# energy&fuels

# Unsteady-State Diffusion of Gas in Coals and Its Relationship with Coal Pore Structure

Haijun Guo,<sup>†,‡</sup> Yuanping Cheng,<sup>\*,†,‡,§</sup> Liang Yuan,<sup>†,‡</sup> Liang Wang,<sup>\*,†,‡</sup> and Hongxing Zhou<sup>†,‡</sup>

<sup>†</sup>Key Laboratory of Coal Methane and Fire Control, Ministry of Education, China University of Mining and Technology, Xuzhou, Jiangsu 221116, China

<sup>‡</sup>National Engineering Research Center of Coal Gas Control, China University of Mining & Technology, Xuzhou, Jiangsu 221116, China

<sup>§</sup>School of Civil, Mining & Environmental Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

ABSTRACT: Coalbed methane (CBM) is under consideration as a potential energy resource because of its global abundance. The exploitation and development of CBM depends on the correct characterization of coal structure and gas migration properties. In this paper, four coal samples with different degrees of metamorphism were collected from the northern China mining area. The gas desorption properties of these samples were studied using a modified gas desorption experimental setup. A nonconstant diffusion coefficient (non-CDC) model was introduced to analyze the gas diffusion properties. In addition, both mercury intrusion porosimetry (MIP) and low-pressure nitrogen gas adsorption (LP-N<sub>2</sub>GA) were used to investigate the coal pore structure. The results indicate that gas desorption and diffusion vary significantly in coal samples with different degrees of metamorphism and that the non-CDC model could accurately describe gas diffusion in coal. In bituminous and anthracite coal, gas desorption and diffusion abilities increased with the increasing degree of metamorphism, but both properties were greater in lignite coal. Comparing the pore structure characteristics and the gas desorption and diffusion properties showed that lignite's particular pore structure resulted in a higher gas adsorption capacity than for high-volatility bituminous coal. The initial desorption and diffusion in lignite were also greater than in medium-volatility bituminous coal or anthracite coal. These results suggest that lignite has significant potential for CBM exploitation and development.

# 1. INTRODUCTION

Gas migration in coal is commonly observed during coal mining. The process of coal mining releases the gas in coal bodies due to the destruction of the coal's structure. This can result in coal and gas outbursts<sup>1–6</sup> and gas explosions,<sup>7–10</sup> which are caused by increased methane concentrations resulting from the accumulation of desorbed coalbed methane (CBM). CBM exploitation depends on the characteristics of gas desorption, diffusion, and seepage in a particular area, which affect gas production and the difficulty of exploitation.<sup>11–13</sup> For these reasons, it is important to understand gas migration in coal.

One step of the coal gas migration processes is gas diffusion, which is a concentration equilibrium process where gas flows from high to low concentrations because of random molecule movement.<sup>14,15</sup> Gas diffusion is involved in the release of gas from coal during mining, gas emission from the broken coal during the outburst development process, and the gas desorption indices of drilling cuttings that are used to predict coal and gas outbursts in China. The gas concentration in coal changes over time as gas diffuses. This means that gas diffusion in coal is unsteady-state gas diffusion. Coal is generally regarded as a porous medium for the purpose of studying gas migration. For porous media, pore structure plays an important role in gas migration.<sup>16</sup> Based on their physical adsorption properties and capillary condensation theory, pores in the porous media are classified into the following three categories by the International Union of Pure and Applied Chemistry (IUPAC): micropores ( $\leq 2$  nm in diameter), mesopores (2-50 nm in diameter), and macropores ( $\geq$ 50 nm in diameter).<sup>17,18</sup> This article follows these IUPAC pore standards.

Studies of gas diffusion in coal began in the early 1950s, leading to many mathematical models of gas desorption and diffusion in porous media.<sup>19</sup> Some investigators later modified the associated analytical solutions, combining them with the results of experimental research on coal samples to create many empirical or semiempirical equations describing gas diffusion properties in coal. $^{20-24}$  In China, the studies by Yang and Wang were especially important.<sup>25,26</sup> They combined diffusion mass transfer theory with experimental analysis to investigate coal gas emission and coal and gas outbursts. They proposed the limit particulate size hypothesis, which states that pores only exist in coal particles if the coal particles are small enough and if their gas diffusion can be described by Fick's law. This allowed them to construct and solve differential equations describing gas diffusion in coal particles. Later, Wu<sup>27</sup> and Guo et al.<sup>28</sup> tested the diffusion coefficients and convective mass transfer coefficients and discussed the transformation of the gas diffusion boundary conditions. Coal gas diffusion theory has continued to develop in recent years, with a large number of experimental and theoretical models.<sup>29-36</sup> In the previous studies, the diffusion coefficient is considered and used as a constant.<sup>20,25,26,29</sup> Generally, for calculating the constant diffusion coefficient, only the initial desorption period, for

Received:May 23, 2016Revised:July 29, 2016Published:August 9, 2016

Table	1.	Proximate	and	Petrograj	phic A	Analyses	of	the	Coal	Samples	s <sup>u</sup>
-------	----	-----------	-----	-----------	--------	----------	----	-----	------	---------	----------------

 ${}^{a}M_{ad}$  = moisture content on air-dried basis;  $A_{ad}$  = ash content on air-dried basis;  $V_{daf}$  = volatile matter content on dry ash-free basis;  $F_{cad}$  = fixed carbon content on air-dried basis;  $V_{L}$  = Langmuir volume;  $P_{L}$  = Langmuir pressure;  $R_{0max}$  = maximum vitrinite reflectance.

example where  $Q_t/Q_{\infty} \leq 0.5$ , is considered because the gas desorbs relatively fast. The models based on the constant diffusion coefficient were set and used in certain engineering cases with low accuracy. However, it is found that the current constant diffusion coefficient models could not accurately characterize the gas migration properties in coals, which cannot well involve the entire process of gas diffusion in coal pores.

In this article, the unsteady-state gas diffusion properties in coal were investigated based on traditional gas diffusion theory and using a non-CDC model. Using a modified gas desorption experimental setup, gas desorption and diffusion in coal samples with different degrees of metamorphism were analyzed. Additionally, the pore structure characteristics of the different coal samples were measured using MIP and LP-N<sub>2</sub>GA tests, and the effects of the coal pore structure on gas desorption and diffusion were investigated. Finally, the implications of the degree of metamorphism in coal samples on CBM exploitation and development are discussed.

