

Time-Dependent Model and the Evolution Mechanism of Dynamic Diffusion Coefficient for Gas Desorption in Gas-Containing Coal

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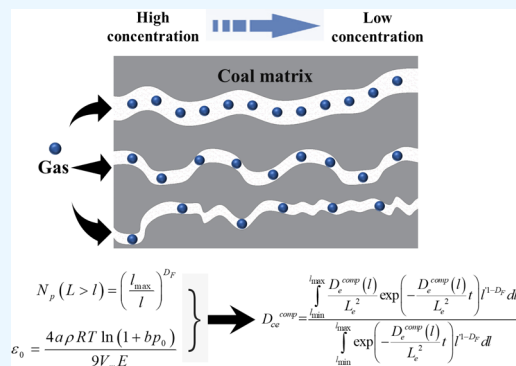
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ABSTRACT: Coalbed methane drainage has important significance for providing clean energy and reducing the risk of coal and gas outburst. Coalbed methane mainly exists in the adsorbed state in coal seam and diffuses from the pore network to the drainage pipelines. The diffusion coefficient is of strategic importance for the accurate prediction of the coalbed methane drainage process, while the currently reported dynamic diffusion coefficient models were found to lack systematic theoretical proof. Therefore, this study focuses on the dynamic diffusion coefficient model, which comprehensively adopts theoretical analysis, numerical calculation, and experimental verification. First, an evolution mechanism was proposed according to the fractal theory, the surface physical chemistry theory, and the diffusion theory in porous media. Then, a time-dependent model of dynamic diffusion coefficient was deduced based on the evolution mechanism. The numerical computation and experimental verification were then carried out to validate the established model. Results showed that the diffusion coefficient of gas desorption in gas-containing coal exhibited dynamic characteristics. The diffusion coefficient was negatively correlated with pore fractal dimension and gas desorption effect but positively correlated with coal matrix adsorption capacity. The pore structure plays a leading role in the dynamic characteristic of diffusion coefficient, followed by the adsorption capacity of the coal matrix, and the gas desorption effect was the weakest. The calculated results according to the proposed time-dependent model agreed well with the experimental data, with correlation coefficients above 96.0%. This research will provide a theory foundation for the in-depth understanding of the gas diffusion mechanism in coal.



1. INTRODUCTION

Coalbed methane is one of the important hazard sources that causes coal and gas outburst, while it is also an important source of clean fuel. Thus, coalbed methane drainage has important significance for providing clean energy and reducing the risk of coal and gas outburst. Coal seam has a double porosity texture composed of pores and fractures, which are interconnected to form a crisscrossed network of gas flow. Coal gas mainly exists in the adsorbed state and diffuses from pores to fractures driven by the concentration gradients during the gas drainage. Therefore, gas diffusion is an important part of the gas migration process during gas drainage. As the key parameter of gas diffusion, the diffusion coefficient will play an important role in accurately predicting coalbed methane production.

The initial diffusion model was a unipore model proposed by Crack according to the Fick law.¹ The unipore model assumed that the isotropic pore structure in coal-rock was uniform with a single diffusion coefficient. However, the fitting results always showed a few deviations with the experimental data.² Based on the unipore model, Pan et al.³ then established a bidisperse model in which the pores in coal-rock were simply divided into macroscopic pores and microscopic pores with

different diffusion coefficients. The two sorts of pores were considered to distribute homogeneously and isotopically in coal-rock. The gas content in macroscopic pores and microscopic pores was in certain proportion and diffused independently in coal.⁴ Thus, the gas diffusion amount could be calculated by adding two unipore models with different diffusion coefficient. The fitting results derived by the bidisperse model could reach perfect agreement with the experimental data. Furthermore, Li et al.⁵ established a multiple diffusion model in which gas diffusion in coal-rock was divided into Knudsen diffusion, transitional diffusion, and Fick diffusion according to the relationship between the pore diameter and the mean free path of gas molecule. The diffusion model can be analogously extended to a multiple diffusion

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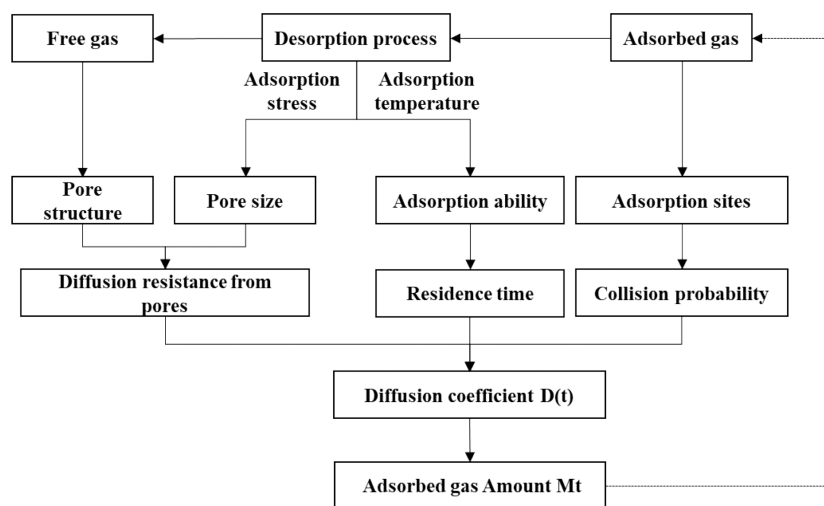


Figure 1. Mechanism of the dynamic diffusion coefficient during gas desorption.

model with three diffusion coefficients. The multiple diffusion model presented a high accuracy of fitting results.

