Investigation of adsorption-diffusion behaviors of elementary O2, CO2 and N2 in coal particles: Influence from temperature

Wei Liu (liuwei7230@cumtb.edu.cn)
China University of Mining and Technology Beijing Campus

Minghui Qi
China University of Mining and Technology - Beijing

Xiangyu Chu
China University of Mining and Technology - Beijing

Shiyang Peng
China University of Mining and Technology - Beijing

Dongyang Han
China University of Mining and Technology - Beijing

Research Article

Keywords: Temperature, Free gas density gradient diffusion, Adsorption constants, Adsorption capacity, Microchannel diffusion coefficient

Posted Date: March 28th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2599080/v1

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Adsorption-diffusion behaviors of gases (i.e., O₂, CO₂ and N₂) in coal are directly related to the coal spontaneous combustion (CSC), in which the temperature is the key factor affecting the gas migration process in coal. In this work, isothermal adsorption experiments of O₂, CO₂ and N₂ under different temperatures were carried out on bituminous coal and anthracite coal samples at 0.5 MPa, respectively. Based on the free gas density gradient diffusion (FDGD) model, the microchannel diffusion coefficients of different gases at different temperatures were calculated, and the effects from temperature were quantitatively evaluated. The results acquired from the experiment and simulation show that (i) the adsorption capacity of these three gases decreases as the temperature increases, and the adsorption capacity at the same temperature satisfies CO₂ > O₂ > N₂; (ii) the FDGD model is verified to be still applicable at high temperatures, indicating that the adsorption-diffusion behavior of O₂, CO₂ and N₂ in coal particles at different temperatures is still consistent with the free gas density gradient diffusion; (iii) the microchannel diffusion coefficient $K_m$ of the three gases gradually increases when the temperature goes up. The present work contributes to the understanding of the gases migration process in the development of CSC.

1 Introduction

As coal mining continues to develop deeper underground, the strata are getting warmer and warmer, resulting in the coal spontaneous combustion (CSC) in longwall gobs becoming increasingly prominent (Wei et al. 2020; Chao et al. 2022). Inert gas injection into the gob is an important means to prevent the CSC (Zheng et al. 2020; Liu et al. 2022), while the temperature significantly affects the behaviors of adsorption and diffusion of gases in coal after the inert gas was injected (Zhang et al. 2011). Therefore, the effect of temperature on the gases migration in coal needs to be quantitatively evaluated to investigate the fire-prevention performance of inert gas (Liu et al. 2022).

The temperature varies considerably from mine to mine depending on the mining depth and climatic conditions (Saghaif et al. 2007; Zhao et al. 2022), and it is one of the most vital factors impressing the gas adsorption capacity (Guan et al. 2018). The effect of temperature on gases adsorption of coal has been studied by scholars using different research methods. Tang et al. (Tang et al. 2015) found that the Langmuir adsorption constant $a$ of methane didn't vary significantly with temperature, but the Langmuir adsorption constant $b$ linearly declines with the rising of temperature. Wang et al. (Wang et al. 2015) carried out isothermal adsorption experiments on methane to find that the Langmuir constant $a$ depended on temperature, which increases linearly with the decline of temperature, while Langmuir constant $b$ increases exponentially with the reciprocal rising of temperature. Skoczylas et al. (Skoczylas et al. 2020) found that the values of the $a$ parameter of the Langmuir isotherm for CH₄ decrease linearly with rising temperature, which declines strongly for CO₂ over temperature; the values of the $b$ parameter for both CH₄ and CO₂ declines exponentially as the temperature increases. Other studies suggested that the adsorption of CO₂ and CH₄ by coal was temperature dependent, and the results indicated that the adsorption capacity for CO₂ and CH₄ decreased with increasing temperature (Chamire et al. 2010; Pan et al. 2012; Perera et al. 2012; Yu et al. 2022). It can be seen that the visible effect of temperature on the adsorption constants of coal is not yet uniformly recognized and needs to be further investigated.

