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# Methane/CO<sub>2</sub> Sorption Modeling for Coalbed Methane Production and CO<sub>2</sub> Sequestration

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A thorough study of the sorption behavior of coals to methane and carbon dioxide (CO<sub>2</sub>) is critical for carbon sequestration in coal seams and enhanced coalbed methane recovery. This paper discusses the results of an *ad/de*-sorption study of methane and CO<sub>2</sub>, in single gas environment, on a set of coal samples taken from the San Juan and Illinois Basins. The results indicate that, under similar temperature and pressure conditions, coals exhibit higher affinity to CO<sub>2</sub> as compared to methane and that the preferential sorption ratio varies between 2:1 and 4:1. Furthermore, the experimental data were modeled using Langmuir, BET, and Dubinin–Polanyi equations. The accuracy of the models in quantifying coal–gas sorption was compared using an error analysis technique. The Dubinin–Radushkevich equation failed to model the coal–gas sorption behavior satisfactorily. For methane, Langmuir, BET, and Dubinin–Astakhov (D-A) equations all performed satisfactorily within comparable accuracy. However, for CO<sub>2</sub>, the performance of the D-A equation was found to be significantly better than the other two. Overall, the D-A equation fitted the experimental sorption data the best, followed by the Langmuir and BET equations. Since the D-A equation is capable of deriving isotherms for any temperature using a single isotherm, thus providing added flexibility to model the temperature variation due to injection/depletion, this is the recommended model to use.

## Introduction

The prospects of geological sequestration and storage of CO<sub>2</sub> as a means to reduce global emission of this greenhouse gas has recently attracted worldwide attention among researchers as well as different regulatory and governmental agencies. Possible sites for geological sequestration of CO<sub>2</sub> include unminable coal seams, depleted oil and gas reservoirs, abandoned and sealed mines, saline aquifers, oceans, etc. The injection of CO<sub>2</sub> in gas-bearing coal seams has the added advantage since it can also result in a significant improvement in coalbed methane (CBM) recovery. The revenues from this enhanced coalbed methane recovery (ECBM) process can, to a large extent, offset the cost of CO<sub>2</sub> sequestration. Understanding and quantifying the coal–gas interaction is, therefore, an important area of research.

For evaluation of gas deliverability from CBM or ECBM operations, it is essential to study the complete sorption behavior of methane and CO<sub>2</sub> on coals. It is generally accepted that coal seams can adsorb more CO<sub>2</sub> than methane and, under competitive sorption scenario, CO<sub>2</sub> is preferentially adsorbed in the coal structure over methane.<sup>1,2</sup> A preferential adsorption ratio of CO<sub>2</sub> to methane of 2:1 has been widely reported in the literature.<sup>2–4</sup> However, the results from a few recent studies indicate widely

varying ratios, all the way from 10:1 for low rank coals to less than 2:1 in low and medium volatile bituminous coals.<sup>5–7</sup> Although the adsorption of gases on coal is believed to be reversible in nature, some recent studies have suggested the existence of a hysteresis during adsorption–desorption cycles.<sup>6,8,9</sup> The differential sorption behavior of coals to gases such as CO<sub>2</sub> and methane has been reported, based on rank, moisture content, maceral content, temperature, etc. Moisture-equilibrated coal samples have generally shown an increase in adsorption capacity with increasing rank, while for dry coals, the reverse trend has also been reported.<sup>6,10–12</sup> The difference in rank dependency of

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dry and moist coals may be due to the increasing affinity of lower rank coals to water.<sup>13</sup> However, Bustin and Clarkson<sup>14</sup> observed that, on a global scale, there are no statistically significant linear or nonlinear correlations between rank and adsorption capacity. Moisture content plays a very important role in gas adsorption. The adsorption capacity of coal decreases with increasing moisture content and has been attributed to a reduction in pore sizes due to water adsorption or swelling of coal.<sup>10,15,16</sup> Various studies have reported an increase in gas sorption capacity with increasing vitrinite content, suggesting a prominent role of this maceral in coal composition, especially in higher rank coals.<sup>16–19</sup> Finally, studies have shown a negative influence of temperature on the sorption capacity of coals. Higher temperatures provide more favorable condition for the gases to be in free state rather than sorbed state.<sup>10,11,14</sup> All of the above factors contribute to the variability of sorption behavior of coals, making it important to study this on a case by case basis.

The gas retention capacity of a reservoir at in situ temperature and pressure conditions can be estimated from a sorption isotherm. Detailed knowledge of the sorption isotherms for methane and CO<sub>2</sub> is a required input parameter for methane production simulations from CBM or ECBM operations. This information is also needed to estimate the coal seam CO<sub>2</sub> storage capacity and the overall economics of the entire process. Gas sorption isotherms in coal are most often modeled using the Langmuir approach, as it usually exhibits excellent correlation with the experimental sorption data. However, a few other models such as the loading ratio correlation (LRC); Brunauer, Emmett, and Teller (BET); Dubinin–Polyanyi (D-P); and two-dimensional equation-of-state models have also been used to correlate single-component experimental sorption data.<sup>11,20–22</sup> Hall et al.<sup>23</sup> observed that various models, such as two-dimensional equation of state, Langmuir, and LRC, performed well for pure gas sorption. Similar observations were made by Gasem et al.<sup>24</sup> Clarkson et al.<sup>25</sup> showed that, for 13 Australian coals tested, both D-P and BET equations performed better than the Langmuir equation for high-pressure methane and low-

pressure CO<sub>2</sub> sorption. All these studies indicate that the modeling exercise should be continued further to evaluate the relative accuracy of various models in predicting the sorption behavior of coals.

This study was aimed at examining the complete ad/desorption behavior of several U.S. coals for pure gas sorption. The sorption isotherms of methane and CO<sub>2</sub> were established for various coal samples in the laboratory. The sorbed coals were then desorbed to check for any hysteresis. The results of the sorption analysis were utilized for isotherm modeling using the Langmuir, BET, and D-P equations. Finally, a statistical analysis was performed to determine which of the models fits the experimental sorption data the best. This paper provides a brief review of these models, followed by details of the experimental work and results, and the findings of the modeling exercise.

### Sorption Isotherm Models

**Langmuir Model.** The most commonly applied isotherm model for adsorption of gases on solids, the Langmuir model, is based on the concept of dynamic equilibrium between the rates of adsorption of gas on a solid and desorption from the solid surface.<sup>26</sup> It is assumed that the adsorption is restricted to a single layer. The equation for the Langmuir isotherm is given as

$$\frac{V}{V_L} = \frac{bP}{1 + bP} \quad (1)$$

where  $V$  is the adsorbed volume at equilibrium pressure  $P$ ,  $b$  is a constant known as the pressure constant,  $V_L$  is the maximum monolayer capacity, also known as the Langmuir volume. At high pressures, all the sites available on the adsorbent are occupied by the adsorbate. Hence, beyond a certain pressure, the adsorbent can adsorb no more adsorbate. This pressure is known as the saturation pressure, and the sorbed volume corresponding to the saturation pressure is the Langmuir volume.

