



Effect of pressure on diffusion characteristic coefficient and dynamic diffusion coefficient of granular coal gas

Ding yan ning¹

¹School of Safety Science and Engineering, Henan Polytechnic University, Jiaozuo Henan 454100, China

Abstract In order to study the micro-mechanism of adsorptive gas (CH₄) and non-adsorptive gas (He) in granular coal, a self-developed gas diffusion coefficient testing system was used, the experimental results show that the initial diffusion coefficient D_0 and the diffusion attenuation coefficient β of He are greater than those of CH₄. According to the comparison between the desorption law of non-adsorptive gas and adsorptive gas, the equilibrium pressure has no significant effect on the gas diffusion coefficient. The initial diffusivity of He and CH₄ fluctuates irregularly with the increase of equilibrium pressure, and the variation of diffusivity β is related to the gas distribution in the granular coal.

Keywords Equilibrium pressure; diffusion coefficient; diffusion law; diffusion characteristic parameter; gas

1. Introduction

The movement of gas molecules through micro-pores to the external fissure system under the effect of concentration gradient is called diffusion process when gas molecules are desorbed and adsorbed on the surface of coal matrix and changed from adsorbed state to free state. The molecular diffusion coefficient, referred to as diffusion coefficient, is closely related to the internal pore structure, porosity, specific surface area and pore capacity of coal itself, and refers to the difficulty of gas diffusion in the coal medium. The study of gas diffusion characteristics has a positive effect on the prevention of coal mine gas protrusion accidents and provides a reliable basis for the rational utilization of coalbed methane and the reduction of environmental pollution.

Therefore, it is necessary to study the diffusion law of gas in coal seam through micromechanism, to find out the influence law of equilibrium pressure on gas diffusion coefficient and diffusion characteristic parameters, and then to find out the influence mechanism of equilibrium pressure on gas diffusion. Some scholars have carried out related studies: based on adsorption kinetics, Qiluan Yang and Zhaofeng Wang [1,2] showed that the diffusion rate of gas in micropores is smaller than that in large pores and fissures, and thus inferred that the key to control gas desorption from coal particles is CH₄ diffusion movement in mesopores-micropores, and the higher the proportion of the number of small pores, the more significant the gas diffusion movement. For the effect of adsorption equilibrium pressure on gas diffusion coefficient, some scholars believe that the gas diffusion coefficient increases with the increase of adsorption equilibrium pressure [3]; some scholars believe that the diffusion coefficient decreases with the increase of equilibrium pressure [4,5]. Li [6] et al. pointed out that the coal body is distributed from surface to surface, and the pores are graded from large to small, and this decreasing pore morphology causes the diffusion mechanism that the gas diffusion coefficient decays with time. Thus, the two parameters of initial diffusion coefficient and diffusion decay coefficient are considered to reflect the dynamic decay characteristics of diffusion coefficient. Nie Baisheng [7] et al. showed that the larger the adsorption equilibrium pressure, the larger the initial diffusion coefficient D_0 and gas desorption rate; the larger the particle size of the coal sample, the larger the D_0 value, the smaller the D_0 value, and the smaller the methane desorption rate in the same desorption time.



In view of this, this paper explores the effects of different equilibrium pressures on the initial diffusion coefficient D_0 , diffusion coefficient D_0 , and diffusion decay coefficient β of He and CH₄ by conducting experimental studies on the diffusion of non-adsorbed gas (He) and adsorbed gas (CH₄) under different equilibrium pressure conditions, and indirectly measuring the diffusion coefficients and diffusion characteristic coefficients of different gases of granular coal using the dynamic diffusion coefficient model.

2. Analysis of basic parameters of experimental coal samples

2.1 Basic parameter determination

The coal samples were collected from the second 1 coal (ZG) of Jiaozuo Zhaogu Second Mine in Henan Province, China, and then screened and prepared with different particle sizes. The industrial analysis was carried out by thermogravimetric method according to MT/T 1087-2008 standard. The adsorption characteristics were tested by high pressure capacity method according to GB/T 23561.2-2009 standard. The true and false densities of the coal were measured by the specific gravity bottle method according to GB/T 23561.2-2009 standard, and the porosity of the coal samples was obtained. The results of the determination of the basic parameters of the coal samples are shown in Table 1.

