Enhanced porosity and permeability in carbonate CO$_2$ storage reservoirs: An experimental and modeling study

Project Number: FWP-FEW0174 – Task 5
Presentation Outline

- Benefit to Program
- Project Overview
- Technical Status
- Accomplishments
- Summary
- Appendix
Benefit to the Program

- This research project quantifies relationships between fluid flow, heterogeneity, and reaction rates specific to carbon storage in carbonate reservoirs by integrating characterization, solution chemistry, and simulation data.

- This project meets the Carbon Storage Program goals to develop technologies that will support industries’ ability to predict CO$_2$ storage capacity in geologic formations to within ±30 percent.
Project Overview

Goals and Objectives

- The goal of this project is to calibrate key parameters in reactive transport models that will be used to predict final storage of CO$_2$ in carbonate EOR fields.

- This project will advance science-based forecasting for the transition of CO$_2$ – EOR operations to storage sites.

- Success is tied to the ability to scale reactive-flow and transport parameters over a range of carbonate rock types and permeability.
Technical Status

The research scope consists of three major tasks:

- Model calibration against existing experimental database of carbonate rocks from Midale-Weyburn Carbon Storage Project

- Study of a wider permeability range using cores from the Wellington, KS, CO$_2$ demonstration site (focus of presentation)

- Refined model and parameter scaling towards predicting changes in reservoir porosity and permeability
Motivation behind choices of characterization techniques and experimental scales

- Geochemical mineral-fluid interactions induced by CO₂ injection have a major effect on rock porosity and permeability evolution, which may potentially alter the behavior or performance of CO₂ geological storage and EOR operations;

- The mineral dissolution/precipitation and associated flow and reactive transport processes in porous media are described at different scales;

- Reactive transport modeling represents a critical component in assessment of geochemical impact of CO₂ water-rock interactions;

- However, a lack of proper calibration or upscaling of the effective macroscopic parameters over large field-scales hinders accurate reactive-transport modeling of CO₂ fate and transport.
Wellington, Kansas, flow unit model & samples

A. Mississippian pay zone
3700'

B. Caprock
3999'

C. Simpson Sandstone
4100'

D. Arbuckle - top
4170'

E. Arbuckle - baffle zone
4815'

F. Arbuckle - injection zone
4775'

#1-32 w/GR log (right) & porosity (left)
Shales = more red

KGS #1-32

KGS #1-28

model image, cores courtesy of KGS
Wellington, KS, samples extend permeability range

A) Vuggy limestone
B) Marly dolostone
C) Evaporite caprock
D) Simpson sandstone & carbonate cement
E) Arbuckle injection zone (large)
F) Arbuckle injection zone, 2
G) Arbuckle baffle zone
Subcores exhibit lower permeability compared to well log data – larger samples are better.

Permeability, mD – reported vs. measured (log scale)

2.5x increase in diameter for “second-generation” Injection zone samples

1.5in / 38mm
Core-flood set-up adapted for new KS samples

- 60°C temp, 25 MPa confining pressure
- constant flowrate 0.05 mL/min
- 1.1m NaCl brine with $p\text{CO}_2 = 3$ MPa, at carbonate equilibrium
Brine-CO$_2$ exposure caused little change to properties of Simpson sandstone sample.

Unreacted Simpson cross-section, (smaller) 15-mm diameter gray-scale tomography image, located ~17mm from inlet.

Quartz grains, less cemented.

Pyrite grains (bright).

Highly-cemented regions.

Calcite.

Dolomite.

$t = 0$, transition to CO$_2$-rich brine flow.

Log, saturation index vs. time [days].

Pre-rxn and post-rxn images showing changes in the sample.
Within larger samples, (macro)pore clusters isolated by finer-grained matrix material.

Connected macro-pores, large deep injection zone sample.
**Reactive transport model adaptations for CO₂ core flooding experiments**

- 3-D continuum-scale reactive transport model (NUFT)
- CO₂-equilibrated brine with pCO₂ = 3 MPa injected into core sample at a constant 0.05 mL/min rate.
  - Handles either core size (15, 38-mm diameter).
- Model lateral boundaries kept impermeable; constant pressure and flux conditions imposed at top and bottom boundaries.
- Dolomite reaction kinetics
  
  \[
  \frac{dm}{dt} = -S \left[ k_{\text{acid}}^{298.15K} e^{-\frac{E_{\text{acid}}}{R} \left( \frac{1}{T} - \frac{1}{298.15K} \right)} d_{H^+}^n + k_{\text{neutral}}^{298.15K} e^{-\frac{E_{\text{neutral}}}{R} \left( \frac{1}{T} - \frac{1}{298.15K} \right)} \right] \left[ 1 - Q \frac{K}{K} \right]
  \]
- Utilizes nonlinear porosity–permeability correlation and surface area–porosity relationship

<table>
<thead>
<tr>
<th>Reactions</th>
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<tbody>
<tr>
<td>Dolomite + 2H⁺ = Ca²⁺ + Mg²⁺ + 2 HCO₃⁻</td>
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<tr>
<td>CO₂(aq) + H₂O = H⁺ + HCO₃⁻</td>
</tr>
<tr>
<td>MgHCO₃⁺ = Mg²⁺ + HCO₃⁻</td>
</tr>
<tr>
<td>CaCO₃(aq) + H⁺ = Ca²⁺ + HCO₃⁻</td>
</tr>
<tr>
<td>CaHCO₃⁺ = Ca²⁺ + HCO₃⁻</td>
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</tbody>
</table>
Important lessons from previous Weyburn results carried forward in new simulations

