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Comparison of high-pressure CO_2 sorption isotherms on Eastern and Western US coals

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ABSTRACT

Accurate estimation of carbon dioxide (CO_2) sorption capacity of coal is important for planning the CO_2 sequestration efforts. In this work, we investigated sorption and swelling behavior of several Eastern and Western US coal samples from the Central Appalachian Basin and from San Juan Basin. The CO_2 sorption isotherms have been completed at 55 °C for as received and dried samples. The role of mineral components in coal, the coal swelling, the effects of temperature and moisture, and the error propagation have been analyzed. Changes in void volume due to dewatering and other factors such as temporary caging of carbon dioxide molecules in coal matrix were identified among the main factors affecting accuracy of the carbon dioxide sorption isotherms. The (helium) void volume in the sample cells was measured before and after the sorption isotherm experiments and was used to build the volume-corrected data plots.

INTRODUCTION

Carbon dioxide geologic sequestration in deep unmineable coal seams has been identified as one of the key strategic options that will allow us to reduce greenhouse gas emissions. As an added benefit, such geological formations generally contain significant quantities of coalbed methane that can be recovered by using the CO_2 flood [1,2] known as

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enhanced coal bed methane (ECBM) production technique. Accurate estimates of the gas storage capacity of coals are important for planning and effective execution of the large-scale CO_2 sequestration projects.

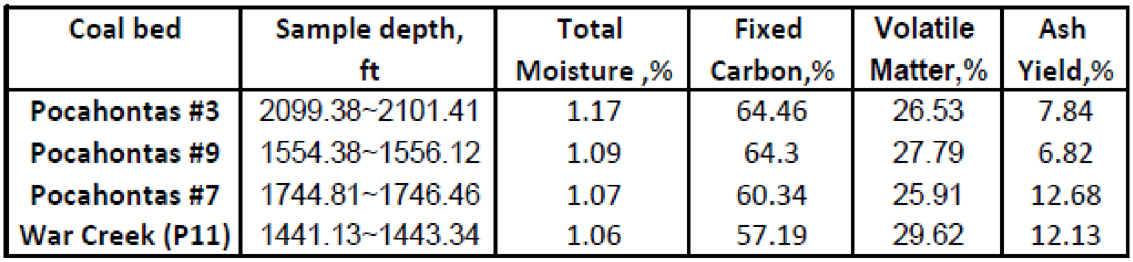
The manometric sorption isotherm characterization is one of the main methods used for measurement of the CO_2 storage capacity of primarily powder coal samples. In order to estimate the Gibbs excess adsorption, this method makes use of the helium void volume that is initially measured using helium displacement techniques, for the actual void volume in sample cell occupied by neither the solid coal sample nor by the adsorbed CO_2 during the test is an inaccessible parameter [3,4]. The carbon dioxide sorption isotherms are normally conducted up to the storage reservoir pressures which usually correspond to supercritical CO_2 phase.

EXPERIMENTAL

In this work, the manometric apparatus was used to conduct CO_2 sorption isotherm experiments on moist and dry coals. The coal cuttings were received from the SECARB Regional Partnership, in support of the Central Appalachian Basin ECBM field test in the Honaker District of Russell County (Pocahontas No. 3, Pocahontas No. 7, Pocahontas No. 9, and Pocahontas No. 11 coal seams) as well as from the Southwest Regional Partnership (SWP), in support of Phase 2 of the San Juan Basin ECBM Pilot Project (Upper and Middle Coals of Fruitland Formation). The experimental work was designed to include three major steps: (1) CO_2 sorption and desorption isotherms on moisture-equilibrated coal; (2) heating the (partially dried) coal *in situ* at 100 °C for 24 hours in vacuum to remove the residual moisture; (3) CO_2 sorption and desorption isotherms on the almost completely dry coal, including the repeated calibration process. The helium void volume in the sample compartment was measured before and after the carbon dioxide sorption isotherms to account for moisture loss during the test. The sorption measurements were performed at 55^oC by introducing CO_2 into the cell to build the pressure step-wise up to 12 MPa. The reference and sample cells that consist of the manometric apparatus were immersed into a temperature-controlled bath, as described by Romanov *et al.* [5]. The heat bath maintained a constant temperature (55±0.02 °C) and the purity of both gases (CO_2 and He) was 99.999%. Prior to the sorption experiments, the Fruitland Fm. coal samples were removed from the sealed water-filled natural-gas-desorption autoclaves (canisters), after degassing for several months and draining the water, physically separated from water and homogenized. All coal samples were then handled under nitrogen atmosphere to minimize surface oxidation.

