

Dynamic nature of supercritical CO₂ adsorption on coals

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Abstract Adsorption on non-rigid solids was shown to be a dynamic process. Excess adsorption and desorption isotherms of CO₂ on eight Argonne Premium coal samples were measured at 55 °C and pressures up to 14 MPa by manometric method. The excess adsorption isotherms of CO₂ on powdered coals showed almost Langmuir-like to rectilinear shape behavior at low pressures up to 9 MPa, and it increased noticeably at pressures higher than 9 MPa. There was a significant hysteresis between the excess adsorption and desorption isotherms for each rank of coals, which was related to the volumetric uncertainties occurring during the adsorption isotherm measurements. The parameters related to the adsorption capacity and micro porous characteristics of the coal were obtained at different pressure ranges by fitting the experimental data to the modified Dubinin-Astakhov (D-A) equation at the increasingly larger pressure ranges, using only the first 4 data points of the excess adsorption isotherm initially, and progressively using additional data points for the subsequent values. It was shown that the curve fit parameters vary with pressure, and therefore, concluded that the adsorption on non-rigid solids such as CO₂ on coal is indeed a dynamic process. It was suggested that new adsorption isotherm equations need to be developed considering the dynamic nature of the adsorption on solid adsorbents.

Keywords Coal · Swelling · CO₂ sequestration · Dynamic · Adsorption · Isotherm

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1 Introduction

Coal is a pseudo-plastic material (Goodman et al. 2006). It shrinks upon moisture lost and swells when moisture or other gasses and organic vapors adsorb (Ozdemir and Schroeder 2009). Similar behavior is observed in adsorption of organic vapors on polymers and other viscoelastic materials (Shimizu et al. 1998; Takanohashi et al. 2000). A breathing effect was seen in metal–organic frameworks (MOFs) (Chang et al. 2015; Ye et al. 2016). However, adsorption equations used to interpret the adsorption isotherm on the non-rigid solids assume them as a rigid solid and report one curve-fit parameter for the entire isotherm. Considering the dynamic nature occurring during the adsorption on non-rigid solids, the adsorption equations need to be reconsidered. Here, CO₂-coal system was investigated to address the variation in the curve-fit parameters throughout the adsorption isotherm at elevated pressures.

The high pressures excess adsorption isotherms of CO₂ on coals have been reported to be different comparing to the conventional low pressure adsorption isotherms (Bae and Bhatia 2006; Busch and Gensterblum 2011; Do 1998; Donohue and Aranovich 1998; Xing et al. 2015). For instance, for a rigid solid, such as activated carbon, the measured adsorbed amount generally increases monotonically at low-pressures, and then, decreases as the pressure further increases, exhibiting a maximum (Bae and Bhatia 2006; Busch and Gensterblum 2011; Chen et al. 1997; Gensterblum et al. 2009; Humayun and Tomasko 2000; Pini et al. 2010). On the other hand, the excess adsorption isotherms of, not only CO₂, but also H₂O, CH₃OH, and organic vapors on coals, and also on other non-rigid solids such as polymers show monotonically increasing trend exhibiting almost a rectilinear shape (Busch and Gensterblum 2011; Goodman et al. 2006; Kelemen et al. 2006;

Mastalerz et al. 2008; Mazumder and Wolf 2008; Ozdemir et al. 2003; Romanov et al. 2006; Sharma 1996; Shimizu et al. 1998; Takanohashi et al. 2000; Yi et al. 2009). Desorption isotherms of these adsorbates typically show a hysteresis (Harpalani et al. 2006; Ozdemir et al. 2003; Reucroft and Patel 1983). The hysteresis between the excess adsorption and desorption isotherms was related to swelling and other experimental uncertainties (Mohammad et al. 2009a; Ozdemir 2004; Ozdemir et al. 2003, 2004; Ozdemir and Schroeder 2009; Sakurovs et al. 2009). Interestingly, excess adsorption isotherms of neither CH₄ nor N₂ showed unusual behavior as occurred in CO₂ isotherms (Bae and Bhatia 2006; Bae et al. 2009; Krooss et al. 2002; Pini et al. 2010).

The excess adsorption isotherms of CO₂ on coals have been interpreted in various ways (Busch and Gensterblum 2011; Do 1998; Dubinin 1960; Goodman et al. 2005; Milewska-Duda et al. 2000; Milewska-Duda and Duda 2002; Mohammad et al. 2009b; Ozdemir et al. 2003; Pini et al. 2010; Sakurovs et al. 2007). Milewska-Duda et al. (Milewska-Duda et al. 2000) studied the adsorption behavior of CH₄ and CO₂ on coal and proposed a dual sorption model describing adsorption on the surface and absorption within the coal matrix as two subprocesses. Shimizu et al. (1998) and Taknohashi et al. (2000) interpreted the sorption isotherms of various organic alcohols on the Argonne Premium coals using a dual-mode sorption equation that has been widely used to describe the sorption isotherms of glassy polymers (Fleming and Koros 1986). The first excess adsorption isotherm equation was developed by Ozdemir group considering the volumetric effects during the adsorption isotherm measurements (Ozdemir 2004; Ozdemir et al. 2002, 2003). The suggested equation was applied successfully by several other groups for the interpretation of high pressure adsorption of CO₂ and CH₄ on coals (Busch and Gensterblum 2011; Day et al. 2008a, b, c; Pini et al. 2010; Sakurovs et al. 2008, 2009, 2010; Svabova et al. 2012; Xing et al. 2015). Bae et al. (2009) applied the suggested equation accounting the absolute adsorption with the Toth equation, in which fugacity was used instead of pressure as the variable to account for the non-ideality. Sakurovs et al. (Day et al. 2008a, b, c; Sakurovs et al. 2007, 2008) applied the suggested equation by replacing the absolute adsorption with the Dubinin-Radushkevich equation, in which density was used as the variable instead of pressure, in order to fit the excess adsorption data at higher pressures and/or higher densities, because defining the saturation pressure and adsorbed phase density were difficult at supercritical conditions. Pini et al. (2010) modified the suggested equation by replacing a Langmuir-like model for the absolute adsorption which was a combination of adsorption and absorption, respectively. However, how the adsorption

