Exploring the Behavior of Shales as Seals and Storage Reservoirs for CO$_2$

Project Number 90210

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NETL ORD, Predictive Geosciences Division
Presentation Outline

• Benefits to Program
• Project Goals and Objectives
• Technical Status
• Accomplishments to Date
• Summary
Technical Scope

Shales as Seals

Shales as Storage Reservoirs

Benefit to the Program

• Carbon Storage Program Goals Addressed:
  – Support industry’s ability to predict CO₂ storage capacity in \((\text{unconventional})\) geologic formations to within \(\pm 30\) percent
  – Ensuring 99 percent storage permanence.

• Project Benefits:
  – Improve understanding of injection/storage performance of unconventional formations
  – Inform efficiency estimation for resource assessment
  – Insights feeding to seal characterization in integrated assessment of risk
Project Overview:
Goals and Objectives

• Project Objectives
  – Evaluate matrix response to CO₂ exposure (sorption, swelling/shrinkage, geochemical interactions)
  – Characterize effective permeability and porosity of shale to CO₂
  – Experimental and simulation-based performance of CO₂ storage in/transport through shale with natural and engineered fractures
  – Reduced order characterization to improve resource estimation and quantitative risk assessment of geologic CO₂ storage
Science Base Feeding to Higher-Level Assessments

Micro-Scale Data Collection (CT, SEM, etc)

Core-Scale Flow and Imaging

Data Conversion & Computational Fluid Dynamics

Gas/liquid flowing in rock fractures

National-Scale Assessment

Well and Field-Scale Simulation

Multiscale Data Analysis

Comparison of Shale Density from CT Scans and Well Logs
CO₂ and CH₄ Sorption capacity as function of %TOC (single-fluid isotherms)

**CO₂ Isotherms**

**CH₄ Isotherms**

**CO₂ Sorption Mechanisms: Fourier Transform-Infrared Spectroscopy (FT-IR)**

15 min CO₂ exposure at 40°C, 0-800 psi

**Physically Sorbed CO₂ IR Peaks: 2350-2330 cm⁻¹**
CO₂ Sorption on Shale Samples

**FT-IR Data:**
Area of 2343 cm⁻¹ CO₂ Sorption Peaks

Peak Area vs Pressure for Clay Infrared Spectra at 40°C

- Ca-Smectite
- Illite-Smectite
- Illite
- Kaolinite

Integrated CO₂ peak area is not quantitative

**FT-IR Data:**
Area of 2331 cm⁻¹ CO₂ Sorption Peaks*

Peak Area vs Pressure of Shale Infrared Spectra at 40°C

TOC-content (wt. %): MS-4 (9.2) > MS-1 (6.5) > US-1 (0.5)

*2343 cm⁻¹ peak not strong enough to obtain reliable area measurements

FT-IR trends compliment results of CO₂ isotherm measurements
Geochemical Model Sensitivity and Caprock Interface

**Study Problem:** Geochemical calculations rely on uncertain thermodynamic & kinetic databases

**Goal:** Characterize the mineral precipitation and dissolution processes that are important at brine/aquifer/caprock interfaces.

**Finding:** The precipitation and dissolution processes for minerals Chlorite, and carbonates Cc, Dol, Ank contribute to autosealing at the brine/aquifer/caprock interfaces.

**Source:** Balashov, V. N. Brantley, S. L. Guthrie, G. D. Lopano, C. L Hakala, and J. A. Impact of geochemical kinetics at the reservoir/shale interface on long term CO2 storage. Goldschmidt Conference June 8 – 13, 2014
Steady-State Permeameter

Capable of reproducing in-situ net stress, and measuring gas flow under partial liquid saturation

**Effective porosity of shale as function of net stress**

**Effective permeability of shale as function of net stress**

Marcellus Shale, Seneca Falls, NY

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Image from: Kashiar Aminian; Discussion of PPAL capability at: SPE/DOE 11765, Symposium on Low Permeability Gas Reservoirs, Denver, CO, March 13-16, 1983
Coupling Mechanical Changes of Fractures to Hydraulic Changes

Cycling of confining pressure causes fracture asperities to break down, reducing effective fracture aperture.
Modeling CO₂ Flow in Fractured Geologic Media

