An Inter-laboratory Comparison of CO₂ Isotherms Measured on Argonne Premium Coal Samples

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Adsorption isotherms, which describe the coal's gas storage capacity, are important for estimating the carbon sequestration potential of coal seams. This study investigated the inter-laboratory reproducibility of carbon dioxide isotherm measurements on dry Argonne Premium Coal Samples (Pocahontas No. 3, Upper Freeport, Illinois No. 6, Wyodak-Anderson, and Beulah Zap). Four independent laboratories provided isotherm data for the five coal samples at temperatures of either 22 °C or 55 °C and pressures up to 7 MPa. The differences among the data sets in this study appeared to be rank-dependent in that the data among the laboratories agreed better for high-rank coal samples than for low-rank coal samples. A number of parameters such as sample size, equilibration time, and apparatus dimensions were examined to explain the rank effect, but no trend could be found that explained the differences. The variations among the data are attributed to different procedures for removing moisture to obtain the "dried" coal.

Introduction

Recently, carbon dioxide (CO₂) sequestration in coal seams has been identified as an attractive option that may aid in mitigating emissions of greenhouse gases.[1-5] Of special interest is the CO₂ storage capacity of coal seams at various pressures. Most often, a coal seam's CO₂ storage capacity is estimated from isotherm measurements using the coal of interest. Measurement of the amount of CO₂ adsorbed per unit mass of coal with increasing pressure produces an isotherm that describes the coal's gas storage capacity. Although individual laboratories often determine their own intra-laboratory

isotherm reproducibility, inter-laboratory isotherm reproducibility has not been reported. This makes it difficult to compare the results obtained from different laboratories. Thus, questions arise concerning the extent to which differences in results can be attributed to the coal sample rather than to the details of the measurement technique.

Strict control must be placed on experimental methodology and variables in order to obtain reproducible results.[6] The need for inter-laboratory accuracy is well recognized by regulatory agencies and industry. This need drives the development of standard methods.[7] Further, the research community recognizes that several factors including the operator, the equipment, the calibration of the equipment, and the laboratory environment including temperature and humidity can influence the variability of a test result.

Because no standard method or equipment for obtaining CO₂ isotherm data is available, labs reporting isotherms use their own, usually home-built, apparatus and procedures. Thus, it is possible that various laboratories report different storage capacities for the same coal samples. To investigate the inter-laboratory repro-

(1) Reeves, S. Geologic Sequestration of CO₂ in Deep, Unmineable Coalbeds: An Integrated Research and Commercial-Scale Field Demonstration Project. 2001. SPE paper 71749 presented at the Annual Technical Conference and Exhibition, Society of Petroleum Engineers, New Orleans, LA, September 30–October 3.
(2) Gentzis, T.; Hirosue, H.; Sakaki, T. *Energy Sources* **1996**, *18*, 119–129.
(3) Gentzis, T. *Int. J. Coal Geol.* **2000**, *43*, 287–305.
(4) Allis, R.; Chidsey, T.; Gwynn, W.; Morgan, C.; White, S.; Adams, M.; Moore, J. Natural CO₂ Reservoirs on the Colorado Plateau and Southern Rocky Mountains: Candidates for CO₂ Sequestration. DOE/NETL-2001/1144-CDROM, 1–19. 2001. NETL Publications. 5-14-2001.
(5) White, C. W.; Strazisar, B. R.; Granite, E. J.; Hoffman, J. S.; Pennline, H. W. *J. Air Waste Manage. Assoc.* **2003**, *52*, 645–715.

(6) Mavor, M. J.; Owen, L. B.; Pratt, T. J. Measurement and Evaluation of Coal Sorption Isotherm Data. 1990. SPE paper 20728 presented at the 65th Annual Technical Conference and Exhibition, Society of Petroleum Engineers, New Orleans, LA, September 23–26, pp 157–70.
(7) ASTM E 691-99 Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method. In *Annual Book of ASTM Standards*; West Conshohochken, PA, 2000; pp 264–285.

Table 1. Inter-laboratory Comparison Participants

participants	affiliation
J. Levy, G. Duffy	CSIRO Energy Technology, Australia
K. A. M. Gasem, R. L. Robinson, Jr., M. Sudibandriyo, Z. Pan, J. E. Fitzgerald	Oklahoma State University
B. M. Krooss, A. Busch, Y. Gensterblum	Aachen University (RWTH), Germany
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ducibility for CO_2 isotherms, the U.S. Department of Energy–National Energy Technology Laboratory (DOE-NETL) initiated an inter-laboratory comparison study of CO_2 isotherms on five different coal samples. This paper presents the first reported study in which the results among laboratories are compared. Each laboratory used the same coals and followed the same general procedure; however, each laboratory used its own apparatus and isotherm measurement techniques. This is not a formal inter-laboratory study with a full statistical analysis report as required by ASTM standards.[7] Our intent is to address the issue of whether the differences currently found among laboratories influence the outcome, or if all published isotherms are comparable. This work provides guidance for estimating the reproducibility that might be expected when comparing published adsorption isotherms from different labs.

