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Carbon dioxide sorption and diffusion in coals: Experimental investigation and modeling

JIAN Xing, GUAN Ping^{*} & ZHANG Wei

MOE Key Laboratory of Orogenic Belts and Crustal Evolution, School of Earth and Space Sciences, Peking University, Beijing 100871, China

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CO₂ sorption and diffusion in coal are closely related to the occurrence of coal and gas outburst, geological sequestration of CO_2 in coalbeds, and enhancing coalbed methane recovery by injecting CO_2 . Hence, it is significant to investigate the sorption properties and diffusion models of CO_2 in coal. Here we used a newly designed experimental apparatus at Peking University to investigate the sorption and diffusion properties of CO₂ in natural coal samples from Dashucun Mine and Wutongzhuang Mine in Handan city, Hebei province, and Jinhuagong Mine in Datong city, Shanxi province, and obtained CO₂ sorption isotherms and diffusivity models. The results indicate that, in a certain pressure range, CO_2 sorption isotherms for the coal samples are consistent with the Langmuir model, which assumes that monolayer sorption occurs at the interface between coal matrix and CO_2 molecules, and the sorption isotherms feature nonstandard hyperbolas in mathematics. At the same pressure and temperature, as the vitrinite content increases, coal adsorbs more CO_2 molecules. The relation between the sorption capacity and the coal rank may be described as a "U-type" trend, and medium rank coal has the least sorption capacity. The bulk diffusivity of CO2 in coal is not constant; in the range of CO2 mass fraction greater than 1%, it increases roughly linearly with increasing mass fraction of CO_2 adsorbed (or CO_2 partial pressure) in coal. CO_2 diffusivity in coal is approximately 10^{-4} to 10^{-2} mm²/s in magnitudes, and the diffusivity ranges in coal samples are 3×10^{-4} to 8×10^{-3} mm²/s from Dashucun Mine, 2×10^{-4} to 4×10^{-3} mm²/s from Wutongzhuang Mine, and 2×10^{-4} to 4×10^{-3} mm²/s from Jinhuagong Mine. The results of the CO₂ sorption and diffusion study can be applied to help predict and prevent coal and gas outburst as well as to evaluate the feasibility in geological sequestration of CO₂ and to enhance coalbed methane recovery.

coal, CO₂, sorption isotherm, CO₂ desorption, diffusion, diffusivity

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Coal outbursts are one of the major hazards during coal mining. It has been shown recently that high CO_2 content in coal can drive coal outbursts in process similar to explosive volcanic eruptions [1,2]. CO_2 is the main component of gas in coal [3], and CO_2 sorption and diffusion are directly related to the dynamics of coal outbursts (especially those driven by CO_2 gas; coal outbursts can also driven by CH_4 gas). Another important aspect of CO_2 in coal is related to the ability of coal to store CO_2 . As CO_2 emissions increase

on a global scale, the average concentrations of CO_2 in the atmosphere reached 390 ppmv in 2010 (http://co2now.org/), compared to about 280 ppmv almost 100 years ago [4]. Therefore, increased attention is paid to CO_2 emissions reduction. It is confirmed that the deep unminable coal seams are a favorable geologic medium for CO_2 sequestration [5–7], and CO_2 injection to coalbed methane reservoir has been utilized to enhance coalbed methane (CO_2 -ECBM) recovery [8]. CO_2 sorption study might help estimate the sorption capacity of coal seams and the results of CO_2 diffusion research can be employed to evaluate the feasibility

^{*}Corresponding author (email: pguanl@pku.edu.cn)

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of CO_2 sequestration in coal and CO_2 -ECBM. Hence, it is significant to study CO_2 sorption and diffusion properties.

Previous studies of gas sorption in coal include theoretical derivation and modeling [9–12], mechanism and data on the capacity of methane sorption in coal and the influencing factors [13–15]. Often, sorption isotherms are determined using isothermal sorption and desorption instrument [16–18]. Tang et al. [19–21] carried out experiments on binary-component or multi-component gas sorption to discuss the methods and techniques of ECBM. However, some experimental samples in previous references were powdered coal, which could not represent the properties of natural coal.