Currently, some studies have been done previously on the variation pattern of the diffusion coefficient for coal over temperature (Liu et al. 2020a; An et al. 2022). However, different diffusion models lead to large differences in the magnitude of the diffusion coefficients, so the impact of temperature on the gas diffusion coefficient is not clear (Meng and Li 2016; Yang et al. 2018; Teixeira Palla Braga and Kudasik 2019; Zhao et al. 2019; Liu et al. 2020a; Tun and Chen 2021; Wang et al. 2021). Long et al. (Long et al. 2021) studied the adsorption and diffusion characteristics of CH₄, CO₂ and N₂ in coal pores by using Monte Carlo and molecular dynamics methods, the strength order for the diffusion properties of these three gases in the pore was CH₄ > N₂ > CO₂. Norbert et al. (Saghaif et al. 2007) showed that the effective diffusivity was strongly dependent on temperature, the rise of temperature pushed up the value of the effective diffusivity for CH₄ and CO₂. Delphine et al. (Chamire et al. 2010) set the temperature range from 283.15K to 333.15K to study the diffusion kinetics of CO₂ and CH₄, the results indicated that the diffusion coefficients estimated from experimental data were enlarged with rising temperature. Dai (Dai 2016) studied the diffusion pattern of methane gas in coal particles, the results showed that the diffusion coefficient decreased with the elevated temperature in a short time, and when the time exceeds 10 minutes, the variation of temperature has little effect on the diffusion coefficient. It can be seen that researchers have done a lot of investigations on the diffusion behavior of CO₂ and CH₄ in coal, but rarely on the diffusion dynamics of O₂ in coal. However, O₂ is involved in the whole process of CSC (Arisoy and Beamish 2015), and it is essential to study the migration behavior of O₂ in coal.

In this work, the isothermal adsorption experiments of different gases (O₂, CO₂ and N₂) at different temperature conditions were carried out, and the Langmuir adsorption isotherm was applied to investigate the variation of adsorption constants over temperature. The free gas density gradient diffusion theoretical model was used to simulate and invert the microchannel diffusion coefficient of gas at different temperatures. The aim is to quantitatively evaluate the effect of temperature on the adsorption and diffusion characteristics of coal particles.

2 Establishment Of The Density Gradient Model

2.1 Mathematical model

The gas that exists in the interior of the coal particles is composed of adsorbed state and free state, and the amount of the gas in the coal particles is described by the Langmuir equation as:

$$C = \frac{abp}{1 + bp} + Dkp$$
where \( C \) is the gas amount per unit quality of coal particle, \( \text{cm}^3/\text{g} \); \( a \) is the ultimate adsorption capacity, \( \text{cm}^3/\text{g} \); \( b \) is the adsorption constant, \( \text{Mpa}^{-1} \); \( D \) is the coefficient, \( \text{m}^2/(\text{g\cdot MPa}) \); \( k \) is the porosity of the coal; \( p \) is the pressure of the gas, MPa.

\[
D = \frac{T_0}{\rho_s p_0 T}
\]

where \( T_0 \) is the standard state temperature, taken as 273.15 K; \( T \) is the thermodynamic temperature, \( K, T = t + 273 \); \( \rho_s \) is the apparent density of coal, \( g/cm^3 \); \( p_0 \) is the standard atmospheric pressure and the value is 0.101325 MPa.

Our previous paper proposed a model in which the mass flow rate of gas in the coal matrix was proportional to the free gas density gradient (FGDG) (Liu et al. 2018, 2021b, a). The following is the mathematical equation of the FGDG diffusion within coal particles:

\[
J_m = -D_m \frac{M_{ol}}{R_s T} \frac{dp}{dr} = -K_m \frac{dp}{dr}
\]

where \( J_m \) is the gas mass flux, \( g/(m^2 \cdot s) \); \( D_m \) is the diffusion coefficient of free gas in microchannels, \( m^2/s \); \( R_s \) is the universal gas constant, 8.314 \( J/(mol K) \); \( M_{ol} \) is the molar mass of the free gas, \( g/mol \); \( r \) is the radius of the spherical coal particle, \( m \); \( K_m \) is defined as the microchannel diffusion coefficient, \( g/(MPa \cdot m \cdot s) \).

Assuming that the gas flow in the coal particle is spherical flow, and the spherical shell with thickness \( dr \) in the coal particle is regarded as the research object, the gas transportation and immigration process follows the law of conservation of mass, the consecutiveness equation of gas flow in the spherical coal particle is derived as

\[
\frac{\partial}{\partial t} \left( \frac{\partial p}{\partial t} + \frac{T_0}{R_s \rho_s T} \frac{\partial p}{\partial r} \right) = \frac{K_m}{\rho_g} \frac{1}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial p}{\partial r} \right) \right)
\]

where \( \rho_g \) is the normative density of the gas, \( g/cm^3 \); \( r \) is the semidiameter of the spherical shell, \( cm \); \( R_s \) is the gas constant, \( J/(g \cdot K) \).

