Novel Geochemical Signal Methodologies

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Carbon Management Research Project Review Meeting
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Need: Low-cost, easily implemented monitoring strategy for carbon storage reservoir leak detection

• Monitoring costs associated with CO₂ storage are projected to be 3 – 20% of the operational costs of a geological carbon storage site.¹

• Injected chemical tracers are demonstrated to provide a low-cost and reliable option for monitoring and quantifying migration of CO₂ from the primary storage reservoir.²

• What if naturally-occurring chemical analytes could be used for low-cost, early detection of CO₂ and brine migration events?

¹Calculated from values presented in Rubin et al., IJGHGC, 2015, 40, 378-400
²Roberts et al., IJGHGC, 2017, 65, 218-234
Geochemical Monitoring of Groundwater Impacts – Novel Geochemical Signal Methodologies Summary

NETL-RIC Advanced Storage (Task 21)

Prior Year Results (Tasks 20 & 21)

New Lab- and Field-Based Chemical Analysis
- Reduced analytical time and increased confidence in data from high-salinity bines = lower cost for monitoring
- Isotope techniques (Sr, Li, Ba, B)
- Metals by Ion Chromatography
- Direct field monitoring (CO₂, Fe, S)

Robust Field Data Sets
- Two CO₂-EOR sites with multiple geologic formations monitored (3y)
- Comprehensive statistical analysis to identify mixing trends
- Identified of major geochemical signals that will indicate CO₂ migration into shallower formations

New Lab- and Field-Based Chemical Analysis
- Reduced analytical time and increased confidence in data from high-salinity bines = lower cost for monitoring
- Isotope techniques (Sr, Li, Ba, B)
- Metals by Ion Chromatography
- Direct field monitoring (CO₂, Fe, S)

Final Product: Predictive Model for Geochemistry-Based Early Leak Detection
- Merge key geochemical reactions identified with statistical approach
- Use to develop low-cost monitoring strategies where chemistry can ID issues not detectable by other techniques
If chemical constituents from the storage reservoir are detected in an intermediate reservoir, or shallow groundwater aquifer, then a CO$_2$ or brine migration event may have occurred.

**Opportunity 1:** Leverage difference in chemistry between geologic formations to identify fluid mixing events

**CO$_2$ or Brine Migration:** Overlying geologic units show chemical signatures similar to primary storage reservoir that differ from the original condition.

**Original Condition:** Distinct chemical composition between geologic units

**Challenge:** What if the major aqueous chemical signatures between formations are similar or influenced by multiple processes?
If chemical signatures specific to CO₂-impacted reservoir fluids are detected in overlying formations, then there is likelihood that a migration occurred.

**CO₂ Reservoir Origin**: CO₂ and brine are expected to carry chemical signatures associated with the reservoir, that are transferred to the receptor geologic formation.

**Other Origin**: Sudden changes in chemical composition in overlying geologic units do not carry reservoir-specific chemical signatures.

**Challenge**: Can we identify the migration pathway?
If chemical signatures specific to certain migration pathways (e.g., along the well, or via fractures in the seal) are known, then mitigation techniques specific to those pathways may be developed to ensure long-term storage permanence and environmental sustainability.

Opportunity 3: Leverage knowledge of geochemical reaction paths along different migration pathways to identify the source.

**Migration along well:** CO₂ and brine are expected to carry chemical signatures associated with the reservoir and well that are transferred to the receptor geologic formation.

**Migration across seal:** CO₂ and brine are expected to carry chemical signatures associated with the reservoir and seal that are transferred to the receptor geologic formation.