capacity, heat of adsorption, and pore size vary with pressure during the adsorption isotherm measurements have not been addressed due to the measurement difficulties (Romanov et al. 2006). Therefore, the objective of this manuscript was to address the variation in the curve fit parameters during the adsorption isotherm measurements and lead to develop new and advanced adsorption isotherm equations to interpret the dynamic nature of the excess adsorption isotherm of microporous and mesoporous soft materials as occurred in CO₂-coal system.

1.1 Adsorption equation for non-rigid solids

Adsorption equation for rigid and non-rigid solids were developed previously (Ozdemir et al. 2002, 2003). Briefly, construction of an adsorption isotherm using the manometric method requires three steps as shown in Fig. 1. First, the empty volume of the sample cell, V_s , is estimated (Fig. 1a). Next, the volume of the adsorbent, V_c , or the free volume (void volume) remaining in the sample cell after adding the adsorbent, V_o , is measured (Fig. 1b). These two volumes are usually measured using the He displacement method (Malbrunot et al. 1997; Sircar 1999). The volume, V_{co} , as well as the density of the adsorbent can also be estimated from these two measurements (Ozdemir and Schroeder 2009). In the third step, the adsorption isotherm is measured using the adsorbate gas of interest (Fig. 1c, d).

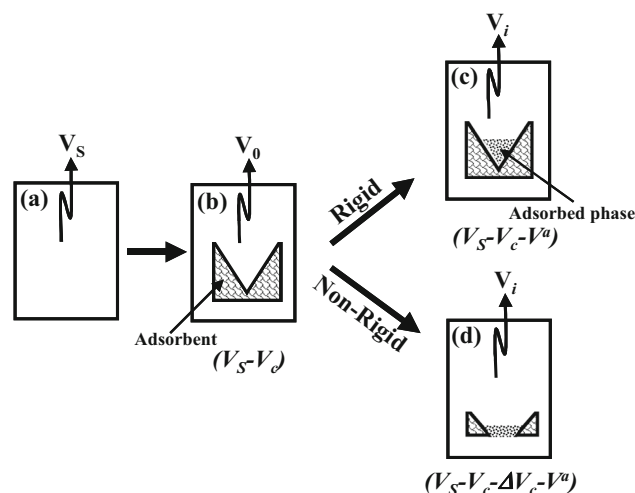


Fig. 1 Construction of an excess adsorption isotherm by manometric method: **a** estimation of the empty volume of the sample cell (V_s), **b** estimation of the void volume of the sample cell (V_o) and, from the difference, the volume of the sample (V_c), **c** measurement of the adsorption isotherm of "rigid" solids during which the void volume (V_o) in the sample cell decreases (to V_i) due to the volume occupied by the adsorbed phase (V^a), **d** measurement of the adsorption isotherm of "non-rigid" solids during which the void volume (V_o) in the sample cell decreases (to V_i) due not only to the volume occupied by the adsorbed phase (V^a) but also to the volume change of the sample (ΔV_c) in response to contraction or expansion of the coal sample

The V-shaped notch in the adsorbent in Fig. 1c, d represents the pores that are occupied to various extents (depending on the pressure) during the adsorption experiments.

The relationship between the experimentally measured adsorption, so called Gibbs adsorption or the excess adsorption, n^{ex} , and the absolute adsorption, n^{abs} , can be given as

$$n^{ex} = n^{abs} + \rho \Delta V \tag{1}$$

where ΔV , is the difference between the void volumes in the presence and absence of the adsorbed phase, respectively, and is defined as

$$\Delta V = V_i - V_o \tag{2}$$

For a rigid solid, Eq. (2) takes the form

$$\Delta V = V_i - V_o = -V^a = -\frac{n^{abs}}{\rho^a} \tag{3}$$

where V^a and ρ^a are the volume and molar density of the adsorbed phase, respectively. Thus, the excess adsorption isotherm can be represented by the well-known adsorption equation for a rigid solids (Sircar 1999), Eq. (4), which includes the correction for the volume occupied by the adsorbed phase:

$$n^{ex} = \left(1 - \rho/\rho^a\right)n^{abs} \tag{4}$$

Here, any deviation or ill-estimation of the adsorbed phase density will create an error in the estimation of the curve fit parameters, and therefore, the adsorption isotherm equation for non-rigid solids as derived below must be used in order to make the necessary corrections.

For a non-rigid solids, the nature of the volume change, ΔV in Eq. (1), includes not only the volume of the adsorbed phase (V^a), but also the nascent volume created by the swelling or shrinkage of the solid adsorbent as well as the volume change due to the dissolution of the adsorbing gas (ΔV_c) and the over- or under-estimation of the void volume due to adsorption of He and/or the extra volume due to sieving effect (ΔV_o) (Ozdemir et al. 2002, 2003). The volumetric compressibility at higher pressures also creates a volume change over extent of higher pressures. Thus, the change in the void volume in the sample cell for a non-rigid solid can be given as

$$\Delta V = V_i - V_o = -V^a - \Delta V_c \mp \Delta V_o \tag{5}$$

Ignoring the over- or under- estimation term for the void volume, ΔV_o , the excess adsorption originally defined for a rigid solid in Eq. (4) now can be written for “non-rigid” solids as:

$$n^{ex} = \left(1 - \rho/\rho^a\right)n^{abs} - \rho \Delta V_c \tag{6}$$

Furthermore, volumetric compressibility of a material, that is, the relative change of the volume of an adsorbent per unit original volume can be related to the pressure change at isothermal condition by the following equation, Eq. (7) (Greenkorn 1983):

$$\gamma = -\frac{1}{V_c} \left(\frac{\partial V_c}{\partial P}\right)_T \tag{7}$$

where γ is the expansion coefficient, MPa^{-1} , and V_c is the volume of the adsorbent at any pressure, cm^3/g . Integrating Eq. (7) from initial pressure of P_o to the any pressure of P and from initial volume of the adsorbent, V_{co} , to any volume, V_c , yields

$$V_c = V_{co}e^{-\gamma(P-P_o)} \tag{8}$$

Assuming the initial volume of the adsorbent is the volume of the adsorbent initially measured by the helium expansion method, and the initial pressure, P_o , is sufficiently small and negligible compared to P , the difference between the final and the initial volumes of the adsorbent, ΔV_c , becomes

$$\Delta V_c = V_{co}(e^{-\gamma P} - 1) \tag{9}$$

Inserting Eq. (9) in Eq. (6), the modified equation for a non-rigid adsorbent will take the form

$$n^{ex} = \left(1 - \rho/\rho^a\right)n^{abs} - \rho V_{co}(e^{-\gamma P} - 1) \tag{10}$$

The general equation, Eq. (10), can now be used to interpret the adsorption isotherms of non-rigid solids accounting for the volume changes. There are three unknowns in the general equation namely the adsorbed phase density, the absolute adsorbed amount, and the volumetric change or the compressibility parameter, which were shortly reviewed as follows.

1.2 Density of the adsorbed phase (ρ^a)

Because the density of the adsorbed phase cannot be measured directly, several approximations have been used, some of which are shown in Table 1. The approximations are based on one of two assumptions: Either that the density of the adsorbed phase remains constant and additional adsorbate occupies additional volume, or that the volume available for adsorption remains constant and additional adsorption causes an increase in the density of the adsorbed phase. The first class of approximations can be further divided depending on whether the temperature at which the adsorption occurring is below or above the critical temperature of the adsorbate. For temperatures below the critical point, the liquid density at the boiling point (Relch et al. 1980), a linear interpolation between the densities at the boiling and critical temperatures (Dubinin 1960), the

Table 1 Constant density approximation for the adsorbed phase

	Approximation	Relationship	Eq. no.
$T < T_c$	Liquid density (Relch et al. 1980)	$\rho^a = \rho_{liq}$	(14)
	Linear approximation (Dubinin 1960)	$\rho^a = \rho_b - (\rho_b - \rho_{vdw}) \left(\frac{T - T_b}{T_c - T_b} \right)$	(15)
	Superheated liquid (Wakasugi et al. 1981)	$\rho^a = \rho_{liq} e^{-k_T(T - T_b)}$	(16)
$T > T_c$	Inverse Van der Waals volume (Humayun and Tomasko 2000; Murata et al. 2001)	$\rho^a = \rho_{vdw} = \frac{8MP_c}{RT_c}$	(17)
	Critical density (Murata et al. 2001)	$\rho^a = \rho_c$	(18)
	Solid density (Zhou 1994)	$\rho^a = \rho_{solid}$	(19)

density of the super-heated liquid (Murata et al. 2001; Relch et al. 1980), and the density at the critical point (Murata et al. 2001) have been used as the adsorbed phase density. At temperatures above the critical temperature, the inverse of the van der Waals volume (Murata et al. 2001; Relch et al. 1980) and, rarely, the density of the solid adsorbate (Zhou 1994) have been used as the density of the adsorbed phase. For the cases involving the constant volume approximation, the adsorbed phase has been assumed to fill the pore volume of a microporous adsorbent (Salem et al. 1998), which is considered to be constant, and an effective film thickness (Wakasugi et al. 1981) has been assigned to describe the adsorbed phase volume. These latter two approximations view the solid and the pore volume as a rigid structure that does not change during the adsorption process. For this reason, they were not considered here further.

The conditions used for measuring CO₂ isotherms often include both the subcritical and supercritical regions. Figure 2 shows a number of proposed adsorbed phase densities of CO₂ at various temperatures. As can be seen in the figure, the estimates of the density of the adsorbed phase generally decrease as the temperature is increased to the

critical temperature. Extrapolation into the supercritical region would result in even smaller densities. For example, the saturated liquid density decreases almost exponentially and equals the critical density at the critical temperature. If this were the true adsorbed phase density, adsorption would occur in neither the liquid state nor above the critical temperature. However, Humayun and Tomasko (2000) have shown that this is clearly not the case. Using a microbalance technique, they estimated adsorbed phase densities at temperatures higher than T_c and found that the adsorbed phase densities were higher than the saturated liquid density (12.78 mol/cm³), and the compressed liquid density (20.19 mol/cm³), and were very near the van der Waals density (23.45 mol/cm³). Assumption of any adsorbed phase density a constant value will influence the curve fit parameters in evaluation of adsorption isotherm data.