At half-coverage, that is, when the sorbed volume is half of the Langmuir volume, the pressure value is referred to as the Langmuir pressure,  $P_L$ . The above equation can be rewritten in terms of  $V_L$  and  $P_L$ , the commonly used form of the Langmuir isotherm, as:

$$\frac{V}{V_L} = \frac{P}{P + P_L} \quad (2)$$

where  $P_L$  is the inverse of  $b$ .

The Langmuir equation correctly expresses the adsorption behavior for a wide range of pressures. The pressure constant is a measure of the isotherm curvature. The larger the value of  $b$ , the greater is the initial slope of the isotherm.  $V_L$  and  $P_L$  are important parameters for economic assessment of CBM resources. While  $V_L$  is the maximum sorption capacity of the coal, which is the value of gas content at very high pressures,  $P_L$  represents the pressure to which the coalbed reservoir has to be depleted to obtain a 50% recovery.

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**BET Model.** The BET model is an extension of the Langmuir model that accounts for the formation of a multilayer. Originally, the model was developed for interpretation of Type II and the reversible part of Type IV isotherms. However, it was later observed that, under certain conditions, it can describe other types of isotherms as well.<sup>27</sup> The BET isotherm equation is expressed as

$$\frac{1}{V(P_0/P - 1)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{P}{P_0} \quad (3)$$

where  $V_m$  is the monolayer volume,  $C$  is a constant,  $P_0$  is the saturation vapor pressure (at a given temperature, the maximum partial pressure that the vapor molecules would exert if the air was saturated with the vapor only), and the remaining variables have their usual connotations. The larger the value of  $C$ , the earlier that the multilayer formation occur.

The BET equation is used almost universally because of its ease of use, its definitiveness, and its ability to accommodate each of the five isotherm types. Although the BET equation rarely matches with the experimental isotherm exactly over its entire range of relative pressures, it is a useful tool in a qualitative sense because it does provide a theoretical foundation for the various isotherm shapes.<sup>27</sup> The range of validity for the BET model is usually between relative pressure values ( $P/P_0$ ) of 0.05–0.35.<sup>28</sup>

**Models Based on Polanyi's Potential Theory.** Similar to the gravitational potential around a planet, for multilayer adsorption, Polanyi assumed the existence of a potential field around the surface of the solid into which each adsorbed gas molecule falls. The surface force field can be represented by equipotential contours, where the space between each set of equipotential surfaces corresponds to a definite adsorbed volume. The adsorption potential is defined as the work done per mole of adsorbate in transferring molecules from the gaseous state to the adsorbed state and represents the work done by the temperature-independent dispersion forces. The potential curve is, therefore, not dependent on temperature and is a function of only the volume enclosed by an equipotential surface surrounding the adsorbent surface. The sorbed volume becomes a function of the adsorption potential,  $A$ , represented as

$$V = f(A) \quad (4)$$

The above relationship is characteristic of a gas–solid system and is known as the characteristic curve.<sup>29</sup> Assuming the adsorbate to behave as an ideal gas, the adsorption potential is given as

$$A = RT \ln\left(\frac{P_0}{P}\right) \quad (5)$$

where  $R$  is the universal gas constant,  $T$  is the adsorption temperature in absolute units,  $P$  is the adsorption pressure, and  $P_0$  is the saturation vapor pressure of the adsorbate at temperature  $T$ . The potential theory has been substantiated by the work of many researchers. Although the concept of the original theory has not changed, its mathematical functional relations have changed significantly in order to improve its predictive

capability.<sup>30</sup> Dubinin<sup>31</sup> used this theory to describe adsorption on microporous adsorbents and proposed a new theory, which is known as the Theory of Volume Filling of Micropore (TVFM). Dubinin postulated that, in micropores, the adsorbate occupies the pore volume by the mechanism of volume filling and, hence, does not form a discrete monolayer in the pores. Based on this, Dubinin and Astakhov proposed an equation representing the isotherms that obeyed the TVFM.<sup>32</sup> Known as the Dubinin–Astakhov (D-A) equation, it is expressed as

$$V = V_0 \exp\left[-D\left\{\ln\left(\frac{P_0}{P}\right)\right\}^n\right] \quad (6)$$

where  $V$  is the amount adsorbed;  $V_0$  is the volume of micropores;  $n$  is the structural heterogeneity parameter, a small number varying between 1 and 4;  $D$  is a constant for a particular adsorbent–adsorbate system and is equal to  $(RT/\beta E)^n$ , where  $E$  is the characteristic energy of the adsorption system and  $\beta$  is the adsorbate affinity coefficient.  $P_0$  is the saturation vapor pressure of the adsorbate at temperature  $T$ , and  $P$  is the equilibrium vapor, or free gas, pressure. Dubinin and Radushkevich suggested that the value of  $n = 2$  may be appropriate for some cases, and the equation can be modified as

$$V = V_0 \exp\left[-D\left\{\ln\left(\frac{P_0}{P}\right)\right\}^2\right] \quad (7)$$

The above equation is known as the Dubinin–Radushkevich (D-R) equation. The D-A and D-R equations are also known as the Dubinin–Polanyi (D-P) equations.

One unique advantage of the D-P isotherm equations is that the characteristic curve can be derived from a single isotherm at a particular temperature, and from the characteristic curve, the isotherm for the same solid–gas system at any other temperature can be obtained. This feature of the D-P models can be very useful for resource assessment of CBM reservoirs, where the spatial in situ temperature variation is significant and availability of the experimental sorption data is limited. Also, the characteristic curve concept can be used to predict the sorption isotherm for coals at different locations, provided the in situ temperature at the location is known.

The BET model is an extension of the Langmuir model and is generally applied to the adsorption on a single flat surface or on a pore surface when the radii of the pores are large. Aranovich and Donohue<sup>33</sup> observed that the application of this is not appropriate for microporous adsorbents for which the pore sizes are only a few molecules wide. On the other hand, although the Langmuir monolayer and Dubinin TVFM equations provide different adsorption capacities, there is a good correlation between the monolayer adsorption capacity and micropore volume.<sup>20</sup>

## Study Approach

**Sample Preparation and Experimental Work.** Four representative samples were prepared from cores and blocks of bituminous coals representing different seams of the San Juan and Illinois

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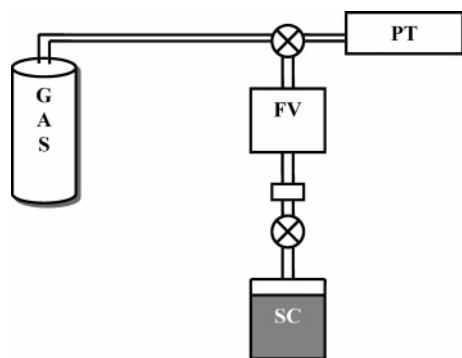
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**Figure 1.** Experimental setup for the sorption study: PT, pressure transducer; FV, fixed volume cylinder; SC, sample container.

