



Experimental and theoretical characterization of methane and CO₂ sorption hysteresis in coals based on Langmuir desorption



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ABSTRACT

Sorption hysteresis is important for primary gas production and CO₂ sequestration in coalbed methane (CBM) reservoirs. We represent the degree of hysteresis using an areal hysteresis index (AHI) method incorporating a hysteresis parameter β , representing the ratio of available sorption sites for desorption relative to adsorption. This approach was applied to quantify the gas-coal sorption hysteresis to both methane and CO₂ on sub-bituminous and bituminous coals and on anthracite. A theoretical desorption model describes hysteresis based on the molecular dynamic equilibrium between gas adsorption and desorption rates. Volumetric excess ad-/desorption isotherms of methane and CO₂ show that adsorption capacities for anthracite are higher than those for the sub-bituminous and bituminous coals over the entire experimental pressure range. Hysteresis for CO₂ is greater than for methane for all four coal samples investigated. The relationships between β and Langmuir pressure, Langmuir volume and final equilibrium pressure are weakly negative with null relationships between β and coal properties. Sorption hysteresis is caused by Langmuir pressure and gas type based on theoretical and experimental analyses although its physical mechanism remains unclear. A $\beta_{\text{CH}_4} - \beta_{\text{CO}_2}$ plot is proposed as a screening tool to determine likely gas substitution contents for enhanced coalbed methane (ECBM) and CO₂ sequestration in coals.

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1. Introduction

With the rapid development of coalbed methane (CBM), CBM reservoir assessments of both original gas-in-place (GIP) and anticipated recoverable reserve by secondary gas injection become increasingly important (Moore, 2012). Gas sorption on coal is one of the most important parameters for CBM reservoir assessment (Busch and Gensterblum, 2011). For primary CBM production, gas transport is a multi-stage process. Gas initially desorbs from internal pores, then diffuses from the surrounding coal matrix and flows through cleats and/or fractures to the wellbore. During enhanced coalbed methane (ECBM) production, CO₂ is introduced via injection wells into the coal cleat/fracture system, diffuses into the matrix and adsorbs on the internal pores. Simultaneously, methane desorbs from these pores and diffuses from the matrix and flows towards the wellbore. Therefore, sorption behavior is critical for both primary CBM production and for ECBM operation.

The irreversibility of sorption hysteresis is defined as the difference between adsorption and desorption isotherms. Methane sorption hysteresis affects CBM production behavior because gas recovery is controlled by desorption rather than by adsorption (K. Wang et al., 2014). Sorption hysteresis was first reported in gas-coal sorption experiments (Anderson et al., 1966), and interpreted as excess activation energy

between gas and coal macromolecules in the desorption process (Bell and Rakop, 1986). Systematic analyses of adsorption and desorption of both methane and CO₂ on dried Argonne Premium coals (Busch et al., 2003) showed that the hysteresis of CO₂ decreased with an increase in coal rank. However, this rank dependent hysteresis was not observed for methane ad-/desorption. The observed hysteresis was attributed to the metastable state of interaction between gas and coal, which in turn is closely related to thermodynamic equilibrium (Busch et al., 2003). The rank dependent hysteresis to CO₂ was also observed in other studies, and interpreted as related to the residual moisture in the coal matrix (Ozdemir et al., 2003, 2004). Residual-moisture-induced hysteresis was confirmed by an inter-laboratory comparison of CO₂ ad-/desorption on a set of Argonne Premium coals (Goodman et al., 2004). In addition to the effects of residual moisture, irreversible coal matrix swelling and CO₂ trapped in ink-bottle pores were also identified as potential root causes for the sorption hysteresis (Goodman et al., 2004). In addition, gas sorption hysteresis may also result from absorption and/or dissolution of gas molecules into the structure of the solid coal matrix (Weishauptova et al., 2004) or the formation of gas clusters in mesopores (Romanov and Soong, 2008). This latter effect is dependent on the maximum equilibrium pressure for methane (Jessen et al., 2008). Furthermore, CO₂ sorption experiments on both dried and as-received coals indicate that CO₂ hysteresis is greater for dried rather than as-received samples for low rank coals (Ozdemir and Schroeder, 2009) and smaller for wet samples in anthracites (He et al., 2010). An unexpected

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crossover is apparent between the adsorption and desorption isotherms near the CO₂ critical point for dry coal, while for wet coals, the adsorption isotherm is greater than that for desorption (He et al., 2010). Additionally, sorption hysteresis may result from an activation barrier for volatile matter presenting at pore throats in heat-treated coals (Bae et al., 2009). Hysteresis to CO₂ ad-/desorption increases with an increase in moisture content (Pan et al., 2010). This hysteresis is negligible for methane but discernable for CO₂ for dry coal, where the desorption isotherm is below the adsorption curve at -65 °C but switches to above the adsorption curve at -45 °C (Battistutta et al., 2010). Alternately, this CO₂ hysteresis may be caused by residual moisture, insufficient equilibrium time, gas absorption and the influence of coal particle size (Zhang et al., 2014). The discrepancy of Langmuir volume between adsorption and desorption increases with an increase in particle size for both methane and CO₂. Adsorption isotherms remained constant during four cycles of subcritical CO₂ sorption (G. Wang et al., 2014), while desorption isotherms depended on the maximum equilibrium pressure — agreeing with previous methane sorption study (Jessen et al., 2008). This hysteresis effect was explained as caused by kinetic restriction or by the accessibility of narrow pore throats in the coal matrix (G. Wang et al., 2014). An improved HI method (K. Wang et al., 2014) identified the role of energy difference between gas entering and leaving narrow pore throats in micropores as a potential mechanism. Further laboratory studies exploring methane and CO₂ hysteresis on coals can be found elsewhere (Dutta et al., 2011; Harpalani et al., 2006; Kim et al., 2011; Pillalamarri et al., 2011; Zhou et al., 2013).