Different from the abovementioned conventional diffusion models, Li et al.⁶ believed that the gas diffusion in coal-rock was a transition process from the surface to the interior and from the large pores to the small pores. As a result, the diffusion coefficient exhibited time-dependent characteristics and decayed exponentially with time. Liu et al.⁷ proposed that the diffusion coefficient decayed in the form of power function, which was attributed to the pore throat shrink caused by the gas pressure release during gas diffusion. Long et al.⁸ owed the time-dependent characteristic of diffusion coefficient to the comprehensive effects of the adsorbing capacity and the complex pore structure. Yuan⁹ attributed the dynamic diffusion coefficient to the dynamic gas concentration gradient between the coal-rock and external environment as well as the interior and surface. Also, the diffusion coefficient decayed in the form of the Langmuir formula. Li et al.¹⁰ found that the gas concentration decreased faster in large pores, while slower in small pores, leading to the gradual decline of diffusion inhibition in small pores. According to their research, the gas diffusion transition from large to small pores was dominated by the gas diffusion rate difference of pores. The time integral of the diffusion coefficient conformed to an equation like the Langmuir formula. Given that the abovementioned mechanisms and models were qualitative analysis, Liu and Lin¹¹ and Zhang et al.¹² respectively put forward a theoretical dynamic model of the gas diffusion coefficient according to the fluid mechanism through capillary driven by gas pressure.

In short, the dynamic diffusion models have such defects as that the empirical formulas belong to qualitative analyses, and the theoretical models go against the fact that gas diffusion is driven by concentration. In this article, the mechanism of the dynamic diffusion coefficient in coal-rock will be systematically put forward. A time-dependent model of dynamic diffusion coefficient will be also proposed according to the fractal theory, the surface physical chemistry theory, and the diffusion theory in porous media. This research will provide theoretical guidance for the in-depth understanding of gas diffusion in coal.

2. EVOLUTION MECHANISM OF DYNAMIC DIFFUSION COEFFICIENT IN GAS-CONTAINING COAL

As shown in Figure 1, the dynamic diffusion coefficient during gas desorption in gas-containing coal is the combined result of gas (adsorbed gas and free gas), pores (pore diameter and topological structure), and coal matrix (adsorption ability and adsorption sites). Most important of all, the pore diameter and topological structure lead to the transition of dominate pores for gas diffusion from large pores to small pores. During the gas diffusion process in pores, gas molecule collision happens in two forms, that is, collisions between gas molecules and collisions between gas molecules and pore wall. Also, the collisions between gas molecules and pore wall have higher resistance to gas diffusion. As the dominate pore diameter decreases, the collision probability between gas molecules and pore wall increases. As a result, the diffusion resistance increases, and the diffusion coefficient decreases. Second, the adsorption sites will be released as the adsorbed gas desorbs from the pore surface. The collision probability between gas and coal matrix during gas diffusion will be enhanced. Due to the adsorbing effect of coal matrix, the diffusion resistance will be enlarged, while the diffusion coefficient will decrease. Third, the desorption process of adsorbed gas into free gas is both affected by temperature and coal matrix shrink. As the temperature decreases, the adsorbing ability of coal matrix and the diffusion resistance are increased, while the pore diameters of coal matrix are enlarged and the diffusion resistance is reduced with the decreasing coal matrix shrink. Therefore, it is the combined effect of the pore structure, the adsorbing capacity of coal matrix, and the gas desorbing effect that eventually leads to the dynamic diffusion coefficient during gas diffusion in gas-containing coal.

3. TIME-DEPENDENT MODEL OF DYNAMIC DIFFUSION COEFFICIENT IN GAS-CONTAINING COAL

3.1. Relationship between the Effective Diffusion Coefficient and the Pore Structure in Coal. 3.1.1. Relationship between the Surface Area and the Pore Diameter.

A large number of studies have indicated that the pore structure in coal exhibits fractal characteristic. For the porous

media with fractal characteristic, the distribution of pores satisfies eq 1.¹³

$$N_p(L > l) = \left(\frac{l_{\max}}{l}\right)^{D_F} \quad (1)$$

where N_p is the cumulative number of pores, l is the pore diameter, l_{\max} is the maximum pore diameter, m , and D_F is the fractal dimension of the specific surface area.

According to eq 1, the number of dN_p for the pores with a diameter range of $l \sim l + dl$ can be calculated by eq 2.

$$-dN_p = D_F l_{\max}^{D_F} l^{-(D_F+1)} dl \quad (2)$$

Assuming the pores to be sphere geometry, the surface area of dS for the pores with a diameter range of $l \sim l + dl$ can be calculated by eq 3.

$$dS = -\pi D_F l_{\max}^{D_F} l^{1-D_F} dl \quad (3)$$

Integrating eq 3, the total surface area of S can be obtained as shown in eq 4.

$$S = \frac{\pi D_F l_{\max}^2}{2 - D_F} \left[1 - \left(\frac{l_{\min}}{l_{\max}}\right)^{2-D_F} \right] \quad (4)$$

According to eqs 3 and 4, the proportion of the surface area of pores with a diameter range of $l \sim l + dl$ to the total surface area expressed in $\delta(l)$ can be calculated by eq 5.

$$\delta(l) = \frac{dS}{S} = \frac{(D_F - 2) l_{\max}^{D_F-2}}{1 - \left(\frac{l_{\min}}{l_{\max}}\right)^{2-D_F}} l^{1-D_F} dl \quad (5)$$

3.1.2. Relationship between the Effective Diffusion Coefficient and the Pore Diameter. Gas diffusion in coal-rock can be divided into Knudsen diffusion, transitional diffusion, and Fick diffusion. Among them, the Knudsen diffusion coefficient can be expressed by eq 6.¹⁴

$$D_K = \frac{2\sqrt{2} k_B^{0.5} T^{0.5}}{3\pi^{0.5} m^{0.5}} \quad (6)$$

The Fick diffusion coefficient can be expressed by eq 7.¹⁵

$$D_B = \frac{2k_B^{1.5} T^{1.5}}{3\pi^{1.5} d^2 p m^{0.5}} \quad (7)$$

The transition diffusion coefficient satisfies eq 8.¹

$$D_p = D_B \left(1 - \exp\left(-\frac{l}{\lambda}\right) \right) \quad (8)$$

For eq 8, the mean free path of the gas molecule denoted as λ can be further expressed by eq 9.

$$\lambda = \frac{k_B T}{\sqrt{2} \pi p d^2} \quad (9)$$

where K_B is the Boltzmann constant, 1.38×10^{-23} J/K, T is the temperature, K, d is the diameter of gas molecule, m , p is the gas pressure, Pa, m is the mass of gas molecular, kg, and λ is the mean free path of gas molecule, m.