Basins in the United States. Samples from the Illinois Basin were from Herrin, Davis, and Seelyville seams. As per standard procedure for volumetric sorption experiments, the samples were pulverized to  $-40$  to  $+100$  mesh size ( $0.149$ – $0.420$  mm) to optimize the sorption time and yet keeping the error in estimation of the sorption capacity to a minimum.<sup>34</sup> The samples were moisture equilibrated by keeping them in an environmental chamber at the experimental temperature and  $\sim 95\%$  humidity level. Ash and moisture content of each sample were determined in accordance with the ASTM standard procedures.<sup>35,36</sup>

The schematic of the experimental setup used for the volumetric sorption experiments is shown in Figure 1. It consisted of two stainless steel cylinders—the fixed volume cylinder (FV), of  $\sim 150$  cm<sup>3</sup> capacity, for calculation of the amount of injected gas and the sample container (SC), of capacity  $\sim 175$  cm<sup>3</sup>, to hold the pulverized samples. These two cylinders were separated by a valve, and a small filter was placed to prevent coal particles from the SC from entering the FV. Since the sorption capacity of coal is sensitive to temperature, the entire setup was kept immersed in a constant-temperature water bath, which was maintained at in situ temperature ( $\pm 0.1$  °C) of the gas reservoir. Accordingly, sorption experiments for the San Juan sample were carried out at  $45$  °C ( $113$  °F), and those for the Illinois Basin were carried out at  $23.5$  °C ( $70$  °F). The two Illinois seams were in close proximity with in situ temperature less than  $1$ ° apart. A pressure transducer (PT), with accuracy of  $0.1\%$  FS, attached to the FV was used to measure the pressure variation in the cylinders with ad/de-sorption.

The void volume in the SC, including the free volume up to the valve, was determined by helium expansion. The adsorbate gas was then injected into the FV and allowed to stabilize. Next, the valve between the cylinders was opened, and the gas was allowed to expand into the SC and sorb on to coal. The setup was left for  $24$  h to attain equilibrium. After that, pressure measurements were made every  $30$  min until at least four constant readings were recorded. Typically, equilibrium time for single gas sorption is not high. After attaining equilibrium, the pressure was recorded, and the volume of the sorbed gas was calculated based on standard gas laws and equations of state. The same process was repeated for  $6$ – $8$  increasing pressure steps to obtain the sorbed volume at each pressure step. For methane, the highest sorption pressure was  $\sim 1500$  psia, the maximum in situ reservoir pressure for the seams. For CO<sub>2</sub>, the highest sorption pressure was limited to  $\sim 900$  psia, which was higher than the anticipated maximum CO<sub>2</sub> injection pressure in the seams in Illinois. Finally, after reaching the highest pressure step, desorption steps were carried out in a similar manner to determine the volume of gas desorbed with reduction in pressure.

**Establishment of Sorption Isotherm.** The amount of gas sorbed at different pressures expressed in terms of volume at standard pressure and temperature (STP) conditions was calculated. The sorbed gas volume, as measured in the laboratory, is known as the Gibbs excess sorption or simply the Gibbs sorption. Although it is apparent that sorbed gas occupies a certain volume in the pore space of the adsorbent, the concept of Gibbs sorption ignores this volume. At low pressures, the volume occupied by the sorbed gas is not significant, and the actual sorbed volume is not much different from the Gibbs sorption volume measured. However, at higher pressures, the volume occupied by the sorbed gas can be significant, and the actual sorbed gas amount can be substantially greater than the Gibbs sorption values.<sup>37</sup> To accommodate this difference, the concept of absolute sorption, which takes into account the volume occupied by the sorbed gas, is used.<sup>2,38</sup> The absolute sorption is calculated using the following equation:

$$n_{\text{abs}} = \frac{n_{\text{Gibbs}}}{\left(1 - \frac{\rho_{\text{gas}}}{\rho_{\text{sorbed}}}\right)} \quad (8)$$

where  $n_{\text{abs}}$  and  $n_{\text{Gibbs}}$  are the absolute and Gibbs sorption values in mol/gm, respectively;  $\rho_{\text{gas}}$  and  $\rho_{\text{sorbed}}$  are the respective densities of gas in gaseous and sorbed phases. The value of the sorbed gas density,  $\rho_{\text{sorbed}}$ , must be known in order to calculate the absolute sorption. Since direct measurement of the sorbed phase density/volume is difficult, empirical approaches are typically used to calculate the adsorbed phase volume/density.<sup>2</sup> For analysis in this study, it was assumed that the sorbed phase density is equal to the liquid density at atmospheric pressure boiling points. For methane, the sorbed density was assumed to be  $0.421$  g/mL. CO<sub>2</sub>, being solid at atmospheric pressure boiling point temperature, its density at this point cannot be used. The density of the liquid CO<sub>2</sub> at the triple point, which is  $1.18$  g/mL, was used instead.<sup>2</sup>

**Sorption Isotherm Modeling.** Sorption data for methane and CO<sub>2</sub> on coals was correlated using the isotherm equations of Langmuir, BET, and D-P models and tested for their applicability for absolute adsorption on coals. Also, these models were compared in order to determine the best model for applications on coals.

**Langmuir Model.** To establish the adsorption isotherm using the Langmuir equation (eq 2) from the sorption data, it is necessary to determine the Langmuir constants  $V_L$  and  $P_L$ . To obtain the values of these constants, the experimental pressure ( $P$ ) versus pressure/volume ( $P/V$ ) was plotted, and the best fit straight-line was obtained. The inverse of the slope of the Langmuir plot provided the Langmuir volume, and the product of the Langmuir volume with the  $Y$ -intercept gave the Langmuir pressure. The  $R^2$  value, an indicator of the degree of fit of the experimental data with the model, was calculated. With the calculated values of  $V_L$  and  $P_L$ , the isotherms were developed using eq 2.

**BET Isotherm Model.** The absolute sorption results were analyzed to test the applicability of the BET isotherm equation (eq 3) for adsorption of methane and CO<sub>2</sub> on coal samples. Prior to the analysis, it was necessary to calculate the saturation vapor pressure ( $P_0$ ) of the adsorbate (CH<sub>4</sub> and CO<sub>2</sub>) at the experimental temperature and pressure conditions. For experimental temperatures below the critical temperature ( $T_c$ ), the saturation vapor pressures of the adsorbates were used directly. However, for experimental temperatures above  $T_c$ , the concept of vapor pressure does not exist, and the concept of pseudo-vapor pressure, as discussed in Agarwal and Schwarz,<sup>39</sup> was used. The critical temperature for methane and CO<sub>2</sub>

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are  $-82.7$  and  $31$  °C, respectively. Hence, for experiments using methane, all the experimental temperatures were above its critical temperature. For CO<sub>2</sub>, while the San Juan sample was tested above the critical temperature, the experiments for other samples were conducted below the critical temperature.