The structural properties of the Appalachian coal samples were investigated using X-ray diffraction (XRD; Philips PW3710 based X'pert Diffraction System, λ = 0.15405 nm) scattering technique. These coals are relatively homogeneous and well characterized. The detailed proximate analyses and depth information are shown in Table 1.

Table 1. Proximate analyses and depth information of coal samples



Coal bed	Sample depth, ft	Total Moisture ,%	Fixed Carbon,%	Volatile Matter,%	Ash Yield,%
Pocahontas #3	2099.38~2101.41	1.17	64.46	26.53	7.84
Pocahontas #9	1554.38~1556.12	1.09	64.3	27.79	6.82
Pocahontas #7	1744.81~1746.46	1.07	60.34	25.91	12.68
War Creek (P11)	1441.13~1443.34	1.06	57.19	29.62	12.13

The Fruitland coals were characterized by Softrock Geological Services, Inc. as follows.

C3 (sample depth, 3110-3122 ft) and C4 (sample depth, 3123-3138 ft): 60% satiny black intermediate, 35% glassy black bright laminar matrix, 5% sub lustrous black dull at margins; brittle, blocky, well cleated, with hexagonal translucent black smoky quartz in open fractures and Carboniferous fire clay volcanic ash (tonstein) in coal section.

C5 (sample depth, 3152-3155 ft): 70% silky and satiny black intermediate matrix with 20% sub glassy semi-bright and 10% greasy black dull laminations; firm, shardy to powdery, fairly cleated, with brown (rust colored) powder fines.

The C4 coal appears to be more heterogeneous and brittle than C5, due to higher mineral ash content (~30% wt.). The drained water with suspended particulates (from the autoclaves) was tested for pH, which was 10.6 and 9.0 for C4 and C5 respectively, as well as the trace metals. The particulates in water from the C3 canister were identified as primarily tonstein or smectite.

RESULTS AND DISCUSSION

Assuming the Gibbs model, we calculated the excess fluid sorption on the coal samples using the NIST Pure Fluids software package, Database 12, ver. 5.0 [8]. To estimate uncertainty propagation in the sorption isotherms, similar-size standard samples (of stainless steel and clean sand) were used under the same experimental conditions.

Figure 1 shows uncertainty propagation in sorption isotherms of carbon dioxide on the standard samples as a function of pressure. Assuming that under the conditions of the experiments there is no measurable adsorption of CO_2 on the reference samples, the results obtained from several tests consistently indicate that the measurement errors increase with CO_2 pressure. Under low CO_2 pressure, the errors were negligible (within 0.01 mmol/g), but they increased abruptly (up to ~0.05 mmol/g) at 8-9 MPa, upon CO_2 transition to supercritical phase.

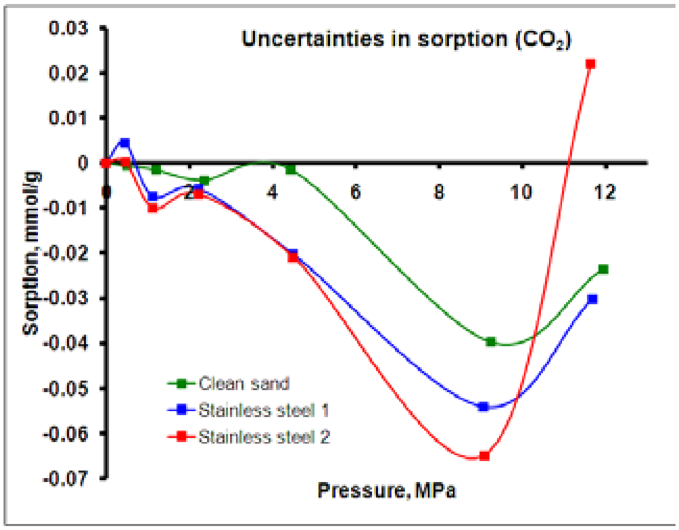


Fig. 1. Uncertainties (errors) in sorption isotherms of carbon dioxide (CO_2) on standard samples.