Table 1: Measurement results of basic parameters of coal samples

Coal samples Number	Water content $M_{ad}/\%$	Ash $A_{ad}/\%$	Volatile matter $V_{daf}/\%$	True Density TRD(g/c m^3)	Apparent density ARD(g/c m^3)	Porosity $\Phi(\%)$	Adsorption constant	
							a/(mL·g ⁻¹)	b/MP a ⁻¹
ZG	2.18	17.97	17.97	1.51	1.38	8.29	38.61	1.57

2.2 Coal sample pore size analysis

The fugacity and flow of different gases in the coal seam are inseparable from the coal pore structure, and the pore structure of coal samples with different degrees of metamorphism and tectonic types vary greatly, which directly affects the determination of gas diffusion coefficient. Therefore, the pore structure of the experimental coal samples is tested. Mercury-pressure method is one of the most commonly used methods for pore analysis in porous media, and the coal samples were analyzed by using AUTO PORE 9505 fully automatic mercury-pressure instrument [8], and the pore volume distribution was obtained as shown in Figure 1.

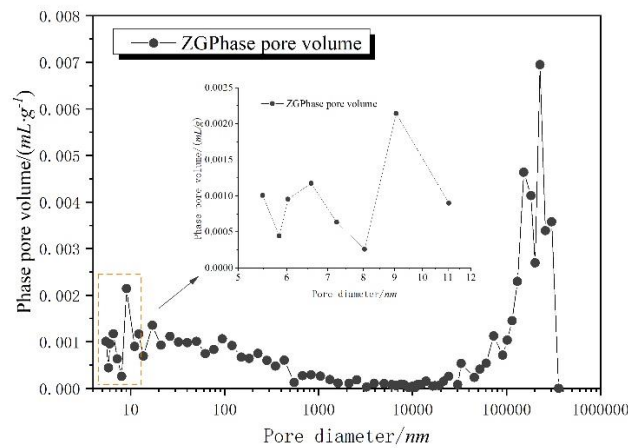


Figure 1: Pore volume distribution of test coal samples

According to the classification of B.B. Hodot, the pores in coal can be divided into micro-pores (<10 nm), small pores (10-102 nm), medium pores (102-103 nm), large pores (103-105 nm) and visible pores and fissures (>105 nm). As can be seen from the figure, the visible pores and fissures of ZG coal sample are more distributed, and the medium and large pores are relatively less. The stage pore capacity of micropores (<10nm) shows spikes at about 5nm and 9nm, which indicates that the coal sample has better development of micropores, as shown in Table 2.



Table 2 Pore volume distribution of experimental coal samples tested by the mercury-pressure method

Coal sample Number	Total pore volume (cm ³ /g)	Pore volume distribution of each pore size stage (cm ³ /g)					Percentage of pore volume at each pore size stage (%)				
		Microporous	Small pore	Medium pore	Large pore	Visible pores and fissures	Microporous	Small pore	Medium pore	Large pore	Visible pores and fissures
ZG	0.0599	0.0066	0.0107	0.0064	0.0061	0.0302	11.1	17.8	10.7	10.1	50.3

3. Indirect test method for diffusion coefficient of coal

3.1 Experimental sample and experimental procedure

In order to analyze the gas diffusion law of granular coal, different gas diffusion parameters were measured indirectly by transient method, and the experimental setup is shown in Figure 2. The ZG coal sample was sieved 1-3mm and the amount of He and CH₄ desorbed under different equilibrium pressure conditions was measured. The experimental steps were as follows: ① weighed 50g of 1mm-3mm particle size coal sample into the coal sample tank; ② vacuumed the coal sample for more than 12 hours; ③ injected gas into the coal sample tank and then put it into the thermostat (25 °C) to equilibrate; ④ after the coal sample was equilibrated, the valve of the coal sample tank was quickly opened and the pressure gauge value just dropped to 0, then the desorption cylinder/soap bubble flow meter was quickly turned on and the amount of gas desorbed in the device was recorded every minute. The accumulated gas desorption amount in the device was recorded every minute until the accumulated gas desorption amount basically stopped changing with time, which was the end of the adsorption and desorption experiment. ⑤ Repeat steps ①-④ to determine the constant temperature desorption process of granulated coal at each equilibrium pressure.

