

# "Inter-laboratory reproducibility of CO<sub>2</sub> adsorption isotherms measured for the Argonne premium coal samples



*Coal-Seq II - Second  
International Forum on  
Geologic Sequestration of CO<sub>2</sub>  
in Deep, Unmineable Coal  
Seams*

*March 6-7, 2003  
Washington, D.C.*

Angela Goodman  
National Energy Technology Laboratory



---

## Why Isotherm Measurements are Important

- Measurement of CO<sub>2</sub> adsorption on coal produces an isotherm that gives the gas storage capacity (volume) as a function of pressure
- Important for carbon sequestration storage estimates
- Gas storage capacity is a function of pressure, temperature, coal rank, and coal moisture content.

*How reproducible are these measurements?*



# Inter-laboratory Project Progress Report

- Five participants (four sets of data analyzed)
- Coal samples (five) from Argonne Premium Coal Sample Program
- Same procedure followed by each group
- Isotherms collected with each lab's experimental apparatus

- **MAIN Goals**

- Determine the reproducibility of CO<sub>2</sub> adsorption isotherms
- Develop a standard method for measuring CO<sub>2</sub>/coal adsorption isotherms

- **MAIN Conclusion**

- Interlab reproducibility is rank dependent - may be related to moisture content



# Participants in Inter-laboratory Comparison

<b>PARTICIPANTS</b>	<b>AFFILIATION</b>
<b>Greg Duffy</b> <b>John Levy</b>	<b>Energy Technology, Australia</b> <b>CSIRO Division of Energy Technology, Australia</b>
<b>Khaled A.M. Gasem</b> <b>Robert. L. Robinson, Jr.</b>	<b>Oklahoma State University</b>
<b>Chad Hartman</b> <b>Matt Mavor</b> <b>Tim Pratt</b>	<b>TICORA Geosciences, Inc., Arvada, Colorado</b>
<b>Bernhard Krooss</b> <b>Frank van Bergen</b>	<b>Aachen University, Germany</b> <b>Department of Geo-Energy, The Netherlands</b>
<b>Ekrem Ozdemir</b> <b>Karl Schroeder</b> <b>Curt White</b>	<b>U.S. DOE-NETL</b> <b>University of Pittsburgh</b>

**Many thanks to all participants' hard work  
and dedication to this project**



## Argonne Premium Coal Samples Studied

<b>Coal (100 mesh)</b>	<b>Rank</b>	<b>%C MAF</b>	<b>% Moisture</b>	<b>% Ash</b>
<b>Pocahontas #3</b>	<b>Low Vol. Bit.</b>	<b>91.1</b>	<b>0.65</b>	<b>4.74</b>
<b>Upper Freeport</b>	<b>Med. Vol. Bit.</b>	<b>85.5</b>	<b>1.13</b>	<b>13.03</b>
<b>Illinois #6</b>	<b>High Vol. Bit.</b>	<b>77.7</b>	<b>7.97</b>	<b>14.25</b>
<b>Wyodak-Anderson</b>	<b>Sub bituminous</b>	<b>75.0</b>	<b>28.09</b>	<b>6.31</b>
<b>Beulah-Zap</b>	<b>Lignite</b>	<b>72.9</b>	<b>32.24</b>	<b>6.59</b>



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

---

# Argonne Premium Coal Samples are Homogeneous

- The Premium Coal Sample Program is intended to provide the basic coal research community with the highest quality samples of a limited number (8) of coals for basic research.
- The premium coal samples produced from each coal and distributed through this program are chemically and physically as identical as possible, have well-characterized chemical and physical properties, and will be stable over long periods of time.
- One of the reasons for preparing these samples was to permit workers to determine if the apparent difference in results between two laboratories was due to the samples or the experimental technique.

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



---

# The Importance of Generating Good Experimental Protocols

- For any laboratory procedure, strict control upon the experimental methodology is required in order to obtain accurate, reproducible data
- At the present time, no standard procedures for CO<sub>2</sub> sorption isotherm measurements on coal are available
- Procedures followed by commercial and research laboratories may vary

Mavor, M. J.; Owen, L.B.; Pratt, T. J. "Measurement and Evaluation of Coal Sorption Isotherm Data" *SPE 20728*, 1990, 157-170.

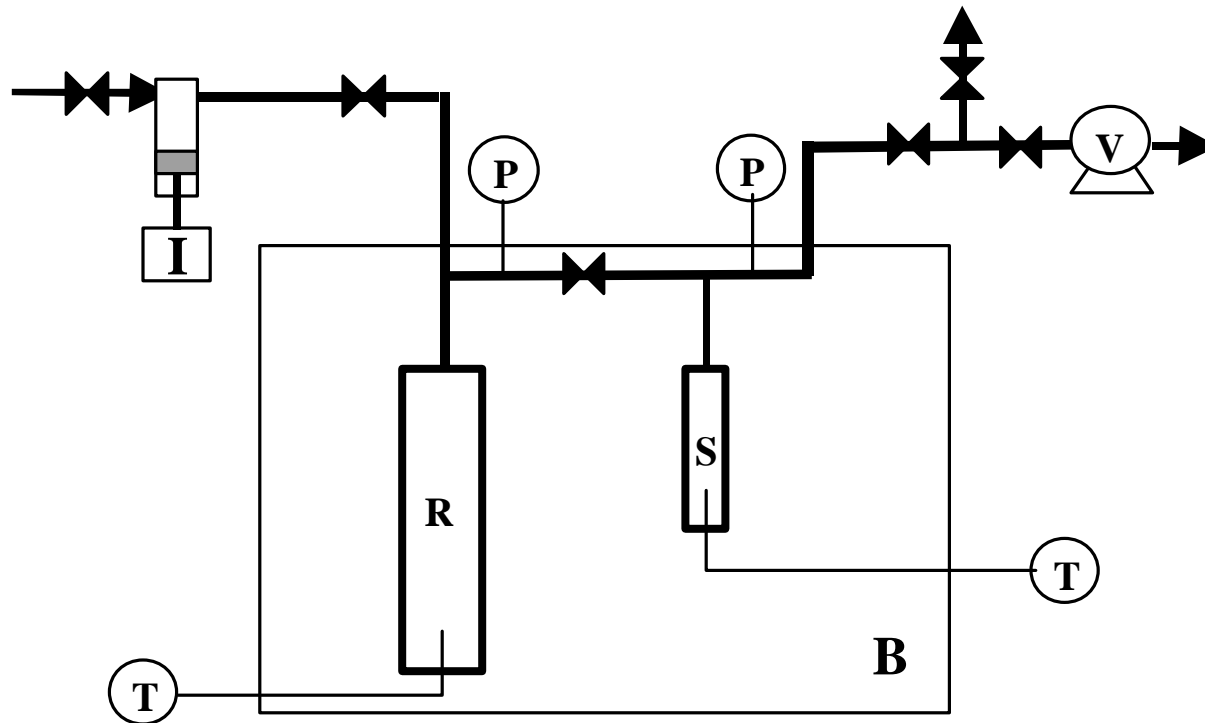


## **Isotherm Procedure Given to Each Lab**

- **Each group measured the CO<sub>2</sub> adsorption and desorption isotherm one time on five different Argonne coals with their own apparatus (5 total isotherms). Coal samples were handled under an inert environment using either nitrogen or helium.**
- **Before measuring isotherms, each coal sample was dried under vacuum for 36 hours at 80°C.**
- **The adsorption experiments were carried out at 22°C (3 labs) and 55°C (2 labs).**
- **Pressures ranged between 0 and 600 Psia at 25°C and 0 to 2000 psia at 55°C.**