In eq 8, the representation of $1 - \exp(-l/\lambda)$ is approximately equal to l/λ when $l/\lambda \ll 1$. D_p is approximately equal to D_K in this situation. When $l/\lambda \gg 1$, the representation of $1 - \exp(-l/\lambda)$ is approximately equal to 1, and D_p is equal to D_B . Therefore,

eq 8 can be used to express the diffusion coefficient in porous media.

In the porous media, the diffusion path of gas molecules always represents spatial curves. The actual diffusion distance is usually expressed by eq 10.¹⁶

$$L(l) = l^{1-D_t} L_c^{D_t} \quad (10)$$

where L_c is the linear distance along the concentration gradient, m , and D_t is the fractal dimension of diffusion path and is in the range of 1–3 for three-dimensional space.

The tortuosity of the diffusion path denoted as τ can be calculated by eq 11.

$$\tau(l) = \frac{L(l)}{L_c} = \left(\frac{L_c}{l}\right)^{D_t-1} \quad (11)$$

Given that the diffusion time and resistance will be enhanced with the increasing diffusion distance, the effective diffusion coefficient is usually employed to characterize the diffusion property in porous media, as shown in eq 12.

$$D_e = \frac{D_p}{\tau^2} \quad (12)$$

3.1.3. Relationship between Gas Diffusion Amount and the Pore Diameter. Due to the complex pore structure, the coal body is usually simplified into three parts, that is, cracks, coal matrix, and pores. Also, the adsorbed gas mainly diffuses from the coal matrix to the cracks through the pore network.¹⁷ Assuming that the gas diffusion network is composed of independently tortuous pipes, which evenly distribute in the coal matrix with fractal characteristics. Taking any direction x as the research object, eq 13 can be obtained according to Fick's law.

$$\frac{dM_{xlt}}{M_{xlt}} = -\frac{D_e}{L_0 L_c} dt \quad (13)$$

where D_e is the effective diffusion coefficient of the coal matrix, m^2/s , M_{xlt} is the cumulated gas diffusion amount along the x -direction for the pores with diameters of l at time t , m^3/kg , \bar{M}_{xlt} is the remaining gas content along the x -direction for the pores with diameter of l at time t , m^3/kg , and L_0 is the average distance of diffusion paths, m .

Integrating eq 13 by the time t , we can get eq 14.

$$\frac{M_{xlt}}{M_{x\infty}} = 1 - \exp\left(-\frac{D_e}{L_0 L_c} t\right) \quad (14)$$

where $M_{x\infty}$ is the cumulated gas diffusion amount at the ultimate time along the x -direction for the pores with diameters of l , m^3/kg .

Using $L_e = \sqrt{L_c L_0}$ as the effective diffusion distance, eq 15 can be obtained.

$$\frac{M_{xlt}}{M_{x\infty}} = 1 - \exp\left(-\frac{D_e}{L_e^2} t\right) \quad (15)$$

According to surface physical chemistry theory, the amount of adsorbed gas is directly proportional to the surface area. Namely, it can be expressed by eq 16.

$$M_{x\infty} = \delta(l) M_{x\infty} \quad (16)$$

where $M_{x\infty}$ is the cumulated gas diffusion amount at the ultimate time along the x -direction, m^3/kg .

Substituting eq 16 into eq 15, the gas diffusion amount can be calculated according to eq 17.

$$M_{\text{slt}} = \delta(l)M_{\text{xoo}} \left[1 - \exp\left(-\frac{D_e}{L_e^2}t\right) \right] \quad (17)$$

3.1.4. Model of Dynamic Diffusion Coefficient in Gas-Containing Coal. Differentiating eq 17 by the time t , the instantaneous diffusion amount for the pores with a diameter of l at the time of t can be expressed by eq 18.

$$dM_{\text{slt}} = \delta(l)M_{\text{xoo}} \frac{D_e}{L_e^2} \exp\left(-\frac{D_e}{L_e^2}t\right) dt \quad (18)$$

The total instantaneous amount of gas diffusion at the time of t can be obtained by eq 19.

$$dM_{\text{slxt}} = \int_{l_{\text{min}}}^{l_{\text{max}}} \delta(l)M_{\text{xoo}} \frac{D_e}{L_e^2} \exp\left(-\frac{D_e}{L_e^2}t\right) dt \quad (19)$$

According to eq 17, the residual gas content at the time of t can be shown in eq 20.

$$\overline{M}_{\text{slt}} = \int_{l_{\text{min}}}^{l_{\text{max}}} \delta(l)M_{\text{xoo}} \exp\left(-\frac{D_e}{L_e^2}t\right) dt \quad (20)$$

According to eq 13, the effective diffusion coefficient along the x -direction of the coal matrix meets eq 21.

$$D_{\text{ce}} = \frac{D_{\text{m}}}{L_{\text{m}}^2} = \frac{dM_{\text{slxt}}}{dt} \frac{1}{\overline{M}_{\text{slt}}} \quad (21)$$

where L_{m} is the average effective distance of gas diffusion, m.

Substituting eqs 5, 19, and 20 into eq 21, we can obtain the model of the effective diffusion coefficient as shown in eq 22.

$$D_{\text{ce}} = \frac{\int_{l_{\text{min}}}^{l_{\text{max}}} \frac{D_e(l)}{L_e^2} \exp\left(-\frac{D_e(l)}{L_e^2}t\right) l^{1-D_{\text{F}}} dl}{\int_{l_{\text{min}}}^{l_{\text{max}}} \exp\left(-\frac{D_e(l)}{L_e^2}t\right) l^{1-D_{\text{F}}} dl} \quad (22)$$

According to the assumptions that the independent tortuous pipes evenly distribute in the coal matrix with fractal characteristics, the diffusion coefficient is equal along the arbitrary direction in the coal matrix. Equation 22 can be used to express the model of effective diffusion coefficient in the coal matrix.

