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

Project Number FEAA-045

David E. Graham$^1$, Joachim Moortgat$^2$
DR Cole$^2$, SM Pfiffner$^3$, TJ Phelps$^3$
Benefit to Program
Monitoring, Verification, Accounting and Assessment

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

- Ground-truth behavior of fluids, CO₂ transport properties to constrain reservoir simulation models, predicting CO₂ storage capacity & designing efficient MVA programs.

- Address CCUS Priority Research Directions:
  - Optimizing Injection of CO₂ by Control of the Near-Well Environment
  - Realizing Smart Monitoring to Assess Anomalies and Provide Assurance
FEAA-045 Timeline

< 2009  Frio Brine pilot site tracer tests  
2009-2015  Cranfield CO₂ storage project tracer tests and measurements (with SECARB)  
2015-2022  Enhanced models integrating tracer results with CO₂ storage reservoir simulations  
2020-2022  Chester-16 reef simulations (with MRCSP)  
2015-2022  Improved perfluorocarbon analytical methods for tracer tests
### Tracers for Evaluating CO$_2$ Storage in Brine Reservoirs

<table>
<thead>
<tr>
<th>Trapping Mechanisms</th>
<th>Processes</th>
<th>Tracers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Migration, structural, and stratigraphic trapping of scCO$_2$</td>
<td>Advection, Dispersion, Mixing &amp; Dilution</td>
<td>CO$_2$ isotopes&lt;br&gt;Methane (CH$_4$)&lt;br&gt;Perfluorocarbons (PFTs)&lt;br&gt;Noble gases</td>
</tr>
<tr>
<td>Residual trapping in rock pores</td>
<td>Capillary Forces</td>
<td>(As above)</td>
</tr>
<tr>
<td>Dissolution of CO$_2$ into formation brine</td>
<td>Diffusion, Partitioning</td>
<td>Water isotopes&lt;br&gt;CO$_2$ isotopes&lt;br&gt;pH&lt;br&gt;DIC, Alkalinity</td>
</tr>
<tr>
<td>Chemical trapping of CO$_2$ through fluid-rock geochemical reactions</td>
<td>Dissolution, Precipitation, Water-Rock Interactions</td>
<td>CO$_2$ isotopes&lt;br&gt;Cations, Sr isotopes&lt;br&gt;Anions</td>
</tr>
</tbody>
</table>
Cranfield, MS
Detailed Area of Study (DAS)

Wells sampled in Jan 2015

Wells reported in 2nd FY 2014 quarterly

Thanks to:
- Hovorka & Hosseini @UT BEG
- LBNL, SECARB
- Sandia Technology
- Denbury Resources
Carbon Isotopes ($^{13}$C/$^{12}$C) of Injected CO$_2$ Gas from Jackson Dome Show Good Mixing with Tuscaloosa CO$_2$

Simple two-component fluid mixing dominates at the DAS site

No obvious evidence of CO$_2$ reaction with reservoir rock carbonates
Modeling of O isotope shifts in CO$_2$

Magnitude of oxygen isotope shift largely a function of brine/CO$_2$ ratio vs carbon isotope variation due to mixing of formation CO$_2$ with injectate
Conservative Perfluorocarbon Tracers (PFTs)

- Non-reactive, non-toxic, inexpensive and stable to 500°C
- Several PFTs can be quantified in a single analysis
- Detectable at pg-fg levels (fmoles)
- Different PFT “suites” (PMCP, PMCH, PECH, PDCH, PTCH), and SF₆, assess multiple breakthroughs → flow regime indicator
2009 Campaign PFTs at F2

<table>
<thead>
<tr>
<th>Time</th>
<th>PFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PMCH</td>
</tr>
<tr>
<td>6</td>
<td>PTCH</td>
</tr>
<tr>
<td>31</td>
<td>PECH</td>
</tr>
<tr>
<td>33</td>
<td>SF₆</td>
</tr>
<tr>
<td>75</td>
<td>PDCH</td>
</tr>
<tr>
<td>269</td>
<td>PMCH</td>
</tr>
<tr>
<td>436</td>
<td>PTCH</td>
</tr>
</tbody>
</table>

Injections

Pressure Front

PFT concentrations (M)

Experiment Hours

F2 SF₆
F2 PMCH
F2 PECH
F2 PTCH
2010 Campaign PFTs Relative to PTCH

Relative Concentration (%)

Experiment Hours

- PMCP
- PDCH
- PECH
- F2 PMCP
- F3 PCMP
- F2 PECH/PDCH
- F3 PECH/PDCH
PFTs Present After 5 Years of Experiment!

