High Pressure Supercritical Carbon Dioxide Adsorption in Coal: Adsorption Model and Thermodynamic Characteristics

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Abstract: This work uses a dual-site Langmuir adsorption model to describe supercritical carbon dioxide (scCO₂) adsorption in coal up to 20MPa and 253K. The isosteric heat of adsorption for scCO₂ in coal is calculated analytically by considering both the real gas behavior and the adsorbed phase, which are ignored in the classic Clausius-Clapeyron approximation. It was found that the proposed model can not only reasonably interpret observed test phenomena but also has the intrinsic ability to extrapolate adsorption isotherms under different temperatures beyond test data. The crossovers of the observed adsorption isotherms under different temperatures are caused by the changing volume of the adsorbed phase during the adsorption process. Both the temperature dependence and adsorption uptake dependence of isosteric heat of adsorption are revealed; the higher the temperature and the adsorption uptake, the lower the isosteric heat of adsorption. The ideal gas law overestimates the isosteric heat of adsorption for scCO₂ in coal. The application of the dual-site Langmuir model allows for estimating the CO₂ storage capacity of deep unminable coal seams, modeling CO₂ transport behavior via differentiating the true ratio between bulk phase and adsorbed phase, and investigating the true thermodynamic characteristics of CO₂ in coal under high pressures.

Key words: carbon dioxide, adsorption, coal, Langmuir, isosteric heat of adsorption

1. Introduction

Because of global warming and climate change concerns, global efforts have been made to decrease the concentration of carbon dioxide in the atmosphere (Grubb et al., 1995; Stern, 2009; Morgan et al., 2014; Paris Protocol, 2015). Carbon dioxide capture, utilization and storage are considered crucial ways to meet the carbon dioxide emission reduction targets. Onshore geological sequestration of carbon dioxide typically involves capturing, transporting and injecting carbon dioxide into suitable underground formations for storage such as depleted oil and conventional gas reservoirs, unconventional natural gas reservoirs (unminable coal seams and shale formations), deep saline formations, and basalt formations (Herzog et al., 2001; White et al., 2003; Metz et al., 2005; Benson et al., 2008; Orr, 2009; Figueroa et al., 2008). Among these geological formations, unminable coal seams are one of the promising options because of their potential for enhancing coalbed methane (ECBM) recovery while simultaneously sequestering carbon dioxide (White et al., 2005; Mazzotti et al., 2009; Busch et al., 2011; Godec et al., 2014). The enhanced natural gas will help to offset the cost of carbon dioxide sequestration. However, there are still some concerns about the long-term effect of sequestration of CO₂ in coal seams and potential environmental consequences (White et al., 2005; Hedges et al., 2005). Carbon dioxide injection issues arise during the field injection process because of the permeability decrease induced by coal swelling (Reucroft, et al., 1987; Pan et al., 2007 & 2010; Cui et al., 2007; Day et al., 2008). The existing phases of the injected carbon dioxide in the subsurface are crucial for the carbon dioxide storage capacity estimation. Therefore, field tests of ECBM with carbon sequestration were and are being conducted around the world, which are helpful to understand the potential benefits and practical issues (Steven et al., 1998; Yamasaki, 2003; Gunter et al., 2004; Sams et al., 2005; White et al., 2005; Van Bergen, et al., 2006; Wong et al., 2007; Ripepi, 2009; Connell et al., 2013; Gilliland et al., 2013; Wei et al., 2015).