Challenge: Which signals indicate specific migration pathways for unique CS reservoirs?
Early-stage geochemistry-based leak detection

Characterizing what a geochemical signal looks like under CO$_2$/brine leakage scenarios

1. Characterize expected signals of brine migration between geologic formations – mixing models developed with field data

2. Identify which combinations of chemical signatures indicate CO$_2$ migration – geochemical-statistical model to identify the probability that a leak occurred using common geochemical parameters
Approaches for geochemistry-based leak detection

- Identify which chemical tracers can: A) be reliably identified and measured in field samples with techniques of varied time and cost, and B) can be used to identify major processes that may occur during CO2 and brine leakage.

**Completed**

Application of Field Data from Permian Basin CO2-EOR Sites to Quantify Operational Baseline and Fluid Mixing

**Completed**

Development of Reaction Matrix for Testing with Bayesian Belief Network Statistical Modeling

**In Progress**

Development of Bayesian Belief Network Statistical Model for Expected Signals from Migration Event
Monitoring geochemical changes at a CO\textsubscript{2}-EOR site in West Texas, USA

**East Seminole Field Data**

Opportunity to:
1. Observe CO\textsubscript{2} induced changes in produced water
2. Monitor overlying groundwaters for produced water intrusion

**Potential Implications/Impact**
1. Understand CO\textsubscript{2} water-rock-interactions
2. Develop applications of geochemical tools for monitoring, measurement, and verification

## Target CO\textsubscript{2}-EOR reservoir, Intermediate Formation, and Groundwater

### Major sampling zones for East Seminole field sampling

<table>
<thead>
<tr>
<th>System</th>
<th>Series</th>
<th>Central Basin Platform Group/Formation</th>
<th>Lithology</th>
<th>Average Depth (m) of Samples at field area</th>
<th>Hydrostratigraphic Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary</td>
<td></td>
<td>Alluvium</td>
<td>Silty sand</td>
<td></td>
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</tr>
<tr>
<td>Tertiary</td>
<td>Upper</td>
<td>Ogallala</td>
<td>Fluvial and lacustrine clastics</td>
<td>45-55</td>
<td></td>
</tr>
<tr>
<td>Cretaceous</td>
<td>Albian</td>
<td>Fredericksburg</td>
<td>Limestone</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Antler / Paluxy</td>
<td>Sandstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triassic</td>
<td>Upper</td>
<td>Dockum Group / Santa Rosa Fm.</td>
<td>Fluvial-deltaic and lacustrine clastics</td>
<td>960</td>
<td>Evaporite Confining System</td>
</tr>
</tbody>
</table>

| Permian      | Ochoan    | Dewey Lake                                  | Halite, Anhyd., Sylvite                 |                                            |                                 |
|              |           | Rustler                                     |                                          |                                            |                                 |
|              |           | Salado                                      |                                          |                                            |                                 |
|              |           | Tansill                                     |                                          |                                            |                                 |
| Guadalupian  |           | Yates                                       | Sandstone and Anhydrite                  |                                            |                                 |
|              |           | Seven Rivers                                |                                          |                                            | Deep Basin Aquifer System       |
|              |           | Queen                                       |                                          |                                            |                                 |
|              |           | Grayburg                                    |                                          |                                            |                                 |
|              |           | San Andres                                  | Dolomite                                 | 1630                                       |                                 |
| Leonardian   |           | Holt                                        | Limestone and Dolomite                   |                                            |                                 |
|              |           | Glorieta                                    |                                          |                                            |                                 |
|              |           | Clear Fork Group                            |                                          |                                            |                                 |
|              |           | Wichita                                     |                                          |                                            |                                 |
| Wolfcampian  |           | Wolfcamp                                    |                                          |                                            |                                 |

| Pennsylvanian|           | Cisco “Clint”                                | Shelf limestones, minor shale            |                                            |                                 |
|              |           | Canyon                                      |                                          |                                            |                                 |
|              |           | Strawn                                      |                                          |                                            |                                 |
|              |           | Atoka                                       | Shale                                    |                                            |                                 |
| Mississippian|           | Barnett                                     | Limestone                                |                                            |                                 |
|              |           | Mississippian                               |                                          |                                            |                                 |
Approach for identifying brine migration demonstrated through application of data transformation techniques to Permian Basin CO₂-EOR field results