CO₂ diffusion studies in coal are also often on theoretical modeling [12, 22-28]; experimental work is rare. Recent references reported some new methods or experimental apparatus, such as "solid coal discs" method [29, 30] (measured CO₂ diffusion from a chamber of CO₂ gas through a coal slab to a chamber of N2 gas under uniform pressure), volumetric method [31-34] (powdered coal samples were kept in a stainless-steel cell with a calibrated volume). In these studies, it was found that the CO₂ diffusivity and sorption in coal are highly variable. Therefore, it is necessary to determine the diffusivity and storage capacity for specific types of coal and to examine how they vary with coal properties. Furthermore, these studies were based on the assumption that diffusivity (D) is constant, which is not necessarily correct. Hence, new technique and method are needed to solve this problem.

Here, we apply a newly built experimental apparatus at Peking University [1] to study the sorption and diffusion properties of CO_2 in natural coal samples from Dashucun, Wutongzhuang, and Jinhuagong Mines. We then obtain a diffusivity model of CO_2 in coal by applying the bulk technique in desorption method [35].

1 Samples and experimental method

Three kinds of coal samples were collected from Dashucun

Mine, Wutongzhuang Mine in Handan City, Hebei Province and Jinhuagong Mine in Datong City, Shanxi Province in China [1] (Figure 1). The maceral components and vitrinite reflectance values of the samples are shown in Table 1. Coal from Dashucun Mine represents vitrinite and mineral components enrichment, with a much higher vitrinite reflectance as compared to other two coal samples. Coal samples from Wutongzhuang Mine and Jinhuagong Mine have similar maceral content and vitrinite reflectance, with a high inertinite content and low vitrinite reflectance.

Table 1 Maceral components and vitrinite reflectance (R_{max}^0) of coal samples

| Samples | Volume fraction content of maceral components (%) | | | | |
|----------------------|--|------------|---------|---------|------|
| ~F | Vitrinite | Inertinite | Exinite | Mineral | (%) |
| Dashucun Mine | 81.7 | 9.4 | 0 | 8.9 | 2.54 |
| Jinhuagong Mine | 79.2 | 20.2 | 0.2 | 0.4 | 0.93 |
| Wutongzhuang Mine | 76.3 | 22.6 | 0 | 1.1 | 1.02 |

Sorption and diffusion experiments were carried out in the Coal Outburst Research Lab in Peking University. Figure 2 reveals the scheme of our experimental apparatus, and the details were described in ref. [1].

The experimental procedure is as follows: (1) The natural coal samples are ground into equal-size spheres (approximately 25 mm in diameter), and the mass and diameter are measured, and then glued to the base of the test cell (Figure 2) in preparation for the experiments. (2) The test cell is connected to the larger decompression tank (Figure 2) and separated by layers of aluminum foils (the number of layers of aluminum foils depends on the desired pressure). (3) The cell is evacuated to remove air. (4) CO₂ is let into the test cell to reach a desired high pressure (such as 3 MPa). The cell is maintained at the constant CO₂ pressure for a few days to allow CO₂ diffusion into coal and reach the sorption



Figure 1 Sample locations shown in traffic maps. (a) Dashucun Mine and Wutongzhuang Mine in Hebei Province; (b) Jinhuagong Mine in Shanxi Province.



Figure 2 Sketch map of experimental apparatus.

equilibrium. For coal spheres of 12.5 mm in radius, a duration greater than 5 days is enough. The duration at the constant CO₂ pressure is roughly estimated from $t = r^2/D$ where *t* is time, *r* is the radius of the coal sphere, and *D* is CO₂ diffusivity in coal. (5) Sudden decompression is achieved by pushing a switch button, triggering the electromagnetically driven knife in the tank downward to cut the aluminum foils, and then the time is recorded. (6) After the coal spheres are taken out of the test cell, the mass of the spheres is continuously measured by a high-precision electronic balance until the mass is almost invariant.

2 Results and data processing

The original experimental data and primary processing results are shown in Figure 3 and Table 2.

One observation is that the mass of coal spheres does not return to the mass before experiment, but is slightly larger or smaller than the initial mass (Table 2). This may be attributed to (1) loss of small particles of coal during the experiment, (2) initial air and moisture absorbed in coal, which were replaced and/or flushed out by CO_2 , and (3) alteration of pore structure in coal, due to CO_2 sorption-swelling and desorption-shrinkage [36–39]. Larsen [40] explained that the adsorbed CO_2 seemed to act as a plasticizer, enabling physical structure rearrangements in coal.

