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CO adsorption-diffusion model in coal seams

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Abstract

Through the adsorption experiment for CO at different temperatures and different pressures, we get a result showing that, at a normal temperature, adsorption isotherms of CO in coal seams is part of class I adsorption isotherm. The CO adsorption quantity can be calculated by the Langmuir equation. Diffusion mode of gas in coal seam is determined by the index Kn, which determines the magnitude of coal hole diameter and average free moving distance of molecules. According to the calculation value of Kn, it is confirmed that diffusion modes of CO in coal seams are mainly Knudsen style and transition type diffusion. The samples of coal are mainly in the bituminous coal of low metamorphic grade, and the coal hole structure is mainly pore and transition hole. Therefore, in the coal seams, the proliferation transition model of proliferation of CO is mainly the Knudsen proliferation.

Keywords: Langmuir equation; monomolecule layer adsorption model; Kn; diffusion model; CO

1. Introduction

The adsorption of desorption and diffusion of coal-bed methane precursors within coal particles is a complex process of series and parallel. With coal mining, adsorbed gas has a continuous desorption and diffusion, transporting to the coal mine roadway and emitting to the atmosphere, which threatens Mine Safety and pollutes the atmosphere. Studies point out \cite{1, 2} that the seam is aggregately formed by the ultimate size. Thus, the study of coal gas adsorption-proliferation laws is very important for solving gas problems and coal mining. Coal-bed methane mainly exists in two states, the free state and the adsorbed state, in which the adsorbed state accounts for more than 90\% existing in the inner surface of coal-hole and micro-porous transition. Arony, Crosdale \cite{3}, and others generally believe that methane in coal is mainly micro-porous based on “the theory of full cubage”, and the view that methane mainly exists with adsorbed “solid solution” state in the space among molecules, is inconsistent with the Langmuir equation which is based on monolayer adsorption model. Therefore, in theory, to calculate the amount of coal methane adsorption by using Langmuir equation is not correct. However, both domestic and foreign researchers calculate equation by Langmuir equation, because the adsorption isotherms by using methane as adsorbate for
studying coal adsorption are almost of type I, the characteristics of type I adsorption isotherm, the characteristics of which is not necessarily monolayer adsorption. Because when the pores cohesion, micropore filling and adsorption isotherms occur to the micropore or microporous solids multi-layer adsorption, it often shows the characteristics of type I.

The diffusion mechanism of coal-bed methane in coal seams: for the first time the Literature [4] analyzed the diffusion mechanism of gas molecules in coal seam gas. According to the Mean Free Path of pore diameter and gas molecules, Literature [5, 6] put forward several diffusions, and provided a useful help for us to understand coal seam gas in the pores of migration on which this paper is based. The author has a further exploration about microproliferation mechanism of the pore gas CO adsorption in the pores of coal. And the experimental group collected 12 coal samples from Kailuan Group for mercury injection test, showing that the CO often exceeds limit.

2. Experiments and experimental results

2.1. Experimental equipment and coal examples

Micromeritics 9310 mercury of Mike Company in the United States was used to measure the porosity of coal samples. Meanwhile, the experts used IS-100 Isotherm Adsorption and Desorption produced by America to test the experimental data of the adsorption of coal sample in condition of 30 °C with different pressures.

Experimental coal samples contain 12 coal samples from Donghuantuo Kailuan Mining Corporation, Jinggezhuang Mining Corporation, Cuijiazha Mining Corporation, Linnancang Mining Corporation.

2.2. The experimental results

Table 1 shows that the experimental results of CO adsorption properties of coal samples under the condition of 30 °C and different pressures.

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Temperature (°C)</th>
<th>Absorption quantity Q (mL·g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1 MPa</td>
</tr>
<tr>
<td>1#</td>
<td>25</td>
<td>0.6400</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.6743</td>
</tr>
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<td></td>
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<tr>
<td>2#</td>
<td>50</td>
<td>0.3643</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.3540</td>
</tr>
<tr>
<td></td>
<td>35</td>
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<td>40</td>
<td>0.2893</td>
</tr>
<tr>
<td>50</td>
<td>0.2437</td>
<td>1.1553</td>
</tr>
</tbody>
</table>

2.3. The study on CO adsorption model in coal seams

He Xue-qiu and others [7] put forward the nature of gas adsorption of coal based on the theory that physical structure affects the gas adsorption and that gas adsorption on the surface of coal is physical adsorption, and its essence is the result of the attraction between surface molecules of coal and the gas molecules. It is the acting force between coal gas molecules and the gas molecules that makes the gas stay on the surface of the coal. Many researchers believe that the relationship between the pressure and gas adsorption can be measured by the general Langmuir equation.

Langmuir monolayer adsorption theory is based on the following four basic assumptions:

(1) The adsorption of solid surface for gas is single-molecule. (That is, each adsorption site of solid surface can only adsorb one molecular, and only when touching the blank surface of solid, can the gas molecules be adsorbed)
(2) Solid surface is equal with regard to its adsorption capacity. (That is, all parts of the surface have the same adsorption capacity)

(3) There is no interaction among adsorbed gas molecules. (That is, the difficulty in adsorption or in desorption is unrelated to neighboring adsorbed molecules).

(4) Adsorption equilibrium is dynamic equilibrium (That is, when adsorption equilibrium is going on, the process of adsorption and desorption will be done at the same time and at the same speed)

Its mathematical equation is showed by (1)-type.

\[ Q = \frac{abP}{1 + bp} \]  \hspace{1cm} (1)

where Q is the amount of adsorption gas on a certain solid surface; a the amount of saturation and adsorption gas on a certain solid surface; and b the parameter related to adsorbent, adsorbate characteristics and temperature.