There are several ways to calculate the pseudo-saturation vapor pressure,  $P_0$ , at supercritical temperature. For this study,  $P_0$  was calculated by extrapolating the plot of log of vapor pressure (VP) versus the reciprocal of absolute temperature (log VP vs  $1/T$ ) to the desired temperature, as described by Clarkson et al.<sup>25</sup> The vapor pressure data was obtained from the standards handbook.<sup>40</sup>

For BET analysis, the BET plots were first drawn for all the samples. To obtain the BET plot,  $1/V(P_0/P - 1)$  was plotted as a function of the relative pressure ( $P/P_0$ ), and the best fit line was obtained along with  $R^2$  values indicating the degree of fit. The monolayer volume ( $V_m$ ) and the BET constant ( $C$ ) were calculated from the slope and intercept of the BET plot, respectively. These values were utilized to establish the BET isotherm.

**Dubinin–Polyanyi (D-P) Equations.** As a part of this study, the ability of the D-A equation (eq 6) was tested for its suitability in describing the experimental methane and CO<sub>2</sub> adsorption results on coals and establishing methane and CO<sub>2</sub> isotherms for various coals. The D-R equation (eq 7), being a specific case of the D-A equation for  $n = 2$ , was not examined separately.

For ease of plotting, eq 6 can be linearized as

$$\ln V = \ln V_0 - D \left( \ln \frac{P_0}{P} \right)^n \quad (9)$$

To determine the value of  $V_0$  and  $D$ ,  $\ln V$  was plotted against  $(\ln P_0/P)^n$ , and the resulting line, known as the potential or the D-P plot was obtained. The exponent,  $n$ , was determined by an optimization technique that minimizes the average relative error, defined later. The micropore volume,  $V_0$ , was then obtained by taking the exponential of the  $Y$ -intercept, while the slope of the line provided the value of the constant,  $D$ . Using the values of  $V_0$  and  $D$ , a set of isotherms was developed using eq 6 with values of  $n$  from 1 to 4. Residuals, as defined below, were calculated for each of the isotherms:

$$r = \frac{(V_{\text{exp}} - V_{\text{eq}}) \times 100}{V_{\text{exp}}} \quad (10)$$

where  $r$  is the residual; and  $V_{\text{exp}}$  and  $V_{\text{eq}}$  are the experimental and calculated sorbed volume, respectively. The average relative error (ARE), as defined below, was calculated for each isotherm and corresponding to each value of  $n$ :

$$\text{ARE} = \frac{1}{j} \sum_{i=1}^j \text{abs}(r_i) \quad (11)$$

where  $j$  is the number of experimental data points. The value of  $n$ , for which the ARE was minimum, was taken to be the exponent for the D-A equation. For the D-R equation, of course, the value of  $n$  was considered to be 2.

## Results and Discussion

**Single-Component Gas Sorption.** A summary of the experimental results for the sorption experiments is presented in Table 1. The methane sorption isotherms for the four samples, shown in Figure 2, indicate that the sorption trend follows the Type I isotherm behavior. Methane isotherms for the San Juan, Herrin, and Seelyville samples show a steady increase with pressure and do not attain saturation levels at the final

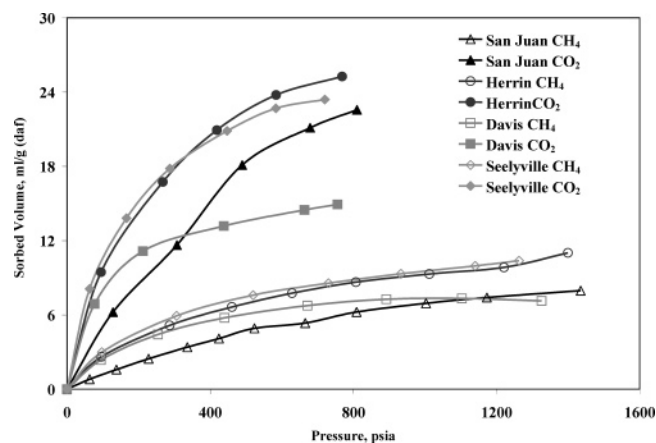


Figure 2. Adsorption isotherms for different samples.

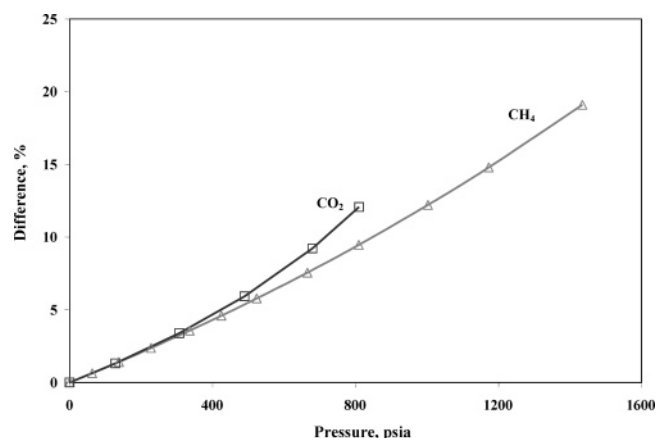


Figure 3. Difference between Gibbs and absolute sorption for the San Juan sample.

Table 1. Overview of the Sorption Experiments

seam	adsorbent	max exptl pressure (psia)	max Gibbs sorption (mL/g)	max absolute sorption (mL/g)
San Juan	methane	1435	10.1	12.0
	CO <sub>2</sub>	809	22.6	25.3
Herrin	methane	1399	11.0	13.4
	CO <sub>2</sub>	769	25.3	29.1
Davis	methane	1325	7.1	8.6
	CO <sub>2</sub>	755	14.9	17.1
Seelyville	Methane	1263	10.4	12.3
	CO <sub>2</sub>	721	23.2	26.3

experimental pressure, while for the Davis sample this level is reached. Again, while the CO<sub>2</sub> isotherm for the San Juan sample does not tend to maximize at the final experimental pressure, the other three definitely exhibit maximizing trend within the range of experimental pressures.

The difference between the absolute and Gibbs sorption values, as presented in Table 1, is substantial for all samples. The difference, as a function of pressure for the San Juan sample, both for methane and CO<sub>2</sub>, is shown in Figure 3. It is clear from the figure that, up to a pressure of 300 psia, the difference is almost negligible. In the mid-pressure range (300–500 psia), the difference is discernible although it stayed within a relatively small range—up to 5%. Also, the difference is similar for both methane and CO<sub>2</sub>. However, in the high-pressure region, the difference is rather significant—12% for CO<sub>2</sub> at ~800 psia and 19% for methane at ~1400 psia. Similar results, although not shown here, were obtained for other samples as well, and the difference was more pronounced for CO<sub>2</sub> than methane in all cases.

(40) Lide, D. R. *Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boston, 1991; Section 6-82.

Table 2. CO<sub>2</sub>:Methane Adsorption Ratio

sample	Gibbs adsorption		absolute adsorption	
	$P = 100$ psia	$P = 800$ psia	$P = 100$ psia	$P = 800$ psia
San Juan	4.0:1	3.3:1	4.0:1	3.6:1
Herrin	4.0:1	2.9:1	4.1:1	2.9:1
Davis	3.2:1	2.1:1	3.2:1	2.2:1
Seelyville	4.0:1	2.6:1	3.8:1	2.6:1

It can be summarized that the isotherms generally follow the Type I behavior. This finding corroborates the findings of several other researchers.<sup>10,15,25</sup> Coals exhibit Type I behavior because of its microporous nature, where the narrow pores cannot accommodate more than a single layer on their walls, and the plateau in the isotherm corresponds to the completion of the monolayer.<sup>28</sup> At higher pressures, absolute sorption is more representative of the actual sorption condition, and this should be used for all practical applications.