The isothermal adsorption experiment on gases of coal particles was constant volume adsorption. When the gas required for the initial pressure was filled into the sampling tube and the solenoid valve was closed, the coal particles started to adsorb gas, the gas content of the free body in the sampling tube was reduced and the pressure decreased. It can be obtained that the initial and fringe conditions of the model are as follows:

\[
\begin{aligned}
& p = 0, \tau = 0 \\
& \frac{dp}{dr} = 0, r = 0 \\
& p = p_w = p_{w0} = \frac{R_s T}{V_s} \cdot \frac{3 G}{R_s T} \int_0^R K_m \frac{dp}{dr} dt, r = R
\end{aligned}
\]

where \( p_w \) is the gas pressure on the external superficial of coal particle, \( MPa \); \( p_{w0} \) is the incipient pressure of gas in the sample tube, \( MPa \); \( V_s \) is the free volume in the sample tube, \( \text{cm}^3 \); \( G \) is the quality of coal sample, \( g \).

2.2 Finite difference model

The spherical coal particle was taken apart to \( N \) nodes along the semidiameter of the sphere. The closer it is to the superficial of the coal particle, the more drastic the variation in gas pressure and content, and the equal ratio of node spacing decreased. The centre point of two contiguous nodes was regarded as a concentric sphere, and the spherical coal particle was split into three parts. Then the \( N \) spherical shells including nodes, a solid sphere centered on node 0 and the external surface of the spherical coal particle are obtained, the node partition of spherical coal particle is shown in the Fig. 1.

For a spherical shell inside coal particle, the differential equation for the gas flow is:

\[
K_m \cdot \left( \frac{\frac{\tau_{m+1} - \tau_m}{2}}{\tau_{m+1} - \tau_m} \right)^2 \cdot 4\pi \cdot \left( \frac{\tau_{m+1} + \tau_m}{2} \right)^2 - K_m \cdot \left( \frac{\frac{\tau_{m+1} - \tau_m}{2}}{\tau_{m+1} - \tau_m} \right)^2 \cdot 4\pi \cdot \left( \frac{\tau_{m+1} + \tau_m}{2} \right)^2 = 4 \pi \left( \frac{\tau_{m+1} + \tau_m}{2} \right)^3 - 4 \pi \left( \frac{\tau_{m+1} + \tau_m}{2} \right)^3 \cdot \left( \frac{\frac{\tau_{m+1} - \tau_m}{2}}{\frac{\tau_{m+1} - \tau_m}{2}} \right)^2 + \left( \frac{a b \rho_s p_0}{1 + \frac{\tau_{m+1} + \tau_m}{2}} \right) + \left( n = 1, 2, \ldots, N; m = 1, 2, \ldots \right)
\]

(6)

where the superscript \( n \) of the pressure \( p \) represents the time node number, and the subordinate \( m \) represents the node number of the shell; \( \Delta t \) is the nth time step.
For the solid ball centered at node 0, there is only inflow of gas without outflow during the adsorption procedure. Thus, the equation of the change of internal gas content is as follows:

\[
K_m \left( \frac{P_n - P_{n-1}}{2} + \frac{P_{n-1} - P_0}{2} \right) \right)^2 = \frac{1}{3} \left( \frac{r_1}{2} \right)^3 \left[ \frac{ab \rho_c \rho_s}{\left( 1 + b \frac{\rho_0}{\rho_n} \right)^2} + Dk \rho_c \rho_s \right] \frac{P_0 - P_{n-1}}{\Delta t_n}
\]

The pressure on the external surface of coal particles is:

\[
P_n^0 = P_w = P_{w0} - \frac{R_g T G}{V_2} \cdot Q_{n-1}, \quad r = R
\]

Cumulative gas adsorption mass of regular spherical coal particle per unit mass:

\[
Q_z = \frac{3}{\rho_c 4\pi R^4} \int_0^t 4\pi R^2 K_m \frac{\partial P_w}{\partial r} dt = \frac{3}{\rho_c R} \int_0^t K_m \frac{\partial P_w}{\partial r} dt
\]

### 3 Experiments

#### 3.1 Experimental coal samples

In this experiment, the coal samples from Yangquanwu Coal Mine(YW) and Silaogou Coal Mine(SLG) were selected for isothermal adsorption experiments. The coal samples were smashed by a coal pulverizer, and the samples with a particle measurement of 60–80 meshes were screened out. The industrial analysis of coal samples is displayed in Table.1.

