Changes in Pore Structure and Connectivity Induced by CO₂ Injection in Carbonates: a Combined Pore-Scale Approach.

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Abstract

We investigate at the pore-scale fluid-rock interactions that occur in the context of carbon dioxide (CO₂) storage in saline carbonate aquifers. Brine saturated with super critical CO₂ is injected into two carbonate samples (Estaillades limestone and an aquifer sample) at typical storage conditions (9MPa and 50°C). Dry high resolution micro-computed tomography scans are obtained prior to and after the experiments and the pore structure, connectivity and computed flow fields are compared using image analysis and pore-scale modeling techniques. We perform direct simulations of transport properties and velocity fields on the 3D scans and we extract representative pore-throat networks to compute average coordination number and assess changes in pore and throat size distributions. In this study, we experimentally mimic near wellbore region conditions by injecting fluids at relatively high flow rates. For high Péclet and Damköhler numbers, experimental observations confirm the formation of highly conductive channels i.e wormholes. A significant increase in porosity and permeability is found with fewer pore and throats after dissolution while the average coordination number does not change significantly. Flow becomes concentrated in the wormhole regions after reactions although a very wide range of velocities is still observed.

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1. Introduction

It is well established that more than half of the world’s hydrocarbon reserves are contained in carbonate reservoirs [1]. Therefore, carbonate formations such as depleted oil and gas reservoirs and deep saline aquifers potentially represent huge storage volumes for Carbon and Capture Storage (CCS) technology. However, due to complex pore structures, micro-porosities, wide heterogeneities at different scales, and high reactivity, carbonate porous media remain very challenging to characterize [2-4]. Prior to
wide-scale implementation of CCS in carbonates, it is vital to investigate experimentally and numerically different phenomena that occur during carbon dioxide (CO$_2$) injection. In this context, pore-scale experimental and numerical studies can add valuable – in some cases predictive - information regarding the physics of single and multi-phase flow and transport properties [5-8].

During CO$_2$ injection in deep saline carbonate aquifers, a series of physical and chemical phenomena take place. At typical storage conditions the CO$_2$ is injected at depths below 800m in a supercritical phase (P$>7.39$MPa and T$>31.04^\circ$C) [9-11]. First, a portion of the injected supercritical-CO$_2$ (sc-CO$_2$) dissolves in the saline brine (solubility trapping) and a plume of the CO$_2$-saturated/enriched brine simultaneously flows along with the sc-CO$_2$ phase throughout the aquifer [12]. However, due to the formation and dissociation of the formed carbonic acid (see reactions 1-4 below), the pH decreases; consequently, the host formation is exposed to dynamic fluid-rock interactions where dissolution or precipitation may occur. Dissolution of the host formation can lead to an increase in porosity possibly increasing injectivity and storage capacity; however this dissolution could compromise the integrity of any seals, allowing the CO$_2$ to escape. On the other hand, precipitation of carbonate can effectively transform the CO$_2$ into solid minerals contributing to another important trapping mechanism (mineral trapping) [13, 14]. The reaction kinetics is strongly dependent on the pH, salinity, temperature and sc-CO$_2$ partial pressures [15]. Characterizing transport properties and reaction regimes that are caused by the plume migration is a reactive transport problem where, advection is coupled with diffusion and chemical reaction [16]. This is a challenging phenomenon to describe since reaction rates and transport properties vary over different time and spatial scales [17-20]. This complexity is exacerbated in carbonates where complex pore structures, wide heterogeneities and non-uniform mineralogical compositions are present. In this paper we start at the pore scale to obtain an understanding of dissolution processes.

Several experimental investigations have reported calcite dissolution reaction rates using high pressure and temperature CO$_2$ batch reactors and rotating disks [21-26]. However, only a few experimental studies were conducted at the pore scale in order to mimic reactive transport in the context of CO$_2$ injection in carbonate rocks. Noiriel et al. (2008) investigated the impact of CO$_2$ injection on reactive surface area, permeability and porosity changes on cylindrical limestone samples (9mm diameter and 15mm length) that were mainly composed of micrite and sparite [27]. The injections were performed at ambient temperatures (T=20$^\circ$C) and pressures below the supercritical threshold. Micro-computed tomography and chemical analysis of effluent concentrations showed a non-uniform increase of porosity, connectivity and reactive surface area induced by dissolution. Luquot and Gouze (2009) reported experimental results at typical storage conditions (100$^\circ$C and 12MPa) where sc-CO$_2$ was used [28]. A set of four core flooding experiments with varying sc-CO$_2$ partial pressures were performed on cylindrical carbonate samples (9mm diameter and 18mm length). Results showed the changes in permeability and porosity induced by dissolution and precipitation. The measured experimental porosity evolution with time was matched by a simplified form of the Bleasdale-Nelder equation.