**Comparison of CO<sub>2</sub> and Methane Sorption Capacities.** It is generally believed that coal adsorbs at least twice as much CO<sub>2</sub> than methane. To verify this, the ratio of adsorbed CO<sub>2</sub> to adsorbed methane was calculated for the samples at different pressures. Table 2 shows the calculated values of the preferential sorption ratios at three different pressures, ~100, 400, and 800 psia. The 800 psia pressure value was chosen to reflect the actual field conditions for the Illinois Basin, where CO<sub>2</sub> injection pressure will probably not exceed 800 psia, and thus provides the upper limit of the amount of CO<sub>2</sub> that can be sequestered.

Table 2 shows that the sorption ratio of CO<sub>2</sub> over methane is not constant for this set of samples and can be broadly placed in the range of 2:1 to 4:1. The results are in conformity with other similar studies.<sup>5–7</sup> Samples from the San Juan, Herrin, and Seelyville seams exhibit greater preferential affinity for CO<sub>2</sub> as compared to that from the Davis seam. Also, the ratio is always higher at low pressure and lower at high pressure. Because of the lower preferential adsorption for CO<sub>2</sub>, Davis seams appears to be more suitable for enhanced gas recovery. Lower preferential adsorption for CO<sub>2</sub> on coals from this seam suggests that fewer volumes of CO<sub>2</sub> will have to be injected to displace 1 vol of methane. However, if the objective is CO<sub>2</sub> storage, then the San Juan, Herrin, and Seelyville samples are better candidates since several volumes of CO<sub>2</sub> will be required to displace 1 vol of methane due to their greater affinity for CO<sub>2</sub>.

The reason for greater sorption of CO<sub>2</sub> than methane onto coal is still not well understood.<sup>5</sup> However, several studies in the past have tried to explain this behavior. Ettinger et al.<sup>41</sup> argued that preferential adsorption occurs due to a difference in atmospheric boiling points between different gases and that higher boiling point corresponds to increasing sorption strength. CO<sub>2</sub> has a higher boiling point (−78.5 °C) as compared to methane (−161.6 °C); therefore, the adsorption affinity of CO<sub>2</sub> is higher than that of methane. Cui et al.<sup>42</sup> explained that CO<sub>2</sub> is preferentially adsorbed over methane due to its higher adsorption energy for all pore sizes and smaller particle size. CO<sub>2</sub> can diffuse into not only the micropores but also the ultramicropores. Milewska-Duda et al.<sup>43</sup> related this difference to the difference in sorption mechanisms between these two

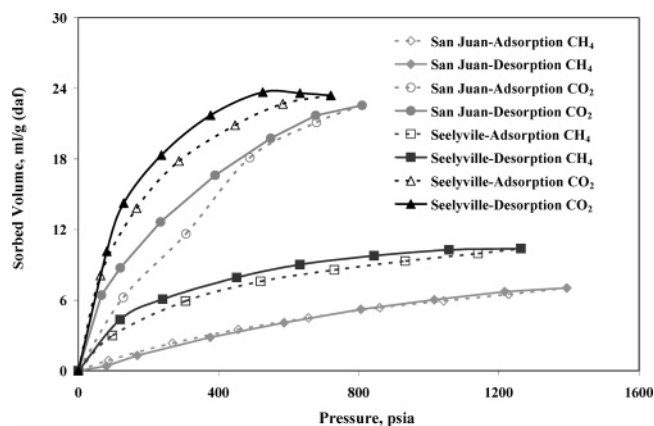


Figure 4. Comparison of CO<sub>2</sub> and methane adsorption–desorption isotherms.

adsorbents. They argued that, in case of methane, adsorption into the micropores was the only major mechanism of gas retention. However, for CO<sub>2</sub>, adsorption into the micropores and absorption into the solid/elastic organic structure of coal occurred.

In summary, this study confirms the findings of other researchers that CO<sub>2</sub> is preferentially sorbed in coal over methane for all coals. However, there is no unanimity among the researchers on the reasons for this preferential behavior, and further studies are needed to explain this phenomenon.

**Sorption Hysteresis.** Ideally, desorption isotherms for coal and N<sub>2</sub>/CH<sub>4</sub>/CO<sub>2</sub> should not deviate from the adsorption isotherms, since the sorption process is physical in nature and is reversible.<sup>15,44</sup> The complete adsorption–desorption isotherms for two representative samples, for which desorption was carried out, are shown in Figure 4.

It can be seen in Figure 4 that, with the exception of the methane isotherm for San Juan sample, some hysteresis exists for all others. Both for methane and CO<sub>2</sub>, desorption isotherms lie above the adsorption isotherms.

Desorption hysteresis of methane and CO<sub>2</sub> sorption on coals, although not common, is not a new finding and has been reported by several researchers in the past.<sup>1,6,8,9</sup> Desorption hysteresis on coals (or any adsorbent) may occur due to two different reasons—changes in the adsorbent properties/structures or the capillary condensation in the adsorbent micropores.<sup>28</sup> Busch et al.<sup>6</sup> observed a significantly positive deviation both for methane and CO<sub>2</sub> desorption curves. This was attributed to a metastable sorbent–sorbate system that prevents ready release of gas to the extent corresponding to the thermodynamically equilibrium value with decrease of pressure during desorption. For CO<sub>2</sub>, the deviation was found to be smaller for higher rank coals. This was also confirmed by Ozdemir et al.,<sup>9</sup> where the positive deviation of CO<sub>2</sub> desorption was attributed to swelling of the coal matrix. Shrinkage/swelling of coal matrix is believed to be associated with desorption/adsorption process.<sup>45–47</sup> Changes in moisture content can also lead to desorption hysteresis.

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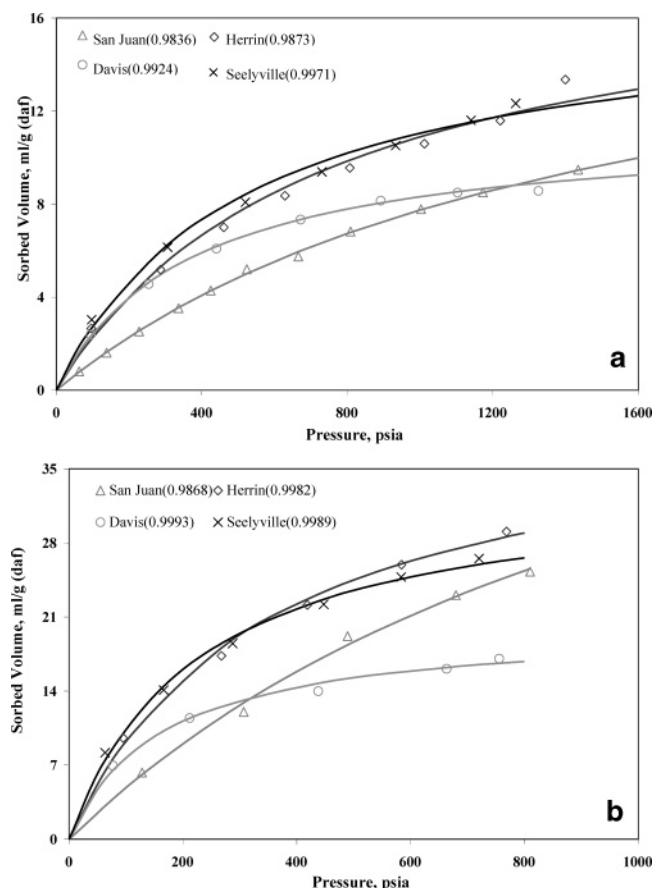
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(41) Ettinger, I.; Eremin, I.; Zimakov, B.; Yanovskaya, M. Natural factors influencing coal sorption properties. I: Petrography and sorption properties. *Fuel* **1966**, 45, 267–275.

