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Adsorption isotherms and kinetic characteristics of methane on block anthracite over a wide pressure range

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Abstract

It is important to quantitatively understand the methane adsorption and transport mechanism in coal for an evaluation of the reserves and for its production forecast. In this work, a block coal sample was chosen to perform the CH_4 adsorption experiments using the gravimetric method at temperatures of 293.60 K, 311.26 K, 332.98 K and 352.55 K and pressures up to 19 MPa. The excess adsorption capacity of CH_4 in dry block anthracite increased, followed by a sequence decrease with the increasing pressure. High temperature restrained the growth of the excess adsorption due to that the adsorption is an intrinsically physical and exothermic process. The excess adsorption peak decreased slowly with the increase of temperature and intersected at a pressure of more than 18 MPa; meanwhile, the pressure at the excess adsorption peak increased. The existing correlations were examined in terms of density rather than pressure. The DR+k correlation, with an average relative deviation of $\pm$0.51%, fitted our data better than the others, with an average relative deviation of up to 2.29%. The transportation characteristics of CH_4 adsorption was also investigated in this study, including the adsorption rate and diffusion in block coal. The kinetic data could be described by a modified unipore model. The adsorption rates were found to exhibit dependence on pressure and temperature at low pressures, while the calculated diffusivities exhibited little temperature dependence. In addition, the kinetic characteristics were compared between CH_4 and CO_2 adsorption on the block coal. The excess adsorption ratios of CO_2 to CH_4 obtained from the DR+k model decreased with the increasing pressure.

Key words

adsorption isotherm; thermodynamic model; adsorption rate; diffusion

1. Introduction

With the consumption of conventional energy, such as coal, petroleum and natural gas, the exploitation of unconventional gas reservoirs is attracting increasing attention. Coalbed methane (CBM) is an unconventional natural gas resource that is associated with coal. As the key component, approximately 88%–98% of CH_4 is retained in the coalbed, mainly in the adsorbed state [1−3]. The growing interest in CH_4 recovery from coal seams has led to extensive study of the gas adsorption behavior in coal.

In recent years, numerous data for CH_4 adsorption on crushed coal have been reported when the temperature and pressure are higher than 308 K and 8 MPa, respectively [4−13]. However, some fundamental issues still exist for the effects of pressure and temperature on the adsorption behavior. Most researchers suggested that the excess adsorption isotherms for CH_4 on crushed coal belonged to the type I isotherm because the amount of excess adsorption increased and then reached equilibrium with the increasing pressure. However, some scholars found that the excess adsorption capacity for CH_4 adsorption on dry coal initially increased, followed by a decrease with pressure [14,15]. Therefore, the data quality of high-pressure adsorption isotherms must be further refined under the realistic reservoir conditions. Mohammad et al. [16,17] estimated the uncertainty of CH_4 adsorption on moist and dry coals associated with each data point by propagating the errors from the pressure, temperature and volume in the volumetric method. In addition, the adsorption isotherms are performed mostly using different particle sizes of powdered coal, while CH_4 adsorption data on block coal remain scarce. The properties of block coal are close to those of the

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raw samples from a coal reservoir. Therefore, an accurate measurement of the adsorption behavior of CH_4 on block coal is required to enable the data to be more reliable at the pressure and temperature prevailing in deep coal seams.

It is important to predict the adsorption capacity and estimate the recovery potential in exhausted coal reserves, therefore, a model that can accurately describe the adsorption behavior is required. The Langmuir monolayer model and the Dubinin-Radushkevich (DR) pore filling model were used by Clarkson et al. [18,19] under low pressure. Hao et al. [20] also demonstrated that these models were valid when the pressure was less than the saturation pressure of gas. Sakurovs et al. [21,22] proposed that the Langmuir and DR equations could be applied under supercritical conditions by replacing the pressure by density and introducing a term k. In this work, the free fluid density can be determined directly using a magnetic suspension balance (MSB), and the modified models are applied to fit the adsorption isotherms of CH_4 on block coal.