1.3 Model equations for the absolute adsorption (n^{abs})

The absolute adsorption, n^{abs} , is the amount of material actually adsorbed on a solid adsorbent. Many adsorption-model equations have been proposed to represent the absolute adsorption amount. Some of these equations are based on a theoretical foundation, such as the (Langmuir 1918), B.E.T. (Brunauer et al. 1938), Eyring (Chaback et al. 1996), and virial equation of state (Chaback et al. 1996), while others are derived to provide empirical curve fits such as the Langmuir–Freundlich (Do 1998), Toth (Do 1998), UNILAN (Do 1998), modified B.E.T., (BETn) (Brunauer et al. 1938), and (Dubinin 1966) equations. Empirical equations, which are not related to physical factors, however, do not allow extrapolation beyond the range of the variables for which the parameters have been determined (Suzuki 1990). Some of the model equations used to represent the amount of gas in the adsorbed phase were summarized in Ozdemir et al. (2003) according to the mechanism of adsorption and the surface properties of the

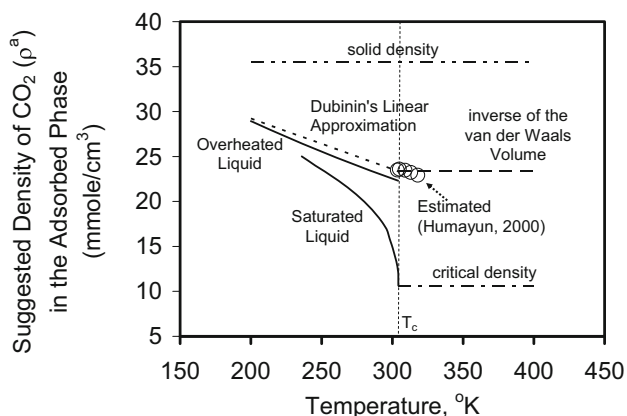


Fig. 2 Proposed adsorbed phase densities of CO₂ at various temperatures

solid adsorbent. For instance, the Dubinin-Astakhov (D-A) and Dubinin-Radushkovich (D-R) equations are based on a pore filling rather than surface adsorption mechanism. The B.E.T. is based on infinite numbers of adsorbed layers rather other than the monolayer adsorption as in the Langmuir equation. Among these, the D-A pore filling model was reported to fit better to the adsorption isotherms of gases on microporous coal (Busch and Gensterblum 2011; Clarkson and Bustin 1999; Harpalani et al. 2006; Ozdemir 2004; Ozdemir et al. 2003, 2004; Ozdemir and Schroeder 2009; Sakurovs et al. 2007, 2009). However, these equations do not account the creation of additional surface areas or pore volumes during the adsorption isotherm measurement for non-rigid solids.

1.4 Saturation pressure for CO₂ (P_s)

Some of the model equations to interpret the adsorption isotherms include the saturation pressure (P_s). For instance, the D-A equation, which is used to interpret the adsorption isotherms for microporous adsorbents according to a pore filling mechanism, contains the saturation pressure. While the saturation pressure can be defined at temperatures below the critical temperature, it does not have a physical meaning at temperatures greater than the critical temperature. However, as shown in Table 2, several relationships were suggested for curve-fit purposes to represent the saturation pressure at temperatures greater than the critical temperature. Figure 3 shows the suggested saturation pressure for CO₂ below and above its critical temperature. Although the saturation pressure has no physical meaning at temperatures above the critical temperature, the suggested saturation pressure relationships have been used for modeling purposes. As such, good fits have been reported for supercritical adsorption using estimated saturation pressures above critical temperatures (Clarkson and Bustin

1996; Dubinin 1960; Gil and Grange 1996; Sobolik et al. 1992).

2 Experimental

2.1 Coal samples

Isotherms describing the excess adsorption and desorption of CO₂ on the eight Argonne Premium coal samples (Vorres 1990, 1993) were measured at 55 °C and pressures up to 14 MPa using the manometric method as shown in Fig. 4. The as-received samples had an average particle diameter of about 150 μm (–100 mesh). To minimize surface oxidation (Schmidh 1945), sample handling was performed in a helium flushed glove bag under a positive pressure of He. A 0.6–1.3 g aliquot of as-received coal samples was used for each experiment. Before removing the coal samples from their sealed glass ampoules, they were mixed well according to the Argonne instructions (Vorres 1993). Each sample was dried in situ at 80 °C under vacuum for 36 h before any measurements were performed. The void volume of each sample cell containing the coal sample, V_o, was estimated using helium prior to the measurement of the adsorption isotherms.

2.2 Isotherm measurement method

After removing the helium under vacuum, the reservoir cell was pressurized with CO₂. Fifteen minutes were allowed to achieve thermal equilibrium, although a stable temperature reading was achieved in less than 5 min. Then, a portion of the gas was transferred from the reference cell into the sample cell. Pressure with 0.25 % of full scale accuracy and temperature (±0.1 °C) were monitored in both cells to verify thermal and adsorption equilibration. In initial tests

Table 2 Relationships for saturation pressure of CO₂

	Relationship	Ref.	Eq.
T < T _c	$P_s = P_c \exp [A(T_r) + wB(T_r)]$ where $A(T_r) = 5.92714 - 6.9648T_r^{-1} - 1.28862 \ln (T_r) + 0.169347T_r^6$ $B(T_r) = 15.2518 - 15.6875T_r^{-1} - 13.4721 \ln (T_r) + 0.43577T_r^6$	(Reid et al. 1977)	(20)
T > T _c	$P_s(CO_2, MPa) = -155.4953 + 1.75862T - 6.829149 \times 10^{-3}T^2 + 9.231018 \times 10^{-6}T^3$	(Kamiuto et al. 2001)	(21)
	$P_s = P_c \left(\frac{T}{T_c}\right)^2$	(Dubinin 1960)	(22)
	$f_s = P_c \left(\frac{T}{T_c}\right)^t$ $P_s(CO_2, MPa) = 7.382 \exp \left(9.98144 - 3036.254/T\right)$	(Amankwah and Schwarz 1995) (Kamiuto et al. 2001)	(23) (24)