(42) Cui, X.; Bustin, R. M.; Gregory, D. Selective transport of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in coals: insights from modeling of experimental gas adsorption data. *Fuel* **2004**, 83, 293–303.

(43) Milewska-Duda, J.; Duda, J.; Nodzenski, A.; Lakatos, J. Absorption and adsorption of methane and carbon dioxide in hard coal and activated carbon. *Langmuir* **2000**, 16, 5458–5466.





**Figure 5.** Langmuir isotherms for (a) methane and (b) CO<sub>2</sub> with  $R^2$  values.

**Table 3.** Langmuir Isotherm Parameters for Absolute Sorption

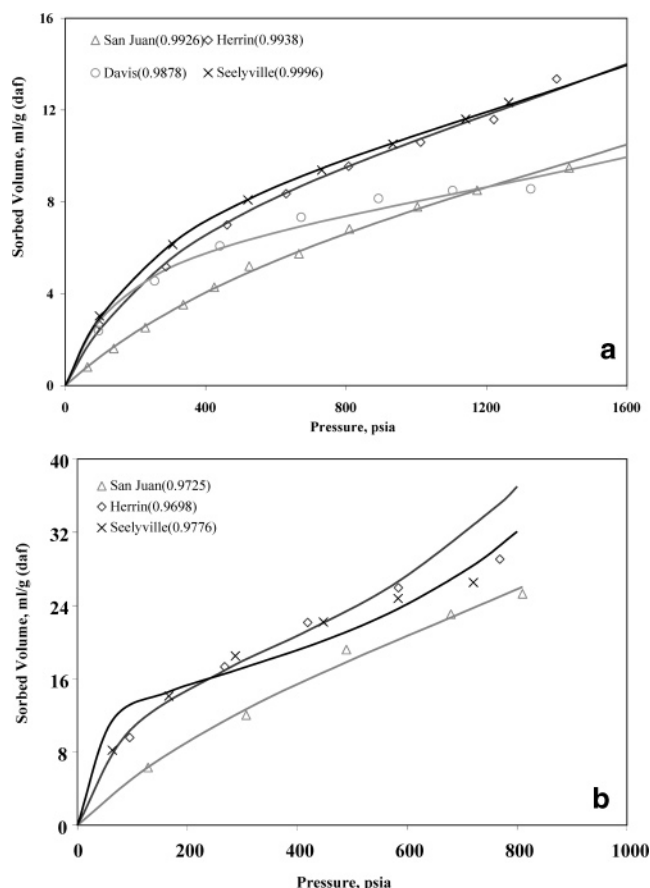
sample	methane		CO <sub>2</sub>	
	$V_L$ (mL/g)	$P_L$ (psia)	$V_L$ (mL/g)	$P_L$ (psia)
San Juan	19	1492	64	1209
Herrin	18.9	736	41.5	347
Davis	11.4	372	20.2	162
Seelyville	16.7	512	34.4	229

Moisture content of any sample decreases while bleeding gas from the sample container during desorption. With decrease in sample moisture, the capacity of coal to adsorb gas increases, thus increasing sorbed gas content significantly.

**Sorption Isotherm Modeling. Langmuir Model.** The  $P/V$  versus  $P$  plots from methane and CO<sub>2</sub> experimental data were drawn for all the samples. From statistical analyses of the plots, the Langmuir volume ( $V_L$ ) and pressure ( $P_L$ ) constants for all samples were calculated, and the results are presented in Table 3. The Langmuir isotherms, developed using these constants in eq 2, are shown in Figure 5. It can be seen from this figure that the adsorption of methane and CO<sub>2</sub> are very well correlated by the Langmuir model, with an  $R^2$  value in all cases greater than or equal to 0.97. This is in agreement with the results of previous researchers on the ability of the Langmuir model to describe methane adsorption data on a variety of coals.<sup>21,48,49</sup> For sorption of CO<sub>2</sub> on coal at in situ conditions, on the other hand, there appears to be a paucity of work in the literature. However, the results do confirm the findings of Busch et al.<sup>6</sup> and Clarkson et

(48) Yang, R. T.; Saunders, J. T. Adsorption of gases on coals and heat treated coals at elevated temperature and pressure: 1. Adsorption from hydrogen and methane as single gases. *Fuel* **1985**, 64 (5), 616–620.

(49) Joubert, J. I.; Grein, C. T.; Bienstock, D. Sorption of methane on moist coal. *Fuel* **1973**, 52 (3), 181–185.



**Figure 6.** BET isotherms for (a) methane and (b) CO<sub>2</sub> with  $R^2$  values.

**Table 4.** BET Parameters for Methane and CO<sub>2</sub> Sorption

sample	methane		CO <sub>2</sub>	
	$V_m$ (mL/g)	$C$	$V_m$ (mL/g)	$C$
San Juan	10.7	8	24.8	6
Herrin	11	14	17	18
Davis	7.3	31		
Seelyville	10.6	19	14.3	70

al.<sup>25</sup> that Langmuir equation can be used to describe adsorption of CO<sub>2</sub> on coal.

**BET Isotherm Model.** Using the experimental results, both for methane and CO<sub>2</sub>,  $1/V(P_0/P - 1)$  versus  $P/P_0$  were plotted. From these plots, the BET parameters,  $V_m$  and  $C$ , were calculated following the procedure detailed in the previous section. The values shown in Table 4, and the BET isotherms, using eq 3, are shown in Figure 6.

The BET plots exhibited excellent correlation, with the correlation coefficient ( $R^2$ ) varying between 0.93 and 0.99. Overall, the correlation was better for methane than for CO<sub>2</sub>. The relative pressure values for methane experiments were in the range of 0.01–0.35, whereas for CO<sub>2</sub>, the range was between 0.05 and 0.50. The BET equation is normally assumed to be valid over the relative pressure range 0.05–0.30, and BET plots are typically linear in this range.<sup>28</sup> However, linear plots were obtained for relative pressures smaller than 0.05 for methane and for relative pressures larger than 0.3 for CO<sub>2</sub> as well. The CO<sub>2</sub> BET plots for Davis sample showed a negative  $Y$ -intercept. The BET equation, therefore, could not be used to correlate the adsorption of CO<sub>2</sub> for this sample. Negative  $Y$ -intercepts, in this case, resulted in negative  $C$  value, which has not been reported in the literature. It is not clear whether this was a mathematical problem or one with some theoretical significance.