1- Gas cylinder; 2-Vacuum pump; 3-Thermal water bath; 4-Coal sample tank; 6-Shut-off valve; 7-Desorption cylinder; 8-Soap bubble flow meter

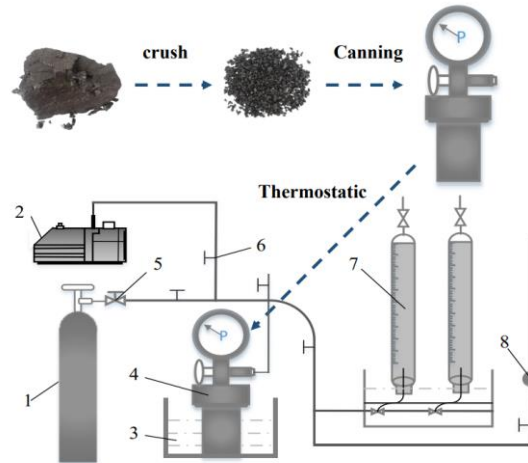


Figure 2: Experimental steps of desorption diffusion of granular coal by transient method

The diffusion coefficient is measured by the transient method, and the diffusion coefficient is obtained by back-calculating the experimental data of coal desorption diffusion for different gas grains using the dynamic diffusion coefficient model and the Barrell method.

(1) The dynamic diffusion coefficient model assumes that the coal grains are isotropic spheres and the diffusion pores consist of multi-scale, non-homogeneous multistage voids of different sizes and satisfy Fick's diffusion law; the diffusion coefficient decays exponentially with increasing time t [9,10].

$$\left\{ \begin{array}{l} \frac{\partial c}{\partial t} = D(t) \left(\frac{\partial^2 c}{\partial^2 r} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \\ \frac{\partial c}{\partial r} = 0 (r = 0, t \geq 0) \\ c = c_0 (t = 0, 0 \leq r \leq r_0) \\ D(t) = D_0 \exp(-\beta t) \end{array} \right. \quad (1)$$

Where, $\frac{\partial c}{\partial r}$ is the concentration gradient; $D(t)$ is the dynamic diffusion coefficient $\text{cm}^2 \cdot \text{s}^{-1}$ that decays with time; D_0 is the initial diffusion coefficient, $\text{cm}^2 \cdot \text{s}^{-1}$, which reflects the diffusion coefficient of the outermost large pore; β is the diffusion decay coefficient s^{-1} , which reflects the transition degree of the outer large pore to the inner small pore, and the larger its value, the larger the difference between the diameters of adjacent pores.

The analytical equation of diffusivity is obtained after using the separation variable method to find the analytical equation (1) as follows:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ -\frac{n^2 \pi^2 D_0}{r_0^2 \beta} [1 - \exp(-\beta t)] \right\} \quad (2)$$

In order to solve the exponential model accurately, the diffusion model is solved by MATLAB software in this paper, and finally D_0 and β are obtained by fitting with high accuracy.

(2) The process of solving the analytical solution of the constant coefficient diffusion model includes the method^[11] and the logarithmic method^[12,13,14], of which the logarithmic method is most commonly used, and the analytical solution of the single-hole diffusion model is obtained after simplifying:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{i=1}^{\infty} \frac{1}{i^2} \exp \left(\frac{-Di^2 \pi^2 t}{r_0^2} \right) \quad (3)$$

Where, Q_t is the coal grain gas diffusion at moment t , mL/g ; Q_∞ is the gas diffusion at $t \rightarrow \infty$, mL/g ; r_0 is the coal grain radius, m ; Q_t/Q_∞ represents the gas desorption rate.