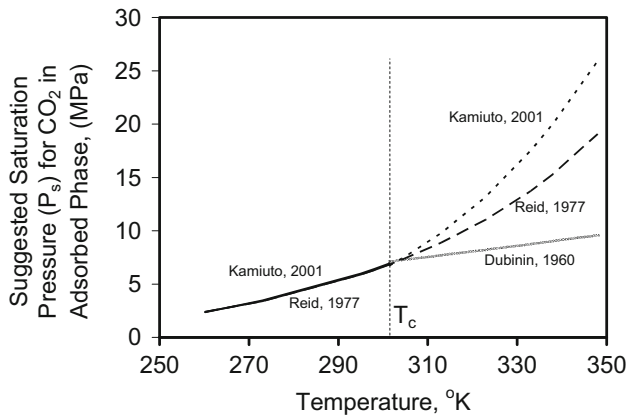


Fig. 3 Suggested saturation pressure for CO₂ at below and above its critical temperature

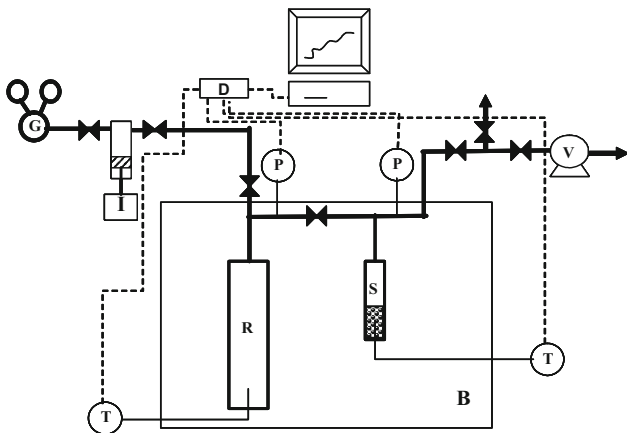


Fig. 4 Volumetric gas adsorption apparatus: R reservoir cell, S sample cell, P pressure transducer, T thermocouple, G gas cylinder, I ISCO syringe pump, D data acquisition system, V vacuum pump, B constant temperature bath

of up to 20 h, it was found that 20–30 min was sufficient to reach equilibrium for the adsorption of CO₂ on the powdered coal samples with a particle size of about 150 μm. The amount of CO₂ within both the reference and sample cell were calculated using the real gas law, which accounts for the gas compressibility (Span and Wagner 1996). From the mass balance, the difference between the moles of CO₂ transferred from the reservoir cell, n^r , and the moles of CO₂ calculated to be present in the He-estimated free-gas phase in the sample cell, V_o , was considered to be the Gibbs excess adsorption, n^{ex} (Ozdemir et al. 2003; Sircar 1999). The reference cell was then pressurized with additional CO₂ and the process was repeated. Adsorption isotherms were plotted as the total amount of excess adsorbed CO₂, n^{ex} , versus the measured equilibrium pressure.

2.3 Evaluation of the adsorption isotherm data

The CO₂ adsorption isotherm data were interpreted using Eq. (11). Here, the Dubinin-Astakhov (D-A) equation (Dubinin 1960), was employed to define the physical adsorption, n^{abs} , assuming a pore filling mechanism.

$$n^{ex} = \left(1 - \rho/\rho^a\right) n_o e^{-\left[\frac{RT}{\beta E_o} \ln(P_s/P)\right]^j} - \rho V_{co} (e^{-\gamma P} - 1) \quad (11)$$

where n^{ex} is the experimentally measured amount of adsorption, ρ is the density of the gas phase, ρ^a is the density of the adsorbed phase, n_o is the adsorption/micropore capacity, β is the affinity coefficient between CO₂ and the coal ($\beta = 0.35$ for CO₂) (Medek 1977), E_o is the characteristic heat of adsorption, j is the structural heterogeneity parameter, P_s is the saturation pressure, R is the universal gas constant, T is the temperature, V_{co} is the volume of the coal sample initially estimated by the helium expansion method, and γ is the expansion coefficient. The saturation pressure (P_s) and the density of the adsorbed phase (ρ^a) were calculated using the relationships suggested by Reid et al. (1977) and Dubinin (1960), respectively. The calculated values were $P_s = 12.317$ MPa and $\rho^a = 22.007$ mol/cm³ at 55 °C. Curve fitting was performed using the *SigmaPlot*[®] spreadsheet regression data analysis.

2.3.1 Calculation of isosteric heat of adsorption

The characteristic heat of adsorption, E_o , can be related to the isosteric heat of adsorption, Q_{st} , Eq. (12) (Aoshima et al. 2000) at the fractional filling ϕ of e^{-1} using the enthalpy of vaporization ΔH_v at the boiling point (17.1548 kJ/mol for CO₂) (Reid et al. 1977).

$$Q_{st, \phi=e^{-1}} = \Delta H_v + \beta E_o \quad (12)$$

2.3.2 Calculation of average pore size of coals from CO₂ adsorption isotherm

The Dubinin-Astakhov exponent, j , and the characteristic heat of adsorption, E_o , are related to the surface heterogeneity of the adsorbent (Debelak and Schrodt 1979; Medek 1977). From these two parameters, the average pore sizes of coals can be calculated from Medek's approach (Debelak and Schrodt 1979; Medek 1977):

$$r_e = \frac{(k/E_o)^{1/3}}{\Gamma\left(\frac{3j+1}{3j}\right)} \quad (13)$$

where k ($= 3.145$ kJnm³mol⁻¹ for CO₂) is a constant (Debelak and Schrodt 1979) and Γ is the gamma function.