# 2. EXPERIMENTAL WORK

**2.1. Coal Samples.** In the paper, four coal samples with different degrees of metamorphism were collected directly from working faces of the northern China mining area. The samples were sealed in canisters to prevent oxidization and then immediately transported to the laboratory for analysis. The four coal samples were labeled 1–4. Table 1 shows the results of proximate analysis, gas adsorption experiments, vitrinite reflectance measurements, and coal rank.

The coal rank is a measure of the degree of coalification, and can be quantified by  $V_{daf}$ <sup>37</sup> As  $V_{daf}$  decreases, the coal rank increases; thus, the degree of metamorphism of the coal samples increases from sample #1 to sample #4. This is consistent with the maximum vitrinite reflectance of the four coal samples.

2.2. Experimental Methods. 2.2.1. Gas Desorption. In the most cases, coal sampled from the mining area is in a broken or pulverized state; that is, most coal samples are in particulate form.<sup>19,38</sup> Therefore, the gas diffusion properties in coal sample are generally measured via desorption or sorption methods.<sup>14</sup> In this paper, the desorption method was used. Once the coal particles had achieved adsorption equilibrium at a certain pressure, the free gas in the coal sample tank was released rapidly, after which desorption reflecting the gas pressure relief was recorded. These data were used to study the gas diffusion law and compute the diffusion coefficient. For a sufficiently small coal particle size, most of the fractures are destroyed. Thus, compared to the gas diffusion resistance from pores during gas migration, the gas seepage resistance from fractures can be ignored. Hence, it can be assumed that the gas migration in coal particles is solely due to gas diffusion.<sup>39–41</sup> To compare the measurements from the different coal samples, the coal particles should be sieved to the same size prior to analysis. However, the coal particle size should not be too small. Based on the China National Standards AQ/T 1065-2008 and GB 474-2008, the four coal samples were sieved to a particle size range of 1-3 mm and dried in a vacuum drying oven at 105 °C for 12 h.

In this study, the traditional gas desorption experimental setup was modified. As shown in Figure 1, a reference tank and a gas sample bag were added to the conventional gas desorption experimental setup to eliminate the experimental error caused by human operation.



**Figure 1.** Modified gas desorption experimental setup. (1) High pressure  $CH_4$  cylinder; (2) pressure reducing valve; (3) reference tank; (4) vacuum pump; (5) constant temperature bath; (6) coal sample tank; (7) gas desorption measuring cylinder; (8) gas sample bag; (a–d) pressure gauge; (e–g) valve.

In this study, the gas desorption experiments included the following steps:

- The density ( $\rho$ ) of a coal sample was measured using an Ultrapyc 1200e Automatic Gas Pycnometer for Density from Quantachrome; the instrument has a resolution and accuracy of 0.0001 g/mL and 0.02%, respectively. Next, coal particles (weighing  $m_c$ ) were placed in the coal sample tank. The temperature of the thermostatic water bath was adjusted to 60 °C, and the coal particles were outgassed for approximately 24 h under high vacuum to remove air and other impurities. Once the pumping had ceased, the temperature of the thermostatic water bath was adjusted to 30 °C and the coal sample tank was filled with methane (>99.9% purity) to an adsorption equilibrium pressure. It was considered that adsorption equilibrium had been reached after 6 h of unchanged pressure.
- The volume  $(V_c)$  of the coal sample in the coal sample tank was obtained using the following equation:

$$V_{\rm c} = \frac{m_{\rm c}}{\rho} \tag{1}$$

The volume of gas molecules adsorbed onto the coal pore surfaces is extremely small, which means that it can be ignored. Thus, combining the volume  $(V_{\rm ct})$  of the coal sample tank with  $V_{ct}$  the free gas volume  $(V_{\rm f})$  in the coal sample tank at adsorption equilibrium was calculated using the following equation:

$$V_{\rm f} = V_{\rm ct} - V_{\rm c} \tag{2}$$

The free gas volume ( $V_{\rm fo}$ ) under the standard conditions was obtained with the following equation:

$$\frac{P_{\rm eq}V_{\rm f}}{T_{\rm eq}} = \frac{P_{\rm 0}V_{\rm f0}}{T_{\rm 0}}$$
(3)



Figure 2. Gas migration process in coal bodies.

where  $P_{\rm eq}$  is the adsorption equilibrium pressure in the coal sample tank, MPa;  $T_{\rm eq}$  is the temperature of the coal samples in the coal sample tank, K;  $P_0$  is the standard pressure of 0.101325 MPa; and  $T_0$  is the standard temperature of 273.15 K.

• Next, the valve (g; see Figure 1) was opened to link the coal sample tank to the gas sample bag, allowing the pressure to reduce to atmospheric pressure. As soon as possible, the valve (g) was then turned to connect the coal sample tank to the gas desorption measuring cylinder. The desorbed gas volumes at different times (t) were measured by recording the liquid level. Based on the atmospheric pressure and temperature outside the coal sample tank, the volumes were converted into volumes at STP ( $V_t$ ). The gas volume in the gas sample bag was measured and converted into the volume at STP ( $V_{co}$ ), and then the modified volume ( $Q_t$ ) of the desorbed gas per unit mass at various times t was obtained using the following equation:

$$Q_{t} = \frac{V_{t} - (V_{f0} - V_{co})}{m_{c}}$$
(4)

The ultimate desorption volume  $(Q_{\infty})$  as t approached  $\infty$  was calculated as follows:<sup>40</sup>

$$Q_{\infty} = \left(\frac{V_{\rm L} P_{\rm eq}}{P_{\rm L} + P_{\rm eq}} - \frac{V_{\rm L} P_{\rm a}}{P_{\rm L} + P_{\rm a}}\right) (1 - M_{\rm ad} - A_{\rm ad})$$
(5)

where  $P_{\rm a}$  is the atmospheric pressure outside the coal sample tank, MPa.

2.2.2. Evaluation of the Diffusion Coefficients. As a naturally fractured organic rock, coal offers a large amount of promising storage space and provides channels for CBM transportation.<sup>37,42-44</sup> Gas migration in coal is a complex process. According to molecular movement theory, gas molecules are instantly adsorbed and/or desorbed by the coal pore surface.<sup>19</sup> However, gas migration in coal must last for some time because of the resistance caused by gas diffusion out of various types of pores in the coal matrix and its flow through the fractures in coal. Thus, when studying gas migration in coal, the dual porosity media model is generally accepted. This model regards coal as a porous medium consisting of coal matrices and fractures.  $^{45-50}$  Adsorbed gas and free gas occur in the coal matrix pores, while the fractures act as channels for free gas migration. As shown in Figure 2, gas migration in coal can be simplified to three processes: first, adsorbed gas on the coal pore surface is desorbed; second, free gas diffuses from the coal matrices to the fractures; and finally, the gas flows out of the coal bodies.<sup>30,51,52</sup> Thus, gas diffusion is important because it constitutes the initial stage of gas migration in coal.

