Monitoring of Geological CO$_2$ Sequestration Using Isotopes and Perfluorocarbon Tracers

Project Number FEAA-045

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Presentation Outline

• Tracers & their applications to C storage
• Cranfield CO$_2$ storage pilot site
  – PFT simulations
  – CH$_4$ exsolution tracer
• Coupling reaction modeling with transport simulations
• Hydrocarbon interference with PFT analysis
• Accomplishments & Synergies
Candidate Tracers
(substances used to follow the course of a process)

**Brines:** Native non-conservative tracers that respond to changes

- pH, alkalinity, electrical conductivity
- Cations: Na, K, Ca, Mg, \( \Sigma Fe \), Sr, Ba, Mn
- Major anions: Cl, HCO\(_3\), SO\(_4\), F, Br
- Organic acids: acetate, propionate, formate, oxalate, etc.
- Other organics: DOC; methane, CO\(_2\), benzene, toluene

**Gases:** Native conservative tracers or added conservative tracers

- Gases: N\(_2\), H\(_2\), O\(_2\), CO\(_2\), CO, CH\(_4\), C\(_2\) – C\(_{n+}\)
- Noble gas tracers: Ar, Kr, Xe, Ne, He (and their isotopes)
- Perfluorocarbon tracers (PFTs):
  - PMCP, PECH, PMCH, PDCH, PTCH (SF\(_6\))

**Isotopes:** D/H, \(^{18}\)O/\(^{16}\)O, \(^{87}\)Sr/\(^{86}\)Sr in water, DIC, minerals;

- \(^{13}\)C/\(^{12}\)C in CH\(_4\), CO\(_2\), DIC, DOC, carbonates
Benefit to Program
Geologic Storage, Simulations, and Risk Assessment

- Provide information on physical and geochemical changes in reservoir, ensuring CO₂ storage permanence.

- Facilitate fundamental understanding of processes impacting behavior of fluids—diffusion, dispersion, mixing, advection, capillarity, and reaction—to improve storage efficiency.

- Ground-truth behavior of fluids, CO₂ transport properties that can be used to constrain reservoir simulation models, predicting CO₂ storage capacity & designing efficient MVA programs.
Project Overview
Current Goals and Objectives

Provide methods to interrogate the subsurface that will allow direct improvement of CO$_2$ storage

- Incorporate CO$_2$-brine chemical and isotopic reactions and transport into simulations
- Assess efficiency of perfluorocarbon tracer analysis using capillary adsorption tubes in a hydrocarbon-rich matrix
Thanks to:
• Hovorka & Hosseini @UT BEG
• LBNL, SECARB
• Sandia Technology
• Denbury Resources

Extracted from > 60 million element model by UTBEG Hosseini et al., *IJGCC* (2013)

• 155 × 195 × 24 m³, inclined in x and y
• 64 × 51 × 79 = 257,856 unstructured grid cells,
• F2 and F3 well locations (70, 100 m) from Ajo-Franklin et al., *IJGCC*, 2013
• Petro-physical properties for 8 facies
Simulating PFT Injection Campaign
2009-2010 Breakthrough Curves

Competitive Dissolution of CO$_2$ Versus CH$_4$ in Brine

Simulated CH$_4$ Breakthrough Agrees With Field Data

Coupling Flow & Transport with Geochemical Reactivity

Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations

Chapter 43 of
Section A, Groundwater
Book 6, Modelling Techniques

Techniques and Methods 6–A43

U.S. Department of the Interior
U.S. Geological Survey
Validation Example: Transport & Cation Exchange

![Graph showing transport and cation exchange](image)

- **CaCl$_2$**
- **Na$^+$ K$^+$ NO$_3^-$**
- **?**
Same Problem in 2D Homogeneous & Heterogeneous Domains

Permeabilities field (mD)

Porosity field

Effluent concentration, mmol/kg

Line: 2D FD homogeneous+IPhreeqc
Dash line: 2D FD heterogeneous+IPhreeqc
Modeling Overview & Next Steps

• 2016: CO$_2$-H$_2$O flow & transport in high-resolution static model of DAS with advanced EOS.

• 2017: Addition of perfluorocarbon and SF$_6$ tracers.

• 2018 (early): Addition of CH$_4$ to study competitive dissolution/exsolution, formation of free gaseous CH$_4$. Excellent agreement with field data for all above.

• 2018 (late): Addition of reactive transport to complete comprehensive model of all trapping mechanisms.

• 2018-2019: Collaborate with NETL RIC to validate geochemistry and then use model to interpret lab-to-field data (e.g., Mt Simon core to Cranfield DAS).

• Consider reactive transport both in target formation but also in potential cap-rock failures.
Do Hydrocarbons Interfere with PFT Sampling & Analysis?

