Dynamic pore-scale imaging of reactive transport in heterogeneous carbonates at reservoir conditions

Hannah Menke\textsuperscript{a*}, Branko Bijeljic\textsuperscript{a}, Matthew Andrew\textsuperscript{a}, Martin J. Blunt\textsuperscript{a}

\textsuperscript{a}Imperial College London Department of Earth Science and Engineering, South Kensington Campus, London, SW7 2AZ, United Kingdom

Abstract

Two carbonate rocks were studied experimentally at reservoir conditions at two flow rates using dynamic X-ray tomography. Cores of both homogeneous (Ketton) and heterogeneous (Portland) carbonates, were injected with CO\textsubscript{2}-saturated at 10 MPa and 50°C. Images were taken at between 30-second and 40-minute time-resolutions during injection. Reaction-induced changes in porosity, permeability, and structure were obtained by segmenting the images and extracting a pore/throat network. Differences in dissolution type and magnitude were found for each rock and flow rate. At the highest flow rates, Ketton displayed uniform dissolution. Conversely, Portland formed wormholes at high and compact dissolution at low flow rates.

© 2013 The Authors. Published by Elsevier Ltd. Selection and peer-review under responsibility of GHGT.

Keywords: Pore-scale; Reactive Transport; Carbonate; Reservoir Condition; X-ray Microtomography; Synchrotron

1. Introduction

Fluid-rock chemical interaction in the subsurface is an important mechanism with regard to storage permanence in Carbon Capture and Storage (CCS) [1,2]. When CO\textsubscript{2} is injected into the host brine it forms an acid solution [3,4,5] that has the potential to dissolve the surrounding rock structure, especially in carbonates, compromising seal

* Hannah Menke. Tel.: +44 2075941359; fax: +44 2075947444.
E-mail address: h.menke12@imperial.ac.uk
integrity and thus allowing CO₂ to escape [6]. However, the magnitude and type of dissolution is dependent on the flow and transport conditions of the brine and the intrinsic properties of the host rock and are known to be a strong function of temperature and pressure [7,8,9,10]. Understanding reaction in the fluid-rock system and fluid distribution and movement within the reservoir is thus imperative for accurate predictive modelling [11,12,13,14]. This paper will focus on the experimental measurements by X-Ray microtomography to assess the impact of flow and pore structure on reaction between acidic brine and rock.

X-Ray microtomography is now the predominant method for studying pore-scale processes [16,17]. This method offers significant advantages over traditional methods including the ability to study dynamic time-dependent processes non-invasively. Expanding on the reservoir condition pore-scale imaging experimental apparatus developed by Andrew et al. (2013) [18], Menke et al. (2014) [19], have developed a flow test-rig for imaging pore-scale reaction in situ. This study was for a single reservoir condition dynamic experiment on a Ketton carbonate micro-core and provided a direct-simulation based analysis of the dynamic changes in the pore-scale velocity field directly on the experimentally obtained micro-CT images. Additionally, Pereira-Nunes et al. (2014) [20] have used these images to verify a pore-scale reactive transport model.

In this study we expand on these results to include pore-scale imaging of two distinct carbonate rock types of varying heterogeneity at two flow and transport conditions. For each experiment we acquire the series of images to track the alteration in pore structure and the corresponding changes in porosity as dissolution progresses. Furthermore, we employ pore scale network modelling to characterize permeability and the evolving pore structure, and provide insights into pore scale dissolution patterns for rocks of different pore heterogeneity under varying flow conditions.

2. Materials and Methods

Our experimental apparatus is adapted from that of Andrew et al. (2013, 2014a,b) [18,21,22] and is identical to that in Menke et al., (2014) [19] [Figure 1]. A 1% KCl/5% NaCl by weight brine was loaded into a Hastelloy reactor (Parr instruments Co., IL, USA) and pre-equilibrated at 50°C and 10 MPa and fully saturated with super-critical (sc) CO₂. The carbonate core was wrapped in 3 layers of aluminum foil to deter any CO₂ diffusion and confined in a Viton sleeve with deionized water within a carbon fiber Hassler cell at 13MPa. The combination of a thermocouple inside the confining fluid and a flexible heating tape wrapped around the cell maintained reactor temperature in the cell. A separate brine of 6% KI was loaded into the back end flow pump and used to fully saturate the core before being ejected from the system to avoid contaminating the reactor fluid.

