Carbon Dioxide Storage in Coal Seams: High-Pressure CO₂-Coal Isotherm Uncertainties

Angela Goodman

Project Partners:
- Oklahoma State University
- TICORA Geosciences
- CSIRO, Australia
- University of British Columbia, Canada
- Aachen University, Germany

Sixth Annual Conference on Carbon Capture and Sequestration
Sheraton Station Square May 7-10, 2007, Pittsburgh PA

Why Isotherm Measurements are Important?

- Measurement of CO₂ adsorption on coal produces an isotherm that gives the gas storage capacity as a function of pressure. Important for carbon sequestration storage estimates
- The research community lacks a standard method for determining carbon dioxide adsorption isotherms
  - Unknown affects of:
    - Different Apparatus
    - (manometric, volumetric, and gravimetric)
    - Different Procedures
    - Different Operators

How reproducible are these measurements?

Inter-laboratory comparison of CO₂ sorption on moisture-equilibrated Argonne premium coal

- Six participants
- Coal samples (three) from Argonne Premium Coal Sample Program
- Same procedure followed by each group
- Isotherms collected with each lab’s experimental apparatus

MAIN Goal
- Determine the reproducibility of CO₂ sorption isotherms

MAIN Conclusion
- At CO₂ pressures above 8 MPa, sorption isotherms diverged significantly

Inter-laboratory Partners

<table>
<thead>
<tr>
<th>Participants</th>
<th>Affiliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. Duffy, R. Sakurovs, S. Day</td>
<td>CSIRO Australia</td>
</tr>
<tr>
<td>B.M. Krooss, A. Busch, Y. Gensterblum</td>
<td>Aachen University, Germany</td>
</tr>
<tr>
<td>K.A.M. Gasem, R. L. Robinson, J.E. Fitzgerald, C. Jing, S. Mohammed</td>
<td>Oklahoma State University, OK</td>
</tr>
<tr>
<td>T. Pratt, C. Hartman</td>
<td>TICORA Geosciences, Colorado</td>
</tr>
<tr>
<td>M. Bustin, L. Chikatamarla</td>
<td>University of British Columbia</td>
</tr>
<tr>
<td>Slava Romanov, K. Schroeder, C. White</td>
<td>U.S. DOE-NETL, USA</td>
</tr>
</tbody>
</table>

Argonne Premium Coal Samples

<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 #3</td>
<td>Low Vol. Bit.</td>
<td>91.1</td>
<td>0.65</td>
<td>4.74</td>
</tr>
<tr>
<td>Illinois #6</td>
<td>High Vol. Bit.</td>
<td>77.7</td>
<td>7.97</td>
<td>14.25</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>

Moisture-Equilibration Procedure

- Modifications
  - Moisture equilibrated at 55°C
  - Handled coals under nitrogen environment
- Pocahontas No. 3 and Illinois No. 6 were equilibrated for 72 hours and Beulah Zap was equilibrated for 48 hours.
- Exception: lab 6 used Beulah Zap and Pocahontas No. 3 as-received from the Argonne coal bank

http://www.anl.gov/PCS/pcshome.html
Moisture-Equilibrated Coals

Moisture-Equilibration Results

- Moisture contents of the coal samples varied significantly among the labs and from the as-received moisture contents of the as-received Argonne samples.
- Small modifications of the ASTM procedure has an unexpectedly large effect on the interlaboratory reproducibility for the coal moisture – equilibration content.

CO₂-Coal Isotherm Procedure

- Used their own apparatus
  - manometric (four labs), volumetric (one lab), and gravimetric (one lab).
- Same conditions:
  - moisture-equilibrated coals
  - 55°C
  - 2000 psia (14 MPa)

Equipment to Measure Sorption Isotherms

Manometric Technique

Gravimetric Technique

- R: reservoir chamber, S: sample chamber, P: pressure transducer, I: syringe pump, V: vacuum pump, T: thermocouples B: constant temperature bath.
Differentiating Between the Reference Volume, Sample Volume, and Void Volume

reference volume: \( V_{\text{reference}} \)

sample cell volume: \( V_{\text{void}} = V_{\text{sample cell}} - V_{\text{sample}} \)