To quantify the gas diffusion process from a mathematical point of view, the Fick's law is used:  $^{14,25,34}$ 

$$J = -D\frac{\partial c}{\partial h} \tag{6}$$

where *J* is the diffusive flux, kg/(m<sup>2</sup>·s); *D* is the diffusion coefficient or diffusivity, which reflects the diffusion "rate", m<sup>2</sup>/s; *c* is the concentration, kg/m<sup>3</sup>; *h* is the distance, m; and  $\frac{\partial c}{\partial h}$  is the concentration gradient (a vector). The negative sign indicates that the direction of the diffusive flux is opposite to the direction of the concentration gradient.

Coal is a complex porous material and the mechanisms of gas diffusion are affected by many factors. However, pore size and pore structure are generally considered have the greatest effect. Some studies have suggested the following analytical solution for the gas diffusion coefficient of a spherical coal particle:<sup>14,25</sup>

$$\frac{Q_{t}}{Q_{\infty}} = \frac{6\sqrt{Dt}}{\sqrt{\pi}a} - \frac{3Dt}{a^{2}}$$
(7)

where  $\frac{Q_t}{Q_{\infty}}$  is the desorption ratio; and *a* is the radius of the spherical coal particle, m.

For coal, the gas diffusion coefficient D is far less than 1; hence, if the desorption time is very short, the above equation can be simplified as follows:<sup>25,53</sup>

$$\frac{Q_t}{Q_\infty} = \frac{6\sqrt{Dt}}{\sqrt{\pi}a} = K\sqrt{t}$$
(8)

where  $K = \frac{6\sqrt{D}}{\sqrt{\pi}a}$ .

Eq 8 indicates that there is a linear relationship between  $\frac{Q_t}{Q_{\infty}}$  and  $\sqrt{t}$  if the desorption time is very short. In the Cartesian coordinate system, a linear fit of  $\frac{Q_t}{Q_{\infty}}$  versus  $\sqrt{t}$  yields a value of K; this allows the calculation of the gas diffusion coefficient *D*. Eq 8 is generally used to determine the coalbed gas content.

The above method assumes a constant diffusion coefficient and is only accurate for short desorption times. Recently, some investigators<sup>14,39</sup> have proposed a non-CDC model, in which the diffusion coefficient depends on the time *t*; the relationship between  $\frac{Q_t}{Q_{\infty}}$  and *t* is as follows:

$$\frac{Q_t}{Q_{\infty}} = \frac{6\sqrt{\int_0^t Ddt}}{\sqrt{\pi}a} - \frac{3\int_0^t Ddt}{a^2}$$
(9)

Assuming the following:

#### **Energy & Fuels**

$$\begin{cases} x = \frac{\sqrt{\int_0^t Ddt}}{a} \\ F = \frac{Q_t}{Q_{\infty}} \end{cases}$$
(10)

Eq 9 can be converted into the following unary quadratic equation:

$$3x^2 - \frac{6}{\sqrt{\pi}}x + F = 0$$
 (11)

Solving eq 11 gives the following solution:

$$x = \frac{\frac{6}{\sqrt{\pi}} - \sqrt{\frac{36}{\pi} - 12F}}{6} = \frac{1}{\sqrt{\pi}} - \sqrt{\frac{1}{\pi} - \frac{F}{3}}$$
(12)

Assuming that  $y = \int_0^t Ddt$ :

$$y = a^{2}x^{2} = a^{2} \left(\frac{1}{\sqrt{\pi}} - \sqrt{\frac{1}{\pi} - \frac{F}{3}}\right)^{2}$$
(13)

Given this value of *y*, the diffusion coefficient *D* can be calculated as follows:

$$D = \frac{dy}{dt} \tag{14}$$

From eq 10, we can see that the F and  $Q_t$  are closely related. An indirect way to calculate the D could be adopted in order to smooth the data in the above differential calculation. F calculated from a high degree polynomial is used to obtain y, and central differentials can be used to obtain D.

2.2.3. Coal Pore Characteristics Test. In this article, mercury intrusion porosimetry (MIP) and low-pressure nitrogen adsorption (LP-N<sub>2</sub>GA) were used to analyze the pore characteristics of the four coal samples.

MIP is widely used to analyze the pore size distribution of porous materials including coal.<sup>54–56</sup> The pore structure differences were determined using an AutoPore IV 9510 (Micromeritics, USA), and the data were modeled using the Washburn equation:  $^{55,57-59}$ 

$$r = \frac{2\sigma\cos\theta}{p_c}$$
(15)

where *r* is the pore radius of porous materials (nm),  $\sigma$  is the surface tension of Hg (dyn/cm<sup>2</sup>),  $\theta$  is the contact angle between Hg and the coal surface (deg), and  $p_c$  is the external pressure (MPa).

The LP-N<sub>2</sub>GA technique is typically used to measure the nanoscale pore size distribution in porous materials. The principle of the technique is based on using porous materials as the adsorbent and N<sub>2</sub> as the adsorbate; the volume of gas adsorption is recorded while the gas pressure is gradually increased to the saturated vapor pressure at a constant temperature of 77 K.<sup>60</sup> The adsorption/desorption isotherm is obtained from the volume of the pores and the pore sizes or the relative pressure. Equilibrium isotherms of N<sub>2</sub> at 77 K can detect pore sizes from 0.3 to 300 nm.<sup>61</sup>

#### 3. EXPERIMENTAL RESULTS

r

**3.1. Gas Desorption and Diffusion Properties.** Figure 3 and Table 2 show the gas desorption volumes, initial gas desorption rates, and ultimate desorption volumes of the four coal samples at the different adsorption equilibrium pressures. The desorption tests demonstrate that sample #1 had the largest initial desorption capacity; its desorption volume reached approximately 70% of the ultimate desorption volume in a short time (approximately 20 min), after which its desorption behavior rapidly tends to be stable. The desorption rates of coal samples #2, #3, and #4 were also relatively large, but they did not tend to be stable until approximately 2-3 h



Figure 3. Gas desorption volumes and the initial desorption rates of the four coal samples at the different equilibrium pressures.