The aim of this paper is to address fluid-rock interactions induced by CO$_2$ injection at typical storage conditions by combining experimental core flooding, with high resolution micro-computed tomography and pore-scale modeling calculations. First, we briefly present the chemical reactions and describe the dissolution regimes. Then, the experimental apparatus and methodology will be presented. Subsequently, first imaging and modeling results will be discussed. Finally, we will highlight future work directions.
2. Theory and experimental methodology

2.1 Chemical reactions and reactive transport theory

In a \( \text{CO}_2(g) - \text{H}_2\text{O} - \text{calcite (CaCO}_3): \text{calcium carbonate}) \) system, a series of chemical reactions occur [29]:

\[
\begin{align*}
\text{CO}_2(g) & \leftrightarrow \text{CO}_2(aq) \quad (1) \\
\text{CO}_2(aq) + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CO}_3 \quad (2) \\
\text{H}_2\text{CO}_3 & \rightarrow \text{H}^+ + \text{HCO}_3^- \quad (3) \\
\text{HCO}_3^- & \rightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (4) \\
\text{CaCO}_3 + \text{H}^+ & \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad (5) \\
\text{CaCO}_3 + \text{H}_2\text{CO}_3 & \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (6) \\
\text{CaCO}_3 & \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \quad (7)
\end{align*}
\]

In reactive transport problems, calcite dissolution chemical reactions (Equations 5, 6 and 7) are coupled with transport (advection and diffusion) of reactants and products. The understanding and modeling of reactive transport in general and wormholing phenomenon in particular has been widely investigated in the context of acid stimulation in carbonate oilfields. Calcite dissolution patterns have been experimentally shown to depend on two dimensionless numbers namely the Péclet and Damköhler numbers (and/or the Péclet-Damköhler number). The Péclet number is defined as the ratio of advection rate to diffusion rate: \( \text{Pe} = \frac{u l}{D} \), where \( u \) (m.s\(^{-1}\)) is the interstitial velocity (the Darcy velocity \( v \) divided by the porosity), \( l \) (m) is a typical length scale (a representative pore size) and \( D \) (m\(^2\).s\(^{-1}\)) is the molecular diffusion coefficient. The Damköhler number is here defined as the ratio of the reaction rate to the advection rate: \( \text{Da} = \frac{k l}{u} \). In our system, the Péclet number is equal to 3.5 (Estaillades) and 4.7 (aquifer sample). The diffusion coefficient for Ca\(^{2+}\) cations is \( D = 7.5 \times 10^{-10} \) m\(^2\).s\(^{-1}\) [28]. For the typical length scale, we use the average pore radius which is obtained from the network extraction. Damköhler number was estimated from Luquot and Gouze (2009) where, for similar experimental conditions measured Damköhler numbers ranged from 1 to 6 [28].

![Schematic diagram](image)

Figure 1 Schematic diagram representing the dependence of dissolution regimes and patterns on Péclet (Pe) and Damköhler (Da) numbers obtained from Golifère et al. [31]. Note that the transition values were computed for a particular system and specific reactants. Changes in the system and chemical composition will shift the transitions values. The blue point is an indication of the area investigated in this study.
2.2 Experimental methodology

Injection of single aqueous phase brine saturated with sc-CO$_2$ was performed at 50°C and 9MPa using a specially built core flood apparatus which is shown Figure 2. An equilibration reactor (1000 mL C276 autoclave with a gas entrainment stirrer – Parr instruments CO., IL, USA) was used to generate equilibrium between the brine and sc-CO$_2$ phases and produce the reactant fluid - brine saturated with sc-CO$_2$. High precision syringe pumps (Teledyne ISCO 1000D and 100D, Lincoln, NE, USA) were used to maintain pressure and inject fluids at constant pressures and flow rates. The temperature of the system was controlled at the target value using water heating jackets for the pumps and insulation throughout the lines and valves. In addition, an electrical oven was used to accommodate the flow cell and maintain the temperature. The brine composition used was 5wt. % NaCl and 1wt. % KCl. The cylindrical samples have a diameter of 5mm and a length of 20mm. Injections of brine saturated with sc-CO$_2$ were performed at a constant flow rate $Q = 1.667 \times 10^{-9} \text{m}^3\cdot\text{s}^{-1}$ ($v=8.49 \times 10^{-5} \text{m} \cdot \text{s}^{-1}$). This is quite high flow rate (around 10m/day) representing the near well-bore region.