Experimental Section

Approximately a dozen laboratories that were collecting adsorption data were invited to participate in this study. However, because of funding or time constraints, a subset of four independent laboratories volunteered to participate at their own expense, excluding the cost of the coal samples. Located throughout the world, the participants included government, academic, and industrial laboratories. Table 1 lists the participants and their affiliations. The data each laboratory contributed will remain anonymous; the laboratories will be referred to as laboratory A, B, C, or D throughout the paper.

For this study, DOE-NETL chose a set of five coal samples from the Argonne Premium Coal Sample Program: Pocahontas No. 3, Upper Freeport, Illinois No. 6, Wyodak-Anderson, and Beulah Zap.[8,9] The Argonne Premium Coal Samples provide the research community with the highest quality samples for basic research. Each coal sample is as chemically and physically identical as possible. The coals are well-characterized and are stable over long periods of time because they were prepared and stored under inert gas. This ensures that all participants received identical, homogeneous coal samples, and any variations in the measured results were unlikely to be due to sample variability. The samples were supplied as powders (−100 mesh). Proximate and ultimate analyses for the Argonne Premium Coal Samples are shown in Table 2.

Each laboratory collected CO_2 isotherm measurements for the five coal samples. All laboratories handled the coal samples in an inert environment of either nitrogen or helium to minimize surface oxidation. Before measuring the CO_2 isotherm, each laboratory dried the coal samples under vacuum either continuously or intermittently for 36 h at 80 °C to achieve a common initial state of near-zero moisture content. Literature reports have suggested that moisture plays a key

role in determining the adsorption capacity of coal for both methane and carbon dioxide.[10–13] Each laboratory collected the adsorption isotherms at temperatures and pressure ranges suitable for their adsorption equipment. Laboratories A, B, and C measured adsorption data at 22 °C and pressures up to 5.5 MPa, and laboratories A and D collected adsorption data at 55 °C and pressures up to 14 MPa. For the 55 °C data, only pressures up to 7 MPa are discussed because the error for laboratory A became too large for the comparison to be meaningful. Laboratories A and C measured the intra-laboratory isotherm reproducibility on two separate coal samples at 22 °C. Results are reported on a MAF (moisture- and ash-free) basis.

All laboratories measured CO_2 adsorption isotherms using their own equipment. The following laboratory equipment parameters varied: sample weight, sample cell volume, reference cell volume, void volume, equilibration time, and data collection method. Table 3 presents the values of these parameters. Each laboratory utilized one of two basic types of equipment to measure the CO_2 isotherms: Apparatus 1 or Apparatus 2 (Figure 1). Apparatus 1 typically consists of a reference cell (R) and a sample cell (S), both contained within a temperature-controlled environment (B). Pressure gauges or pressure transducers (P) are calibrated over the pressure range studied. Some systems have a provision for temperature measurements (T) to ensure thermal equilibration during the gas transfers. A vacuum system (V) is used to evacuate the apparatus before admitting the adsorbing gas. A pressurized inlet system (I) is used to provide gas at a pressure appropriate for the measurement. Cell volumes (R and S) and the void volume, the volume not occupied by the coal sample in the sample cell, are usually determined by the helium expansion method. Apparatus 2 consists of a pump and cell sections that are maintained in a constant temperature air bath. The equilibrium cell is partially filled with the adsorbent to be studied. The cell is placed under vacuum prior to gas injection. Volumes are determined by injecting known quantities of helium from a calibrated injection pump (Ruska Pump).

The exact details of the measurements varied for each laboratory, but a typical isotherm measurement would consist of the following steps. First a known pressure of CO_2 is introduced into the reference volume. That gas is then expanded into the sample volume. During this period, both temperature and pressure are monitored to ensure both thermal and adsorptive equilibrium is reached. Once equilibrium is established, the pressures of the reference and sample volume are recorded. The process is repeated as the sample is subjected to successively higher pressures during the adsorption experiments. Desorption experiments would consist of similar steps except that the higher pressure in the sample cell would be lowered stepwise into the reference cell. Neither the individual pressures at each step nor the equilibration times were controlled in this inter-laboratory comparison. The experimental conditions employed at the participating laboratories are listed in Table 3.

For the laboratories using Apparatus 1, the amount of CO_2 adsorbed on the coal sample (moles of CO_2 sorbed per unit mass of coal), also known as the Gibbs excess adsorption, is calculated by the real gas law shown in eq 1

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

where R is the molar gas constant, T_{iso} is the isothermal temperature, m_c is the mass of the coal, V_R is the volume of

(8) Vorres, K. S. Users Handbook For The Argonne Premium Coal Sample Program, 1993: accessed December 9, 2003 at URL http://www.anl.gov/PCS/pcshome.html.

(9) Vorres, K. S. *Energy Fuels* **1990**, *4*, 420−426.

(10) Clarkson, C. R.; Bustin, R. M. *Int. J. Coal Geol.* **2000**, *42*, 241−271.

(11) Ozdemir, E.; Schroeder, K.; Morsi, B. I.; White, C. W. *Prepr. Pap− Am. Chem. Soc., Div. Fuel Chem.* **2003**, *47*.

(12) Krooss, B. M.; van Bergen, F.; Gensterblum, Y.; Siemons, N.; Pagnier, H. J. M.; David, P. *Int. J. Coal Geol.* **2002**, *51*, 69−92.