FRACGEN stochastically generates fracture networks

NFFLOW models flow in discrete fracture networks

Images from: Sams, N. Overview of NFFLOW & FRACGEN. June 3, 2013
**Goal:** Develop a robust characterization of site-scale CO$_2$ storage and EGR potential of gas-bearing shale formations

**Scenario:** Dry gas window, Marcellus, SW PA, Depth of 6,700 ft (~ 2,000 m), gross interval thickness of 120 ft (37 m), 145ºF (63ºC), Initial pressure 4,000 psi (27.6 MPa), matrix permeability 0.1 -1 (μD)

**Sensitivity of CO$_2$ storage/EGR performance to:**
- Fracture network characteristics
- Matrix CO$_2$ and CH$_4$ sorption characteristics
- Injector/producer distance
- Injection pressure
- Stress-dependent matrix perm.
Representing Fracture Networks

Semi-stochastic fracture network and flow modeling
Modified dual porosity, multiphase, compositional, multidimensional flow model
Discrete Fracture Modeling coupled with conventional reservoir simulation
Semi-stochastic fracture network and flow modeling
Single Lateral CO₂ Storage Scenario

Scenario: Constant pressure at 5000 psi, single lateral

Uncertain Parameters: \( h_{\text{net}}, \Phi_{\text{matrix}}, \Phi_{\text{fracture}}, k_{\text{matrix}}, k_{\text{fracture}}, \) fracture spacing, Langmuir constants

MC with 1000 realizations

<table>
<thead>
<tr>
<th></th>
<th>( P_{90} )</th>
<th>( P_{50} )</th>
<th>( P_{10} )</th>
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<tr>
<td>OGIP (BSCF)</td>
<td>111</td>
<td>138</td>
<td>165</td>
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<tr>
<td>CH₄ Production over 30 Years (BSCF)</td>
<td>20.1</td>
<td>23.7</td>
<td>27.4</td>
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<tr>
<td>CO₂ Stored after 30 Years (BSCF)</td>
<td>15.3</td>
<td>16.9</td>
<td>18.5</td>
</tr>
</tbody>
</table>
CO₂ Storage and Enhanced Gas Recovery Scenario

- CO₂ Injection for EGR not expected to start until primary production complete (nominally 40 years)
- Models predict EGR recovery (technical) potential between 0 and 11% (above primary production)
- Time to breakthrough of 10% mole fraction in produced stream decreases significantly as SRV overlap of adjacent laterals increases

Flux through Fractured Seal ROM
NSEALR

- Assumes thin, relatively impermeable, fractured rock unit, initially saturated with a saline water.
- Two-phase, relative permeability approach and 1-D Darcy flow of carbon dioxide through the horizon in the vertical direction
- User defined or stochastically varying permeability, porosity, seal thickness
- Correction for in situ stress on aperture values generated by the fractured rock model, including shear stress options

Accomplishments to Date

– Well/pad-scale characterization of CO$_2$ storage and EGR performance in depleted shale gas formations
– Preliminary experimental characterization of:
  • Shale sorption characteristics
  • Mechanisms of CO$_2$/shale interactions
  • Matrix permeability
  • Fracture flow
  • Pore imaging
– Reduced physics model characterizing flux through fractured seal
– Contributing to methodology for CO$_2$ storage in shale
Summary

– Future Plans

• Understanding shale pore type and structure
• Flow through nanopores on molecular scale
• Importance of pore effects at core-scale
• Matrix swelling/shrinkage effects
• Oil wet versus water wet (black shale vs. gray)
• Liquid and condensate reservoirs
• Simulation refinement and validation
Organization Chart

• NETL Office of Research & Development
  – Predictive Geosciences Division
  – Engineered Natural Systems Division
  – Material Characterization Division

• URS Corp.

• West Virginia University, Penn State University, Carnegie Mellon University
## Gantt Chart