Figure 2 High pressure and temperature reactive transport experimental apparatus. The apparatus consisted of five precision pumps, a high pressure and temperature mixing unit used to generated sc-CO$_2$ enriched brines, an oven and a specific flow cell that allow the injections at pressures and temperatures up to 20MPa and 80°C. Sampling vessels are used to collect effluent samples and monitor changes in chemical concentrations.

The core samples were drilled in a way that allows the bedding lines to be perpendicular to the length of the core. The samples were wrapped with aluminum and were contained in Vitton sleeves. The confining pressure applied here was constant and equal to 110% of the injection pressure i.e. 10 MPa. In a reactive
transport type core flood it is important to control the radial confining pressure in order to maintain the core integrity. Table 1 summarizes the petro-physical and mineralogical compositions of the dry native samples – note that permeability and porosity were measured on larger cores drilled from the same block of stone (37.84 mm diameter and 76.49 mm length for Estaillades and 25 mm diameter and 39.2 mm length for the aquifer sample). Mineralogical composition was obtained from X-Ray Diffraction (XRD) measurements (Weatherford laboratories) on grains obtained from the same samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>Permeability (mD)</th>
<th>XRD-Mineralogical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estaillades</td>
<td>29.5</td>
<td>151</td>
<td>Calcite: 97.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Quartz: 2.1</td>
</tr>
<tr>
<td>Aquifer sample</td>
<td>28</td>
<td>217</td>
<td>Calcite: 97.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Quartz: 2.8</td>
</tr>
</tbody>
</table>

Table 1 Experimental measurements of porosity and permeability and mineralogical characterizations for the two samples studied: Estaillades limestone and the aquifer sample.

Estaillades is a quarry limestone with heterogonous pore size. The aquifer sample is a carbonate obtained from a deep saline aquifer in the Middle East. In brief, the main steps of the experimental procedures are:

1- The system (including the core holder and sample) is set under vacuum for 24 hours.
2- Carbonate pre-equilibrated brine is injected to saturate the core. More than 1,000 pore volumes (PV) are injected.
3- Brine saturated with CO₂ was prepared using the high pressure and temperature reactor. The same experimental procedure as El Maghraby et al. (2012) is used [32].
4- Brine saturated with sc CO₂ is injected through the core at constant flow rate, (100±15) PV are injected.
5- Clean the samples by flushing out the liquids using a solvent (iso-propanol) and allow the samples to dry using a vacuum oven.

2.2.2 Micro-Computed Tomography using a Synchrotron

Dry scans of the selected carbonate samples (prior to and after the core flooding) were made at the SYRMEP (Synchrotron Radiation for Medical Physics) beamline at the Elettra synchrotron in Trieste, Italy [33]. The images were obtained using energies between 27-30 keV. A detector of 3.85 µm was used and the 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 voxel size 7.7 µm.

3. Results

3.1 Image Analysis

At the target flow rate, dissolution is not uniform and as expected wormholes are observed in the scans. During approximately the first 300 -350µm, face dissolution is observed where the rock is subject to significant reaction. Then the wormhole forms and propagates - in most cases – around the center of the sample and through the most permeable pores. The length of the wormhole varies with the sample. Therefore, during the segmentation, only the region corresponding to the wormhole propagations were
selected – the face dissolution region (300-350 µm) was ignored. Figure 3 represents the methodology that was used to select the 3D areas for image analysis, network extraction and direct computations.

Figure 3 Example schematic of the cropping methodology for the aquifer sample. Important face dissolution occurs at the inlet of the sample. The remaining solid structure is cropped and segmented into a 3D binary representation of the pore space. Blue indicates the pore space and green represents the solid.