<table>
<thead>
<tr>
<th>Coal samples</th>
<th>Ash content $A_{ad}$(%)</th>
<th>Fixed carbon $F_C$(%)</th>
<th>Moisture content $M_{ad}$(%)</th>
<th>Volatile content $V_{ad}$(%)</th>
<th>Apparent coal density $\rho_c$(g/m³)</th>
<th>Porosity $n_0$(%)</th>
<th>Coal types</th>
</tr>
</thead>
<tbody>
<tr>
<td>YW</td>
<td>14.210</td>
<td>76.190</td>
<td>0.750</td>
<td>8.850</td>
<td>1449000</td>
<td>8.783</td>
<td>Anthracite</td>
</tr>
<tr>
<td>SLG</td>
<td>8.881</td>
<td>65.841</td>
<td>0.681</td>
<td>22.598</td>
<td>1490000</td>
<td>5.521</td>
<td>Bituminous</td>
</tr>
</tbody>
</table>

#### 3.2 Experimental system and procedures

The H-sorb 2600 adsorber was used in the gas adsorption experiments, as shown in Fig. 2. The instrument was composed of a gas cylinder zone, adsorption zone, and computer-controlled zone, with the temperature control accuracy of ± 0.1 °C. The purity of $O_2$ and $N_2$ used in the experiment reached 99.99% and the purity of $CO_2$ was 99.999%.

Isothermal adsorption experiments of coal particles on $O_2$, $CO_2$ and $N_2$ were divided into single-point pressure adsorption experiments and step pressure adsorption experiments. The experimental procedure consisted of two main parts: drying of coal samples and isothermal adsorption experiments. First, about 6.5 g of coal was weighed out with an electronic balance, and then coal was loaded into the sample tube with a funnel. The iron ingots and sponges were clamped into the sample tube with tweezers to fix the coal powder. The purpose was to prevent the accuracy of the instrument from being affected by the spillage of coal particles. The coal sample tube was connected to the sample processing area of the instrument, and then the parameters were set, and then the coal sample tube was dried in a vacuum environment at 105°C for 4 hours. Subsequently, the isothermal adsorption experiment was performed, which was divided into three main steps: calibration of the free chamber volume of the coal sample tube, introduction of adsorption gas and determination of the isothermal adsorption line. The pressure was set to 0.5 Mpa for the single point pressure adsorption experiments, and the step adsorption experiments were carried out respectively at 0.57143 MPa, 0.66667 MPa, 0.8 MPa, 1.0 MPa, 1.33333 MPa, 2 MPa and 4 Mpa. The experimental temperatures were 20°C, 30°C, 40°C, 50°C, and 60°C, respectively.

### 4 Experimental Results

#### 4.1 Results of adsorption capacity

Figure 3 illustrates the results of single-point isothermal adsorption experiments for different gases at different temperature conditions. The cumulative adsorption of $O_2$, $CO_2$ and $N_2$ on YW and SLG coal samples decreased gradually with the increase of temperature from 20°C to 60°C.
adsorption amounts of different gases under the same temperature conditions for both YW and SLG coal samples satisfied CO₂ > O₂ > N₂. It can be seen that the cumulative adsorption of anthracite (YW) is larger than that of bituminous coal (SLG) for each gas at the same temperature.

### 4.2 Calculation of adsorption constant

The Langmuir adsorption isotherm, also known as the single molecule adsorption theory, the equation as follows:

\[
Q = \frac{abp}{1 + bp}
\]

where \(Q\) is the gas adsorption capacity of coal when adsorption reaches equilibrium, cm³/g.

