Impact of pore structure on gas adsorption and diffusion dynamics for long-flame coal

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ABSTRACT

The pore structure of coal has a "U-shaped" relation with coal rank. Adsorption pores (pore size smaller than 2 nm) and seepage pores (2 nm < pore size<50 nm) greatly influence gas adsorption and diffusion. Thus, the pore structure of five coal samples (R_o between 0.57% and 0.62%) from eastern China was investigated in this study. Scanning electron microscopy was used for the qualitative analysis of the pore structure. Additionally, mercury porosimetry and the adsorption of CO_2 at 273 K were used for the quantitative analysis of the pore size distribution. #15 and #16 coal samples were used to study gas adsorption properties at different temperature, while #12, #13, #14 and #16 coal samples were used to study gas diffusion characteristics. The results show that the micropores of long-flame coal are well developed and that micropores (pore size smaller than 2 nm) greatly affect gas adsorption properties, whereas mesopores (2 nm < pore size<50 nm) affect gas diffusion characteristics. The adsorption ability of long-flame coal increases with the microinvasion capacity and specific surface area. From the perspective of adsorption dynamics, V_L increases with temperature, whereas P_L does not change appreciably. Methane's effective diffusion coefficient, obtained from adsorption data based on Fick's laws of diffusion, was observed to increase with the development of mesopore structure and decrease with time. Initially, the effective diffusion coefficient decreased sharply and stabilized after 15 min. The results may have significant implications for the control of methane in coal.

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1. Introduction

Coal and gas outburst, the most common accident in coal mines and one of the most destructive dynamic phenomena of methane (Hodot, 1966; Valliappan and Zhang, 1999), is a serious threat to safe production in coal mines. Coal and gas outburst accidents are attributed to the dynamic effects of methane in coal seams and methane adsorption and diffusion phenomena. The pore structure of coal seam has a decisive effect on the dynamic phenomena of methane.

Pore structures and fissures have a wide range of distributions in coal and play a significant role in methane occurrence and flow. According to the IUPAC classification (Rouquerol et al., 1994) of coal pore size, the pore structures of coal are divided into micropores (<2 nm), mesopores (2 nm-50 nm) and macropores (>50 nm).

Micropores form the adsorption volume, and mesopores constitute the gas diffusion space, whereas macropores compose the gas laminar penetration volume (Yu, 1992). More than 95% of gas adsorbs onto the interface of the coal matrix (Gray, 1987). The internal pore structure of coal is mainly composed of the matrix and cleats; fluids follow different migration mechanisms in these two structures. Micropores and mesopores primarily exist in the coal matrix (White et al., 2005). Fluid migration in the matrix occurs mainly through diffusion, described by Fick's laws, and concentration gradients drive this migration. Fluid migration in the cleats occurs mainly through laminar flow, described by Darcy's law (Charrière et al., 2010), which is driven by pressure gradients. An investigation of bituminous and subbituminous coals from northeast China revealed that the pore size (6.65 nm < r < 16.2 nm) is highly suitable for methane adsorption and that micropores occupy more than 90% of the total pore volume (r < 10 nm) (Cai et al., 2013). Clarkson and Bustin (1999a) studied the pore structure of coal and the effect of pressure on the diffusion characteristics of methane and CO_2 using a combination of experiments and simulations.

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Other research has shown that coal maceral controls pore structure and methane adsorption (Beamish and Crosdale, 1995; Bustin et al., 1995; Clarkson and Marc Bustin, 1996; Lamberson and Bustin, 1993; Unsworth et al., 1988). Songhang Zhang et al. (2010) found that coal rank is the key factor controlling the development of micropores and excessively large pores and that the petrographic composition of coal affects seepage pores. Research on the coal pore structure, especially quantitative analysis of pore structure, has great value to the study of the diffusion and adsorption characteristics of CH_4 in coal (Cai et al., 2013).

Many studies have focused on the adsorption and diffusion characteristics of coal samples from China and abroad. An investigation of bituminous and subbituminous coals from northeast China focused on coal samples with R_o values ranging from 0.54% to 1.19% (Cai et al., 2013). In addition, Maria Mastalerz et al. (2004) studied the adsorption characteristics of bituminous coal with a high volatile content from Indiana, USA, with R_o values ranging from 0.48% to 0.62%. Lila W. Gurba et al. (2000) studied the relation between the elemental composition of coal macerals and vitrinite reflectance in samples from the Gunnedah Basin, Australia, with R_o values ranging from 0.63% to 0.99%. Gürdal and Yalcın (2000) studied the gas adsorption capacity of carboniferous coals from the Zonguldak Basin (northwest Turkey) and the factors controlling gas adsorption. Moreover, Yao (2011) studied the influence of igneous intrusions on coal rank, coal quality and adsorption capacity in samples with R_o values ranging from 1.53% to 6.17% and studied the methane and carbon dioxide adsorption properties of samples with R_o values ranging from 0.49% to 3.65% (Garnier et al., 2011).