In order to investigate the effects of moisture, the experimental work was designed to include the three major steps as described in the experimental procedure. Figure 2 shows carbon dioxide excess adsorptions on Pocahontas No. 3 and Pocahontas No. 9 (wet and dry) coals. The amount of the adsorbed carbon dioxide on the dry coals is significantly higher than on the wet coals; less so in Pocahontas No. 9 because of the noticeable swelling above 4 MPa and especially above 9 MPa, which results in eventually negative slope of the excess sorption plot. This increase in sorption capacity indicates that the moisture in coal organic matrix interrupts carbon dioxide interactions with coal by clogging the micro-pores where most of the sorption presumably takes place.

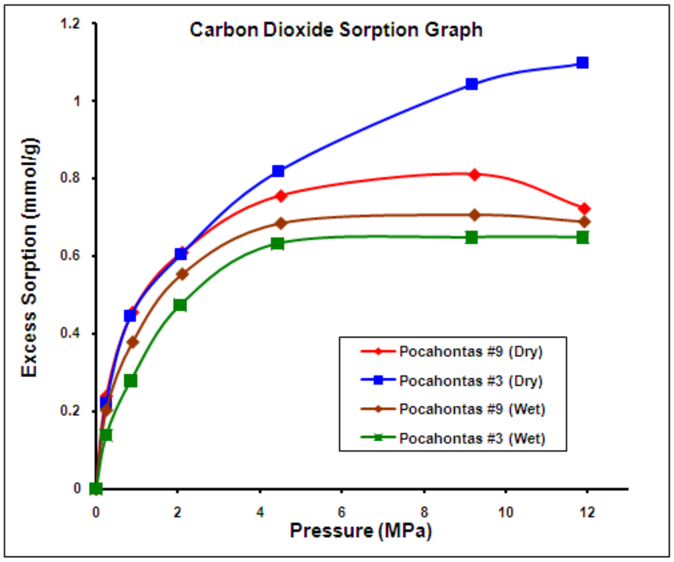


Fig. 2. Carbon dioxide excess sorption isotherms (dry basis) on wet and dry Appalachian coals (Pocahontas No. 3 and Pocahontas No. 9).

Manometric sorption isotherm experiments on Pocahontas No. 7 and War Creek (P11) coals that have relatively lower fixed-carbon content and higher ash yield were conducted as well, as shown in Figure 3. War Creek (P11) test results show a smaller increase in the amount of adsorbed carbon dioxide, after removal of moisture by heating. One possible explanation is the War Creek (P11) coal has a somewhat different mineral and maceral composition, which may result in different pore rearrangements upon heating. It appears (Figure 3) that this coal swells more noticeably after sorbing the CO_2, especially in its supercritical phase, resulting in apparent negative slope of the excess sorption plot.

Interesting changes in sorption behavior of the wet coals are observed shortly after transition to the supercritical CO_2 phase. Unlike the other two Central Appalachian coals (Figure 2), these coals (Figure 3) produce a noticeable rise in CO_2 sorption capacity above 9 MPa, when the CO_2 density becomes comparable to water density, which may facilitate the water displacement and increased micropore volume available for CO_2 adsorption.