# Typical Design of a Volumetric Apparatus to Measure Adsorption Isotherms



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

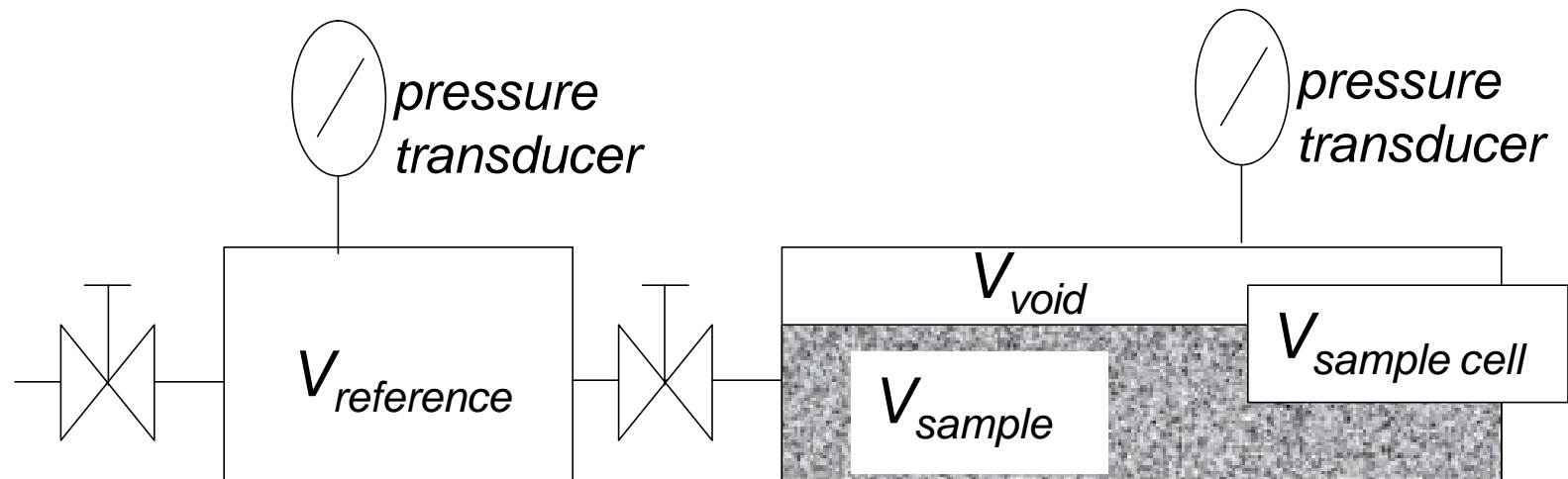
# Differentiating Between the Reference Volume, Sample Volume, and Void Volume

reference volume:

$V_{reference}$

sample cell volume:

$V_{sample\ cell} = V_{sample} + V_{void}$



# Calculating the Amount of CO<sub>2</sub> Adsorbed (n<sup>ex</sup> = Gibbs Excess Adsorption)

$$PV = nRTZ$$

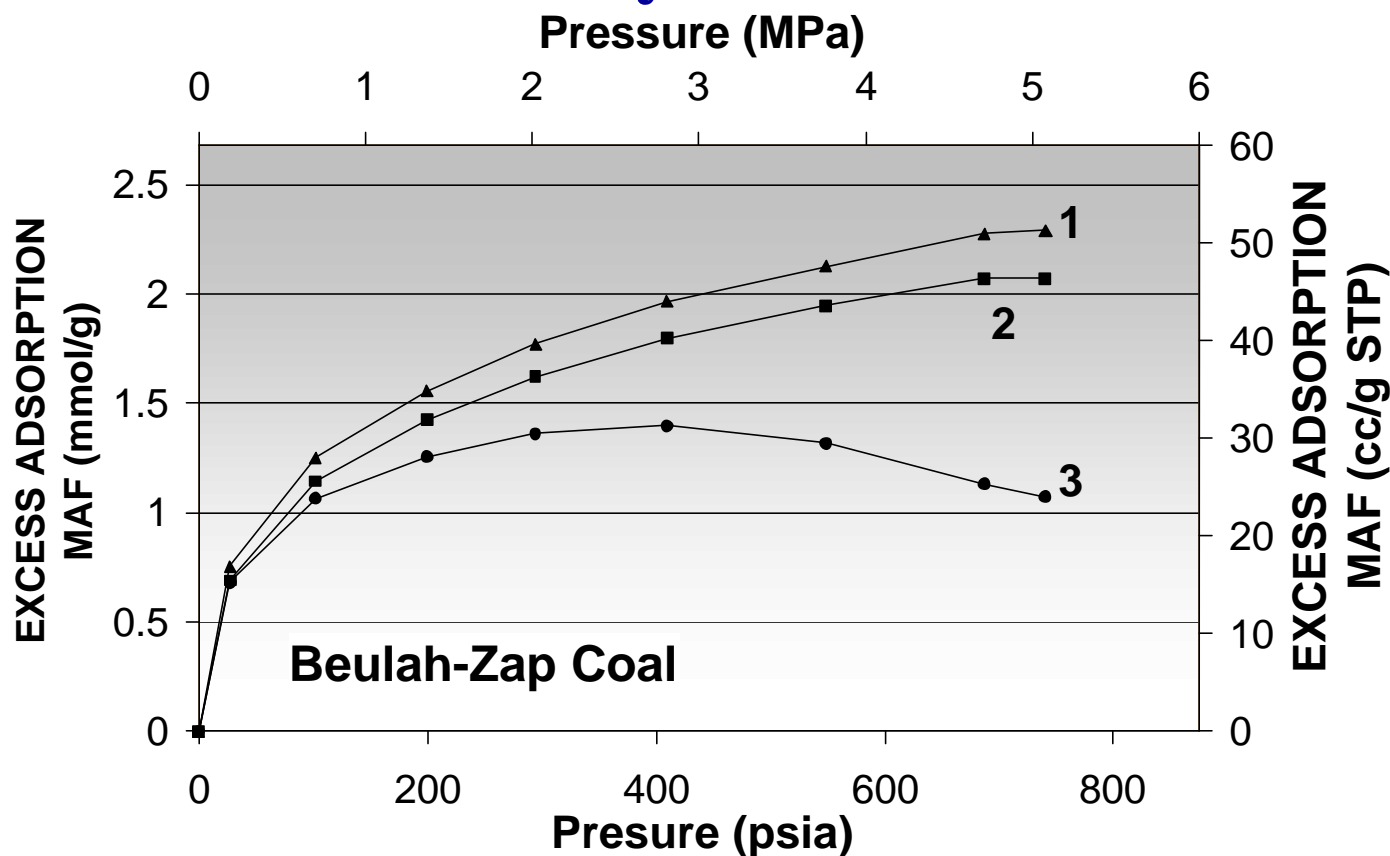
$$\Delta n^{ex} = \left( \frac{1}{RT_{iso} m_c} \right) * \left( V_R \left( \frac{P_{ri}}{Z_{ri}} - \frac{P_{rf}}{Z_{rf}} \right) - V_V \left( \frac{P_{sf}}{Z_{sf}} - \frac{P_{si}}{Z_{si}} \right) \right)$$

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

m <sub>c</sub>	Mass of coal, g	T <sub>iso</sub>	Isothermal temperature, K
n	Number of moles of gas	V <sub>R</sub>	Reference cell volume, cm <sup>3</sup>
P <sub>ri</sub>	Initial reference cell pressure, MPa	V <sub>V</sub>	Void volume, cm <sup>3</sup>
P <sub>rf</sub>	Final reference cell pressure, MPa	Z <sub>ri</sub>	Initial reference real gas compressibility factor <sup>3</sup> , dimensionless
P <sub>si</sub>	Initial sample cell pressure, MPa	Z <sub>rf</sub>	Final reference real gas compressibility factor <sup>3</sup> , dimensionless
P <sub>sf</sub>	Final sample cell pressure, MPa	Z <sub>si</sub>	Initial sample real gas compressibility factor <sup>3</sup> , dimensionless
R	Molar gas constant, 8.314510 J K <sup>-1</sup>	Z <sub>sf</sub>	Final sample real gas compressibility factor <sup>3</sup> , dimensionless



# Z Compressibility Factors can Contribute to Variability in the Data



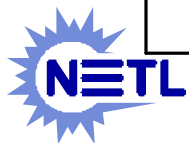
- 1) R. Span, W. Wagner, *J. Phys. Chem. Ref. Data* **25**, 6, 1996
- 2) Z value from Air Liquid Gas Encyclopedia, 1976
- 3) Z = 1 (ideal gas law)



