CO₂ Isotherms Measured on Moisture-Equilibrated Argonne Premium Coals at 55°C and 15 MPa

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ABSTRACT

Sorption isotherms, which describe the coal’s gas storage capacity, are important for estimating the carbon sequestration potential of coal seams. The DOE-NETL initiated a second inter-laboratory isotherm comparison of coals where CO₂ sorption isotherms were collected on moisture-equilibrated coals at temperatures and pressures relevant to CO₂ sequestration. Each laboratory used the same coal samples and followed the same general procedure; however, each laboratory used their own apparatus and isotherm measurement technique. This study investigated the inter-laboratory reproducibility of carbon dioxide isotherm measurements on moisture-equilibrated Argonne premium coal samples (Pocahontas #3, Illinois #6, and Beulah Zap). Six independent laboratories provided isotherm data on the three moisture-equilibrated coal samples at 55°C and pressures up to 15 MPa. Agreement among the laboratories was good up to 8 MPa. At the higher pressures, the data among the laboratories diverged significantly for two of the laboratories and coincided reasonably well for four of the laboratories. This work provides guidance for estimating the reproducibility that might be expected when comparing published sorption isotherms on moisture-equilibrated coals from different laboratories.

INTRODUCTION

Carbon dioxide storage in coal seams has recently received increased attention as a potential option to reduce greenhouse gas emissions to the atmosphere. Accurate measurements of CH₄ and CO₂ sorption isotherms are vital for the optimum development of techniques to either sequester CO₂ or to combine CO₂ storage with an enhancement of CH₄ recovery ¹ ². For a given coal seam, sorption isotherm measurements provide information about the storage capacity, the overall economics of the process, and the types of operating conditions that can be used ³. The storage capacity of a coal seam is traditionally estimated from manometric, volumetric, or gravimetric isotherm measurements ⁴ ⁶. Since there is no standard procedure or technique for measuring the isotherm, results obtained from different laboratories need to be compared to determine their accuracy.

In order to better understand the variation in estimates of the storage capacity of coal seams, the U.S. Department of Energy-National Energy Technology Laboratory (DOE-NETL) initiated a second inter-laboratory isotherm comparison of coals where CO₂ sorption isotherms were collected on moisture-equilibrated coals at temperatures and pressures relevant to CO₂ sequestration. Results are compared amongst six laboratories worldwide. Results of this second comparison among laboratories for moisture-equilibrated coals were recently published in International Journal of Coal Geology (COGEL-01407), 2007, “Inter-laboratory Comparison II: CO₂ Isotherms Measured on Moisture-Equilibrated Argonne Premium Coals at 55°C and 15 MPa.” All experimental details, results and conclusions can be found in this reference. Table 1 identifies the authors who contributed to this study and their affiliations.

The main conclusions of the published study are as follows: The overall agreement between the laboratories was good up to 8 MPa with the exception of those instances where moisture content of the coals were either higher or lower than the as-received moisture threshold. At CO₂ pressures above 8 MPa, the reported sorption isotherms diverged significantly. Further studies need to be conducted in order to address deviations and experimental problems associated with measuring high-pressure CO₂ sorption isotherms.
DISCUSSION

Until recently, there have been very few high-pressure studies of CO$_2$-coal sorption isotherms under in-seams conditions.$^7$-$^10$ This void is being filled because of interest in ECBM and CO$_2$ sequestration.$^3$ According to the metric for success of carbon sequestration technologies published in the 2006 DOE road map, DOE requires that the ability to predict CO$_2$ storage capacity within +/- 30% accuracy be demonstrated by 2012.$^{11}$ According to the data in this study, the low-pressure isotherm measurements are already meeting this goal. Further studies, however, need to be conducted in order to address the errors associated with the high-pressure isotherm measurements.

The main point of the study was to compare the isotherms measured by different laboratories worldwide. If all laboratories used the same coal samples, same equation of state, and same adsorbed layer density, then the laboratories should get the same isotherms. The laboratories did get the same CO$_2$-coal isotherms up to 8 MPa. After that the data deviated significantly. Examination of the experimental apparatus and parameters failed to explain the differences at higher pressures. When using manometric, volumetric, and gravimetric techniques, the CO$_2$-coal isotherm is calculated from changes in pressure, volume, or mass. These techniques treat coal as a rigid solid. In some cases coal may be treated as a polymer-like network that can be affected by the gas or solvent in which it is in contact.$^3$ If the coal volume changed during the isotherm measurement at high pressures, the calculated isotherm from manometric, volumetric, and gravimetric techniques may be in error.

Factors that may cause the coal volume to change upon exposure to CO$_2$ require experimental investigation. The direct interaction of CO$_2$ and coal is poorly defined, especially at the higher pressures.$^{12}$ Research groups are investigating the possibility of multi-layer CO$_2$ sorption at the higher pressures.$^3$,$^{13}$ Coal swelling and shrinkage is a known phenomenon.$^{3}$,$^{13}$-$^{20}$ Reucroft reported that coal swells by 4.18% at 1.5 MPa and that lower rank coals swell more than higher rank coals.$^{16}$,$^{17}$ Ozdemir et al. incorporated a swelling term in their curve fit model in order to account for swelling when calculating the isotherm.$^{13}$ Coal structural changes have also been reported.$^{21}$-$^{24}$ Recently, the solubility of CO$_2$ in water was shown to affect the final isotherm calculation by over-estimating the CO$_2$ storage capacity in coals.$^{25}$ This result is in contrast to work published by Hall et al in that they find no significant effect on the sorption with water content values above the equilibrium water content.$^{26}$ Mavor et al discusses the uncertainties associated with isotherm measurements and stresses the importance accurate pressure and temperature measurements.$^{27}$,$^{28}$ Recent review articles outline ten hypotheses on how CO$_2$ interacts with a coalseam and suggests that experimental work is needed to verify these propositions, especially for high-pressure CO$_2$-coal interactions.$^3$,$^{29}$ Another selective review article focuses on how CO$_2$ dissolves in coals and changes the coals’ physical structures, properties, and behaviors.$^{30}$ However, there are no reported studies that measure coal swelling, shrinkage, or structure changes while conducting high-pressure CO$_2$-coal isotherm measurements using traditional techniques such as manometric, volumetric or gravimetric methods.

Table 1

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References