(13) Joubert, J. I.; Grein, C. T.; Bienstock, D. *Fuel* **1972**, *52*, 185.

Table 2. Proximate and Ultimate Analyses of the Argonne Premium Coal Samples

coal sample		proximate analysis (wt %)			ultimate analysis (wt %, MAF)[b]				
seam	state	rank	moisture	ash[a]	VM[a]	C	H	O	S	N
Pocahontas No. 3	VA	low vol. bit.	0.65	4.74	18.48	91.05	4.44	2.47	0.50	1.33
Upper Freeport	PA	med. vol. bit.	1.13	13.03	27.14	85.50	4.70	7.51	0.74	1.55
Illinois No. 6	IL	high vol. bit.	7.97	14.25	36.86	77.67	5.00	13.51	2.38	1.37
Wyodak-Anderson	WY	subbit.	28.09	6.31	32.17	75.01	5.35	18.02	0.47	1.12
Beulah Zap	ND	lignite	32.24	6.59	30.45	72.94	4.83	20.34	0.70	1.15

[a] Dry Basis. [b] MAF = Moisture and Ash Free.

Table 3. Experimental Parameters for Each Laboratory

	LAB A	LAB B	LAB C	LAB D
maximum CO₂ pressure (MPa)	3.6 ± 0.005	5.131 ± 0.001	4.7 ± 0.008	8.3 ± 0.007
temperature (°C)	22 ± 0.1			
	55 ± 0.1	22 ± 0.02	22 ± 0.1	55 ± 0.1
coal mass (g)	1.1–1.5	89.7–111.7	5–6.7	54.5–64.7
sample cell Volume (cm³)	7.2 ± 0.2	150 ± 0.01	9.23 ± 0.006	110 ± 0.3
reference cell volume (cm³)	11.7 ± 0.2	320.3 ± 0.01	1.67 ± 0.01	250± 0.01
average void volume (cm³)	6.6	93.6	4.9	75
equilibration time	30 min	6–12 h	30 min	6–12 h
CO₂ purity	99.999%	99.95%	99.995%	99.99%

the reference cell, V_v is the void volume, Z is the compressibility factor, and P is the pressure in the subscripted cells (ri is the reference initial, rf is the reference final, sf is the sample final, and si is the sample initial). Equation 1 expresses the difference between the moles of CO₂ transferred from the reference cell and the moles of CO₂ present in the previously determined void volume of the sample cell. The coal volume, and thus the void volume of the sample chamber, is assumed to be constant throughout the adsorption measurement. Finally, the estimate of the total amount of Gibbs excess adsorbed gas, n^{ex}, at the end of the ith step is the sum of the incremental adsorptions obtained at each step (eq 2).

$$n^{ex} = \Delta n_1^{ex} + \Delta n_2^{ex} + \Delta n_3^{ex} + ... + \Delta n_i^{ex} \qquad (2)$$

The isotherm curve is created by plotting the total amount of Gibbs excess adsorbed CO₂ as a function of the measured equilibrium pressure.

For laboratories using Apparatus 2, the procedure to calculate the Gibbs excess adsorbed CO₂ is similar to the above description with the exception that the pump's volume displacement was used to calculate the moles transferred to the sample cell rather than the change in pressure in the reservoir cell (eq 3).

$$n_{inj} = \left(\frac{P\Delta V}{ZRT}\right)_{pump} \qquad (3)$$

Because this system involves the measurement of displaced volume at constant pressure, it is a true volumetric technique. The other technique, which measures a pressure change for a constant volume, is more appropriately called a manometric technique.

When calculating the Gibbs excess adsorption as shown in eqs 1 and 3, the gas compressibility coefficient Z at each pressure is required to determine the mass balance. This parameter describing the nonideality of the gas should be known with the highest degree of precision because the shape of the CO₂ adsorption isotherm and the calculated amount of excess adsorption are affected by the choice of the compressibility factor. The importance of Z is demonstrated in Figure 2. The bottom curve shows the extent of Gibbs excess adsorption calculated if the compressibility is ignored and the ideal gas law is applied ($Z = 1$). When compressibility factors taken from an older reference are used,[14] the calculated extent of adsorption increases dramatically as shown by the center line in Figure 2. A number of methods are available to calculate
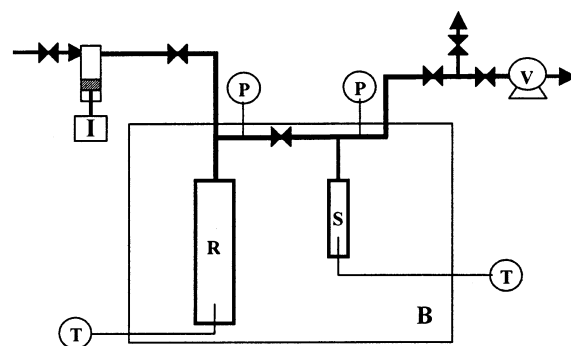
Apparatus 1
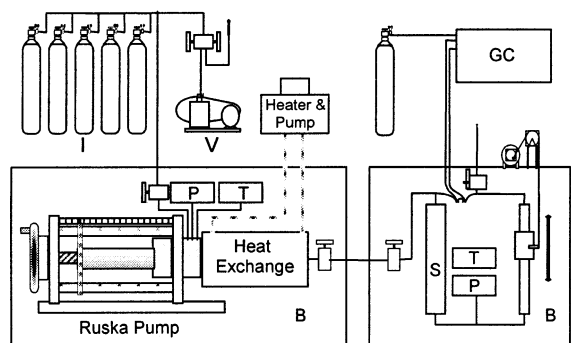
Apparatus 2

