Carbon Dioxide Storage in Coal Seams: High-Pressure CO_2-Coal Isotherm Uncertainties

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Why Isotherm Measurements are Important?

- **Measurement of CO_2 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?

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Inter-laboratory comparison of CO_2 sorption on moisture-equilbrated 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 CO_2 sorption isotherms

- **MAIN Conclusion**
  - At CO_2 pressures above 8 MPa, sorption isotherms diverged significantly

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Inter-laboratory Partners

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

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Argonne Premium Coal Samples

Coal (100 mesh)	Rank	%C MAF	% Moisture	% Ash
Pocahontas #3	Low Vol. Bit.	91.1	0.65	4.74
Illinois #6	High Vol. Bit.	77.7	7.97	14.25
Beulah-Zap	Lignite	72.9	32.24	6.59

http://www.anl.gov/PCS/pcshome.html

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Moisture-Equilibration Procedure

- **ASTM procedure D 1412-99 " Standard Test Method for Equlibrium Moisture of Coal at 96-97 Percent Relative Humidity"**
- **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**

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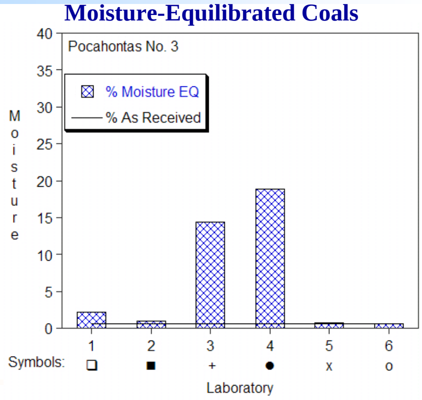
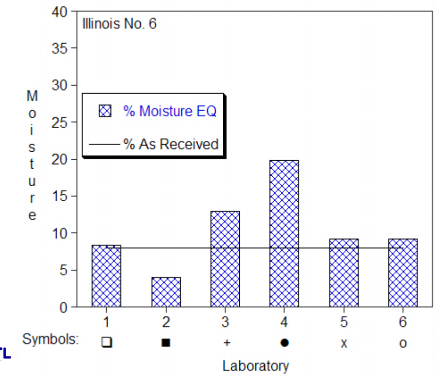
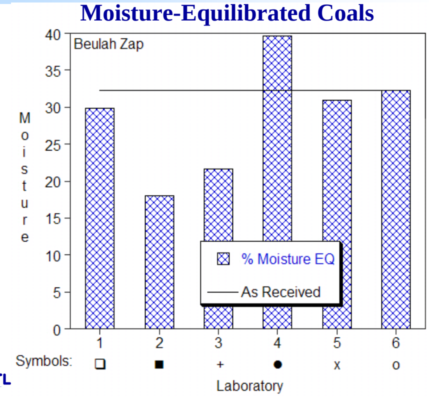
Moisture-Equilibrated Coals



Moisture-Equilibrated Coals



Moisture-Equilibrated Coals



Moisture-Equilibration Results

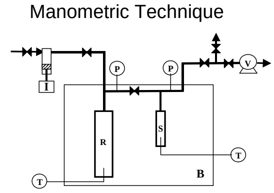
- Moisture contents of the coal samples varied significantly among the labs and from the as-received moisture contents of the as-received Argonne samples.
- Small modifications of the ASTM procedure has an unexpectedly large effect on the inter-laboratory reproducibility for the coal moisture – equilibration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

CO_2-Coal Isotherm Procedure

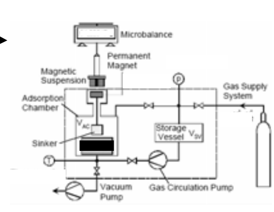
- Used their own apparatus
  - **manometric (four labs), volumetric (one lab), and gravimetric (one lab).**
- Same conditions:
  - **moisture-equilibrated coals**
  - **55°C**
  - **2000 psia (14 MPa)**

Equipment to Measure Sorption Isotherms

Manometric Technique



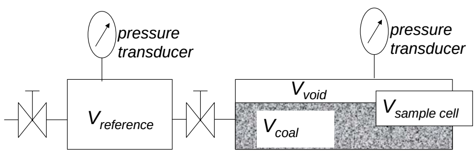
Gravimetric Technique



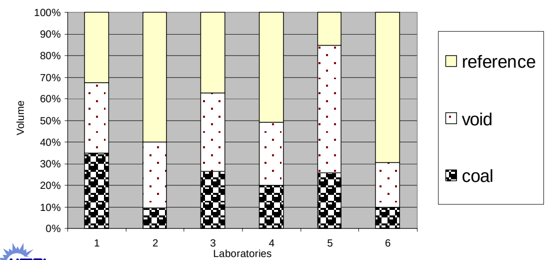
- **R: reservoir chamber, S: sample chamber, P: pressure transducer, I: syringe pump, V: vacuum pump T: thermocouples B: constant temperature bath**

