Reactive Transport Models with Geomechanics to Mitigate Risks of CO₂ Utilization and Storage

Project: DE-FE009773

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Objectives

- Experiments to study pore level and petrophysical property changes in experiments of carbon dioxide and brine with different rock types
- Validation of models using experimental results
- Coupling of geomechanical models with flow
Experimental Strategy

Experimental systems and reactive transport model

- **Core flooding system**
  - CO₂ injection rate
  - Petrophysical changes
  - Mineralogical changes

- **Batch reactor system**
  - Petrophysical changes
  - Mineralogical changes
  - Changes with time

- **Modeling**
  - Evaluate experimental data
  - Geomechanics and Flow

Comprehensive measurements

- **BET, He Porosimeter, and Micro-CT**
  - Analyze porosity changes, surface area and pore structure

- **ICP-MS and pH meter**
  - Measure pH and cation concentration of the effluent

- **XRD and QEMSCAN**
  - Mineralogical analysis of core samples
Sample Preparation

Batch Reactor System

Core Flooding System

He porosimeter
QEMSCAN
XRD
Micro-CT
BET
ICP-MS

Micro-CT for Limestone

8 inch
Sandstone
Limestone
Dolomite

1 inch

1/2 inch

Core plugs

Micro-CT

BET

QEMSCAN

XRD
Core flooding system conditions

- Core pressure: 2,000 psi
- Confining pressure: 3,000 psi
- Reaction temperature: 60 °C
- Reaction time: 14 days
- Cores: sandstone, limestone, and dolomite
- CO₂ : Brine ratio: Variable
- (1.5 inch diameter, 7 inch length)
Sandstone Effluent Analysis

Mineralogical changes: Effluent analysis using ICP-MS, sandstone

Iron involvement observed by Carroll et al. (2012)

Fe, Ca, and Mg concentrations peak and decrease

Slightly higher peaks at higher flow rates
Limestone Effluent Results

Mineralogical changes: Effluent analysis using ICP-MS, limestone

Significant changes with respect of Ca
Dolomite Effluent Results

Mineralogical changes: Effluent analysis using ICP-MS, dolomite

Ca and Mg dissolution consistent with the mineralogical composition of dolomite
Core flooding conducted at sequestration conditions shows effluent peaks of key cations – Fe, Ca and Mg

The level of iron dissolution in sandstone – even over short durations was higher than expected – may have major implications in practical sequestration scenarios

Ankerite and siderite are the main iron bearing reactive minerals in sandstone and they dissolve almost completely in the two-week experiment

In XRD spectra, differences were observed in sandstone, but not in limestone or in dolomite

Higher flow rates led to higher levels of mineral dissolutions
**Porosity Changes - Sandstone**

Petrophysical changes: Porosity measurement using helium porosimeter, sandstone

<table>
<thead>
<tr>
<th>Unreacted Sandstone</th>
<th>Brine: 1 ml/min CO(_2): None</th>
<th>Brine: Initially saturated CO(_2): 1.41 ml/min</th>
<th>Brine: 1 ml/min CO(_2): 1.41 ml/min</th>
<th>Brine: 1 ml/min CO(_2): 2.82 ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlet</td>
<td>21.263 %</td>
<td>21.462 %</td>
<td>22.822 %</td>
<td>22.650 %</td>
</tr>
<tr>
<td>Average porosity of sandstone</td>
<td>21.307 %</td>
<td>21.175 %</td>
<td>21.739 %</td>
<td>21.110 %</td>
</tr>
<tr>
<td>Inlet</td>
<td>21.110 %</td>
<td>21.706 %</td>
<td>21.739 %</td>
<td>21.634 %</td>
</tr>
</tbody>
</table>

**Porosity changes:**

- Unreacted Sandstone: 0.18 %
- Brine: 1 ml/min CO\(_2\): None: 0.12 %
- Brine: Initially saturated CO\(_2\): 1.41 ml/min: 0.60 %
- Brine: 1 ml/min CO\(_2\): 2.82 ml/min: 1.01 %
Limestone Porosity Changes