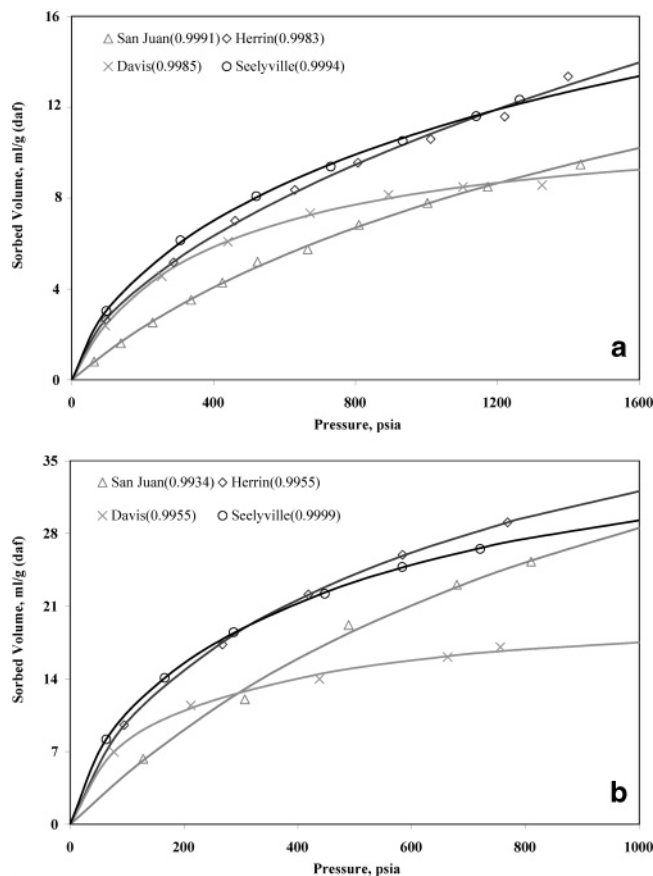


Figure 7. D-A isotherms for (a) methane and (b) CO<sub>2</sub> with  $R^2$  values.

Table 5. D-A Parameters for Methane and CO<sub>2</sub> Sorption

sample	methane			CO <sub>2</sub>		
	$V_0$ (mL/g)	$D$	$n$	$V_0$ (mL/g)	$D$	$n$
San Juan	16.9	0.3081	1.5	40.4	0.3552	1.5
Herrin	24.7	0.4896	1.1	35.2	0.3574	1.3
Davis	10.3	0.0804	2.1	18.1	0.1716	1.6
Seelyville	18.8	0.263	1.4	30.6	0.2723	1.4

Overall, the BET equation showed fair to excellent match for the methane adsorption data for all the coals tested. In most cases, for both methane and CO<sub>2</sub>, BET equation overpredicted significantly at higher pressures. For CO<sub>2</sub>, the match was not very good except for the San Juan sample. This is rather surprising, given the fact that  $R^2$  values of the BET plot for CO<sub>2</sub> were very high (0.93–0.98). This discrepancy suggests that high correlation of the BET plot does not imply high accuracy of the model in describing the sorption data. Rather the  $R^2$  value only seems to be mathematical in nature without much practical significance. Using the BET equation, adsorption data for methane could be explained well in contrast to the poor match for CO<sub>2</sub> adsorption. Regarding applicability of the BET equation to the adsorption of methane and CO<sub>2</sub> on coal, the following conclusion can be made: The BET equation is able to describe the adsorption data of methane on coals at in situ reservoir condition very well but fails to describe the same for CO<sub>2</sub> under similar conditions.

**D-A and D-R Isotherms.** For purpose of analysis, the D-P plots were drawn following the procedure detailed earlier. The  $R^2$  coefficients for all the plots are greater than 0.99, both for methane and CO<sub>2</sub>, suggesting that the D-P equation may be applied satisfactorily to adsorption on coals tested. The D-A parameters ( $V_0$ ,  $D$ , and  $n$ ) determined for all four samples are listed in Table 5.

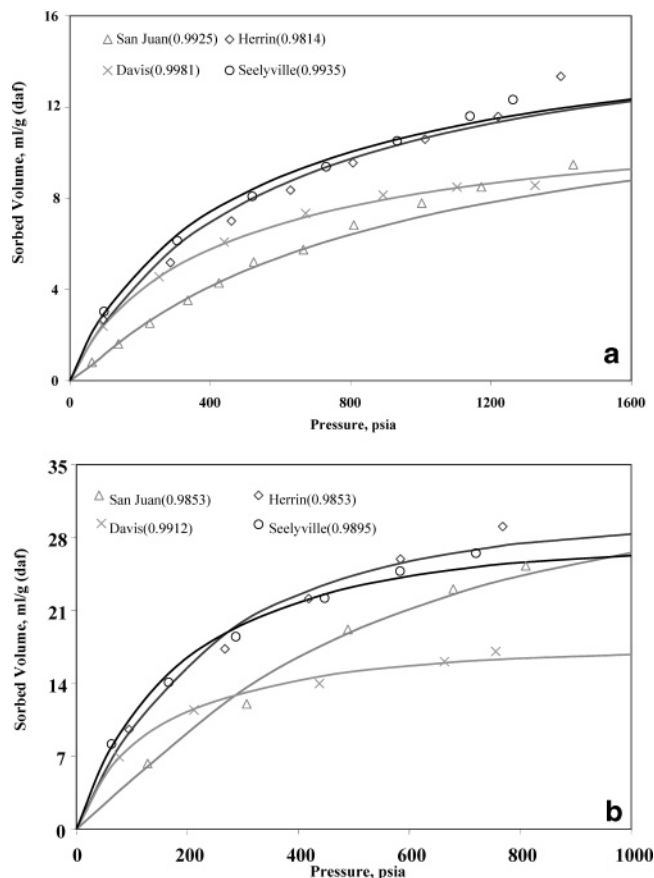
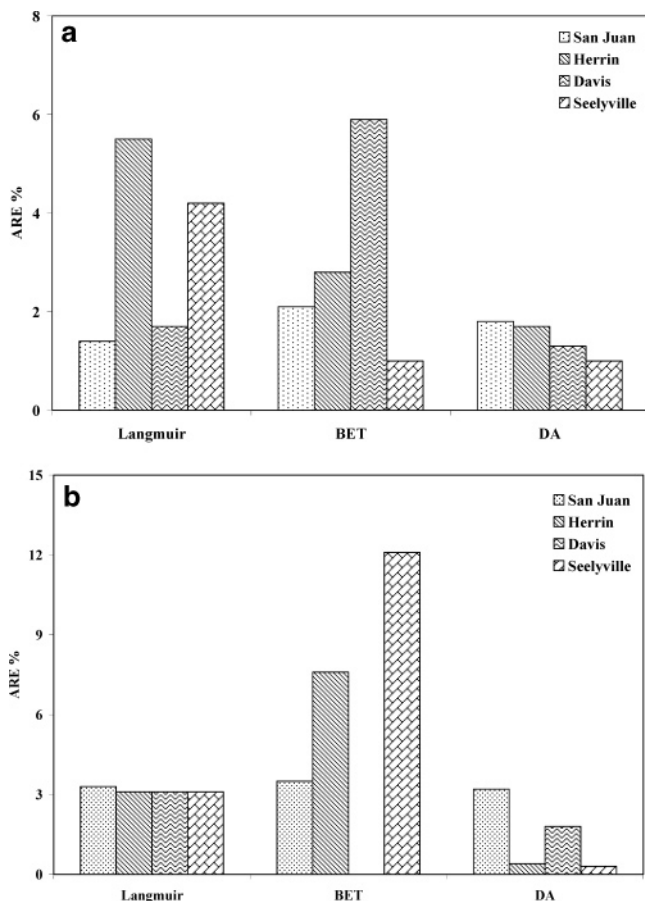


