2.59</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>14.37</td>
<td>9.32</td>
<td>13.05</td>
<td>18.60</td>
<td>29.79</td>
<td>56.27</td>
</tr>
<tr>
<td>Permeability (m²)</td>
<td>3.23×10⁻¹⁴</td>
<td>1.37×10⁻¹³</td>
<td>5.69×10⁻¹³</td>
<td>9.40×10⁻¹³</td>
<td>3.72×10⁻¹³</td>
<td>2.20×10⁻¹¹</td>
</tr>
</tbody>
</table>

Table 1. Description of the extracted networks. Average coordination number is the average number of throats connected to each pore. The average aspect ratio is the average of the ratio of the pore radius to the mean radius of the throats connected to it. The permeability is computed from a flow simulation through the network.
Figure 3. Pore inscribed radius distributions in microns for (a) Middle Eastern sample 1 (b) Portland limestone (c) Indiana limestone (d) Middle Eastern sample 2 (d) Guiting carbonate and (f) Mount Gambier limestone. In this and subsequent figures, samples are presented in order of increasing coordination number: from a low connectivity sample (a) to a very high connectivity sample (f).
Microporosity. Thin section analysis of some of the samples indicates that the samples contain microporosity. There are small pores below the resolution of the scans (7.7 µm and 9 µm) and the grains are, in most cases, themselves porous. In our methodology we neglect the role of microporosity in the computation of multiphase properties: we assume that microporosity is poorly connected does not impact our relative permeability predictions. In reality, most of the microporosity will remain water-filled throughout the displacement sequence. This will result in an apparent connate or irreducible water saturation which we do not capture and may lead to a larger water relative permeability than calculated here [Oren et al., 1998; Blunt et al., 2002]. This is discussed later in the paper.

Methodology and overview of the network simulations
Capillary controlled displacement is simulated using the pore network model developed by Valvatne and Blunt [2004]. Initially the medium is assumed to be filled with the wetting phase (brine) and oil is then injected. After oil invasion, we alter the wettability of the pore spaces in direct contact with oil to represent mixed-wet conditions. Waterflooding is then simulated and relative permeability curves are generated.

We study the impact of wettability in mixed-wet media where some fraction, $f$, of the pore space occupied by oil is made oil-wet and a fraction $1-f$ remains water-wet. We vary the oil-wet fraction from zero (a strongly water-wet case) to 1 (strongly oil-wet rock). In addition to modelling mixed-wet media, this methodology reproduces wettability alteration which is due to asphaltene deposition/precipitation in carbonates. This alteration, governed by oil composition, brine salinity and rock mineralogy is difficult to predict a priori.

Where oil has been in contact with the carbonate surface (pores and throats), random contact angles with no spatial correlation are assigned with different distributions – given in Table 2 – for the water-wet and oil-wet pores and throats.
**Layer Flow.** The 3D networks are composed of individual elements (pores and throats) with circular, triangular or square cross-sectional shapes. Using square or triangular-shaped networks elements allows for the explicit modelling of wetting layers where non-wetting phase occupies the centre of the element and wetting phase remains in the corners. The pore space in carbonates is highly irregular with water remaining in the grooves and crevices after primary oil flooding due to capillary forces. The wetting layers might not be more than a few microns in thickness, with little effect on the overall saturation or flow. Their contribution to wetting phase connectivity is, however, of vital importance, ensuring low residual wetting phase saturation by preventing trapping. Wetting layers of water are always present in the corners, while layers of oil-sandwiched between water in the corners and water in the centre can be observed in oil-wet regions. Layer drainage is when oil flows in these layers, allowing, slowly, very low saturations to be reached.

<table>
<thead>
<tr>
<th>Input parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial contact angle (degrees)</td>
<td>0</td>
</tr>
<tr>
<td>Interfacial tension (mN/m)</td>
<td>48.3</td>
</tr>
<tr>
<td>Water-wet contact angles (degrees)</td>
<td>0-60</td>
</tr>
<tr>
<td>Oil-wet contact angles (degrees)</td>
<td>100-160</td>
</tr>
<tr>
<td>Oil viscosity (mPa.s)</td>
<td>0.547</td>
</tr>
<tr>
<td>Water viscosity (mPa.s)</td>
<td>0.4554</td>
</tr>
</tbody>
</table>

Table 2. Input parameters for relative permeability computations. Values of viscosity were obtained from Pentland et al. [2010].

**3. Results**

Five wettability distributions are studied: \( f=0, \ f=0.25, \ f=0.5, \ f=0.75 \) and \( f=1 \). Figure 5 shows a completely water-wet case (\( f=0 \)) as a reference. As expected, water remains in the smallest portions of the pore space, giving very low water relative permeability and significant trapping of oil in the larger pores at the end of waterflooding, mainly caused by snap-off. In the case of poorly connected carbonates (ME1, Portland and Indiana limestones), up to 75% of the pore space can be trapped. However, for the better connected networks, namely ME2, Guiting and Mount Gambier, the water relative permeability is higher and there is less trapping (there are more pathways for the oil to escape), although the residual saturation is around 40% or higher in all cases.

Figure 6 shows a mixed-wet case with \( f=0.25 \). A small fraction of oil-wet pores tends to increase the amount of oil trapping, particularly in the less connected networks where now there is little or no range of saturation when two phases flow simultaneously, except very slow flow in wetting layers. The water phase connectivity is reduced and the water relative permeability is in general lower than the strongly water-wet case. The water-wet regions fill first in a capillary-controlled displacement at the pore scale: these are the small pores and poorly connected; however, they surround most of the oil-wet pores that are then trapped. These pores cannot then be displaced during forced water injection, which explains the increase in residual oil saturation. Here again, for the highly connected networks, the water relative permeability is higher since the water has more possible pathways through the system and there is both spontaneous and forced displacement by water.
Figure 5. Waterflood relative permeability for the strongly water-wet case (f=0). Curves are presented in order of increasing connectivity. (a) Middle Eastern sample 1. (b) Portland limestone. (c) Indiana limestone. (d) Middle Eastern sample 2. (d) Guiting carbonate. (f) Mount Gambier limestone.
When the fractional wettability is 0.5, an equal mix of water-wet and oil-wet pores, at low water saturations, a similar behaviour is observed regardless of the connectivity of the pore space (Figure 7). At the beginning of the water flooding, the water is still poorly connected and flows only through the smallest water-filled pores and thin wetting layers of the pore space; therefore the water relative permeability is low. However, in an equal mix of water-wet and oil-wet fractions of the pore space, depending on the connectivity, an important increase in the water relative permeability is noticeable. After spontaneous imbibition, a significant forced displacement of oil occurs as the oil-wet pores and throats connect through the network. The residual oil saturation is generally lower since oil remains connected in the oil-wet region in layers. This effect is noticeable in the shape of the oil relative permeability, for the well-connected samples, that show a long region where the oil relative permeability is very low, but there is still displacement – this behaviour is controlled by slow flow in oil layers [Salathiel, 1971]. The poorly connected samples still show a water-wet controlled behaviour, where there is a sharp decrease in the oil relative permeability and significant trapping. Here there is little connectivity of the oil-wet regions and as a consequence layer drainage is unable to achieve low residual saturations. In addition, the maximum water relative permeability varies from very low to very high values dependent on the degree of trapping and the connectivity of the water phase. Where the residual saturation is low, water can fill most of the pore space – and the larger pores in the oil-wet regions – and has a high end-point value. A wide range of behaviour is seen in this case dependent on the pore structure of the medium.

When the oil-wet fraction is higher, f=0.75 (Figure 8), the residual saturation is now very low as the oil remains connected in layers throughout the displacement. The water relative...

Figure 6. Waterflood relative permeability for the mixed-wet case (f=0.25). Curves are presented in order of increasing connectivity. (a) Middle Eastern sample 1. (b) Portland limestone. (c) Indiana limestone. (d) Middle Eastern sample 2. (d) Guiting carbonate. (f) Mount Gambier limestone.
permeability can rise to high values in all cases as the water fills the centres of the larger regions of the pore space. This is a sign of a more typical oil-wet behaviour with displacement over a wide saturation range and low relative permeabilities of both oil and water at low saturations of their respective phases, controlled by wetting layer flow [Valvatne and Blunt, 2004]. This behaviour is generically similar to network modelling calculations for sandstones [Valvatne and Blunt, 2004; Zhao et al., 2010]. The jumps in some of the curves reflect the relatively small size of the networks studied: improvements in imaging should soon allow larger networks to be constructed.

Figure 7. Waterflood relative permeability for the mixed-wet case (f=0.5). Curves are presented in order of increasing connectivity. (a) Middle Eastern sample 1. (b) Portland limestone. (c) Indiana limestone. (d) Middle Eastern sample 2. (e) Guiting carbonate. (f) Mount Gambier limestone.
Figure 8. Waterflood relative permeability for the mixed-wet case (f=0.75). Curves are presented in order of increasing connectivity. (a) Middle Eastern sample 1. (b) Portland limestone. (c) Indiana limestone. (d) Middle Eastern sample 2. (d) Guiting carbonate. (f) Mount Gambier limestone.

Figure 9 shows the case of the fully oil-wet case (f=1). The behaviour is generally quite similar to that observed for the mixed-wet case (f=0.75): very low residual oil saturation, a prolonged layer drainage regime (low oil relative permeability at low oil saturation) and high end-point water relative permeability.
Figure 9. Waterflood relative permeability for the strongly oil-wet case ($f=1$). Curves are presented in order of increasing connectivity. (a) Middle Eastern sample 1. (b) Portland limestone. (c) Indiana limestone. (d) Middle Eastern sample 2. (e) Guiting carbonate. (f) Mount Gambier limestone.

Analysis of results
In order to summarize the previous description, we analyze the impact of wettability and average coordination number on the relative permeability behaviour. The evolution of residual oil saturation with the fractional wettability (Figure 10) shows that the residual oil saturation reaches a maximum for the fractionally-wet case with $f=0.25$, and then decreases sharply to very low saturations as the medium becomes more oil-wet. Waterflooding gives a high local displacement efficiency for the cases $f=0.75$ and $f=1$, where the behaviour is controlled by oil layers.
Figure 10. Residual oil saturation as a function of fractional wettability for: Guiting (triangles), Indiana (rectangles), Portland (circles), Mount Gambier (diamonds), Middle Eastern sample 1 (crosses), and Middle Eastern sample 2 (stars).
Figure 11. Residual oil saturation as a function of the average coordination number for: Guiting (triangles), Indiana (rectangles), Portland (circles), Mount Gambier (diamonds), Middle Eastern sample 1 (crosses), and Middle Eastern sample 2 (stars).