- Low-cost analytical techniques leveraged to monitor chemical composition of water samples: Na⁺, Ca²⁺, K⁺, Cl⁻, alkalinity, and TDS
- Leakage into groundwaters could be detected using these parameters, however competing inputs of these ions from agriculture complicate signal interpretation
- Solution: Focus on an intermediate geologic formation, that already contains installed wells, for monitoring
- Applying isometric-log ratios (ilr), a data transformation technique, provides a more robust source attribution tool
  - Produced water (PW) ilr are consistent during CO₂ injection \( \rightarrow \) stable tracer
  - PW ilr distinct from Santa Rosa groundwater

Small amount (5%) of reservoir mixing with overlying formation water would result in significant chemical shift

Gardiner et al., 2020, App. Geochem.
Early-stage geochemistry-based leak detection

Characterizing what a geochemical signal looks like under CO\textsubscript{2}/brine leakage scenarios

1. Characterize expected signals of brine migration between geologic formations – mixing models developed with field data

2. Identify which combinations of chemical signatures indicate CO\textsubscript{2} migration – geochemical-statistical model to identify the probability that a leak occurred using common geochemical parameters

Reactions underlying response

1. \( \text{CO}_2 + \text{H}_2\text{O} \approx \text{H}_2\text{CO}_3 \approx \text{H}^+ + \text{HCO}_3^- \)

2. \( 2\text{H}_2\text{O} + \text{CO}_2 + \text{CaMg(CO}_3)_2 \approx \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- \)

3. \( \text{H}_2\text{O} + \text{CO}_2 + \text{CaCO}_3 \approx \text{Ca}^{2+} + \text{HCO}_3^- \)

4. \( 2\text{H}_2\text{O} + \text{CO}_2 + \text{SrMg(CO}_3)_2 \approx \text{Sr}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- \)

5. \( \text{H}_2\text{O} + \text{CO}_2 + \text{SrCO}_3 \approx \text{Sr}^{2+} + \text{HCO}_3^- \)

6. \( \text{H}_2\text{O} + \text{CO}_2 + \text{BaCO}_3 \approx \text{Ba}^{2+} + \text{HCO}_3^- \)

7. \( \text{H}_2\text{O} + \text{CO}_2 + \text{BaMg(CO}_3)_2 \approx \text{Ba}^{2+} + \text{Mg}^{2+} + \text{HCO}_3^- \)
What does a leak look like (geochemically) and when do we need to do something about it?

Applying predicted geochemical reactions towards the statistical model

Identify which combinations of chemical signatures indicate CO₂ migration – geochemical-statistical model to identify the probability that a leak occurred using common geochemical parameters.
Identified reaction matrix to represent dominant CO₂-sandstone aquifer reactions

- Reaction matrix identifies relevant CO₂-rock reactions
- Mineral assemblages emphasize abundant minerals
  - Geochemical parameters are sensitive to these reactions
### Step 1. Generating Reaction Matrix and Model based on Previous Research