It is well known that the affinity of carbon dioxide in coal is higher than methane, and the amount of carbon dioxide adsorbed in coal is always higher than methane at the same pressure. In order to evaluate the carbon dioxide storage potential of unminable coal seams, the first step is to evaluate the adsorption capacity of carbon dioxide in coal via isothermal sorption tests. However, because of the heterogeneous properties of coal, scCO₂ adsorption behavior in coal has not garnered research attention like it has for manmade materials. There are inconsistent test phenomena reported regarding scCO₂ adsorption in coal. Some researchers show peculiar test phenomena for scCO₂ in coal such as the bimodal Gibbs excess adsorption isotherms (Krooss et al., 2002; Toribio et al., 2004; Busch et al., 2007; Simons et al., 2007; Busch et al., 2008). Other researchers exhibit smooth CO₂ excess adsorption isotherms in coal when the pressure rises up to 20MPa (Sudibandriyo et al., 2003; Fitzgerald et al., 2005; Bae et al., 2006; Ottiger et al., 2006; Sakurovs et al., 2007; Day et al., 2008; Pini et al., 2010; Weniger et al., 2010; Song et al., 2015; Luo et al., 2015). Since the latter test phenomena can be reproduced and the former cannot, the peculiar test phenomenon is attributed to artificial test errors (Ottiger et al., 2006; Pini et al., 2010). Even though the smooth CO₂ excess adsorption isotherms have been observed, an optimized model for modeling both the Gibbs excess and absolute adsorption uptake is still needed. Despite extensive research for scCO₂ adsorption in manmade materials, a number of semi-empirical models have been adopted by revising the classic D-A, D-R, Langmuir and Toth equations to describe the sorption behavior of scCO₂ in coal by fitting each isothermal adsorption curves independently (Sudibandriyo et al., 2003; Fitzgerald et al., 2005; Bae et al., 2006; Ottiger et al., 2006; Sakurovs et al., 2007; Day et al., 2008; Pini et al., 2010; Schell et al., 2012; Weniger et al., 2010; Song et al., 2015; Luo et

al., 2015; Moreira et al., 2017). However, all these models are based on either the empirical density of adsorbed carbon dioxide (density of liquid carbon dioxide) in coal or the assumed constant volume of adsorbed carbon dioxide in coal. Even though good fitting results are obtained by each researcher, the physical meaning of the obtained parameters from these revised classical equations still needs to be confirmed. Furthermore, even though the coal swelling phenomena has been observed, few models include coal swelling to obtain absolute isotherms from Gibbs excess isotherms (Ozdemir et al., 2003; Romanov et al., 2006; Pini et al., 2010). Considering both the adsorption and penetration (absorption) CO_2 in coal may explain the coal swelling effect during the sorption process. The penetration CO_2 can not only compensate the elastic energy change associated with volume change but also can change the macromolecular structure of coal (Jakubov et al., 2002; Larsen, 2004; Pini et al., 2010). In addition, these models cannot be used to extrapolate isotherms beyond test temperatures. The prediction of adsorption isotherms under high pressure and high temperature geological conditions are critical for carbon dioxide storage capacity estimations in the deep subsurface. Therefore, to reasonably interpret the adsorption behavior of scCO_2 in coal and predict adsorption isotherms under high temperature and high pressure in-situ conditions, a more concise and robust adsorption model is needed.

As a crucial evaluation index for the thermodynamic process in physical adsorption tests, the isosteric heat of adsorption for scCO_2 in coal has rarely been considered by researchers. There are still several issues that exist regarding the calculation of this index for scCO_2 adsorption in coal (Pan et al., 1998; Chakraborty et al., 2006; Stadie, 2012; Baran et al., 2013; Stadie et al., 2013 & 2015). First, the absolute adsorption isotherms must be obtained from the observed adsorption isotherms in order to calculate the isosteric heat of adsorption, where a robust model is needed (Herbst et al., 2002; Bae et al., 2006). Under low pressure conditions, the observed adsorption isotherm approximates the absolute adsorption isotherm, and there is no need to obtain the absolute adsorption isotherm. However, when the Gibbs excess adsorption behavior becomes obvious under higher pressure conditions, a reliable adsorption model is necessary to obtain the absolute adsorption uptake from observed adsorption isotherms. Second, even though the absolute adsorption isotherms can be obtained, the classic Clausius-Clapeyron approach is not appropriate because it cannot take the real gas behavior of scCO_2 and the adsorbed gas phase into consideration (Pan et al., 1998; Chakraborty et al., 2006; Stadie et al., 2015). Figure 1 shows the deviation of CO_2 behavior compared with ideal gas under different temperatures and pressures. The usage of the Clausius-Clapeyron approach therefore will hide the true behavior of the isosteric heat of adsorption because the Clausius-Clapeyron approach uses the ideal gas assumption and neglects the adsorbed gas phase volume (Chakraborty et al., 2006; Stadie et al., 2015). It has been found that both the gas behavior and the adsorbed gas phase volume can significantly influence the isosteric heat of adsorption (Chakraborty et al., 2006; Mertens, 2009; Stadie et al., 2015). Therefore, in order to obtain the true behavior of the isosteric heat of adsorption, the real gas behavior and the adsorbed gas phase volume must be reasonably considered.