Under medium and low pressure conditions, the adsorption of O₂, CO₂ and N₂ by dried coal samples is in accordance with the Langmuir monolayer adsorption theory, according to the Langmuir single molecular layer adsorption isothermal formula, the reciprocal of both sides of the formula is:

\[
\frac{1}{Q} = \frac{1}{ab} \cdot \frac{1}{p} + \frac{1}{a}
\]

A linear relationship was fitted using data on the step adsorption pressure and adsorption capacity of a single substance gas with \(1/Q\) as the dependent variable and \(1/p\) as the independent variable. The slope of the relationship is \(1/ab\) and the intercept is \(1/a\), and thus the adsorption constants \(a\) and \(b\) can be calculated. Figure 4 indicates that the reciprocal of the gas adsorption capacity of coal samples is linearly related to the reciprocal of the pressure, and the fitting degree is more than 0.98, as a result, the relevant calculation of the isothermal adsorption experiment using the Langmuir equation is reasonable. The adsorption constants \(a\) and \(b\) were calculated as shown in Table 2.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Adsorption constant (a) (cm³/g) and (b) (MPa⁻¹) values of coal sample for individual gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YW-O₂</td>
</tr>
<tr>
<td>Tempe</td>
<td>a</td>
</tr>
<tr>
<td>ature</td>
<td></td>
</tr>
<tr>
<td>20 °C</td>
<td>33.113</td>
</tr>
<tr>
<td>30 °C</td>
<td>32.154</td>
</tr>
<tr>
<td>40 °C</td>
<td>31.746</td>
</tr>
<tr>
<td>50 °C</td>
<td>31.056</td>
</tr>
<tr>
<td>60 °C</td>
<td>32.573</td>
</tr>
</tbody>
</table>

### 4.3 Effect of temperature on the adsorption constant

The adsorption constant \(a\) is Langmuir volume, which represents the maximum adsorption capacity of coal particles to gas, the magnitude of the \(a\) value can be used to reflect the performance of coal adsorption (Singh and Javadpour, 2016; Ye et al., 2016; Zhao and Tang, 2002), which satisfies the equation:

\[
a = \frac{V_mS}{\delta N_a}
\]

where \(S\) is the specific superficial area of the coal, cm²/g; \(N_a\) is Avogadro's constant, 6.022×10²³ mol⁻¹; \(\delta\) is the area of one gas molecule in the adsorption layer, cm²; \(V_m\) is the molar volume in the standard state, 22.4 L/mol.

It can be seen from Eq. (12) that the parameters \(N_a\), \(\delta\) and \(V_m\) are constants when the adsorbed gases are the same, so the value of \(a\) is determined only by the size of the specific surface area \(S\) of the coal, and is independent of the temperature. Figure 5 shows the variation curve of the adsorption constant \(a\) with temperature. It can be seen that the value of \(a\) remains essentially constant with increasing temperature. The slight fluctuation of \(a\) value may be also due to the trace changes of parameters such as pressure of coal particles under experimental conditions. Furthermore, the adsorption constant \(a\) of the coal sample was the largest for CO₂, followed by O₂ and finally N₂, indicating that the coal particles had the strongest adsorption capacity for CO₂ and the weakest adsorption capacity for N₂.

The adsorption constant \(b\) is the proportion of the adsorption rate constant to the desorption rate constant, its value is related to the properties of coal and gas, and represents the strength of the coal's ability to adsorb gas, which satisfies the following equation (Shi, 2015):
where \( k_2 \) is the adsorption rate constant, \( \text{mol/(s\cdot MPa)} \); \( k_1 \) is the desorption rate constant, \( \text{mol/s} \).

Based on the adsorption kinetics, when the adsorption reaches equilibrium, the adsorption proportion is equivalent to the desorption proportion, yielding an adsorption constant \( b \) that satisfies the relation formula (Shi, 2015):

\[
b = \frac{k_2}{k_1}
\]

In above equation, the temperature is variable, other parameters are constants. Let \( c_1 = c\tau_0/a, c_2 = E/R, c_3 = 2\pi kMRT \), deforming the \( b \)-value formula into:

\[
b = \frac{c_1 e^{\frac{c_2}{T}}}{\sqrt{c_3 T}}
\]