Further simplifying, the logarithmic method equation used to calculate the diffusion coefficient is obtained as

$$\ln \left(1 - \frac{Q_t}{Q_\infty} \right) = -\lambda t + \ln A \quad (4)$$

Among them, $\lambda = \frac{\pi^2 D}{r_0^2}$, $A = \frac{6}{\pi^2}$. The diffusion coefficient is then calculated by fitting the data Q_t/Q_∞ versus t .

4 Results and Analysis

4.1 Transient method diffusion experimental results

Transient method granular coal in He adsorption equilibrium conditions, Figure 3(a) Experimental results of He desorption with time, Figure 3(b) Experimental results of He diffusivity with time. The experimental results of granular coal in CH_4 in adsorption equilibrium conditions are shown in Fig. 4(a) and (b).



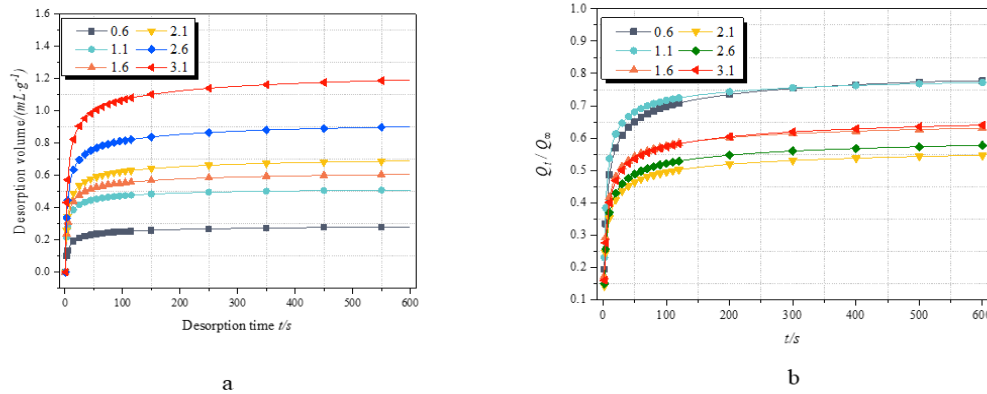


Figure 3: He grain coal diffusion experiment results

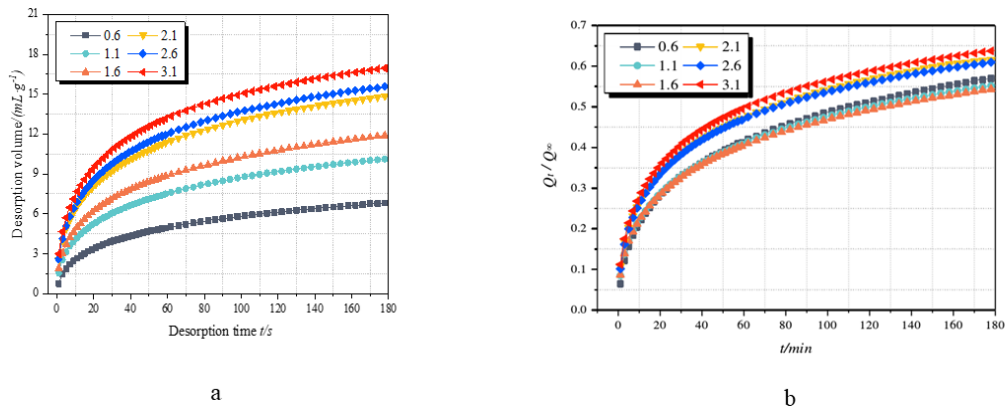


Figure 4: Experimental results of CH₄ particle coal diffusion

From Fig. 3, the relationship of desorption rate of coal sample with t shows that He diffuses out from the coal matrix rapidly within 10s and gradually stabilizes after 150s. At the equilibrium pressure of 0.6 MPa and 1.1 MPa, the desorption rate is higher and reaches 77% at 10 min of desorption; at the equilibrium pressure of 2.1 MPa, the desorption rate is the smallest at 55%; overall when the equilibrium pressure is 0.6~3.1 MPa and the desorption time is 10 min, the He desorption rate is in the range of 55%~77%. Since He is a non-adsorbed gas, the diffusible amount is small, and the experiments only measured the He desorption data in 10 min. As can be seen from Figure 4, CH₄ desorption gradually increased with the desorption time, and the desorption amount was small in the later period and decreased with the prolonged diffusion time. Unlike He, the CH₄ desorption rate Q_i/Q_∞ varies linearly at the initial stage and gradually stabilizes with the change of desorption time. CH₄ has high desorption rate at high pressure (2.1 MPa, 2.6 MPa, 3.1 MPa). Overall, when the equilibrium pressure was 0.6~3.1 MPa and the desorption time was 10 min, the CH₄ desorption rate was in the range of 24%~30%, and when the desorption time was 180 min, the CH₄ desorption rate was in the range of 60%~70%.