Figure 1 Deviation behavior of the CO₂ under different temperatures and pressures (Data is obtained from the NIST Standard Reference Database 23 (REFPROP: Version 8.0.))

To tentatively solve the above-mentioned issues, this work first uses a dual-site Langmuir model to describe scCO₂ adsorption behavior in coal by considering both the adsorbed phase and the absorbed (penetrated) phase. Then, the published data of high pressure scCO₂ adsorption in two different coals are obtained from literature in order to validate the proposed model. Last, isosteric heats of adsorption for scCO₂ are calculated analytically by considering the real gas behavior of scCO₂ and the contribution of the adsorbed phase.

2. Absolute adsorption model

Coal swelling is a pronounced phenomenon associated with CO₂ injection into coal seams, which can result in injectivity issues during field tests (White et al., 2005; Van Bergen, et al., 2006). Researchers have used different approaches such as dilatometric method, optical or strain gages, and X-ray and small-angle scattering techniques to study the coal swelling effects in a laboratory scale, but have not reached an agreement on whether the coal swelling is universal or not. Radlinski et al. (2009) found that coal microstructures were unaffected by exposure to CO₂ over a period of days based on the SANS and USANS tests. Most other researchers agree that the uptake of CO₂ in coal results in the swelling monotonically with pressure which can be modeled by Langmuir-type curves based on laboratory evidence (Levine, 1996; Palmer and Mansoori, 1998; Shi and Durucan, 2004a; Cui et al., 2007; Pini et al., 2009 & 2010),

$$\varepsilon_s = \varepsilon_0 \cdot \frac{k_s P}{1 + k_s P} \quad (1)$$

where ε_s is the swelling strain under specific pressure, P , ε_0 and k_s are fitting coefficients.

Based on the assumption that coal swelling is induced by the CO₂ penetration (absorption) in the macrostructure of coal, the dual-site model is used for describing both the CO₂ adsorption and the CO₂ absorption in coal as shown in equation (2) (Fornstedt et al., 1996; Graham et al., 1953; Larsen, 2004; Pini et al., 2010). Figure 2 shows how the CO₂ phase changes before and after CO₂ sorption: the absolute adsorption is the sum of net adsorption and absorption uptake. The dual-site model therefore combines both the adsorption and absorption content of CO₂ in coal, represented by a Langmuir-type term. In addition, the absorption term essentially has similar properties with the coal swelling behavior.

$$n_a = n_{ad} \frac{K_1(T)P}{1 + K_1(T)P} + n_{ab} \frac{K_2(T)P}{1 + K_2(T)P} \quad (2)$$

where n_a is the absolute adsorption content under specific pressure, P , n_{ad} is the net adsorption content, n_{ab} is the absorption content, $K_1(T)$ and $K_2(T)$ are corresponding Langmuir contents ($K_1(T) = A_1 \cdot \exp(-\frac{E_1}{RT})$ and $K_2(T) = A_2 \cdot \exp(-\frac{E_2}{RT})$), T represents temperature, E_1 and E_2 are corresponding adsorption energies, A_1 and A_2 are corresponding prefactors, R is universal gas constant), P is pressure.

Figure 2 The difference of CO₂-coal sorption system before and after CO₂ adsorption.

If the absorbed and adsorbed phase can be weighted by a parameter, α , and equation (2) is rearranged, the following form can be obtained,

$$n_a = n_{\max} \cdot \left[(1 - \alpha) \left(\frac{K_1(T)P}{1 + K_1(T)P} \right) + \alpha \left(\frac{K_2(T)P}{1 + K_2(T)P} \right) \right] \quad (3)$$

where $n_{\max}$ is the maximum adsorption capacity. Notably, the physical meaning of $n_{\max}$ in equation (3) is different from the conventional Langmuir equation which is composed of both the net adsorption content and the absorption content. The term “adsorbed” will be used in the following sections as a simplification which actually refers to both adsorbed and absorbed (penetrated) phases for CO₂ in coal.