Figure 8. D-R isotherms for (a) methane and (b) CO<sub>2</sub> with  $R^2$  values.

The isotherms established using the D-A equation for adsorption of methane and CO<sub>2</sub> are shown in Figure 7. These figures show that, in general, the D-A equation gave excellent fit to adsorption data of both methane and CO<sub>2</sub> for the entire pressure range tested for all samples. The D-R isotherms for methane and CO<sub>2</sub> for all samples are shown in Figure 8. Unlike the D-A equation, the degree of fit of the D-R equation with adsorption data of methane and CO<sub>2</sub> varied from excellent to poor. For example, for methane isotherms of the San Juan and Herrin samples, the match was very good at low to medium pressures (<800 psia) but poor at high pressures. In general, the match was better for methane than CO<sub>2</sub>. Also, at high pressures, the D-R equation usually under-predicted both methane and CO<sub>2</sub>.

As a comparison between D-A and D-R equations, the D-A isotherm was found to be more accurate for most of the cases. Thus, D-A isotherm is a better model than the D-R isotherm for adsorption of methane and CO<sub>2</sub> on coals tested. The D-R isotherm fitted the data well in some cases, but in most cases, the fit was moderate to poor. The difference between these two equations lies in the value of the structural heterogeneity parameter,  $n$ , which accounts for the pore size distribution in the coal structure. As apparent from the best fit values of the three parameters of the D-A equation presented in Table 5, the value of  $n$  varies within the range of 1.4–2.6. However, in the D-R equation, the value of this parameter is constrained to 2, resulting in relatively poor fit of this equation to the experimental sorption data. The moderate success of D-R equation suggests that the energy distribution of coal micropores does not follow the Gaussian distribution, one of the assumptions in the D-R equation. Rather, the results suggest that the energy distribution of micropores of coals can be approximated by the Weibull



**Figure 9.** Average error analysis for adsorption of (a) methane and (b) CO<sub>2</sub> with different isotherm models.

distribution, as assumed by the D-A equation. Hence, for all further analysis of D-P models, only the D-A equation is discussed.

**Comparison of Different Isotherm Models: Error Analysis.** To conduct a quantitative comparison and to determine which isotherm models are the best fit to the experimental data, residual analysis discussed in the Study Approach, was performed for all models. The model with the least ARE is suggested as the best isotherm model to describe methane and CO<sub>2</sub> adsorption data on coal. The results of the ARE analysis for methane and CO<sub>2</sub> are presented in Figure 9. For adsorption of methane, the D-A equation gave the lowest ARE for two samples—the Langmuir model for one sample and the BET model for one sample. No model is therefore consistently more accurate than the other. However, in case of San Juan sample, where the Langmuir model has the lowest ARE, it is only slightly better than the D-A equation. Figure 9 also shows that, for CO<sub>2</sub>, the D-A model has the smallest ARE for all the samples, with a value as low as 0.3% in the case of Seelyville sample. The small values of ARE indicates the accuracy of the model in predicting the adsorption behavior of CO<sub>2</sub> on coals. The BET equation is the most accurate model for adsorption of methane for Seelyville sample. However, in other cases, BET equation is not as good as the Langmuir and D-A equations. It is obvious that overall the D-A equation has the lowest ARE. It can, therefore, be concluded that the D-A equation is the best model, followed by the Langmuir equation, for application on methane and CO<sub>2</sub> adsorption data for coals. Clarkson et al.<sup>25</sup> had also observed that the D-A equation was the most accurate

model for adsorption on coals. However, their results had also suggested that the BET equation was more accurate than the Langmuir equation, a finding that is not supported by this study.

### Summary and Conclusions

The study presented here provided experimental data for adsorption and desorption of methane and carbon dioxide for a set of moisture-equilibrated coal samples taken from the San Juan and Illinois Basins in the United States. The experiments were conducted following the standard volumetric method at the expected reservoir temperatures for different coals. The experimental results were analyzed using Langmuir, BET, and D-P isotherm model equations to evaluate the relative performance of these equations in describing the experimental results. The following conclusions are drawn from this study:

(1) The sorption results indicate that, barring a few aberrations observed in some samples, the sorption isotherm trend generally follows Type I isotherm behavior.

(2) The difference between the absolute and Gibbs sorption values, especially for CO<sub>2</sub>, may be substantial at higher pressure range (>500 psia). For accurate estimation of the sorption capacity of coals at high pressure, absolute sorption values should ideally be considered.

(3) Under similar temperature and pressure conditions, coals exhibit higher affinity for CO<sub>2</sub> as compared to methane. The preferential sorption ratio of CO<sub>2</sub> to methane observed for these set of samples varies from 2:1 to 4:1.

(4) Comparison of the adsorption and desorption isotherms, both for methane and CO<sub>2</sub>, reveal some degree of hysteresis with the desorption isotherms lying above the adsorption curve. This apparent irreversibility of the ad/de-sorption process may be attributed to various reasons. However, any change in sorption behavior due to coal matrix shrinkage/swelling associated with ad/de-sorption should be investigated further.

(5) Evaluation of experimental results with the sorption isotherm equations indicates that, for methane, all the equations perform satisfactorily and no one equation can be regarded as consistently better than the others to explain the experimental results. For CO<sub>2</sub>, the Langmuir equation provides only a reasonable fit to the experimental results, and the match for the BET equation is rather poor. The D-A equation, however, is more accurate than the Langmuir or BET equations in explaining the experimental sorption results for CO<sub>2</sub>.

(6) Overall, to explain the sorption behavior of both gases, the performance of the D-A equation is the best, followed by Langmuir and BET equations, respectively.

(7) The characteristic curve drawn from a single isotherm at a particular temperature using D-A equation can be utilized to derive the isotherms for other temperatures. Since the process of adsorption is associated with release of heat and desorption with cooling, the temperature of the coal reservoir varies during both desorption of methane and injection of CO<sub>2</sub>. The D-A equation is, therefore, useful in evaluating the CO<sub>2</sub> sequestration potential and/or methane release under such variable temperature regime.

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