Physical Properties of Dry Block Argonne Premium Bituminous Coal Related to CO₂, CH₄, and N₂ Adsorption

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Abstract

CO₂, CH₄, and N₂ adsorption and swelling were quantified for dry Blind Canyon, Pittsburgh #8 and Pocahontas Argonne Premium coals and their kinetics were analyzed. Strain measurements were made perpendicular and parallel to the bedding plane on ~7x7x7 mm³ 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 P<1.8 MPa. There is a strong non-linear correlation between strain and the quantity of gas adsorbed. The dependence of the coal matrix shrinkage/swelling coefficient (Cgc) on both the type and quantity of gas adsorbed is seen by plotting the ratio between the strain and the adsorbate concentration against the adsorbate concentration. Cgc increases with increasing CO₂ and CH₄ concentration measured both parallel and perpendicular to the bedding plane for a given coal and the Cgc data for CH₄ and CO₂ overlap. The gas-induced strain (S) and adsorption amount (M) were measured as a function of time at 30 °C following step changes in CO₂, CH₄, and N₂ 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) of 0.51 ± 0.02, 0.53 ± 0.02, 0.53 ± 0.02 were determined for CO₂, CH₄, and N₂ respectively. These data support the use of a Fickian diffusion model framework for analyzing these kinetic data. The kinetic constant k was determined using a unipore diffusion model for each experiment and the data were pooled for ANOVA analysis. Statistically significant differences for k were found among the gases (CO₂>N₂>CH₄) and coals (Pocahontas>Blind Canyon>Pittsburgh #8) but not for the method of the kinetic measurement (e.g. strain, gas uptake).

1. Introduction

The prospect of storing CO₂ in unmineable coalbeds with the potential for enhanced production of natural gas has renewed interest in quantifying the basics of gas-coal interactions [1-3]. Currently there are gaps in our fundamental understanding about aspects of coal interactions with adsorbates. Among these are the kinetics of gas transport through the coal matrix and swelling/shrinkage response of coal to adsorbates that are introduced and removed from coal. Native coal is considered to be in a strained glassy state with the potential for structural rearrangements upon exposure to CO₂ [4-7]. Initial exposure of briefly dried coal to CO₂ lead to physical structural rearrangement [6]. Water is an integral part of coal physical structure and moisture loss from coal results in significant shrinkage [8-11]. This shrinkage is only partially reversible [9, 10]. Initial exposure of briefly dried coal to CO₂ lead to physical structural rearrangement [7]. Adsorption studies have been conducted using moisture equilibrated coal [12-17] but there is little information about the effect of moisture on the strain response of coal to gas sorption [18]. The effects of native moisture on the kinetics and amount of gas sorption require additional investigation. Many adsorption studies have been conducted using dried coal. CO₂ [19-21] and CH₄ [19] adsorption isotherms on well-defined dry powder bituminous Argonne Premium coals have been measured. Once coal is dried it responds reproducibly toward CO₂ and CH₄ adsorption over many adsorption and desorption cycles [22]. Recently companion strain measurements were made for some of the Argonne Premium bituminous dry powder coal samples at P≤0.6 MPa) and found a non-linear correlation between strain and the quantity of gas.
adsorbed. [22]. The present work extends these adsorption and strain measurements to blocks of dry Blind Canyon, Pittsburgh #8 and Pocahontas Argonne Premium coal.

There have been many kinetics studies dealing with CO₂ and CH₄ adsorption/desorption on coal that have been interpreted within a Fickian diffusion model framework [13, 23-29]. Unipore [13, 24-28], bi-dispersive pore [23], and refined bi-dispersive pore [13] models have been used. The kinetics of CO₂ swelling has been interpreted as anomalous diffusion (Case II) [30]. Time dependent strain data for CO₂ adsorption on coal have been reported but not kinetically interpreted [31-36]. The present work considers the kinetics of CO₂, CH₄, and N₂ gas-induced strain using blocks of dry Blind Canyon, Pittsburgh #8 and Pocahontas Argonne Premium coal. These kinetic studies serve as a foundation for future experiments conducted with native coal in the presence of moisture.

2. Experimental

Large pieces of Blind Canyon, Pittsburgh #8 and Pocahontas coals were obtained from the Argonne Premium Coal Sample program [37]. The coal lumps were roughly cut into ~7x7x7 mm³ 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 three days using a dry turbo-molecular pump to a pressure of 1x10⁻⁸ Torr measured near the inlet to the pump. Samples were also exposed to CO₂ at P≤1.8 MPa and further evacuated prior to kinetic studies. Once dried and exposed to CO₂ the samples gave repeatable results toward gas-induced strain and the adsorption kinetics.