3 Results and discussion

3.1 Adsorption and desorption isotherms of supercritical CO₂ on coals

Figure 5 shows the excess adsorption and excess desorption isotherms of CO₂ on Argonne Premium Pocahontas No. 3, Upper Freeport, Pittsburgh No. 8, Lewiston-Stockton, Blind Canyon, Illinois No. 6, Wyodak, and Beulah-Zap coals at 55 °C and pressures up to 14 MPa. The error bars show the expected error as estimated from the error analysis for the manometric gas adsorption apparatus used (Ozdemir 2004). The lines represent the best fit of the excess adsorption isotherm data to Eq. (11). As shown in the figure, the excess adsorption isotherms of CO₂ on powdered coals showed almost Langmuir-like to rectilinear shape behavior at low pressures up to 9 MPa. At pressures greater than 9 MPa, the excess adsorbed amount increased dramatically. At pressures larger than 12 MPa, the excess adsorbed amount slightly decreased. Following the excess adsorption isotherm measurements, excess desorption isotherms of CO₂ on each coal was obtained. As shown in the figure, there is a significant hysteresis between the excess adsorption and excess desorption isotherms for each rank of coals. During the desorption steps, the calculated excess amount is first increased, and then decreased as the pressure further reduced. Although the hysteresis between the excess adsorption and excess desorption isotherms was higher than expected due to volumetric changes occurring during the excess adsorption isotherm measurements and, as can be seen from the figure, to the experimental uncertainties since the expected error increases considerably at pressures higher than the critical pressure, P_c , of 7.38 MPa. Therefore, the desorption isotherms no longer considered for evaluation.

3.2 Variation of physical parameters during the adsorption isotherm measurements

By fitting the excess supercritical CO₂ adsorption data to the modified D-A equation, Eq. (11), the values of the physical constants including the adsorption capacity (n_0), characteristic heat of adsorption (E_0), Dubinin exponent (j), and expansion coefficient (γ), were obtained. To determine the variations of the physical parameters during the adsorption isotherm measurements, these values were estimated for increasingly larger pressure ranges, using only the first four data points of the excess adsorption isotherm initially for curve fitting, and progressively using additional data points for the subsequent values, and finally using the full range of data at about 12.317 MPa, which is the theoretical saturation pressure for CO₂ at 55 °C.

Therefore, the physical parameters and the changes in coal properties during the adsorption isotherm measurement were estimated at various pressures and adsorption levels.

3.2.1 Adsorption capacity of CO₂ on dried argonne coals

Figure 6 shows the adsorption capacity of CO₂ on dried Argonne coals as obtained by fitting the excess adsorption isotherm data to Eq. (11) over increasing pressure ranges. As shown in the figure, the general trend for the adsorption capacity is to increase as pressure increases up to 9 MPa. At pressures greater than 10 MPa, the adsorption capacity decreases slightly. The adsorption capacity of the Beulah Zap coal showed a different maximum at 5 MPa, after which the capacity decreased as the pressure increased further. The increase in the adsorption capacity is in very good agreement with the direct measurement of the CO₂ adsorption on coals using in situ infrared spectroscopy (Goodman 2009; Goodman et al. 2005). The increase in the adsorption capacity can be related to pore volume increase as a result of the swelling of coal during the CO₂ adsorption measurement.