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction Pathways</strong></td>
<td><strong>Base Case Brine</strong></td>
<td><strong>Base Case Brine + CO₂</strong></td>
<td><strong>Mechanisms Underlying Responses</strong></td>
<td><strong>Parameters related to Leakage Pathway</strong></td>
<td><strong>Confidence in Detecting Change</strong></td>
</tr>
<tr>
<td>1</td>
<td>Dolomite (1° res.) → Wellbore migration</td>
<td>Equilibrium with formation</td>
<td>CO₂ Induced Water-Rock Rxns</td>
<td>·Carbonate dissolution</td>
<td>·Dissolved ions [Ca²⁺, Mg²⁺, Sr²⁺, Fe²⁺] ·Barium and strontium isotopes</td>
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<td></td>
<td></td>
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<td>·Cement dissolution</td>
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<td>2</td>
<td>Dolomite (1° res.) → Shale (seal) → Overlying Units</td>
<td>Box B1 + Shale Rxns</td>
<td>CO₂ Induced Water-Rock Rxns</td>
<td>·Carbonate dissolution</td>
<td>·Dissolved ions [Ca²⁺, Mg²⁺, Sr²⁺] ·Strontium isotopes</td>
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<td></td>
<td></td>
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<td>·Shale dissolution</td>
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<tr>
<td>3</td>
<td>Sandstone (1° res.) → Wellbore migration</td>
<td>Equilibrium with formation</td>
<td>CO₂ Induced Water-Rock Rxns</td>
<td>·Silica dissolution</td>
<td>·Dissolved ions [Na⁺, Ca²⁺, Mg²⁺, Fe²⁺] ·Barium strontium isotopes</td>
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<td></td>
<td></td>
<td>·Cement dissolution</td>
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<tr>
<td>4</td>
<td>Sandstone (1° res.) → Shale (seal) → Overlying Units</td>
<td>Box B3 + Shale Rxns</td>
<td>CO₂ Induced Water-Rock Rxns</td>
<td>·Carbonate dissolution</td>
<td>·Dissolved ions [Na⁺, Ca²⁺, Mg²⁺, Fe²⁺] ·Strontium isotopes</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>·Shale dissolution</td>
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</table>
Calculated changes in water chemical signals based on CO₂ reaction with the defined reaction matrix

- 18 mineral assemblages tested, involving different amounts of:
  - carbonate (calcite), feldspar (albite and anorthite), mica (annite and phlogopite), and chlorite (ripidolite)

- Quartz and kaolinite included in all reactions as the major sandstone phases

- Each mineral assemblage first equilibrated with Santa Rosa groundwater average fluid data, then reacted with different concentrations of dissolved CO₂
Application of statistical model to identify when dissolved ion combinations could relate to CO₂ leak

Reactions Associated with CO₂ Leakage → Leakage Event Simulation: Geochemical Reaction Path Model → Identifying CO₂ Leakage: Bayesian Belief Network

Identifying CO₂ Leakage: Bayesian Belief Network

Model Output

Regression Curves

Std. Deviation: Residuals
Mean-predicted value

Multiple Ion Concentrations + Observed Fluid Network

Probability of CO₂ Leakage
Using the Geochemical-Statistical model to identify priority parameters for monitoring – 1 Parameter Example

Bayesian Belief Network (BBN) model for leak inference with low magnesium concentrations.

Example: Mg data input (only) from field data → inconclusive results
Using the Geochemical-Statistical model to identify priority parameters for monitoring – 3 Parameter Example

Example: Mg$^{2+}$, HCO$_3^-$, and SO$_4^{2-}$ data input (only) from field data → likely occurrence of large CO$_2$ leak
Lessons Learned & Synergy Opportunities

- **Lessons Learned**
  - CO₂ concentration alone may not provide information on “early leaks”
  - Simple geochemical parameters can provide a first-pass check on whether fluid communication or CO₂ leakage occurred
  - More advanced geochemical analytical techniques can be used to better pinpoint the cause for unwanted migration

- **Synergy Opportunities**
  - Apply isometric log ratio and the geochemical-statistical model at field demonstration sites
  - Interface with NRAP IAM
Identify which chemical tracers can: A) be reliably identified and measured in field samples with techniques of varied time and cost, and B) can be used to identify major processes that may occur during CO₂ and brine leakage.

Refine the Reaction Matrix for Testing with Bayesian Belief Network Statistical Modeling - incorporate isotope-based tracers as part of the decision tree of key aqueous species for identifying migration pathway.