3. Gibbs excess adsorption model and isosteric heat of adsorption

3.1 Gibbs excess adsorption model

For a pure gas and solid sorption system, the excess adsorbed amount (n_e) can be shown by the Gibbs equation (4) (Gibbs, 1878),

$$n_e = n_a - V_a \cdot \rho_g = n_a \left(1 - \frac{\rho_g}{\rho_a} \right) \quad (4)$$

where n_e is the excess adsorption content, n_a is the absolute adsorption content, V_a is the total volume of both the absorbed and adsorbed phases, ρ_a is the density of adsorbed phase and ρ_g is the density of bulk phase under specific temperature and pressure. When the V_a is very small, the contribution of the

adsorbed phase can be neglected and n_e is the approximation of the n_a (Zhou et al., 2001). However, for a high pressure sorption system, the contribution of the adsorbed phase must be taken into consideration to physically interpret the abnormal gas adsorption behavior. For example, the observed adsorption uptake increases, reached maximum and then decreases with increasing gas pressure. Therefore, it is imperative to find a reasonable approach for obtaining the absolute isotherms from Gibbs excess isotherms for the gas-solid sorption system under high pressure and temperature.

Considering the accepted assumption that the density of the adsorbed phase can be treated as an unknown constant (Agarwal et al., 1988; Zhou et al., 2001; Do et al., 2003; Mertens, 2009; Stadie et al., 2012; Schell et al., 2012; Stadie et al., 2013 & 2015; Tang et al., 2016), the volume of the adsorbed gas phase can be obtained by equation (5),

$$V_a = \frac{n_a}{\rho_a} \quad (5)$$

Combining with equation (3), equation (5) can be rewritten as,

$$V_a = V_{\max} \cdot \left[(1 - \alpha) \left(\frac{K_1(T)P}{1 + K_1(T)P} \right) + \alpha \left(\frac{K_2(T)P}{1 + K_2(T)P} \right) \right] \quad (6)$$

where V_a is the total volume of the adsorbed phase under specific temperature and pressure, $V_{\max}$ is the maximum volume at maximum adsorption content, $V_{\max} = n_{\max} / \rho_a$. Based on equations (3), (4) and (6), both excess adsorption (n_e) and surface coverage (θ) equations can be obtained as shown in equation (7) and (8)

$$n_e(P, T) = (n_{\max} - V_{\max} \cdot \rho_g) \cdot \left[(1 - \alpha) \left(\frac{K_1(T)P}{1 + K_1(T)P} \right) + \alpha \left(\frac{K_2(T)P}{1 + K_2(T)P} \right) \right] \quad (7)$$

$$\theta = \frac{n_a}{n_{\max}} = (1 - \alpha) \frac{K_1(T)P}{1 + K_1(T)P} + \alpha \left(\frac{K_2(T)P}{1 + K_2(T)P} \right) \quad (8)$$

If the observed adsorption isotherms (Gibbs excess adsorption isotherms) are obtained through isothermal adsorption tests, equation (7) is able to describe the adsorption behavior where the parameters ($V_{\max}$, $n_{\max}$, $K_1(T)$, $K_2(T)$, α) can be obtained via curve fitting. The absolute adsorption content can then be solved for via equation (5).

3.2 Isosteric heat of adsorption

Based on the Clausius–Clapeyron relationship (Clausius, 1850), it is known,

$$\Delta H_{ad} = \left(\frac{dP}{dT} \right)_{n_a} \cdot T \cdot \Delta v = \left(\frac{dP}{dT} \right)_{n_a} \cdot T \cdot (v_a - v_g) \quad (9)$$

where ΔH_{ad} is the isosteric heat of adsorption, $\Delta v(= (v_a - v_g))$ is the volume change of the phase change, v_g is the molar volume of the bulk gas phase, v_a is the molar volume of the adsorbed phase, and T is temperature.