Petrophysical changes: Porosity measurement using helium porosimeter, limestone

Unreacted Sandstone

<table>
<thead>
<tr>
<th>Brine: 0.5 ml/min</th>
<th>Brine: Initially saturated 0.5 ml/min</th>
<th>Brine: 0.5 ml/min</th>
<th>Brine: 0.5 ml/min</th>
<th>Brine: 1 ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂: None</td>
<td>CO₂: 0.71 ml/min</td>
<td>CO₂: 0.71 ml/min</td>
<td>CO₂: 1.41 ml/min</td>
<td>CO₂: 1.41 ml/min</td>
</tr>
<tr>
<td>Outlet</td>
<td>20.812 %</td>
<td>20.321 %</td>
<td>20.349 %</td>
<td>20.349 %</td>
</tr>
<tr>
<td></td>
<td>20.704 %</td>
<td>20.402 %</td>
<td>20.403 %</td>
<td>20.715 %</td>
</tr>
<tr>
<td></td>
<td>20.822 %</td>
<td>20.314 %</td>
<td>20.680 %</td>
<td>20.650 %</td>
</tr>
<tr>
<td></td>
<td>Average porosity</td>
<td></td>
<td></td>
<td>20.646 %</td>
</tr>
<tr>
<td>Of limestone</td>
<td>19.973%</td>
<td></td>
<td></td>
<td>20.390 %</td>
</tr>
<tr>
<td></td>
<td>20.619 %</td>
<td>20.619 %</td>
<td>29.847 %</td>
<td>25.720 %</td>
</tr>
</tbody>
</table>

Inlet

| Porosity changes: | 0.70% | 0.55 % | 1.12(5.46) % | 1.59 % | 2.79 % |

Porosity changes: Unreacted Sandstone

Outlet: 20.812 %, 20.704 %, 20.822 %

Average porosity of limestone: 19.973%

Inlet: 20.619 %

Porosity changes: 0.70%, 0.55%, 1.12%, 1.59%, 2.79%
## Petrophysical changes: Porosity measurement using helium porosimeter, dolomite

<table>
<thead>
<tr>
<th>Unreacted Sandstone</th>
<th>Brine: 0.6 ml/min CO₂: None</th>
<th>Brine: 0.6 ml/min CO₂: 0.85 ml/min</th>
<th>Brine: 0.6 ml/min CO₂: 1.70 ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity changes</td>
<td>0.42%</td>
<td>1.58%</td>
<td>2.52%</td>
</tr>
<tr>
<td>Average porosity of sandstone</td>
<td>14.016 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Outlet**

- **Inlet**

- **Unreacted Sandstone**

- **Brine: 0.6 ml/min CO₂: None**

- **Brine: 0.6 ml/min CO₂: 0.85 ml/min**

- **Brine: 0.6 ml/min CO₂: 1.70 ml/min**

- **Porosity changes:** 0.42%, 1.58%, 2.52%
Permeability Changes

Petrophysical changes: Permeability calculation

Sandstone:
- 1.41 ml/min CO₂
- 2.82 ml/min CO₂
- Blank (No CO₂)

Limestone:
- 0.71 ml/min CO₂ (0.5 ml/min brine)
- 1.41 ml/min CO₂ (0.5 ml/min brine)
- Blank (No CO₂)
- 1.41 ml/min CO₂ (1 ml/min brine)

Dolomite:
- 0.85 ml/min CO₂
- 1.70 ml/min CO₂
- Blank (No CO₂)

Permeability change ranges

Sandstone: from 0.21 % to 1.43 %
Limestone: from 1.06 % to 3.42 %
Limestone: from 0.51 % to 2.41 %
Micro-CT Imaging

Petrophysical changes: Limestone core analysis using Micro-CT

Images of different sections of limestone core using Micro-CT Pre- (left, orange color) images and post (right, gray color) flooding experiments

Brine: 0.5 ml/min  
CO₂: None

Brine: Initially saturated  
CO₂: 0.71 ml/min

Brine: 0.5 ml/min  
CO₂: 0.71 ml/min

Brine: 0.5 ml/min  
CO₂: 1.41 ml/min

Brine: 1 ml/min  
CO₂: 1.41 ml/min
Summary of Petrophysical Changes

- Changes in porosity and permeability were quantified.
- Porosity changes were measured by helium porosimeter. In the sandstone, limestone, and dolomite the porosity change ranged from 0.12 % to 1.01 %, from 0.55 % to 2.79 %, and from 0.42 % to 2.52 %, respectively.
- In sandstone, permeability change ranged from 0.21 % to 1.43 %. Also limestone and dolomite showed increase, from 1.06 % to 3.42 % and from 0.51 % to 2.41 %, respectively.
- Higher flow rates led to larger changes.
- Pore morphology changes were found in limestone using Micro-CT. At lower flow rates beginnings of wormhole type structures were observed, and higher flow rates fully developed wormhole was shown.
Mineralogical changes: Comparison between experiment and simulation results

