Transition of CO₂ Enhanced Oil Recovery to Carbon Storage: Experimentally Constrained Reactive Transport Model

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Goals and Benefits

- To quantify key relationships in reactive transport models to constrain final CO$_2$ storage estimates.
- To calibrate down hole logging measurement methods to estimate carbonate formation permeability.
- Our results improve prediction of changing CO$_2$ storage capacity in carbonate reservoirs as a consequence of enhanced oil recovery (±30%)
Weyburn Demonstration

- calcite, \( \text{CaCO}_3 \), and
- dolomite, \( \text{(Ca,Mg)}\text{CO}_3 \)
Wellington, Kansas Demonstration

- Dolomite \((Ca,Mg)CO_3\)

![Graph and images showing permeability and injection zones.](image)
Dissolution yields preferential flow paths in more heterogeneous carbonate rocks

![Diagram showing permeability contrast (k_f/k_i) and dissolution front patterns.](Image)
Dissolution yields preferential flow paths in more heterogeneous carbonate rocks

Figure 12: Qualitative correlation between permeability contrast \((k_f/k_i, \text{ increasing towards the right})\) and evolution of dissolution patterns from stable to less stable.
Model parameters are constrained by characterization, pressure, and solution data.
Reactive Transport Model

Mineral Reaction Rates

\[ \frac{dn}{dt} = -S k_{298.15} K e^{-\frac{E}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right)} \left( 1 - \frac{Q}{K} \right) \]

Permeability-Porosity \( n - \) best fit

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

Surface Area-Porosity \( m - \frac{2}{3} \)

\[ S_t = S_0 \left( \frac{\theta_t \phi_t}{\theta_0 \phi_0} \right)^m \]

Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
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<tbody>
<tr>
<td>calcite + H⁺ = Ca²⁺ + HCO₃⁻</td>
</tr>
<tr>
<td>dolomite + 2H⁺ = Ca²⁺ + Mg²⁺ + 2HCO₃⁻</td>
</tr>
<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>
</tr>
</tbody>
</table>
Evolution of permeability is tied to the heterogeneity and the mineral reactivity

<table>
<thead>
<tr>
<th></th>
<th>Dolostone, homogeneous</th>
<th>Dolostone, heterogeneous</th>
<th>Limestone, heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>8.0</td>
<td>3.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Min</td>
<td>2.5</td>
<td>1.6</td>
<td>6.0</td>
</tr>
<tr>
<td>Median</td>
<td>3.0</td>
<td>3.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Greater permeability change with limestone

$$K_t = K_0 \left( \frac{\phi_t}{\phi_0} \right)^n$$
Mineral dissolution rates vary by 100 times and may require calibration of reactive surface area

\[
\frac{dn}{dt} = -Sk_{298.15}e^{\frac{E}{RT} - \frac{1}{298.15}} \left(1 - \frac{Q}{K}\right)
\]
Validation Study – Big Sky Demonstration, Duperow Formation (Lee Spangler and Stacey Fairweather)

- CHARACTERIZATION
  - X-ray CT, XRD, SEM, NMR
- FORWARD MODELING
- REACTIVE EXPERIMENT
- MODEL – DATA COMPARISON

Dolomite
5% $\phi$ and low $k$

Mixed carbonate
17% $\phi$ and high $k$
How do you scale lab experiments to the field?
Larger grid size reduces the permeability change

Initial porosity: 0.2
bulk permeability: 0.32 mD

- Increase the grid area by 64
- Decreases permeability change

bulk permeability increase

150%  100%  50%
Calibration of down hole logs to better estimate variable permeability with depth in carbonate reservoirs
NMR signal can be used to estimate down hole permeability

Weyburn,  Wellington, Kansas

\[ k = A \cdot T_{2,LM}^2 \cdot \phi^4 \]  
(Schlumberger Doll Research)
Predicted permeability differs by orders of magnitude using standard value of $A$
Calibrate using independent measures

- $\varphi$ : porosity (Nuclear Magnetic Resonance)
- $\nu$ : pore shape factor ($2.5$ for elliptical pores)
- $\tau$ : tortuosity ($X$-Ray Tomography, Nuclear Magnetic Resonance)
- $\rho$ : surface relaxivity (Calibrated Nuclear Magnetic Resonance)

$A = \frac{\rho^2}{\varphi^3 \nu \tau^2}$

Daigle and Dugan JGR 2011
Tortuosity ($\tau$) is extracted from high resolution tomography images and the NMR porosity.

Matrix porosity assessed by difference between XRCT and NMR porosity.

- Use a random walk algorithm to extract tortuosity from segmented pore network.

\[
A = \frac{\rho^2}{\varphi^3 u \tau^2}
\]
Test – Initial estimates of caprock-like permeability from SDR equation and standard A is due to high Fe concentrations

- Solve for $A = 5.33 \times 10^{-09} \text{m}^2/\text{s}^2$
- NMR Porosity; $\phi = 21.7\%$
- NMR – $T_{2,LM}$
- Measured Permeability; $k = 0.027 \text{ mD}$

\[
k = A \cdot T_{2,LM}^2 \cdot \phi^4
\]

- Solve for Relaxivity; $\rho = 65.6 \mu\text{m/s}$
  - Standard for carbonates is 2 $\mu\text{m/s}$
  - Reflects high paramagnet content
- NMR Porosity; $\phi = 21.6\%$
- XRCT Tortuosity; $\tau = 3.53 \text{ m/m}$
- Pore shape factor; $\nu = 2.5 \text{ m}^2/\text{m}^2$
  - elliptical pores
  - could be refined with XRCT data
Surface relaxivity ($\rho$) depends on mineralogy and Mn and Fe content

But $\rho$ cannot resolve difference between estimated and measured permeability

\[ y = 0.6207x + 2.3218 \]
\[ R^2 = 0.8597 \]

\[
A = \frac{\rho^2}{\varphi^3 \nu \tau^2}
\]
Next steps in the calibration

\[ k = A \cdot T_{2,LM}^2 \cdot \varphi^4 \]

\[ A = \frac{\rho^2}{\varphi^3 \nu \tau^2} \]

- Measure the Fe/Mn content for all samples
- Conduct a sensitivity study of the parameters and power functions
Synergy

- Weyburn-Midale Carbon Storage Demonstration
- Wellington, Kansas Carbon Storage Demonstration
- Big Sky Carbon Storage Demonstration
Summary and Future Plans

- Derived key reactive-transport parameters and their ranges for carbonate rocks over a wide range of heterogeneity and initial permeability
- Conducting a validation study using core from an independent CO₂ storage formation
- Developing a protocol for calibrating the NMR signal to provide meaningful in-situ permeability measurements
- Using numerical methods to scale laboratory parameters to reservoir
- Write final topical report on CO₂ storage potential in carbonate rocks.
Bibliography


