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Determining the diffusion coefficient of gas diffusion in coal: Development of numerical solution

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ABSTRACT

Determining gas diffusion coefficient from experimental data is a key step of reproducing and predicting the diffusion process in coal. Previously analytical solution, including the unipore diffusion model and the bidisperse diffusion model, has been used extensively to estimate the gas diffusion coefficient(s) in coal. The utilization of analytical solution is convenient, however, there are some defects which may affect the accuracy of the results. For example, it is not suitable for fitting manometric sorption data, and the assumption of linear adsorption isotherm is not true.

In this paper, we present a numerical solution to determine the gas diffusion coefficients. Three models were developed based on different assumptions of pore system and diffusion forms, i.e., unipore model assuming one kind of pore and diffusion, bidisperse model I (BM I) assuming independent macropore diffusion and micropore diffusion, bidisperse model II (BM II) assuming dependent macropore diffusion and micropore diffusion. Nitrogen diffusion experiment was conducted and the adsorption isotherm was measured. Sphere geometry was built for numerical simulation and the proposed models were used to fit the experimental data to determine the diffusion coefficients. Results show that neither the analytical unipore model nor the numerical unipore model can describe the diffusion process perfectly. By giving the same diffusion coefficient, the modelled fractional uptake ratio of numerical unipore model is smaller than the result of analytical unipore modeling at early stage while greater at later stage, which is due to the different assumptions of adsorption isotherm. Both BM I and BM II can describe the diffusion process well. The determined macropore diffusion coefficients of the two models are similar, while the micropore diffusion coefficient and the macropore adsorption ratio of BM II are greater than that of BM I. These can be explained by the different roles of the macropore diffusion in the two models. The gas pressure change at the center of the coal sphere was examined, from the modeling result of BM I, the macropore pressure increases sharply and then drops along with the external gas pressure, while the initial increasing rate of macropore pressure of BM II is much smaller and tends to be stable at later stage. No apparent impacts of initial gas pressures on diffusion coefficients can be observed, the change of diffusion coefficients and macropore adsorption ratio are actually small with increasing gas pressure.

The numerical solution of determining gas diffusion coefficients can easily relax the assumptions and restrictions of the analytical solution. It can be used to test different kinds of coal samples, investigate different diffusion mechanisms and match all kinds of experimental data. The measured sorption isotherm and coal properties can also be incorporated into the modeling, which makes the determined diffusion coefficients more reliable. This paper is a preliminary attempt and we hope it can bring the researchers some new ideas about studying the gas diffusion characteristics in coal.

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1. Introduction

For coalbed methane (CBM) production and coal mine gas management, gas diffusion in coal refers to the gas exchange between coal cleat and coal matrix. It plays an important role in controlling the gas production rate together with gas sorption capacity and

coal permeability. A diffusion process may be related to three mechanisms, i.e., molecular diffusion, Knudsen diffusion and surface diffusion [1,2]. Different mechanisms prevail in different scale of pores, for example: the molecular diffusion dominates the gas flow in macropores where the pore diameter is way greater than the mean free path of gas molecules; the Knudsen diffusion is apparent when the mean free path is approaching the pore diameter; gas flow in micropores (<2 nm) is mainly controlled by surface flow. As a heterogeneous material, coal has a very complicated pore system which includes all kind of pores from micro- to macro- and this has been confirmed by various researchers [3–5].

Different laboratory methods have been used to measure the gas diffusion process in coal, such as sorption method, steady state method and inverse diffusion method [6–8], among them the sorption method was most extensively used due to the simpleness and reliability of the experimental setup. The way of studying diffusion phenomenon through sorption experiment is also called sorption kinetic study, as it can be measured along with determining adsorption capacity of gas in coal. A key problem for reproducing and predicting the diffusion process is to estimate the effective diffusion coefficient/coefficients. During the past decades, the influences of gas type [9–11], coal properties [3,12,13], sample size [9,14,15], gas pressure [16,17], moisture [18] and temperature [19,20] on diffusion coefficient(s) have been discussed widely. Even though the nature of heterogeneous coal structure makes it appear to be difficult to fit diffusion data with a simple model, a unipore model with single diffusion coefficient was indeed found to be sufficient in some experiments [21–23], while bidisperse model with two diffusion coefficients was found to fit well in other experiments [1,11,14,24].