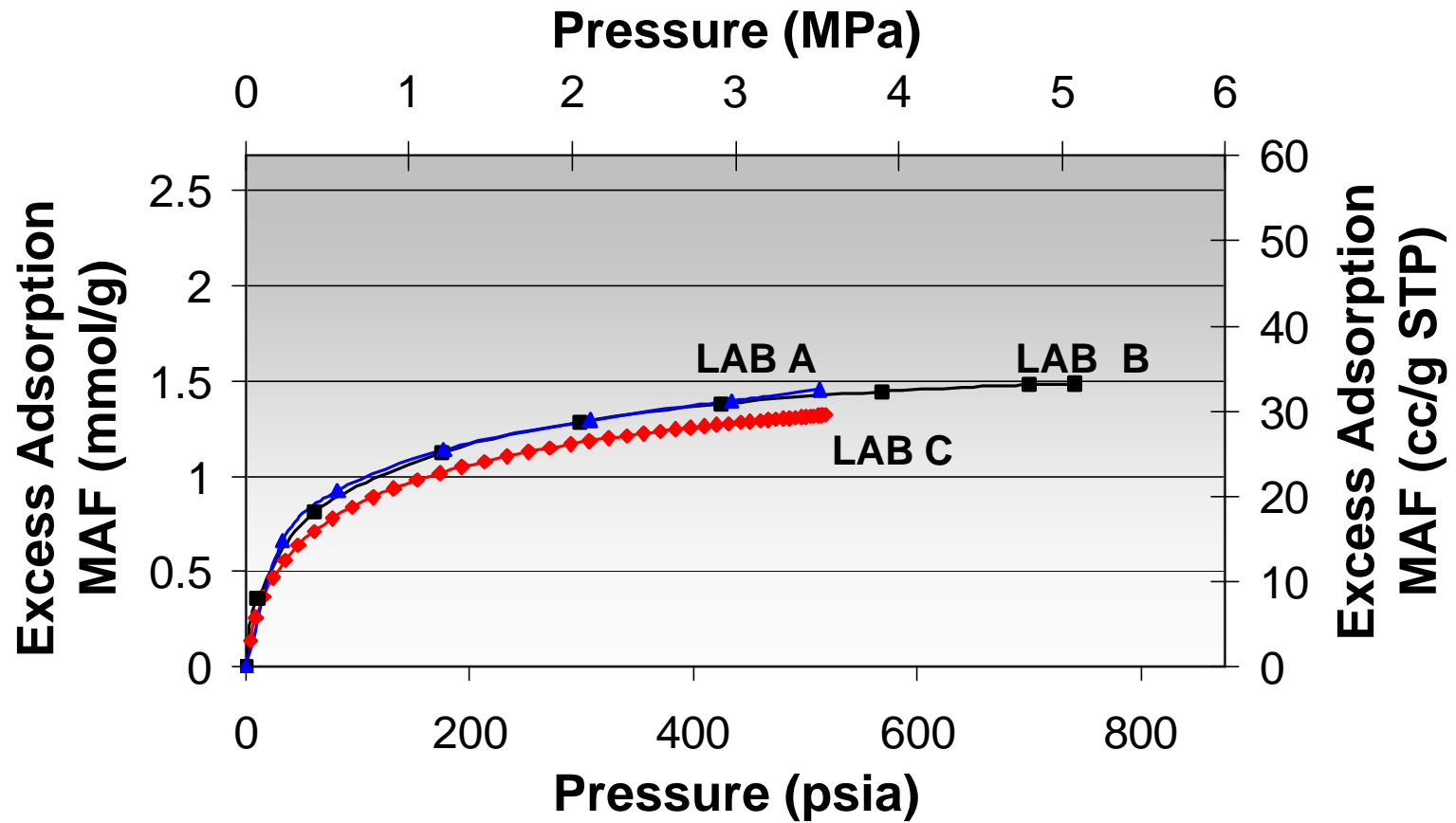
# Compilation of Experimental Parameters

Participant	Maximum CO <sub>2</sub> pressure (MPa)	Temperature (°C)	sample weight range (g)	Volume of sample cell (cm <sup>3</sup> )	Volume of reference cell (cm <sup>3</sup> )
<b>A</b>	3.6 +/- 0.1	22 +/-0.1	1.1 - 1.5	7.2 +/- 0.2	11.7 +/- 0.2
<b>B</b>	5.131 +/- 0.001	22 +/-0.02	89.7 - 111.7	150.00 +/- 0.01	320.30 +/- 0.01
<b>C</b>	4.700 +/- 0.008	22 +/-0.1	5.0 - 6.7	9.230 +/- 0.006	1.67 +/- 0.01
<b>D</b>	8.300 +/- 0.007	55 +/-0.1	54.5-64.7	110.0 +/- 0.3	250 +/- 0.01

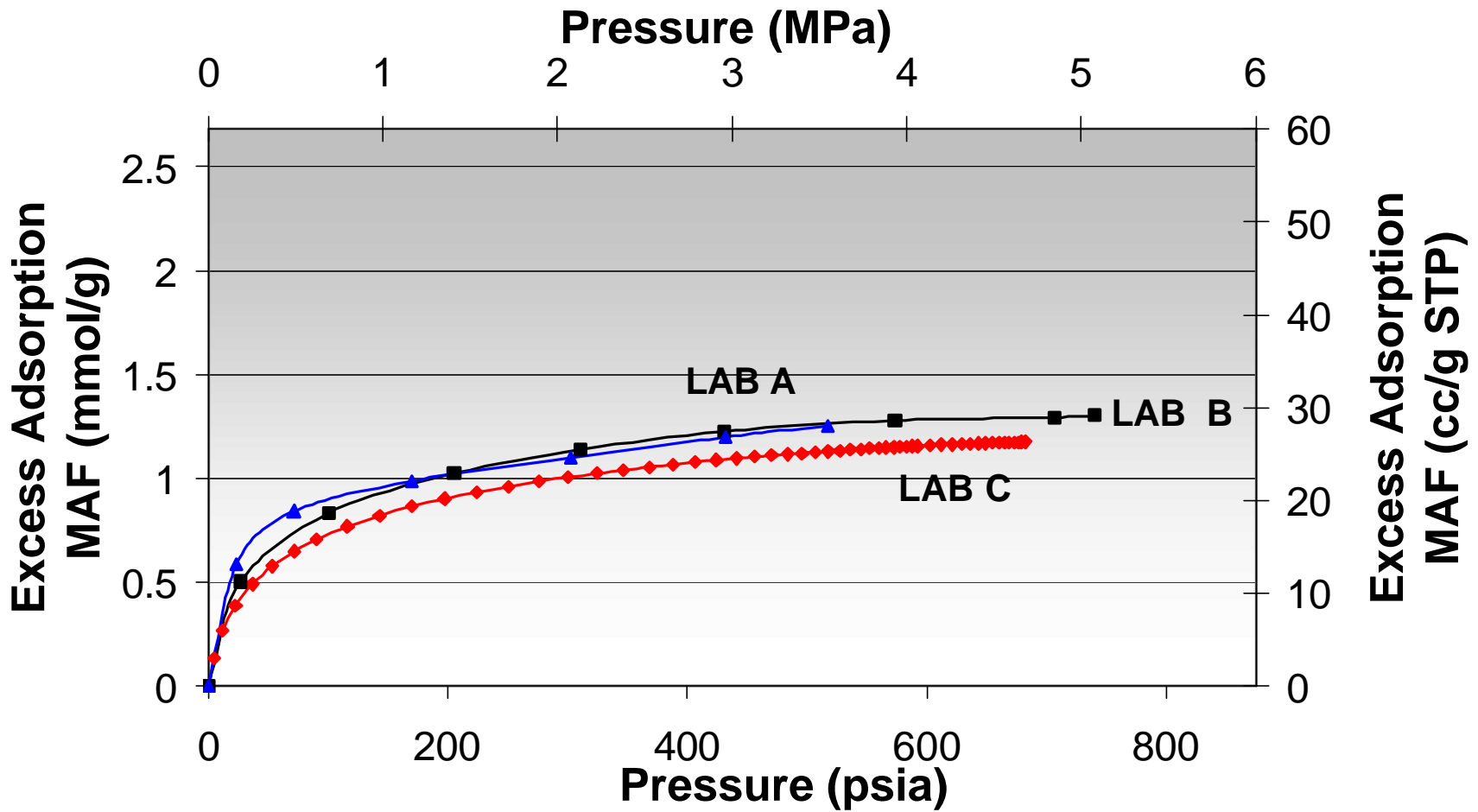
Participant	Average Void Volume (cm <sup>3</sup> )	Equilibration Time (minutes)	DATA COLLECTION	CO <sub>2</sub> Purity
<b>A</b>	6.6	30	MANUAL	99.999%
<b>B</b>	93.6	80	AUTOMATED	99.95%
<b>C</b>	4.9	30	AUTOMATED	99.995%
<b>D</b>	75	6-12 hours	SEMI-AUTOMATED	99.99%



