CO₂ Sequestration in Coal Seams: Understanding the Interactions Between CO₂ and Coal

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Goals and Objectives
Support of DOE/NETL Program Objectives

- Priority Research Pathways:
  - Geologic formations: unmineable coal seams
  - Trapping mechanisms: CO₂ sorption on coal
- Goal: “2012 Demonstrate ability to predict CO₂ storage capacity with +/-30% accuracy”
  Carbon Sequestration Roadmap (Table 1 “Top Level”)
- Goal: “Capability to predict CO₂ storage capacity” and “Injection techniques to enhance CO₂ contact with coal seam”
  Carbon Storage Roadmap (Cross Cut Pathways, Table 5)
- Goal “2008 Develop an understanding of trapping mechanism for coal seams”
  Carbon Storage Roadmap (Program Goals, Table 5)
CO$_2$ sequestration in coal seams

- **STORAGE CAPACITY:**
  - Isotherms
    - Accuracy
    - Reproducibility
    - Coal powders versus confined cores

- **TRAPPING MECHANISM:**
  - Chemical and physical interaction
  - Swelling
    - Loss of permeability (Darcy Flow)
  - Structure changes
    - CO$_2$ plasticizes the coals and reduces the T$_g$ value causing a structural rearrangement
Working Hypotheses: CO$_2$ Injection into a Coalbed


**Selected Hypotheses**

- 1) The glass-to-rubber transition temperature (T$_g$) of the coal will be dramatically reduced by imbibition of CO$_2$. The coal will become plasticized.

- 2) The cleat system within the coalbed will begin to close and become restricted, slowing Darcy flow within that area of the seam due to swelling.

- 3) There will be a substantial increase in the self diffusivity of CO$_2$ in coal once it has become plasticized and is above its T$_g$.

- 4) Injection of dry CO$_2$ will dry the coal, particularly in those areas where the flow rate of CO$_2$ is highest. Drying the coal will result in coal shrinkage proportional to the amount of water removed from the coal and an increase in permeability.
NETL Tools

Traditional Methods
- Volumetric/Gravimetric techniques
  - CO$_2$-coal isotherms
  - Interlab study on moisture-equilibrated coals up to 2000 psia
  - Gravimetric study indicating coal swelling
- Dilatometry
  - Coal swelling or shrinkage upon exposure to CO$_2$

Novel Methods
- IR spectroscopy
  - Understanding mechanism, coal structure changes, swelling, and isotherms
- Core Flow Lab
  - Permeability measurements
  - Estimate swelling
# Argonne premium coals

- coals are well-characterized, providing the research community with a large database of physical and chemical properties of coal
- samples were supplied as powders (-100 mesh).
- prepared in an inert environment

<table>
<thead>
<tr>
<th>Coal (100 mesh)</th>
<th>Rank</th>
<th>%C MAF</th>
<th>% Moisture</th>
<th>% Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pocahontas No. 3</td>
<td>Low Vol. Bit.</td>
<td>91.1</td>
<td>0.65</td>
<td>4.74</td>
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<tr>
<td>Upper Freeport</td>
<td>Med. Vol. Bit.</td>
<td>85.5</td>
<td>1.13</td>
<td>13.03</td>
</tr>
<tr>
<td>Pittsburgh No. 8</td>
<td>High Vol. Bit.</td>
<td>83.2</td>
<td>1.65</td>
<td>9.10</td>
</tr>
<tr>
<td>Lewiston-Stockton</td>
<td>High Vol. Bit.</td>
<td>82.6</td>
<td>2.42</td>
<td>19.36</td>
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<tr>
<td>Blind Canyon</td>
<td>High Vol. Bit.</td>
<td>80.7</td>
<td>4.63</td>
<td>4.49</td>
</tr>
<tr>
<td>Illinois No. 6</td>
<td>High Vol. Bit.</td>
<td>77.7</td>
<td>7.97</td>
<td>14.25</td>
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<tr>
<td>Wyodak-Anderson</td>
<td>Sub bituminous</td>
<td>75.0</td>
<td>28.09</td>
<td>6.31</td>
</tr>
<tr>
<td>Beulah-Zap</td>
<td>Lignite</td>
<td>72.9</td>
<td>32.24</td>
<td>6.59</td>
</tr>
</tbody>
</table>

The phases of most interest are gaseous and supercritical CO$_2$.