The experimental results were fitted according to Eq. (15), and the results are shown in Fig. 6. It can be seen that the \( b \) decreases with increasing temperature, which proves that the ratio of adsorption rate to desorption rate of coal decreases with increasing temperature. The fitting coefficients exceed 0.96, and thus the \( b \) varies with temperature in accordance with the negative exponential relationships. The higher the temperature, the more active the gas molecules are, the less they are adsorbed by the coal particles, and the fewer molecules reach the coal surface per unit time, so the adsorption rate constant \( (k_2) \) is smaller (Pillalamarry et al. 2011). However, the desorption rate constant \( (k_1) \) is positively related to temperature. Because the activation energy required for desorption is also certain, the kinetic energy of gas molecules is enhanced when the temperature increases, which is more favorable for moving to free space. The more molecules are detached from the surface of coal particles per unit time, the shorter the time to reach adsorption equilibrium, and the shorter the residence time of the gas in the coal exterior and porous structure, resulting in a larger the \( k_1 \). Therefore, the \( b \) decreases with the increase in temperature, i.e., the high temperature should suppress the physical adsorption properties of gases in coal, resulting in the decrease in the adsorption capacity of gases in coal (Sakurovs et al. 2008; Pini et al. 2010; Wang et al. 2017).

5 Model Validation And Discussion

5.1 Inversion of the microchannel diffusion coefficients

In our previous articles, the numerical simulation software of coal particle gas flow had been developed to slove the FDDG model (Liu et al. 2018, 2021b, a). The simulated adsorption curves were compared with the experimental adsorption data to invert the microchannel diffusion coefficients \( K_m \), and the inversion process is described in our previous articles (Liu et al. 2020c, b). When the simulated adsorption curves matched well with the experimental adsorption curves, the values of the \( K_m \) of different gases at different temperatures were then determined, as shown in Fig. 7. It can be seen that the simulated curves of each coal sample for different gases at different temperatures are in good agreement with the experimental data in both conventional and logarithmic coordinates, so the simulated data can better reflect the whole experimental process of the gas adsorption. This indicates that the gas migraion model based on the free gas density gradient diffusion can better describe the adsorption-diffusion behaviors of elementary \( O_2 \), \( N_2 \) and \( CO_2 \) in coal particles at different temperature conditions.

5.2 Effect of temperature on migration behaviors

By comparing and analyzing the simulation and experimental results by the above inversion method, we obtained the \( K_m \) for \( O_2 \), \( CO_2 \) and \( N_2 \) at different temperatures in Table 3. Figure 8 further shows the variation curves of the \( K_m \) with temperature rising for different gases. As the temperature increases, for both YW and SLG coal samples, the \( K_m \) of different gases increases in the range of 20°C to 60°C. This indicates that temperature has an important positive enhancement on the microchannel diffusion coefficients \( (K_m) \). The increase in the \( K_m \) value of \( CO_2 \) is the most pronounced as the temperature increases.
5.2 Discussion

Figure 9 shows that the microchannel diffusion coefficient kept $\text{CO}_2 > \text{O}_2 > \text{N}_2$ at the same temperature condition. The mechanism of temperature manipulation on adsorption-diffusion is complex. According to thermodynamic principles, thermal stresses are generated through the alternation of temperature as coal is a porous medium with a well-developed pore structure, and thermal expansion and thermal fracture lead to the pores/fractures expansion of the coal particle (Zhou, 2011; Zhou et al. 2020). In fact, the pores/fractures structural changes in coal play a key role in the dynamics of diffusion. In order to determine the effect of temperature on the structure of coal pores and fractures, the electron microscope scanning experiments were performed on YW and SLG samples at temperatures of 20$^\circ$C and 60$^\circ$C, respectively. The electron micrographs of the pores/fractures are shown in Fig. 10. It can be seen that the pore/fractures of coal at different scales expand further with the increase of temperature, thus confirming the above theoretical inference, i.e., the high temperature promotes the development of pores/fractures of the coal particle, which is more conducive to gas diffusion.

Furthermore, the temperature also affects the coal’s adsorption characteristics, and plays a vital role in the diffusion process. According to the molecular kinematics theory, the root mean square velocity and mean free path of gas molecules increase with the elevated temperature (Li et al. 2010). The thermal motion of the molecules is intensified, which enhances the percolation capacity. The diffusion rate of gas in the coal is then accelerated, which boosts the diffusion flow of the gas from the coal particles, thus increasing the diffusion coefficient of the gas (Akbarzadeh and Chalaturnyk 2014; Tang et al. 2016; Gao et al. 2021).