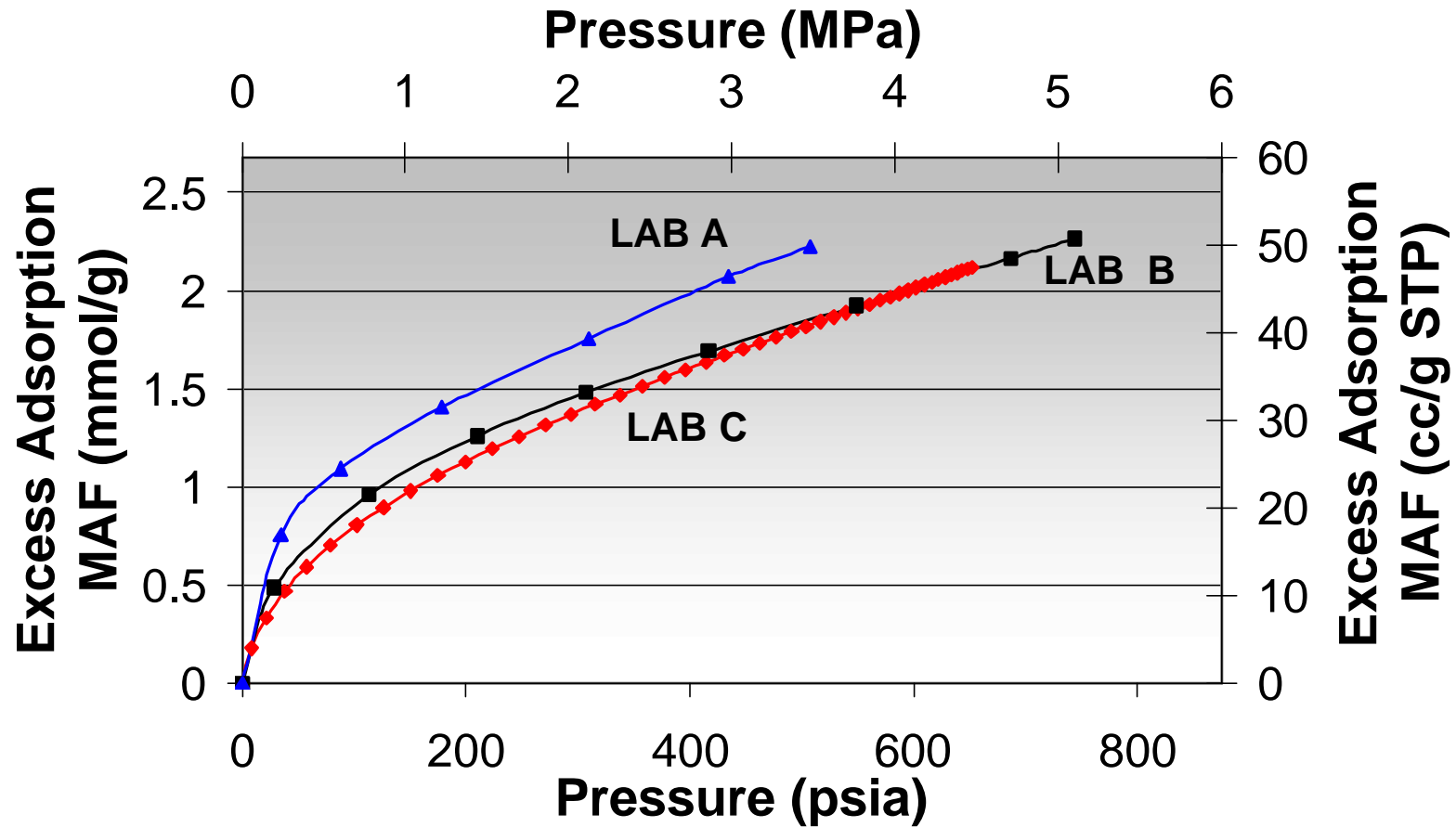
## Pocahontas #3 Coal (91.1% C) at 22°C



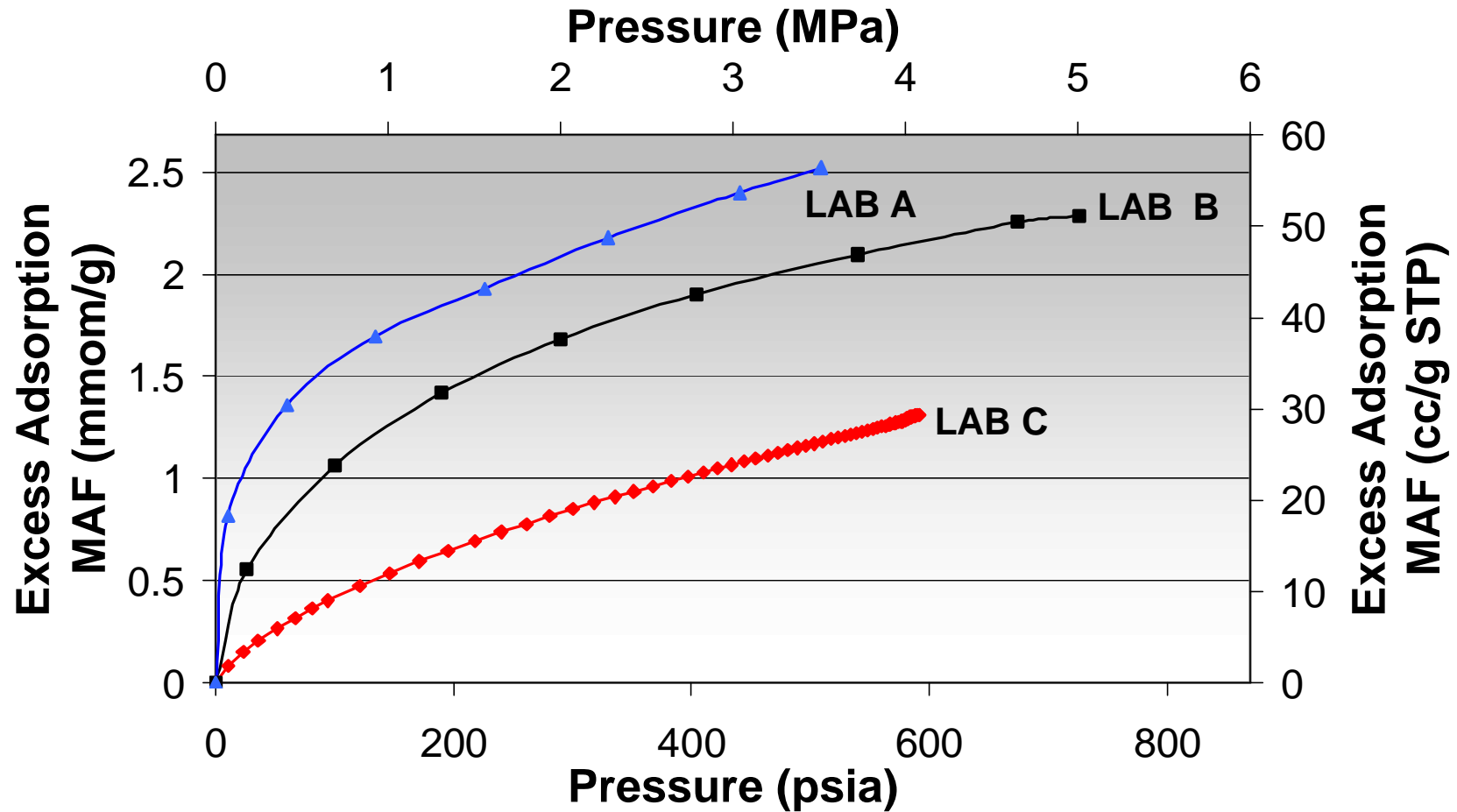
# Upper Freeport Coal (85.5% C) at 22°C



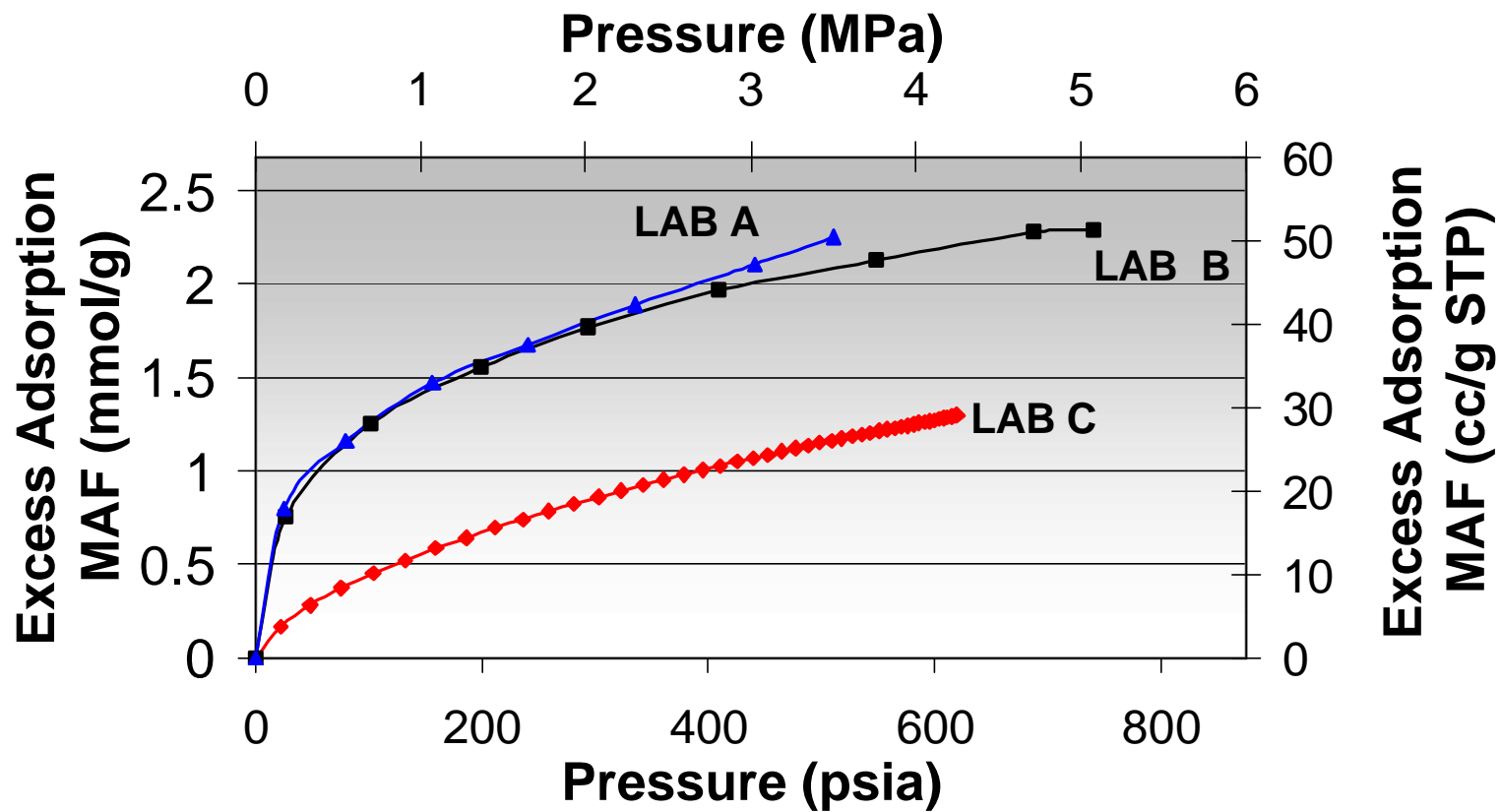
## Illinois #6 Coal (77.7% C) at 22°C



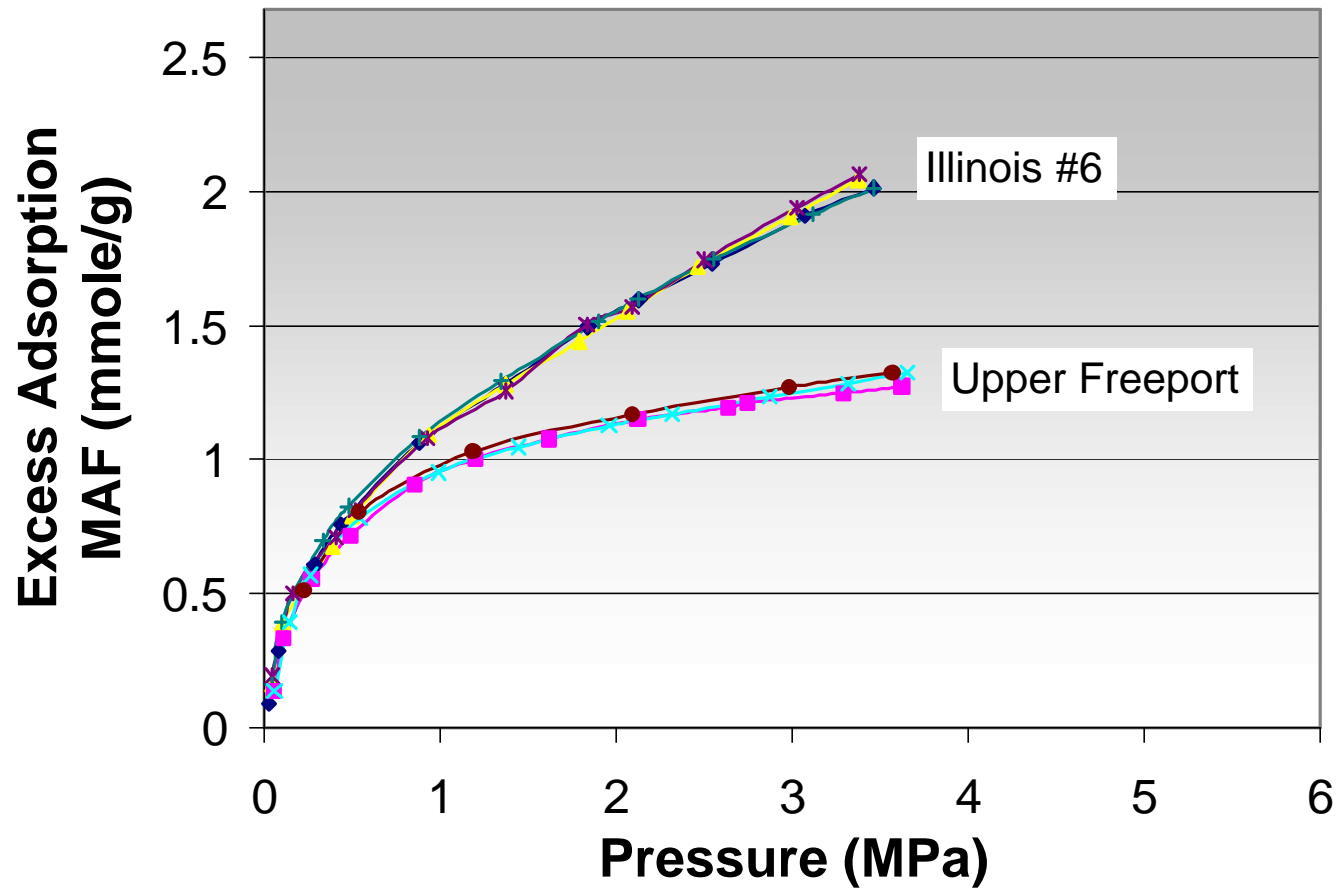