The DL coal mine is an inland accumulation in eastern China with R_o values ranging from 0.57% to 0.62%. It is a low-rank, long-flame coal. Because there are few studies on long-flame coal in China, we used the long-flame coal of the DL mine to study the relation between coal pore structure and methane dynamics. This relation is significant for controlling gas in coal mines.

2. Methods

2.1. Coal samples and preparation

Five coal samples were selected from five coal seams (#12, #13, #14, #15 and #16) of the DL coal mine. The DL coal mine formed during the Cretaceous period (K_1F) of the Mesozoic Era and is a continental, sedimentary, concealed coalfield. In addition to the localized exposure of the coalfield at the western edge, almost the entire coalfield was covered by Quaternary period. The detailed sampling area and the labels of these coal samples are shown in Table 1.

After sample acquisition, the coal samples were crushed. For the coal sample extracted from each coal seam, approximately 10 g of coal sample pieces measuring 0.074–0.2 mm were sifted for proximate analysis and approximately 100 g of coal sample pieces measuring 0.2–0.25 mm were sifted for petrographic analysis, a methane adsorption test and a CO_2 adsorption test. Simultaneously, a coal sample piece measuring approximately $10 \times 10 \times 10$ mm was

extracted for electron microscopy and approximately 300 g of pieces measuring 1–3 mm were sifted for desorption.

2.2. Proximate analysis

A 5E-MAG6600 automatic proximate analyzer, used to perform proximate analysis through thermogravimetric analysis, was employed (China State Administration of Work Safety: MT/T 1087-2008, 2009) in accordance with the MT/T 1087-2008 test methods for the proximate analysis of coal.

2.3. Petrographic analysis

To determine the maceral group composition and minerals and the reflectance of vitrinite in coal in accordance with the GB/T 16773-2008 method for preparing coal samples for coal petrographic analysis (General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China and Standardization administration of the People's Republic of China (2008a)), polished sections of the coal samples measuring 0.2–0.25 mm were prepared. The maceral group composition and the minerals in the coal were determined in accordance with the GB/T 8899-1998 method (State Bureau of Quality Technology Supervision of the People's Republic of China, 1998). The maximum reflectance of the vitrinite in the coal samples was determined in accordance with the GB/T 6948-2008 method for microscopically determining the reflectance of vitrinite in coal (General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China and Standardization administration of the People's Republic of China (2008b)).

2.4. Scanning electronic microscopy

In accordance with the GB/T 20307-2006 method (Inspection and Quarantine of the People's Republic of China and Standardization administration of the People's Republic of China (2007)), we prepared coal samples measuring $10 \times 10 \times 10$ mm to qualitatively determine the pore and fracture characteristics. In the laboratory, the coal rock samples were shaped into small cubic blocks measuring 1–2 cm^3 small blocks. We selected a relatively smooth natural fracture surface as the observation face. A HITACHI S-3000N scanning electron microscope was used to observe the coal samples on the micron scale. Images of the coal samples are shown in Fig. 1.

2.5. Methane adsorption test

According to the Langmuir adsorption law, using the high-pressure volumetric method based on the theory of static volumetric determination (Sing, 1985), we performed methane adsorption experiments on the long-flame coal in the laboratory. The Langmuir equation is $V = VP_L/(P + P_L)$ (Langmuir, 1918). The Langmuir volume V_L represents the monolayer adsorption capacity of coal, which is assumed to be the maximum adsorption capacity, and the Langmuir pressure P_L represents the adsorption pressure P at which the adsorbed volume V reaches half of the Langmuir volume V_L. In the experiment, we tested the methane adsorption isotherm of dry coal according to the MT/T752-1997 method for the determination of the methane adsorption capacity in coal (China Department of Coal Industry (1997)). Approximately 50 g of coal sample measuring 0.2–0.25 mm was weighed and placed in a vacuum drying oven. The coal sample was dried for 2 h at 378 K and 4 Pa, cooled to room temperature and placed in a coal sample tank for evacuation at 4 Pa for 8 h. Then, we tested the adsorption at 303 K using the volumetric method.

Table 1
Sampling location and proximate analysis.

Samples	Proximate analysis			
	Mad/%	Ad/%	Vdaf/%	Fcad/%
#12	6.32	5.63	44.15	49.18
#13	6.30	33.31	44.89	33.28
#14	7.55	10.64	39.04	49.87
#15	7.33	7.68	40.93	50.20
#16	4.89	10.86	44.43	46.82