Good match of peak and trends for iron

Reactions of a few other minerals may be relevant
Petrophysical Changes

Petrophysical changes: Porosity and permeability changes

Figures show the comparison between pre-experiment and post-experiment values of porosity and permeability distribution in the core.

Slightly larger changes at the inlet. Maximum amount is predicted to be 0.5 % and 1.4 % for porosity and permeability, respectively. This is consistent with experimental data.
Trends and peaks of effluent ion concentrations (particularly, Fe) were matched by the simulations.

Simulations showed that ankerite dissolution was fast relative to siderite leading to the characteristic iron effluent peak observed in the experiments.

Porosity and permeability changes predicted in the simulation were reasonably close to the experimental values.
**Batch Reactors**

**Schematic diagram of the batch reactor system**

**Batch reactor system conditions**

- Reaction pressure: 2,400 psi
- Reaction temperature: 60°C
- Reaction time: 14 days
- Core samples: sandstone, limestone, and dolomite
  - (Powder, fractures, and 0.5 inch core plug)
**Batch Systems – Main Results**

**Mineralogy changes with different surface area: Effluent analysis using ICP-MS**

Table 7. ICP-MS results for core plug, fractured core, and powdered core after two week

<table>
<thead>
<tr>
<th></th>
<th>Na (mg/kg)</th>
<th>Mg (mg/kg)</th>
<th>Al (mg/kg)</th>
<th>Si (mg/kg)</th>
<th>K (mg/kg)</th>
<th>Ca (mg/kg)</th>
<th>Fe (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LOD</strong></td>
<td>2</td>
<td>0.004</td>
<td>0.06</td>
<td>0.06</td>
<td>7</td>
<td>13</td>
<td>0.05</td>
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<tr>
<td><strong>Core plug samples</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>7024</td>
<td>0.68</td>
<td>0.64</td>
<td>0.22</td>
<td>&lt;7</td>
<td>&lt;13</td>
<td>1.92</td>
</tr>
<tr>
<td>Sandstone</td>
<td>7108</td>
<td>60.2</td>
<td>27.2</td>
<td>3.8</td>
<td>72</td>
<td>154</td>
<td>126</td>
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<tr>
<td>Limestone</td>
<td>7024</td>
<td>24</td>
<td>2.43</td>
<td>1.16</td>
<td>64</td>
<td>571</td>
<td>0.08</td>
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<tr>
<td>Dolomite</td>
<td>7188</td>
<td>302</td>
<td>0.87</td>
<td>5.04</td>
<td>80</td>
<td>428</td>
<td>0.08</td>
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<tr>
<td><strong>Fracture samples</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Blank</td>
<td>7096</td>
<td>0.82</td>
<td>&lt;0.06</td>
<td>0.25</td>
<td>&lt;7</td>
<td>&lt;13</td>
<td>1.14</td>
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<tr>
<td>Sandstone</td>
<td>7103</td>
<td>109</td>
<td>64.9</td>
<td>8.4</td>
<td>140</td>
<td>204</td>
<td>192.1</td>
</tr>
<tr>
<td>Limestone</td>
<td>7028</td>
<td>29</td>
<td>1.39</td>
<td>3.07</td>
<td>96</td>
<td>708</td>
<td>0.07</td>
</tr>
<tr>
<td>Dolomite</td>
<td>7097</td>
<td>444</td>
<td>0.15</td>
<td>2.37</td>
<td>137</td>
<td>543</td>
<td>0.08</td>
</tr>
<tr>
<td><strong>Powder samples</strong></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>Blank</td>
<td>7018</td>
<td>0.74</td>
<td>0.32</td>
<td>1.68</td>
<td>&lt;7</td>
<td>&lt;13</td>
<td>1.53</td>
</tr>
<tr>
<td>Sandstone</td>
<td>6904</td>
<td>167.2</td>
<td>98.5</td>
<td>17.2</td>
<td>211</td>
<td>384</td>
<td>271.44</td>
</tr>
</tbody>
</table>

Enhanced changes are observed as we go from core plugs to fracture samples to powders.
Mineralogical changes: Limestone core plug analysis using QEMSCAN

Background area increased from 14.58% to 23.54%

Widespread dissolution including internally
The cross sectional 2D images the pore morphology change is easily recognized.