The coefficient $K_m$ is different for different gases due to the fact that the molecular dynamics diameter of gas has the difference. The molecular dynamics diameter of $O_2$ is 0.346 nm, that of $\text{CO}_2$ is 0.33 nm and that of $N_2$ is 0.364 nm (Cui et al. 2004). Being compared with $O_2$ and $N_2$, $\text{CO}_2$ has the smallest molecular dynamics diameter, and the smaller the molecular diameter, the easier it is for gas molecules to flow in the micropores. Thus, the $\text{CO}_2$ is easier to penetrate into the superfine pores of coal than $O_2$ and $N_2$. Moreover, another main reason is that the gas adsorption capacity is influenced by the interaction between gas molecules and coal surfaces. The $\text{CO}_2$ has lower diffusion activation energy and higher apparent diffusion rate. The charged $\text{CO}_2$ adsorbed by coal atoms has strong van der Waals energy with a strong electrostatic effect, while the uncharged $N_2$ (or $O_2$) adsorbed by coal atoms have less van der Waals energy and no electrostatic effect (Wu et al., 2017). There also has been a factor that needs to be taken into consideration is the rectangular shape of the quadrupole moment of $\text{CO}_2$ (Skoczylas et al. 2020), which favors the transport of $\text{CO}_2$ gas in the microchannels. All these factors contribute to the stronger adsorption-diffusion behavior of $\text{CO}_2$ with respect to $O_2$ and $N_2$, which explains the order of the microchannel diffusion coefficients of $\text{CO}_2 > \text{O}_2 > \text{N}_2$ (Cui et al. 2004; Sander et al. 2020).

6 Conclusions

In this work, the isothermal adsorption experiments were performed on pure $O_2$, $\text{CO}_2$ and $N_2$, and the adsorption-diffusion characteristics of these gases in coal particles were investigated by numerical simulation using the free gas density gradient model. The major findings are as follows:

- i. The experimental cumulative adsorption capacity of $O_2$, $\text{CO}_2$ and $N_2$ decreases with the elevated temperature, and the adsorption capacity of three gases by coal satisfies $\text{CO}_2 > \text{O}_2 > \text{N}_2$. The experimental results also show that the adsorption constant $a$ decreases slightly with increasing temperature, but the adsorption constant $b$ decreases negatively exponentially.
- ii. The simulation results of the FGDG model agree well with the experimental data at different temperature conditions, which verifies the accuracy of this model. This indicates that the adsorption-diffusion behavior of $O_2$, $\text{CO}_2$ and $N_2$ in coal particles at high temperatures still obeys the free gas density gradient diffusion theory.
- iii. The microchannel diffusion coefficients $K_m$ of $O_2$, $\text{CO}_2$, and $N_2$ at various temperatures are obtained using the inversion method. In the range of 20$^\circ$C to 60$^\circ$C, the coefficient $K_m$ increases with the rising of temperature, but the coefficient $K_m$ of $\text{CO}_2$ is much larger than that of $O_2$ and $N_2$ at the same temperature, while the $K_m$ of $O_2$ and $N_2$ are closer.

Declarations

Funding

We gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (52074303, 51874315). This work is also the funded project of the Fundamental Research Funds for the Central Universities (2022JCCXAQ06).
Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

WL: Conceptualization, Methodology, Software, Writing - review & editing, Funding acquisition. MQ: Methodology, Software, Validation, Writing - original draft, Data Curation. XC: Investigation, Resources, Conceptualization. SP: Supervision, Visualization. DH: Methodology, Visualization.

Ethics declarations

Ethics approval

The manuscript is not be submitted to more than one journal for simultaneous consideration. The submitted work is original. This study does not involve any animal and human sample.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

Data will be made available on request.

References


Figures

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Schematic diagram of the H-Sorb 2600 adsorber
Figure 3

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Figure 4

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Figure 5

The curves of adsorption constant $a$ with temperature.
Figure 6

The curves of adsorption constant $b$ with temperature.

(a) YW-O$_2$

(b) SLG-O$_2$

(c) YW-CO$_2$

(d) SLG-CO$_2$

(e) YW-N$_2$

(f) SLG-N$_2$
Figure 7
Matching diagram of simulated data and experimental data of O\textsubscript{2}, CO\textsubscript{2} and N\textsubscript{2} at different temperatures

(a) YW

(b) SLG

Figure 8
Variation of $K_m$ values for different gases over temperature
Figure 9
Comparison of $K_m$ values for different gases

(a) YW

(b) SLG

Figure 10
Scanning electron microscope image of coal samples