The impact of connectivity on the residual oil saturation is shown Figure 11. The residual oil saturation tends to decrease with increasing connectivity, regardless of wettability.

One indication of waterflood displacement efficiency that is used to characterize the wettability is the water saturation value at which the oil and water relative permeabilities are equal ($S_w$ where $k_{rw} = k_{ro}$) [Craig, 1971]. For water saturations higher than the crossover saturation, waterflooding becomes less efficient, since (for equal viscosities) more water flows than oil. The water saturation at the cross-over as a function of wettability for the different carbonate samples is shown in Figure 12. In most cases, the water saturation is highest for the mixed-wet case $f=0.75$. This confirms that waterflooding is most effective for mixed-wet carbonates that have preference to an oil-wet behaviour. The smallest water saturation at the crossover point is reached for the water-wet and weakly mixed-wet cases ($f=0.25$): these are least efficient for waterflooding. This contrasts with traditional analyses of relative permeability that suggests that the cross-over point is at more than 50% water saturation for water-wet cases and less than 50% water saturation for mixed-wet or oil-wet samples [Craig, 1971]. We only see this trend in the near oil-wet region; this rule does not apply in general because of the low estimated water relative permeability.
Figure 12. The water saturation at the relative permeability cross-over point ($S_w$ where $k_{rw}=k_{ro}$) with fractional wettability for Guiting (triangles), Indiana (rectangles), Portland (circles), Mount Gambier (diamond), Middle Eastern sample 1 (crosses), and Middle Eastern sample 2 (stars).

**Comparison with measured data**

We compare our computations to measurements found in the literature on reservoir carbonate samples. The approach is not necessarily predictive as scans of the reservoir samples and an independent measurement of wettability are not available: we simply make an assessment if the estimated connectivity and wettability are plausible for the experimental sample studied. Also, the objective of this comparison is not to have a perfect match between the laboratory measurements and the results of the network modelling by fine-tuning the oil-wet fraction or the contact angles; rather, the goal is to determine if our calculated behaviour is supported by the available experimental evidence and discuss the impact of wettability and pore structure on field-scale recovery.

We study three sets of waterflood relative permeabilities measured on Middle Eastern carbonate reservoir samples. A summary of the petrophysical and geological description of the samples is provided in Table 3.
| Case 1. Al-Sayari [2009] measured steady-state waterflood relative permeability on an aged (restored state) reservoir carbonate sample from the Middle East. Through analysis of thin sections, mercury injection capillary pressure and NMR response, the reservoir sample was described as having a well-connected pore structure with a relatively low fraction of microporosity.

A similar relative permeability to that measured can be observed for the case of $f=0.25$ for the well-connected Guiting and Mount Gambier networks (Figure 13). The relatively low residual oil saturation and the shape of the oil relative permeability curve indicate a mixed-wet behaviour. For Guiting, the discrepancies in the water relative permeability can be explained by the un-resolved microporosity.
Figure 13. Comparison between waterflood relative permeability measurements from a Middle Eastern reservoir (oil relative permeability, circles, water relative permeability, crosses; Al-Sayari [2009]) with (a) Guiting limestone and (b) Mount Gambier limestone for a fractional wettability of \( f = 0.25 \).

**Case 2.** Meissner et al. [2009] performed detailed measurements on several samples from the Arab-D reservoir of the Dukhan field, onshore Qatar. They reported the results of several steady-state relative permeability tests for oil/brine and gas/oil systems. Results were reported for both native and the restored state cores. The results were reported in terms of normalized saturations and relative permeabilities:

\[
S_{\text{WR}} = \frac{(S_W - S_{WR})}{(1 - S_{WR}) - S_{\text{orw}}} \tag{1}
\]

where \( S_{\text{WR}} \), the initial water saturation, is determined after primary drainage and \( S_{\text{orw}} \) is the residual oil saturation determined by extrapolation of the oil relative permeability as it asymptotically approaches zero. This is only slightly different from the true residual oil saturation \( S_{\text{or}} \) that is best determined through the waterflood capillary pressure.

In this case, to introduce an initial water saturation, we set the maximum primary drainage capillary to be equal to 690 KPa (approximately 100 psi). This value is chosen based on the different capillary pressure measurements that showed a sharp increase in the pressure for an average pressure of around 100 psi.

Figure 14 shows a comparison between the four measurements reported of water/oil relative permeability on the native state subsurface cores with the relative permeability generated for the strongly oil-wet case \( f = 1 \) for ME1. The suggestion here is that the reservoir is strongly oil-wet with a structure similar to that observed in the subsurface sample from which we extracted a network.
Figure 14. A comparison between the waterflood relative permeability for the Middle Eastern sample 1, for a strongly oil-wet case $f=1$ with measurements on native state subsurface reservoir cores (oil relative permeability, circles, and water relative permeability, crosses) obtained from Meissner et al. [2009].

**Case 3.** Okasha et al., [2007] reported unsteady-state relative permeability measurements on carbonate reservoir samples from the Arab-D reservoir of the Ghawar field in Saudi Arabia. This is the world’s largest conventional oilfield. Three data sets were presented for three samples obtained from different areas of the Ghawar field: Utmaniyah, Hawiyah and Haradh. Here, since the measured values are presented in a non-normalized form; we simply compare with the data, without changing the initial water saturation.

Figure 15 shows a good agreement between the measurements and the relative permeability generated by network modelling for the mixed-wet Mount Gambier network ($f=0.25$) for one of the three samples. Note that we suggest that in this field the wettability and pore structure are different from the subsurface Middle Eastern sample in the previous section. Figure 16 shows good agreement for the second measured sample with low connectivity carbonates i.e. Portland and ME1 for a strongly oil-wet case. The difference of the wettabilities is evidence of local variations of wettability within the reservoir.

Good agreement was not obtained for the third sample which had high connate water saturation. This limitation in our modelling will be discussed later.

**Implications for field-scale recovery**

In waterflooding, for oil and water of similar viscosity, the saturation at which the relative permeabilities cross - as discussed above – gives a useful and simple indicator of the recovery. For water saturations beyond the crossover point, more water will be produced than oil. Our simulations, Figure 12, indicate that the optimal waterflood efficiency is observed for a mixed-wet system with a large fraction of oil-wet pores, around 0.75. The highest waterflood efficiency is implied for the less well-connected samples, since in these cases the waterflood relative permeability is very low and this holds back the movement of water, allowing oil to be displaced. For better connected samples, there is less sensitivity to wettability and overall a lower crossover saturation, indicating less favourable recoveries.
This is a somewhat surprising conclusion and implies that waterflooding in mixed to oil-wet carbonates of poor pore-space connectivity may be an effective process. This behaviour stands in contrast to sandstones, where network modelling studies indicate that more neutrally-wet conditions provide optimal recovery [Øren et al, 1998; Valvatne and Blunt, 2004]. Moreover, experimental measurements presented by Jadhunandan and Morrow [1995] have shown that oil recovery by waterflooding in sandstones reach a maximum at close to neutral wettability.

However, there is one complexity that we have not addressed. Many carbonate reservoirs are extensively fractured. In these cases, waterflooding rapidly invades the fractures, while recovery from the lower permeability matrix (the rock studied here) is mediated by a balance of viscous, gravitational and capillary forces. In these circumstances, it is better to have a more water-wet system to allow capillary imbibition into matrix [Blunt et al, 2012]. A discussion of this is beyond the scope of this paper, but we note that both geological structure and multiphase flow properties impact displacement efficiency and overall recovery.

Figure 15. Mount Gambier waterflood relative permeability for the mixed-wet case with an oil-wet fraction of f=0.25 (solid) compared to measurements on a reservoir sample obtained from Okasha et al. [2007] (oil relative permeability, circles, and water relative permeability, crosses).
Figure 16. Middle Eastern sample 1 (right) and Portland limestone (left) waterflood relative permeability for the strongly oil-wet case with an oil-wet fraction of $f=1$ (solid) compared to measurements on reservoir samples obtained from Okasha et al. [2007] (oil relative permeability, circles, and water relative permeability, crosses).

**Limitations of the analysis**

There are three major limitations of the work we have presented. The first is that the images on which the network extraction is based have a resolution of around 8 µm, meaning that significant fractions of the pore space in intra-granular porosity or other small features cannot be resolved. This leads to two problems with our analysis. First, we tend to find rather low water relative permeabilities, since we only allow the water to flow through the larger pores that we capture in the imaging: in reality water is likely to fill most of the microporosity as well, leading to better connectivity, particularly at low water saturation. Second, for most imposed capillary pressures in primary drainage, as mentioned above, the microporosity will remain largely water-filled, leading to an apparent connate water saturation. This is not captured in our models, which allow the pore space to be drained to effectively zero saturation. To image microporosity adequately would require resolutions of around 0.1 µm or better, limiting scans to small samples: a realistic model of a carbonate needs to employ a multi-scale approach that combines microporosity – possibly in a statistical sense – with an explicit description of the connectivity of the larger pores [Bauer et al., 2012].

The second limitation is our treatment of oil layers and pore geometry. We allow oil layers to be present in pores and throats of triangular cross-section if it is possible to construct such a layer geometrically. In reality, the formation and collapse of layers is controlled by thermodynamic stability constraints that are, in general, more severe. We tend to underestimate the residual oil saturation in mixed-wet and oil-wet systems. Furthermore, the use of more complex pore shapes, such as multi-pointed stars, allows a richer description of corner and layer flow. These features have been implemented into network models [Ryazanov et al., 2009; Sorbie et al., 2011] but not considered here.

The third limitation concerns our assignment of contact angle. This is done at random from uniform distributions for water-wet and oil-wet regions. There is not direct confirmation that this is indeed a representative wettability condition. The characterization of wettability at the pore scale remains a topic for future work.

**Conclusions**

We have studied the impact of wettability and connectivity on relative permeability for a set of carbonate samples with different pore structures using pore network modelling. Both connectivity and the wetting state of the porous media affect the relative permeability. The impact of wettability alteration is less pronounced in highly connected carbonates. We suggest
that waterflooding leads to higher recovery for mixed-wet systems with a high fraction of oil-wet pores (around 75%) compared to strongly water-wet or oil-wet cases. We show that waterflooding leads to lower residual oil saturation in the case of highly connected samples, but that recovery is most effective for the poorly connected samples under mixed-wet conditions.

