Monitoring of Geological CO$_2$ Sequestration Using Isotopes & PFTs

Project Number FEAA-045

David E. Graham$^1$, Joachim Moortgat$^2$
David R Cole$^2$, Susan M Pfiffner$^3$, Tommy J Phelps$^3$
Mengnan Li$^2$ & Derrick James$^2$

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage Project Review Meeting
2021 Virtual Review Webinar
August 9, 2021
Project Overview

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

Tasks
1. Numerical modeling of reactive transport at Cranfield and Chester 16 CCS Site(s) to
   • Better interpret field data
   • Predict long-term evolution of fluids & formation
   • Apply lessons learned to other projects
2. Assess efficiency of PFT analysis using capillary adsorption tubes in a hydrocarbon-rich matrix
Task 1 Objective

- Constrain **structural, solubility, and chemical** trapping mechanisms that guarantee storage permanence, through novel subsurface signals & modeling.
  - Non-trivial migration patterns in heterogeneous formations
  - Diffusion driven convection and cross-flow into low-perm. facies
  - Chemically driven mineralization of CO$_2$ and formation alterations

- Iteratively coupled workflow of field data and modeling
Modeling Tools

• Unique combination of capabilities in Osures:
  – 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\textsubscript{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
  – New Reactive transport by coupling to iPHREEQC geochemistry (2019-2020) and PhreeqcRM (2020-2021), which is faster / parallelizable.
Prior Accomplishments

Modeling of pure CO$_2$ injection into brine at Cranfield

Excellent match to observed pressure response and CO$_2$ breakthrough times in observation wells

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

CO$_2$ migration in 2009 (left) & 2010 (right)
Prior Accomplishments

Modeling of perfluorocarbon tracers co-injected with CO$_2$

Remarkable match to breakthrough curves (at exceedingly low concentrations)

CO$_2$ and PFT migration (Soltanian et al., GGST 2018)
Prior Accomplishments

Modeling of the exsolution of methane dissolved in formation brine

Match to observed breakthrough curves (Soltanian et al., *Groundwater* 2018)
Prior Accomplishments

2020: Reactive transport by coupling to iPhreeqc and PreeqcRM interfaces, only single-phase

Excellent agreement to benchmark studies and experimental results:

but now with advanced numerical methods and more physics (Moortgat et al. Sci Rep 2020):
Technical Status

Two main accomplishments on Task 1 in 2021:

• Development of two-phase reactive transport with full equation-of-state based multi-component phase-split computations.

• Initial modeling of CO$_2$ transport in challenging Chester 16 reef system.
**Two-Phase Geochemistry**

New reactions + EOS phase-split computation formalism that strictly satisfies thermodynamic equilibrium

Effect of **dissolved salts** on CO$_2$ solubility, compared to experimental data
Two-Phase Geochemistry

Carbon isotope evidence for mixing of formation CO₂ with injectate

Oxygen isotope shift in brines reveals the fraction of CO₂ “communicating” with fluid

Carbon isotope evidence for mixing of formation CO₂ with injectate

Carbon isotope evolution of DIC in DAS and production wells from pre- to post-breakthrough
Two-Phase Geochemistry

Measured pH change in formation brine during CO$_2$ injection
Two-Phase Reactive Transport

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

**Time:** 0
Synergistic collaboration developed with Battelle to model CO$_2$ transport in complex Chester 16 reef system (MRCSP)

- 2020 (and ongoing): develop alternative static models on tetrahedral grids
Chester 16

- Industry-standard is logically Cartesian corner-point grids
- For complex geometry, like domes, many dead and pinched cells
- Can truly unstructured, e.g., tetrahedral, grids offer advantages?
Chester 16

- Tetrahedral static model for Chester 16 reported in 2020
- 361,210 tetrahedral grid elements, 1,250 m × 700 m × 215 m
Chester 16

- Multiple injection and ‘soak’ periods
- Model CO₂ injection into water at BHP of 130 bar and T = 104 F where CO₂ is supercritical

<table>
<thead>
<tr>
<th>Injection Period</th>
<th>Date Range</th>
<th>Days Injected</th>
<th>Target Formation</th>
<th>CO₂ 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>
</tr>
<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\textsubscript{2} injection (higher-order DG)
- Two viewing angles, 1 year of injection, 1 mol\% CO\textsubscript{2} contours (and perm.)
Lessons Learned

- (Task 2) Perfluorocarbon and isotope tracers offer powerful tools to track migration of injected CO$_2$ through arrival times and breakthrough curves in observation/production wells, measure degree of mixing with brine.