In order to obtain ΔH_{ad} , the $(\frac{dP}{dT})_{n_a}$ must be obtained first (Chakraborty et al., 2006; Stadie et al., 2015).

Based on the surface coverage concept (equation (3)), the following relationship can be obtained using the chain rule (Mertens, 2009; Stadie et al., 2014 & 2015),

$$(\frac{dP}{dT})_{n_a} = (\frac{\partial P}{\partial \theta})_{n_a} \cdot (\frac{\partial \theta}{\partial K})_{n_a} \cdot (\frac{\partial K}{\partial T})_{n_a} \quad (10)$$

Combining with equation (9) and (10) and applying the ideal gas law ($Pv_g = RT$), we can obtain one form of isosteric heats of adsorption mathematically (equation (11)),

$$-\Delta H_{ads(n_a), IGL} = (\frac{\partial P}{\partial \theta})_{n_a} \cdot (\frac{\partial \theta}{\partial K})_{n_a} \cdot (\frac{\partial K}{\partial T})_{n_a} \cdot T \cdot (\frac{RT}{P} - \rho_a^{-1}) \quad (11)$$

If we combine equation (10) and (11) and apply the real gas law, another analytical form of the isosteric heat of adsorption can be obtained (equation (12)),

$$-\Delta H_{ads(n_a), RGL} = (\frac{\partial P}{\partial \theta})_{n_a} \cdot (\frac{\partial \theta}{\partial K})_{n_a} \cdot (\frac{\partial K}{\partial T})_{n_a} \cdot T \cdot (\rho_g^{-1} - \rho_a^{-1}) \quad (12)$$

Equation (12) and (13) are much easier to solve using the analytical approach. Equation (13) shows the analytical solution of $(\frac{dP}{dT})_{n_a}$ (Mertens, 2009; Stadie et al., 2013 & 2015),

$$(\frac{\partial P}{\partial \theta})_{n_a} \cdot (\frac{\partial \theta}{\partial K})_{n_a} \cdot (\frac{\partial K}{\partial T})_{n_a} = \frac{\frac{(1-\alpha)P}{(1+K_1(T)P)^2} \cdot \frac{-E_1 K_1(T)}{RT^2} + \frac{\alpha P}{(1+K_2(T)P)^2} \cdot \frac{-E_2 K_2(T)}{RT^2}}{\frac{(1-\alpha)K_1(T)}{(1+K_1(T)P)^2} + \frac{\alpha K_2(T)}{(1+K_2(T)P)^2}} \quad (13)$$

Using the dual-site Langmuir adsorption model, absolute adsorption isotherms can be obtained from the excess adsorption isotherms. The isosteric heat of adsorption can then be calculated considering the real gas behavior and the contribution of the adsorbed phase, neither are considered in the classic Clausius-Clapeyron approximation.

2. Data set acquisition and processing

High pressure (over 7.4 MPa) scCO₂ adsorption isotherms in coals are limited, and only two sets of data are directly retrieved from the literature (Song et al., 2015; Ottiger et al., 2006). These data were measured using the gravimetric approach to obtain the scCO₂ sorption isotherms in dry coal under different temperatures and pressures (≥ 15 MPa). Detailed information about these tests can be found in the original publications (Song et al., 2015; Ottiger et al., 2006). The pertinent data from these papers are shown in Figure 3.

Figure 3 Experimental data retrieved from Song et al. (2015), Ottiger et al. (2006); the dotted line is to connect data points for visualization.

The observed adsorption isotherms under different temperatures are fitted simultaneously using equation (7) within the limits of the fitting parameters ($0 < n_{\max} < 100$ mmol/g, $0 < V_{\max} < 100$ cm³/g, $0 < \alpha < 1$, 10 kJ/mol $< E_1, E_2 < 100$ kJ/mol, $0 < A_1, A_2$). The test data is processed using the Universal Global Optimization (UGO) method of the Auto2Fit software (7D-soft High Technology Inc., China), and the UGO can find the global maximum/minimal value of any functions without using the initial start values. The obtained fitting parameters are shown in Table 1.