 Table 2. Ultimate Desorption Volumes of the Four Coal

 Samples at the Different Adsorption Equilibrium Pressures

	ultimate desorption volume $(m^3/t)$				
coal sample number	1 MPa	2 MPa	3 MPa		
#1	10.93	14.73	16.51		
#2	9.78	13.56	15.41		
#3	15.34	17.27	19.79		
#4	17.23	18.77	22.77		

later. Additionally, the initial desorption rates, cumulative desorption volumes, and ultimate desorption volumes of coal samples #2, #3, and #4 increased with the increasing degree of metamorphism.

Based on Figure 3 and eq 8, the data of four coal samples at the adsorption equilibrium pressure of 2 MPa were used and analyzed as an example, and the linear fitting to the desorption data in the initial desorption period where  $Q_t/Q_{\infty} \leq 0.5$  was carried out, and the results are shown in Figure 4.

Figure 4 shows that, except for sample #1, the correlation coefficients of the other three coal samples are very small, especially sample #3 with the correlation coefficient of 0.7208. Therefore, the constant diffusion coefficient model cannot accurately characterize the gas diffusion in coal samples.

If *D* depends on the time *t*, the relationship between *t* and *F* can be determined using polynomial fitting. The fitting formula and eq 13 were substituted into eq 14, allowing *D* to be determined at a given time t (Figure 5).

Figure 5 shows that the non-CDC model can describe the gas diffusion characteristics in the coal samples well. For all of the samples, the gas diffusion coefficients decreased over time. The initial gas diffusion coefficient of coal sample #1 was the largest, followed by samples #4 and #3, and finally sample #2. For sample #1, the rate of decrease of the gas diffusion



**Figure 4.** Linear fitting results of the four coal samples at the equilibrium pressure of 2 MPa based on the constant diffusion coefficient.

coefficient was also largest, and after approximately 30 min, the diffusion coefficient of sample #1 had decreased to a value smaller than the other three coal samples. Similar to the gas desorption properties, the gas diffusion coefficients of samples #2, #3, and #4 also increased with the increasing degree of metamorphism.

Moreover, in order to confirm the calculation accuracy, a theoretical calculation of F as a function of t using the calculated D(t) from the polynomial and eq 7 was carried out and compared with the experimental results  $Q_t/Q_{\infty}$  of the four coal samples at the adsorption equilibrium pressure of 2 MPa. The contrastive analysis results are shown in Figure 6.

Figure 6 shows that the calculated values are essentially consistent with the measured values, which reflects that the calculation method is applicable and the non-CDC model meets the requirement of characterizing the coal gas diffusion.

**3.2. Mercury Intrusion Porosimetry (MIP).** Previous studies<sup>37,60</sup> have used the degree of pore connectivity to classify the types of pores in coal as interconnected, passing, dead end, and closed pores (Figure 7). The first three pore types have important effects on gas adsorption/desorption, diffusion and seepage in coal.

Figure 8 shows the MIP curves for the four coal samples. The pore structure and connectivity can be evaluated based on the characteristics of the MIP curves.<sup>16,62</sup> Generally, the MIP curves of open pores have hysteresis loops; in contrast, the MIP curves of semiclosed pores do not have hysteresis loops because the mercury ejection pressure is equal to the mercury intrusion

pressure. However, the MIP curves from certain semi-enclosed pores called bottleneck pores (one example is the ink-bottle pore) that also have hysteresis loops because of the difference in the mercury ejection pressure between the bottleneck and the wider bottle body. Broad hysteresis loops indicate excellent pore connectivity.<sup>62</sup> From Figure 8, it can be deduced that sample #1 has much better pore connectivity than samples #2, #3, and #4. Considering the compression effect and the damage to the coal structure caused by MIP at high pressure,<sup>63,64</sup> pore diameters larger than 50 nm (macropores) measured by MIP (i.e., the mercury intrusion curves that are not covered by the shadow in Figure 8), are used in this article. Thus, the macropore volume and specific surface area of the four coal samples were determined (Table 3).

3.3. Low-Pressure Nitrogen Gas Adsorption (LP-N<sub>2</sub>GA). Figure 9 shows the LP-N<sub>2</sub>GA isotherms of the four coal samples. The mesopore (2-50 nm in diameter) and micropore ( $\leq 2$  nm in diameter) data are of principal interest in this study (Table 3). Similar to the MIP curves, the LP-N<sub>2</sub>GA isotherms also have conspicuous hysteresis loops, although these are produced by a markedly different process. The adsorption branch is associated with capillary condensation, while the desorption branch is associated with evaporation of the condensed liquid.<sup>65,66</sup> The presence of a pronounced hysteresis loop indicates that evaporation from pores is a different process than capillary condensation in the pores; to some extent, this suggests that capillary condensation occurred in the mesoporous solids.<sup>65</sup> Zsigmondy seems to be the first to use the Kelvin equation to interpret these phenomena.<sup>65,67</sup> The equation relates the relative pressure  $(P/P_0)$  of gas at equilibrium with a liquid meniscus to the mean radius of curvature r of that meniscus, as follows:

$$k_{\rm B}T(\rho_1 - \rho_{\rm g})\ln(P_0/P) = \frac{2\gamma_{\rm lg}}{r}$$
(16)

where  $\rho_{\rm l}$  and  $\rho_{\rm g}$  are the number densities of the coexisting liquid and gas, respectively; and  $\gamma_{\rm lg}$  is the liquid–gas surface tension at the temperature *T*. Based on this, five types of hysteresis loops have been identified and associated with various pore shapes;<sup>37,66,68</sup> these are shown in Figure 10.

Figure 9 demonstrates that there are large differences between the coal samples based on their degree of metamorphism. Sample #1 exhibits a type E hysteresis loop, indicating the presence of numerous bottleneck pores. When the relative pressure  $(P/P_0)$  increases to the value corresponding to  $r_n$ , the bottleneck fills with the liquid-vapor, after which the whole bottleneck pore is saturated by fluid with an increasing relative pressure. Hence, its adsorption curve increases gradually. However, large-scale gas desorption begins



Figure 5. Variation of diffusion coefficients of the four coal samples with the time at the different equilibrium pressures.