## Wyodak Coal (75% C) at 22°C



## Beulah-Zap Coal (72.9% C) at 22°C

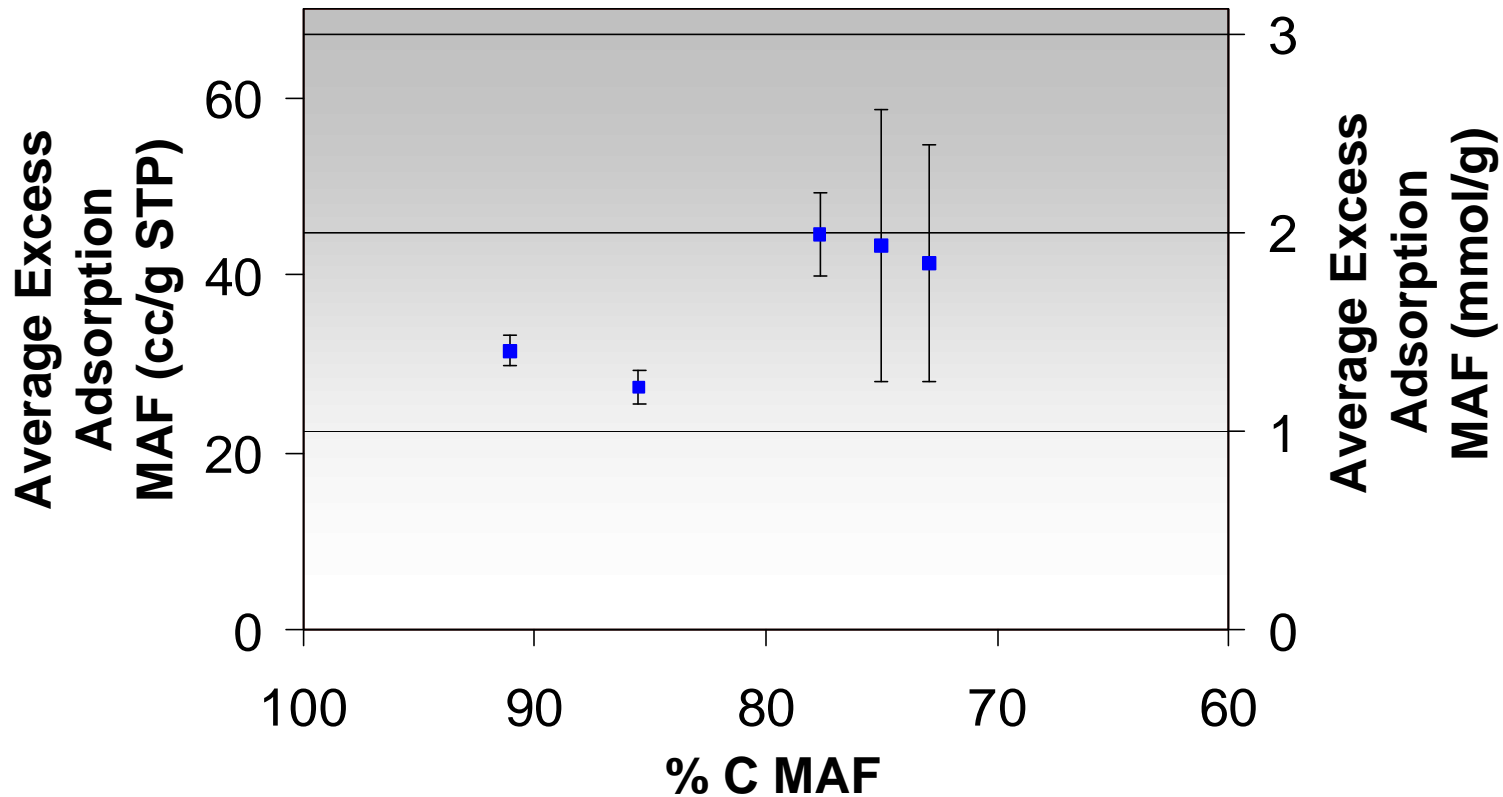


## Intra-laboratory Reproducibility for Lab A at 22°C



# The Data Vary More for Low Rank Coals

CO<sub>2</sub> Adsorption Capacity versus Carbon Content  
at 3.5 MPa (508 psia), 22°C