A comparison of the generated results with measurements obtained from carbonate reservoirs showed similar behaviour and confirmed the capabilities of the network modelling to reproduce the relative permeability observed in mixed and oil-wet reservoir carbonate samples.

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Part 2

Predictions of non-Fickian solute transport in different classes of porous media using direct simulation on pore-scale images


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Abstract

We present predictions of transport through micro-CT images that includes the analysis of correlation structure, velocity and the dynamics of the evolving plume. We simulate solute transport through millimeter-sized three-dimensional images of a beadpack, a sandstone and a carbonate, representing porous media with an increasing degree of pore-scale complexity. The Navier-Stokes equations are solved to compute the flow field and a streamline simulation approach is used to move particles by advection, while the random walk method is employed to represent diffusion. We show how the computed propagators (concentration as a function of displacement) for the beadpack, sandstone and carbonate depend on the width of the velocity distribution. A narrow velocity distribution in the beadpack leads to the least anomalous behavior, where the propagators rapidly become Gaussian in shape; the wider velocity distribution in the sandstone gives rise to a small immobile concentration peak, and a large secondary mobile peak moving at approximately the average flow speed; in the carbonate with the widest velocity distribution, the stagnant concentration peak is persistent, with a slower emergence of a smaller secondary mobile peak, characteristic of highly anomalous behavior. This defines different types of transport in the three media and quantifies the effect of pore structure on transport. The propagators obtained by the model are in excellent agreement with those measured on

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1. Introduction

Solute transport in porous media is of importance in a broad range of scientific fields and engineering applications, notably for contaminant migration in subsurface hydrology [1,2], geological storage of carbon-dioxide[3], packed bed reactors and chromatography in chemical engineering[4,5], and tracer studies and miscible displacement in enhanced oil recovery [1,6]. A considerable body of research has been devoted to describe transport that results in a non-linear growth of the variance of displacement with time. These processes cannot be described by the solution of the governing transport equations in a homogeneous medium with Fick’s law used to describe the dispersive flux; hence this type of transport is said to be non-Fickian [2].

The interplay of simple physical processes – advection and diffusion – results in a rich macroscopic transport behavior that is a consequence of the wide range of local flow speeds experienced by the moving particles, combined with local mixing (see recent reviews [2,7] and references therein). The non-Fickian nature of dispersive processes in heterogeneous porous media has been demonstrated experimentally from pore to field scales [8-16]. However, the predictive understanding of the relationship between pore structure, the velocity field and transport is still limited. Our goal is to investigate and explain the origin of non-Fickian transport behavior as a function of pore-scale heterogeneity by simulating flow and solute transport directly on micro-CT
images of pore space in simple homogeneous beadpacks and more complex geological porous media, namely sandstone and carbonate rocks.

In the asymptotic limit, assuming that the porous medium is homogeneous, when the velocity field is fully sampled by solute, macroscopic transport parameters, such as the dispersion coefficient $D$, are constant and can be used in an averaged advection-dispersion equation. However, until the velocity field is fully sampled, transport is non-Fickian and $D$ possesses temporal or spatial variation. This variation is observed in varying plume shapes and the corresponding description of the probability density function (PDF) of either displacement or transit times of the solute particles. These PDFs have been studied experimentally by Nuclear Magnetic Resonance (NMR) measurements on unconsolidated beadpacks [12, 17-21] and samples of geological rock [12, 22-27]. Notable progress has been made in matching the experimental NMR propagator data with numerical models that either simulate transport directly on the pore space of the beadpacks [19,20,28], sandstones [22,29] and a carbonate [30], or use pore networks extracted from micro-CT images in a sandstone [31] and dolomite [27].

A landmark comparative experimental NMR study of propagators in a beadpack, a sandstone and a carbonate rock was presented by Scheven et al. [12]. This study has demonstrated that the propagators measured in the beadpack rapidly reach a symmetric Gaussian-like shape about the mean displacement, consistent with Fickian transport; however for Bentheimer sandstone and Portland carbonate two asymmetric peaks for stagnant and mobile fluid are observed at different observation times. In Bentheimer sandstone, at early times there is a pronounced peak representing the
stagnant fluid regions that gradually disappears over time with the emergence of a dispersed plume of mobile fluid approximately centered about the mean displacement. A much larger stagnant peak is observed for Portland carbonate that persists for longer times – consequently the formation of a highly dispersed mobile plume is delayed.

No predictive model has been able to explain the relationship between pore structure, velocity field and transport. In this study we examine the non-Fickian behavior of solute transport simulated directly on micro-CT images of the pore space. We simulate solute transport through three-dimensional images of a beadpack (a disordered close packing of spheres), Bentheimer sandstone and Portland carbonate, representing porous media with an increasing degree of pore-scale complexity. The Navier-Stokes equations are solved to compute the flow field. A streamline method is used to represent advection, while a random walk approach models diffusive transport.

In earlier work, we have used this approach to study transport in a sandpack, sandstone and carbonate to compute the distribution of transit time across image voxels and to predict the asymptotic dispersion coefficient [30,29]. We showed good agreement between NMR-measured and predicted propagators at one time for Bentheimer sandstone and Portland carbonate [29,30]. Herein, we extend this work to provide a more detailed and accurate comparison with experiment at all the times measured for the three media listed above. Moreover, we explain the results in terms of the distribution of velocities in the pore space. We present a methodology for making transport predictions on micro-CT images that includes analyses of
variograms of porosity and velocity, the velocity fields and velocity distributions, and the dynamics of the evolving plume.

2. Images, Mathematical Model and Flow Fields

Our transport simulations require a description of the pore space, a method for calculating the flow field, and a particle tracking method for moving solute by advection and diffusion.

2.1 Pore-space images

We study transport in the three porous media mentioned in the Introduction, with increasing pore-scale complexity. First is an experimental beadpack image with $300^3$ voxels comprised of a disordered close packing of spherical grains of the same size$[32,33]$ with diameter $d_g = 100\mu m$; the porosity is $35.93\%$ and the permeability is $5.63 \times 10^{12}m^2$. Second is a Bentheimer sandstone $300^3$ micro-CT image with a porosity of $21.51\%$ and permeability $3.53 \times 10^{12}m^2$. Third is a Portland limestone $320^3$ X-ray synchrotron image with a porosity of $8.62\%$ and permeability $2.47 \times 10^{13}m^2$. The porosity and permeability values were computed on the images. The porosity is calculated as the ratio of number of pore voxels, $N_{pvox}$ divided by total number of voxels, $N_{vox}$. The voxels that have no connection through the pore space to either the inlet or outlet are excluded from the flow calculations and further analysis.

The voxel sizes are $2\mu m$, $3\mu m$ and $9\mu m$ for the beadpack, Bentheimer sandstone, and Portland carbonate respectively. The images have been binarized into solid and void, which for the abovementioned image sizes, represent cubes of side length of $0.6mm$, $0.9mm$ and $2.88 mm$ for the beadpack, Bentheimer sandstone, and Portland carbonate respectively. Figures 1a-c shows two-dimensional cross-sections of the segmented
image of the beadpack and the gray scale images for Bentheimer sandstone and Portland carbonate.

The dry scan image for Bentheimer sandstone was acquired on a cylindrical core of 5 mm diameter and length 25 mm with an Xradia Versa micro-CT scanner (provided by iRock Technologies). The dry scan image for Portland carbonate was acquired on a cylindrical core of the same size with a synchrotron beamline (SYREMP beamline at the ELETTRA synchrotron in Trieste, Italy) at a resolution of 9 µm, corresponding to two different detector pixel sizes of 3.85 µm and 4.5 µm; the CDD camera binned the results giving the final resolution of twice the detector pixel size. Reconstruction and image analysis was performed by in-house software, resulting in images of around 600$^3$ pixels from which a central cubic section was taken for our simulations.

2.2 Mathematical model for flow

For calculating the flow field we use a standard finite volume method implemented in OpenFOAM [34]. Incompressible steady viscous flow is simulated directly through the pore-space images by solving the volume conservation equation (1) and the Navier-Stokes equations (2):

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

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

where $\mathbf{u}$ is the velocity vector, $\mu$ is viscosity of water ($\mu = 0.001$ Pa s), $\rho$ is the density of water ($\rho = 1000$ kg/m$^3$) and $p$ is pressure. The pressure and velocity are solved iteratively based on the pressure implicit with splitting of operators (PISO) algorithm.
of Issa [35]; further details can be found in [36]. We impose no flow, \( u = 0 \), on solid boundaries.

The simulations are run at a Reynolds number \( Re = \frac{u_{av} L}{\mu} \ll 1 \) assuming steady-state \( \frac{\partial u}{\partial t} = 0 \). The average flow speed is calculated as \( u_{av} = q/E \), where \( q = Q/(L_y L_z) \) is the Darcy velocity, \( Q \text{[m}^3\text{/s]} \) is the total volumetric flux calculated as \( Q = \int u \ dA_x \), where \( A_x \text{[m}^2\text{]} \) is the cross-sectional area of void voxels perpendicular to the direction of flow \( x \) and \( u \) is the face velocity that is normal to \( A_x \); \( L_x, L_y, L_z \) are the image lengths in each direction, and \( E \) is porosity. Each voxel in the image is converted to a grid block in the finite volume mesh. Since we simulate slow flow, the second term on the left in Eq. (2) is small compared to the second term on the right (viscous) term.

The flow domain is cubic. We use constant pressure boundary conditions for pressure at the left and the right faces of the images (the pressure drop is \( \Delta P \)). For the other faces of the images and for the solid walls, no-slip boundary conditions are used. By solving the Navier-Stokes equations we obtain the velocities and pressures for each voxel, and calculate absolute permeability \( k \text{[m}^3\text{]} \) from Darcy’s law:

\[
  k = \frac{\mu Q L_x}{\Delta P L_y L_z} \tag{3}
\]

The steps in the flow field computation are presented in Figures 2a-i for the images of beadpack, Bentheimer sandstone and Portland carbonate. The pore-space geometry, pressure and velocity field are shown. The velocity field figures show a subset of pore voxels where advection is dominant in comparison with diffusion (see later for a fuller discussion) – the stagnant flow voxels are not represented on the figure.
We can define a characteristic length $L$ (related to a typical grain size) that is given by $\pi V/S$, where $V$ is the volume of the porous medium (pore plus grain) and $S$ is the area of the pore-grain interface [37]. The area $S$ is measured directly on the image from the number of voxel faces separating void from grain: this method is employed for consolidated media where it is not possible to extract an unambiguous mean grain size. Using this method we estimate the values of for the characteristic length of $139.9\ \mu\text{m}$ and $327.0\ \mu\text{m}$ for the sandstone and carbonate respectively. The grain diameter $100\ \mu\text{m}$ is used as the characteristic length for the beadpack.