The results of pore size analysis of coal samples showed that the percentage of small and micro pores in granular coal was high. Some research results suggest [15,16] that gas is firstly desorbed from macropores and transition pores, and as the desorption time increases, the gas concentration in macropores and transition pores decreases, and gas desorption gradually develops from macropores and transition pores to micropores under the effect of concentration difference. This kind of pore form, forming gas desorption rate and desorption volume grows more slowly.

4.2 Relationship between equilibrium pressure and diffusion characteristic parameters

The exponential model considers the negative exponential decay of the diffusion coefficient with desorption time, the diffusion decay coefficient β and the initial diffusion coefficient D_0 values for He and CH₄. Figure 5 and Figure 6 show the comparison of β and D_0 values for He and CH₄ at different equilibrium pressures.

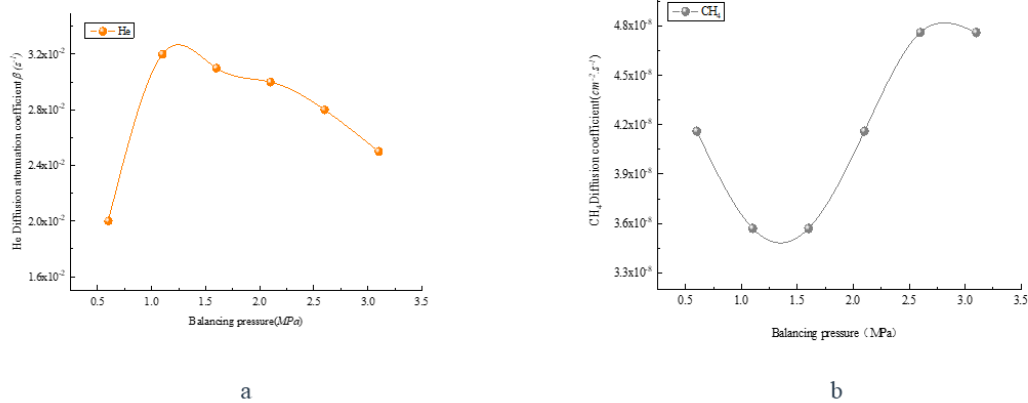


Figure 5: Variation of β value of He and CH_4 versus equilibrium pressure

As can be seen from Fig. 5, with the increase of the equilibrium pressure, the fluctuation of the diffusion decay coefficient β value of CH_4 is relatively large compared with that of He. For non-adsorbed gas He is instantly discharged from the pores of granular coal, the diffusion is large at the early stage of β and small at the later stage of β , with a decaying trend. For the CH_4 diffusion process, in addition to free gas, the diffusion process becomes complicated due to the presence of adsorbed gas. The exponential model calculates the average diffusion decay coefficient of order $10^{-2} s^{-1}$ for He and $10^{-4} s^{-1}$ for CH_4 .