Figure 1. Apparatus 1 (manometric) and Apparatus 2 (volumetric) are two types of equipment used by laboratories to measure the CO₂ sorption isotherms in this study.

the compressibility coefficients of real gases, such as the Peng–Robinson approximation. All methods rely on the precision of experimental measurements of the thermodynamic properties of the gas. The most recent and widely accepted method for computing the compressibility coefficients of CO₂ is the formulation published by Span and Wagner.[15] The amount of excess adsorption calculated using this correction is shown as the top line in Figure 2. To ensure that the data from all of the laboratories are on the same basis, all the adsorption isotherms were calculated using the Z values from Span and Wagner.

The experimental error in the adsorption data was estimated for laboratories A, B, and D using the theory of

(14) *Gas Encyclopaedia, L'Air Liquide*; Elsevier: Amsterdam, 1976.

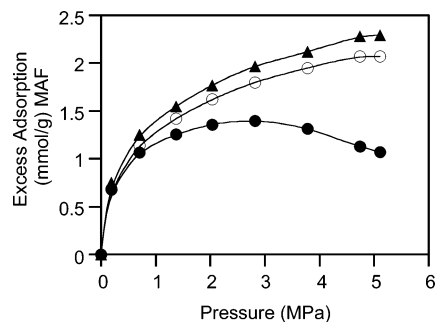(15) Span, R.; Wagner, W. *J. Phys. Chem.* **1996**, *25*, 1509–1596.

Figure 2. CO_2 adsorption calculated using three different compressibility factors for the same set of experimentally determined values: Z value from ideal gas ($Z = 1$) (●), Z value from *Air, Liquid, and Gas Encyclopedia*[14] (○), and Z value from Span and Wagner equation[15] (▲).

multivariate-error propagation.[16] The method describes how random errors in the experimental measurements are propagated into errors in the quantity calculated based on those measurements. To determine the expected uncertainty or standard error in a given quantity, the quantity calculated is expressed as an analytical function of its measured and determined variables. Specifically, for a given function y, calculated from a set of input variables ($x_1, x_2, … x_{NV}$), the uncertainty in the function y is shown in eq 4

$$\sigma_y^2 = \sum_{i=1}^{NV}\left[\left(\frac{\partial y}{\partial x_i}\right)^2 \sigma_{x_i}^2\right] \quad (4)$$

where NV is the number of variables, i is the variable index, and σ_{x_i} is the standard deviation of the measurement x_i. Equation 4 assumes that the input variables are uncorrelated and that first-order approximations are sufficient. The specific errors accounted for in the inter-laboratory measurements are the following: temperature, pressure, void volume, reference volume, compressibility factor, and coal mass. For the isotherm measurements at 22 °C and pressures up to 5 MPa, the errors were small compared to the differences observed between data sets (Figure 3, top graph). For the isotherm measurements at 55 °C where higher pressures are attained (7 MPa), the errors become larger (Figure 3, bottom graph). At pressures higher than 7 MPa, the calculated error for one laboratory became too large for the comparison to be informative. Therefore, only the region for which there is confidence for both laboratories is shown.

Results

The major goal of this study was to determine if the reproducibility of the CO_2 adsorption isotherm methods, as they were being employed, was acceptable. Thus, these results and the discussion that follows should be considered a discovery process which was undertaken to determine if stricter control is needed to obtain good inter-laboratory precision in the development of CO_2 adsorption isotherms. The data are examined for possible sources of error, but only as a guide for future investigations, not to provide unequivocal answers to specific questions. Currently, there is no standard test method as assumed by ASTM procedure E-691.[7] On the basis of the results to be presented, it may be argued that there is a need for one.

(16) *NIST/SEMATECH e-Handbook of Statistical Methods*, Propagation of error considerations: accessed December 9, 2003, at URL http://www.itl.nist.gov/div898/handbook/mpc/section5/mpc55.htm.
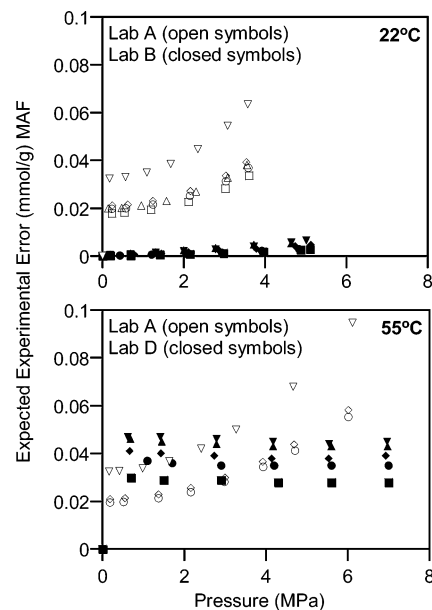

Figure 3. Experimental error associated with isotherm measurements for laboratories at 22 °C and 55 °C. Laboratory A (top and bottom graph) is represented by open symbols [(○) Pocahontas No. 3, (□) Upper Freeport (top graph only), (◇) Illinois No. 6, (△) Wyodak-Anderson (top graph only), (▽) Beulah Zap]. Laboratory B (top graph) and Laboratory D (bottom graph) are represented by closed symbols [(●) Pocahontas No. 3, (■) Upper Freeport, (◆) Illinois No. 6, (▲) Wyodak-Anderson, (▼) Beulah Zap].