Table 1 Fitting parameters (equation (7)) for observed adsorption isotherms using four adsorption isotherms

Samples	Temperatures (K)	$n_{\max}$ (mmol/g)	$V_{\max}$ (cm ³ /g)	α	E_1 (kJ/mol)	E_2 (kJ/mol)	A_1 (MPa ⁻¹)	A_2 (MPa ⁻¹)
Chinese coal	293.29, 311.11, 332.79, 352.55	1.6675	0.0752	0.4941	26.702	25.497	2.15E-04	1.10E-05
Sulcis coal	318.15, 333.15	6.3932	0.2220	0.6612	28.019	36.940	5.16E-05	1.54E-08

Once all the fitting parameters are obtained from fitting the observed adsorption isotherms using equation (7), the absolute adsorption isotherm can be calculated using equation (5). Then, the isosteric heat of adsorption can also be obtained using equations (11) & (12).

5. Modeling results and discussions

5.1 Observed and absolute adsorption isotherms

Figure 4 shows the dual-site Langmuir model fits observed adsorption isotherms very well. It is clear that the predicted absolute adsorption content of scCO₂ increases continuously with increasing pressures. The absolute adsorption content is much higher than Gibbs excess adsorption isotherms. The distinguishable difference between observed and absolute adsorption isotherm implies the significant contribution of the adsorbed layer of scCO₂ in coal for absolute adsorption content.

Figure 4 Fitting adsorption isotherms using dual-site Langmuir model for five coals; solid line: Gibbs excess fitting (equation (8)) and dotted line: absolute adsorption uptake (equation (5))

For both coals, there are consistent crossovers of the observed adsorption isotherms under different temperatures after the observed adsorption content reached the maximum value. After the crossover, the observed adsorption content at higher temperatures is greater than at low temperatures under the same pressure. However, the temperature-dependent property of adsorption uptake under different temperatures can be shown via the absolute adsorption uptake, where the higher the temperature the lower the adsorption uptake. The abnormal crossover phenomenon of the observed adsorption isotherms appears because the pressure is used as the independent variable, instead of the density of scCO_2 . Figure 5 shows two components of Gibbs excess adsorption uptake (equation (7)), surface coverage (Θ) and the term $(n_{\max} - V_{\max} * \rho(P, T))$, as a function of pressure and density. When the pressure is treated as a variable, the term $(n_{\max} - V_{\max} * \rho(P, T))$ show temperature as well as pressure dependency feature because of the density of scCO_2 , $\rho(P, T)$. However, when the pressure is treated as a density, the term $(n_{\max} - V_{\max} * \rho(P, T))$ only show the pressure-independency feature. Therefore, the cross-over is simply caused by the PVT behavior of scCO_2 .

Figure 5 Surface coverage (solid line, left axial) and the term $(n_{\max} - V_{\max} * \rho(P, T))$ (dotted lines, right axial) with increasing pressure (density) for both Chinese and Sulcis coals

5.2 Adsorption isotherm prediction

For geological storage of carbon dioxide in subsurfaces such as unminable coal seams and shale formations, one of the crucial issues is to estimate the storage capacity of carbon dioxide under real geological conditions. With increasing depth, both in-situ reservoir pressure and geothermal effect become pronounced, and there will be a phase change of carbon dioxide from subcritical status to supercritical status. Thus, carbon dioxide storage capacity must take high pressure and high temperature conditions into consideration. However, it is impractical to measure all isotherms under different temperatures. Therefore, finding an adsorption model capable to predict higher temperature adsorption isotherms using lower temperature data pique researchers' interests.

Predicting isotherms under different temperatures are possible using the proposed model because the temperature dependency of adsorption isotherms are only exhibited through the Langmuir constant ($K_1(T)$ and $K_2(T)$ in equations (3 and 7)). Figure 6 (left part) shows that the predicted adsorption isotherms have the same feature of the observed adsorption isotherms, where both the crossovers and the abnormal phenomenon (the higher the temperature the high the observed adsorption uptake) occur. When the adsorption isotherms are plotted as a function of bulk density, the crossovers disappear, which means the higher the temperature the lower the observed adsorption uptake. This behavior can also be shown in the predicted adsorption isotherms (Figure 6, right part).