3.2. Relationship between the Effective Diffusion Coefficient and the Adsorption Capacity of Coal Matrix. According to surface physical chemistry theory, the average residence time of gas molecules on the adsorbate surface meets eq 23.¹⁸

$$t_{\text{s}} = t_{\text{g}} \exp(\xi/RT) \quad (23)$$

where t_{g} is the residence time of gas molecules colliding with each other, s , R is molar gas constant, 8.31 J/(mol/K), and ξ is the adsorption potential energy, J/mol.

The average velocity of gas-to-solid collisions denotes as v_{s} , and the average velocity of gas-to-gas collisions denotes as v_{g} . The relationship between v_{s} and v_{g} satisfies eq 24.

$$\frac{v_{\text{s}}}{v_{\text{g}}} = \frac{t_{\text{g}}}{t_{\text{s}}} = \exp\left(-\xi/RT\right) \quad (24)$$

Assuming that the total number of gas molecules is N at the equilibrium state. The number of gas molecules within a velocity range of $v \sim v + \Delta v$ is ΔN among which the number of gas molecules colliding with solids is ΔN_{s} . Then, the collision probability between gas and solid denoted as P can be calculated by eq 25.

$$P = \frac{\Delta N_{\text{s}}}{\Delta N} \quad (25)$$

According to the gas speed distribution function,¹⁹ the speed distribution of gases colliding with solid denoted as f_{s} can be expressed by eq 26.

$$\begin{cases} f_{\text{s}}(v) = \lim_{\Delta v \rightarrow 0} \frac{\Delta N_{\text{s}}}{N \Delta v} = \frac{1}{N} \frac{dN_{\text{s}}}{dv} \\ f_{\text{s}}(v) = \lim_{\Delta v \rightarrow 0} \frac{P \Delta N}{N \Delta v} = P \frac{1}{N} \frac{dN}{dv} \end{cases} \quad (26)$$

Similarly, the speed distribution of gas colliding with gas denoted as f_{g} can be expressed by eq 27.

$$\begin{cases} f_{\text{g}}(v) = \lim_{\Delta v \rightarrow 0} \frac{\Delta N_{\text{g}}}{N \Delta v} = \frac{1}{N} \frac{dN_{\text{g}}}{dv} \\ f_{\text{g}}(v) = \lim_{\Delta v \rightarrow 0} \frac{\Delta N - \Delta N_{\text{s}}}{N \Delta v} = (1 - P) \frac{1}{N} \frac{dN}{dv} \end{cases} \quad (27)$$

The average speed of gas molecules denoted as \bar{v} can be obtained by eq 28.

$$\bar{v} = \frac{\sum_{i=1}^m v_{\text{s}}^i \Delta N_{\text{s}}^i + \sum_{j=1}^n v_{\text{g}}^j \Delta N_{\text{g}}^j}{N} \quad (28)$$

Since the value of gas molecular speed varies from 0 to infinity, average speed can be calculated by the integral operation shown in eq 29.

$$\bar{v} = \frac{\int_0^{\infty} v_{\text{s}} dN_{\text{s}} + \int_0^{\infty} v_{\text{g}} dN_{\text{g}}}{N} = \int_0^{\infty} v_{\text{s}} \frac{dN_{\text{s}}}{N} + \int_0^{\infty} v_{\text{g}} \frac{dN_{\text{g}}}{N} \quad (29)$$

Substituting eqs 24, 26, and 27 into eq 29, we can obtain eq 30.

$$\bar{v} = \{1 - [1 - \exp(-\xi/RT)]P\} \int_0^{\infty} v_{\text{g}} \frac{dN}{N} \quad (30)$$

The gas speed is assumed to still satisfy the Maxwell's distribution law as shown in eq 31.²⁰ Also, dN/N can be expressed by eq 32.

$$f(v) = 4\pi \left(\frac{m}{2\pi k_{\text{B}} T}\right)^{3/2} \exp\left(-\frac{1}{2}mv^2/k_{\text{B}}T\right) v^2 \quad (31)$$

$$\frac{dN}{N} = f(v) dv \quad (32)$$

Combining eqs 30, 31, and 32, eq 33 can be obtained.

$$\bar{v} = \{1 - [1 - \exp(-\xi/RT)]P\} \sqrt{\frac{8RT}{\pi M}} \quad (33)$$

As the mean free path of the gas molecule has no relation with the average speed, the diffusion coefficient can be written as eq 34.

$$D_p = \frac{1}{3} \bar{v} \bar{\lambda} = D_B \{1 - [1 - \exp(-\xi/RT)]P\} \quad (34)$$

As shown in eq 35, the expression of $[1 - \exp(-\xi/RT)]P$ is defined as P_s .

$$P_s = [1 - \exp(-\xi/RT)]P \quad (35)$$

Then, eq 34 can be simplified into eq 36.

$$D_p = D_B(1 - P_s) \quad (36)$$

where P_s can be used to assess the declined degree of diffusion coefficient caused by the collision between the gas and solid.

Comparing eq 8 with eq 36, P_s can also be expressed as eq 37.

$$P_s = \exp\left(-\frac{l}{\lambda}\right) \quad (37)$$

For the steady-state diffusion, the collision probability between gas and solid in the unit diffusion distance can be regarded as a constant. However, gas desorption in gas-containing coal belongs to unsteady-state diffusion. As the adsorbed gas desorbs from the surface, the potential adsorption sites are released, and the collision probability between gas and coal matrix is increased. The dynamic collision probability can be calculated by eq 38.

$$\frac{P(t)}{P} = 1 - \frac{M_\infty - M_t}{a} \quad (38)$$

where M_∞ can be expanded into eq 39.

$$M_\infty = \frac{abp_0}{1 + bp_0} - \frac{abp_c}{1 + bp_c} \quad (39)$$

where a is the Langmuir adsorption constant, m^3/kg , b is the Langmuir equilibrium constant, Pa^{-1} , p_0 is the equilibrium pressure of gas adsorption, Pa , p_c is the atmospheric pressure, Pa , M_t is the cumulative amount of gas diffusion, m^3/g , and M_∞ is the ultimate amount of gas diffusion, m^3/g .