To study the correlation structure, in Figures 3a-c we plot variograms for porosity, $\gamma_p$, and velocity in the direction of flow, $\gamma_{u_x}$, for the images of beadpack, Bentheimer sandstone and Portland carbonate. The functions are calculated as:

$$
\gamma_p(\Delta x) = \frac{\sum_{n=1}^{N} (I(x_n) - \bar{I})^2}{2N} \tag{4}
$$

$$
\gamma_{u_x}(\Delta x) = \frac{\sum_{n=1}^{N} [u_x(x_n) - \bar{u}_x]^2}{2N} \tag{5}
$$

$I(x_n)$ is the indicator function for porosity ($I(x_n) = 1$ for pore voxels and $I(x_n) = 0$ for grain voxels), $u_x(x_n)$ are velocities in the direction of flow across faces oriented normal to the $x$-direction, and $N$ is the number of voxels. Plotted are $\gamma_p$ and $\gamma_{u_x}$ values normalized to the theoretical values at infinite range (uncorrelated limit) $\gamma_p,\gamma_{u_x} = (1-\varepsilon)\varepsilon$ and $\gamma_{u_x,\text{max}} = \langle u_x^2 \rangle - \langle u_x \rangle^2$.

The variograms for both porosity and velocity for all three samples indicate that the system becomes uncorrelated beyond the characteristic length, which is much smaller
than the total system size. This suggests that the images are sufficiently large to obtain representative results to compare with experiments on larger core samples.

### 2.3 Velocity distributions

Figures 2g-i show the very different nature of the velocity fields: in the beadpack flow is well-connected, evenly distributed throughout the sample and characterized by less tortuous channels; in Bentheimer sandstone similar features are observed but with a higher degree of tortuosity; however in the poorly connected Portland carbonate, flow is concentrated in a few channels with considerable stagnant regions of the pore space. Furthermore, the velocity distributions obtained on the images reveal considerable differences for the three porous media studied. In Figure 4 the probability density functions of the ratio of the magnitude of $\mathbf{u}$ (at the voxel centers) divided by the average flow speed $u_{av}$ are presented for the beadpack, Bentheimer sandstone and Portland carbonate as semi-log and log-log plots. The analytical probability density function of $|\mathbf{u}|/u_{av}$ for a single circular cylindrical tube is also shown to represent the homogeneous limit. The PDF is a histogram of the velocity distribution is sampled uniformly in 256 bins of $\log(|\mathbf{u}|/u_{av})$. The PDFs exhibit different characteristics in terms of the spread between low and high velocities, and the magnitude of the peak centered approximately on $|\mathbf{u}|/u_{av}=1$.

Figure 4 demonstrates that there are over eight orders of magnitude of variation in flow speed, but, unlike for the single tube, a significant fraction of the pore space for beadpack, Bentheimer sandstone and Portland carbonate experiences very low velocities. The beadpack has a PDF that – for low velocities – is similar to a single tube – again emphasizing the homogeneous nature of the system. The spread of
velocity in Portland carbonate is considerably wider than in Bentheimer sandstone, which in turn has a distribution that is much wider than the beadpack. In Portland carbonate many velocities are one thousandth of the average or lower. Fewer voxels are effectively stagnant for Bentheimer sandstone, and even fewer for the beadpack. At the fast extreme of the distributions, locally, the velocity can be more than 100 times the average. There is the greatest spread of these fast speeds for Portland, less for Bentheimer and least for the beadpack. Note also that the peak of the distributions are close to the average, Darcy velocity ($|u|/u_{av}=1$); this peak is largest for the beadpack. We will use these characteristics to interpret the shapes of transport propagators in Section 3 and to explain different generic transport behavior. We will also demonstrate that we are able to make quantitative predictions of experimental results.

2.4 Transport model

For moving solute by advection, we use a particle tracking method that employs a semi-analytic description of the velocity field within a grid block for all combinations of solid boundaries [37]. For a known velocity $u$ within a voxel we move solute by a displacement $u dt$ in each time step. A random-walk method is used to describe molecular diffusion: a particle instantaneously jumps over a mean-free path $\zeta = \sqrt{6D_m}$ in a random direction. The time step for the simulation is $10^{-4}$ s; the average motion of particle at each time step is less than one voxel. The diffusion coefficient is $2.2 \times 10^{-9}$ m$^2$s$^{-1}$ which is the free self-diffusion coefficient of water[38]. Particles are initially placed in uniformly-spaced voxels. Within each voxel the particle is placed at random. We place 1,000,000 particles in the pore space. This
boundary condition represents the conditions in NMR experiments, where the transport of water through water is measured: the solute is distributed uniformly throughout the medium. We apply a reflection boundary condition for particles that hit the surface of the solid voxels. If a particle exits the inlet or outlet face of the image, it is randomly reassigned to the opposite face – flux-weighted during the advective step and area-weighted for the diffusive step [39]. Reflecting boundary conditions are used for the other image faces. We track particles and plot concentration profiles as a function of particle displacement (propagators).

3. Results and Discussion

We study the different generic types of non-Fickian transport in porous media by analyzing displacement probabilities (propagators) on the images of the beadpack, Bentheimer sandstone and Portland carbonate. We use the velocity distributions from Figure 4 to explain the behavior. Furthermore, we predict accurately the propagators measured in NMR experiments by Scheven et al. [12].

3.1 Propagators and the effect of pore structure

The evolution of the propagators relative to the expected mean displacement in the main flow direction are presented in Figure 5 for the beadpack (Figure 5a) that has a relatively narrow distribution of velocities (as shown in Figure 4b); for Bentheimer sandstone (Figure 5b) with a wider spread of velocities; and Portland carbonate (Figure 5c) with the widest spread. The probabilities of displacement are plotted for different times t = 0.106s, 0.2s, 0.45s, 1s and 2s, as a function of displacement at the same flow conditions as reported in the NMR experiments by Scheven et al.[12] – that
is $u_{av} = 0.91\text{mm/s}, 1.03\text{mm/s},$ and $1.3\text{mm/s}$ for the beadpack, Bentheimer sandstone and Portland carbonate respectively.

Pore structure complexity determines quantitatively different generic transport behavior that is evident in Figure 5 as very different shapes of propagators in the beadpack, Bentheimer sandstone and Portland carbonate. At early times ($t=0.1\text{s}$), in the beadpack, the majority of the solute is moving, although the propagator is asymmetric. This means that the distribution is not Gaussian as would result from a solution of the transport equation in one dimension employing Fick’s law. However, as time progresses, solute particles start to sample the entire velocity field, and for $t=0.45\text{s}$ onwards the propagator rapidly becomes Gaussian about the mean displacement, thus representing Fickian behavior. A very different response is observed at early times for Bentheimer sandstone. A considerable peak in concentration around zero is present – this is stagnant solute that moves by diffusion (note the negative displacement values due to random motion by diffusion). The immobile peak gradually narrows due to mass transfer exchange between immobile and mobile fluid regions by diffusion. At longer times ($t=2\text{s}$) there is a formation of a dominant secondary mobile fluid peak in concentration that is centered approximately on 1. For Portland carbonate, a large immobile fluid concentration peak is observed that is persistent with time. The mobile fluid peak starts to form only at late times ($t>1\text{s}$) and its magnitude is much lower than that in the beadpack and Bentheimer sandstone. This implies a delayed exchange between flowing and stagnant regions of the pore space. The difference in transport through the three media can be explained by the velocity distributions in Figure 4. The large stagnant peak in Portland carbonate
is a consequence – as mentioned in the previous Section – of a large number of very low velocities in the pore space.

The overall dispersion of the concentration is also related to the spread of the velocity distribution, with Portland carbonate, again, showing the most dispersed profiles. We can use the characteristic length $L=100\mu\text{m}$ for the beadpack and the estimated values of $139.9\mu\text{m}$ and $327.0\mu\text{m}$ for the sandstone and carbonate respectively, to estimate typical times to diffuse across one pore (if we assume that this is the characteristic length). This time is of the order $t_{\text{diff}} = \frac{L}{D_m}$ giving 4.54s, 8.89s and 48.6s for the beadpack, sandstone and carbonate respectively. For reference the Peclet numbers ($\text{Pe} = \frac{u_{\text{av}}L}{D_m}$, where $u_{\text{av}}$ is the average flow speed, $L$ is the characteristic length, and $D_m$ is the molecular diffusion coefficient) are 41.4, 65.5 and 187.3 respectively for the beadpack, sandstone and carbonate. For comparison, the time to transit a characteristic length by advection is equal to diffusion if the velocity is $2.42\times 10^{-2}$, $1.53\times 10^{-2}$ and $5.34\times 10^{-3}$ of the average speed for the three media: regions with a much lower velocity than this are effectively stagnant, since diffusive transport is much faster over the characteristic length.

For the beadpack, the time to diffuse a characteristic length is longer than the time taken to reach asymptotic, Fickian, behavior, indicating a lack of spatial correlation: to sample the velocity distribution, a solute particle only needs to diffuse around one pore length at most, as presented in Figure 3a. For the sandstone and carbonate, however, the stagnant peak persists for longer, giving more anomalous behavior.
If we have a system that is macroscopically homogeneous – that is, displays statistically the same pore structure over much greater lengths than those studied – then, eventually, an asymptotic limit is reached in all cases. The dispersion coefficient is related to the spread of velocities and is greatest for the carbonate, less for the sandstone and lowest for sand or beadpacks[30]. However, real systems display distinct geological structures at several length scales and so this asymptotic limit may never be reached: before the solute has time to sample the local flow field, it is transported into a region with a different pore structure with its own distinctive distribution of velocities. This explains how, at the field scale (100s to 1,000s m) and for transport times of days or months, anomalous behavior can still be observed [13 and references therein, 40,41,15]. The structure at all scales affects the transport, and a firm basis at the pore scale is necessary to account properly for large-scale behavior [42].