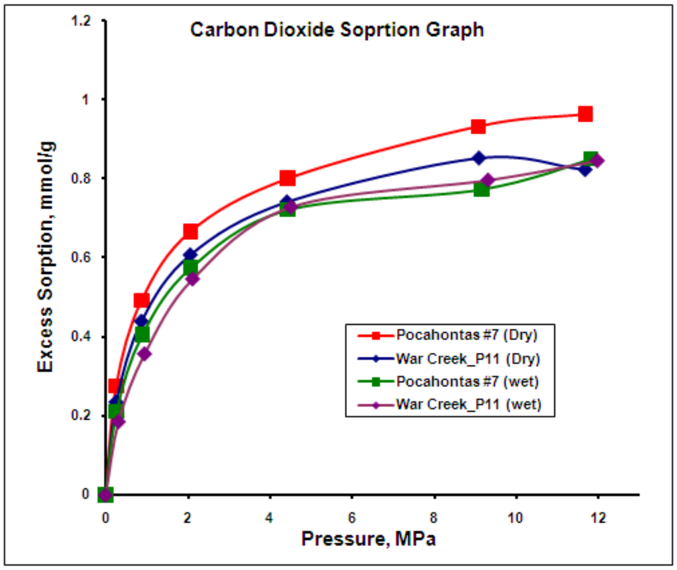


Fig.3. Carbon dioxide excess sorption isotherms (dry basis) on wet and dry Appalachian coals (Pocahontas No. 7 and War Creek/ P11)

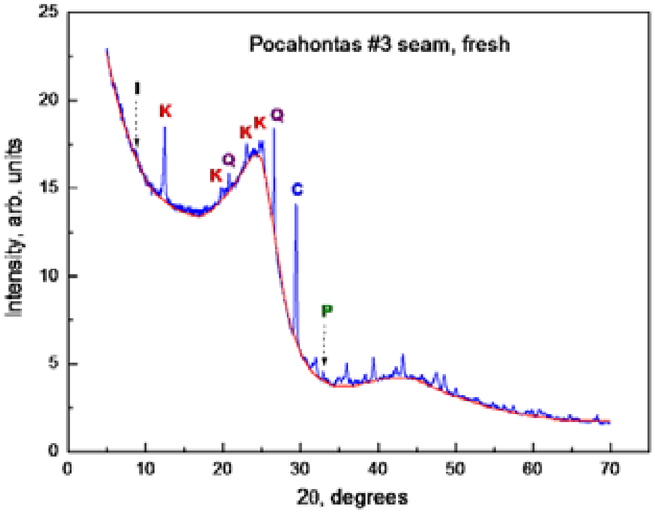
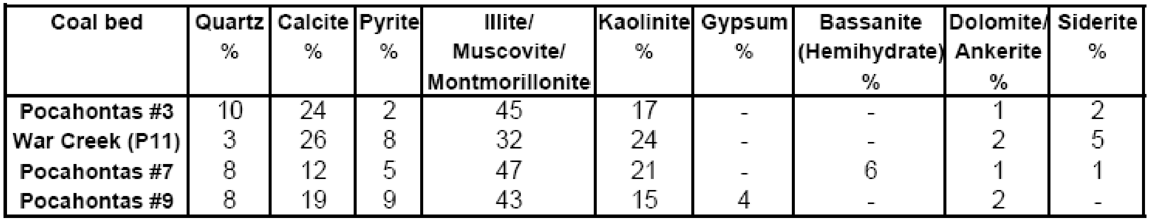


Fig. 4. Powder X-ray diffraction profile of Pocahontas No. 3. The background is due to coal phase and the sharp peaks are due to minerals (Q: quartz, C: calcite, P: pyrite, I: illite/ muscovite/ montmorillonite, K: kaolinite).

In order to see if these coals contain the mineral components strongly interacting with carbon dioxide [6,7]; we investigated into the mineral matter composition using a standard X-ray diffraction technique. Figure 4 shows the powder X-ray diffraction profile of as-received Pocahontas No. 3.

The X-ray diffraction patterns indicate that the coal contains various mineral components, such as calcite, montmorillonite, kaolinite, etc. The relative amount of each mineral component (as shown in Table 2) was roughly estimated by semi-quantitative analysis of the X-ray data. For comparison, the data for coal sample from the Pocahontas No. 3 coal seam are very similar to the data reported for mineral content of the Pocahontas No. 3 coal in the Argonne Premium Coal database. The overall mineral content appears to be small and we were unable to accurately determine the quantity of the swelling clays if any are present in Appalachian coals.