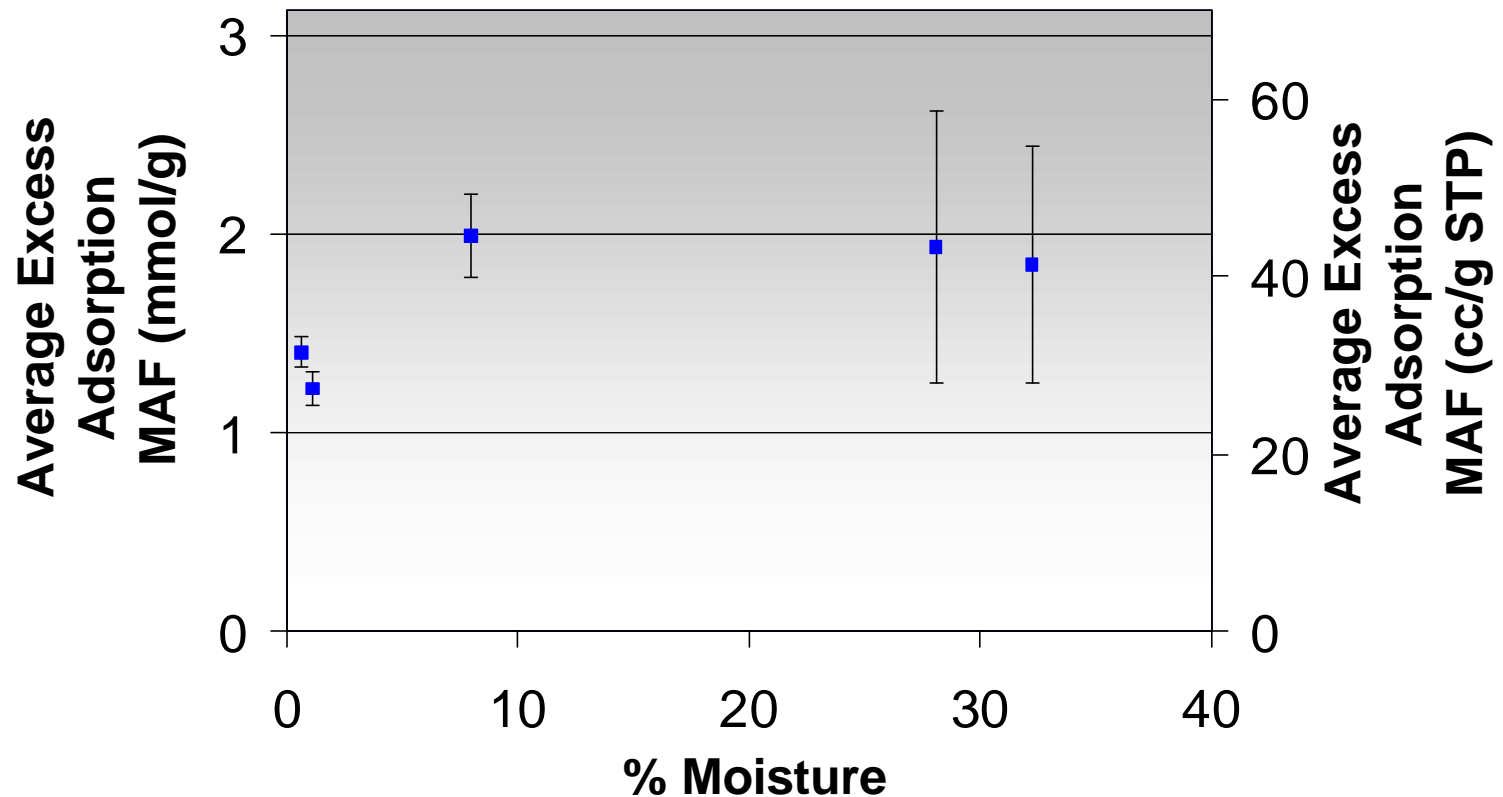


High Rank Coal ←————→ Low Rank Coal



# The Data Vary More for Low Rank Coals

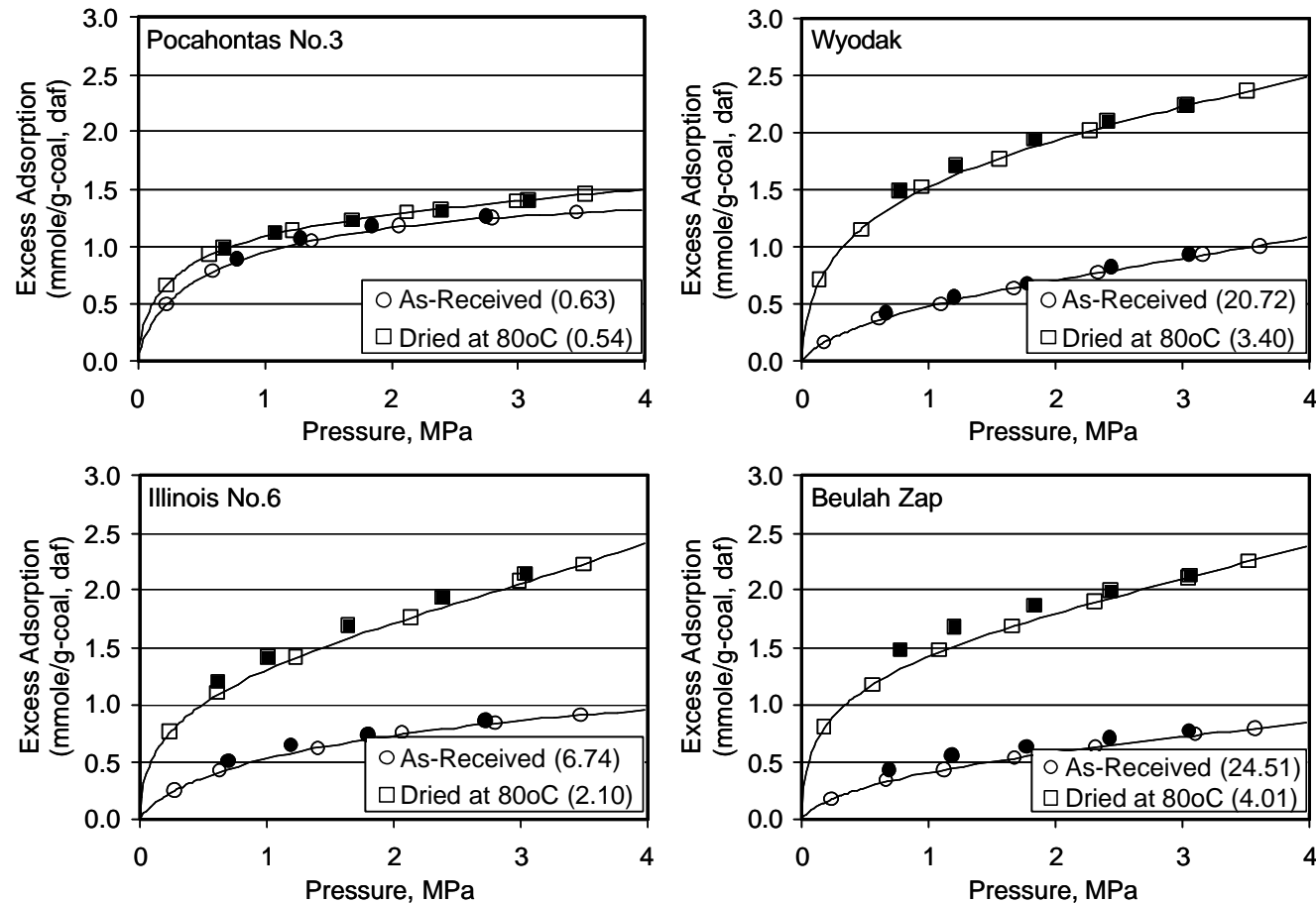
CO<sub>2</sub> Adsorption Capacity versus Moisture Content  
at 3.5 MPa (508 psia), 22°C



High Rank Coal ←————→ Low Rank Coal



# CO<sub>2</sub> Adsorption Capacity Decreases with Increasing Moisture Content



Ozdemir E.; Schroeder K.; Morsi, B.; White C. *Fuel Chemistry Division Preprints*, **2003**, 47 (DATA SHOWN).  
 Clarkson C.R.; Bustin, R.M. *Int. J. Coal. Geology*, **2000**, 42, 241-271.  
 Krooss, B.M.; van Bergen, F.; Gensterblum, Y.; Siemons, N.; Pagnier, H.J.M.; David, P. *Int. J. Coal. Geology*, **2002**, 51, 69-92.