Develop Process-Based Statistical Models using Geochemistry-Based Tools

Key Products:
- 2020: Develop decision tree of key aqueous geochemical signals for identifying potential leakage points from carbon storage reservoirs to groundwater. (Completed)
- 2021: Demonstrate application of process-based model towards identifying the signals most important for monitoring leakage in a geologic system of interest. (Expected EY21-Q4)

Demonstrate Application of Bayesian Belief Network Statistical Model for Expected Signals of a Migration Event
Thank you!

Questions?

Contact: Alexandra.Hakala@netl.doe.gov

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Geochemical Monitoring of Groundwater Impacts – Novel Geochemical Signal Methodologies

Advanced Storage Task 21 Project – Total Project Value $ k

**Products:**

- 2020: Demonstrate hypothetical processes and signals in a carbonate system if migration occurs in a CO₂-EOR reservoir *(Completed EY20-Q2)*

- 2020: Develop decision tree of key aqueous geochemical signals for identifying potential leakage points from carbon storage reservoirs to groundwater. *(Completed EY20-Q4)*

- 2021: Demonstrate application of process-based model towards identifying the signals most important for monitoring leakage in a geologic system of interest. *(Expected EY21-Q4)*
## Direct Sensing Chemical Analysis for CS Monitoring


<table>
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<tr>
<th>Geochemical Tracer</th>
<th>What it Shows</th>
<th>Evaluation Approach</th>
<th>Field Deployment Status</th>
<th>Technology Transfer</th>
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</thead>
<tbody>
<tr>
<td><strong>Direct Monitoring Field-Based Techniques</strong></td>
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<tr>
<td>Direct CO₂ Measurement in Shallow Wells</td>
<td>• Amount of dissolved CO₂ in groundwater via direct measurement</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field sampling at CO₂-EOR and natural analog sites</td>
<td>Field-tested</td>
</tr>
<tr>
<td>Field-Based Electrochemical Sensors</td>
<td>• Presence and concentrations of dissolved iron and reduced sulfur species – identifies intrusion of fluids that impact local reservoir chemical conditions</td>
<td>Laboratory</td>
<td>Verified analytical techniques and applied to measuring iron and sulfur in samples collected at a natural analog site</td>
<td>Deployable (shallow monitoring); NETL-modified technique</td>
</tr>
<tr>
<td>CarboQC for Direct CO₂ measurement</td>
<td>• Direct measurement of dissolved CO₂ through PVT technique</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and tested in emergent groundwaters</td>
<td>Deployable; NETL-modified technique</td>
</tr>
<tr>
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<td>What it Shows</td>
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<td>Field Deployment Status</td>
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<tr>
<td><strong>Ion Chromatography-Based Techniques</strong></td>
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<tr>
<td><strong>Cations</strong></td>
<td>Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺</td>
<td>Screen major cations for large field sample sets within a few days – indicator of water source and whether additional tracers need to be analyzed for prediction/interpretation</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field sampling at CO₂-EOR and natural analog sites</td>
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<tr>
<td><strong>Anions</strong></td>
<td>fluoride, chloride, nitrite, nitrate, bromide, bromate, phosphate, chromate, iodide, sulfate, thiosulfate, sulfite</td>
<td>Screen major anions for large field sample sets within a few days – indicator of water source and whether additional tracers need to be analyzed for prediction/interpretation</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field samples from CO₂-EOR site</td>
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<tr>
<td><strong>Organic Acids</strong></td>
<td>acetate, lactate, formate, butyrate, propionate, pyruvate, succinate, oxalate, citrate</td>
<td>Screen organic acids in for large field sample sets – indicators of biological activity</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field samples from CO₂-EOR site</td>
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## Geochemical Tracer