The second observation is that after a long period of CO_2 desorption, the mass of coal may reach a minimum and then increase or fluctuate slightly (Figure 3). This can be explained as follows. Initially, CO_2 desorption dominates the measured mass change. However, as CO_2 is almost gone, the diffusion of other easily-adsorbed air components (such as moisture) into coal would become significant, and there may be mass gain or decrease. Hence, there are many processes going on even though the outward diffusion of CO_2 is the dominant process in terms of mass change.

Another observation is that desorption of CO_2 is faster with a higher initial experiment pressure, and the duration of the coal mass reaching the minimum is shorter (Figure 3). The explanation can be seen in later discussions.

The initial mass m_1 (the mass of the coal spheres saturated with CO₂, or the mass at t = 0) cannot be measured directly because the weighing did not start right after the decompression (it takes a few seconds to take the samples out of the test cell for weighing). By plotting m(t) versus



Figure 3 The data of CO_2 mass loss record for each experiment (ten experiments in total). X-axis is time (unit: h), and Y-axis is the mass of CO_2 remaining in coal during desorption (unit: g).

time, or square root of time, we can obtain m_1 by extrapolation, as the *m* value at t = 0.

Because the *m* obtained fitting requires extrapolation, this fitting is not trivial. If diffusivity (*D*) is perfectly constant for a curve, m(t) vs. $t^{0.5}$ curve can be approximated by a second-order polynomial for mass loss from 0% to 90% as follows [35]:

$$m(t) = m_1 \left(1 - \frac{6}{\sqrt{\pi}} \frac{\sqrt{D}}{a} \sqrt{t} + 3\frac{D}{a^2} t \right), \tag{1}$$

where a is the radius of spheres. However, when such a curve is used to fit the data, the fit is not good, indicating that diffusivity is variable in each experiment.

In this paper, two methods are used to fit the m(t) vs. $t^{0.5}$ curve for each experiment to obtain the initial mass m_1 . In method 1, m(t) vs. $t^{0.5}$ curve is fit by an unconstrained second order polynomial, but only from mass loss of 0% to 50%. The intercept at $t^{0.5} = 0$ is m_1 . In method 2, m(t) vs. $t^{0.5}$ curve is fit by a fourth order polynomial from mass loss of 0% to 90%, and the intercept at $t^{0.5} = 0$ is m_1 (Figure 4). To estimate the error, the curves are also fit by third order poly-

nomials, and the difference in m_1 from different fits is roughly taken as the error. The results of each experiment can be seen in Table 2. Comparison of the results between method 1 and method 2 demonstrates little difference. Hence, both of them are reliable, and the results of method 2 would be used in later discussions.

3 Discussions

3.1 CO₂ sorption isotherm

IUPAC [41] (International Union of Pure and Applied Chemistry) identified six types of sorption behavior exhibited by various adsorbents and adsorbates. To describe them, many theoretical isothermal sorption models have been established, such as Langmuir monolayer sorption model, BET multilayer sorption model, Polyanyi sorption potential theory (Dubinin-Astakhov equation), theory of volume filling and Freundlich equation. Coal is a typical microporous medium, and the sorption behavior is still in dispute [42, 43].

Table 2 Basic data of coal spheres in the experiments, m_1 and adsorption capacity (V) values^{a)}

| Samples | Exp [#] | No. | Radius (mm) | $M_{0}\left(\mathrm{g} ight)$ | $P (MPa)^{a)}$ | $M_{\infty}\left(\mathrm{g} ight)$ | m_1 (method 1) | m_1 (method 2) | V(cc/g) |
|-------------------|------------------|-----|-------------|--------------------------------|----------------|------------------------------------|------------------|------------------|---------|
| Dashucun Mine | Exp30 | 4 | 12.22 | 47.51 | 1.02 | 47.62 | 1.64 | 1.66 ± 0.03 | 17.67 |
| | Exp32 | 1 | 11.92 | 10.52 ^{a)} | 4.68 | 10.55 | 0.65 | 0.69 ± 0.04 | 33.18 |
| | Exp33 | 4 | 12.22 | 47.62 | 1.55 | 47.65 | 1.91 | 1.93±0.04 | 20.50 |
| | Exp35 | 4 | 12.22 | 47.59 | 2.15 | 47.62 | 2.17 | 2.17 ± 0.08 | 23.06 |
| Wutongzhuang Mine | Exp37a | 3 | 12.56 | 34.93 | 1.02 | 34.88 | 0.98 | 0.99±0.03 | 14.34 |
| | Exp38a | 3 | 12.67 | 33.64 | 2.17 | 33.61 | 1.21 | 1.23 ± 0.01 | 18.49 |
| | Exp39a | 3 | 12.56 | 34.89 | 3 | 34.9 | 1.41 | 1.36 ± 0.07 | 19.72 |
| Jinhuagong Mine | Exp37b | 3 | 12.72 | 34.22 | 1.02 | 34.04 | 1.18 | 1.2±0.05 | 17.74 |
| | Exp38b | 3 | 12.45 | 32.8 | 2.17 | 32.63 | 1.36 | 1.38 ± 0.06 | 21.28 |
| | Exp39b | 3 | 12.72 | 34.04 | 3 | 34.01 | 1.51 | 1.50 ± 0.11 | 22.28 |