The unipore model assumes coal particles used in the experiment are homogeneous spheres with uniform radius r, the fractional uptake of adsorbed gas mass can be written as:

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2\pi^2 t \frac{D}{r^2}\right) \quad (1)$$

where m_t is the amount of adsorbed gas at time t (g), m_∞ is the final adsorbed amount after equilibrium (g), D is the diffusion coefficient (m²/s) and t is the sorption time (s). The value of $\frac{D}{r^2}$ can be written as an effective diffusion coefficient D_e (1/s). Note Eq. (1) is under the assumption that the external/surface gas concentration is constant, thus it is suitable for volumetric and gravimetric sorption method but theoretically it cannot be used for manometric sorption method, where the external gas concentration changes with time. The solution of fitting manometric sorption experimental data can also be found from Crank [25]. By assuming the initial gas concentration in coal is 0, the fractional uptake of adsorbed mass can be expressed as:

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp\left(-\frac{D}{r^2}q_n^2 t\right)}{9 + 9\alpha + q_n^2\alpha^2} \quad (2)$$

Here, q_n are the non-zero roots of:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \quad (3)$$

where α is the ratio of the void volume V_{void} to the volume of the solid spheres (1). The parameter α is calculated from the final fractional uptake of gas by coals:

$$\frac{m_\infty}{V_{void}C_0} = \frac{1}{1+\alpha} \quad (4)$$

where C_0 is the initial gas concentration of void space (mol/m³). Unipore model may be adequate for some bright coals but for most coals with a multimodal pore distribution, bidisperse model was

found to fit better. Generally the idea of bidisperse model divides the diffusion into a macropore diffusion stage and a micropore diffusion stage (or rapid/slow diffusion stages in the strict sense), taking the constant external gas concentration boundary as an instance:

$$\frac{m_a}{m_{a\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2\pi^2 t \frac{D_a}{r_a^2}\right) \quad (5)$$

$$\frac{m_i}{m_{i\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2\pi^2 t \frac{D_i}{r_i^2}\right) \quad (6)$$

where the subscripts a and i represent the corresponding parameters of rapid macropore diffusion and slow micropore diffusion, respectively. $\frac{D_a}{r_a^2}$ and $\frac{D_i}{r_i^2}$ can also be written as the effective diffusion coefficients D_{ae} and D_{ie} (1/s), respectively. The overall uptake is sum of the two stages:

$$\frac{m_t}{m_\infty} = \frac{m_a + m_i}{m_{a\infty} + m_{i\infty}} = \beta \frac{m_a}{m_{a\infty}} + (1 - \beta) \frac{m_i}{m_{i\infty}} \quad (7)$$

where $\beta = \frac{m_{a\infty}}{m_{a\infty} + m_{i\infty}}$ is the ratio of macropore adsorption to the total adsorption (1). Through adjusting D_e in unipore model, D_{ae}, D_{ie} and β in bidisperse model, the best fitting curve of $\frac{m_t}{m_\infty}$ versus time is selected by comparing to the experimental results, and the diffusion coefficient/coefficients can thus be determined.

The above attempts to model diffusion experimental data can be classified as *analytical solution* (mathematical solution), and all of them are in the form of infinite series. Although this method has been extensively utilized since decades ago and the fitting results appeared to be good in most cases, there are still some defects which may affect the accuracy and applicability of analytical solution:

- Both unipore model and bidisperse model are based on the assumption of linear adsorption, while the adsorption of gas in coal is typical Langmuir-type rather than linear-type. This flaw is expected to be more obvious at high pressure stage as been pointed out before [14].
- From the expressions of bidisperse model it can be seen that the rapid macropore diffusion stage and the slow micropore diffusion stage are actually assumed to be independent. However, the independence of the two diffusion stages is related to the pore structure of coal, and this assumption cannot be always true.
- The analytical solution is not suitable for modeling manometric sorption data. Even though modified solution of unipore model was proposed (Eqs. (2)–(4)), it has the assumption that the initial gas concentration in coal is 0, but this is not true for most sorption steps. Moreover, to apply bidisperse model to fit manometric sorption data, two sets of $\frac{D}{r^2}$, α, q_n, V, m_∞ need to be adjusted separately for macropore diffusion and micropore diffusion, which will easily lead to overparameteration.
- The above models restricted to a specific geometry of coal, which are all spheres.

Comparing with analytical solution, *numerical solution* is free from the above restrictions. The basic assumption can be improved by developing different numerical models, and different coal geometries can be easily established. Modern simulation software provides a fast model resolving speed and thus increases the applicability of this method. Preliminary studies on numerical modeling of gas diffusion in coal can be found from Cui et al. [11] and Shi and Durucan [1] who discussed numerical unipore model and bidisperse model. However, afterwards the related research is rare. It should be noted that Both Cui model and Shi & Durucan model