# Differences in Estimated Moisture Content of Original Samples

Coal Sample	Argonne Percent Moisture	Percent Moisture of Samples After Drying		
		A	B	D
Pocohontas #3	0.65	0.54	-0.01	-0.06
Upper Freeport	1.13	0.68	-0.32	
Illinois #6	7.97	2.10	1.01	-0.47
Wyodak-Anderson	28.09	3.40	2.46	
Beulah Zap	32.24	4.01	3.95	-0.37

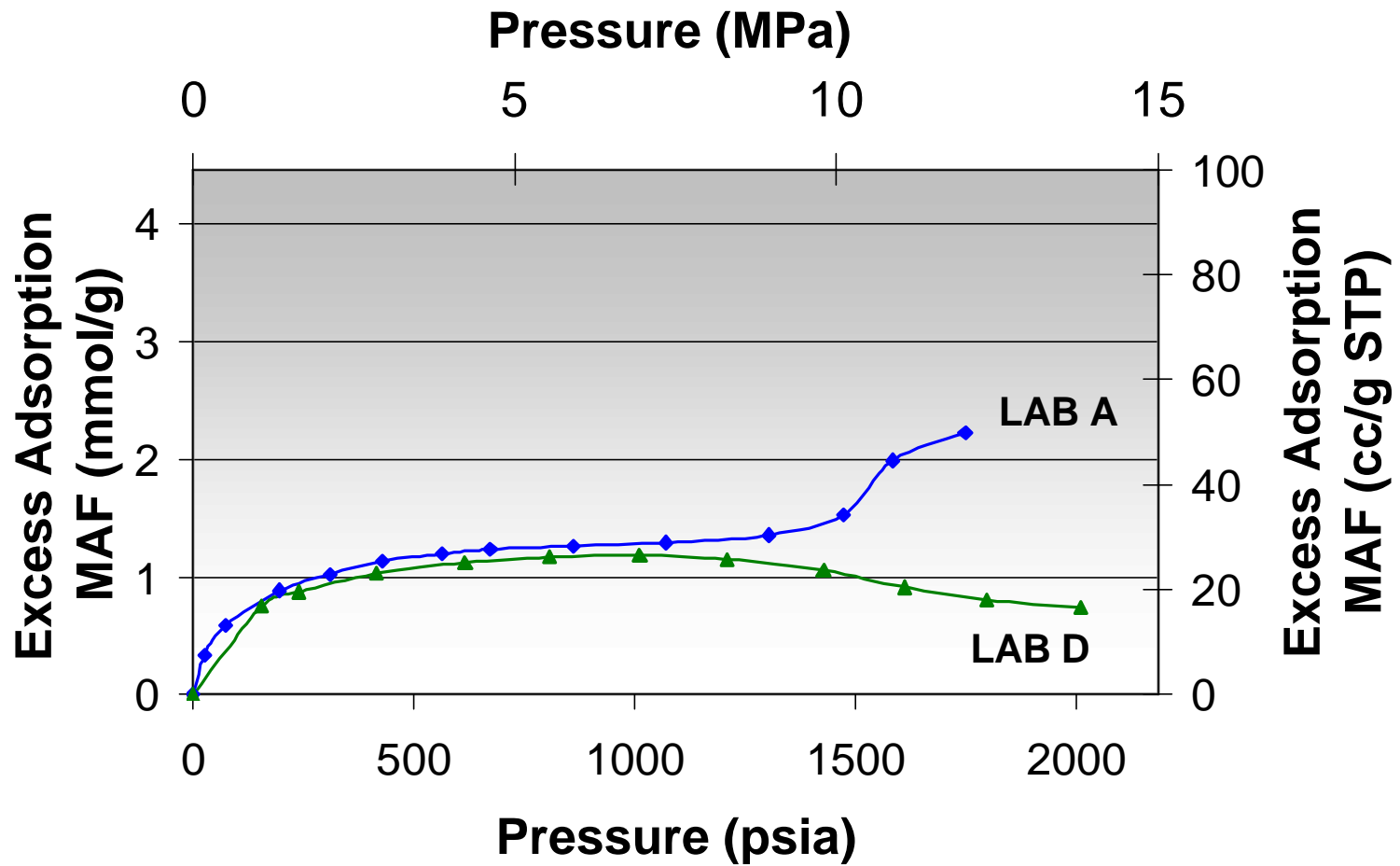


# Inter-lab reproducibility is rank dependent

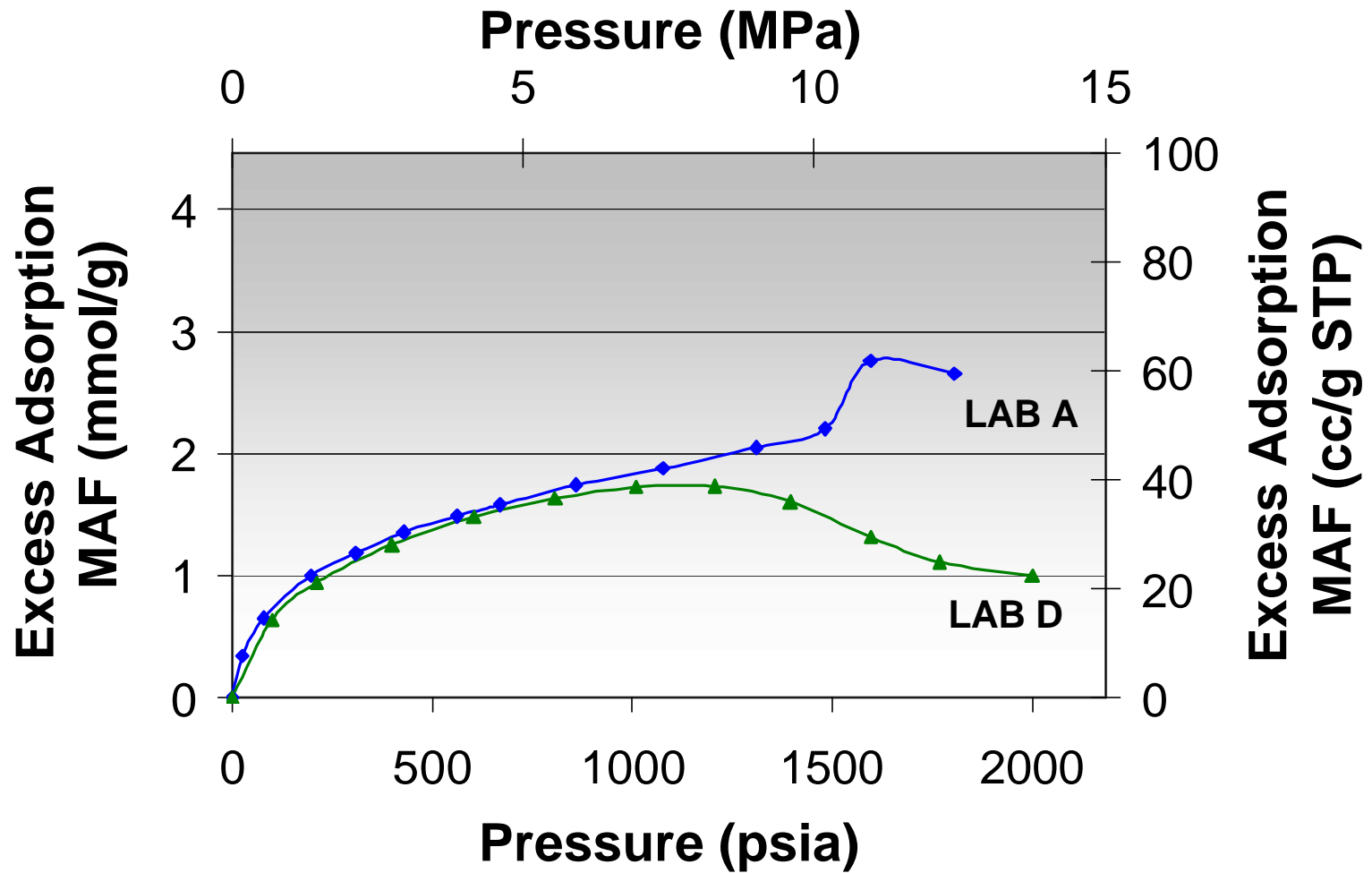
- **General trend from maximum to minimum adsorption appears to be Lab A, Lab B, and Lab C**
- **Variables –**
  - sample size
  - equilibration time
  - apparatus (swelling)
- **All labs should use the same Z**
- **Moisture content is variable and may be the largest source of error**
  - How should moisture content be controlled?
  - “Dry” coal samples until to a certain percent moisture content
  - CO<sub>2</sub> should dry the coal during the isotherm measurement [Iwai, Y.; Murozono, T.; Koujina, Y.; Arai, Y.; Sakanishi, K. *J. Supercritical Fluid* **2000**, *18*, 73-79.]