Adsorption kinetics is of great importance for understanding the transport mechanism of gas in a coal reservoir. The kinetic rate of CH_4 is generally described using an appropriate diffusion model. The diffusion coefficient is commonly calculated by various authors using either unipore or bidispere models to describe the kinetic characteristics [3,12,23−28]. However, disagreements exist in the literature regarding whether one characteristic diffusion coefficient is sufficient to describe the adsorption kinetics of gas in coal and whether the diffusion coefficients increase or decrease with the increasing pressure.

In this work, block coal was used to perform the adsorption experiments at temperatures of 293.60 K, 311.26 K, 332.98 K and 352.55 K and pressures up to 19 MPa, corresponding to the coal reservoir conditions. The CH_4 adsorption and diffusion behaviors in block coal were also investigated using thermodynamic and kinetic models. The adsorption isotherms were fitted by four thermodynamic models: modified Langmuir and DR, Langmuir+k, and DR+k models. In addition, a modified unipore model was used to describe the diffusion data and to obtain the effective diffusivity. Finally, the adsorption characteristics of CH_4 and CO_2 on the same block coal were compared.

2. Experimental

2.1. Sample preparation

All of the adsorption experiments were performed on anthracite coal, which was taken from Datong coal mine located in Shanxi province of China. A block coal sample with a hollow cylinder, inside & outside diameters of 6.4 mm & 16 mm, respectively, and length of 15 mm was used to measure the excess adsorption capacity. The detailed properties of the coal sample are presented in Table 1. Organic petrographic analysis indicates that the coal sample was a typical anthracite. Part of the coal sample was prepared for scanning electron microscope (SEM) analysis, as shown in Figure 1. SEM observations reveal that hollow particles in the sample appeared to roughen the surface, which is favorable to increase the interspace among the particles and to retain the CH_4 adsorption amount on the surface of coal. The coal sample was outgassed under vacuum conditions (approximately 0.007 MPa) over 12 h at 378.15 K to remove the adsorbed moisture.

Table 1. Physical properties of the coal sample used in this work

Proximate analysis		Ultimate analysis		Petrographic analysis	
Element	content (wt%)	element	content (wt%)	element	content (vol%)
Ash	37.48	C	50.73	vitrinite	73.0
Moisture	0.86	H	2.17	liptinite	0
Volatile matter	10.48	N	7.65	inertinite	16.2
Fixed carbon	51.18	O	35.63	mineral	10.8
		S	0.93	Ro'max	3.7

In addition, the He, CH_4 and N_2 for the experiments were supplied by Dalian Da-te Gas Co., Ltd., with purity of 99.999%, 99.99% and 99.999%, respectively.

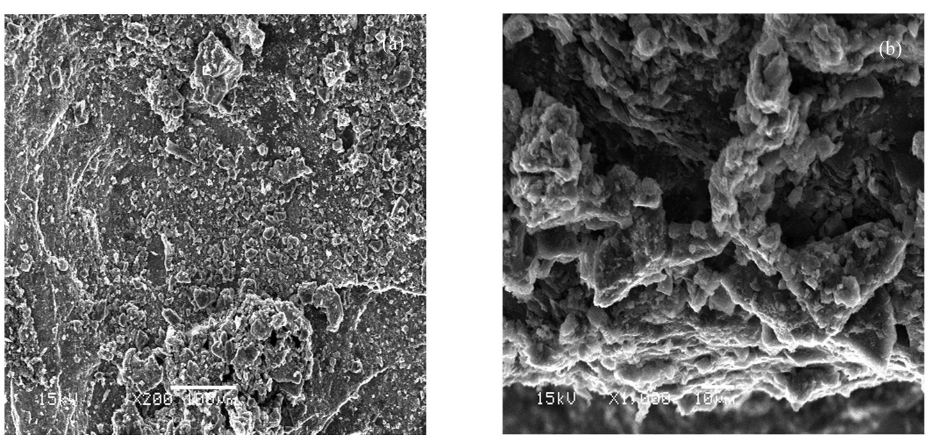

Figure 1. SEM images of the block coal sample with different magnifications