3.2 Comparison with experiment

We compare the computed propagators with those measured in NMR experiments by Scheven et al.[12] in Figure 6. The rock types, flow speeds, diffusion coefficient and displacement times are the same in both the experiments and simulations: there are no adjustable or tunable parameters in our model.

There is a very good agreement between the experiments and simulation. As discussed above we see a rapid approach to Gaussian behavior in the beadpack (Figure 6a); an immobile stagnant peak that gradually disappears and a large mobile peak developing in Bentheimer sandstone (Figure 6b); and a persistent immobile peak and a slow development of the mobile peak concentration in Portland carbonate (Figure 6c). For
the beadpack and Bentheimer sandstone, there appears to be a slight shift in the peak between experiment and the model. This could be due to systematic under-sampling of slow-flow regions in the experiments that led to an apparent higher average speed [12]. The agreement is particularly good for the most heterogeneous sample, Portland carbonate. The implication here is that capturing the wide spread of velocities is the key to capturing transport correctly. These results suggest that given a good image of the pore space it is possible to make a priori predictions of transport.

4. Conclusions

We have described and explained different generic transport behavior in three porous media with increasing pore-scale complexity. In porous media with a relatively homogeneous pore space, giving a narrow spread in local velocity distribution, the exemplar of which is represented by a disordered close packing of equally-sized spheres, Fickian transport is rapidly attained through molecular diffusion at the pore scale. On the other hand, with a wider spread in local velocity distribution such as Bentheimer sandstone, a stagnant peak is seen at early times, with a pronounced mobile peak only emerging later. A greater fraction of the pore space is effectively stagnant and to sample the velocity distribution fully requires diffusive exchange between mobile and immobile regions. Finally and most importantly, in porous media with a very widespread in distribution of local velocities, the exemplar of which is Portland carbonate, there is persistent immobile concentration peak at longer times, with a smaller secondary mobile peak, leading to a highly anomalous behavior. The propagators obtained by the model are in excellent agreement with experimental measurements by Scheven et al. [12]. The work demonstrates that pore-scale modeling can provide reliable predictions of core-scale (mm to cm scale) transport.
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References


Figure Captions

Figure 1. Two-dimensional cross-sections of the segmented image of the beadpack (a) and the three-dimensional gray scale images for Bentheimer sandstone (b) and Portland carbonate (c).

Figure 2. Image geometries of the beadpack (a), Bentheimer sandstone (b), and Portland carbonate (c) shown with the pore volume represented by gray color; normalized pressure fields with a unit pressure difference across the model for beadpack (d), Bentheimer sandstone (e), and Portland carbonate (f); normalized flow fields, where the ratios of the magnitude of $u$ at the voxel centers divided by the average flow speed $u_{av}$ are shown using cones (too small to be seen individually) that are colored using a logarithmic scale spanning from 5 to 500 for the beadpack (g), Bentheimer sandstone (h), and Portland carbonate (i). In the images red color indicates high values and blue color indicates low values.

Figure 3. Variograms showing the normalized functions for porosity, $\gamma_p$, and velocity in the direction of flow, $\gamma_u$, for the images of beadpack (a), Bentheimer sandstone (b), and Portland carbonate (c). Indicated by the vertical line is the characteristic length (representing a mean grain size) for all three samples. We find that the porosity and velocity appears to be largely uncorrelated beyond this characteristic length, which is much less than the total system size.

Figure 4. Probability density function of the velocity distributions for the beadpack, Bentheimer sandstone and Portland carbonate presented on (a) semi-logarithmic axes,
and (b) doubly logarithmic axes. The solid line is the distribution for a single cylindrical tube, representing the homogeneous limit.

**Figure 5.** Probability of molecular displacement $P(\zeta)$ in the images of (a) beadpack, (b) Bentheimer sandstone, and (c) Portland carbonate as a function of displacement $\zeta$ for the set of times $t = 0.106s, 0.2s, 0.45s$, 1s and 2s. The coordinates are rescaled by the expected nominal mean displacement $<\zeta>_0 = u_{av}t$ in the direction of flow. The average velocities are $u_{av} = 0.91$mm/s, 1.03mm/s, and 1.3mm/s for the beadpack, Bentheimer sandstone and Portland carbonate respectively. These correspond to the flow speeds in the experiments [12] with which we compare our results in the next section.

**Figure 6.** Probability of molecular displacements $P(\zeta)$ (solid lines) as a function of displacement $\zeta$ for the set of times $t = 0.106s, 0.2s, 0.45s$, 1s and 2s compared to the propagator obtained in the NMR experiments (dashed lines) by Scheven et al.[12] at the same observation times. (a) the beadpack, (b) Bentheimer sandstone and (c) Portland carbonate. The coordinates are rescaled by the nominal mean displacement $<\zeta>_0 = u_{av}t$, $u_{av} = 0.91$mm/s for the beadpack, $u_{av} = 1.03$mm/s for Bentheimer sandstone and $u_{av} = 1.3$mm/s for Portland carbonate, as in the experiments.
Figures 1a-c
Figures 2a-i
Figures 3a-b
Figure 3c
Figures 5a,b

Figure 5c
Figures 6a-c
Part 3

Insights into non-Fickian Solute Transport in Carbonates

Water Resources Research (submitted, 2012)

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Key points
Transport computed through micro-CT images of six carbonate rocks is anomalous
Highly anomalous transport is explained by the wide local velocity distribution
The effect of pore structure and Peclet number is quantified

Abstract
We study and explain the origin of early breakthrough and long tailing plume behavior by simulating solute transport through three-dimensional X-ray images of six different carbonate rock samples, representing geological media with a high degree of pore-scale complexity. A Stokes solver is employed to compute the flow field and the particles are then transported along streamlines to represent advection, while the random walk method is used to model diffusion. We compute the propagators (concentration vs. displacement) for a range of Peclet numbers (Pe) and relate it to the velocity distribution obtained directly on the images. There is a very wide distribution of velocity that quantifies the impact of pore structure on transport. In samples with a relatively narrow spread of velocities, transport is characterized by a small immobile concentration peak, representing essentially stagnant portions of the pore space, and a dominant secondary peak of mobile solute moving at approximately the average flow speed. On the other hand, in carbonates with a wider velocity distribution, there is a significant immobile peak concentration and an elongated tail of moving fluid. An increase in Pe – increasing the relative impact of advection over diffusion – allows the emergence of a highly dispersed mobile concentration profile. This behavior indicates highly anomalous transport. The implications for modeling field-scale transport are discussed.
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Index Terms: 1829; 1831; 1832; 1869;

Keywords: non-Fickian dispersion; pore-scale modeling; porous media; carbonates; heterogeneity; micro-CT images; X-ray synchrotron images; direct simulation; transport; propagator

1. Introduction

Flow and solute transport play an important role in a number of applications in geological porous media, including storage of carbon dioxide, contaminant transport and the associated access to clean drinking water, safe disposal of nuclear waste and enhanced oil recovery. Although carbonate formations contain more than half of the world’s conventional oil reserves [Chilingar et al., 1972; Ahlbrandt et al., 2005], the interplay of physical processes involving transport through their complex structures with heterogeneities from the pore scale upwards is not fully understood.

Experimental studies of transport behavior in carbonate rock in both the laboratory [Baker, 1977; Bretz and Orr, 1987; Gist et al., 1990; Hidajat et al., 2004; Oshita and Okabe, 2005; Fourar et al., 2005; Fourar and Radilla, 2009] and the field [Cacas et al., 1990; Gelhar et al., 1992 and references therein; Maloszewski and Zuber, 1993; Meigs and Beauheim, 2001; Witthüser et al., 2003; Birk et al., 2005; Gouze et al., 2008a] have typically found an early breakthrough of the solute and a long tailing of the concentration at late times. At the core scale, effluent breakthrough curves (BTCs) of a sucrose tracer injected into brine-saturated San Andres carbonate cores have shown a considerable degree of tailing due to significant core heterogeneity [Bretz and Orr, 1987]. Gist et al.[1990] associated long-time tails of NaCl brine tracer BTCs in heterogeneous carbonate rocks (including dolostone and a Middle Eastern carbonate) with macroscopic permeability heterogeneities on the millimeter-to-centimeter scale,
in contrast to BTCs in less heterogeneous carbonates (including Austin chalk, Oolitic limestone and Indiana limestone) that did not show pronounced tailing. Hidajat et al. [2004], measured both in-situ (by X-ray CT scanning) and outlet NaI tracer concentrations in vuggy carbonate samples from a west Texas field and observed a very early breakthrough followed by a long tail – this implied the existence of a sample-spanning high-permeability streak in a tight matrix. At the field scale, good examples of prolonged tailing of BTCs in carbonate rock can be found in the experimental studies of Meigs and Beauheim [2001], Witthüser et al. [2003], Birk et al. [2005] and Gouze et al., [2008a].

This late-time behavior cannot be modeled by a deterministic advection-dispersion equation (employing Fick’s law at the macroscale) in a homogenous domain; more sophisticated theories are required, including multi-rate mass transfer models [Haggerty and Gorelick, 1995; Haggerty et al., 2000] and continuous time random walks (CTRW) [Berkowitz et al., 2006] that take into account the transport between fast (mobile) and slow (immobile) regions. The review by Berkowitz et al. [2006] provides an excellent overview of these transport modeling approaches. Behavior that cannot be described by the advection-dispersion equation has been coined “anomalous”, or non-Fickian, and is very often encountered in complex geological media, from laboratory studies to the field scale [Levy and Berkowitz, 2003; Becker and Shapiro, 2003; Gouze et al., 2008a].

Studying BTCs is very useful in assessing solute first arrival times. However, having an accurate description of plume concentration as a function of distance in either a core or at the field scale provides full information on the in-situ transport processes. If
the transport is Fickian, described by the advection-dispersion equation, the injected tracer particles rapidly fully sample the velocity field, resulting in a concentration profile whose peak moves with the average flow speed with a Gaussian spread – this is typical of homogeneous media where each particle encounters the relatively narrow range of flow speed after traveling through only a few pores, as shown for unconsolidated beadpacks [e.g. Scheven et al., 2005]. However, in complex porous media, such as carbonate rock, the solute experiences a very wide range of transit times across pores of very different size; consequently the particle transport deviates from Fickian behavior, resulting in large variations of plume shape from a Gaussian profile, as discussed by Berkowitz and Scher [2001] and Scher et al. [2002].