**Chemical Model** – Experiments allow combined reactivity to be calibrated

$$\frac{dm}{dt} = -S \left[ k_{acid}^{298.15K} e^{-\frac{E_{acid}}{R} \left( \frac{1}{T} - \frac{1}{298.15K} \right)} a_{H^+} + k_{neutral}^{298.15K} e^{-\frac{E_{neutral}}{R} \left( \frac{1}{T} - \frac{1}{298.15K} \right)} \right] \left( \frac{1}{K} - \frac{Q}{K} \right)$$

- Rate equations are tied to equilibrium
- Literature equilibrium constants provide starting points
- Calibrations combine rate constants and surface areas
- Pressure changes are not sensitive to reaction rate

**Porosity – Permeability – Surface Area Relationships**

- Change surface area in proportion to decreasing spherical grains

$$S_t = S_0 \left( \frac{\theta_t}{\theta_0} \right)^{2/3} \left( \frac{\phi_t}{\phi_0} \right)^{2/3}$$

$$K_t = K_0 \left( \frac{\phi_t}{\phi_0} \right)^n$$

“n” and permeability contrast terms allow for coupled porosity, permeability evolution.
Effective porosity and mineral phase volume fraction were calculated by a volumetric averaging approach.

\[
\phi = \frac{\sum_{i} \phi_i}{N}, \quad \theta_m = \frac{\sum_{i} \theta_{m,i}}{N}
\]

Permeability distributions were estimated by assessing macro-pore distribution and connectivity. Two porous regions were assumed within the rock sample: one representing interconnected \textit{macro-pore regions}, and the other the \textit{less porous matrix}.
Pre-experiment modeling results — Base Case

- flow rate = \(0.05 \text{ mL/min}\),
- porosity-permeability relation \( n = 6 \),
- permeability contrast \( K_1/K_2 = 100 \),
- \( k_{\text{acid}}^{298.15K} = 10^{-3.2} \text{ mol/m}^2/\text{s} \),
- \( k_{\text{neutral}}^{298.15K} = 10^{-7.5} \text{ mol/m}^2/\text{s} \).
Sensitivity studies — increasing permeability contrast by 10x

Porosity distributions after CO$_2$ flooding of 120 hours (5 days)

low permeability contrast (base case)  
higher permeability contrast
Sensitivity studies — decreasing kinetic constants by 100x (acid) and 10x (neutral mechanism)

Porosity distributions after CO₂ flooding of 120 hours (5 days)

- high reactivity (base case)
- lowered reactivity

Graph showing normalized pressure difference over time (hour) with different rate constants.
Sensitivity studies — decreasing porosity-permeability relation ($n$) from 6 to 3

Porosity distributions after CO$_2$ flooding of **120 hours** (5 days)

$n = 6$ (base case)  

$n = 3$
Accomplishments to Date

- Publication of results of low permeability caprock response to CO₂ exposure (*Smith et al., 2012, ES&T*)
- Weyburn-specific model and scaling results published in special issue (*Carroll et al., 2013, IJGGC*).
- Development of model methodology to incorporate varying scales of characterization data to be published (*Hao et al., in final revision, AWR*).
- Additional samples from Arbuckle reservoir (Wellington, KS, KGS) acquired, imaged via CT, and characterized.
- One full-length Simpson (Wellington, KS) experiment completed; Results of eight Weyburn experiments to be published (*Smith et al., in final revision, AWR*).
- Equipment modified to accept larger core samples (*first larger-scale core to be tested September 2013*).
- Pre-experimental modeling completed to inform upcoming experiments.
Key Findings

- Anisotropic permeability and mineral dissolution play dominant roles in porosity and permeability changes that will occur during CCUS operations.
- Calibrated several reactive transport parameters that scale from microns to centimeters.
- Porosity–Permeability relationships are dependent on sample heterogeneity.
  - Pore regions are not well connected at previous core scales.

Future Plans: Refining the reactive-transport model, calibrating NMR well logs with experiments from the Wellington, KS, CO$_2$ demonstration site.
Appendix

- Organizational Chart
- Gantt Chart
- Bibliography
Organization Chart

- **Carbon Fuel Cycles** (Roger Aines)
- **Carbon Management** (Susan Carroll)
- **LLNL Carbon Sequestration Program**
  - Task 1. Active Reservoir Management
  - Task 2. In Salah
  - Task 3. China
  - Task 4. Snovit
  - Task 5. Carbonates
- **Technical Staff**
  - Bourcier
  - Buscheck
  - Aines
  - White, Chiaramonte, Ezzedine, Hao, White
  - Friedmann
  - Chiaramonte, White, Hao, Wagoner, Walsh
  - Carroll, Hao, Smith
- **Expertise**
  - Subsurface Hydrology
  - Computational Geomechanics
  - Experimental and Theoretical Geochemistry
  - Seismology
  - Structural Geology
## Gantt Chart: Task 5 Carbonates

<table>
<thead>
<tr>
<th>Activity</th>
<th>Fiscal Year 2012</th>
<th>Fiscal Year 2013</th>
<th>Fiscal Year 2014</th>
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<tbody>
<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
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<tr>
<td>5.1.1 Finish model calibration with Weyburn data</td>
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<td>5.1.2 Finish premodel simulations for new experiments</td>
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<tr>
<td>5.1.3 Refine model using new data</td>
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<tr>
<td>5.1.1 Experimental Design</td>
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<tr>
<td>5.2.2 Conduct experiments</td>
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<tr>
<td>5.2.3 Interpret experimental results</td>
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Bibliography