Differentiating Between the Reference Volume, Sample Volume, and Void Volume

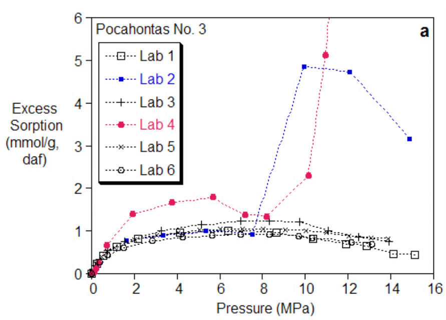
reference volume: ***Vreference***
sample cell volume: ***Vvoid = Vsample cell - Vsample***



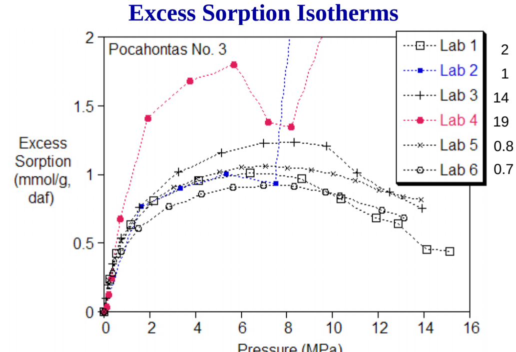
	LAB 1	LAB 2	LAB 3	LAB 4	LAB 5	LAB 6
Coal Mass (g)	110-150	2.1 – 2.7	111.741	79.17	3.73	60.8 – 74.6
Equilibration Time	> 2hours	30 min	6 hours	4-12 hours	60 min	6-12 hours



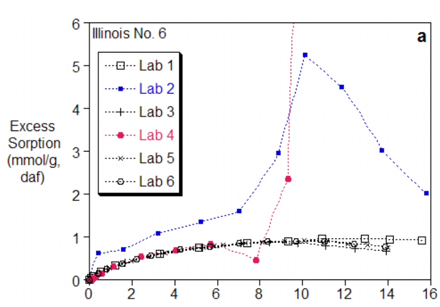
Excess Sorption Isotherms



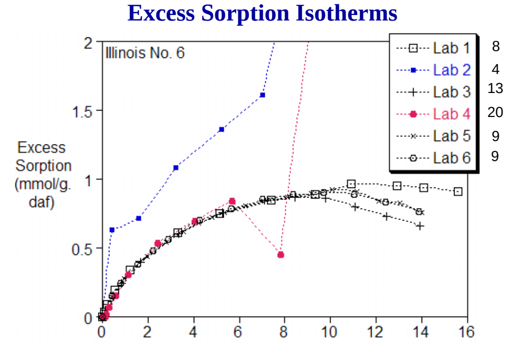
Excess Sorption Isotherms



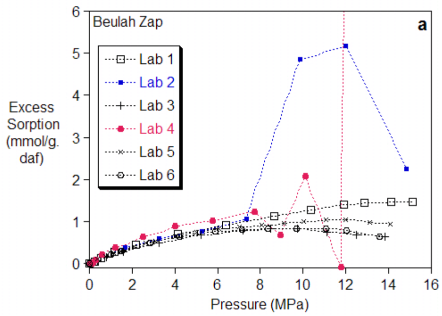
Excess Sorption Isotherms



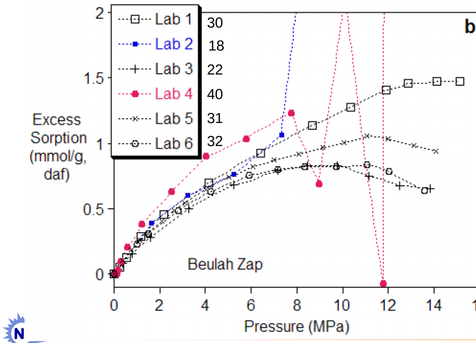
Excess Sorption Isotherms



Excess Sorption Isotherms



Excess Sorption Isotherms



CO_2-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 CO_2 Adsorbed (n^{ex} = Gibbs Excess Adsorption)

$$PV = nRTz$$

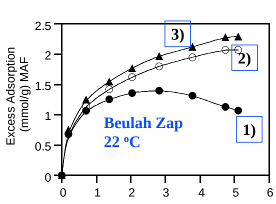
$$\Delta n^{ex} = \left(\frac{1}{RT_{iso}m_c}\right) * \left(V_R\left(\frac{P_{ri}}{z_{ri}} - \frac{P_{rf}}{z_{rf}}\right) - V_V\left(\frac{P_{sf}}{z_{sf}} - \frac{P_{si}}{z_{si}}\right)\right)$$