Figure 4 shows 2D sections of 3D micro-computed tomography scans of the Estaillades carbonate prior to and after injection of brine saturated with sc-CO₂. Here, the same 2D slice is compared. The propagation of the wormhole is clearly visible. In order to better compare the pore space, the cropped segmented images of the same slices are shown in Figure 5. In addition to the wormhole propagation along the sample, we notice the increase of porosity in the regions away from the wormholes. However, this is a local effect which is observed on a single 2D slice - to assess the impact of dissolution on overall pore space connectivity, representative pore-throat networks will be extracted in order to compute the coordination number, and this will be discussed in the following sections.

Figure 4 2D images of 3D micro-computed tomography scans of Estaillades prior to (left) and after (right) reaction. The same physical location is shown in both cases. Images are representing the same slices. The presence of the wormhole can be clearly seen in the image to the right.
3.2 Connectivity analysis

3D scans representing the same physical volume were processed i.e. cropped and segmented in order to generate 3D binary images of the pore space. Topologically representative pore and throat networks were extracted in order to assess the impact of reaction on the pore structure. The maximal ball algorithm developed by Dong and Blunt (2009) was used to extract the networks [34]. A summary of the network properties is presented in Table 2. Overall, the number of pores and throats decreases as a result of the dissolution process: individual pores and throats are merged to form the wormhole and this effect dominates over the formation of new connections in the rest of the pore space. However, the average coordination number (average number of throats connected to a single pore) does not change significantly. The maximum coordination number increases dramatically since this represents the wormhole. Figure 6 shows the comparison of coordination number distributions for native and altered cases and both samples.

<table>
<thead>
<tr>
<th></th>
<th>Number of pores</th>
<th>Number of throats</th>
<th>Average coordination number</th>
<th>Standard deviation coordination number</th>
<th>Maximum coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estaillades</td>
<td>8649</td>
<td>13053</td>
<td>2.98</td>
<td>2.81</td>
<td>37</td>
</tr>
<tr>
<td>native</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estaillades</td>
<td>5853</td>
<td>8084</td>
<td>2.72</td>
<td>3.36</td>
<td>141</td>
</tr>
<tr>
<td>altered</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquifer sample</td>
<td>7564</td>
<td>14328</td>
<td>3.74</td>
<td>3.82</td>
<td>46</td>
</tr>
<tr>
<td>native</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquifer sample</td>
<td>5092</td>
<td>8763</td>
<td>3.39</td>
<td>4.44</td>
<td>112</td>
</tr>
<tr>
<td>altered</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Description of the extracted networks.
Figure 6 Distribution of coordination numbers for the native (solid line) and the altered (dashed line) cases. Coordination number distribution does not change significantly, although the maximum – representing the wormhole – is much larger in the altered samples.

Figure 7 shows a comparison of the pore and throat size distributions of the native and altered networks. The shape of the distributions remains very similar; however fewer pores and throats are present in the altered networks. The shift in the distributions is more pronounced in Estaillades with a greater fraction of larger pores in the altered sample.

Figure 7 shows pore and throat size distributions of the native (solid line) and altered carbonate (dashed line) samples.

3.2 Transport properties

We simulate incompressible viscous steady-state flow directly on the pore space images by solving the volume conservation and momentum balance (Navier Stokes) equations [35,36]. Figure 8 shows the normalised velocity distribution – computed at the centre of each void voxel in the image - for the native and altered Estaillades limestone. In both cases a wide range of velocities is observed. However, in the altered case, the flow is more concentrated in the wormhole regions. Non uniform dissolution leads to a sharpening of velocities within the large channels.
4. Conclusions and future work

A specific experimental apparatus was used to mimic at the pore scale dynamic fluid-rock interactions that occur near the well-bore during CO$_2$ injection in deep saline carbonate aquifers. The samples were imaged at a resolution of around 8µm before and after reaction and the results were analysed using network modelling and direct computation of the flow field in the pore space. At relatively high Péclet and Damköhler numbers, we noticed the formation and propagation of wormholes along the samples. The generation of new connectivity in the regions away from the wormhole is evident, although the total number of pores and throats decrease as connections merge, while the distribution of coordination number remains largely unaffected. The flow field becomes more concentrated in the wormhole, but a very wide range distribution of local velocities – spanning more than eight orders of magnitude – is predicted. For future work we will investigate dissolution regimes at lower Damköhler numbers and will predict transport properties.

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References