Figure 6. Comparison of the desorption ratios from the measured values and the calculated values of the four coal samples at the equilibrium pressure of 2 MPa.



suddenly when the relative pressure decreases to the value corresponding to the  $r_{\rm n}$ . The gas adsorption/desorption isotherms of sample #2 match type A, and the separation of the adsorption and the desorption branches occurs at a relative pressure of 0.5, which demonstrates that there are a large number of cylindrical pores. Additionally, the small hysteresis loop suggests that the coal has poor porosity, implying that many pores in sample #2 have one closed side or dead end

pores. Sample #3's hysteresis loop corresponds to type C, which has many conical pores. The minimum radius and maximum pore radii are  $r_{\rm m}$  and  $R_{\rm m}$  ( $R_{\rm m} \leq 2r_{\rm m}$ ), respectively.<sup>66,68</sup> For the adsorption branch, capillary condensation occurs suddenly when the relative pressure increases to the  $r_{\rm m}$  value, resulting in the formation of a steep adsorption branch. For the desorption branch, the evaporation of condensed liquid begins when the relative pressure decreases to the  $R_{\rm m}$  value and ends when the relative pressure decreases to the  $r_{\rm m}$  value. Sample #4 has type B adsorption/desorption isotherms and its hysteresis loop is large, indicating a large number of slit-like or plate-like pores with all open sides. These results are consistent with the studies of Nie et al.<sup>37</sup> and Fan et al.<sup>69</sup>

# 4. DISCUSSION

The gas adsorption and desorption ability of coal largely depends on its pore volume and specific surface area. The results of this study show that the gas desorption capacity of the four coal samples with different degrees of metamorphism decreased in the following order: #4, #3, #1, and #2. This result is consistent with the LP-N<sub>2</sub>GA analysis showing the volume and total specific surface area of micropores and mesopores in the coal samples (Figure 11). Together, these data suggest that micropores and mesopores control the gas adsorption and desorption capacity of the coal samples, which is consistent with the research result from Nie et al.<sup>37</sup> The gas desorption and diffusion law demonstrates that sample #1 had a greater



Figure 8. MIP curves for the four coal samples.

 Table 3. Pore Structural Parameters of the Four Coal

 Samples

	porosimetry	(MIP)	low-press	(LP-N <sub>2</sub> GA)				
coal sample number	macropore volume s (mL/g)	nacropore specific urface area (m²/g)	mesopore volume (10 <sup>-3</sup> mL/g)	e micropore volume (10 <sup>-4</sup> mL/g)	total <sup>a</sup> specific surface area (m²/g)			
#1	0.0108	0.328	2.347	1.445	1.873			
#2	0.0078	0.165	1.553	1.392	0.919			
#3	0.0089	0.216	3.978	2.218	2.168			
#4	0.0105	0.272	5.201	2.600	2.466			
<sup><i>a</i></sup> Total s mesopor	pecific surface e specific surfac	area = ce area.	micropore	specific surface	e area +			

initial gas desorption and diffusion ability than the other three samples. The gas desorption rates and diffusion coefficients of samples #2, #3, and #4 increased with the degree of metamorphism, which is consistent with the variations in macropore volume and specific surface area measured by MIP (Figure 12). As shown in previous studies,<sup>37,60</sup> macropores likely act as channels for gas flow, controlling the initial speed of gas desorption rate and diffusion in coal. Over time, the gas desorption rate and diffusion coefficients of all four coal samples decreased (Figures 3 and 5); this is probably because the dominant factor affecting gas desorption and diffusion due to the sustained decrease in gas pressure and concentration in the pores as the gas diffused out. In addition, the decrease in

the gas desorption rate and diffusion coefficient of sample #1 were much larger in the other samples. This probably occurred because the gas pressure and concentration in the pores of sample #1 decreased more quickly due to its greater initial gas desorption rate. Furthermore, the micropores and mesopores in coal sample #1 were mostly bottleneck pores, which have greater resistance to gas migration than other pore types.

In summary, compared with high-volatility bituminous coal, the pores in lignite coal matrices were better developed, especially the micropores and mesopores related to the gas adsorption and desorption capacity. Additionally, the macropore development in lignite results in greater initial gas desorption and diffusion than in bituminous or anthracite coal. The MIP curves and LP-N2GA isotherms for lignite show that large hysteresis loops, suggesting good pore connectivity and many open pores that are favorable for gas migration.<sup>62</sup> Finally, the desorption data indicate that it only spends less than 3 min that 60% of the total adsorbed gas in the lignite was desorbed. In contrast, coal sample #2 (the high-volatile bituminous coal), coal sample #3 (the medium-volatile bituminous coal), and coal sample #4 (the anthracite) need 24-40 min, 18-26 min, and 10-18 min, respectively. Consequently, lignite has significant potential for CBM exploitation and development.

#### 5. CONCLUSIONS

In this paper, four coal samples with different degrees of metamorphism from the northern China mining area were studied. A conventional gas desorption experimental setup was modified to analyze gas desorption in the coal samples.



Figure 9. LP-N2GA isotherms of the four coal samples.



Figure 10. LP-N<sub>2</sub>GA hysteresis loops and their corresponding pore shapes.

Unsteady-state gas diffusion properties in the samples were investigated using a non-CDC model. The coal pore structural characteristics were also measured using MIP and LP-N<sub>2</sub>GA, and their effects on gas desorption and diffusion properties in coal were evaluated. Finally, the implications of these results for CBM exploitation and development were discussed. The experimental results suggest the following conclusions:

• The gas desorption and diffusion properties of coal samples with different degrees of metamorphism vary

significantly. The non-CDC model can describe the gas diffusion characteristics in all of these coal samples well. The gas desorption and diffusion capacity of the bituminous and anthracitic coal samples increased with the increasing degree of metamorphism; however, these properties were significantly better in lignite.

 MIP analyses indicated that lignite and anthracite have better pore connectivity than bituminous coal. The lignite sample also had the largest macropore volume and



Figure 11. Relationship between ultimate desorption volume and the micropores and mesopores in the coal samples.



Figure 12. Relationship between the initial gas desorption rate and diffusivity and the macropores in the coal samples.

specific surface, followed by the anthracite and the medium-volatility bituminous coal; the high-volatility bituminous coal had the smallest value. The LP-N<sub>2</sub>GA tests suggested that there were numerous bottleneck pores in the lignite, cylindrical pores in the high-volatility bituminous coal, and conical pores in the low-volatility bituminous coal. Finally, the anthracite sample had a large number of slit or plate-like pores with open sides.