a) 0.13 g fragments drop from coal spheres after sudden decompression in Exp32, the data (10.52 g) in table represents the initial mass reduced by 0.13 g. Exp30, Exp33 and Exp35 use the same group of coal spheres, as well as Exp37a and Exp39a, Exp37b and Exp39b. M_0 is the initial mass of coal spheres before the experiment, P is the experimental pressure, m_1 is the mass of CO₂ when CO₂ reached the adsorption equilibrium in coal spheres at the given pressure, m_1 cannot be directly weighed by an electronic balance, but can be inferred. M_∞ is the mass of coal spheres after complete desorption of CO₂ for a very long time.



Figure 4 m(t) vs. $t^{0.5}$ curve fitting by a fourth order polynomial from mass loss of 0% to 90%, the intercept at $t^{0.5} = 0$ is m_1 .

Here we define V, gas adsorbed volume, as the ratio of the maximum adsorbed volume (unit in cc/g) of CO_2 in unit mass coal and the initial mass of coal spheres at a certain equilibrium pressure. V value of each experiment can be seen in the last column of Table 2. Figure 5 shows the relationship between V values and experimental pressures (P), i.e. the curves are sorption isotherms.

According to Figure 5, the sorption isotherm of coal can be classified as Type I within a certain pressure range (always at subcritical conditions, and the gas pressure is less than 7.39 MPa). This type of isotherm is mathematically represented as a nonstandard hyperbola. The curve of gas adsorbed volume versus experimental pressure exhibits a steep start and then slowly flattens above a certain pressure (known as the saturation pressure), which is similar to the result of previous studies [30].

Type I sorption isotherm (Langmuir model) is based on the concept of dynamic equilibrium between the rates of sorption of gas on a solid and desorption from the solid surface [44]. It is assumed that the sorption is restricted to a single layer. The equation for the Langmuir isotherm is given as

$$\frac{V}{V_{\rm L}} = \frac{bP}{1+bP} \quad \text{or} \quad \frac{V}{V_{\rm L}} = \frac{P}{P+P_{\rm L}},\tag{2}$$

where V (unit in cc/g or m³/t) is the adsorbed volume at equilibrium pressure P, V_L is the maximum monolayer capacity of a given coal, also known as the Langmuir volume; and b is the pressure constant, which is a function of temperature. P_L is the ambient pressure when the adsorbed volume is half of V_L and referred to as the Langmuir pressure, and P_L equals the inverse of b.

In addition to the monolayer sorption assumption, the model also assumes that the surface of coal solid is homogeneous and the energy of sorption is constant over all sorption sites, the adsorbate molecules are held at localized and defined sites and each site can accommodate only one ad-



Figure 5 Adsorption isotherms of three kinds of samples. We get rid of the result of Exp32 which deviates the curve too much.

sorbate molecule; there is no interaction between neighboring adsorbate molecules.

The Langmuir sorption isotherm equations (Figure 5) of Dashucun Mine, Jinhuagong Mine and Wutongzhuang Mine coal samples are

$$\frac{V}{31.72} = \frac{P}{P+0.82}, \quad 1 \text{ MPa} < P < 4.7 \text{ MPa}, R^2 = 0.99976, (3)$$
$$\frac{V}{25.73} = \frac{P}{P+0.46}, \quad 1 \text{ MPa} < P < 3 \text{ MPa}, R^2 = 0.99999, (4)$$
$$\frac{V}{24.54} = \frac{P}{P+0.72}, \quad 1 \text{ MPa} < P < 3 \text{ MPa}, R^2 = 0.99995. (5)$$

The $V_{\rm L}$ and $P_{\rm L}$ of the coal samples adsorbing CO₂ are listed in Table 3, which are roughly consistent with literature data [45].