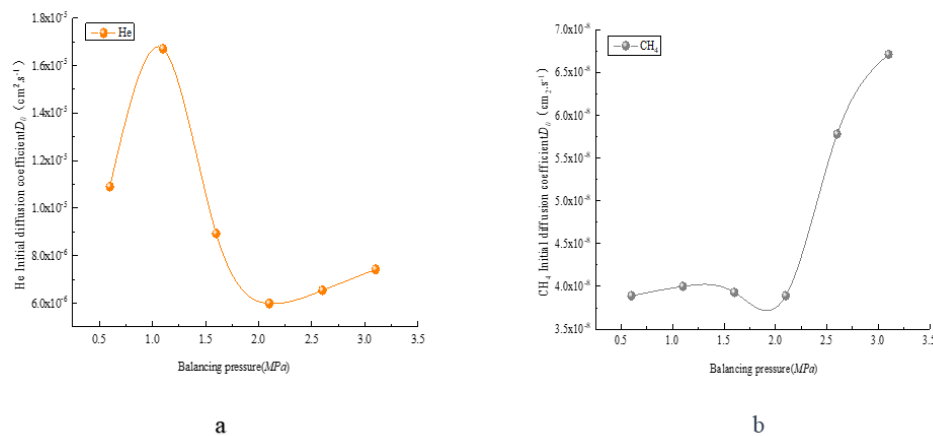


Figure 6: Variation of D_0 value of He and CH_4 versus equilibrium pressure

Comparing with Fig. 5 and Fig. 6, the diffusion decay coefficients β of He and CH_4 are the smallest at the absolute pressure of 0.6 MPa, with the order of $10^{-2} s^{-1}$ and $10^{-4} s^{-1}$, respectively. the trend of D_0 and β values of He is to increase first and then decrease; the trend of β values of CH_4 is to increase first and then decrease and then increase, and its D_0 value tends to stabilize first and then increase suddenly. Combined with the experimental results, with the desorption of CH_4 , the gas pressure in coal particles increases and the β value appears to fluctuate. And the change of pore size caused by the change of adsorbed gas into free gas is the reason for the sudden increase and fluctuation of diffusion decay coefficient β with the increase of gas equilibrium pressure.

Yang Tao ^[17] et al. showed that the initial effective diffusion coefficient was positively correlated with the adsorption equilibrium pressure, temperature and coal sample particle size through the experiments of coal particle gas desorption diffusion under different particle size, temperature and equilibrium pressure conditions. The initial diffusion coefficient is related to the gas equilibrium pressure, and with the increase of the adsorption equilibrium pressure, the kinetic energy of gas molecules increases and the van der Waals force between molecules decreases. Combined with the study in section 2.1, it shows that the initial diffusion coefficient D_0 of non-adsorbed gas is larger than the D_0 value of adsorbed gas, which leads to the rapid growth of desorption amount and desorption rate at the early stage of non-adsorbed gas diffusion; the average diffusion decay coefficient β of non-adsorbed gas is larger than the β value of adsorbed gas, which leads to the flattening of desorption amount and desorption

rate at the late stage of non-adsorbed gas diffusion. However, there is no obvious linear relationship between the adsorption equilibrium pressure and the initial diffusion coefficient of the gas.

4.3 Effect of equilibrium pressure on diffusion coefficient/initial diffusion coefficient

The diffusion coefficients of transient normal grain coal were calculated using diffusion parameter theory to analyze the differences between the diffusion coefficients D and the initial diffusion coefficients D_0 for He and CH_4 at different equilibrium pressures, as shown in Figure 7:

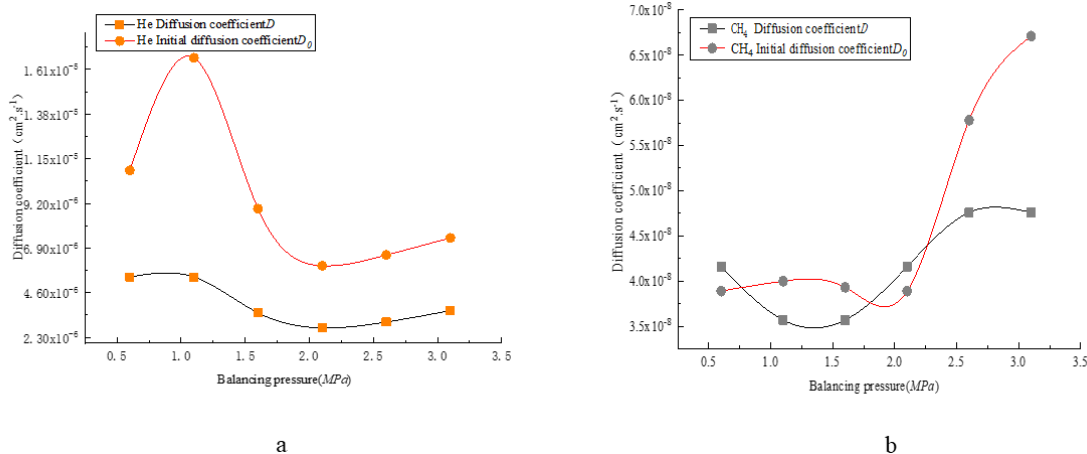


Figure 7: Initial over coefficient/diffusion coefficient of He, CH₄ versus equilibrium pressure