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 built by Theta Industries. The dilatometer was coupled to the gravimetric sorption apparatus by way of 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 ~7x7x7 mm³ 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 pressures from 0.1 to 1.8 MPa.

For kinetic measurements, gas was manually introduced into the gravimetric gas sorption and the dilatometer units by way of a metering valve. A pressure rise from vacuum to 1.8 MPa was achieved within 3 minutes. The pressure was then held constant during the course of the experiment. The gravimetric and dilatometer output were continuously recorded. These data were converted into molar adsorption amounts per coal on a dry ash free (daf) basis and expansion/contraction as parts per million (ppm) respectively. Adsorption and gas induced strain were measured for CO₂, CH₄ and N₂ at 30 °C and repeated several times for each coal. Gas-induced strain was measured parallel and perpendicular to the bedding plane in separate experiments. Following each adsorption experiment the sample was evacuated (T≤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.

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. These results are shown in Table 1 with the 95% confidence interval. The thermal expansion coefficients were statistically indistinguishable measured parallel and perpendicular to the bedding plane for Blind Canyon (80.7 wt% C) and Pittsburgh #8 (83.2 wt% C) coal. For Pocahontas (91.1 wt% C) the thermal expansion coefficient was greater measured perpendicular to the bedding plane. These results are in excellent agreement with earlier work showing the linear thermal expansion coefficient is anisotropic and greater in the axis perpendicular to the bedding only for coal greater than ~90 wt% C [38]. The range for bituminous coal <90 wt% C was 36.5 to 39.5 m/m.Kx10⁻⁶ [38].

3.2 Gas-Induced Strain. The adsorption amount and strain were determined following equilibration P≤1.8 MPa. Figure 1 shows the results for strain measured parallel (left) and perpendicular (right) to the bedding plane. For all coals the amounts of CO₂, CH₄, and N₂ adsorbed are comparable to those found with powdered samples at constant pressure [22]. There is a strong correlation between the quantity of gas adsorbed and strain. The dependence of the coal matrix shrinkage/swelling coefficient (Cgc) on both the type and quantity of gas adsorbed
is found by plotting the ratio between the strain and the adsorbate concentration against the adsorbate concentration (Figure 2). \( C_{gc} \) increases with increasing CO2 and CH4 concentration measured both parallel and perpendicular to the bedding plane for a given coal. The \( C_{gc} \) data for CH4 and CO2 overlap. \( C_{gc} \) data for Blind Canyon and Pittsburgh #8 coal are indistinguishable, furthermore \( C_{gc} \) data is comparable measured either parallel or perpendicular to the bedding plane. In contrast, \( C_{gc} \) data for Pocahontas coal fall below the data for these coals and \( C_{gc} \) data measured perpendicular to the bedding plane appear slightly above \( C_{gc} \) data measured parallel to the bedding plane. Pocahontas coal exhibits anisotropic behavior in both gas-induced strain and thermal expansion. The fact that all plots in Figure 2 have a non-zero slope indicates that strain is non-linearly correlated with the quantity of gas adsorbed.

### 3.3 Kinetics for Adsorption and Gas-induced Strain

Figure 3 shows typical plots of strain (measured perpendicular to the bedding plane) versus time and adsorption amount versus time following a step change in pressure. Dry Pocahontas coal at 30 °C was exposed to CO2 at 1.8 MPa and followed as a function of time. After approximately 1100 minutes the samples were depressurized and evacuated. Qualitatively, both expansion and adsorption are reversed by evacuation and the appearances of the curves are inverse to the shapes produced during pressurization. Kinetic data for desorption and shrinkage were generally not obtained. The rate of desorption and shrinkage was accelerated by raising the sample temperature to 75 °C until samples returned to their starting weight and sample size.