Figure 6 Prediction of adsorption isotherms (black lines) beyond test data; left part: adsorption uptake as a function of pressure; right part: adsorption uptake as a function of bulk density.

5.3 Confidence of the predicted adsorption isotherms

In order to validate the prediction ability of the proposed model, the Chinese coal sample is taken as an example to show the confidence of the predicted adsorption isotherms. First, only three adsorption isotherms from the four isotherms are fitted using the proposed method. Then, the predicted

adsorption isotherms are compared with the test data to see the difference. Table 2 shows that the fitting parameters use only three adsorption isotherms. Figure 7 shows that all predicted isotherms are consistent with test data. The predicted adsorption isotherms beyond test data are approximately the same. This also means the best-fit parameter can only be achieved using a large set of measured data.

Table 2 Fitting parameters (equation (7)) for observed adsorption isotherms using only three adsorption isotherms

Samples	Fitting isotherms (K)	Predicted isotherms (K)	$n_{\max}$ (mmol/g)	$V_{\max}$ (cm ³ /g)	α	E1(kJ/mol)	E2(kJ/mol)	A1(MPa ⁻¹)	A2(MPa ⁻¹)
Chinese coal	293.29, 311.11, 332.79	352.55, 392.57	1.6837	0.0760	0.5345	26.593	27.244	6.08E-06	1.54E-04
	293.29, 332.79, 352.55	311.11, 392.57	1.6521	0.0745	0.5033	27.632	24.941	1.66E-04	1.44E-05
	293.29, 311.11, 352.55	332.79, 392.57	1.6471	0.0742	0.5050	26.962	25.192	2.05E-04	1.41E-05

Figure 7 Adsorption isotherms comparison between predicted data using three adsorption isotherms (dotted lines). Solid symbol represents test data.

5.4 Thermodynamic analysis of isotherms

Figure 8 shows isosteric heats of adsorption calculated using equations (11) and (12) and it can be seen that (i) the isosteric heat of adsorption decreases with increasing absolute adsorption uptake and (ii) temperature dependence of the isosteric heat of adsorption. It is also clear that the isosteric heats of adsorption using the ideal gas law are always higher than that using the real gas law at the same temperature. This means the isosteric heats of adsorption using the ideal gas law always overestimates the isosteric heat of adsorption. Both the temperature dependency and adsorption uptake dependency of the isosteric heat can also be readily shown using the proposed approach.

Figure 8 Comparison of different isosteric heats of adsorption for scCO₂ in coal: isosteric heat of adsorptions using ideal gas law (dotted lines) and real gas law (solid lines), and the gas phases are supercritical and liquid in the magnified area.

After carbon dioxide becomes scCO₂ (or liquid CO₂), the heat of adsorption shows different behaviors as shown in the magnified area in Figure 8. When the CO₂ is in liquid phase, the isosteric heat of adsorption is the lowest compared with scCO₂. When the CO₂ becomes scCO₂, the isosteric heat of adsorption decreases with increasing absolute adsorption uptake but there are crossovers of isosteric heat of adsorption under different temperatures, which has not been reported in literature. This can be attributed to the enhanced interaction among the adsorbed phase over the coal surface at a higher density (Schaef et al, 2013). Figure 9 shows the density at low temperatures is much higher than that at high temperatures for scCO₂, which may strengthen the enhanced interaction effect.