### Carbon Storage

**FWP Number Car Stor_FY14**

**Schedule and Milestones**

<table>
<thead>
<tr>
<th>Task No.</th>
<th>Activity Name (Task/Sub-task)</th>
<th>Start</th>
<th>Finish</th>
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<tr>
<td>1.0</td>
<td>Project Management</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<tr>
<td>1.1</td>
<td>Project Management</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<td>2.0</td>
<td>Reservoir and Seal Performance</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<td>2.1</td>
<td>Impact of CO₂-Brine-Rock Chemistry on Storage Formations and Seals</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<td>Impact of Microbial Processes on Storage Formations and Seals</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<tr>
<td>2.3</td>
<td>Impact of CO₂ on Shale Formations as Seals</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<tr>
<td>2.4</td>
<td>Characterization of Reservoir and Seal Material Performance</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<td>Understanding of Multiphase Flow for Improved Injectivity and Trapping</td>
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<td>Geochemical Model Sensitivity at Caprock Interfaces</td>
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<td>Monitoring Groundwater Impacts</td>
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<td>9/30/14</td>
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<td>3.1</td>
<td>Natural Geochemical Signals for Monitoring Groundwater Impacts</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<td>Resource Assessments and Geospatial Resource</td>
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<td>9/30/14</td>
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<tr>
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<td>Resource Assessments</td>
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<td>4.2</td>
<td>Geospatial Data Management</td>
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<td>9/30/14</td>
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<tr>
<td>5.0</td>
<td>Monitoring CO₂ and Pressure Plume</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<tr>
<td>5.1</td>
<td>Development of Technology to Monitor CO₂ and Pressure Plume</td>
<td>10/1/13</td>
<td>9/30/14</td>
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<td>6.0</td>
<td>Catalytic Conversion of CO₂ to Industrial Chemicals</td>
<td>10/1/13</td>
<td>9/30/14</td>
</tr>
<tr>
<td>6.1</td>
<td>Catalytic Conversion of CO₂ to Industrial Chemicals</td>
<td>10/1/13</td>
<td>9/30/14</td>
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**FY14**

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<tr>
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<th>Q3</th>
<th>Q4</th>
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**Milestone Summary**

- M1.14.2.A
- M1.14.3.A
- M1.14.4.A
- M1.14.5.A
- M1.14.6.A

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**Page 1 of 1**
Coupled Fluid Flow and Geomechanical Modelling

3-D, single phase Finite Element Model to estimate maximum allowable injection pressure without caprock failure.

**Ground Deformation**
- Maximum computed surface displacements are about 0.07 ft (21.3 mm).
- Can monitor with tiltmeter array.
Related Studies

• Nuttall et al., (2005) – Kentucky Geologic Survey
  – KGS developed the first volumetric estimates of CO\textsubscript{2} storage potential in the Carbonaceous (black) Devonian gas shales that underlie Kentucky, estimating that as much as 28 Gt could be stored there.

• Advanced Resources International (2013)
  – Basin-level assessment of CO\textsubscript{2} and EGR potential, reservoir simulation, novel monitoring, techno-economic assessment

• Tao & Clarens (2013) (U. Virginia)
  – Estimating CO\textsubscript{2} storage in Marcellus shale

• Zobak et al. (Stanford)
  – evaluate physical and chemical interactions between CO\textsubscript{2} and shale, imaging of fluid migration in shale

• Ripepi et al. (Virginia Tech)
  – Simulation and field demonstration in Central Appalachia
(2) Experimental Analysis of CO₂ Storage in Organic-rich Shale

**Purpose:**
Examine & quantify CO₂ sorption capacity of *individual* clay standards & shale samples
Determine relative roles of kerogen, clay, & clay type in CO₂ storage potential of shales

**Analytical work conducted on shale samples and clay standards**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>He Pycnometry</th>
<th>E-SEM</th>
<th>FT-IR (std)</th>
<th>FT-IR (T&amp;P)</th>
<th>CO₂ Adsorption Isotherms</th>
<th>TOC</th>
<th>XRD</th>
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</thead>
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<tr>
<td><strong>Shale Samples</strong></td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>MS-1</td>
<td>Marcellus: <em>Oatka Creek</em></td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>MS-4</td>
<td>Marcellus: <em>Union Springs</em></td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
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<tr>
<td>US-1</td>
<td>Utica: <em>Flat Creek</em></td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
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<tr>
<td><strong>Clay Standards</strong></td>
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<td></td>
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<td></td>
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<tr>
<td>STx-1</td>
<td>Ca-Smectite</td>
<td>Y</td>
<td>-</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IMt-2</td>
<td>Illite</td>
<td>Y</td>
<td>-</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
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<tr>
<td>KGa-1b</td>
<td>Kaolinite</td>
<td>Y</td>
<td>-</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
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<tr>
<td>ISCz-1</td>
<td>Illite-Smectite</td>
<td>Y</td>
<td>-</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Talc</td>
<td>control</td>
<td>-</td>
<td>-</td>
<td>Y</td>
<td>Y</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*All clays are natural standards obtained from the Clay Mineral Society*