**Carbon Dioxide**

- Critical Temp. = 31°C
- Critical Press. = 7.3 MPa
- Hydrostatic gradient = 0.0097 MPa/meter
- Geothermal Gradient = 1.8°C / 100 meters (Sedimentary Rock)
Traditional Methods: Volumetric/Gravimetric Techniques
Determining the CO₂-coal adsorption isotherm quantitatively

Volumetric Technique

Gravimetric Technique
Traditional Methods: Volumetric/Gravimetric Techniques

**Interlab Comparison I:** dry comparison

*Energy & Fuels* 2004, 18, 1175-1182

**Interlab Comparison II:** moisture-equilibrated comparison

- The research community lacks a standard method for determining carbon dioxide adsorption isotherms
  - Unknown effects of:
    - Different Apparatus
    - Different Procedures
    - Different Operators
- A multi-lab determination of CO$_2$ adsorption isotherms.
- Using the same Argonne Premium Coals
- Using their own apparatus.
  - Under the same conditions: moisture-equilibrated, 55°C, 2000 psia (14 MPa)
# Traditional Methods: Volumetric/Gravimetric Techniques

## Interlab Comparison Participants

<table>
<thead>
<tr>
<th>Name</th>
<th>Organization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gregg Duffy</td>
<td>CSIRO Division of Energy Technology, Australia</td>
</tr>
<tr>
<td>Bernhard Krooss</td>
<td>Aachen Germany</td>
</tr>
<tr>
<td>Chad Hartman</td>
<td>TICORA Geosciences, Inc., Arvada, Colorado</td>
</tr>
<tr>
<td>Slava Romanov</td>
<td>NETL, Pittsburgh, PA</td>
</tr>
</tbody>
</table>
Traditional Methods:
Volumetric/Gravimetric Techniques

Interlab Results

Beulah Zap Coal
55°C / moisture-equilibrated
Traditional Methods: Volumetric/Gravimetric Techniques

Interlab Results

- Beulah Zap Coal
  - 55°C / moisture-equilibrated

% Moisture

Laboratory

- BZ moisture EQ at 55 °C
- BZ As received at 25 °C
Traditional Methods:
Volumetric/Gravimetric Techniques

Compressibility Factor ($Z$)

$$\Delta n_{ex} = \left( \frac{1}{RT_{iso}m_c} \right) \ast \left( V_R \left( \frac{P_{ri}}{Z_{ri}} - \frac{P_{rf}}{Z_{rf}} \right) - V_V \left( \frac{P_{sf}}{Z_{sf}} - \frac{P_{si}}{Z_{si}} \right) \right)$$

$$n_{ex} = \Delta n_{1ex} + \Delta n_{2ex} + \Delta n_{3ex} + \ldots + \Delta n_{nex}$$

- 1) $Z = 1$ (ideal gas law)
- 2) $Z$ value from Air Liquid Gas Encyclopedia, 1976

Beulah Zap 22 °C
Traditional Methods:
Volumetric/Gravimetric Techniques

Adsorbed Layer Density

\[ n_{abs} = \frac{n^{ex}}{1 - \left( \frac{\rho_g}{\rho_a} \right)} \]

<table>
<thead>
<tr>
<th>method</th>
<th>Adsorbed layer density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZGR EOS</td>
<td>0.982</td>
</tr>
<tr>
<td>ONO-Kondo Model</td>
<td>0.996</td>
</tr>
<tr>
<td>VDW</td>
<td>1.03</td>
</tr>
<tr>
<td>Solid density estimate</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Traditional Methods:
Volumetric/Gravimetric Techniques

Coal Changes

• Do not account for changes in the coal caused by CO₂
• Designed for non-swelling materials such as inorganic materials (rocks).
• Coal is an organic and inorganic substance that can undergo structure changes, swelling, and shrinkage upon exposure to CO₂ and other fluids.
Traditional Methods: Volumetric/Gravimetric Techniques

- Magnetic suspension balance (Rubotherm) at Leipzig University, Germany.
- Initial and final sample volumes differ by 20%.
- Single point correction - not based on the changes in coal swelling with changes in CO₂ pressure. (Coal swelling is underestimated)

**Pocahontas #3 Coal**

55°C / Dried

Excess Sorption (mmol/g) vs. Pressure P (MPa)

- Initial Volume
- Final Volume
Traditional Methods: Dilatometry

- Adsorption of CO$_2$ on coal can cause changes in the coal structure.
  - CO$_2$ can cause a loss of permeability through swelling or softening.
  - Dramatic softening of a powdered bituminous coal in the presence of CO$_2$ is shown in the figure at right.
  