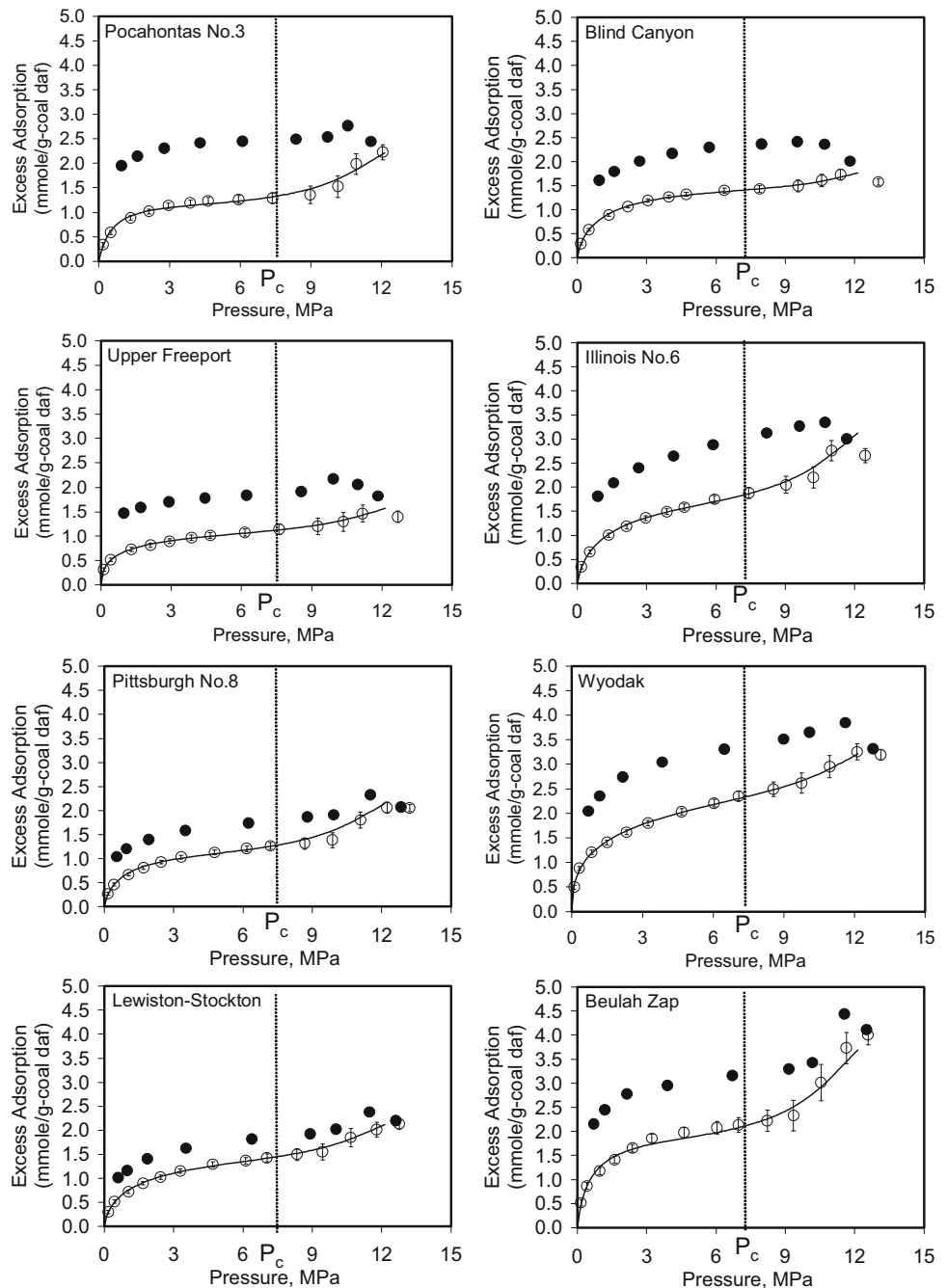
3.2.2 Isothermic heat of adsorption

Figure 7 shows the isosteric heat of adsorption for CO₂ adsorbed on each dried Argonne coal and its response to increasing pressure. As shown in the figure, the isosteric heat of adsorption decreases with pressure up to 6 MPa, goes through a minimum, and increases back as pressure further increases. The decrease in isosteric heat of adsorption can be related to the increasing in the pore sizes. As the pore size increases, the isosteric heat of adsorption is expected to become smaller because of a weakening of the surface potential exerted by the opposite walls of the coal matrix (Dubinin 1960).

3.2.3 Average pore sizes of dried argonne coals estimated from supercritical CO₂ adsorption isotherms

The average pore size can be calculated by using the Dubinin-Astakhov exponent, j , and the characteristic heat of adsorption, E_0 . Figure 8 shows the average pore sizes of dried Argonne coals calculated for increasing pressure ranges. As shown in the figure, the average pore sizes of dried coals goes through a maximum as pressure increases. This is somewhat expected because of the coal swelling (Ozdemir et al. 2003, 2004; Ozdemir and Schroeder 2009). For instance, the coal pores were shown to collapse as a result of the drying that occurred before the adsorption isotherm measurements were conducted (Ozdemir and Schroeder 2009). As shown in the figure, upon CO₂ adsorption, these pores re-open as coal continues to swell upon adsorption

Fig. 5 Excess adsorption and excess desorption isotherms of supercritical CO₂ on Argonne Premium coals at 55 °C



under higher CO₂ pressures. As the pressure approaches 6–10 MPa, the coal becomes saturated with the adsorbed CO₂. As the pressure increases further, the average pore sizes become smaller due in part to filling of those pores with the adsorbed CO₂, and/or to the change in the effective stress within the pores (Kowalczyk et al. 2008, 2010).

3.2.4 Expansion coefficient for the dried argonne coals

The expansion coefficients for the dried Argonne coals were obtained from the excess adsorption isotherms.

Figure 9 shows these values with increasing pressures. As can be seen from the figure, the expansion coefficient for all coal ranks is greatest at low pressures. This indicates that the volumetric change is significant at low pressures when CO₂ is introduced to the dry coal samples as the volume of the coal sample changes rapidly as a result of the recovery of the original volume of the coals which was shrunken as a result of drying (Ozdemir et al. 2003, 2004; Ozdemir and Schroeder 2009).

Figure 10 compares the expansion coefficient, γ , obtained under a CO₂ atmosphere for the Argonne

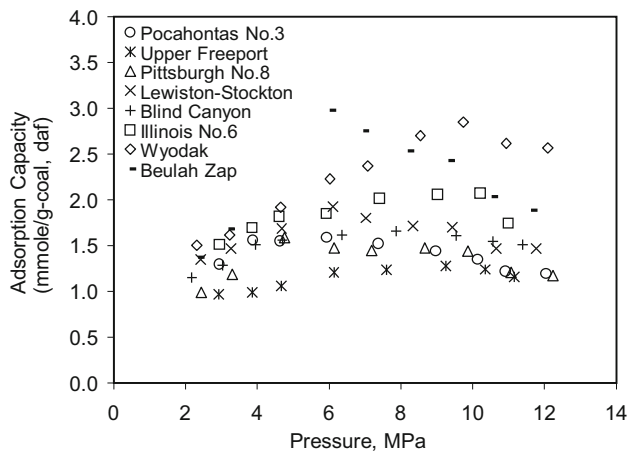


Fig. 6 Variation in adsorption capacity during excess adsorption isotherm measurements obtained from curve fit parameters of CO₂ on the dried Argonne Premium coals at 55 °C

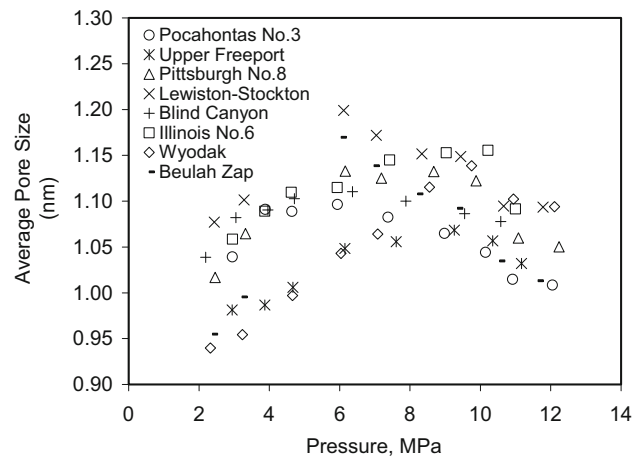


Fig. 8 Variation in average pore size during the excess adsorption isotherm measurements obtained from curve fit parameters of CO₂ on the dried Argonne Premium coals at 55 °C

