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# Investigation of methane diffusion in low-rank coals by a multiporous diffusion model





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### ABSTRACT

To study the methane diffusion behaviors of low-rank coals ( $R_{o,m}$  of 0.45% and 0.58%), a combination of CO<sub>2</sub> adsorption, N<sub>2</sub> adsorption/desorption, and mercury intrusion porosimetry (MIP) measurements were used to characterize the pore structure of coals, and a new multiporous diffusion model was established to model methane diffusion under dry and moist conditions during the methane adsorption process. The results indicate that the pore structure of low-rank coal samples exhibits a multimodal pore size/volume distribution and has a greater percentage of microporosity and mesoporosity. The multiporous model provides a better fit than the bidisperse model, which deviates significantly from the data, especially during the initial diffusion stage. Based on the multiporous diffusion model, the macropore diffusivity  $(10^{-4} \cdot 10^{-3} \text{ s}^{-1})$  is generally one to three orders of magnitude greater than the mesopore diffusivity  $(10^{-5} \cdot 10^{-4} \text{ s}^{-1})$  and micropore diffusivity  $(10^{-6} \cdot 10^{-5} \text{ s}^{-1})$ . Moreover, both the macropore diffusivity and micropore diffusivity show a decreasing trend with increasing pressure, whereas a strong positive correlation exists between the mesopore diffusivities and pressure, indicating that the effect of pressure on methane diffusion in pores with different sizes is different during the adsorption process. This difference may be due to the competition between the different mechanisms of gaseous methane diffusion and the swelling of the coal matrix caused by gas adsorption. Furthermore, the moisturereduced methane diffusivities is mainly due to the moisture in the coal matrix that adsorbs to the pore surface and occupies the pore space, as well as changes the pore structure according to the effect of mineral swelling from the adsorbing moisture. Therefore, these results may have a significant implication for understanding the transport mechanism of methane in coals and the design of enhanced CBM recovery.

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### 1. Introduction

Coalbed methane (CBM) represents an alternative hydrocarbon resource that has attracted global attention in recent years. Compared to conventional natural gas reservoirs, coal reservoirs have unique characteristics, including a dual porosity system, pore structure, gas storage, and flow mechanisms. It has been confirmed that CBM is mainly adsorbed at the pore surface in the coal matrix and that gas is desorbed from the pore surface and diffuses from the pore system to the cleat/fracture systems during production (Clarkson and Bustin, 1999; Shi and Durucan, 2005; Cai et al.,

\* Corresponding author. E-mail address: dmliu@cugb.edu.cn (D. Liu). 2014a,b). Commonly, gas transport in coals is divided into two stages: gas diffusion within the coal matrix and flow in the cleat system (Pillalamarry et al., 2011). Harpalani and Chen (1997) revealed that gas diffusion through the matrix is assumed to be concentration gradient driven and is usually modeled using Fick's Second Law of Diffusion. Moreover, both Shi and Durucan (2003); Pan et al. (2010) found that gas diffusion within the coal matrix is dominated by three diffusion mechanisms in coals, including Fickian diffusion (molecule-molecule collisions dominate), Knudsen diffusion (transport through physically adsorbed layer). Due to the often significant heterogeneity of the pore structure, all three diffusion mechanisms play important roles in gas diffusion within the coal matrix (Xu et al., 2015; Yuan et al., 2014).

A significant amount of work has been completed in modeling

diffusion, and various diffusion models have been applied to characterize the diffusion process, such as the unipore model (Charrière et al., 2010; Jian et al., 2012; Pone et al., 2009; Švábová et al., 2012), the bidisperse model (Busch et al., 2004; Clarkson and Bustin, 1999; Cui et al., 2004; Shi and Durucan, 2003, 2005; Smith and Williams, 1984; Pan et al., 2010), and the Fickian diffusion-relaxation (FDR) model (Staib et al., 2013). Based on these models, one or two diffusion coefficients are obtained to describe the sorption kinetics of coals. By studying the gas diffusion of different rank coals, Crosdale et al. (1998); Clarkson and Bustin (1999) discovered that the unipore model is more suitable for vitrinite-rich bright coals, whereas the bidisperse model may be adequate to describe the sorption kinetics of some inertinite-rich dull or banded coals. This observation indicates that the coal composition may influence gas transport in the coal matrix and the pore structure plays an important role in accurately modeling gas transport through the coal matrix. Previous research using nuclear magnetic resonance suggests that the pore volume distribution of low-rank coals has a triple peak pattern (Cai et al., 2015). Moreover, based on experimental and mathematical simulations, many influencing factors on the diffusion coefficients have been discussed in recent studies. Pan et al. (2010), by studying the effects of matrix moisture on methane and carbon dioxide diffusion, discovered that the diffusion coefficients of dry coal are higher than those of wet coal and that the diffusion coefficients of  $\ensuremath{\text{CO}}_2$  are significantly higher than those of CH<sub>4</sub> under the same conditions. However, a similar study by Wang et al. (2014) also found that diffusivity decreases with increasing moisture for Chinese anthracite, whereas for Chinese bituminous coal, diffusivity varies with the moisture following a U-shaped function. Furthermore, Charrière et al. (2010) demonstrated that the calculated diffusion coefficients of CH<sub>4</sub> and CO<sub>2</sub> from the unipore model increase with increasing temperature and gas pressure on coals from the Lorraine Basin in France. However, it has been proposed that diffusion coefficients may have different trends depending on the model chosen, even when using the same data (Clarkson and Bustin, 1999; Shi and Durucan, 2005; Staib et al., 2013).