![Fig. 1. Typical absorption isotherm concerning methane absorption by coal samples (t=30 °C)](image)

The data from Table 1 shows that the flexible relationship between the volume of coal and adsorption of CO. The pressure is represented by Fig. 2 and Fig. 3.

![Fig. 2. Typical CO absorption isotherm concerning methane absorption (a) By 1# coal sample (=50 °C); (b) By 2# coal sample (=50 °C)](image)

Fig. 2 and Fig. 3 show that both CO adsorption quantity in coal volume and the pressure of the adsorption isotherm represent the characteristics of class I adsorption isotherm. Therefore, we can also use the Langmuir equation to calculate the CO adsorption in the seam. When the ambient temperature arrives at a certain degree (low temperature), the temperature will have a greater impact on adsorption, and with the pressure becoming bigger, coal adsorption of CO will also increase. When the pressure rises to a certain value, adsorption capacity of coal reaches saturation, then, the bigger pressure will not bring further adsorption. Different coal samples’ adsorption needs different saturation pressure to reach saturation.

3. Study of gas diffusion model of CO in coal seam

3.1. Theoretical analysis about diffusion model of coal-bed methane
According to Kinetic Theory, He et al [8] proposed that:

\[ kn = \frac{d}{\lambda} \]  

(2)

where \( d \) is the void mean diameter, m; \( \lambda \) the free path of gas molecules, m

\[ \lambda = \frac{kT}{\sqrt{2\pi d_0^2 p}} \]  

(3)

where \( k \) is the Boltzmann constant, \( 1.38 \times 10^{-23} \, \text{J/K} \); \( T \) the absolute temperature, K; \( d_0 \) the molecule effective diameter, nm; and \( p \) the molecule pressure, MPa.

Fig. 4. The coal bed gas diffusion model in coal seam (a) Fick diffusion; (b) Knudsen diffusion; (c) Transitional diffusion

Diffusion falls into 3 groups: general Fick diffusion, Knudsen diffusion and transitional diffusion. When \( Kn=10 \), the Void Diameter is far larger than the Mean Free Path of gas molecules, at this moment, gas molecules collision takes place among the free gas molecules, and the diffusion still follows Fick’s theorem, which is called Fick’s type. The diffusion model (see Fig. 4 (a). When \( Kn=0.1 \), the Mean Free Path molecular is larger than aperture, and the collisions between the gas molecules and pore wall occupy a leading position, so in this condition, Knudsen diffusion is followed. The diffusion model (see Fig. 4 (b). When \( 0.1<Kn<10 \), the void diameter is close to the Mean Free Path of gas molecules, and the collision among the molecules as well as that between the molecules and pore wall are equally important. At present, transitional diffusion between the Fick diffusion and Knudsen diffusion happens, see Fig. 4(c).

3.2. Instance analysis of model diffusion model of CO in coal seam

According to coal aperture partition by Xo?oT [9], the coal pore structure can be divided into: 1000 nm< macropore, 100 nm< mesopore <1000 nm, 10 nm< transitional pore<100 nm, 1 nm< Millipore <10 nm. According to Xo?oT partition standard of the coal pore structure, the coal pore structures tested in this experiment are: 244.3801 nm<macropore<1004.2 nm<mesopore<105.4 nm<transitional pore<10.8 nm<Millipore<7.2 nm.

Here the coal sample is considered in normal temperature and pressure, \( T=293 \, \text{K}, P=0.1 \, \text{MPa} \), firstly we take mesopore aperture for 100 nm. From the formula (1) we can know that the value of mesopore Kn is 23.7. Because the macropore aperture is greater than mesopore, the mecropore Kn value will be greater than 23.7. From the pressured-mercury test, we can measure the minimum value of aperture: 7.2 nm, and calculate the Millipore Kn value: 0.814. The transitional pore Kn data are showed in Table 2.

Table 2. Kn data of the transition hole of coal samples

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Transition hole (Kn)</th>
<th>Serial number</th>
<th>Transition hole (Kn)</th>
<th>Serial number</th>
<th>Transition hole (Kn)</th>
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<td>2.403</td>
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<td>4#</td>
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<td>8#</td>
<td>2.403</td>
<td>12#</td>
<td>2.406</td>
</tr>
</tbody>
</table>
From the Table 2 we can see that when the transitional pore Kn value varies between $0.1 < Kn < 10$, the main forms of diffusion of CO in coal transitional pore are Knudsen diffusion and transitional diffusion. As the Kn value in milipore is 0.184, which is more than 0.1, the forms of diffusions are also mainly the Knudsen diffusion and transitional diffusion. And while Kn value is more than 10, the CO in coal macropore and mesopore is diffused in the form of Fick’s type diffusion. In our study, the coal is chosen by low or middle standard and metamorphism.

4. Conclusions

(1) When $T=50 \, ^{\circ}C$, the model of the CO adsorption quantity in coal seam conforms to the Langmuir monolayer adsorption theory. Moreover, when the ambient temperature reaches a certain degree (low temperature), it will have a considerable effect on adsorption, and with the pressure becoming higher, coal adsorption of CO will also increase. When the pressure increases to a certain value, adsorption capacity of coal reaches saturation. Then, higher pressure will not bring further adsorption. Different coal samples’ adsorption needs different saturation pressure to reach saturation.

(2) The CO in coal macropore and mesopore is mainly diffused by Fick’s type diffusion. However, in transitional pore and Milipore, Knudsen and transitional diffusion become the main forms. There are mainly two kinds of structures in the coal structure: the transitional pore and the Milipore. So, Knudsen diffusion and Transitional diffusion become the main forms of the diffusion of CO in coal pore.

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