Reactor brine was then pulled through the core at a set flow rate with the pressure regulated by the injection pump at 10 MPa. The difference in attenuation between the two brines allowed for visual confirmation of the start of reaction using the real-time 2-D projections. Within the x-ray transparent carbon fibre Hassler cell, a 4 mm diameter, 1.2 cm long core was imaged approximately 2 mm from the front of the core with a 5 mm³ field of view. This point was chosen to avoid any possible boundary condition effects. Two different imaging apparatuses were used: the first is a lab source (Xradia Versa XRM-500, www.zeiss.com) for conducting reactive transport experiments in the homogenous rock where the changes in solid/fluid interface are slow enough so that it is possible to capture them with a 15-30 minute time resolution; the second is a synchrotron source (Diamond Lightsource Beamline I13-I) for experiments in the heterogeneous rock in which the solid/fluid interface changes are very rapid – this is only possible because the beam is powerful enough to provide time resolutions of 30s. The image voxel size varied between 3.8 and 6.1 μm depending on the lense and detector used.
Fig. 1. (a) The Core Assembly consists of the 1.2mm carbonate core, wrapped in one layer of aluminum followed by the Viton sleeve. This is then wrapped in two additional layers of aluminum to deter carbon dioxide diffusion with a thermocouple in between the layers for heating control. This is confined inside a carbon fiber Hassler cell with two steel end caps and flexible PEEK tubing for fluid transport. The core is imaged only in a 5mm³ field of view; (b) The Flow Rig is comprised of a front pressure and back-end pump, a reactor, and a confining pump. Filters (F) keep particulates from clogging flow lines and PID controllers fix temperature in the reactor and within the flow cell. In the micro-CT all pumps are outside of the lead lined X-ray hutch. At the synchrotron all pumps must necessarily lie inside the hutch and all flow conditions are controlled remotely.

We imaged reaction between calcite and unbuffered scCO₂ saturated brine in two carbonate cores at two flow rates. The two carbonate cores were selected because although they are both relatively pure (<99%) calcite oolites implying very similar reaction rates, they have widely differing pore structures. Ketton limestone is known to have homogenous pore structure, flow and transport properties while Portland limestone is characterized by heterogeneous structural, flow and transport properties [23,24].

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Experimental Time (min)</th>
<th># of scans</th>
<th># of projections</th>
<th>Flowrate (mL/min)</th>
<th>Time per scan (min)</th>
<th>Resolution (microns)</th>
<th>Source Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketton</td>
<td>147</td>
<td>10</td>
<td>400</td>
<td>0.5</td>
<td>15-20</td>
<td>3.8</td>
<td>Lab</td>
</tr>
<tr>
<td>Ketton</td>
<td>220</td>
<td>17</td>
<td>400</td>
<td>0.05</td>
<td>15-20</td>
<td>4.75815</td>
<td>Lab</td>
</tr>
<tr>
<td>Portland</td>
<td>120</td>
<td>97</td>
<td>1000</td>
<td>0.5</td>
<td>0.5-1</td>
<td>6.1</td>
<td>Lab</td>
</tr>
<tr>
<td>Portland</td>
<td>220</td>
<td>17</td>
<td>800</td>
<td>0.5</td>
<td>30-40</td>
<td>4.75815</td>
<td>Synchrotron</td>
</tr>
<tr>
<td>Basebed</td>
<td>10</td>
<td>10</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td>Lab</td>
</tr>
</tbody>
</table>

The images were taken as fast as our sources allowed using between 400 and 1000 projections depending on the desired resolution. The images were then filtered [Figure 2] using the edge-preserving filter non-local means [25,26] and then segmented using the watershed segmentation module in Avizo 8.0 [www.vsg3d.com] keeping all values
the same to avoid user bias [17,27]. Additionally, the filtered images were registered and subtracted to create a difference image used in visualizing dissolution patterns. The segmented images were then input into a network extraction model to analyze permeability changes.