Table 3 $V_{\rm L}$ and $P_{\rm L}$ results of coal samples from experiments

| Samples | Dashucun Mine | Jinhuagong Mine | Wutongzhuang |
|--------------------|---------------|-----------------|--------------|
| $V_{\rm L}$ (cc/g) | 31.72 | 25.73 | 24.74 |
| $P_{\rm L}$ (MPa) | 0.82 | 0.46 | 0.72 |

Although the fits in Figure 5 are good, the Langmuir monolayer sorption model is unlikely perfect in describing CO_2 sorption in coal, as coal seams are heterogeneous. The assumption of homogeneous surface is not applicable to actual coal seams, and the assumption of monolayer sorption is doubtable above subcritical conditions. It is well known that the sorption isotherm of coal could not be presented as a hyperbola at excess gas pressure. This phenomenon may be explained by the change of pore structure of high gas pressure in coal pore. The variation of sorption model can be explained as follows. The physical and chemical property of CO_2 , such as the density, varies drastically at supercritical conditions; capillary condensation of CO_2 occurs easily at high pressure [12]; CO_2 multilayer sorption of coal violates the basic assumption of Langmuir model.

Dutta et al. [42] showed that both Langmuir and D-A (Dubinin-Astakhov) equations fit their experimental data satisfactorily by using Illinois coals (powder coal). However, the overall quality of fitting using the D-A equation is better than that using Langmuir equation. In this study, because the Langmuir equation fits our data well, we decided not to use the more complicated D-A equation.

3.2 Diffusion coefficients

Diffusion coefficients are indispensable in the study of natural mass transport processes involving diffusion. Gas diffusion in coal depends on the properties of gas and coal. The best approach of obtaining the diffusivity is to design some diffusion experiments so that the diffusion problem has a simple analytical solution, and then the experimental results could be compared with (or fit by) the analytical solution. The method of choice depends on given problems. The often used methods include diffusion-couple method, thin-source method, desorption or sorption method, and crystal dissolution method [35].

Gas diffusion in coal includes in-diffusion during sorption experiments and out-diffusion during desorption experiments, and there may be differences between the in-diffusivity and out-diffusivity. Diffusivity studied here is out-diffusivity. In this paper, the bulk technique in desorption method is used to obtain the diffusivity of CO_2 in coal using the mass loss experiments described earlier. Because gas flow is much faster than gas diffusion in coal, compared to the gas diffusion time, the time of gas flow in fractures can be ignored. Hence, diffusion process dominates the gas loss in coal, and this study assumes that coal desorption time is referred as the gas diffusion time.

The process of gas diffusion in micropore, macropore, and fracture is controlled by various diffusion mechanisms. The pore size and pore structure of coal are related directly to the diffusion mechanisms and thus diffusivity. The common simple diffusion model is bi-disperse model referred by Ruckenstein et al. [46] that describes macropore and micropore diffusion, and then modified and improved by Clarkson et al. [47] and Shi et al. [48]. However, coal is so complicated that a bi-disperse model is unlikely going to work. A multi-disperse or continuously disperse model may be necessary.

Comparison of pore size (d) and mean free path (λ) of gas molecule and multi-disperse gas diffusion mechanisms in coal can be classified as follows: pore diffusion or molecule diffusion (sometimes named self-diffusion), where d is larger than λ , and molecular collision mainly occurs among gas molecules; transition diffusion, where d is approximately equal to λ , both gas molecular collision and collision between gas and coal molecules of pore wall are equivalently important; Knudsen diffusion, where d is smaller than λ , molecular collision mainly occurs between gas molecules and coal molecules of pore wall; surface diffusion and configurational diffusion, where d is much smaller than λ ; and free gas molecules cannot access these micropores. The diffusivity of single diffusion mechanism decreases in above-mentioned order [25, 49]. Hence, based on the pore structure of given coal samples, the dominated diffusion mechanism or combinations of them can be determined [34, 50].