$$n^{ex} = \Delta n_1^{ex} + \Delta n_2^{ex} + \Delta n_3^{ex} + \ldots + \Delta n_i^{ex}$$

m_c	Mass of coal, g	T_{iso}	Isothermal temperature, K
n	Number of moles of gas	V_R	Reference cell volume, cm^3
Pr_i	Initial reference cell pressure, MPa	V_V	Void volume, cm^3
Pr_f	Final reference cell pressure, MPa	zr_i	Initial reference real gas compressibility factor[3], dimensionless
Ps_i	Initial sample cell pressure, MPa	zr_f	Final reference real gas compressibility factor[3], dimensionless
Ps_f	Final sample cell pressure, MPa	zs_i	Initial sample real gas compressibility factor[3], dimensionless
R	Molar gas constant, 8.314510 J K^{-1}	zs_f	Final sample real gas compressibility factor[3], dimensionless

Technical Challenges
Excess Sorption: Compressibility Factor (Z)

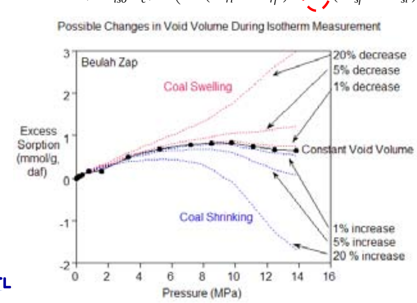
$$\Delta n^{ex} = \left(\frac{1}{RT_{iso}m_c}\right) * \left(V_R\left(\frac{P_{ri}}{Z_{ri}} - \frac{P_{rf}}{Z_{rf}}\right) - V_V\left(\frac{P_{sf}}{Z_{sf}} - \frac{P_{si}}{Z_{si}}\right)\right)$$



- 1) Z = 1 (ideal gas law)
- 2) Z value from Air Liquid Gas Encyclopedia, 1976
- 3) R. Span, W. Wagner, *J. Phys. Chem. Ref. Data* **25**, 6, **1996**

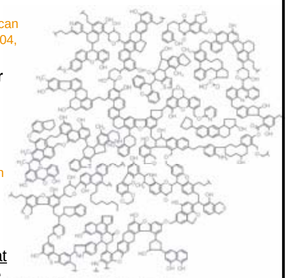
Technical Challenges Excess Sorption: Void Volume

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



Problems with sorption of CO_2 on coal

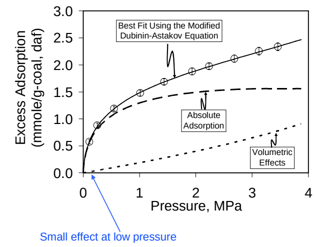
- **CO_2 swells coal** (Larsen, 2004, Karacan 2003, Laximinarayana 2004, Harpalani 2004, Reucroft 1987, 1986)
- **CO_2 dissolves in coal and water** (Larsen 2004, Duan 2003)
- **CO_2 alters the coal chemically** (Burruss 2006)
- **CO_2 causes coal physical structure rearrangement** (Karacan 2003, Goodman 2006)
- **CO_2 shrinks coal** (Ozdemir 2003)



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

Isotherm Model

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



$$n^{ex} = \left(1 - \rho/\rho^{a}\right) n^{abs} + \rho \Delta V$$

n^{ads} = Dubinin – Astakov

$$n^{abs} = n_o e^{-\left[K \ln\left(P_s/P\right)\right]^{t}}$$

"Importance of Volume Effects to Adsorption Isotherms of Carbon Dioxide on Coals"
Ozdemir,Ekrem; Morsi,Badie I.; Schroeder,Karl
***Langmuir* 19, 9764-9773 (2003)**

Conclusions: Inter-laboratory comparison of CO_2 adsorption isotherms Inter-laboratory

- Provided first inter-laboratory comparison for CO_2 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 CO_2 sorption**

- **A. L. Goodman, A. Busch, M. Bustin, L. Chikatamarla, S. Day, G. J. Duffy, J.E. Fitzgerald, K.A.M. Gasem, Y Gensterblum, C. Hartman, B.M. Krooss, Z. Pan, T. Pratt, R. L. Robinson, Jr., V. Romanov, R. Sakurovs, K. Schroeder, M. Sudibandriyo, C. M. White "Inter-laboratory Comparison II: CO2 Isotherms Measured on Moisture-Equilibrated Argonne Premium Coals at 55oC and 15 MPa" published online at www.sciencedirect.com**