The 3D solid image there are many pore changes on the surface of the core plug.

The 3D negative image is cloudier after the batch experiment reaction.
Batch Reactor Observations

• Mineral dissolution caused the growth and expansion of pores in all mineralogies.
• The 2D cross section Micro-CT results showed pore expansion within the sandstone and limestone core plugs.
• The 3D solid images showed pore changes on the surface of sandstone, limestone, and dolomite. The 3D negative images displayed removed particles and increased porosity.
• Surface area changes were measured by BET instruments. Increased surface area in sandstone, limestone, and dolomite ranged from 24.30 % to 35.47 %, 9.98 % to 19.58 %, and 7.45 % to 40.94 %, respectively.
Experimental Conclusions

- Mineralogical changes after two weeks of injection have the potential to cause significant petrophysical and subsequent structural changes in sandstone, limestone and dolomite formations under carbon dioxide sequestration conditions. This was the original hypothesis that was validated using high-pressure core floods in this work.

- Iron chemistry plays an unexpectedly larger role in sequestration in sandstone formations. Dissolution of ankerite and siderite lead to large iron effluent concentrations. A reactive transport model such as TOUGHREACT may be used to explain the complex interconnected reactions with flow. However, some of the flow rate effects observed in the experiments could not be reproduced in the model.

- In limestone and dolomite, calcium and magnesium bearing minerals dissolve leading to formation of large dissolution zones, including wormholes.
Porosity and permeability changes are small – of the order of 1-2% and similar values result from TOUGHREACT.

Batch experiments showed similar trends in iron in sandstones, and calcium and magnesium in limestone and dolomite. As the surface areas increase by using rock chips and then powders, reactivities increase leading to larger cationic concentrations in brine.

Approximate morphology of the reacted volume is viewed using QEMSCAN and Micro-CT for batch samples. Reactions appear to be uniform throughout the volume for limestone and dolomite, whereas they appear to be limited more to the surface in sandstone.
Method: Coupling DEM with Conjugate Network Flow Model (INL)

Prior to fracturing

\[ q_{ij} = \frac{k_0 \cdot A_{ij} \cdot (P_i - P_j)}{\mu \cdot l_{ij}} \]

After fracturing

\[ q_{ij} = \frac{k_{ij} \cdot b_{ij} \cdot (P_i - P_j)}{\mu \cdot l_{ij}}, \quad \text{with} \ k_{ij} \approx b_{ij}^2 / 12 \]

- Directly calculate apertures of micro-fractures;
- Apertures are used as direct input for updating permeability of the flow network;
- More PHYSICS-based hydraulic fracturing model
Mechanistic modeling of reactivations of natural fractures near injection wellbore due to CO2 injection

- Cemented wellbore with open injection interval
- Vertical stress ~10,000psi with H/V ratio of 0.5
- Densely fractured reservoir
- Natural fractures are assumed to be mechanically closed
- Natural fractures have initial permeability of ~$1.4 \times 10^{-12} \text{m}^2$
- The reservoir matrix permeability is low, ~$1.4 \times 10^{-19} \text{m}^2$
Simulations on stress and permeability changes

Fluid pressure distribution shortly after the injection was started

Horizontal displacement field and fracture network colored by fracture permeability

Fluid pressure distribution after flow reached steady-state

Horizontal displacement field and fracture network colored by fracture permeability
Shear slipping vs. opening?

Displacement vector fields
DEM geomechanics model - a robust for either fractured or not-fractured reservoir

Most natural fractures are filled with secondary minerals, and have certain tensile and shear strengths: DEM accounts for such effects in dealing with natural fractures.

We see dilational opening of fractures rather than shear failures.

Geochemical reactions such as mineral dissolution/precipitation weaken mechanical strength natural fractures, leading to reactivation of fractures.
Project Status

- Wrapping up with more data analysis on reaction rates and surface area
- Field implications
- Use of experimentally obtained parameters in INL simulations