Diffusivity is extracted by replotting desorption data in each experiment. We define $F = (m_1-m(t))/m_1$ as the fractional mass loss. Based on the bulk technique, the theoretical relation between *F* and $t^{0.5}$ for *F* from 0% to 90% (the approximate relation has a relative accuracy of 0.1%) [35] is

$$F = \frac{6}{\sqrt{\pi}} \frac{\sqrt{D}}{a} \sqrt{t} - 3\frac{D}{a^2}t,$$
(6)

if D is constant. If D depends on time, then

$$F = \frac{6}{\sqrt{\pi}} \frac{\sqrt{\int_{0}^{t} Ddt'}}{a} - 3 \frac{\int_{0}^{t} Ddt'}{a^{2}}.$$
 (7)

The diffusion model and diffusivity derivation of threedimensional sphere sample with radius of a can be seen in ref. [35]. For mass loss range from 0% to 50%, the data are fit by

$$F = c_1 t^{1/2} - c_2 t, (8)$$

where the intercept is zero, and theoretically c_1 and c_2 are related as in eq. (6) if D is constant. c_1 and c_2 are used to obtain D independently and see if they roughly match (if D is constant in an experiment, D calculated from c_1 and c_2 should be the same). It can be seen that D calculated from c_2 is different from that calculated from c_1 in Table 4. Hence D is not constant, and D varies with time.

The variable D values are obtained at time t using the following approach (Zhang Youxue, personal communication). In eq. (7), we assume that

$$x = \sqrt{\int_0^t Ddt'} / a \tag{9}$$

and eq. (7) is a quadratic equation for x:

$$3x^2 - (6/\sqrt{\pi})x + F = 0.$$
 (10)

| Samples | Exp [#] | C_1 | c_2 | $D (\mathrm{mm^2/s})$ |
|-------------------|------------------|---------|----------|-----------------------|
| Dashucun Mine | Exp30 | 0.00909 | 3.37E-05 | 0.0003-0.001 |
| | Exp32 | 0.0298 | 3.40E-04 | 0.002-0.008 |
| | Exp33 | 0.0118 | 5.72E-05 | 0.0005-0.001 |
| | Exp35 | 0.0144 | 8.75E-05 | 0.0005-0.002 |
| Wutongzhuang Mine | Exp37a | 0.01001 | 4.32E-05 | 0.0002-0.001 |
| | Exp38a | 0.0107 | 3.95E-05 | 0.0005-0.002 |
| | Exp39a | 0.0181 | 1.33E-04 | 0.0005-0.004 |
| Jinhuagong Mine | Exp37b | 0.0123 | 7.21E-05 | 0.0002-0.002 |
| | Exp38b | 0.0164 | 1.16E-04 | 0.0002-0.003 |
| | Exp39b | 0.0199 | 1.51E-04 | 0.0003-0.004 |

Table 4 c_1 and c_2 fit by eq. (8), and the range of *D* value calculated by eq. (12)

We obtain

$$x = \frac{\sqrt{\int_{0}^{t} Ddt'}}{a} = \frac{\frac{6}{\sqrt{\pi}} - \sqrt{\frac{36}{\pi} - 12F}}{6} = \frac{1}{\sqrt{\pi}} - \sqrt{\frac{1}{\pi} - \frac{F}{3}}.$$
 (11)

Then, let $y = \int_0^t D dt' = a^2 x^2$. That is,

$$y = a^2 \left(\frac{1}{\sqrt{\pi}} - \sqrt{\frac{1}{\pi} - \frac{F}{3}}\right)^2.$$
 (12)

Therefore, y as a function of t can be calculated based on mass loss data. Then, the out-diffusivity D at a given time can be obtained as

$$D = \frac{\mathrm{d}y}{\mathrm{d}t}.$$
 (13)

In order to smooth the data in the above differential calculation, instead of direct measurements, F calculated from the fourth order polynomial (the calculations also can be seen in Figure 4, because m(t) and F are related) is used to calculate y, and central differentials are used to obtain D. The CO₂ out-diffusivity in coal obtained using the method is plotted against average absorbed mass fraction of CO₂ in Figure 6 and the last column of Table 4.

Diffusivity was recognized as a constant in many references based on some theoretical derivation and experimental study. Figure 6 demonstrates that CO_2 diffusivity increases with the ambient pressure before decompression starts. This conclusion can explain the third observation mentioned above well. With high equilibrium gas pressure before decompression, coal can adsorb more CO_2 , and the instantaneous concentration gradient of CO_2 in coal is large during the desorption process, so the instantaneous CO_2 diffusivity is large too. In addition, CO_2 diffusivity decreases with the decreasing mass fraction of CO_2 adsorbed in coal (or CO_2 partial pressure) in each experiment (Figure 6).