The transport can be described by a probability density function (PDF) of either the displacement or transit time of solute particles. PDFs have been studied experimentally by Nuclear Magnetic Resonance (NMR) measurements where the distribution of displacement of moving protons is obtained [Callaghan, 1991; Gladden, 1994]; these are also called the NMR flow propagators [Kärger and Heink, 1983]. The propagators have been measured on consolidated rock cores in Fontainebleau sandstone [Packer and Tessier, 1996; Tessier et al., 1997; Tessier and Packer, 1998], Bentheimer sandstone [Waggoner and Fukushima, 1996; Johns et al., 2003; Scheven et al., 2005; Verganelakis et al., 2005; Singer et al., 2006; Mitchell et al., 2008a], Portland carbonate [Scheven et al., 2005; Verganelakis et al., 2005; Mitchell et al., 2008b] and in a dolomite [Zhao et al., 2010]. A critical discussion of these measurements is presented by Gladden and Mitchell [2011]. These experiments clearly distinguish the nature of non-Fickian transport in a homogeneous beadpack from that in sandstones and even further, from that in carbonate rock. Scheven et
al. [2005] have demonstrated that the propagators measured in a beadpack show a non-Gaussian shape only for a short time, then become Gaussian about the mean displacement; for Bentheimer sandstone a pronounced peak is observed representing the stagnant fluid regions that gradually disappears with time; for Portland carbonate the stagnant peak is both larger and more persistent than that for sandstones, implying a much greater degree of particle retardation.

In this modeling study we compute PDFs of solute displacement for a suite of carbonate rock images over a wide range of Peclet numbers ($Pe = \frac{u_{av}L}{D_m}$, where $u_{av}$ is the average flow speed, $L$ is the characteristic length, and $D_m$ is the molecular diffusion coefficient) to demonstrate the nature of non-Fickian transport in different classes of carbonate. To describe advection and diffusion at the pore scale, random walk-based particle tracking techniques have been a common choice, either simulating transport directly on the voxelized images of the pore space, or on extracted pore networks. Network modeling has been widely used for studying solute transport [Saffman, 1959; Saffman, 1960; Sahimi et al., 1986; Sorbie and Clifford, 1991; Damion et al., 2000; Bruderer and Bernabe, 2001; Bijeljic et al., 2004; Picard and Frey, 2007; Acharya et al., 2007; Rhodes et al., 2008]. Advection is solved for analytically in a unit network bond, and random walk movement is superimposed to simulate diffusion. Advances have been made in the description of the asymptotic dispersion coefficients over a wide range of Peclet numbers [Bijeljic et al., 2004; Acharya et al., 2007] including an explanation for the power-law dependence of longitudinal dispersion coefficient as a function of $Pe$, reconciling experiment, pore-scale modeling, and CTRW theory for Berea sandstone [Bijeljic and Blunt, 2006; Dentz et al., 2004]. Propagators have been studied using network models representing
Berea sandstone [Picard and Frey, 2007] and for a dolomite [Zhao et al., 2010]. The latter study has shown a good agreement with NMR experiments using an adjustable parameter to describe the pore dynamics.

In parallel with network modeling, a number of approaches have been developed to simulate transport directly on a three-dimensional voxel representation of the porous medium obtained by direct X-ray (synchrotron or micro-CT) scanning or by reconstructing pore space from two-dimensional thin section images. The finite difference method has been used to compute flow in reconstructed Fontainebleau sandstone [Salles et al., 1993; Tessier et al., 1997; Stapf et al., 2000], reconstructed Vosges sandstone [Yao et al., 1997], reconstructed random spherical and aspherical packings [Coelho et al., 1997], micro-CT images of Berea and Bentheimer sandstones [Bijeljic et al., 2011a; Mostaghimi et al., 2012; Blunt et al., 2012; Bijeljic et al., 2012] and an image of Portland carbonate [Bijeljic et al., 2011a; 2012]. The finite element method was used on a model sand pack [Cardenas, 2008; Cardenas, 2009], while the finite element/finite volume method was employed to compute flow in an image of Fontainebleau sandstone [Zaretskiy et al., 2010]. In addition, particle-based approaches have been used to find the flow field and simulate the transport of solute. The lattice-Boltzmann method has been employed to compute flow in computer model-generated bead packs [Lowe and Frenkel, 1996; Maier et al., 2000; Kandhai et al., 2002]; directly on an NMR image of a spherical bead pack [Manz et al., 1999]; and on an NMR image of a spherical bead pack that was modified to represent a Bentheimer sandstone core [Johns et al., 2003]. The modified moving particle semi-implicit method was used to compute dispersion through micro-CT images of Berea and two other sandstones [Ovaysi and Piri, 2011].
Significant progress in describing Fickian and non-Fickian dispersion has been made in the studies that use direct transport simulation on the pore space. Findings on Fickian dispersion include description of the asymptotic dispersion coefficients over a wide range of Peclet numbers directly in the pore space of unconsolidated beadpacks [Coelho et al., 1997; Maier et al., 2000] on sandstones [Salles et al., 1993; Ovaysi and Piri, 2011; Bijeljic et al., 2011a; Mostaghimi et al., 2012] and carbonate rock [Bijeljic et al., 2011a]. Non-Fickian dispersion results include agreement between direct pore-scale simulations and experimentally measured NMR propagators for bead packs [Manz et al., 1999; Kandhai et al., 2002; Maier et al., 2008], sandstones [Tessier et al., 1997; Blunt et al., 2012; Bijeljic et al., 2012] and a carbonate [Bijeljic et al., 2011a; 2012]. However, almost all of the abovementioned studies deal with bead packs, sandpacks and sandstones that have a considerably lower degree of pore-scale complexity than carbonates.

Despite huge advances in computer power and algorithmic efficiency, studies of dispersion have – to date – been limited to relatively small samples. The Fontainebleau sandstone image used for mesh generation in the study by Zaretskiy et al.[2010] had 200³ voxels with a resolution of 7.5 μm giving an overall size of 1.5×1.5×1.5 mm³. Ovaysi and Piri[2011] used 42×42×190, 66×66×298, and 52×52×234 voxels for Berea and the two other studied sandstones respectively. The corresponding image resolutions were 10.69 μm for Berea and 6.796 μm and 8.683 μm for the other two sandstones, resulting in sample sizes of approximately 0.45 mm in the x and y directions and 2.03 mm in the flow direction.
In our previous work [Bijeljic et al., 2011a] we employed an efficient streamline-based algorithm with a random walk method to study solute dispersion on micro-CT images of a sandpack, Berea sandstone, and Portland limestone containing 300³ grid blocks (voxels) at a resolution (voxel size) of 10 µm, 5.345 µm, and 9 µm, respectively, representing a cube of side length 1.6–3.0 mm. The qualitatively different signature of transport through the major porous rock types encountered in the subsurface – sandpacks, sandstones, and carbonates was demonstrated. A very good agreement was found between the model results and NMR measurements [Scheven et al., 2005; Mitchell et al., 2008b] of the Portland carbonate propagators [Bijeljic et al., 2012].

However, while the connection between non-Fickian transport behavior as a result of a wide range of transit times has been made [Berkowitz and Scher, 2001; Scher et al. 2002; Bijeljic and Blunt, 2006] we provide a systematic study to describe the non-Fickian behavior arising from the relationship between the complex pore structure and velocity field to characterize transport in heterogeneous carbonates. To date, there have been no modeling studies performed directly on images of carbonate rocks for a suite of samples and over a range of Pe: the aim of this work is to predict quantitatively the non-Fickian transport characteristics in carbonate rock of different structure and over a range of flow conditions. We study the nature of early breakthrough and long tailing plume behavior by simulating transport of a solute through three-dimensional X-ray images of six different carbonate rock samples, representing geological media with a high degree of pore-scale complexity. A Stokes solver is employed to compute the flow field and the particles are then transported semi-analytically along streamlines to represent advection, and the random walk
motion is used to model diffusion. We describe the different non-Fickian transport behavior in different types of carbonates by analyzing propagators (concentration vs. displacement) for a wide range of Peclet numbers and explain this behavior by analyzing PDFs of the velocity distribution.

2. X–ray Images and Mathematical Model

*Images*. For transport studies we use four quarry carbonate samples (Indiana, Estaillades, Ketton and Mount Gambier limestones) and two carbonate samples from a Middle East aquifer (denoted ME1 and ME2). The dry scan images were acquired on cylindrical cores having 5 mm diameter and 25 mm length with a synchrotron beamline (SYREMP beamline at the ELETTRA synchrotron in Trieste, Italy) at a resolution of 7.7 µm (for Indiana, Estaillades, Ketton, ME1 and ME2) and 9 µm (for Mount Gambier), corresponding to two different detector pixel sizes of 3.85 µm and 4.5 µm; the CDD camera binned the results giving the final voxel size of twice the detector pixel size. The range of energy used was 27-33 KeV, and each scan lasted between 3 and 4 hours. Reconstruction was performed by in-house software, resulting in images of around $600^3$ pixels from which a central cubic section was taken for our simulations. Two-dimensional cross-sections of three-dimensional gray scale images for the six carbonates studied are shown in Figure 1a-f. Segmentation into binary images was based on a histogram analysis using Otsu’s thresholding algorithm and using ImageJ software [Sahoo et al., 1988]. In addition, we acquired an additional image at higher resolution – 3.3 µm voxel size – for Estaillades using a micro-CT scanner (Xradia Versa).
The voxel size, number of voxels, system size, porosities, permeabilities, characteristic length, and average coordination number of the carbonate rocks studied are given in Table 1. The average coordination numbers are obtained by extracting pore networks from the images using the maximal ball algorithm [Dong and Blunt, 2009; Gharbi and Blunt, 2012]. The pore networks are a topological representation of the pore space as wide pores connected by throats. The coordination number is the number of throats connected to each pore. We define the characteristic length \( L \) (needed for calculating \( Pe \)) for each carbonate image based on a cubic packing of regular spheres. For this idealized system, the grain diameter is \( \pi V/S \), where \( V \) is the volume of the porous medium (pore plus grain) and \( S \) is the area of the pore-solid interface. We use the same definition for our images, since the volume, and the pore-solid area are readily computed, while it is difficult to identify individual grains unambiguously. The image sizes are \( 320^3 \text{–} 380^3 \) voxels in total representing a cube of side length 2.46–3.15 mm, representing 8–43 characteristic lengths; the higher-resolution image is \( 650^3 \) voxels.