### What it Shows
- Evaluation Approach
- Field Deployment Status
- Technology Transfer

### Ion Chromatography-Based Techniques

<table>
<thead>
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</thead>
<tbody>
<tr>
<td>Transition Metals Fe³⁺, Fe²⁺, Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺</td>
<td>• Screen large field sample sets for metals within a few days – identify whether more detailed ICP-based techniques are needed to characterize water source • Identify redox changes that may indicate fluid migration</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field sampling at CO₂-EOR sites</td>
<td>Deployable; NETL-modified technique</td>
</tr>
<tr>
<td>Rare earths La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu</td>
<td>• Screen large field sample sets for REEs within a few days – identify whether more detailed ICP-based techniques are needed to characterize water source</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field samples from CO₂-EOR site</td>
<td>Deployable; NETL-modified technique</td>
</tr>
<tr>
<td>Sulfides sulfide, cyanide</td>
<td>• Complement field-based electrochemical monitoring techniques • Identify redox changes that may indicate fluid migration</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field samples from CO₂-EOR site</td>
<td>Deployable; NETL-modified technique</td>
</tr>
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### Published
- NETL TRS describing use of ion chromatography to screen high-TDS field samples

### In Progress
- NETL TRS describing use of ion chromatography to screen high-TDS field samples
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<tr>
<td><strong>Isotope-Based Techniques</strong></td>
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</table>
| Strontium $^{87}\text{Sr}/^{86}\text{Sr}$ | • As stable isotope indicator of the sources of geologic brines and reservoir CO$_2$-fluid-rock reactions  
• Used to define mixing curves for expected values in receptor formations | Laboratory + Field Assessment | Deployable; May be location-specific (NETL-developed technique) | • Wall et al. JAAS (2013)  
• Wall et al. TRS report  
• Phan et al. App Geochem (2018)  
• Gardiner et al. IJGHGC (2020)  
• Multi-isotopic monitoring of CO$_2$-EOR site in Permian Basin |
| Carbon $^{13}\text{C}/^{12}\text{C}$ | • C indicates source of CO$_2$ detected  
• Used to identify whether CO$_2$ is from the storage reservoir | Laboratory + Field Assessment | Deployable (established techniques) | • Gardiner et al. IJGHGC (2020)  
• Multi-isotopic monitoring of CO$_2$-EOR site in Permian Basin |
| Oxygen $^{18}\text{O}/^{16}\text{O}$ | • Indicates geologic versus atmospheric contributions to water  
• Used to identify whether high TDS fluid is from deep reservoirs | Laboratory + Field Assessment | Deployable (established techniques) | • Gardiner et al. IJGHGC (2020)  
• Multi-isotopic monitoring of CO$_2$-EOR site in Permian Basin |
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<tr>
<td>Lithium $^7\text{Li}/^6\text{Li}$</td>
<td>• Identifies whether reservoir brine contacted the seal layer or organic-rich zones • Identifies whether migrated brine originates from the carbon storage reservoir</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field sampling at CO$_2$-EOR site</td>
<td>Deployable; May be location-specific (NETL-developed technique) • Pfister et al. (2017) • Phan et al. App Geochem (2018) • NETL TRS report on application of Li isotopes as geochemical tracers for carbon storage</td>
</tr>
<tr>
<td>Boron $^{11}\text{B}/^{10}\text{B}$</td>
<td>• Identifies whether leaked CO$_2$ contacted brine, or if it came directly from the sc-CO$_2$ plume</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field sampling at CO$_2$-EOR site</td>
<td>Deployable; May be location-specific (NETL-modified technique) • Phan et al. COGEL (2020) • NETL TRS report on application of B isotopes as geochemical tracers for carbon storage</td>
</tr>
<tr>
<td>Geochemical Tracer</td>
<td>What it Shows</td>
<td>Evaluation Approach</td>
<td>Field Deployment Status</td>
<td>Technology Transfer</td>
</tr>
<tr>
<td>-------------------</td>
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<tr>
<td><strong>Isotope-Based Techniques</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Uranium $^{234}$U/$^{238}$U</td>
<td>• Relevant for regions with elevated uranium present in subsurface reservoirs • Identifies fluid migration and oxidation-reduction processes</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field sampling at CO$_2$-EOR and natural analog sites</td>
<td>Location-specific (need detectable concentrations of U; established techniques) • Phan et al. GCA (2019) • Gardiner et al. IJGHGC (2020)</td>
</tr>
<tr>
<td>Barium $^{138}$Ba/$^{134}$Ba</td>
<td>• Relevant for regions with elevated Ba • Indicates fluid mixing between the CS reservoir and overlying geologic units</td>
<td>Laboratory + Field Assessment</td>
<td>Verified analytical techniques and applied to field samples from CO$_2$-EOR site</td>
<td>Technique developed in 2018-2019 for onshore gas (NETL-developed technique); Modified for carbon storage in 2019-2020 • Multi-isotopic monitoring of CO$_2$-EOR site in Permian Basin • NETL TRS on application of Ba isotopes as geochemical tracers for carbon storage</td>
</tr>
</tbody>
</table>
Appendix 2