In conclusion, a new diffusivity model is presented in this paper.

The dependence of D on CO₂ mass fraction (or CO₂ partial pressure) may be explained as the variation of pore structure (as well as fracture structure) during coal desorption. Because the ambient pressure is one atmosphere, as CO₂ partial pressure in coal increases, the coal sample is under greater tension, widening the numerous micropores (as well as macropores). Because the micropores are likely the major pathways for CO₂ diffusion, CO₂ diffusivity increases.

The production of volumetric strain reduces the pore size, due to the shrinkage of coal matrices desorption [36, 37], which is similar to the explanation of the first observation. At the early stage of the coal desorption process, the partial pressure of CO_2 in coal pore is high, and the pore size is relatively big. Pore diffusion and transition diffusion may dominate the CO_2 diffusion process. As the mass fraction of CO₂ decreases, the pore structure varies, and the pores become small. Pore diffusion is restricted; on the contrary, Knudsen diffusion, surface diffusion, and configurational diffusion may dominate the CO₂ diffusion process. The desorption is a process changing from macropore diffusion (early stage) to micropore diffusion (late stage) actually, explained by the bi-disperse model [46]. The maximum value of diffusivity is two orders of magnitude larger than the minimum value (Figure 6), which is consistent with the previous reference results [47]. After desorption for a long time, the diffusivity decreases to the background level.

Furthermore, the dependence of D on CO₂ mass fraction is in a linear manner in the range of CO₂ mass fraction greater than 1% (Figure 7), and the linear relation equation can be seen in Table 5. The slopes increase with the experimental pressure for the coal samples from Dashucun Mine and Jinhuagong Mine, but the conclusion is incorrect for the samples from Wutongzhuang Mine. Harpalani et al. [36] showed that there is a linear relation between volumetric strain and gas desorption. So we infer that the linear manner between D and CO₂ mass fraction is related to a kind of relation between pore structure and CO₂ mass fraction. Because our experiments lack some data at the early stage of desorption, the exact reason remains unclear, and further



Figure 6 Relation between diffusivity and mass fraction of CO₂ residue adsorbed in coal. (a) Dashucun Mine; (b) Wutongzhuang Mine; (c) Jinhuagong Mine.



Figure 7 Linear relations between diffusivity and mass fraction (>1%) of CO₂ adsorbed in coal samples. (a) Dashucun Mine; (b) Wutongzhuang Mine; (c) Jinhuagong Mine.

Table 5 Linear relation equations of D versus CO_2 mass fraction (C), and the correlation coefficients (R^2)

| Samples | Exp [#] | P (MPa) | D vs. C (C>1%) | R^2 |
|-------------------|------------------|---------|----------------------------------|--------|
| Dashucun Mine | Exp30 | 1.02 | $D = 0.0339C + 2 \times 10^{-5}$ | 0.9979 |
| | Exp32 | 4.68 | D = 0.1845C + 0.0006 | 0.9926 |
| | Exp33 | 1.55 | $D = 0.0501C + 4 \times 10^{-5}$ | 0.9981 |
| | Exp35 | 2.15 | D = 0.0724C - 0.0002 | 0.9981 |
| Wutongzhuang Mine | Exp37a | 1.02 | $D = 0.0571C - 9 \times 10^{-5}$ | 0.9961 |
| | Exp38a | 2.17 | D = 0.0377C + 0.0005 | 0.9523 |
| | Exp39a | 3 | D = 0.1271C + 0.0002 | 0.9962 |
| Jinhuagong Mine | Exp37b | 1.02 | D = 0.0926C - 0.0008 | 0.9876 |
| | Exp38b | 2.17 | D = 0.124C - 0.0009 | 0.9969 |
| | Exp39b | 3 | D = 0.1742C - 0.0005 | 0.9956 |

study is needed to solve it.

However, the linear relation is indistinctive in the range of CO_2 mass fraction smaller than 1% (Figure 7). The explanation can be the same as that of the second observation. Furthermore, at the late stage of coal desorption, the measurement errors may influence the accuracy of experiments data.