 Micropores and mesopores controlled the gas adsorption and desorption capacity of the coal samples. The macropores acted as channels for gas flow, controlling the initial speed of gas desorption and diffusion. The pore structure of lignite resulted in its high gas adsorption capacity, which exceeded that of the highvolatility bituminous coal; lignite's strong initial gas desorption and diffusion also exceeded that of the bituminous coal and the anthracite. Therefore, lignite has significant potential for the exploitation and development of CBM.

#### AUTHOR INFORMATION

#### Corresponding Authors

- \* E-mail: cyp620924@hotmail.com; Tel: +86-516-83885948; Fax: +86-516-83995097.
- \* E-mail: liangw1982@126.com; Tel: +86-516-83885948; Fax: +86-516-83995097.

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

The authors are grateful to the financial support from the National Natural Science Foundation of China (No. 51574229, 51674252), the sponsorship of Jiangsu Overseas Research & Training Program for University Prominent Young & Middle-aged Teachers and Presidents, the Qing Lan Project, the Fundamental Research Funds for the Central Universities (No.2015XKMS008), and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

### NOMENCLATURE

 $M_{\rm ad}$  Moisture content on air-dried basis, %

Article

 $A_{\rm ad}$  Ash content on air-dried basis, %

 $V_{\rm daf}$  Volatile matter content on dry ash-free basis, %

 $F_{\rm cad}$  Fixed carbon on air-dried basis, %

- $V_{\rm L}$  Langmuir volume, m<sup>3</sup>/t
- $P_{\rm I}$  Langmuir pressure, MPa
- $P_0$  The standard pressure, 0.101325 MPa

 $T_0$  The standard temperature, 273.15 K

 $R_{0\text{max}}$  Maximum vitrinite reflectance, %

- $\rho$  Density of coal sample, kg/m<sup>3</sup>
- $m_c$  Weight of coal sample, kg

 $V_c$  Volume of the coal samples in the coal sample tank, mL

 $V_{\rm ct}$  Volume of the coal sample tank, mL

 $V_{\rm f}$  Free gas volume in the coal sample tank, mL

 $V_{\rm f0}$  Free gas volume at STP in the coal sample tank, mL

 $P_{\rm eq}$  Adsorption equilibrium pressure in the coal sample tank, MPa

 $T_{\rm eq}$  Temperature of the coal samples in the coal sample tank, K

t Desorption time, s

V<sub>t</sub> Gas desorption volume at STP, mL

 $V_{co}$  Gas volume in the gas sample bag at STP, mL

 $Q_t$  Desorption gas volume per unit mass at the different times t,  $m^3/t$ 

 $Q_{\infty}$  Ultimate desorption volume as t approaches  $\infty$ , m<sup>3</sup>/t

 $P_a$  Atmospheric pressure outside the coal sample tank, MPa *J* Diffusive flux, kg/(m<sup>2</sup>·s)

D Diffusion coefficient or diffusivity,  $m^2/s$ 

*c* Concentration, kg/m<sup>3</sup>

h Distance, m

a Radius of the spherical coal particle, m

r Pore radius of porous materials, nm

 $\sigma$  Surface tension of Hg, dyn/cm<sup>2</sup>

 $\theta$  Contact angle between Hg and the coal surface

*p*<sub>c</sub> External pressure, MPa

 $\rho_{\rm l}$  Number densities of coexisting liquid

 $\rho_{\rm g}$  Number densities of coexisting gas

 $\gamma_{lg}$  Liquid-gas surface tension at temperature T, N/m

 $r_n$  Radius of the bottleneck in the bottleneck pore, nm

 $R_{\rm n}$  Maximum radius of the bottleneck pore, nm

 $r_{\rm m}$  Minimum radius of the conical pore, nm

 $R_{\rm m}$  Maximum radius of the conical pore, nm

# REFERENCES

(1) Kong, S.; Cheng, Y.; Ren, T.; Liu, H. A sequential approach to control gas for the extraction of multi-gassy coal seams from traditional gas well drainage to mining-induced stress relief. *Appl. Energy* **2014**, *131* (0), 67–78.

(2) Xue, S.; Wang, Y.; Xie, J.; Wang, G. A coupled approach to simulate initiation of outbursts of coal and gas — Model development. *Int. J. Coal Geol.* **2011**, *86* (2–3), 222–230.

(3) Wang, L.; Cheng, Y.; An, F.; Zhou, H.; Kong, S.; Wang, W. Characteristics of gas disaster in the Huaibei coalfield and its control and development technologies. *Natural Hazards* **2014**, *71* (1), 85–107.

(4) Zhang, P.; Peterson, S.; Neilans, D.; Wade, S.; McGrady, R.; Pugh, J. Geotechnical risk management to prevent coal outburst in room-and-pillar mining. *Int. J. Min. Sci. Technol.* **2016**, *26* (1), 9–18.

(5) Skoczylas, N.; Dutka, B.; Sobczyk, J. Mechanical and gaseous properties of coal briquettes in terms of outburst risk. *Fuel* **2014**, *134*, 45–52.

(6) Lunarzewski, L. W. Gas emission prediction and recovery in underground coal mines. *Int. J. Coal Geol.* **1998**, 35 (1-4), 117-145.

(7) Bao, Q.; Fang, Q.; Zhang, Y.; Chen, L.; Yang, S.; Li, Z. Effects of gas concentration and venting pressure on overpressure transients

during vented explosion of methane-air mixtures. *Fuel* **2016**, *175*, 40–48.

(8) Chunli, Y.; Xiangchun, L.; Yanbin, R.; Yiliang, Z.; Feifei, Z. Statistical Analysis and Countermeasures of Gas Explosion Accident in Coal Mines. *Procedia Eng.* **2014**, *84*, 166–171.

(9) Jia, B.; Wen, H.; Liang, Y.; Wang, X. Mechanism characteristics of CO2 and N2 inhibiting methane explosions in coal mine roadways. *Journal of China Coal Society* **2013**, *38* (3), 361–366.

(10) Shao, H.; Jiang, S.; Zhang, X.; Wu, Z.; Wang, K.; Zhang, W. Influence of vacuum degree on the effect of gas explosion suppression by vacuum chamber. *J. Loss Prev. Process Ind.* **2015**, *38*, 214–223.

(11) Beaton, A.; Langenberg, W.; Pană, C. Coalbed methane resources and reservoir characteristics from the Alberta Plains, Canada. *Int. J. Coal Geol.* **2006**, *65* (1-2), 93–113.

(12) Busch, A.; Gensterblum, Y. CBM and CO2-ECBM related sorption processes in coal: A review. *Int. J. Coal Geol.* 2011, 87 (2), 49–71.