From the analysis of Fig. 7, it is clear that the diffusion coefficients of He and CH₄ are not monotonic with respect to the equilibrium pressure under different equilibrium pressure conditions. The results from the order of magnitude show that the adsorption equilibrium pressure is less volatile for the whole diffusion coefficient D for adsorbed or non-adsorbed gases. For the He diffusion process, the instability of the transient diffusion process leads to a large difference in the numerical magnitude between the diffusion coefficient D_0 values at the early stage of diffusion and those at the later stage. With the desorption of CH₄, the adsorbed gas becomes free gas causing the dynamic change of pore size with diffusion time, which may result in the fluctuation of diffusion coefficient D with the increase of gas equilibrium pressure.

Under the same equilibrium pressure conditions, the initial diffusion coefficient D_0 values of He and CH₄ vary significantly, and with the reduction of the particle size scale of granular coal, the gas diffusion channel is smaller and the grade difference of pore change is larger, which makes the phenomenon of D_0 change. As different gases exist in different ways in the pores of granular coal, He diffuses faster than CH₄, and the D_0 variation pattern of gas is not obvious. For non-adsorptive gases the faster the initial diffusion coefficient D_0 decays, the smaller the fluctuation of diffusion coefficient D , the faster the decay. The initial diffusion coefficient D_0 for adsorptive gases tends to increase and then decrease, and the diffusion coefficient D first decreases and then increases. The average values of initial diffusion coefficient D_0 and diffusion coefficient D for non-adsorptive gases are larger than those of D_0 and D for adsorptive gases, and the average order of magnitude difference between D_0 and D values for non-adsorptive gases is the same.

5. Conclusion

The diffusion coefficients and diffusion characteristic coefficients (D_0 , β) were measured indirectly by the transient method, and the diffusion coefficients and diffusion characteristic coefficients of different gas types (He, CH₄) were compared and analyzed under equilibrium pressure conditions.

(1) The initial diffusion coefficient D_0 and diffusion decay coefficient β of non-adsorptive gases are larger than the values of D_0 and β of adsorptive gases, which have more significant effects on the initial desorption amount and desorption rate of gases. Non-adsorptive gases are desorbed instantaneously in the early stage, and their desorption amount and rate tend to be stable phenomena in the late stage of desorption. The influence of equilibrium pressure on the diffusion characteristic coefficients (D_0 , β) of non-adsorptive and adsorptive gases is related to the instability of the transient diffusion process.



According to the comparison of desorption laws of non-adsorbed and adsorbed gases, the equilibrium pressure has no significant effect on the gas diffusion coefficient. Therefore, when the pore size is equal and the resistance is the same, the diffusion coefficient is constant. The initial diffusion coefficient D_0 of He and CH₄ shows irregular fluctuation with the increase of equilibrium pressure, and the change law of diffusion decay coefficient β is related to the internal gas distribution characteristics of the granular coal.