According to eq 35 ~ eq 38, the diffusion coefficient during gas desorption meets eq 40.

$$D_p^{\text{ads}} = D_B \left[1 - \exp\left(-\frac{l}{\lambda}\right) \left(1 - \frac{M_\infty - M_t}{a} \right) \right] \quad (40)$$

Considering the adsorbing ability of the coal matrix, the effective diffusion coefficient will be revised as eq 41.

$$D_e^{\text{ads}} = \frac{D_p^{\text{ads}}}{\tau^2} \quad (41)$$

3.3. Relationship between the Effective Diffusion Coefficient and the Gas Desorption Effect. When the gas adsorption reaches equilibrium, the volumetric strain caused by the expansion of coal matrix meets eq 42.²¹

$$\varepsilon_0 = \frac{4a\rho RT \ln(1 + bp_0)}{9V_m E} \quad (42)$$

where ε_0 is the volumetric strain, ρ is the coal density, kg/m^3 , V_m is the molar volume, $22.4 \text{ L}/\text{mol}$, and E is the elastic modulus of the coal matrix, Pa .

According to the Langmuir isothermal adsorption equation, there is eq 43.

$$bp_0 = \frac{M_\infty}{a - M_\infty} \quad (43)$$

Substituting eq 43 into eq 42, then eq 44 is obtained.

$$\varepsilon_0 = \frac{4a\rho RT}{9V_m E} \ln\left(\frac{a}{a - M_\infty}\right) \quad (44)$$

The adsorbed deformation at the time of t is determined by eq 45.

$$\varepsilon_t = \frac{4a\rho RT}{9V_m E} \ln\left(\frac{a}{a - (M_\infty - M_t)}\right) \quad (45)$$

Associating eqs 44 and 45, we can get the relationship between the desorbed deformation and the gas desorption amount at the time of t , which is shown in eq 46.

$$\Delta\varepsilon = \varepsilon_0 - \varepsilon_t = \frac{4a\rho RT}{9V_m E} \ln\left(\frac{a - M_\infty}{a - (M_\infty - M_t)}\right) \quad (46)$$

During the gas desorption process, the coal matrix continues to shrink with an expanding pore volume. Therefore, the pore diameter can be expressed by eq 47.

$$l' = l(1 - \Delta\varepsilon)^{1/3} \quad (47)$$

The process of gas desorption can be regarded as a changeable process. According to the fundamental principles of thermodynamics,²² the relationship between temperature and gas diffusion amount can be obtained as shown in eq 48.

$$T(t) = T_1 \left(\frac{\gamma\eta}{\gamma\eta + \rho M_t} \right)^{k-1} \quad (48)$$

where T_1 is the temperature of adsorbed gas, K , ρ is the visual density of coal, kg/m^3 , γ is the porosity, m^3/m^3 , η is the content proportion of adsorbed gas, and k is a polytropic index, with a value in the range of 1.000463–1.004183.

Considering the gas desorption effect on the pore and temperature, the effective diffusion coefficient can be revised as shown in eq 49.

$$D_e^{\text{dsp}} = \frac{2k_B^{1.5} T(t)^{1.5} (1 - \exp(-\frac{\sqrt{2}\pi p d^2 l'})}{k_B T(t)}}{3\pi^{1.5} d^2 p m^{0.5} \tau^2} \quad (49)$$

3.4. Time-Dependent Model of Dynamic Diffusion Coefficient Considering Pore Structure, Gas Desorption Effect, and Adsorption Capacity of Coal Matrix. Substituting eqs 7, 11, and 40 into eq 41, the effective diffusion coefficient considering the adsorption capacity of the coal matrix can be obtained as shown in eq 50.

$$D_e^{\text{ads}} = \frac{2k_B^{1.5} T(t)^{1.5} \left[1 - \exp\left(-\frac{l}{\lambda}\right) \left(1 - \frac{M_\infty - M_t}{a} \right) \right]}{\left(\frac{l_c}{l}\right)^{2(D_t - 1)}} \quad (50)$$

Since the gas desorption effect is not considered, the pore diameter of l and the temperature of T in eq 50 can be regarded as constants. However, when the dynamic changes of l and T should be considered in the gas diffusion process, the effective diffusion coefficient considering adsorption capacity of the coal matrix and gas desorption effect can be obtained by substituting eqs 47 and 48 into eq 50 and expressed in eq 51.

$$D_e^{\text{comp}} = \frac{2k_p^{1.5} T(t)^{1.5}}{3\pi^{1.5} d^2 p m^{0.5}} \left[1 - \exp\left(-\frac{l'}{\lambda}\right) \left(1 - \frac{M_{\infty} - M_t}{a}\right) \right] \left(\frac{L_c}{l'}\right)^{2(D_t-1)} \quad (51)$$

Substituting the parameter D_e in eq 21 with D_e^{comp} , the time-dependent model of dynamic diffusion coefficient comprehensively considering pore structure, gas desorption effect, and adsorption capacity of coal matrix can be obtained as shown in eq 52.

$$D_{ce}^{\text{comp}} = \frac{\int_{l_{\min}}^{l_{\max}} \frac{D_e^{\text{comp}}(l)}{L_c^2} \exp\left(-\frac{D_e^{\text{comp}}(l)}{L_c^2} t\right) l'^{1-D_F} dl}{\int_{l_{\min}}^{l_{\max}} \exp\left(-\frac{D_e^{\text{comp}}(l)}{L_c^2} t\right) l'^{1-D_F} dl} \quad (52)$$

As concluded, the time-dependent model of dynamic diffusion coefficient comprehensively considering pore structure, gas desorption effect, and adsorption capacity of coal matrix can be obtained by combining eqs 47, 48, 51, and 52.