Effect of CO$_2$ Pressure on the Softening Temperature of a Bituminous Coal
Traditional Methods: 
Dilatometry

- **High-Pressure Micro-Dilatometer (HPMD)**
  - Identical to device used by Khan and Jenkins.
    - Measurements at Penn State and NETL
  - Refurbished and upgraded temperature control and data acquisition.
  - Test same coal as Khan plus all Argonne premium coal samples.

Schematic from Khan & Jenkins *Fuel* 63, **1984**, p 110

HPMD
Novel Methods: Infrared Spectroscopy
Fundamental Chemistry

- Provide direct evidence of CO$_2$ interaction with coal

**Storage Capacity**
- determine the CO$_2$-coal adsorption isotherm without Z factors and adsorbed layer density values

**Mechanism**
- investigate the nature of the CO$_2$-coal interaction

- Investigate temperatures, pressures, and coal moisture contents relevant to coal seam sequestration
Novel Methods: Infrared Spectroscopy

ATR-FTIR Spectroscopy
(attenuated total reflectance-Fourier transform infrared)

maximum pressure = 10 MPa
maximum temperature = 250°C
Novel Methods: Infrared Spectroscopy
ATR-FTIR adsorption isotherms

Pocahontas #3 (0.5% moisture)
Comparing ATR-FTIR and manometric techniques for CO₂ adsorption on Argonne coals

For the manometric method:

1. Z values calculated from Span and Wagner EOS
2. Adsorbed layer density = 1.03 g/cm³
Novel Methods: Infrared Spectroscopy

CO₂ Sorption Kinetics for Pittsburgh No. 8 Coal

0.35 MPa CO₂ and 55°C
Novel Methods:
Infrared Spectroscopy

CO₂ Sorption Kinetics for Pittsburgh No. 8 Coal

Area of 2333 cm⁻¹ CO₂ IR band vs. time (minutes)

0.35 MPa CO₂ and 55°C
Fickian CO₂ Transport Mechanism

- Fickian Diffusion (rate CO₂ reaches the coal pores)
  - Straight line plot of Mt/M∞ vs. t^{1/2}
- Case II Diffusion (rate determining step is the motion of the coal macromolecules)
  - Straight line plot of Mt/M∞ vs. t

\[ y = 0.85507 + 0.0038194x \quad R = 0.9266 \quad y = 0.86648 + 0.00019275x \quad R = 0.88635 \]
CO₂ is a good plasticizer for many coals

- Exposure to CO₂ changes sequential diffusion rates, solubility, and adsorption isotherms
- Dissolution of organic fluids in coals plasticizes them and enable physical structure changes

- Data obtained using fresh (unexposed to CO₂) coal samples may be irrelevant to CO₂ sequestration because exposure to CO₂ may induce structure changes and the coal may be different before and after the initial CO₂ exposure.
Novel Methods:
Geological Sequestration Core Flow Laboratory (GSCFL)

Central to the GSCFL is the New England Research Inc.,
Modified AutoLab 1500 Core Flow Unit
Novel Methods: GSCFL Activities

- Help determine sequestration suitability of geologic formations
  - Coal seams, depleted gas and oil reservoirs, and brine aquifers
- Contribute to limited database on sequestration technology
- Provide experimental data to verify and validate modeling efforts
  - Porosity and Pore volume compaction
  - Permeability
  - Reservoir integrity – Elastic Moduli – – Poisson’s Ratio and Young’s Modulus
  - Stress/strain relationships & impacts on permeability when CO₂ is injected
    - shrinkage and swelling of coal
  - Petrology measurements – – physical changes and mineralization
 Novel Methods: GSCFL Results

• **Pittsburgh Coal Seam:**
  - 15 cores 1.5" and 2.0" in diameter, 1.0-3.0" long core samples, flow path orientation thru face cleats (horizontal coring) or thru butt cleats (vertical coring)

• **Porosities:**
  - $1.5 \pm 0.25\%$ - no significant porosity differences between horizontal and vertical coring

• **Permeability:**
  - $H_2O$ (15 to 70 $\mu D$) $CO_2$ (0.702 to 0.900 $\mu D$)

• **Radial strain:**
  - $H_2O$ (154 to 254 $\mu \varepsilon$) $CO_2$ (698 to 827 $\mu \varepsilon$)

• **Coal swelling**
  - Permeability decreases with elevated $CO_2$ pressure and with increasing confining pressure
  - 3-fold increase in radial strain with $CO_2$ injection when compared with $H_2O$
Summary

- Developing a fundamental picture of how CO$_2$ interacts with coal
- Observed coal swelling and structure changes upon exposure to CO$_2$
- Additional work is needed to understand CO$_2$-coal interactions at pressures above 7 MPa