Figure 4 shows the initial swelling and strain (measured perpendicular to the bedding plane) versus time and initial adsorption amount versus time corresponding to the experiment shown in Figure 3. At 10 minutes into the experiment CO2 was manually introduced into the gravimetric gas sorption and the dilatometer units. The final pressure of 1.8 MPa was achieved at roughly 13 minutes into the experiment (~3 minutes from the start of gas introduction). The start time \( (T_0) \) for kinetic analysis lies between the start and end of pressurization and is set in the middle for the example in given in Figure 4. During pressurization sample contraction occurs due to increasing hydrostatic pressure while sample expansion occurs due to the adsorption of gas [34]. In separate experiments, pressurization with helium to 1.8 MPa showed a contraction of roughly 100 ppm for all coals studied. The effect of hydrostatic pressure has been shown for coal [34] and this effect will complicate kinetic analysis of gas induced strain. In our studies expansion is observed throughout pressurization with CO2 and this indicates that gas induced expansion masks the contraction due to increasing hydrostatic pressure. During pressurization with CH4 and N2 contraction is initially observed due to less and slower uptake of these gases relative to CO2. In these cases \( T_0 \) coincides generally with the onset of expansion following initial contraction.

The amount of gas uptake \((M)\) and gas induced strain \((S)\) for coal follow respectively the general equations

\[
\frac{M}{M_{\text{max}}} = k t^n \quad \text{and} \quad \frac{S}{S_{\text{max}}} = k t^n
\]

A plot log \( M/M_{\text{max}} \) vs. log time \((t)\) has a slope \( n \) and is often diagnostic of the diffusion mechanism (Fickian, Case II, anomalous etc.) [30]. Figure 5 shows plots of log \( (S/S_{\text{max}}) \) versus log (time) and log \( (M/M_{\text{max}}) \) versus log (time) for CO2 adsorption at 1.8 MPa and 30 °C for dry Pocahontas coal. These data yield values for \( n \) of 0.48 and 0.52. The data for all coals and gases were pooled and the exponent \( (n) \) evaluated using an ANOVA statistical analysis method. The results of the analysis are shown in Table 2. Values for \( (n) \) of 0.51 ± 0.02, 0.53 ± 0.02, 0.53 ± 0.02 were determined for CO2, CH4, and N2 respectively. These results are not significantly different. No significant differences were found among coals and type of measurement. These data support use of a Fickian diffusion model framework for analyzing these kinetic data.

The unipore diffusion model is simple and has been applied to coal for kinetic analysis of CO2 and CH4 adsorption and desorption [23-29]. It assumes a square root of time dependence and that the coal is interspersed with non-connecting cylindrical pores of a single radius. For small times \((t)\) the simplification of the analytical solution of the partial differential equation of Fick's second law results for the amount of gas uptake \((M)\) and gas induced strain \((S)\) respectively [23-28]:

\[
\frac{M}{M_{\text{max}}} = k(t)^{1/2} = 6(D_{et}/\pi)^{1/2} \quad \text{and} \quad \frac{S}{S_{\text{max}}} k(t)^{1/2} = 6(D_{et}/\pi)^{1/2}
\]

By plotting the fraction of adsorbed amount (or fraction of strain) versus the square root of time the kinetic constant \( k \) and the effective diffusivity \( D_{et} \) may be calculated from the slope in the initial uptake region (<50%). The
over simplifications of the unipore model have been discussed in relation to bi-dispersive pore [23], and refined bi-dispersive pore [13] and other models [23]. Nevertheless, it may be adequate for some coals [13]

The left side of Figure 6 shows a plot of S/S_{max} versus the square root of time and on the right is a plot of M./M_{max} versus the square root of time for CO_2 adsorption at 1.8 MPa and 30 °C on Pocahontas coal. The kinetic constant (k) based on adsorption amount and gas induced strain were 2.4x10^{-2} and 1.7x10^{-2} sec^{-1} respectively for this individual experiment. The data for all coals and gases were pooled and the results for k were analyzed using the ANOVA method of analysis. Table 3 expresses the findings as log k for accurate representation of the 95% confidence intervals. Statistically significant differences for log k were found among 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 vs. gas uptake). Table 3 also lists the effective diffusion parameter D_e calculated using equation (2). Consequently the dependencies of k are reflected in the D_e values.

Summary

1) The thermal expansion coefficients were statistically indistinguishable measured parallel and perpendicular to the bedding plane for Blind Canyon and Pittsburgh #8 coal. For Pocahontas coal the thermal expansion coefficient was greater measured perpendicular to the bedding plane.

2) There is a strong non-linear correlation between the quantity of gas adsorbed and strain. The dependence of the coal matrix shrinkage/swelling coefficient (C_{gc}) on both the type and quantity of gas adsorbed is seen by plotting the ratio between the strain and the adsorbate concentration against the adsorbate concentration. C_{gc} increases with increasing CO_2 and CH_4 concentration measured both parallel and perpendicular to the bedding plane for a given coal and the C_{gc} data for CH_4 and CO_2 overlap.

