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Physical properties of selected block Argonne Premium bituminous coal related to CO_2, CH_4, and N_2 adsorption

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ABSTRACT

CO_2, CH_4, and N_2 adsorption and gas-induced swelling were quantified for block Blind Canyon, Pittsburgh #8 and Pocahontas Argonne Premium coals that were dried and structurally relaxed at 75 °C in vacuum. Strain measurements were made perpendicular and parallel to the bedding plane on ~7×7×7 mm^3 coal blocks and gravimetric sorption measurements were obtained simultaneously on companion coal blocks exposed to the same gaseous environment. The adsorption amount and strain were determined after equilibration at $P \leq 1.8$ MPa. There is a strong non-linear correlation between strain and the quantity of gas adsorbed and the results for all gases and coals studied follow a common pattern. The dependence of the coal matrix shrinkage/swelling coefficient (C_{gc}) on the type and quantity of gas adsorbed is seen by plotting the ratio between the strain and the adsorbate concentration against the adsorbate concentration. In general, C_{gc} increases with increasing adsorbate concentration over the range of ~0.1 to 1.4 mmol/g. Results from the dried block coals are compared to CO_2 experiments using native coals with an inherent level of moisture as received. The amount of CO_2 adsorbed using native coals (assuming no displacement of H_2O by CO_2) is significantly less than the dried coals. The gas-induced strain (S) and adsorption amount (M) were measured as a function of time following step changes in CO_2, CH_4, and N_2 pressure from vacuum to 1.8 MPa. An empirical diffusion equation was applied to the kinetic data to obtain the exponent (n) for time dependence for each experiment. The data for all coals were pooled and the exponent (n) evaluated using an ANOVA statistical analysis method. Values for (n) near 0.5 were found to be independent on the coal, the gas or type of measurement (e.g., parallel strain, perpendicular strain, and gas uptake). These data support the use of a Fickian diffusion model framework for kinetic analysis. The kinetic constant k was determined using a unipore diffusion model for each experiment and the data were pooled for ANOVA analysis. For dry coal, statistically significant differences for k were found for the gases (CO_2>N_2>CH_4) and coals (Pocahontas> Blind Canyon>Pittsburgh #8) but not for the method of the kinetic measurement (e.g., strain or gas uptake). For Blind Canyon and Pittsburgh #8 coal, the rate of CO_2 adsorption and gas-induced strain for dry coal was significantly greater than that of the corresponding native coal. For Pocahontas coal the rates of CO_2 adsorption and gas-induced strain for dry and native coal were indistinguishable and may be related to its low native moisture and minimal amount of created porosity upon drying.

1. Introduction

The prospect of storing CO_2 in unmineable coalbeds with the potential for enhanced production of natural gas has renewed interest in quantifying the basics of gas–coal interactions (White et al., 2003, 2005; Reeves, 2003). Currently there are gaps in our fundamental understanding of coal interactions with adsorbates such as the kinetics of gas transport through the coal matrix and the swelling/shrinkage response of coal as adsorbates are introduced and removed. Native coal, defined here as coal possessing its inherent moisture as received with minimal handling and treatment, is considered to be in a strained glassy state with the potential for structural rearrangements upon exposure to CO_2 (Larsen, 2004; Goodman et al., 2005, 2006). Initial exposure of briefly dried coal to CO_2 leads to physical structural rearrangement (Goodman et al., 2006). Significant differences in acoustic emission signal between the first and subsequent adsorption cycles provides further evidence of structural rearrangements during the first CO_2 adsorption cycle for dried coal (Majewska and Zietek, 2007).

Water is an integral part of the coal physical structure and the loss of moisture from coal results in significant shrinkage (Suuberg et al., 1993; Kelemen et al., 2006a); however, these studies were conducted using powdered coal and some of the shrinkage may be associated with better packing of the coal particles induced by shrinkage of the coal matrix upon drying. Adsorption studies have been conducted using moisture-equilibrated coal (Clarkson and Bustin 1999a,b; Kross et al., 2002; Harpalani et al., 2006; Goodman et al., 2007), but there is

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little information about the effect of moisture on the strain response of coal to gas sorption (Ceglarska-Stefanska and Czaplinski, 1992). The effect of native moisture on the kinetics and amount of gas sorption requires additional investigation. Dried coal was used in many adsorption studies. Adsorption isotherms for CO_2 (Busch et al., 2003, 2007; Ozdemir et al., 2004; Goodman et al., 2004) and CH_4 (Busch et al., 2003) were measured for selected well-defined dry powder bituminous Argonne Premium coals. Companion strain measurements were made for selected Argonne Premium bituminous coals for CO_2 and CH_4 at low pressure ($P \leq 1.8$ MPa) that show a non-linear correlation between strain and the quantity of gas adsorbed (Kelemen and Kwiatek, 2007; Kelemen et al., 2006b). The present work extends these adsorption and strain measurements to blocks of native Blind Canyon, Pittsburgh #8 and Pocahontas Argonne Premium coal.