Additional information on Permian Basin CO$_2$-EOR geochemical monitoring
Milestone: Model what a leak would look like in the geochemical signals at different leakage points in a CO$_2$-EOR system.

E. Seminole Field Data

- CO$_2$-EOR field initiating CO$_2$ flood (Fig. 1)

<table>
<thead>
<tr>
<th>System</th>
<th>Series</th>
<th>Group/Formation</th>
<th>Lithology</th>
<th>Average Depth (m) of Samples at field area</th>
<th>Hydrostratigraphic Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary</td>
<td>Alluvium</td>
<td></td>
<td>Silty sand</td>
<td>~45-55</td>
<td>Evaporite Confining</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Upper</td>
<td>Cripple Creek</td>
<td>Fluvial and lacustrine clastics</td>
<td>~45-55</td>
<td></td>
</tr>
<tr>
<td>Cretaceous</td>
<td>Albian</td>
<td>Antrim Group</td>
<td>Antler / Palux</td>
<td>Sandstone</td>
<td></td>
</tr>
<tr>
<td>Triassic</td>
<td>Upper</td>
<td>Dockum Group</td>
<td>Fluvial-delta and lacustrine clastics</td>
<td>~160</td>
<td>Deep Basin Aquifer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Santa Rosa Fm.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pennsylvanian</td>
<td></td>
<td>Wolfcampian</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cisco &quot;Cline&quot;</td>
<td>Shelf limestones, minor shale</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mississippian</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Timeline of sampling history at field site, with dates of sampling trips and major field events below.

Opportunity to:

1. Observe CO$_2$ induced changes in produced water
2. Monitor overlying groundwaters for produced water intrusion

Potential Implications/Impact

1. Understand CO$_2$ water-rock-interactions
2. Develop applications of geochemical tools for monitoring, measurement, and verification

Figure 2. Simplified stratigraphic column$^1$ of the Central Basin Platform; highlighted formations were sampled at E. Seminole field.

$^1$Figure B based on previous editions from Stueber et al. (1998), Engle et al. (2016) and Pfister et al. (2017).
Statistically significant ($p < 0.5$) increases in dissolved inorganic constituents [alkalinity, TDS, Na$^+$, Cl$^-$, SO$_4^{2-}$] in produced waters.

- Alkalinity increases due to dissolution of CO$_2$ into formation water.
- Sulfate increase likely due to sulfur-mineral oxidation.
- Na$^+$, Cl$^-$, and TDS increases due to enhanced mixing with denser formation water below oil-water contact.
- No increase in Ca$^{2+}$ or Mg$^{2+}$, suggesting negligible carbonate reservoir dissolution.