Excess Sorption Isotherms

Excess Sorption Isotherms

<table>
<thead>
<tr>
<th>LAB 1</th>
<th>LAB 2</th>
<th>LAB 3</th>
<th>LAB 4</th>
<th>LAB 5</th>
<th>LAB 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal/Mass (g)</td>
<td>110-150</td>
<td>2.1 - 2.7</td>
<td>111.74</td>
<td>79.17</td>
<td>3.73</td>
</tr>
<tr>
<td>Expiration</td>
<td>2 hours</td>
<td>30 min</td>
<td>6 hours</td>
<td>60 min</td>
<td>6-12 hours</td>
</tr>
</tbody>
</table>

Excess Sorption Isotherms

Excess Sorption Isotherms
CO₂-Coal Isotherm Results

- Isotherm measurements up to 15 MPa
  - Agreement between the labs are in fair agreement with the exceptions of labs 2 and 4
  - No obvious explanation for labs 2 and 4
- Manometric design, sample mass, cell volumes, moisture content
- Isotherm measurements below 8 MPa
  - Minor exceptions: labs 3 and 4 for Pocahontas No. 3 and lab 2 for Illinois No. 6

Calculating the Amount of CO₂ Adsorbed (\(n^{ex} = \text{Gibbs Excess Adsorption}\))

\[
\Delta n^{ex} = \frac{PV}{nRTZ} - \frac{1}{RTm} \left( \frac{P_{i}}{Z_{i}} - \frac{P_{f}}{Z_{f}} \right) - \frac{1}{RTm} \left( \frac{P_{s}}{Z_{s}} - \frac{P_{f}}{Z_{f}} \right) - \frac{1}{RTm} \left( \frac{P_{s}}{Z_{s}} - \frac{P_{f}}{Z_{f}} \right)
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)</td>
<td>Mass of coal, g</td>
</tr>
<tr>
<td>(T_{iso})</td>
<td>Isothermal temperature, K</td>
</tr>
<tr>
<td>(n)</td>
<td>Number of moles of gas</td>
</tr>
<tr>
<td>(V)</td>
<td>Reference cell volume, cm³</td>
</tr>
<tr>
<td>(P_{i})</td>
<td>Initial reference cell pressure, MPa</td>
</tr>
<tr>
<td>(P_{f})</td>
<td>Final reference cell pressure, MPa</td>
</tr>
<tr>
<td>(Z_{i})</td>
<td>Initial reference real gas compressibility factor, dimensionless</td>
</tr>
<tr>
<td>(Z_{f})</td>
<td>Final reference real gas compressibility factor, dimensionless</td>
</tr>
<tr>
<td>(P_{s})</td>
<td>Initial sample cell pressure, MPa</td>
</tr>
<tr>
<td>(Z_{s})</td>
<td>Initial sample real gas compressibility factor, dimensionless</td>
</tr>
<tr>
<td>(P_{f})</td>
<td>Final sample cell pressure, MPa</td>
</tr>
<tr>
<td>(Z_{f})</td>
<td>Final sample real gas compressibility factor, dimensionless</td>
</tr>
</tbody>
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Excess Sorption Isotherms

Technical Challenges Excess Sorption: Compressibility Factor (Z)

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

Technical Challenges Excess Sorption: Void Volume

Possible Changes in Void Volume During Isotherm Measurement

- 15% decrease
- 5% increase
- 10% decrease
- 5% increase
- 15% increase
- 5% decrease
- 10% increase
- 5% decrease
Problems with sorption of CO₂ on coal

- CO₂ dissolves in coal and water (Larsen 2004, Duan 2003)
- CO₂ alters the coal chemically (Burruss 2006)
- CO₂ causes coal physical structure rearrangement (Karacan 2003, Goodman 2006)
- CO₂ shrinks coal (Ozdemir 2003)

Currently – a fundamental model that describes sorption behavior in the supercritical region is still missing (Siemons and Busch 2006)

The Adsorption Isotherms Appear to Be Combinations of a Surface Adsorption Term and a Constant Term

\[ n_{\text{ads}} = n_{\text{Dubinin–Astakov}} \]

The Adsorption Isotherms

Conclusions: Inter-laboratory comparison of CO₂ adsorption isotherms

- Provided first inter-laboratory comparison for CO₂ sorption on moisture-equilibrated coals
  - 4 out of 6 labs agree within 30%
  - Above 8 MPa, sorption isotherms deviate significantly
- Further studies are needed to address deviations and experimental problems for high-pressure CO₂ sorption