Fig. 2. Image processing workflow shown for the experiment on Ketton at the higher flow rate (see Table 1): (a) raw 2-D image; (b) filtered 2-D image; (c) segmented 2-D image (d) 2-D difference image (e) 3-D rendering of the difference image (f) network extraction.
3. Results and Discussion

Figure 3 depicts porosity as a function of time for all four experiments. Porosity is determined using the ratio of solid ‘rock’ voxels to void ‘pore’ voxels in each image. As expected, the overall porosity increases as dissolution occurs throughout the experiments. There is a greater rate of change in porosity for the higher flow rates due to higher availability and rate of renewal of fresh reactive fluid. However, the magnitude and distribution of this dissolution is different in each experiment [Figure 4]. In the high flow rate Ketton experiment we see a largely uniform amount of dissolution both temporally and spatially. The same is true for the low flow rate Ketton experiment with the exception of the region that is very close to the core inlet where we observe slightly more dissolution at later times. In the high flow rate Portland experiments the spatial variation in porosity is uniform; however, the amount of dissolution through time does not remain constant and slows at the later times. Finally, in the low flow rate Portland experiments the dissolution magnitude varies both temporally and spatially with the greatest amount of dissolution happening at later times and nearest to the inlet of the core.

Fig. 3. Porosity as a function of time for Ketton (Ket) and Portland (Port) at high [0.5 mL/min] and low [0.05 mL/min] flow rates. Try dashed lines for lower flow rate experiments and say that in the caption
Pore network extraction directly on the binarized images was employed to characterize the geometry, topology, and permeability alterations during dissolution. This method is based on the maximal ball algorithm [28] that gives a topological representation of the pore space as pores connected by throats and provides basic permeability information. Additionally, the three-dimensional difference images were rendered to give a qualitative sense of the type of dissolution patterns.

Figure 5 shows renderings of both the 3-D difference image and network extraction results of each experiment at approximately halfway through each experiment. We observe that the pore topology has been dramatically altered by reaction in distinct patterns. The Ketton has dissolved rather uniformly [Figure 5a] with the lower flow rate experiment being less uniform at the inlet face of the core [Figure 5b]. The Portland case though shows evidence of preferential dissolution pathways (or wormholes) at high flow rates [Figure 5d] and dramatic dissolution nearer to the inlet face and little dissolution elsewhere at low flow rates [Figure 5c].
These different dissolution patterns have a great effect on the evolution of permeability during reaction. In the high flow rate experiment, the Ketton dissolution is relatively uniform and the change in permeability [Figure 6] is gradual. This is contrasted to the high flow rate experiment in Portland, where there is no observable change in permeability until 40 minutes have elapsed; however then there is a dramatic increase in later times. In the low flow rate experiments we observe this same dramatic permeability increase in Ketton at approximately 120 minutes. In the experiment at the low flow rate Portland has no permeability change. The permeability increases significantly when a connected dissolution pathway is formed across the whole core.
4. Conclusions

We have used a high pressure-high temperature experimental rig to image the dissolution of Ketton and Portland carbonates with sc-CO\textsubscript{2} equilibrated acid brine at reservoir conditions at two flow rates, at 3.8-6.1 µm spatial and 30 second to 40-minute time resolutions. We demonstrate that for dissolution of carbonates with homogeneous pore structure, flow and transport properties a coarser time resolution is sufficient and the lab source can be utilised, whereas for fast reaction in carbonates with heterogeneous structural, flow and transport properties a fine time resolution obtained by the synchrotron source is needed. We find that pore structure, flow and transport heterogeneity has a key impact on the dissolution patterns: at high flow rates we see wormholing for the heterogeneous carbonate and uniform dissolution for the homogeneous carbonate. At low flow rates we observe a more dominant dissolution nearer to the sample inlets for both carbonates. Significant sudden increases in porosity and permeability are seen when the configuration of channels created by dissolution break through – for the constant reaction rates studied here the times for the breakthrough depend on the heterogeneity and flow rate.

Acknowledgements

We would like to thank the Qatar Carbonates and Carbon Storage Research Centre for generously funding this research. Additionally, we would like to thank the Diamond Lightsource I13-I imaging team for their time and expertise in synchrotron science and data analysis.

References

Advances in Water Resources 2013, 51, 197-216.