Table 2. Semi-quantitative analysis of mineral components, wt%



Coal bed	Quartz %	Calcite %	Pyrite %	Illite/ Muscovite/ Montmorillonite	Kaolinite %	Gypsum %	Bassanite (Hemihydrate) %	Dolomite/ Ankerite %	Siderite %
Pocahontas #3	10	24	2	45	17	-	-	1	2
War Creek (P11)	3	26	8	32	24	-	-	2	5
Pocahontas #7	8	12	5	47	21	-	6	1	1
Pocahontas #9	8	19	9	43	15	4	-	2	-

The Fruitland coals had a much lower CO_2 sorption capacity, 0.4-0.7 mmol/g, than the Central Appalachian coals. Figure 5 shows carbon dioxide sorption isotherm plots for wet and dry coal sample, C5 from the Fruitland Fm. (Middle Coals, 3152-3155 ft). The effects of moisture are clearly observed at the lower, gaseous CO_2 pressures, up to 7-8 MPa. In this pressure range, the increase in the amount of sorbed carbon dioxide after drying is about 110%. The sorption profile on the wet coal sample showed an abnormal behavior in the pressure range of about 9-12 MPa, after transition from gaseous to supercritical phase of CO_2. A less prominent behavior, rather similar to the War Creek (P11) coal's, was observed in sorption isotherms of C4 (not shown here) which may have had a more open (pass-through as opposed to dead-end type) pore structure that is easier to flush. The presence of the pass-through pores can allow a larger volume of the micropore water to be flushed out by gaseous CO_2. Most of the measured physical parameters for both samples were similar: the dry-basis sample mass, 24.2 g (C4) and 30.6 g (C5); the pre-test moisture level, 12.2% (C4) and 11% (C5); and the pre-test void volume, 18.1 cm^3 (C4) and 17.3 cm^3 (C5). However, C4 had a much higher density (attributed to quartz and tonstein), >1.7 g/cm^3 vs. 1.4 g/cm^3 for C5.

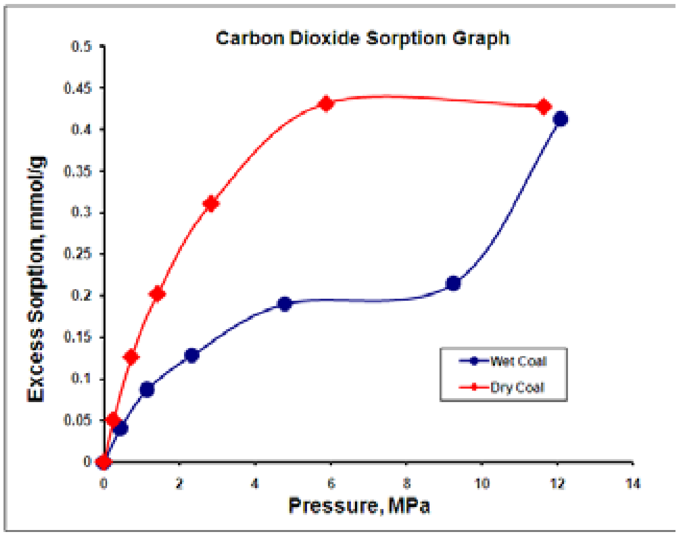


Fig. 5. Carbon dioxide excess adsorptions (dry basis) on wet and dry Fruitland coal samples, C5. Depth: 3152-3155 ft.

SUMMARY

We investigated sorption and swelling behavior of several Eastern and Western US coal samples from the Central Appalachian Basin and from San Juan Basin. The role of mineral components in coal, the coal swelling, the effects of temperature and moisture, and the error propagation have been analyzed. Changes in void volume due to dewatering were identified among the main factors affecting accuracy of the carbon dioxide sorption isotherms. The void volume in the sample cells was measured before and after the sorption isotherm experiments and was used to build the volume-corrected data plots. It was observed that uncertainties in the sorption isotherm data interpretation increase abruptly around the CO_2 critical point.

Acknowledgements

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