(13) Li, S.; Tang, D.; Xu, H.; Yang, Z. The pore-fracture system properties of coalbed methane reservoirs in the Panguan Syncline, Guizhou, China. *Geosci. Front.* **2012**, *3* (6), 853–862.

(14) Zhang, Y. Geochemical Kinetics; Princeton University Press: Boston, 2008.

(15) Pillalamarry, M.; Harpalani, S.; Liu, S. Gas diffusion behavior of coal and its impact on production from coalbed methane reservoirs. *Int. J. Coal Geol.* **2011**, *86* (4), 342–348.

(16) Cai, Y.; Liu, D.; Pan, Z.; Yao, Y.; Li, J.; Qiu, Y. Pore structure and its impact on CH4 adsorption capacity and flow capability of bituminous and subbituminous coals from Northeast China. *Fuel* **2013**, *103*, 258–268.

(17) Rouquerol, J.; Avnir, D.; Fairbridge, C. W.; Everett, D. H.; Haynes, J. M.; Pernicone, N.; Ramsay, J. D. F.; Sing, K. S. W.; Unger, K. K. Recommendations for the characterization of porous solids. *Pure Appl. Chem.* **1994**, *66*, 1739–1758.

(18) Zou, M.; Wei, C.; Zhang, M.; Shen, J.; Chen, Y.; Qi, Y. Classifying coal pores and estimating reservoir parameters by nuclear magnetic resonance and mercury intrusion porosimetry. *Energy Fuels* **2013**, *27* (7), 3699–3708.

(19) Wu, S. Research of methane-coalbed coupling movement theory and its application (Gas-solid coupling movement theory with adsorption). Ph. D. Dissertation, Northeastern University: Shenyang, 2005.

(20) Éttinger, I. Solubility and diffusion of methane in coal strata. J. Min. Sci. 1987, 23 (2), 159–169.

(21) Kuznetsov, S.; Bobin, V. Desorption kinetics during phenomena in collieries. *Soviet Mining Science* **1987**, *23* (2), 159–168.

(22) Vasyuchkov, Y. F. A study of porosity, permeability, and gas release of coal as it is saturated with water and acid solutions. *J. Min. Sci.* **1985**, *21* (1), 81–88.

(23) Mendes, A. M. M.; Costa, C. A. V.; Rodrigues, A. E. Linear driving force approximation for isothermal non-isobaric diffusion/ convection with binary Langmuir adsorption. *Gas Sep. Purif.* **1995**, 9 (4), 259–270.

(24) Dziurzyński, W.; Krach, A. Mathematical model of methane caused by a collapse of rock mass crump. *Archives of Mining Sciences* **2001**, *46* (4), 433–449.

(25) Yang, Q.; Wang, Y. Theory of methane diffusion from coal cuttings and its application [J]. *Journl of China Coal Society* **1986**, *3*, 011.

(26) Yang, Q.; Wang, Y. Mathematical Simulation of the Radial Methane Flow in Spherical Coal Grains [J]. *Journal of China University of Mining & Technology* **1988**, *3*, 007.

(27) Wu, S. Preliminary approach on the low of gas diffussion and permeation on coal seams. *Shanxi Mining Institute Learned Journal* **1994**, 3, 011.

(28) Guo, Y.; Wu, S.; Wang, Y.; He, G. Study on the measurement of coal particale gas diffusion and diffusion coefficient. *Shanxi Mining Institute Learned Journal* **1997**, *15* (1), 15–19.

(29) Charrière, D.; Pokryszka, Z.; Behra, P. Effect of pressure and temperature on diffusion of CO 2 and CH 4 into coal from the Lorraine basin (France). *Int. J. Coal Geol.* **2010**, *81* (4), 373–380.

(30) Guo, J. C.; Nie, R. S.; Jia, Y. L. Unsteady-state diffusion modeling of gas in coal matrix for horizontal well production. *AAPG Bull.* **2014**, *98* (9), 1669–1697.

(31) Hu, H.; Li, X.; Fang, Z.; Wei, N.; Li, Q. Small-molecule gas sorption and diffusion in coal: molecular simulation. *Energy* **2010**, *35* (7), 2939–2944.

(32) Nie, B.; Yang, T.; Li, X. Research on diffusion of methane in coal particles. *Journal of China University of Mining & Technology* **2013**, 42 (2), 975–980.

(33) Pan, Z. J.; Connell, L. D.; Camilleri, M.; Connelly, L. Effects of matrix moisture on gas diffusion and flow in coal. *Fuel* **2010**, 89 (11), 3207–3217.

(34) Zhao, Y.; Feng, Y.; Zhang, X. Molecular simulation of CO2/ CH4 self- and transport diffusion coefficients in coal. *Fuel* **2016**, *165*, 19–27.

(35) Staib, G.; Sakurovs, R.; Gray, E. M. A. Dispersive diffusion of gases in coals. Part II: An assessment of previously proposed physical mechanisms of diffusion in coal. *Fuel* **2015**, *143*, 620–629.

(36) Jian, K.; Lei, D.; Fu, X.; Zhang, Y.; Li, H. Effect of an electrostatic field on gas adsorption and diffusion in tectonic coal. *Int. J. Min. Sci. Technol.* **2015**, 25 (4), 607–613.

(37) Nie, B.; Liu, X.; Yang, L.; Meng, J.; Li, X. Pore structure characterization of different rank coals using gas adsorption and scanning electron microscopy. *Fuel* **2015**, *158*, 908–917.

(38) Cheng, Y.; Wang, H.; Wang, L.; Zhou, H.; Liu, H.; Liu, H.; Wu, D.; Li, W. *Theories and engineering applications on coal mine gas control*;China University of Mining and Technology Press: Xuzhou, China, 2010.

(39) Jian, X.; Guan, P.; Zhang, W. Carbon dioxide sorption and diffusion in coals: Experimental investigation and modeling. *Sci. China: Earth Sci.* **2012**, *55* (4), 633–643.

(40) Lu, S.; Cheng, Y.; Qin, L.; Li, W.; Zhou, H.; Guo, H. Gas desorption characteristics of the high-rank intact coal and fractured coal. *Int. J. Min. Sci. Technol.* **2015**, *25* (5), 819–825.

(41) Lu, S. Q.; Cheng, Y. P.; Li, W.; Wang, L. Pore structure and its impact on CH4 adsorption capability and diffusion characteristics of normal and deformed coals from Qinshui Basin. *Int. J. Oil, Gas Coal Technol.* **2015**, *10* (1), 94–114.

