



Methane adsorption behavior on coal having different pore structures

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ABSTRACT

The adsorption of methane onto five dry coal samples was measured at 298 K over the pressure range from 0 to 3.5 MPa using a volumetric method. The isotherm data were fitted to the Langmuir and the Freundlich equations. The kinetic data were fitted to a pseudo second order equation, the linear driving force equation (LDF), and an intra-particle diffusion model. These results showed that higher methane adsorption is correlated with larger micro-pore volumes and specific surface areas. The adsorption was related to the narrow micro-pore size distribution when the previous two parameters are large. The kinetics study showed that the kinetics of methane adsorption onto these five dry coal samples followed a pseudo second order model very well. Methane adsorption rates are controlled by intra-particle diffusion. The faster the intra-particle diffusion, the faster the methane adsorption rate will be.

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1. Introduction

Coal is a complex polymeric material with a complicated porous structure [1]. It is generally believed that coal contains both micro- and macro-pores [2,3]. Micro-pores are present within the coal matrix and the macroscopic pore system consists of the coal matrix itself. This is called the natural fracture network of the cleat system. The characteristics of methane adsorption on coal affect coal seam gas migration and accumulation. Accurately predicting the methane adsorption capacity requires research on these subjects. There have been many studies of the adsorption of methane on coal. In the large pores a gas pressure gradient causes flow. In the micro-pores a gas concentration gradient causes diffusion where gas molecules diffuse within the coal until equilibrium is reached. More than 90% of the gas is adsorbed within the meso- and micro-pores of coal [4]. It is important to understand the effect on methane adsorption of pore surface area and volume in a coal sample.

There is little current work on methane adsorption and diffusion from a microscopic point of view. In this work, we examine the effect of pore structure on the methane adsorption isotherm of a raw coal sample, as well as the methane adsorption kinetics.

2. Procedures

2.1. Experimental

The porous structure of five coal samples was examined using a NOVA1000e instrument available from Quantachrome Company. The N₂ adsorption data were obtained at a sample temperature of 77 K after degassing at 393 K for 14 h. The specific surface area and pore volume were measured with the assistance of the DFT equation and the pore size distribution was calculated by the NLDFT method.

The methane isotherms and kinetic data were measured by a volumetric method by using a gas sorption apparatus. The schematic arrangement is shown in Fig. 1. A grain size of 150–250 μm was used. The coal samples were collected, crushed, and then screened using two standard sieves of 60 and 100 mesh. Then these samples were dried at 373 K for at least 8 h in a muffle furnace. The coal samples from different coal mines were numbered 1#, 2#, 3#, 4#, and 5#.

2.2. Kinetic modeling

The pseudo second order rate equation used is [5]:

$$\frac{dq_t}{dt} = k_2(q_{e,2} - q_t)^2 \quad (1)$$

After integration with the initial conditions

$$t = 0, q_t = 0; t = t, q_t = q_t,$$

this gives:

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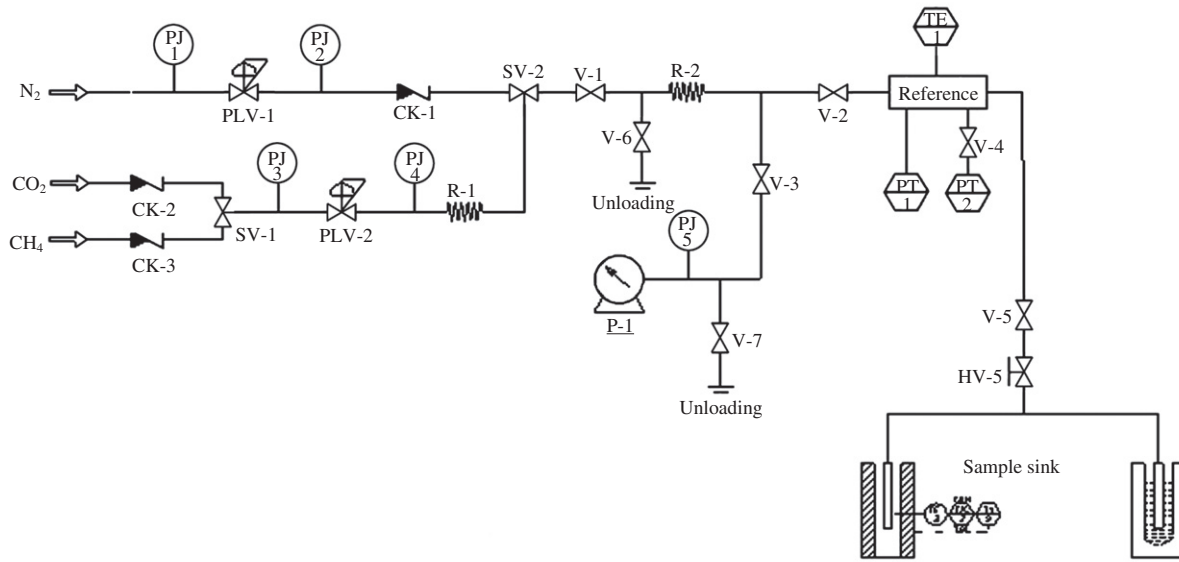