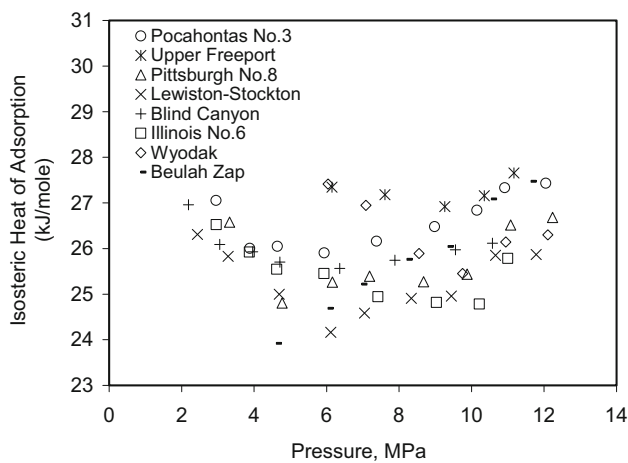


Fig. 7 Variation in characteristic heat of adsorption during the excess adsorption isotherm measurements obtained from curve fit parameters of CO₂ on the dried Argonne Premium coals at 55 °C

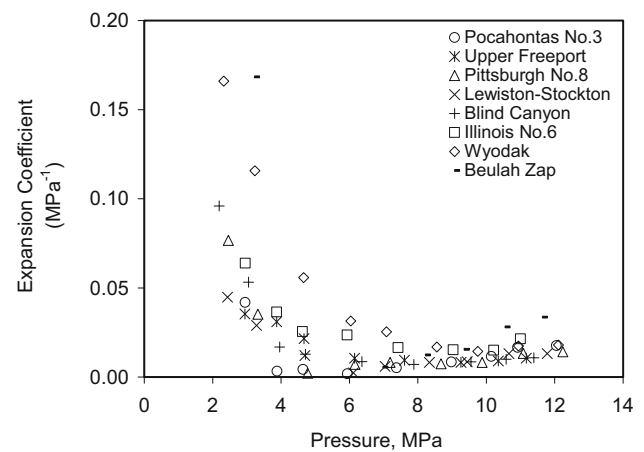


Fig. 9 Variation in expansion coefficient during the excess adsorption isotherm measurements obtained from curve fit parameters of CO₂ on the dried Argonne Premium coals at 55 °C

Premium coals as well as for other coals of various ranks as reported by Walker et al. (1988). In previous one, the expansion coefficient was obtained from the CO₂ adsorption isotherms using the modified Dubinin-Astakhov equation while, in the latter case, the bulk compressibility was estimated from the dimensional change. As shown in the figure, the pore compressibility under CO₂ atmosphere obtained from the adsorption isotherms (this work) is 10 times higher than the bulk compressibility obtained from the dimensional change (Walker’s data). The trend is in good agreement with the literature data although these values are 1–2 orders of magnitude larger than the expansion factors estimated from dimensional changes under triaxial stress tests. For instance, Harpalani et al. (1989) reported the compressibility factor of coal measured

under the triaxial conditions as 1.3×10^{-4} , 66×10^{-4} , and 9.1×10^{-4} MPa⁻¹ for the bulk compressibility, pore compressibility (assuming a 2 % porosity), and matrix shrinkage compressibility, respectively. The compressibility estimated under a CO₂ atmosphere is higher for the low rank coals. It decreases with coal rank up to 83 C %, and then, slightly increases as the coal rank further increases. This is a trend similar to that observed for the shrinkage of coals upon moisture loss (Ozdemir and Schroeder 2009). The values of γ , from which the volume changes can be calculated, clearly show that there is a volumetric effect on the adsorption isotherm measurements and should be treated accordingly.

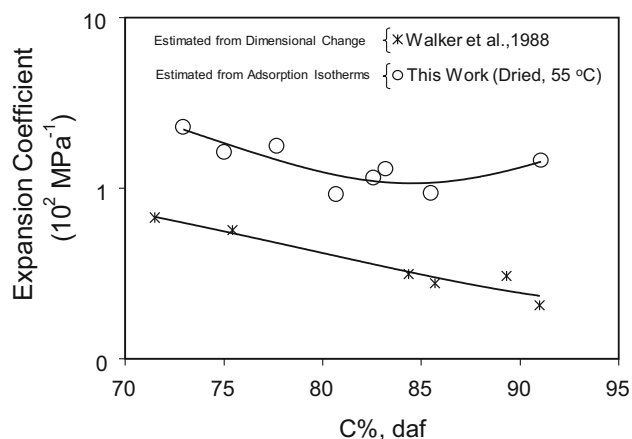


Fig. 10 Comparison of the expansion coefficient, γ , for coals under a CO_2 atmosphere as obtained from the excess adsorption isotherms (pore compressibility) and obtained from the dimensional changes (bulk compressibility) reported by Walker et al. (1988)

4 Conclusion

The variations in curve fit parameters clearly indicate that the adsorption on non-rigid solids is a dynamic process. In a dynamic process, the curve fit parameters must not be constant. The adsorption equation used to represent the absolute adsorbed amount, n^{abs} , must therefore account for the nature of the adsorption process as well as the dynamic changes that occur during the adsorption measurements. In the future, new adsorption equations need to be developed representing the dynamic nature of the adsorption processes.

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