(42) Gilman, A.; Beckie, R. Flow of coal-bed methane to a gallery. Transp. Porous Media 2000, 41 (1), 1-16.

(43) Valliappan, S.; Wohua, Z. Numerical modelling of methane gas migration in dry coal seams. *Int. J. Numer. Anal. Methods Geomech.* **1996**, 20 (8), 571–593.

(44) King, G. R.; Ertekin, T.; Schwerer, F. C. Numerical simulation of the transient behavior of coal-seam degasification wells. *SPE Form. Eval.* **1986**, *1* (02), 165–183.

(45) Liu, J.; Chen, Z.; Elsworth, D.; Qu, H.; Chen, D. Interactions of multiple processes during CBM extraction: a critical review. *Int. J. Coal Geol.* **2011**, *87* (3), 175–189.

(46) Liu, S.; Harpalani, S.; Pillalamarry, M. Laboratory measurement and modeling of coal permeability with continued methane production: Part 2 – Modeling results. *Fuel* **2012**, *94*, 117–124.

(47) Thararoop, P.; Karpyn, Z. T.; Ertekin, T. Development of a multi-mechanistic, dual-porosity, dual-permeability, numerical flow model for coalbed methane reservoirs. *J. Nat. Gas Sci. Eng.* **2012**, *8*, 121–131.

(48) Perera, M.; Ranjith, P.; Viete, D.; Choi, S. The Effects of Injection and Production Well Arrangement on Carbon Dioxide Sequestration in Deep, Unmineable Coal Seams: A Numerical Study. *Int. J. Coal Prep. Util.* **2012**, *32* (5), 211–224.

(49) Vishal, V.; Singh, L.; Pradhan, S.; Singh, T.; Ranjith, P. Numerical modeling of Gondwana coal seams in India as coalbed methane reservoirs substituted for carbon dioxide sequestration. *Energy* **2013**, *49*, 384–394.

(51) Patton, S.; Fan, H.; Novak, T.; Johnson, P.; Sanford, R. Simulator for degasification, methane emission prediction and mine ventilation. *Mining Engineering* **1994**, *46* (4), 341–345.

(52) Valliappan, S.; Wohua, Z. NUMERICAL MODELLING OF METHANE GAS MIGRATION IN DRY COAL SEAMS. Int. J. Numer. Anal. Methods Geomech. **1996**, 20 (8), 571–593.

(53) Clarkson, C. R.; Bustin, R. M. The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modeling study. 2. Adsorption rate modeling. *Fuel* **1999**, 78 (11), 1345–1362.

(54) Guo, H.; Cheng, Y.; Wang, L.; Lu, S.; Jin, K. Experimental study on the effect of moisture on low-rank coal adsorption characteristics. *J. Nat. Gas Sci. Eng.* **2015**, *24* (0), 245–251.

(55) Jin, K.; Cheng, Y. P.; Wang, L.; Dong, J.; Guo, P. K.; An, F. H.; Jiang, L. M. The effect of sedimentary redbeds on coalbed methane occurrence in the Xutuan and Zhaoji Coal Mines, Huaibei Coalfield, China. *Int. J. Coal Geol.* **2015**, *137*, 111–123.

(56) Rong, H.; Bai, H. Pore structure characteristics of the relative water-resisting layer on the top of the Ordovician in Longgu Coal Mine. *Int. J. Min. Sci. Technol.* **2014**, *24* (5), 657–661.

(57) Gürdal, G.; Yalçın, M. N. Pore volume and surface area of the Carboniferous coals from the Zonguldak basin (NW Turkey) and their variations with rank and maceral composition. *Int. J. Coal Geol.* **2001**, 48 (1-2), 133–144.

(58) Hyvaluoma, J.; Raiskinmaki, P.; Jasberg, A.; Koponen, A.; Kataja, M.; Timonen, J. Evaluation of a lattice-Boltzmann method for mercury intrusion porosimetry simulations. *Future Generation Computer Systems* **2004**, *20* (6), 1003–1011.

(59) Washburn, E. W. The Dynamics of Capillary Flow. *Phys. Rev.* **1921**, 17 (3), 273-283.

(60) Wang, F.; Cheng, Y.; Lu, S.; Jin, K.; Zhao, W. Influence of Coalification on the Pore Characteristics of Middle High Rank Coal. *Energy Fuels* **2014**, *28* (9), 5729–5736.

(61) Ravikovitch, P. I.; Vishnyakov, A.; Russo, R.; Neimark, A. V. Unified approach to pore size characterization of microporous carbonaceous materials from N2, Ar, and CO2 adsorption isotherms. *Langmuir* **2000**, *16* (5), 2311–2320.

(62) Chen, S.; Zhu, Y.; Li, W.; Wang, H. Influence of magma intrusion on gas outburst in a low rank coal mine. *Int. J. Min. Sci. Technol.* **2012**, *22* (2), 259–266.

(63) Comisky, J. T.; Santiago, M.; McCollom, B.; Buddhala, A.; Newsham, K. E. In *Sample size effects on the application of mercury injection capillary pressure for determining the storage capacity of tight gas and oil shales*, Canadian Unconventional Resources Conference; Society of Petroleum Engineers, 2011.

(64) Li, Y. H.; Lu, G. Q.; Rudolph, V. Compressibility and fractal dimension of fine coal particles in relation to pore structure characterisation using mercury porosimetry. *Part. Part. Syst. Charact.* **1999**, *16* (1), 25–31.

(65) Evans, R.; Marconi, U. M. B.; Tarazona, P. Fluids in narrow pores: Adsorption, capillary condensation, and critical points. *J. Chem. Phys.* **1986**, *84* (4), 2376–2399.

(66) De Boer, J. In *The structure and properties of porous materials*, Proceedings of the tenth symposium of the colston research society held in the University of Bristol; Butterworths: London, 1958.

(67) Zsigmondy, R. Über die Struktur des Gels der Kieselsäure. Theorie der Entwässerung. Zeitschrift für anorganische Chemie **1911**, 71 (1), 356–377.

(68) Jin, Y.; Huang, Z. Adsorption and pore size distribution; National defense industry press: Beijing, 2015.

(69) Fan, J.; Ju, Y.; Liu, S.; Li, X. Micropore structure of coals under different reservoir conditions and its-implication for coalbed methane development. *Journal of China Coal Society* **2013**, *38* (3), 441–447.