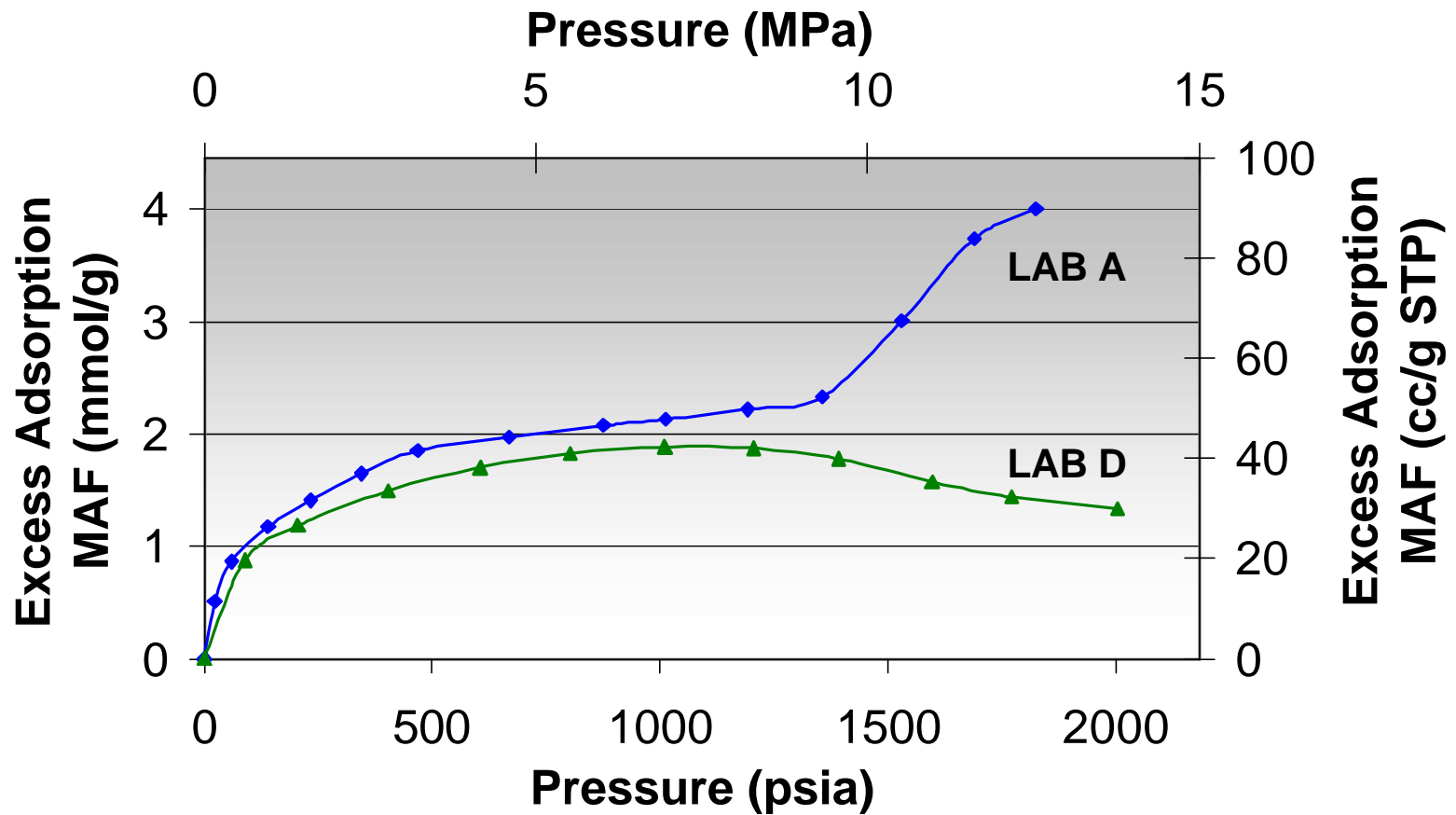
# Pocahontas #3 Coal (91.1% C) 55°C



## Illinois #6 Coal (77.7% C) 55°C

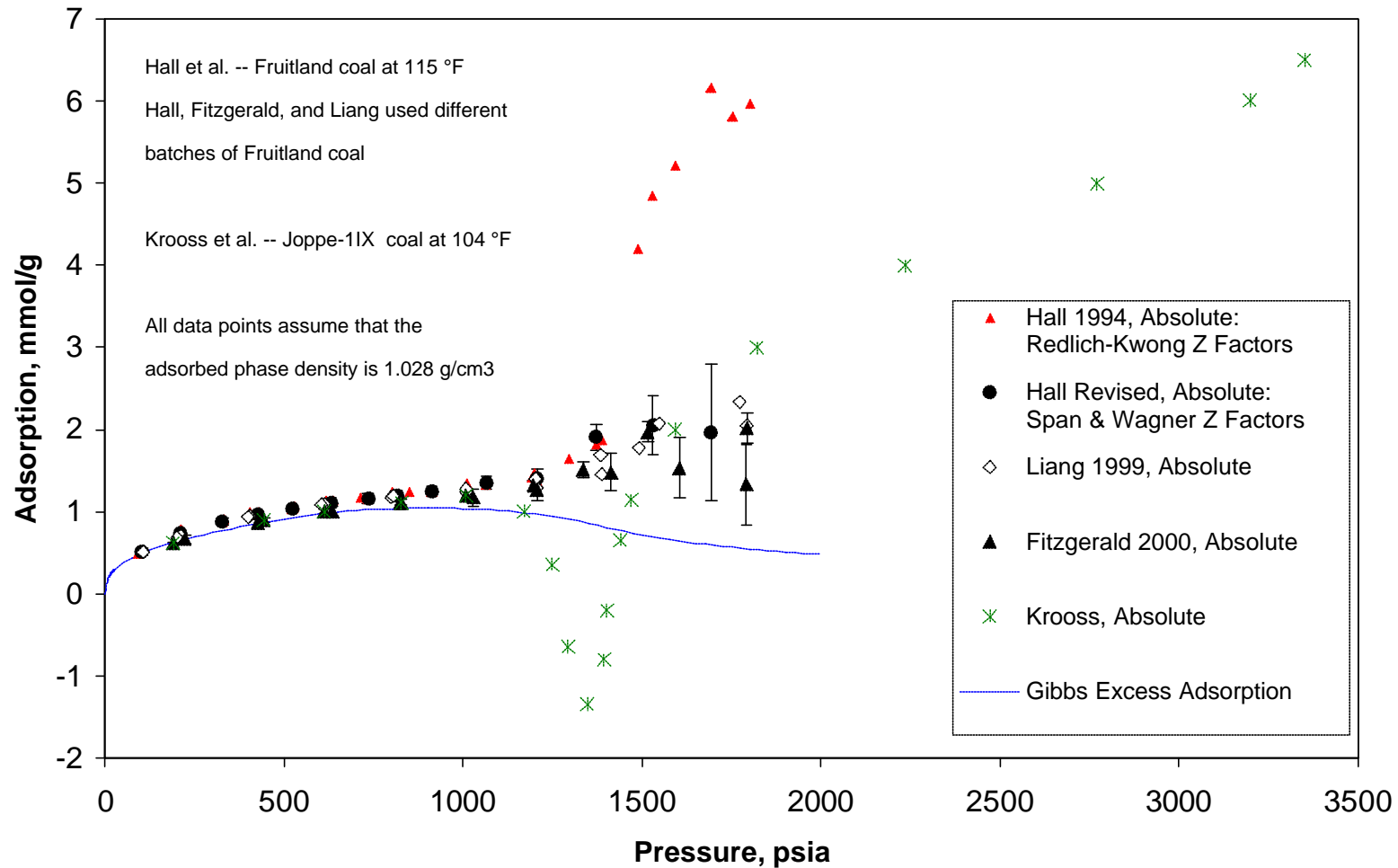


## Beulah-Zap Coal (72.9% C) at 55°C



# High-Pressure CO<sub>2</sub> Experiments on Coal

## CO<sub>2</sub> Adsorption on Fruitland and Joppe-1 IX Coals



# High-Pressure CO<sub>2</sub> Adsorption Experiments

- Shapes of isotherms are more complex than CH<sub>4</sub> isotherms
- Unexpected behavior above 1200 psia (8.3 MPa)
  - volume calculations
  - swelling



---

## Future Work

- Publish results in a peer-reviewed journal
- Largest source of error in gas storage capacity measurements is the use of conditions which are not representative of the reservoir.

**Second Inter-laboratory comparison that simulates conditions of the coal seam**

– Potential Conditions:

- Pressure Range
  - Temperature
  - Moisture (moisture equilibrated?) ASTM D 1412-93
  - Suggestions from the audience
- Questions

*Thank you to all participants*