3) Data from this study support the use of a Fickian diffusion model framework for analyzing these kinetic data. The gas-induced strain (S) and adsorption amount (M) were measured as a function of time at 30 °C 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) of 0.51 ± 0.02, 0.53 ± 0.02, 0.53 ± 0.02 were determined for CO_2, CH_4, and N_2 respectively.

4) The kinetic constant k was determined using a unipore diffusion model for each experiment and the data was pooled for ANOVA analysis. Statistically significant differences for k were found among 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 vs. gas uptake).

Acknowledgements

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References


3) Reeves, S. R., Oil and Gas Journal, 2003, 14, 49.


### Table 1. Thermal expansion coefficient measured parallel and perpendicular to the bedding plane

<table>
<thead>
<tr>
<th></th>
<th>Thermal expansion coefficient (m/m.K x10&lt;sup&gt;-6&lt;/sup&gt;)</th>
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<tr>
<td></td>
<td>Parallel</td>
<td>Perpendicular</td>
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<tr>
<td>Pocahontas</td>
<td>36.4 (± 1.9)</td>
<td>40.9 (± 1.5)</td>
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<tr>
<td>Pittsburgh #8</td>
<td>38.1 (± 1.9)</td>
<td>37.2 (± 1.9)</td>
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<td>Blind Canyon</td>
<td>40.5 (± 1.9)</td>
<td>40.5 (± 1.9)</td>
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### Table 2. Time exponent (n) factor analysis

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<th># of Measurements</th>
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<td></td>
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<td>Pocahontas</td>
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<tr>
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<td>0.02</td>
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<tr>
<td>Blind Canyon</td>
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<td>0.02</td>
<td>18</td>
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<tr>
<td>Gas</td>
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<td></td>
<td></td>
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<tr>
<td>Carbon Dioxide</td>
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<td>0.01</td>
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<tr>
<td>Methane</td>
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<td>Strain parallel</td>
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<tr>
<td>Strain perpendicular</td>
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<td>0.02</td>
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<tr>
<td>Gas adsorption amount</td>
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<td>0.02</td>
<td>19</td>
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### Table 3. Diffusion constant determined for a 1.8 MPa final step pressure

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<th>Coal</th>
<th>Gas</th>
<th>D&lt;sub&gt;e&lt;/sub&gt; (sec&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>log k (sec&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>ANOVA ±95%</th>
<th>Number of Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pocahontas</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.5 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
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<td>0.076</td>
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<tr>
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<td>0.071</td>
<td>7</td>
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<tr>
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<td>5.2 x 10&lt;sup&gt;-6&lt;/sup&gt;</td>
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<td>0.055</td>
<td>10</td>
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<td>-2.525</td>
<td>0.057</td>
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Figure 1. Relationship between strain versus adsorbate concentration for CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2}. (Left) strain parallel to the bedding plane and (right) perpendicular to the bedding plane.
Figure 2. Plots of the strain divided by adsorbate concentration versus adsorbate concentration (left) parallel and (right) perpendicular to the bedding plane for Blind Canyon coal.
Figure 3. Plot of swelling measured perpendicular to the bedding plane (left) and adsorption amount (right) for CO$_2$ adsorption at 1.8 MPa and 30 °C for on Pocahontas coal. The start of pressurization occurred at 10 min and the start of evacuation at 1100 min.

Figure 4. Plot of initial swelling measured perpendicular to the bedding plane (left) and adsorption amount (right) for CO$_2$ adsorption at 1.8 MPa and 30 °C for on Pocahontas coal. The start of pressurization occurred at 10 min and 1.8 MPa was achieved at 13 min.
Figure 5. (Left) plot of \( \log(\frac{S}{S_{\text{max}}}) \) versus \( \log(\text{time}) \) and (right) \( \log(\frac{M}{M_{\text{max}}}) \) versus \( \log(\text{time}) \) for CO\(_2\) adsorption at 1.8 MPa and 30 °C for Pocahontas coal.

Figure 6. (Left) plot of \( \frac{S}{S_{\text{max}}} \) versus the square root of time and (right) \( \frac{M}{M_{\text{max}}} \) versus the square root of time for CO\(_2\) adsorption at 1.8 MPa and 30 °C for Pocahontas coal.