- Minimal interference with GC-ECD analysis by direct injection
- Sorbent tubes can be used to concentrate PFTs from gas samples.
- Potential competition in sorbent tube sampling
- Created a set of PFT standards in 1-L gas matrices:
  - CO₂
  - Natural gas
  - Diesel-saturated CO₂
- Loaded on AMBERSORB™ in quartz sorbent tube
- Analysis at NETL RIC (Sean Sanguinto) using thermal desorption and GC-NICI-MS
Decreased Efficiency of PFT Adsorption, Desorption and Analysis

![Graph showing efficiency of different gas matrices](image-url)

- **Gas Matrix**
  - Diesel/CO₂
  - Natural Gas

- **Efficiency (%)**
  - PMCP
  - PMCH
  - PECH
  - PTCH
Increased PFT Breakthrough to Downstream Sampler Tube

**Diagram:**
- PFTs
- Sorbent Tube 1
- Sorbent Tube 2

**Graph:**
- Concentration Ratio on the y-axis
- PFTs on the x-axis
- Bars for PMCP, PMCH, PECH, and PTCH
  - CO₂
  - Natural Gas
  - Diesel/CO₂

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Lessons Learned & Next Steps

– Hydrocarbons substantially reduce the efficiency of perfluorocarbon adsorption to AMBERSORB™.

– The most volatile PFT (PMCP) dissolved in a CO₂ matrix saturated with diesel could not be detected on sorption tube samples using GC-NICI-MS.

– Diesel matrix also caused early breakthrough of samples during active sampling with sorption tubes, introduced high variability in sorption tube samples, and substantially reduced the sensitivity of analysis for all PFTs.

– Research and development activities are needed to identify new sorbents and PFT capture strategies that are more robust to hydrocarbons in reservoir gas matrices.
Synergy Opportunities

- Collaborate with NETL RIC to validate geochemistry and then use model to interpret lab-to-field data (e.g., Mt Simon core to Cranfield DAS).
- Collaborative PFT sorbent testing in hydrocarbon-rich matrices
- New tracer test campaigns
- Sharing best practices for tracer analysis
Project Summary

- Simulated both PFT experiments at Cranfield DAS
- Validated CH$_4$ exsolution modeling with excellent match to field measurements
- Coupling geochemical reaction modeling with transport modeling for dynamic 3-D reservoir simulations
- Demonstrated significant hydrocarbon interference with sorption tube sampling of PFTs
- Assessing options to reduce interference and increase selectivity using advanced sorbents
- We welcome collaborations
Project Organization

Collaborators:

- Tommy Phelps
- Susan Pfiffner
- Joachim Moortgat
- David Cole
- Reza Soltanian
- Judy Zhu

RCSPs

Sean Sanguinito (NETL RIC)
## Gantt Chart

<table>
<thead>
<tr>
<th>Task</th>
<th>Milestone Description*</th>
<th>Fiscal Year 2018</th>
<th>Fiscal Year 2019</th>
<th>Planned Start Date</th>
<th>Planned End Date</th>
<th>Actual Start Date</th>
<th>Actual End Date</th>
<th>Comment (notes, explanation of deviation from plan)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Prioritization of reactive transport processes for simulation from discussions with NETL researchers</td>
<td></td>
<td></td>
<td>8/17</td>
<td>12/17</td>
<td>8/17</td>
<td>1/18</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Prepare PFT standards in hydrocarbon matrices for sorbent tube test and GC-MS analysis at NETL</td>
<td></td>
<td></td>
<td>9/17</td>
<td>12/17</td>
<td>9/17</td>
<td>12/17</td>
<td></td>
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<tr>
<td>FY17</td>
<td>Universal dynamics of gravity-conductive mixing of CO2 in 3D heterogeneous porous media and implications for geologic carbon sequestration</td>
<td></td>
<td></td>
<td>6/17</td>
<td>12/17</td>
<td>5/17</td>
<td>12/17</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Report on efficacy of sorbents to improve PFT capture and analysis</td>
<td></td>
<td></td>
<td>1/18</td>
<td>6/18</td>
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<tr>
<td>1.2</td>
<td>Improved pattern formation and its evolution can provide unique and easy-to-use predictive tools for the long-term dissolution trapping of CO2, enhanced by gravity-convecitive mixing</td>
<td></td>
<td></td>
<td>10/17</td>
<td>9/18</td>
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<tr>
<td>13, 14</td>
<td>Initial incorporation of geochemical reactions and stable isotope tracers into the Ouestes reservoir simulator</td>
<td></td>
<td></td>
<td>6/18</td>
<td>9/18</td>
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<tr>
<td>2.2</td>
<td>Report on new adsorbent technology for PFT sampling</td>
<td></td>
<td></td>
<td>1/18</td>
<td>9/18</td>
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<tr>
<td>2.2</td>
<td>Survey field test opportunities for enhanced PFT sampling technology</td>
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<td>8/18</td>
<td>12/18</td>
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<td>1.5</td>
<td>Final report on CO2 trapping mechanisms, with a focus on capillary trapping</td>
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<td>10/18</td>
<td>6/19</td>
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<tr>
<td>1.6</td>
<td>Assess the role of fractures on CO2 trapping mechanisms</td>
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<td></td>
<td>10/18</td>
<td>9/19</td>
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Bibliography