Fig. 1. Adsorption equipment.

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \left(\frac{1}{q_{e,2}} \right) t, \quad (2)$$

where $q_{e,2}$ is the amount of methane adsorbed on the coal sample at equilibrium, kg/kg; q_t the adsorbed methane at time t ; and k_2 the rate constant of the pseudo second order model, 1/s.

The linear driving force (LDF) model for adsorption is described by Ashleigh J. Fletcher et al. [6]:

$$\frac{M_t}{M_e} = 1 - e^{-kt}, \quad (3)$$

where M_t is the methane uptake at time t ; M_e the equilibrium uptake for the given pressure increment, of course, $M_t = M_e$ at equilibrium; and k the rate constant.

The intra-particle diffusion model:

Assuming that the resistance to mass transfer is controlled by intra-crystalline diffusion and that a crystal of the sample may be regarded as an approximately spherical object, the diffusion equation in spherical coordinates is [7,8]:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_c \frac{\partial q}{\partial r} \right), \quad (4)$$

where D_c is the intra-crystalline diffusivity; and $q(r, t)$ the adsorbed quantity of gas at time t at radial position r . If gas uptake by the adsorbent is small relative to the total amount of gas in the system the initial boundary conditions are:

$$q(r, 0) = q'_0, q(r_c, 0) = q_0, \left(\frac{\partial q}{\partial r} \right)_{r=0} = 0.$$

The solution of Eq. (4) is:

$$\frac{\bar{q} - q'_0}{q_0 - q'_0} = \frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-\frac{n^2 \pi^2 D_c t}{r_c^2} \right), \quad (5)$$

where $\bar{q}$ is the average adsorption in the particle; q'_0 the initial adsorption in the particle; and q_0 the equilibrium adsorption in the particle.

At short times Eq. (5) may be approximated by:

$$\frac{m_t}{m_\infty} = \frac{6}{\sqrt{\pi}} \sqrt{\frac{D_c t}{r_c^2}} - 3 \frac{D_c t}{r_c^2} \quad (m_t/m_\infty < 0.85). \quad (6)$$

Eq. (6) is used as the diffusion model to which the kinetic data are regressed. The diffusion time constant can be obtained in this way.

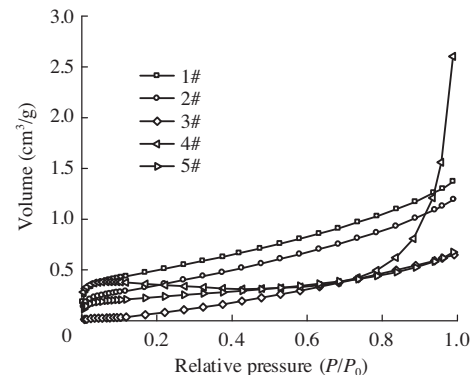
3. Results and discussion

3.1. Porous structure of the five coal samples

The N_2 adsorption isotherms of the five coal samples are presented in Fig. 2. It is obvious that the adsorbed methane increases as the pressure increases.

All five samples with the exception of 4# exhibit Type I adsorption isotherms according to the IUPAC [9] classification. This is characteristic of a material with micro-pores. Over the pressure range from 0 to 0.9 P/P_0 the isotherm fits Henry's law very well but the latter part of the adsorption curve rises more rapidly. The increased adsorption capacity is caused by capillary condensation in the large pores of the coal. These four coal samples (excepting 4#) show a linear relationship between relative pressure and adsorption capacity over the pressure range from 0 to 1 P/P_0 . This phenomenon is probably caused by the low pressure.

The specific surface area and the pore volume were calculated by the DFT equation. The average pore diameter was calculated with the D-R equation. It can be seen that the coal sample specific surface area, and the micro-pore volume, are both small. The corresponding texture parameters are listed in Table 1.

Fig. 2. N_2 adsorption isotherms of the five coal samples (at 77 K).

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