Porosities are computed on the images from the ratio of number of pore voxels, \( N_{p\text{vox}} \) divided by total number of voxels, \( N_{\text{vox}} \). Voxels that are not connected to the inlet or outlet are excluded from the analysis and the flow calculations. It can be seen that the carbonates that have a low porosity tend to be poorly connected and have a lower permeability, provided that the characteristic length is similar.

**Mercury Injection Capillary Pressure (MICP) curves.** Mercury Injection Capillary Pressure (MICP) was measured at a commercial laboratory (Weatherford) on samples taken from the same block of stone from which the images were obtained. Figures 2a-
show the inferred throat radius distributions normalized to a maximum value obtained from MICP for (a) Estaillades, Indiana and ME1, and (b) for Ketton, Mt Gambier and ME2. Plotted also are the straight black solid and dashed lines that mark half the voxel size of the images studied, representing the smallest throat radius that can be detected in the images.

Carbonate rocks are – in general – characterized by a wide range of pore size and significant microporosity: pores less than 1 µm across. This microporosity is not imaged and hence not accounted for in our simulations. With the image resolution we had available, most of the macroporosity of the pore space is captured for Indiana, Estaillades, Ketton, Mt Gambier and ME2, while less of the macropores are scanned for ME1. We will discuss later that consideration of microporosity would further emphasize the findings from this study associated with a large fraction of stagnant solute. A complete discussion of microporosity is beyond the scope of this paper and requires the acquisition of much higher resolution images.

**Flow model.** Incompressible steady viscous flow is simulated directly through the pore-space images by solving the volume conservation equation (1) and the Navier-Stokes equations (2):

\[ \nabla \cdot \mathbf{u} = 0 \]  
(1)

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

where \( \mathbf{u} \) is the velocity vector at the center of each voxel, \( \mu \) is viscosity of water (\( \mu = 0.001 \) Pa s), \( \rho \) is the density of water (\( \rho = 1000 \) kg/m³) and \( p \) is pressure, using a
standard finite volume method implemented in OpenFOAM [OpenFOAM, 2011]. The pressure and velocity are solved iteratively based on the pressure implicit with splitting of operators (PISO) algorithm of Issa[1986]; see Raeini et al.[2012] for further details.

The simulations are run at a \( Re = \frac{\mu u^\prime L}{\nu} \ll 1 \) assuming steady-state \( \frac{\partial u}{\partial z} = 0 \). The average flow speed is calculated as \( u_{av} = q/\varepsilon \), where \( q = Q/(L_x L_y) \) is the Darcy velocity, \( Q [m^3/s] \) is the total volumetric flux calculated as \( Q = \int u \cdot dA \), where \( A_{void} [m^2] \) is the cross-sectional area of void voxels perpendicular to the direction of flow \( x \) and \( u \) is the face velocity that is normal to \( A_x \); \( L_x, L_y, L_z \) are the image lengths in each direction, and \( \varepsilon \) is porosity. Each voxel in the image is converted to a grid block in the finite volume mesh. Slow flow is simulated; the second term on the left in Eq. (2) is small compared to the second term on the right (viscous) term.

The flow domain is cubic. We use constant pressure boundary conditions for pressure at the left and the right faces of the images (the pressure drop is \( \Delta P \)). For the other faces of the images and for the solid walls, no-flow boundary conditions are used. By solving the Navier-Stokes equations we obtain the velocities and pressures for each voxel, and calculate absolute permeability \( k [m^2] \) from Darcy’s law:

\[
k = \frac{\mu Q L_x}{\Delta P L_y L_z}
\]  

(3)

The permeability values in Table 1 are given in mD, where 1mD = 9.869233×10^{-16} m².
An illustration of how flow was computed on the synchrotron images of Estaillades limestone (that is an exemplar for a carbonate with a wide spread of velocities) and Mount Gambier limestone (that is an exemplar for a carbonate with a narrower spread of velocities) is presented in Figures 3a-f. The pore geometry, pressure field and velocity field are shown. The velocity field figures show a subset of pore voxels where advection is dominant in comparison to diffusion – the stagnant flow voxels are not represented on the figure.

Figures 3c and 3f show the very different nature of the velocity fields: while in the low-connectivity Estaillades limestone, flow is concentrated in a few channels with much of the pore space largely stagnant, in the highly connected Mount Gambier limestone flow is evenly distributed throughout the sample and is characterized by less tortuous channels. Qualitatively similar flow fields to that of Estaillades limestone can be seen in Figures 4a,b for Indiana limestone and ME1. Figure 4d represents the flow field in Ketton limestone that is qualitatively similar to that of Mt Gambier and ME2. This will be discussed in more detail later.

The correlation structure is shown in Figure 5, where the variograms for porosity, $\gamma_p$, and velocity in the direction of flow, $\gamma_{u_x}$, for the images of (a) Ketton, Mt Gambier and ME2, and (b) for Indiana, Estaillades and ME1 are plotted. The functions are calculated as:

$$\gamma_p(\Delta x) = \frac{1}{2N} \sum_{i=1}^{N} [p(x_i) - \overline{p}][p(x_i + \Delta x) - \overline{p}]^2$$ (4)

$$\gamma_{u_x}(\Delta x) = \frac{1}{2N} \sum_{i=1}^{N} [u_x(x_i) - \overline{u_x}][u_x(x_i + \Delta x) - \overline{u_x}]^2$$ (5)
\( I(x_i) \) is the indicator function for porosity (\( I(x_i) = 1 \) for pore voxels and \( I(x_i) = 0 \) for grain voxels), \( \mathbf{u}_x(x_i) \) are velocities in the direction of flow across faces oriented normal to the \( x \)-direction, and \( N \) is the number of voxels. Plotted are \( \gamma_p \) and \( \gamma_{av} \) values normalized to the theoretical values at infinite range (uncorrelated limit) \( \gamma_{pc,av} = (1 - e) \) and \( \gamma_{av} = \langle \mathbf{u}_x^2 \rangle = \langle u_x^2 \rangle \). The \( x \)-axes values are normalized to the characteristic length \( L \) estimated for each carbonate sample – the values for \( L \) are presented in Table 1.

The variograms for porosity indicate a correlation length (the distance when the variogram reaches its maximum – sill – value) that is approximately the characteristic length – a typical grain size. The correlation length for the velocity field is, however, larger in some cases, particularly for the more heterogeneous cases shown in Figure 5b.

In Figure 6 probability density functions of the ratio of the magnitude of \( \mathbf{u} \) (at the voxel centers) divided by the average flow speed \( \mathbf{u}_{av} \) are presented as semi-log and log-log plots. The PDFs are calculated as histograms of the velocity distributions sampled uniformly in 256 bins of \( \log(|\mathbf{u}|/ \mathbf{u}_{av}) \). For the reference on the same plots we present the homogeneous limit – that is the analytical probability density function of \( |\mathbf{u}|/ \mathbf{u}_{av} \) for a single circular cylindrical tube. The PDFs of \( |\mathbf{u}|/ \mathbf{u}_{av} \) exhibit different characteristics in terms of the spread between low and high velocities, and the magnitude of the peak centered on \( |\mathbf{u}|/ \mathbf{u}_{av} = 1 \). It is evident from Figure 6a that in all the carbonate samples many velocities are close to zero, while the values for higher velocities show different spreads. We will use these characteristics to interpret the shapes of dispersion propagators in the results section that explain the origin of early breakthrough and long tailing plume behavior.
Indicated on Figure 6b by the vertical line is the velocity $u_{\text{min}}$ at which the time taken to traverse a voxel of size $\Delta x$ by advection $t_{\text{adv}} = \frac{\Delta x}{u_{\text{min}}}$ is 100 times longer to that traversed by diffusion $t_{\text{diff}} = \frac{(\Delta x)^2}{2D_m}$ for a base-case Peclet number of 200. The base-case value for molecular diffusion coefficient $D_m$ was $1.5 \times 10^{-9}$ m$^2$/s which for Indiana limestone yields $P_e = 200$ (using the characteristic length of $L = 0.2996$ mm and $u_{\text{av}} = 1$ mm/s). Smaller velocities are unlikely to have much impact on transport in these regions of the pore space, since diffusion will dominate. As we discuss later, for larger $P_e$ this limit is shifted to smaller velocities. Note that there are always a significant number of very small speeds, indicating that some diffusion is always necessary to allow solute to move throughout the pore space.

**Transport model.** We simulate transport by moving an ensemble of particles by advection along streamlines, using a semi-analytic description of the velocity field within a grid block for all combinations of solid boundaries [Mostaghimi et al., 2012]. A random-walk method is used to describe molecular diffusion: a particle instantaneously jumps over a mean-free path $\xi = \sqrt{6D_m dt}$ in a random direction. The time step $dt$ for all simulations is $10^{-4}$ s and it does not change with $P_e$; the average motion of particle at each time step is less than one voxel. We simulate the range of $P_e$ by varying $D_m$. Particles are injected in the total image volume by placing them in uniformly-spaced voxels and within each voxel the particle is placed at random. The number of injected particles ranges from 1,000,000 to 2,000,000. We apply a reflection boundary condition for the particles that hit the surface of the solid voxels. If a particle exits the inlet or outlet face of the cubic image, it is randomly reassigned to the opposite face — flux-weighted during the advective step and area-
weighted for the diffusive step [Bijeljic and Blunt, 2004]. Reflecting boundary conditions are used for the other image faces.

We track particles and plot concentration profiles as a function of particle displacements (propagators). Propagators are calculated such that \[ \int_{-\infty}^{\infty} P(\zeta) \, d\zeta = 1, \] where \( P(\zeta) \) is the probability of particle displacement \( \zeta \). The propagator is the probability that a particle has moved a distance \( \zeta \) in the main flow direction and is equivalent to the concentration profile resulting from an initial delta-function pulse (mathematically the Green function for the transport).

3. Transport Results

Firstly, we study the impact of structure on the nature of early breakthrough and long tailing plume behavior by analyzing displacement probabilities (propagators) on our suite of carbonate images (as reported in Table 1) for \( Pe=200 \). Secondly, we extend our study to examine the impact of Peclet number. For both parts, we use the velocity distributions from Figure 6 to explain the behavior.