4. INFLUENCING FACTORS OF THE EFFECTIVE DIFFUSION COEFFICIENT IN GAS-CONTAINING COAL

4.1. Effect of Pore Structure on the Effective Diffusion Coefficient. According to the previously reported results,^{23,24} parameters of numerical calculation were determined and are listed in Table 1. Equation 22 was then used to calculate the effective diffusion coefficient in gas-containing coal with different pore structures. The calculation results are listed in Figure 2.

Table 1. Calculation Parameters of the Model

parameters	values	parameters	values
l_{\min}	1×10^{-9} m	a	30.89 mL/g
l_{\max}	1×10^{-6} m	b	0.9434 MPa ⁻¹
L_c	1×10^{-3} m	p_0	0.5 MPa
T	298 K	p_c	0.1 MPa

As shown in Figure 2, the effective diffusion coefficient decays dramatically first and then slowly with the increasing time, which is consistent with previous reports.^{6–11} The effective diffusion coefficient decreases with the increase in the

fractal dimensions D_F and D_t . The effective diffusion coefficient obtained by increasing D_F from 2.9 to 1.0 is approximately equal to that by increasing D_t from 1.5 to 1.22, indicating that the effect of D_t would be even more obvious. The specific surface areas of pores in coal matrix are mainly dominated by the micropores with diameter less than 10 nm, followed by the mesopores with diameter ranging from 10 to 100 nm and the macropores with diameter above 100 nm.²⁵ In the early stage of diffusion, the diffusion coefficient in macropores is large but with a poor gas adsorption capacity. The gas content in the macropores decreases rapidly in a short time, resulting in the rapid transition of dominant diffusion from macropores to micropores and mesopores. Therefore, the diffusion coefficient exhibits rapid attenuation in the early stage of diffusion. In the later stage of diffusion, gas diffusion is mainly dominated by the micropores for the slow decrease of the proportion of surface area in macropores with increasing diameter. Then, the attenuation rate of the effective diffusion coefficient slows down in the later stage of diffusion. The fractal dimension D_F is negatively correlated with the proportion of surface area in macropores.²⁶ Similarly, the fractal dimension D_t is negatively correlated to the connectivity of pores. As the proportion of surface area in macropores and the connectivity of pores increase, the fractal dimensions D_F and D_t will decrease, while the effective diffusion coefficient will increase.

4.2. Effect of Adsorption Capacity of Coal Matrix on the Effective Diffusion Coefficient. According to the parameters listed in Table 1, eqs 22 and 41 were employed to calculate the effective diffusion coefficient considering the adsorption capacity of the coal matrix under the conditions of $D_F = 2.9$ and $D_t = 1.5$. The effective diffusion coefficient without considering the adsorption capacity of coal matrix is also calculated. The calculation results are shown in Figure 3.

As shown in Figure 3, the effective diffusion coefficient considering the adsorption capacity of the coal matrix significantly increased by 30–120% compared with that without considering the adsorption capacity, while the difference value between them gradually decreases with the increasing time. According to the surface physical chemistry theory and the kinetic theory of gas molecules, as the gas adsorption capacity increases, the adsorption vacancy on the pore wall increases. The number of collisions between free gas and the pore wall will be reduced and the diffusion time in unit distance will decrease, resulting in the decrease of the diffusion

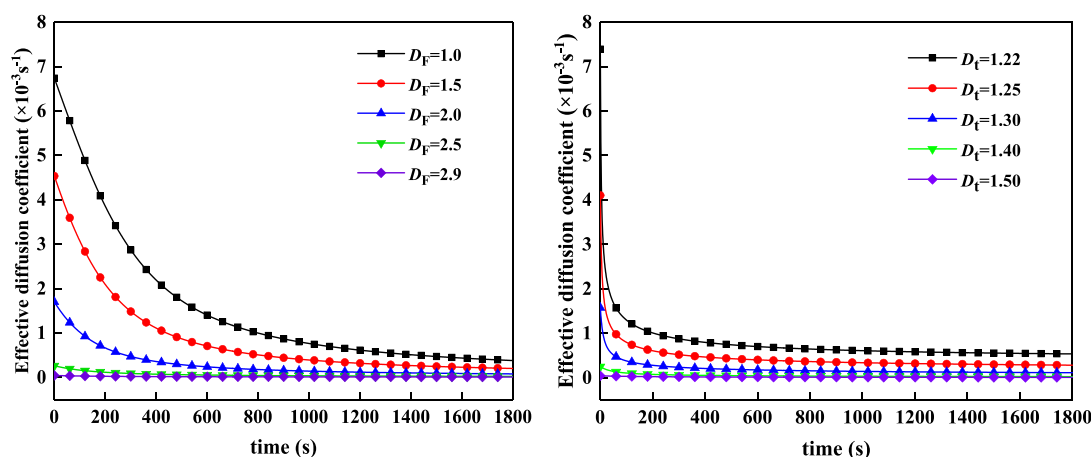


Figure 2. Effect of D_F ($D_t = 1.5$) and D_t ($D_F = 2.9$) on effective diffusion coefficient.

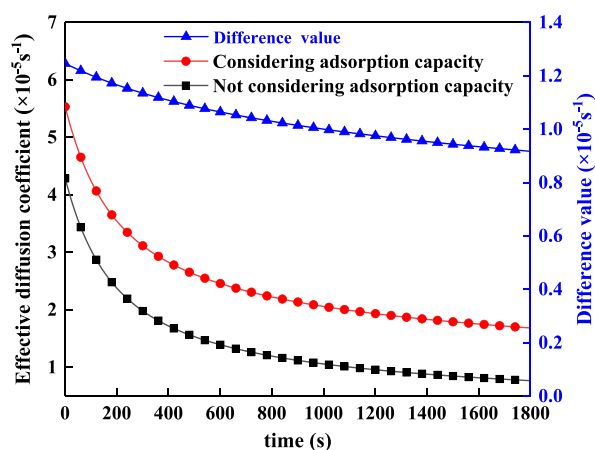


Figure 3. Effect of the adsorption capacity of the coal matrix on effective diffusion coefficient.

resistance and the increase of effective diffusion coefficient.²⁷ However, the effect of adsorption capacity on the effective diffusion coefficient will decrease gradually with the continuous decrease in adsorbed sites on the pore wall during the gas desorption. Finally, the difference value between the two conditions considering the adsorbing ability of the coal matrix decreased gradually with the increasing diffusion time.