References

- [1]. Wang Zhaofeng. Gas Desorption Law and Application Research of Coal in Air, Water and Slurry Media [D]. Safety Technology and Engineering, China University of Mining and Technology, 2001.
- [2]. Yang Qiluan. Preliminary study on the law of coal chip gas dispersion with time [J]. Coal Mine Safety, 1986(4):3-11. Long, Wei-Cheng. Research and Application of Gas Fugacity Law Based on Multi-source Gas Data Fusion[D]. Henan University of Science and Technology, 2007.
- [3]. Cui X, Bustin R M, Dipple G. Selective transport of CO₂, CH₄, and N₂ in coals: insights from modeling of experimental gas adsorption data [J]. Fuel, 2003,83:293-303.
- [4]. Pandey G N, Tek M R, Katz D L. Diffusion of fluid through porous media with implications in petroleum geology [J]. Aapg Bull, 1974,58(2):291-303.
- [5]. Schomer S, Krooss B M. Molecular transport of methane, ethane and nitrogen and the influence of diffusion on the chemical and isotopic composition of natural gas accumulations [J]. Geofluids, 2004 (4): 81-108.
- [6]. Li ZQ, Wang SJ, Liu YW, Song DANYU, Wang YG. Mechanism of gas diffusion in tectonic coal based on a new diffusion model with dynamic diffusion coefficient [J]. Journal of China University of Mining and Technology, 2015, 44(05): 836-842.
- [7]. Nie Baisheng, Yang Tao, Li Xiangchun, Li Li, Lu Hongqi. Experiment on the diffusion law of coal particle gas desorption[J]. Journal of China University of Mining and Technology, 2013,42(06):975-981.
- [8]. Carlos A León y León. New Perspectives in Mercury Porosimetry [J]. Advances in Colloid & Interface Science, 1998, 76: 341-372.
- [9]. Li ZQ, Wang DK, Song DY. Effect of temperature on dynamic diffusion coefficient of coal grain gas under new diffusion model [J]. Journal of Coal, 2015, 40(5): 1055-1064.
- [10]. Li ZQ, Liu Y, Xu YP, et al. New model of gas diffusion mechanism and dynamic diffusion coefficient in multi-scale pore space of coal particles [J]. Journal of Coal, 2016, 41(03): 633-643.
- [11]. Charrière D, Pokryszka Z, Behra P. Effect of pressure and temperature on diffusion of CO₂ and CH₄ into coal from the Lorraine basin (France) [J]. International Journal of Coal Geology, 2010, 81(4): 373-380.
- [12]. Guo YY, Wu SY, Wang YM, et al. Study on the diffusion and diffusion coefficient of coal gas [J]. Journal of Shanxi Mining Institute, 1997,15(1):17-21.
- [13]. Yang Qiluan, Wang Youan. Coal chip gas diffusion theory and its application [J]. Journal of Coal, 1986 (3): 87-94.
- [14]. Nie Baisheng, Wang Enyuan, Guo Yongyi, et al. A mathematical and physical model of coal particle gas diffusion [J]. Journal of Liaoning University of Engineering and Technology (Natural Science Edition), 1999, 18(6): 582-585.
- [15]. Xue W. T. Study on the variation law of coal particle gas diffusion coefficient with dispersion time[D]. Henan University of Technology, 2016.
- [16]. Xu Chao, Wang Shuo, Guo Hai, et al. Model of unsteady state diffusion characteristics of gas in coal and experimental validation [J]. Coal Mine Safety, 2018, 49(5): 1-5.
- [17]. Yang T, Nie Baisheng. Initial effective diffusion coefficient in coal grain gas desorption experiments [J]. Journal of Liaoning University of Engineering and Technology (Natural Science Edition), 2016, 35(11): 1225-1229.
- [18]. Nie Baisheng, Guo Yongyi, Wu Shiyue, et al. Theoretical model of coal particle gas diffusion and its analytical solution [J]. Journal of China University of Mining and Technology, 2001, 30(1): 19-22.
- [19]. Zhou Shining. Mechanism of gas flow in coal seams [J]. Journal of Coal, 1990, 15(1): 15-24.



- [20]. Xue W. T. Study on the variation law of coal grain gas diffusion coefficient with dispersion time [D]. Henan University of Technology, 2016.
- [21]. Wen Zhihui, Duan Xinjun, Wang Honglei. Study on the time response law of coal chip gas diffusion coefficient [J]. Journal of Henan University of Technology (Natural Science Edition), 2017, 36(6): 33-39.
- [22]. Zhao Y, Zhang J, Ding S. A new method for solving the fission gas diffusion equations with time varying diffusion coefficient and source term considering recrystallization of fuel grains [J]. Nuclear Materials and Energy, 2019, 20: 100686.