3.1 Non-Fickian propagators in carbonates – impact of pore structure

We first present the evolution of the propagators relative to the expected mean displacement in the main flow direction in carbonates with a relatively narrow spread of velocities (as shown in Figure 6): Ketton (Figure 7a), Mt Gambier limestones (Figure 7b) and ME2 (Figure 7c). These will be later compared to the propagators in carbonates with a wider spread of velocities.
We define a dimensionless time $t_d = t/\tau_{eff}$, where $\tau_{eff} = \frac{L^2}{D_m}$. This is the ratio of the time to the time to traverse a characteristic length by diffusion. In this paper we study pre-asymptotic, non-Fickian transport where $t_d < 1$; for $t_d >> 1$ (the limit for Fickian behavior, as suggested by Salles et al.[1993]) we see the development of a Gaussian plume and Fickian behavior, once diffusion has allowed the solute to sample to entire flow field. Dimensionless time $t_d$ multiplied by the Peclet number $Pe$ represents the number of characteristic lengths the solute has traveled on average. Our focus is on $t_d < 1$ but where $t_d Pe > 1$.

Probabilities of displacement are plotted in Figure 7 for dimensionless times $t_d = 0.0015, 0.015, 0.075,$ and $0.15$ for $Pe = 200$. At early times time ($t_d = 0.0015$), due to a significant portion of fluid residing in stagnant zones for which diffusion is the main mechanism of transport, the solute can move against the main flow direction (a negative displacement). There is a concentration peak of stagnant solute centered around zero, while the flowing solute has an elongated moving tail with no pronounced mobile peaks. As time progresses, more and more particles diffuse out of the stagnant regions, which results in the stagnant peak becoming narrower with time on rescaled distance axes, while there is a formation of a secondary mobile solute peak in concentration that becomes prominent around $t_d = 0.075$, and dominates at later times ($t_d = 0.15$). This reflects the particles that eventually diffuse out from the slow moving regions and then move rapidly through the better connected wider regions. The diffusion time for the particles to diffuse a characteristic length (say the distance between pores) is $t_d = 1$. This is $14.4s$ for Mt Gambier limestone, $32.3s$ for ME2 and $64.1s$ for Ketton limestone. The emergence of Gaussian behavior can be
seen in Figure 8, where propagators for Mt. Gambier are plotted for $t_d=0.8$ and $t_d=1.2$. The mobile peak in solute concentration increases with time and almost entirely dominates the slow-moving region that is gradually disappearing at longer times.

More persistent non-Fickian behavior is observed for the carbonates with a wide spread of velocities. Figures 9 shows the propagators for Estaillades limestone, Indiana limestone, and ME1, where large, more persistent concentration peaks in stagnant fluid are seen. This indicates that more solute is retarded in diffusion-dominated stagnant zones, while less is free to flow through connected channels resulting in an elongated plume tail at early times and a smaller mobile peak at later times ($t_d = 0.15$).

The characteristic time to diffuse out of a single stagnant pore is similar in these cases and yet the approach to Gaussian-like behavior is slower than in the less heterogeneous samples. This indicates that there is correlated heterogeneity in the flow field, as indicated in Figure 5b, meaning that to reach a fast-flowing domain, particles have to diffuse through several stagnant pores, giving a much larger timescale to see the emergence of approximately Gaussian behavior.

We can explain the complex non-Fickian transport behavior of propagators described in Figures 7-9 by looking at the velocity distribution curves in Figure 10. The exemplars taken are Mt Gambier limestone for a narrow spread of velocities and Estaillades limestone for a wide spread. Note that they are different in both low-velocity field dominated regions where diffusion is the only mechanism of transport leading to stagnant concentration peaks, and in the high-velocity region which
produces the elongated tail of fast-moving solute. These characteristics define the nature of transport revealed by the different shapes of the propagators.

In the carbonates with a narrow spread of velocities (Ketton and Mt Gambier and ME2 in Figure 7), transport is characterized by a smaller immobile concentration peak and a significantly larger secondary peak in mobile tracer concentration. On the other hand, in samples with a wider spread of velocity (Estaillades, Indiana and ME1 in Figure 9), transport is characterized by a significant immobile peak concentration and an elongated tail of fast-moving solute.

The generic transport behavior can be predicted from the velocity distribution (Figures 6 and 10), pore size distribution (Figure 2) and the connectivity combined with the velocity field (Figures 3 and 4). While a lower porosity and connectivity with a wide spread of velocities result in most anomalous transport (Estaillades, Indiana and ME1), a higher porosity and connectivity and a narrow spread of velocities result in less anomalous transport behavior (Ketton, Mt Gambier and ME2).

We explore the effect of image resolution in Figures 11a,b where we compare the velocity fields and propagators for Estaillades for the $350^3$ image with a resolution of 7.7 µm and the $650^3$ image with a voxel size of 3.3 µm. The velocity fields are virtually identical with, perhaps, more slow-flowing regions identified in the higher resolution image. There is very little difference in the predicted propagators. Improving the image resolution allows more of the pore space to be captured, although there is still unresolved micro-porosity. However, there is – with finite computational resources – a trade-off between resolution and total system size. We
cannot both resolve micro-porosity and run simulations on an image that spans several characteristic lengths, and which is therefore representative of core-scale transport.

The complex non-Fickian transport behavior of propagators described has significant implications for mixing and large-scale transport. In order to describe long tailing plume behavior from the core scale, the plume retardation arising from stagnant flow regions needs to be incorporated, while the early breakthrough behavior needs to be described by taking into account secondary mobile peaks. This requires, as discussed in the Introduction, a transport model based on CTRW or multi-rate transfer models [Haggerty and Gorelick, 1995; Haggerty et al., 2000; Berkowitz et al., 2006].

### 3.2 Dependence on Peclet number

We study the effect of Pe on transport by taking exemplars representing the two generic types of behavior mentioned previously: Mt Gambier and Estaillades limestone.

Figure 12a,b compares the propagators for Mt Gambier at dimensionless times $t_d = 0.015$ and $t_d = 0.15$, for Pe=10, 50, 200 and 700. At early times ($t_d = 0.015$) lower Pe leads to a more diffusive transport with displacement centered on zero. On the other hand, the fast flow in mobile zones is more pronounced at higher Pe, where advection is more important, leading to the faster formation of the secondary mobile peaks (as seen for $t_d = 0.15$).

The impact of Pe on propagators for Estaillades is presented in Figure 13a,b for the same set of dimensionless times and Pe as in the case of Mt Gambier. Immobile fluid
regions are seen for both times and all Pe. For late times ($t_d = 0.15$) the formation of mobile peak is seen at highest Pe=700, although even in this case the persistent stagnant peak exists.

The impact of Pe on the shape of propagators can be analyzed by looking at the velocity distributions. In Figure 10 we plotted diffusive cut-offs at Pe=10, 50, 200 and 700 for which the time taken to traverse a voxel by advection is 100 times longer to that traversed by diffusion for Mt Gambier limestone. This means that essentially the only transport mechanism for these voxels is diffusion. With an increase in Pe, the diffusive cut-off moves to a lower value resulting in fewer voxels for which diffusion is the dominant mechanism of transport. Hence, as we vary Pe (either the overall flow rate or diffusion coefficient), the sampling of the velocity distribution changes. Thus, the diffusion-controlled stagnant peaks of concentration are less pronounced at higher Pe, as shown in Figures 12 and 13.

4. Discussion and Conclusions

We suggest that the characteristic transport behavior in carbonates is characterized by a stagnant peak concentration and a long fast-moving tail, controlled by the relative impact of diffusion and advection coupled to a wide range of flow velocities in a heterogeneous pore space.

In carbonates with a wide pore size distribution coupled with a low connectivity that consequently exhibit a wide distribution of velocities, the peak plume position is retarded relative to the mean flow field with a very wide spread, with a very slow moving peak concentration and an elongated tail of fast-moving solute, characterized
by peaks in mobile plume concentration. This is consistent with other studies of transport from the pore to the field scales in heterogeneous media (see, for instance, Berkowitz et al. [2006], Gouze et al., 2008b). For the carbonates where the impact of structure – a narrow pore size distribution and/or a highly connected pore space – results in a narrow distribution of velocities, quantitatively different non-Fickian behavior is observed, as the concentration peak of stagnant fluid is much smaller, on account of more fluid flow through connected channels that results in an elongated plume tail at early times and a single mobile peak moving at the average flow speed at later times. This behavior of propagators has significant implications for mixing and large-scale transport: in order to describe long tailing plume behavior, the plume retardation arising from stagnant flow regions needs to be incorporated, while accounting for the early breakthrough with secondary single or multiple mobile peaks.

This implies that simple average values for transport parameters, based on a Fickian formulation at the core scale cannot be used for accurate upscaling in geological media with multiple heterogeneity scales. Appropriate approaches to deal with multiple-scale heterogeneity, from the pore scale upwards, have been discussed by Berkowitz et al. [2008] and Bijeljic et al. [2011b].

We have provided the evolution of propagators for different carbonates as a function of Peclet number and quantified the impact of flowrate and diffusion on the nature of non-Fickian transport. These can – in principle – be used in a larger-scale simulation of transport without the need to presume a governing transport equation. The propagator $P(x,t; Pe)$ is simply the Green function for displacement. As a consequence, the concentration profile can formally be computed from
for an arbitrary initial concentration $C(x,0)$. In a numerical simulation, permeability heterogeneity at, say, the core (cm) scale could be computed to find a flow field. This then defines a locally-varying Peclet number $Pe(x)$. If we have characterized the propagators as a function of $Pe$, then Eq. (6) allows the time evolution of an arbitrary initial plume to be computed in a domain that is heterogeneous at the core-to-field scale. Further details of a possible approach to this problem using a generalized network analysis and a continuous time random walk approach can be found in Rhodes et al. [2008]. The development of this methodology is a topic for future work.

Geological structures are heterogeneous on all scales. Hence, it is not realistic to presume that given sufficient time the concentration profile will assume a Gaussian profile: the plume will encounter different scales of velocity heterogeneity, resulting in a highly dispersed transport from the pore to the field scales [Berkowitz et al., 2006]. Another promising topic for future work is to couple this methodology with chemical reaction at the pore scale, to provide a fundamental basis for larger-scale treatments of reactive transport.

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References


Table Captions

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