Figure 9 Density of liquid and scCO₂; dotted line represents liquid carbon dioxide and solid line represents scCO₂

6 Implications for geological carbon dioxide storage

Carbon dioxide storage in deep unminable coal seams and deep shale formations are two promising geological sites for onshore carbon sequestration. Since the adsorption phase of carbon dioxide in coal is one of the main components of the total carbon dioxide gas-in-place in the subsurface, the accurate prediction of adsorption carbon dioxide in coal is crucial. With the increasing reservoir depth, high pressure and high temperature geological situations have to be considered. Such geological conditions result in the change of carbon dioxide from subcritical phase to supercritical phase, and an optimized model is needed to analyze such behavior. The proposed dual-site Langmuir model can describe both the observed adsorption and the absolute adsorption of sub- and super-critical carbon dioxide in coal. In

order to accurately assess the storage capacity of scCO₂ in coal, equation (14) should be used for the total carbon dioxide gas-in-place (GIP) in the subsurface (Tang et al., 2016),

$$GIP_{CO_2} = n_e + V_{tot}\rho_g \quad (14)$$

Where n_e is the observed adsorption uptake (Gibbs excess adsorption uptake), V_{tot} is the total pore space of coal measured by Helium intrusion test, and ρ_g is the density of bulk gas. Equation (14) supports the fact that if the observed adsorption isotherms are obtained from laboratory tests, the carbon dioxide storage capacity can be accurately assessed and there is no need to differentiate absolute adsorption content from observed adsorption isotherms. However, this is only valid for estimating the total storage capacity of coal seams. In order to understand the existing status of injected carbon dioxide in coal and carbon dioxide transport behavior under reservoir conditions, the true ratio between bulk carbon dioxide and the adsorbed phase must be known. Using the observed adsorption isotherms (Gibbs excess adsorption isotherms) will always underestimate the true content of the adsorbed phase as shown in Figure 4. The dual-site Langmuir model can solve this problem by extrapolating the true content of the adsorbed phase (equation (3)) from observed adsorption isotherms. Furthermore, for large scale carbon dioxide injection tests in deep coal seams, one of the fundamental issues is to understand how the injected carbon dioxide transports within the coal matrix (Tang et al., 2015). Since carbon dioxide exists in coal seams mainly in two states (free gas and adsorbed phase), the adsorbed phase influences the transport behavior of carbon dioxide because it not only occupies space in nanopores but also interacts with pore walls. It has been found that the adsorbed gas phase significantly affects adsorptive gas (methane) transport in coal seams and shale formations (Yu et al., 2014; Akkutlu et al., 2012; Civan et al., 2011; Singh et al., 2016; Naraghi et al., 2015; Wu et al., 2016). This situation will also occur with respect to carbon dioxide transport in coal. Therefore, in order to build a reasonable gas transport model for carbon dioxide transport in coal seams, the first step is to obtain the true ratio of the free phase to the adsorbed phase (Tang et al., 2016). The proposed dual-site Langmuir adsorption model makes this possible.

7 Conclusions

This work uses a dual-site Langmuir adsorption model to describe high pressure carbon dioxide adsorption in coal by considering both the adsorbed and absorbed phases. Then, the isosteric heat of adsorption are calculated analytically by considering both the real gas behavior and the adsorbed gas phase. Last, the published data for high pressure carbon dioxide adsorption in coal are utilized to verify the proposed model.

Modeling results reveal the proposed model can not only reasonably address observed test phenomena but also has the intrinsic ability to extrapolate adsorption isotherms under different temperatures beyond test data. It was found that the crossovers of the observed adsorption isotherms under different temperatures are caused by the changing volume of the adsorbed and absorbed phases during the adsorption process.

Both the temperature dependence and absolute adsorption uptake dependence of the isosteric heat of adsorption are readily investigated for scCO₂ in coal; for subcritical carbon dioxide, the higher the temperature and the higher the absolute adsorption uptake, the lower the isosteric heat of adsorption. The gas behavior significantly affects the quantity of the isosteric heat of adsorption: the isosteric heat

of adsorption using the ideal gas law always overestimates the isosteric heat of adsorption for scCO_2 in coal. For scCO_2 adsorption in coal, there exists an abnormal phenomenon that the higher the temperature the higher the isosteric heat of adsorption, which has not been previously reported in the literature.

The proposed adsorption model lays the foundation for accurately estimating the storage capacity of carbon dioxide, differentiating the true ratio between the adsorbed phase and bulk phases and developing gas transport models that consider the adsorbed phase effect. The thermodynamic analysis is useful for interpreting temperature related phenomena associated with carbon dioxide adsorption in coal as well as shale gas reservoirs.

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