In this work, we investigated the methane adsorption and diffusion behaviors in two Chinese low-rank coals through experimental study and modeling. The pore structure, as a factor of methane diffusion, is required. Therefore, the pore structure of the coal samples was first investigated via the CO<sub>2</sub> adsorption, N<sub>2</sub> gas adsorption/desorption, and mercury intrusion porosimetry (MIP) techniques. Then, a new multiporous diffusion model, based on the bidisperse model, was proposed to describe the methane diffusivity in the coal matrix. Finally, the effects of moisture and pressure on methane diffusion under dry and moist conditions were discussed in detail.

## 2. Material and methods

# 2.1. Coal samples and preparation

The coal samples used in this work were collected from the Taian coal mine and Wangtian coal mine in the Baode mining area, Shanxi Province. The maximum vitrinite reflectance ( $R_{o,m}$ ), petrographic, and proximate analyses for the coal samples were carried out in our laboratory, and the experimental procedures were the same as those of our previous work (Cai et al., 2011). The ranks of the two coals are lignite for Taian (TA) and long-flame coal for Wangtian (WT), with maximum vitrinite reflectance ( $R_{o,m}$ ) reaching 0.45% (TA) and 0.58% (WT), respectively. The results of the petrographic and the proximate analysis are presented in Table 1.

The coal lumps were pulverized and the particles between 0.18 and 0.25 mm were selected for  $CH_4$  adsorption and diffusion

experiments. The powder samples were divided into two parts. One part was dried in a 50 °C vacuum oven for more than one week to remove any pre-existing moisture. The other part was used to prepare the moisture-equilibrated samples. The samples were prepared using a saturated K<sub>2</sub>SO<sub>4</sub> solution, with a relative humidity of approximately 97%. The wet samples were weighed periodically during moisture-equilibrated process. Over a period of two months, the moisture of the coal samples reached an equilibrium state, as described in detail by Pan et al. (2010). The moisture content of coal samples is defined as:

$$w\% = \frac{m_{\text{moisture}}}{m_{coal}} \times 100\% \tag{1}$$

where w% is the moisture content,  $m_{moisture}$  is the total mass of water uptake in coal,  $m_{coal}$  is the total mass of the dry coal.

The dry and moisture-equilibrated samples were prepared for CH<sub>4</sub> isotherm adsorption and diffusion experiments.

#### 2.2. Mercury intrusion porosimetry analysis

Many methods, including scanning electron microscope (SEM), low-temperature  $N_2$  adsorption/desorption, MIP, and nuclear magnetic resonance (NMR) techniques, have been adopted to acquire the pore structure information. In this study, the pore structure and pore size distribution of the coal samples were investigated using the MIP method. The block sample was selected for MIP analysis following the rock capillary pressure measurement standard process (the Chinese Oil and Gas Industry Standard of SY/T 5346-2005) (Yao and Liu, 2012) and conducted using the PoreMasterGT60 (Quantachrome, US). The measurements run up to a pressure of 206 MPa, at which pore throats as small as four nm can be penetrated. Mercury intrusion/extrusion curves were obtained, and the cumulative mercury injection volume, pore radius, and pore size distribution could be inferred from the curves. The results of the MIP analysis are listed in Table 2.

#### 2.3. $CO_2$ adsorption and $N_2$ adsorption/desorption analysis

Although the MIP method is commonly used to characterize the pore size distribution of coal from a few nanometers to tens of micrometers, the pore compressibility of coals is inevitable at high pressures (normally higher than 20 MPa) (Patrick et al., 2004), which can easily lead to inaccurate results. Therefore,  $CO_2$  adsorption and N<sub>2</sub> gas adsorption/desorption experiments are used to characterize pores with diameters less than 300 nm. The experiments were conducted using a modified Micromeritics ASAP-2000 automated surface area analyzer.

Prior to CO<sub>2</sub> adsorption and N<sub>2</sub> gas adsorption/desorption analyses, 0.18-0.25-mm particle size coal samples were sieved and dried at 105 °C for 24 h in a vacuum oven to remove air, free water, and other impurities (Yao et al., 2008; Nie et al., 2015). The CO<sub>2</sub> adsorption data (273.15 K or 0 °C) were collected at a relative pressure  $(P/P_0)$  range from 0.01 to 0.035, and the N<sub>2</sub> gas adsorption/ desorption (77 K or -196.15 °C) isotherms were measured at a relative pressure  $(P/P_0)$  range from 0.01 to 0.995. As discussed by Clarkson et al. (2013), CO<sub>2</sub> adsorption at 273 K can be used to investigate pores with diameters less than 1.5 nm and N<sub>2</sub> adsorption at 77 K can be used to investigate pores with diameters greater than 1.7 nm. Furthermore, the CO<sub>2</sub> adsorption data were interpreted using the Dubinin-Astakhov (D-A) and Dubinin-Radushkevich (D-R) models, and the N<sub>2</sub> adsorption/desorption data were analyzed using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) theories. The results of the CO<sub>2</sub> adsorption and N<sub>2</sub> adsorption/desorption analysis are listed in Download English Version:

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