“Y” indicates the procedure has been conducted on the sample
Organic-rich Shale Outcrop Samples

Marcellus - *Union Springs*

Marcellus - *Oatka Creek*

Utica - *Flat Creek*

TOC = 9.20 wt. % (σ 0.60)  
TOC = 6.51 wt. % (σ 0.22)  
TOC = 0.45 wt. % (σ 0.17)

Quartz + Clay (e.g. illite, chlorite, kaolinite) + Carbonate + Pyrite + Kerogen ± Feldspar
Key Findings: CO₂ Storage in Shale

• Without HF and natural gas production, CO₂ can not be injected
• Storage predominantly as free-phase CO₂ in fractures – low permeability matrix limits amount of matrix available for sorption
• Favorable assumptions about Langmuir characteristics results in only a small increase in storage (sorbed phase)
• Storage ~ 50,000 tonnes per fractured stage
• CO₂ storage is not much greater in injector/producer scenario, and can be less in cases with significantly overlapping SRV
Potential Fluid Leakage Pathways from Unconventional HC Formations (US EPA, 2012)

- Leakage through the annuli of the vertical drilling well
- Leakage through a natural fault
- Leakage through an abandoned well
Representation of Horizontal Wells with Transvers Hydraulic Fractures
Evaluating the potential viability of an Equivalency Network

Equivalent hydraulic fracture representations:
- Maximum cumulative production error between the two representations is within 15%

Discrete transverse fracture representation
Crushed zone representation

Content Contributed by: Turgay Ertekin, Penn State University Department of Energy and Mineral Engineering
NETL ORD Multi-Scale CT Flow and Imaging Facilities

**Micro CT Scanner**
- Resolution $10^{-6}$ to $10^{-5}$ m
- Pore scale

**Industrial CT Scanner**
- $10^{-6}$ to $10^{-3}$ m
- Pore & core scale
- Pressure & flow controls

**Medical CT Scanner**
- $10^{-4}$ to $10^{-2}$ m
- Core scale
- P, T, and flow controls
Effective porosity and permeability of shale to $\text{CO}_2/\text{CH}_4$ over range of effective stress, and characterization of hysteresis effects

- Steady-state flow measurement, research quality data
- Capable of running different gases under different pressures, including nitrogen, methane and carbon dioxide.
- Capable of reproducing in-situ net stress, and measuring gas flow under partial liquid saturation.
- Can also measure pore volume to gas, adsorption isotherms and PV compressibility using $\text{N}_2$, $\text{CH}_4$ or $\text{CO}_2$
- Uses stable gas pressure as a reference for flow measurement
  - Temperature controlled
  - Stable to one part in 500,000
  - Target flow measurement is $10^{-6}$ standard cm$^3$ per second

*Image from: Kashiar Aminian; Discussion of PPAL capability at: SPE/DOE 11765, Symposium on Low Permeability Gas Reservoirs, Denver, CO, March 13-16, 1983*
Linked SRM-Economic Screening Tool
Modeling Approach

Field Properties
- Site location/properties
- Well/Completion details
- TOC

Flood Scenario Definition
- Configuration of well pad (# laterals/adjacency)
- Injection Schedule

Scenario Technical Performance
CO₂ injectivity over time, bottomhole pressure over time, produced gas rate/composition over time

Calculate Mass of CO₂ stored through flood

Financial Parameters
- CO₂ storage / NG value
- Electricity cost
- Interest rate
- Debt/equity ratio

Operational Parameters
- Source/sink distance
- Pipeline pressure
- Workover frequency

Economic Screening Model

Dynamic link library

Scenario Economic Performance
Cumulative Probability
UTC of Storage ($/tonne Stored CO₂)
CO₂–Clay Interactions: FT-IR Spectroscopy*

Chemically Sorbed CO₂ IR Peaks: 1400, 830, 720 cm⁻¹

*measured at 40°C
No changes observed in IR spectra with addition of CO₂ and pressure
CO$_2$–Clay Interactions: FT-IR Spectroscopy:

Chemically Sorbed CO$_2$ IR Peaks: 1400, 830, 720 cm$^{-1}$

Clay Standards at 0 and 800 psi CO$_2$

Absorbance

Wavenumber (cm$^{-1}$)