4.3. Effect of Gas Desorption Effect of Coal Matrix on the Effective Diffusion Coefficient. According to the parameters listed in Table 1, eqs 41 and 49 are employed to calculate the effective diffusion coefficient considering the desorption effect under the conditions of $D_F = 2.9$ and $D_t = 1.5$. The effective diffusion coefficient without considering the desorption effect is also calculated. The calculation results are listed in Figure 4.

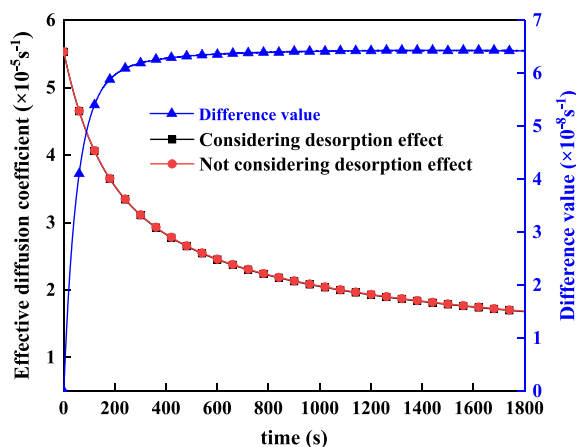


Figure 4. Effect of gas desorption on the effective diffusion coefficient.

As can be seen from Figure 4, the effective diffusion coefficient considering the desorption effect is slightly less with 3 orders of magnitude than that without considering the desorption effect. Also, the difference value between them increases rapidly at first and then maintains a smooth upward trend with increasing time. The results indicate that the desorption effect has minimal influence on the effective diffusion coefficient. This could be attributed to that the coal matrix deformation and temperature change caused by gas desorption is relatively small.^{21,22} However, the cumulative

pore deformation and temperature change increase with an increase in diffusion time. As a result, the effect of gas desorption and the difference value between the two effective diffusion coefficients gradually increase with time.

5. RESULTS AND DISCUSSION

5.1. Experimental Results. Coal samples from the Hebi No.6 coal mine were ground to particles with different sizes. A proximate analysis of coal was conducted on 20 g of coal samples with particle size in the range of 0.74–0.25 mm according to “Proximate analysis of coal (GB/T 212–2008)”. Results showed that moisture content was 1.02%, ash content was 9.50%, and volatile content was 15.79% based on an air-dried coal sample. Four hundred grams of coal samples with particle size in range of 0.2–0.25 mm were employed to measure the adsorption constants according to the experimental method of high-pressure isothermal adsorption to coal (GB/T 19560–2008). The adsorption constants a and b were measured to be 29 mL/g and 1.05 MPa^{-1} , respectively. Six hundred grams of coal samples with particle size in range of 0.25–0.50 mm was evenly divided into four groups for gas desorption experiments. The experimental system is shown in Figure 5. In a typical procedure, the gas pressure in the coal

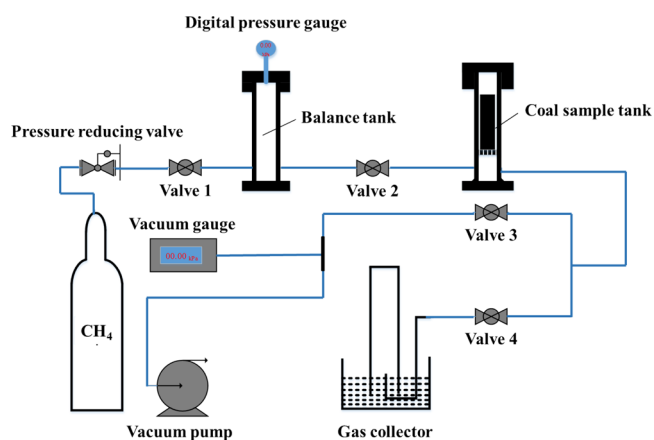


Figure 5. Diagram of the experimental system.

sample tank and balance tank was first vacuumed to below 10 Pa by the vacuum pump. Then, methane was repeatedly inflated into the coal sample tank from the gas cylinder through the balance tank until the expected balance pressure was reached. Finally, the gas desorption process was recorded by the drainage method using a gas gathering device. The measured scope of the gas pressure gauge is 10 MPa with a measurement accuracy of 0.01 MPa. The range of the vacuum gauge is 0.01–10 kPa with a measurement accuracy of 0.01 kPa. The maximum measurement of the gas gathering device is 800 mL with a measurement accuracy of 5 mL. CH_4 with a purity of 99.99% was employed as the experimental gas. During the experiment process, the indoor temperature should always be maintained at $25 \pm 2 \text{ }^\circ\text{C}$ by air-conditioning.

Methane is the main constituent of gas in a coal mine, and the gas pressure is usually below 2 MPa in a coal seam. Therefore, the adsorption equilibrium pressure of CH_4 for gas desorption experiments was set as 0.5, 1.0, 1.5, and 2 MPa. The experimental results are shown as the scatter in Figure 6. In order to calculate the effective diffusion coefficient, the experimental data were fitted using the eq 53 previously

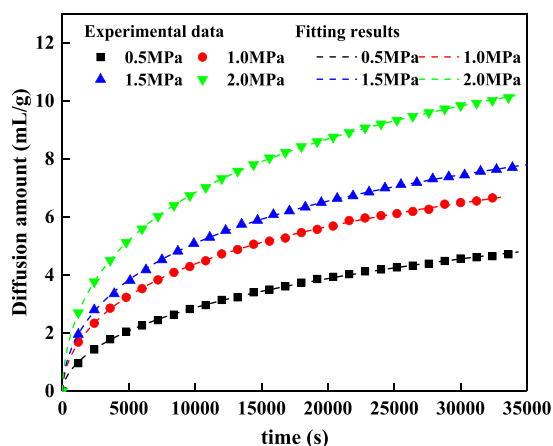


Figure 6. Experimental data and fitting results of the diffusion amount.