Based on previous mentioned studies, gas-coal adsorption/desorption hysteresis for both methane and CO₂ is influenced by numerous parameters. These include influences of both sample state (coal rank, moisture and volatile contents) and experimental procedures (coal particle size, maximum equilibrium pressure). The posited causes for gas-coal sorption hysteresis can be summarized as: gas absorption into the coal matrix; physical (swelling/shrinkage) or thermodynamic (energy barrier) limits on accessibility to pore throats and pores; and systematic instrumental and experimental errors such as insufficient equilibrium time for sorption capacity estimation. These posited mechanisms are based on direct experimental observations, although fundamental mechanisms of sorption hysteresis are not fully understood. In this study, four coal samples representing a spectrum of ranks were used to estimate adsorption and desorption capacities for both methane and CO₂. A hysteresis parameter β was introduced to characterize the hysteresis to both methane and CO₂. The proposed methodology for the characterization of hysteresis was compared with the areal hysteresis index (AHI) method utilizing the difference in area under both desorption and adsorption isotherms (Zhu and Selim, 2000). A Langmuir model was used to represent the gas adsorption isotherms and a proposed Langmuir desorption model was applied to model gas desorption. Hysteresis of both methane and CO₂ isotherms for tested coals was evaluated. The correlations between β and the modeled parameters and coal properties were discussed based both on these and prior observations (Busch et al., 2003; Dutta et al., 2011). Mechanisms for, as well as the implications of, methane and CO₂ sorption hysteresis are also discussed.

2. Experimental methods

2.1. Sample preparation and characterization

Four samples, one each of sub-bituminous and bituminous coal together with two anthracites, were collected from four different mines. The sub-bituminous coal was obtained from the northern San Juan basin in New Mexico. The bituminous coal was collected from the Pittsburgh No. 8 seam in Pennsylvania. The two anthracites were collected from Good Spring and Williamstown in Pennsylvania. Hand-pulverized powders were used for the sorption experiments. These were hand-crushed using a high strength ceramic pestle and mortar (rather than by mechanical mill) to minimize the influence on coal micro-structure,

the over-crushing of resulting coal fines, and to limit external sample contamination.

Proximate analyses were conducted on all four coal samples with the results summarized in Table 1. San Juan coal has the highest moisture and ash contents but the lowest fixed carbon and sulfur contents. Conversely, Pittsburgh No. 8 coal has the highest volatile matter and sulfur contents, but the lowest ash content. The two anthracite samples (Good Spring and Williamstown coals) have approximately the same moisture, fixed carbon, and sulfur contents. All sorption experiments were carried out under *as-received* conditions.

2.2. Sorption experiment protocol

The schematic of the experimental setup is shown in Fig. 1. The setup consisted of stainless steel reference and sample cells fabricated to withstand pressure up to 20 MPa. A set of two- and three-way valves (V_1 , V_2 , V_3 and V_4) were used to achieve the desired flow and storage of gas. The cells were placed in a high precision constant temperature water bath (± 0.1 °C) to maintain the desired constant temperature and related control on gas pressures (measured by dual high accuracy transducers).

Incremented then decremented pressure steps for the experiments are as shown in Fig. 2. The sorption experiments were conducted at 35 °C rendering both methane (supercritical transition temperature - 82.6 °C) and CO₂ (31.1 °C) as potentially supercritical. For each sample, methane sorption was measured before that for CO₂. Pressures were first incremented in five to six pressure steps to record the gas adsorption isotherm, followed by five to eight decrements for the desorption isotherm. For methane, the maximum sorption pressure was <9 MPa for all samples and for CO₂, it was set at ~6.5 MPa, to retain the CO₂ (7.38 MPa) as subcritical avoiding the inherent complexity of phase transition during the sorption experiment. Excess adsorption and desorption capacities were estimated as shown in Appendix 1.

3. Sorption model

3.1. Adsorption

There are many adsorption models that can be used to estimate absolute adsorption capacity for coals. These include Freundlich (Freundlich, 1906), Langmuir (Langmuir, 1918), Brunauer-Emmett-Teller (BET) (Brunauer et al., 1938), Dubinin-Radushkevich (D-R) (Dubinin et al., 1947) and Dubinin-Astakhov (D-A) (Dubinin and Astakhov, 1971) models, among others. However, the most applicable and widely used adsorption model is Langmuir model (Langmuir, 1918). The derivation of this model is based on the supposed molecular dynamic equilibrium of adsorption and desorption rates of gas, where the adsorbate is represented as a monolayer-adsorbed on the surface of the adsorbent (Langmuir, 1918). The classic form of the Langmuir model can be expressed as:

$$V_{ab} = \frac{V_L P}{P_L + P} \quad (1)$$

where V_{ab} is the absolute adsorption capacity; P is the gas equilibrium pressure; V_L is the maximum absolute adsorption capacity; P_L is the gas equilibrium pressure at half of V_L ; V_L and P_L are known as Langmuir

Table 1
Coal sample basic information.

Sample	Particle size (mm)	Moisture (%)	Volatile (%)	Fixed carbon (%)	Ash (%)	Sulfur (%)
San Juan	0.500–0.595	4.66	35.42	40.75	19.17	0.55
Pittsburgh No. 8	0.177–0.250	2.13	39.01	55.02	3.84	1.63
Good Spring	0.177–0.250	1.58	8.33	77.52	12.57	0.62
Williamstown	0.177–0.250	2.06	6.03	76.42	15.49	0.64

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