  - Indicates geologic leakage out of producing formation unlikely at this time.
San Andres Fm. Produced Waters

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Geochemical changes: Producing Formation

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E. Seminole Field Data

- **Produced Water Results**
  - After CO₂ injection, significant shifts in certain analytes [alkalinity, TDS, Na⁺, Cl⁻, SO₄²⁻]
  - No significant shifts in others [Ca²⁺, Mg²⁺]

- **Interpretation**
  - Injected CO₂ is dissolved in water [solubility trapping] and not likely causing carbonate dissolution → Reservoir integrity preserved
  - Produced water geochemistry reflects CO₂ injection → Track CO₂ plume in reservoir
Milestone: Model what a leak would look like in the geochemical signals at different leakage points in a CO2-EOR system.

E. Seminole Field Data

- **Distinctive geochemistry**
  - Applied data transformation tool (isometric log-ratios) to produced water
  - Despite shifts following CO₂ injection, E. Seminole produced water still occupies a small, distinctive range *(Fig. A)*

- **Groundwater Results: Detecting Leakage**
  - E. Seminole produced water occupies small range relative to local produced waters *(Fig. B)*
  - Mixing model demonstrates **hypothetical** detection of leakage from producing formation into overlying, intermediate groundwater *(Fig. C)*
Bayesian Belief Network: Incorporating Reaction Matrix

Dolomite reservoir

Prior Network
(no measurements)

Nothing found in measurements

Mg, Sr, and Ba found in measurements

Reaction Occurring?

Reaction 2 Occurring?

No

Yes

50.0

50.0

Ca

No

Yes

42.5

57.5

Mg

No

Yes

38.7

61.3

Sr

No

Yes

45.0

55.0

Ba

No

Yes

46.3

53.8

Reaction Occurring?

Reaction 3 Occurring?

No

Yes

75.0

25.0

Ca

No

Yes

100

0

Mg

No

Yes

100

0

Sr

No

Yes

100

0

Ba

No

Yes

100

0

Reaction Occurring?

Reaction 4 Occurring?

No

Yes

84.2

15.8

Ca

No

Yes

0

100

Mg

No

Yes

0

100

Sr

No

Yes

0

100

Ba

No

Yes

0

100

Reaction Occurring?

Reaction 5 Occurring?

No

Yes

75.0

25.0

Ca

No

Yes

70.9

29.1

Mg

No

Yes

77.4

22.6

Sr

No

Yes

34.5

65.5

Ba

No

Yes

20.2

79.8

Reaction Occurring?

Reaction 6 Occurring?

No

Yes

84.7

15.3

Ca

No

Yes

0

100

Mg

No

Yes

0

100

Sr

No

Yes

0

100

Ba

No

Yes

0

100

Reaction Occurring?

Reaction 7 Occurring?

No

Yes

75.0

25.0

Ca

No

Yes

70.9

29.1

Mg

No

Yes

77.4

22.6

Sr

No

Yes

34.5

65.5

Ba

No

Yes

20.2

79.8

Reaction Occurring?

Reaction 7 Occurring?

No

Yes

50.0

50.0

Ca

No

Yes

50.0

50.0

Mg

No

Yes

50.0

50.0

Sr

No

Yes

50.0

50.0

Ba

No

Yes

50.0

50.0

Ion Increased?

Mg

No

Yes

38.7

61.3

Ca

No

Yes

42.5

57.5

Ba

No

Yes

46.3

53.8

Reaction Occurring?

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No

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45.0

55.0

Ca

No

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42.5

57.5

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61.3

Sr

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55.0

Ba

No

Yes

46.3

53.8

Reaction Occurring?

Reaction 4 Occurring?

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84.2

15.8

Ca

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Yes

100

0

Mg

No

Yes

100

0

Sr

No

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0

Ba

No

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100

0

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25.0

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100

Sr

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Yes

0

100

Ba

No

Yes

0

100

Reaction Occurring?

Reaction 7 Occurring?

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50.0

50.0

Ca

No

Yes

50.0

50.0

Mg

No

Yes

50.0

50.0

Sr

No

Yes

50.0

50.0

Ba

No

Yes

50.0

50.0