- Long-term diffusive tail (50 X longer than Frio)
- Tracer reservoir in F3 vicinity (>20,000 hr of previous inactivity)
- Revealed differential transport of \( \text{SF}_6 \) and PECH (and others)

<table>
<thead>
<tr>
<th>PFT</th>
<th>F3 Pre-Vent 01-13-15</th>
<th>F3 Post Vent 01-23-15</th>
<th>F3 Post Vent 01-26-15</th>
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</thead>
<tbody>
<tr>
<td>SF6</td>
<td>185,245</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PMCP</td>
<td>571</td>
<td>173</td>
<td>37</td>
</tr>
<tr>
<td>PMCH</td>
<td>1079</td>
<td>428</td>
<td>121</td>
</tr>
<tr>
<td>PECH</td>
<td>2017</td>
<td>1233</td>
<td>377</td>
</tr>
<tr>
<td>PTCH</td>
<td>541</td>
<td>376</td>
<td>107</td>
</tr>
</tbody>
</table>
Lessons Learned

- Long-term experiments are important (long-tail)
- Carbon isotopes are valuable for mixing models
- Flow paths evolve in the reservoir
- Sensitive tracer detection is critical
- Suites of tracers are essential for interpreting flow
- Multiple suites of tracers are required for monitoring with repeated injections
- Models & simulations help to interpret tracer results
Modeling CO₂ Injection at the Cranfield Pilot Site

Numerical Modeling of Reactive Transport

- **Better interpret Cranfield field data**
- **Predict long-term evolution of fluids & formation**
- **Simulate critical CO₂ transport and reaction processes**
- **Apply lessons learned to other projects**

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., *IJGGC*, 2013
- Petro-physical properties for 8 facies
Modeling Tools

- Unique combination of capabilities in Oasures:
  - Higher-order finite element (FE) methods for flow and transport: allow unstructured grids, tensor permeability, discrete fractures, heterogeneity
  - Low numerical dispersion (e.g., resolves small-scale onset of instabilities)
  - Cubic-plus-association (CPA) equation of state (non-ideal) phase behavior modeling of water, CO$_2$, hydrocarbons, tracers (capture, e.g., competitive dissolution and brine compressibility)
  - Fickian diffusion with self-consistent composition + $T + p$ -dependent full matrix of diffusion coefficients for multicomponent multiphase fluids
  - Capillary-driven flow with composition + $p$ -dependent surface tension
  - Reactive transport by coupling to iPHREEQC geochemistry (2019-2020) and PhreeqcRM (2020-2021), which is faster / parallelizable.
Modeling of pure CO₂ injection into brine at Cranfield

Excellent match to observed pressure response and CO₂ breakthrough times in observation wells.

Pressure response in injection well
(Soltanian et al., IJGGC 2016)

CO₂ migration in 2009 (left) & 2010 (right)
Simulating PFT Injection Campaign
2009-2010 Breakthrough Curves

PMCH Tracer

F2

PMCP Tracer

F2

F3

Conclusions from Simulations

- Qualitative agreement with previous studies, but closer to field data due to high-resolution static model, higher-order FE methods, and robust physics.
- Agreement (mostly) on static model and wettability.
- However, pressures at highest rate and CO$_2$ breakthrough in F3 overestimated in all models.
- Most likely cause: missing fluvial conduits of flow.
- Tracer breakthrough in F3 before F2 suggests the same.
Modeling of the exsolution of methane dissolved in formation brine

Match to observed breakthrough curves (Soltanian et al., (2018) *Groundwater* 56:176.)
Reactive transport by coupling to iPhreeqc and PreeqcRM interfaces, only single-phase

but now with advanced numerical methods and more physics (Moortgat et al. Sci Rep 2020):
Two-Phase Geochemistry

Measured pH change in formation brine during CO₂ injection
Two-Phase Reactive Transport

Modeling of the pH change in formation brine during CO$_2$ injection

Time: 8.5
New synergistic collaboration developed with Battelle to model CO$_2$ transport in complex Chester 16 reef system (MRCSP)

- First milestone: develop alternative static model
Chester 16

- Industry-standard is logically Cartesian corner-point grids.
- For complex geometry, like domes, many dead and pinched cells.
- Advantages of unstructured, e.g. tetrahedral, grids.
Chester 16

- Multiple injection and ‘soak’ periods
- Model CO$_2$ injection into water at BHP of 130 bar and $T = 104$ F where CO$_2$ is supercritical

<table>
<thead>
<tr>
<th>Injection Period</th>
<th>Date Range</th>
<th>Days Injected</th>
<th>Target Formation</th>
<th>CO$_2$ Injected (MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/11/17 - 1/14/17</td>
<td>3</td>
<td>A1 Carbonate</td>
<td>804</td>
</tr>
<tr>
<td>2</td>
<td>2/22/2017 - 4/6/2017</td>
<td>43</td>
<td>A1 Carbonate</td>
<td>9,039</td>
</tr>
<tr>
<td>3</td>
<td>4/22/2017 - 7/24/2017</td>
<td>93</td>
<td>A1 Carbonate</td>
<td>20,585</td>
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<tr>
<td>4</td>
<td>9/29/2017 - 11/27/2017</td>
<td>59</td>
<td>Brown Niagaran</td>
<td>18,314</td>
</tr>
<tr>
<td>5</td>
<td>12/16/2017 - 1/16/2018</td>
<td>31</td>
<td>A1 Carbonate</td>
<td>9,010</td>
</tr>
<tr>
<td>7</td>
<td>5/26/2018 - 8/14/2018</td>
<td>80</td>
<td>A1 Carbonate and Brown Niagaran</td>
<td>18,320</td>
</tr>
<tr>
<td>8</td>
<td>10/20/2018 - 7/29/2019</td>
<td>Continuing</td>
<td>A1 Carbonate and Brown Niagaran</td>
<td>55,390</td>
</tr>
</tbody>
</table>
Chester 16