reported by the author in the literature²⁸ and the fitting results are listed in Table 2. The results indicated that the correlation

Table 2. Fitting Results by eq 50.

p_0 (MPa)	M_∞ (mL/g)	ζ ($\times 10^{-3}$)	κ	R^2 (%)
0.5	13.8	1.375	0.57	99.99
1.0	14.4	2.302	0.57	99.95
1.5	16.0	2.457	0.57	99.97
2.0	19.7	2.797	0.57	99.98

coefficient R^2 was more than 99.95% under equilibrium pressures of 0.5–2 MPa. It was indicated that the fitting results exhibited perfect consistency with the experimental data, which could be intuitively observed from the curves shown in Figure 6.

$$M_t = M_\infty \frac{\zeta t^\kappa}{1 + \zeta t^\kappa} \quad (53)$$

where ζ , κ were related to the effective diffusion coefficient, and $0 < \kappa < 1$.

5.2. Model Verification. According to the parameters in Table 2, eq 21 was used to calculate the effective diffusion coefficient in gas-containing coal. The calculation results are shown as scatters in Figure 7. The time-dependent model of dynamic diffusion coefficient expressed in eq 52 was used to fit

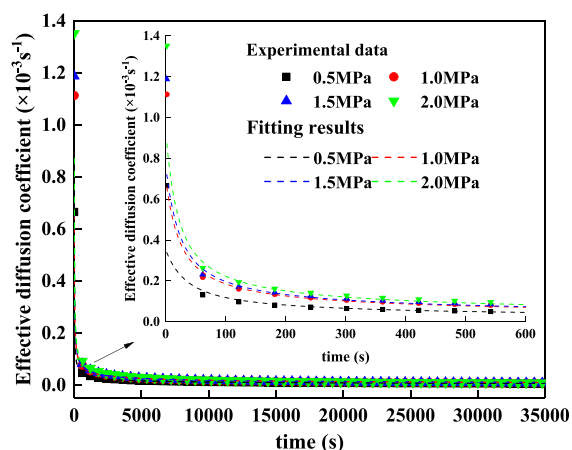


Figure 7. Effective diffusion coefficient during gas desorption.

the experimental data by iterative operation. First, the values of the key variables were determined as follows. The minimum pore diameter of l_{\min} and maximum pore diameter of l_{\max} were set as 10^{-9} and 10^{-6} m, respectively. The effective diffusion distance of L_e ranged from 0.1 to 0.5 mm. The fractal dimensions of D_F and D_t were within the ranges of 2.0–3.0 and 1.1–1.5, respectively. Then, the fitting results were iteratively calculated based on the effective diffusion distance step size of 0.01 mm, pore diameter step size of 10^{-9} mm, and fractal dimension step size of 0.01. When the correlation coefficient between the fitting results and the experimental data was in the given confidence of 96%, the key variable values and R^2 would be output. Finally, the output values with the best correlation coefficient were selected as the calculation results and are shown in Table 3. The results showed that the correlation

Table 3. Calculation Results by the Model

parameters	equilibrium pressure of gas adsorption (p_0 , MPa)			
	0.5	1.0	1.5	2.0
l_{\min} (10^{-9} m)	1.0	1.0	1.0	1.0
l_{\max} (10^{-6} m)	1.0	1.0	1.0	1.0
L_e (10^{-4})	3.5	3.5	3.5	3.5
D_F	2.72	2.67	2.65	2.64
D_t	1.64	1.61	1.61	1.60
R^2 (%)	96.06	96.73	96.81	96.86

coefficient R^2 between the fitting results and the experimental data was more than 96.00%, indicating the perfect accuracy and good consistence of the established model.

As mentioned above in the section 4, the adsorption capacity of the coal matrix has a greater influence than the gas desorption effect on the effective diffusion coefficient. Therefore, the more the gas content in the coal, the larger the effective diffusion coefficient. As shown in Table 3, the fractal dimensions D_F and D_t slightly decrease with the increase in gas equilibrium pressure under the same conditions of pore distribution and effective diffusion distance. In order to get eq 49, it is assumed that gas diffusion was independent of each pore. In fact, the pores are connected with each other in coal matrix. Therefore, the fractal dimensions D_F and D_t in eq 5 represent not only the surface distribution of pores but also the gas content distribution of pores. As the adsorption equilibrium pressure of gas increases, the gas concentration in larger pores drops rapidly for the increased effective diffusion coefficient and rapid diffusion speed. Then, gas will flow into large pores from the connecting small pores driven by concentration gradient. It is equivalent to the increase in the surface area of large pores and the decrease in that of small pores, resulting in the decrease of the fractal dimensions D_F and D_t .

6. CONCLUSIONS

In this study, a time-dependent model of diffusion coefficient considering the comprehensive effects of pores, coal matrix, and gas was established according to the fractal theory, the surface physical chemistry theory, and the diffusion theory in porous media. The effects of pore structure, coal matrix adsorption capacity, and gas desorption effect on the effective diffusion coefficient were discussed in detail. The numerical computation and experimental verification were then carried out to validate the established model. Results showed that the diffusion coefficient of gas desorption in gas-containing coal

exhibited dynamic characteristics. The dynamic change of effective diffusion coefficient was essentially attributed to the comprehensive effects of the gradual decrease of dominant diffusion pores, the enhancement of coal matrix adsorption capacity, and the pore deformation and temperature change caused by gas desorption. Among the influence factors of effective diffusion coefficient, the pore structure plays a leading role, followed by the adsorption capacity of the coal matrix, and the gas desorption effect was the weakest. The fitting results according to the proposed time-dependent model agreed well with the experimental data, with a correlation coefficient above 96.0%, indicating the perfect accuracy and good consistence of the established model. The greater the adsorption equilibrium gas pressure, the greater the diffusion coefficient and the smaller the fractal dimension.

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Notes

The authors declare no competing financial interest.

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