- (Task 1) Numerical models have matured enough to match and interpret field data and make predictions for future CO$_2$ storage projects.

- (Task 1) Predictive capabilities sensitive to accuracy of static models, i.e., capturing formation heterogeneity, and relative permeability / capillarity relations, which are generally facies dependent.
Project Summary (Task 1)

- Completed:
  - 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 Osure+IPhreeqc/PhreeqcRM

- Ongoing & Future work:
  - Investigation of multiphase flow and reactive transport at Cranfield
  - Modeling of independent Chester 16 field site
  - Technology improvements (specifically parallelization / HCP)
  - Final summary report in April 2022
Project Summary (Task 1)

• Completed:
  – PFT and isotope tracer field experiments at Cranfield
  – Lab experiments of best practices in use of PFTs, investigating effects of hydrocarbons and improved substrates in sorbent tubes (e.g., Carbonex 569)

• Future work:
  – Final synthesis of geochemical data and PFT analysis best practices reported in April 2022
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. 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
Organization Chart

David Graham, PI

Tommy Phelps
Susan Pfiffner

Joachim Moortgat
David Cole
Postdocs: Soltanian, Zhu, Li

Collaborators:
<table>
<thead>
<tr>
<th>Task</th>
<th>Milestone Description*</th>
<th>Fiscal Year 2019</th>
<th>Fiscal Year 2020</th>
<th>Fiscal Year 2021</th>
<th>Planned Start Date</th>
<th>Planned End Date</th>
<th>Actual Start Date</th>
<th>Actual End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Survey field test opportunities for enhanced PFT sampling technology</td>
<td>9/18</td>
<td>12/18</td>
<td>9/18</td>
<td>12/18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Thermal desorption system installed on ORNL’s gas chromatography system</td>
<td>2/19</td>
<td>3/19</td>
<td>2/19</td>
<td>3/19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Sorbent selected for PFT-hydrocarbon experiments</td>
<td>3/19</td>
<td>6/19</td>
<td>7/19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>Initial transport modeling of aqueous equilibrium reactions with Osures+Phreeqc</td>
<td>3/19</td>
<td>9/19</td>
<td>3/19</td>
<td>9/19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Data sharing planned with partner institution(s) for future modeling of a CCS project independent of the Cranfield DAS</td>
<td>3/19</td>
<td>12/19</td>
<td>12/19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Validation of PFT sorbent sampling method in hydrocarbon matrices</td>
<td>7/19</td>
<td>12/19</td>
<td>3/20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Best practices identified for PFT sampling in hydrocarbon-rich environments</td>
<td>9/19</td>
<td>12/20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Static model developed for a modeling benchmark study of an independent CCS project</td>
<td>7/19</td>
<td>6/20</td>
<td>8/20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>First demonstrations of reactive transport modeling of the multiphase brine-CO2-rock system using higher-order accurate methods</td>
<td>7/19</td>
<td>12/20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Modeling of CO2-brine flow and transport for a field site different from CranfieldDAS</td>
<td>1/20</td>
<td>3/21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>Final model of geochemistry and reactive transport at Cranfield</td>
<td>7/20</td>
<td>6/21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>Complete CO2-brine-rock geochemistry and reactive transport incorporated into CSS simulations</td>
<td>10/20</td>
<td>9/21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Final report on Monitoring of Geological CO2 Sequestration Using Isotopes and Perfluorocarbon Tracers</td>
<td>1/20</td>
<td>9/21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>