Laboratories A, B, and C reported isotherm data for carbon dioxide adsorption on Argonne coals at 22 °C and pressures up to 5.5 MPa (Figure 4, closed symbols). The participants measured the CO_2 isotherms for five coals: Pocahontas No. 3, Upper Freeport, Illinois No. 6, Wyodak-Anderson, and Beulah Zap. The isotherm curves for laboratories A, B, and C agree well for the high-rank coals: Pocahontas No. 3 and Upper Freeport. The curves begin to vary for the mid-rank coal, Illinois No. 6. Finally, the isotherm curves vary widely for the low-rank coals: Wyodak-Anderson and Beulah Zap. For the isotherm data set, laboratory A always reported the highest adsorption values and laboratory C always reported the lowest values. Laboratory B was usually between the other two laboratories but often close to laboratory A. In general, the difference between data sets for laboratory A (always highest) and laboratory C (always lowest) increased with decreasing rank (Figure 4 and Table 2).

The CO_2 desorption isotherms at 22 °C were measured by laboratories A and C (Figure 4, open symbols). Some hysteresis was noted by both laboratories for all coal samples. However, the hysteresis was more pronounced for the low-rank coals. It appears that laboratory C measured a larger hysteresis than laboratory A, but laboratory A discontinued the desorption experiments before the full curve was developed.

Laboratories A and C also investigated their intra-laboratory reproducibility at 22 °C for two coal samples (Figure 5). Laboratory A measured adsorption isotherms for Illinois No. 6 and Upper Freeport coals three and four consecutive times, respectively, on fresh coal samples. The isotherms were essentially identical. Laboratory C measured the adsorption isotherms for Pocahontas No. 3 and Upper Freeport coals twice on
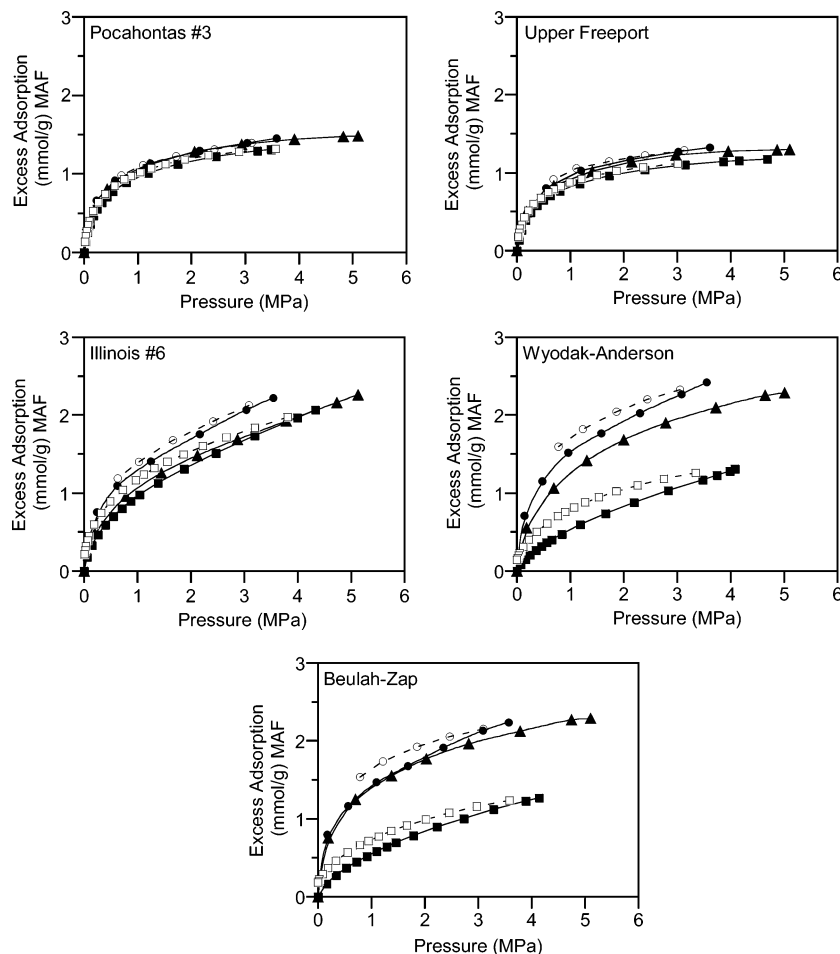
Figure 4. Adsorption and desorption isotherms of CO_2 on dried Argonne Premium Coals at 22 °C for laboratories A (●, ○), B (▲), and C (■, □). Closed symbols and solid lines represent adsorption, and open symbols and dashed lines represent desorption. Lines are to guide the eye.

fresh coal samples. The curves for the Pocahontas No. 3 samples were essentially identical; however, the curves for the Upper Freeport differed. The difference between the two Upper Freeport samples may indicate that the samples were not dried to the same extent (vide infra).