Many kinetics studies dealing with CO_2 and CH_4 adsorption/desorption on coal have been interpreted within a Fickian diffusion framework including unipore (Kissell and Bielicki, 1972; Bielicki et al., 1972; Nandi and Walker, 1975; Smith and Williams, 1984; Marecka and Mianoeski, 1998; Clarkson and Bustin, 1999b; Busch et al., 2004), bi-dispersive pore (Smith and Williams, 1982), and refined bi-dispersive pore (Clarkson and Bustin, 1999b) models. The kinetics of CO_2 swelling has been interpreted as anomalous diffusion (Case II) (Mazumder et al., 2006). Time dependent strain data induced by CO_2 adsorption on coal have been reported but not kinetically interpreted for powdered coal (Reucroft and Patel, 1986; Reucroft and Sethuraman, 1987; Walker et al., 1988) and coal blocks (St. George and Barakat, 2001; Robertson and Christiansen, 2004; Robertson, 2005; Majewska and Zietek, 2007; Day et al., 2008). The present work considers the kinetics of CO_2, CH_4, and N_2 gas-induced strain using blocks of dry Blind Canyon, Pittsburgh #8 and Pocahontas Argonne Premium coal at 30 °C. Measurements also were made using CO_2 and native coal at 30 °C and dry coal at 75 °C

2. Experimental

2.1. Sample preparation

Powder and large pieces (~100 cm^3) of Blind Canyon, Pittsburgh #8 and Pocahontas coals were obtained from the Argonne Premium Coal Sample program (Vorres, 1990). The large coal pieces were stored in nitrogen flushed canisters containing water saturated paper towels prior to sample preparation. Samples referred to as dry coals were pretreated prior to study. The coal lumps were roughly cut into ~7 mm^3 block samples. The length, height and width of the blocks were 7 ± 2 mm. The coals were extensively dried ($T < 75$ °C) for up to 3 days using an oil-free turbo-molecular pump to a pressure of 1×10^{-8} Torr measured near the inlet to the pump. Samples also were exposed to CO_2 at $P \leq 1.8$ MPa and further evacuated prior to kinetic studies. Once dried and exposed to CO_2 the samples gave repeatable results toward gas-induced strain and the adsorption kinetics.

In contrast, native coals possessing their inherent as received moisture were given minimal treatment and each sample was used for only one gas sorption experiment. Sample preparation involved transferring coal into a glove bag containing water saturated paper towels where they were roughly cut into ~7 mm^3 blocks. These cut samples were immediately transferred into the gas sorption and dilatometer analysis units that were connected via a common vacuum and gas delivery manifold. A H_2O source, maintained at 16 °C, was opened during pumping using an oil-free turbo-molecular pump (Pfeiffer). In this way, N_2, O_2 and other gases from air were removed while maintaining a background H_2O gas pressure of 14 Torr. After pumping ~10 min, the samples were further exposed to H_2O at 14 Torr until a stable sample weight and dilatometer output reading were observed prior to starting an adsorption experiment.

2.2. Gas sorption and strain measurements

Gravimetric gas sorption measurements were made using a Hiden IGA gas sorption system. One coal block was placed into a quartz sample bulb and suspended from a thermostated microbalance. Swelling and shrinkage measurements of coal were made using a pressurized dilatometer unit built by Theta Industries. The dilatometer was coupled to the gravimetric sorption apparatus by the vacuum and gas dosing system. Coal samples were treated identically in the dilatometer gravimetric sorption units. The dilatometer sample holder was a 20 mm high by 8 mm diameter open top quartz cylinder. Two ~7 mm^3 samples were stacked together in the dilatometer with a quartz disk placed on top. A probe rod was positioned on top of the quartz disk with an applied mechanical pressure of 25 g cm^{-2}. The sample in the dilatometer unit was sealed and evacuated simultaneously with the sample in the gravimetric gas sorption unit. The adsorption amount and gas-induced strain were determined following equilibration at 1.8 MPa.

For kinetic measurements, gas was manually introduced into the gravimetric gas sorption and the dilatometer units by a metering valve. A pressure rise from vacuum to 1.8 MPa was achieved within 3 minutes and then held constant during the course of the experiment. Gravimetric and dilatometer output were continuously recorded and converted into molar adsorption amounts per coal on a dry ash free (daf) basis and linear strain (expansion/contraction) as parts per million (ppm), respectively. Adsorption and gas-induced strain were measured for CO_2, CH_4 and N_2 at 30 °C and repeated several times for each coal using freshly prepared samples. Gas-induced strain was measured parallel and perpendicular to the bedding plane in separate experiments. Following each adsorption experiment the sample was evacuated ($T \leq 75$ °C) for a time period sufficient to return the sample to its starting weight and sample size. Analysis of variance (ANOVA) was performed using Statview statistical software. The length of each experiment varied depending on the gas, coal and coal treatment with a maximum length of ~2 months.

3. Results and discussion

3.1. Thermal expansion coefficient

Samples were linearly heated in vacuum from 30 to 75 °C and the thermal expansion of coal was quantified. The linear thermal expansion coefficient (α) definition is:

$$\alpha = 1/l(\mathrm{d}l/\mathrm{d}T)_P \left[K^{-1}\right] \quad (1)$$

Where l is length, T is temperature and P is pressure (Van Krevelen, 1993). The results for α are shown in Table 1 with the 95% confidence intervals. The thermal expansion coefficients measured parallel and perpendicular to the bedding plane are statistically indistinguishable for the Blind Canyon (80.7 wt.% C) and Pittsburgh #8 (83.2 wt.% C) coals. For the Pocahontas (91.1 wt.% C) coal, the thermal expansion coefficient was greater measured perpendicular to the bedding plane. These results are in excellent agreement with earlier work showing that the linear

Table 1
Linear thermal expansion coefficient measured parallel and perpendicular to the bedding plane

	Thermal expansion coefficient (m/m K × 10^{-6})	
	Parallel	Perpendicular
Pocahontas	36.4 (±1.9)	40.9 (±1.5)
Pittsburgh #8	38.1 (±1.9)	37.2 (±1.9)
Blind Canyon	40.5 (±1.9)	40.5 (±1.9)

Variance describes the 95% confidence interval.