*measured at 40°C
CO₂ Sorption on Shale Samples

CO₂ Sorption Isotherms:
All Isotherm Data: 0-220 psi at -25, -15 & 0°C

FT-IR Data:
Area of 2331 cm⁻¹ CO₂ Sorption Peaks*

CO₂ Sorption Isotherms vs Relative Pressure for Shale Samples at -25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sorbed CO₂ (cm³/g)</th>
<th>P/P₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS-4</td>
<td>7.2 (± 0.5)</td>
<td>0.8</td>
</tr>
<tr>
<td>US-1</td>
<td>1.7 (± 0.6)</td>
<td></td>
</tr>
<tr>
<td>MS-1</td>
<td>1.5 (± 0.6)</td>
<td></td>
</tr>
</tbody>
</table>

MS-4 > US-1 ≥ MS-1

Peak Area vs Pressure of Shale Infrared Spectra at 40°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS-4</td>
<td>0.20</td>
</tr>
<tr>
<td>MS-1</td>
<td>0.18</td>
</tr>
<tr>
<td>US-1</td>
<td>0.16</td>
</tr>
</tbody>
</table>

*2343 cm⁻¹ peak not strong enough to obtain reliable area measurements

TOC-content (wt. %): MS-4 (9.2) > MS-1 (6.5) > US-1 (0.5)
CO₂ Sorption on Clay Standards

**CO₂ Sorption Isotherms:**
All Isotherm Data: 0-220 psi at -25, -15 & 0°C

**FT-IR Data:**
Area of 2343 cm⁻¹ CO₂ Sorption Peaks

FT-IR trends compliment results of CO₂ isotherm measurements.
Experimental Analysis of CO$_2$ Storage in Organic-rich Shale

**Results:**

(1). Smectite > Illite-Smectite > MS-4 ≥ Illite ≥ Kaolinite > US-1 ≥ MS-1

Summary of CO$_2$ Sorption Isotherm Data at 0.8 P/P$_0$ & -25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Smectite</th>
<th>Illite-Smectite</th>
<th>MS-4</th>
<th>Illite</th>
<th>Kaolinite</th>
<th>US-1</th>
<th>MS-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm$^3$/g</td>
<td>36.5</td>
<td>18.5</td>
<td>7.2</td>
<td>5.7</td>
<td>5.6</td>
<td>1.7</td>
<td>1.5</td>
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<tr>
<td>error +/-</td>
<td>1.3</td>
<td>0.5</td>
<td>0.5</td>
<td>0.6</td>
<td>1.0</td>
<td>0.6</td>
<td>0.6</td>
</tr>
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</table>

(2). Two CO$_2$ sorption peaks observed at 2343 and 2331 cm$^{-1}$ on IR spectra of the shale samples (possibly also clays)

(3). No changes were observed in the IR spectra of clays or shales after 15 min of exposure to CO$_2$ at pressures between 0-800 psi and 40°C.

**Interpretations:**

(1). Shale formations with high smectite, illite-smectite, and/or high TOC-content may have high CO$_2$ storage potential (e.g. Busch et al., 2008; Busch et al., 2009; Ross and Bustin, 2009)

(2). There may be two CO$_2$ sorption sites in shales & clays: in the interlayer* of clay structures & in the interpore space of minerals & kerogen. (*e.g. Rother et al., 2012; Geisting et al., 2012; Loring et al., 2012)

(3). At experimental conditions, exposure to CO$_2$ does not induce chemical changes in clays & shales of these compositions
Field: 77 wells, 652 stages, and 1893 clusters

Representative "Qualified Site"
CO₂ Storage in Depleted Shale combining conventional/ML-based reservoir modeling

- Acquire real-time gas production from a set of shale gas wells
- Use that set of data to develop population statistics
- Develop a history-matched model of shale gas production (29 month production history) using a conventional reservoir model
- Project forward to economic limit before initiating CO₂ injection
- Develop a surrogate reservoir model based on the history matched model to predict wellpad performance under CO₂ loading

Field: 77 wells, 652 stages and 1893 clusters

Representative “Qualified Site”

Content Contributed by: Shahab Mohaghegh, West Virginia University Department of Petroleum & Natural Gas Engineering
CO₂ and CH₄ Sorption capacity as function of %TOC (single-fluid isotherms)

- Sorption capacity of CO₂ and CH₄ exhibit linear relationship with TOC