Laboratories A and D contributed CO_2 isotherm data at 55 °C and pressures up to 7 MPa (Figure 6). The participants measured the isotherms for five coals: Pocahontas, Upper Freeport, Illinois No. 6, Wyodak-Anderson, and Beulah Zap. Closed symbols represent adsorption data; open symbols represent desorption data (laboratory D only). The five isotherms agreed very well, with the exception of the Wyodak-Anderson coal where a small difference between the two laboratories was noted. The desorption data collected by laboratory D showed that the hysteresis was larger for the low-rank coal samples than for the high-rank coal samples, which was similar to what was seen at the lower temperature.

Discussion

The 22 °C CO_2 isotherm experiments showed little variance in the data for high-rank coals (Pocahontas No. 3 and Upper Freeport) and large variance in the data for low-rank coals (Wyodak-Anderson and Beulah Zap) (Figure 4). The variability of the results for the mid-rank Illinois No. 6 coal was between these two extremes. The isotherms for laboratories A and B were often, but
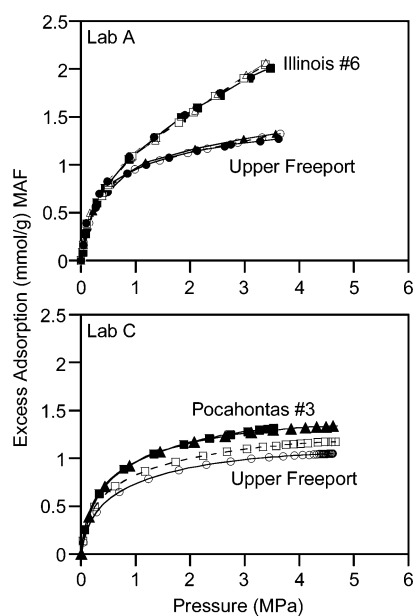

Figure 5. Intra-laboratory isotherm reproducibility of CO_2 adsorption on fresh samples of Argonne Premium Coals at 22 °C. Laboratory A repeated measurement three times for Upper Freeport (●, ○, ▲) and four times for Illinois No. 6 (■, □, △, ●) coals (top graph). Laboratory C repeated measurements twice for both Upper Freeport (○, □) and Pocahontas No. 3 (▲, ■) coals (bottom graph).
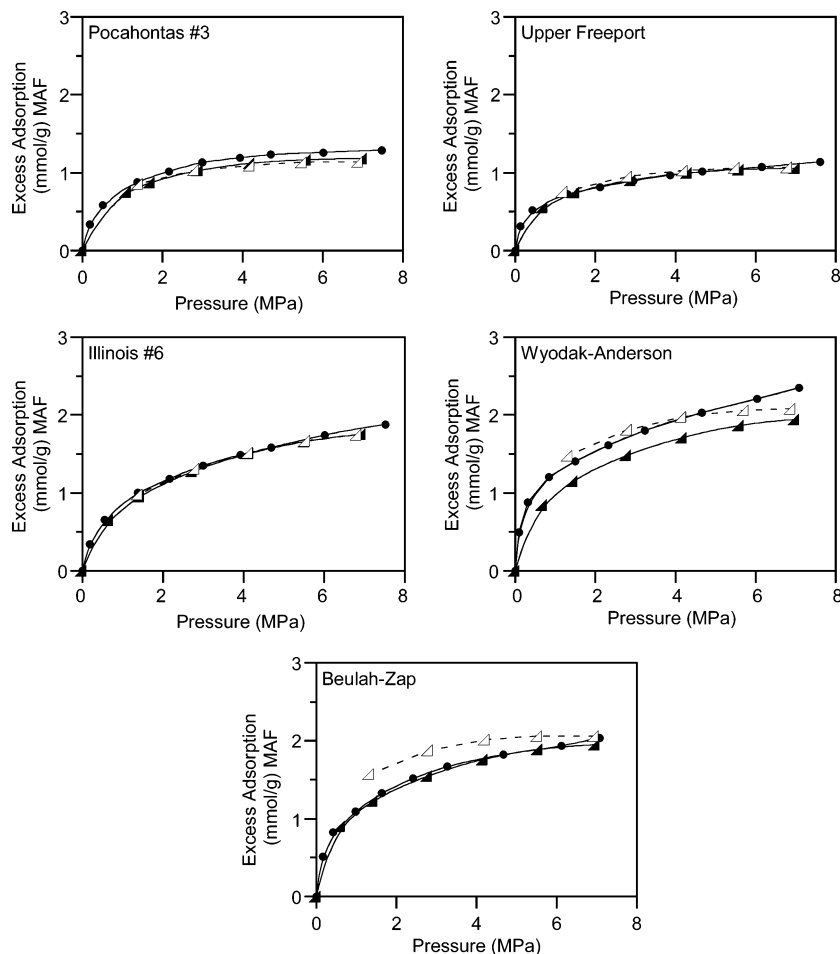
Figure 6. Adsorption and desorption isotherms of CO_2 on dried Argonne Premium Coals at 55 °C for laboratories A (●) and D (▲,△). Closed symbols and solid lines represent adsorption, and open symbols and dashed lines represent desorption. Lines are to guide the eye.

not always, in good agreement, while the isotherms for laboratory C were consistently lower. Examination of the experimental apparatus and parameters listed in Table 3 failed to explain these differences. For example, the equilibration times were shortest for laboratories A and C and longest for laboratory B; yet laboratory A always reported the highest sorption capacities and laboratory C always reported the lowest, contrary to what would be expected if equilibrium were not attained at the shorter time. Laboratory B sometimes agreed more closely with laboratory C than with laboratory A. Therefore, equilibration time is probably only a minor source of variability.