- Preliminary modeling of CO$_2$ injection (higher-order DG)
- Two viewing angles, 1 year of injection, 1 mol% CO$_2$ contours (and perm.)
Project Summary (Task 1)

- Modeling of CO$_2$, CH$_4$, brine, and perfluorocarbon tracers at Cranfield
- Fundamental analyses of solubility trapping (mixing and spreading of dissolved CO$_2$)
- Initial implementation and benchmarking of coupled flow and reactive transport with Osures+iPhreeqc/PhreeqcRM
- Investigation of multiphase flow and reactive transport at Cranfield
- Modeling of independent Chester 16 field site
- Technology improvements (specifically parallelization / HCP)
Task 2. Improving PFT Tests

- Develop methods to improve the analysis of perfluorocarbons in a hydrocarbon-rich matrix, found in many EOR and EGR monitoring well samples.
- Detect lower concentrations in gas samples
- Reduce sampling frequency
- Simplify sample collection, transport and storage

- BNL researchers (Senum et al) in the 1980’s sampled PFTs with capillary adsorbent tracer samplers (~60 mg AMBERSORB™)
- Concentrates PFTs from a large gas volume on a single sorption tube
No significant interference for PFTs diluted into gas matrices and analyzed directly by GC-ECD
Decreased Efficiency of PFT Analysis by Sorption Tube Sampling

AMIERSORB matrix. GC-MS Analysis by Sean Sanguinito, NETL
Increased PFT breakthrough to downstream tube in the presence of hydrocarbons

PFTs → Ambersorb Tube 1 → Ambersorb Tube 2

Concentration Ratio (Tube1/Tube2)

PMCP  PMCH  PECH  PTCH

- Black: CO₂
- Red: Natural Gas
- Blue: Diesel/CO₂

GC-MS Analysis by Sean Sanguinito, NETL
Five different types of sorbent tubes loaded with PFT standards in CO$_2$ were analyzed using thermal desorption with GC-ECD analysis. Measurements were performed on triplicate samples.
PFTs in CO₂ + Diesel Volatiles

Air Toxics tube contains ~2:1 GCB:CMS.
Inverse Air Toxics tube contains ~1:3 GCB:CMS.
New Sorbents Reduced Breakthrough

Alternative sorbents trapped more PFTs than Ambersorb with CO₂ & diesel volatiles

PFTs

Sorbent Tube 1 → Sorbent Tube 2

Sum of both tubes
Improved Sensitivity and LOD with Carboxen 569 Sorbent Tubes

<table>
<thead>
<tr>
<th>PFT</th>
<th>Ambersorb XE-347 LOD (pmoles/L)</th>
<th>Carboxen 569 LOD (pmoles/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMCP</td>
<td>5.8</td>
<td>0.5</td>
</tr>
<tr>
<td>PMCH</td>
<td>1.6</td>
<td>0.1</td>
</tr>
<tr>
<td>PECH</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>PTCH</td>
<td>1.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Hydrocarbons substantially reduce the efficiency of perfluorocarbon adsorption to AMBERSORB™.

The most volatile PFT (PMCP) may not be adsorbed in the presence of HCs using some sampling tubes.

Larger bed volumes of high specific surface area carbon molecular sieve sorbents or mixed beds significantly and substantially improves detection.

Carboxen 569 is a recommended replacement for AMBERSORB in sorbent tubes for PFT sampling.

PFT response factors (sensitivities) vary significantly, but LOD is similar and limited by background contamination.
APPENDICES
Lessons Learned

• Critical uncertainties in modeling/predicting two-phase migration of supercritical CO$_2$ into brine-saturated formation:
  – Subsurface heterogeneity
  – Relative permeability & capillary pressure relations: especially facies-dependence.

• Convective mixing of dissolved CO$_2$ relatively insensitive to multimodal facies heterogeneity when porosity and permeability are correlated. Simple scaling laws in terms of formation/fluid properties apply broadly.

• Rock-fluid reactions likely modest on short time-scales but may affect long-term storage. Predictions require costly (parallelized) numerical modeling & further research.
Synergies

- Established collaborative simulation opportunities with MRCSP regarding complex reef systems.
- Open to other partnerships, incl. future large-scale projects.
- Addressing priority research directions:
  - PRD S-1: Advancing Multiphysics and Multiscale Fluid Flow to Achieve Gton/yr Capacity
  - PRD S-2: Understanding Dynamic Pressure Limits for Gigatonne-scale CO$_2$ Injection
  - PRD S-6: Improving Characterization of Fault and Fracture Systems
- Collaborative PFT sorbent testing in hydrocarbon-rich matrices. Planned GC-MS experiments with NETL RIC.
- Sharing best practices for tracer analysis
  - Potential applications for CCUS Research Priority areas: Locating, Evaluating, and Remediating Existing and Abandoned Wells & Wellbore leakage