The effect of the moisture content of the coals was also examined. The CO_2 adsorption capacity has been reported to decrease with increasing moisture content of the coal.[10−12] As can be seen in Figure 7, a moisture effect is clearly present for the Argonne coals used in this study. The effect is strongest for the mid- and low-rank coals: Illinois No. 6, Wyodak-Anderson, and Beulah Zap, but it is weak for the high-rank coals such as the Pocahontas No. 3. The Pocahontas coal had an as-received moisture content of 0.63%. Upon drying for 36 h at 80 °C under continuous vacuum, the moisture content decreased to 0.54%. The two isotherms for the Pocahontas coal show a small but discernible increase in the extent of CO_2 adsorption for the dried sample. Drying the mid- and low-rank coals under the same

conditions caused a significant loss of moisture. The moisture content of Beulah Zap coal, for example, decreased from 24.54% to 4.01%. The CO_2 adsorption isotherms for the moist low- and mid-rank coals in Figure 7 are less than for the dry coal samples. Thus, moisture can play a significant role in the extent of CO_2 adsorption reported for the Argonne coals.

The divergence in the inter-laboratory results appears to follow a moisture-related trend. This can be seen in Figure 8 where the average and range of values reported by the labs at 3.5 MPa and 22 °C has been plotted as a function of the as-received moisture content. The deviation is low for coals that contained little moisture, but it is high for those coals that naturally contain high amounts of moisture. The deviations can be large with one lab reporting more than twice the adsorption capacity for the same Argonne Premium Coal. It would be instructive to compare the final moisture contents of the coals. Unfortunately, this value was not recorded by all labs in this study. However, there were recorded differences in the drying procedure. Laboratories A and B dried the coal samples under vacuum for 36 h continuously. Laboratory C followed a slightly different drying procedure. Here the coal was also dried for 36 h under vacuum; however, the vacuum pump was switched on and connected to the system intermittently for 15 min and then disconnected and switched off for 15 min. Between the pumping cycles the vacuum was not
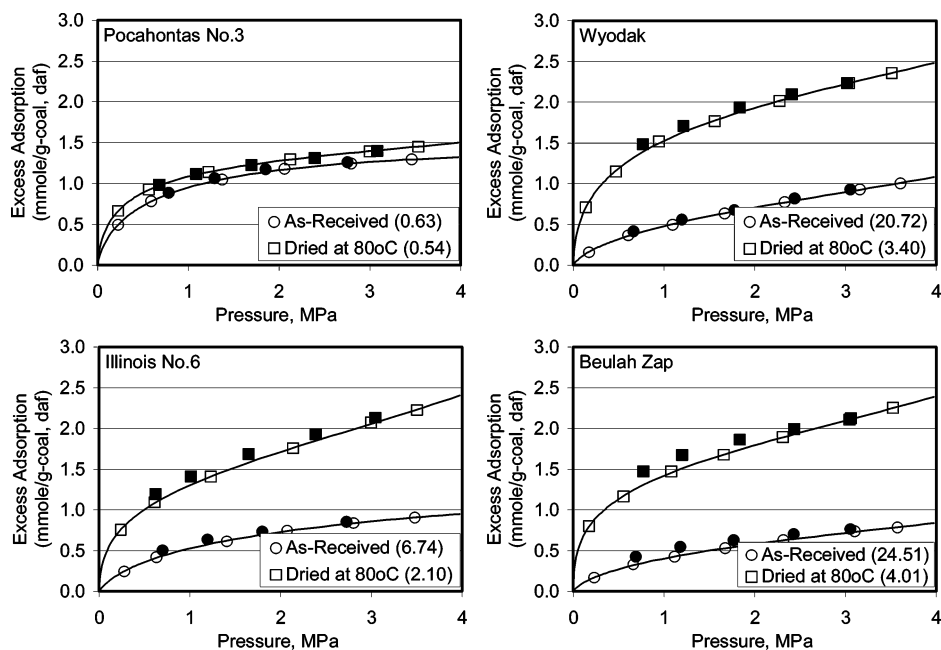
Figure 7. Adsorption and desorption isotherms of CO_2 on as-received and dried Argonne Premium Coals at 22 °C. Open symbols represent adsorption, and closed symbols represent desorption. Lines are to guide the eye. The moisture content of the coal samples is given as percent moisture in parentheses.
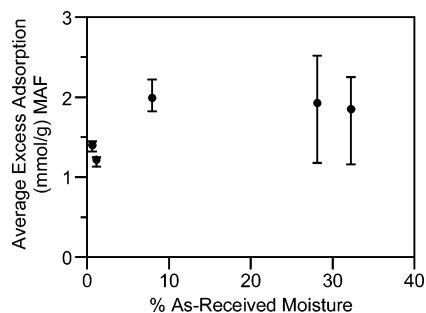

Figure 8. Average (closed circles) and range (bars) of adsorption values obtained at 3.5 MPa and 22 °C.

measurably lost so that the total time under vacuum was essentially the same for all three laboratories. This seemingly slight difference in the drying procedure may have caused the observed differences in the sorption isotherms.

Alternatively, the differences seen for the lower-ranked coals may have been due to differences in the structure, and hence the surface area, of the dried material caused by the details of the drying procedure. This is especially true for the low-rank coals which have been described as having a gel-like structure[17,18] in which water is an intimate structural unit rather than just an adsorbed phase. Also, low-rank coals are notorious for their propensity to undergo surface oxidation at ambient temperatures, and surface oxidation has been reported to decrease the CO_2 surface area.[19] This would be especially important for fine-mesh samples such as were used in these comparisons. While general precautions to avoid exposure to the air were given, no explicit procedure for minimizing oxidation was adopted in this study.

In addition to the comparison at 22 °C, a more limited comparison was made at 55 °C. This temperature was of interest because it is above the CO_2 critical temperature which will be exceeded at sequestration depths greater than about 3000 feet. As can be seen in Figure 6, the agreement between laboratories A and D was very good for four of the five coal samples studied. Only the Wyodak-Anderson coal exhibited a small deviation between the two laboratories. At this higher temperature and for these two laboratories, there was no apparent effect of experimental differences in sample size, equilibration time, apparatus dimensions, and moisture content. Whether this was because both laboratories were able to control the coal environment to the same extent or whether it was a result of the higher temperature could not be determined. The drying of coal with supercritical CO_2 has been reported to be as effective as oven drying.[20] Thus, exceeding the supercritical temperature of CO_2 may provide in-situ drying not attainable at the lower temperature.

Hysteresis upon desorption was measured by three of the four laboratories. Laboratories A and C performed desorption experiments at 22 °C, and laboratory D measured the desorption isotherm at 55 °C. The hysteresis observed upon desorption of CO_2 appeared to be rank-dependent. All labs reported small or no hysteresis for the higher-ranked Pocahontas and Upper Freeport coals and large hysteresis for the low-rank Wyodak-Anderson and Beulah Zap coals. The desorption data for the intermediate Illinois No. 6 coal varied among the laboratories; laboratory C reported considerably larger hysteresis than laboratories A and D. Hysteresis has been reported to be due to changes in the moisture content of the coal.[6] Thus, different residual moisture contents of the coal samples after drying would be expected to play a role in hysteresis. Also, hysteresis due to different residual moistures would be consistent

(17) Suuberg, E.; Otake, Y.; Yun, Y.; Deevi, S. *Energy Fuels* **1993**, *7*, 384−392.
(18) Deevi, S. C.; Suuberg, E. M. *Fuel* **1987**, *66*, 454−460.
(19) Swann, P. D.; Allardice, D. J.; Evans, D. G. *Fuel* **1974**, *53*, 85−87.

(20) Iwai, Y.; Amiya, M.; Murozono, T.; Arai, Y. *Ind. Eng. Chem. Res.* **1998**, *37*, 2893−2896.

with the previous discussion where Laboratory C reported lower adsorption capacity. Other explanations include irreversible matrix swelling of the coal samples and CO_2 trapped in ink-bottle pores.[21] Further investigations are necessary to explain the hysteresis phenomena.

Although other explanations cannot be ruled out completely, residual moisture appears to play a dominate role in affecting the measured adsorption isotherms of CO_2 on dried coals. It is the common denominator that can explain the rank-dependence of the inter-laboratory precision, the better agreement at the higher temperature, and the hysteresis observed upon desorption. In the future, a strict procedure for controlling the coal moisture content will be needed. On the basis of the long history of surface area measurements on coal (nitrogen BET, CO_2, and others),[22] it was thought that drying and degassing the coals in-situ would provide the best method of obtaining reproducible isotherms. It now appears that assumption was false. If adsorption isotherms are to be obtained for dried coals, stricter control on the drying and/or handling conditions will be required for good inter-laboratory comparisons.

Conclusion

This study provides the first inter-laboratory comparison of carbon dioxide isotherm measurements for coal samples. The overall agreement among laboratories was very good for high-rank coals, but the mid- and low-rank coals showed large variations. The presence of different amounts of residual moisture can explain the rank-dependence of the inter-laboratory precision, the better agreement at the higher temperature, and the hysteresis observed upon desorption. Measurements at temperatures above the CO_2 critical temperature may not be as sensitive to residual moisture as those obtained at lower temperatures. In the future, a strict procedure for obtaining measurements will be needed if reproducible, moderate-temperature isotherms are to be obtained for dried coals.

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(21) Adamson, A. W. *Physical Chemistry of Surfaces*; John Wiley & Sons Inc.: New York, 1990; p 662.

(22) Mahajan, O. P. *Carbon* **1991**, *29*, 735−742.