According to Figure 6 and Table 4, the range of variational diffusivity values of coals from Dashucun, Wutongzhuang and Jinhuagong Mines are 3×10^{-4} to 8×10^{-3} , 2×10^{-4} to 4×10^{-4} 10^{-3} , 2×10^{-4} to 4×10^{-3} mm²/s, respectively, which are slightly greater in comparison of results by Saghafi et al. [29] (the range of diffusivity is 1.2×10^{-4} to 1.02×10^{-3} mm²/s for 15 coal samples from Sydney basin, Australia), who measured CO₂ diffusion from a chamber of CO₂ gas through a coal slab to a chamber of N₂ gas under uniform pressure. In our experiments there was a significant pressure gradient (not uniform pressure) from the interior to the surface of coal spheres, and the high internal pressure caused tension, widening the pores and fractures and increasing CO2 diffusivity. The background CO₂ diffusivity when the sample is not under high internal stress (meaning not very high CO₂ mass fraction) is from 2×10^{-4} to 5×10^{-4} mm²/s, which is similar to other referential results [29, 47]. Because in nature CO₂ diffusion occurs often when there is a significant pressure gradient (e.g. when coal containing high CO₂ concentration is exposed to atmosphere, especially when there

was a coal and gas outburst), our experimental results are more applicable to these situations of CO_2 diffusion in coal.

3.3 Influencing factors of sorption and diffusion

The sorption capacity of coal may be influenced by temperature, pressure, moisture content, ash, coal rank, and maceral components, which also influence gas transport in coal and the diffusivity of gas. In the CO₂-coal system, the influencing factors can be summarized into two aspects: the coal seams temperature and pressure setting, and properties of coal.

The coal sorption process is exothermic. Hence the sorption capacity decreases with temperature [7]. However, the sorption capacity increases with gas pressure in a certain range, which is described as sorption isotherm. The coal seams temperature and pressure setting also can influence gas diffusion. The dependence can be described well by the Arrhenius relation [35]. Hence, diffusivity increases with temperature [32], but can either decrease or increase with pressure [49].

Maceral components in coal also affect the sorption capacity and diffusion. There is a trend that the gas (CO₂ or CH₄) sorption capacity of coal increases with vitrinite content (Figure 8(a)), which agrees with existing literatures [51]. Vitrinite develops a large specific surface area due to the high degree of micropore development, compared with other components. Hence, vitrinite can adsorb more gas



Figure 8 Relations between adsorption capacity of coal and maceral components (a) and coal rank (b). Dash lines show the variation trend; hollow circles stand for the data from Hildenbrand et al. [51]; solid circles stand for the data in our experiments.

molecules [50]. However, inertinite develops relatively more macropore, and adsorbs less gas molecules. Besides, the mineral-matter cannot be ignored in discussing the influencing factors [52]. In this paper, we cannot find a certain relation between diffusivity and maceral components because of the variation of pore structure during gas diffusion, so further study is needed.

The sorption capacity and diffusivity vary with the coal rank. Comparison of previous research and our experiment results (Figure 8(b)) shows that coal in a medium rank has the least capacity, which agrees with previous references [18, 51]. The result can be explained in coal chemistry as follows [15]. Fatty group low molecular weight compounds that adsorb gas easily reduce dramatically in low rank coal during coalification. At this stage, the oxygen-containing functional groups content (restrain sorption) is relatively large; on the contrary, the increase of the aromatic ring (promotes sorption) condensation degree is not obvious. Hence, the sorption capacity may decrease to a minimum value at this stage. However, the variation of high rank coal structure during coalification represents that aliphatic chains are shortened, oxygenated groups decreased, aromatic hydrocarbons enriched, and aromatic ring condensation degree increased, and hence the sorption capacity increases with the coal rank at this stage.

The sorption capacity and diffusivity is strongly affected by the presence of moisture in coal, though dry coal samples are used in our experiments. The sorption capacity of natural coal is much smaller than that of dry coal [53]. The role of moisture is confirmed as a competitor to gas molecules for sorption sites [38, 51]. Sang et al. [16] believed that the sorption capacity differences among dry coal, injection water coal and equilibrium water coal might be explained by the wettability differences of coal. Water is described as a good swelling agent [54] and can be adsorbed on the coal surface in multi-layers [55]. Water sorption can reduce the effective pore size of coal, and hence lowering the gas diffusivity [32, 47, 56, 57].

The pore structure of coal directly influences the sorption

capacity and gas diffusion. The sorption capacity increases with the degree of micropore development in coal. Based on the bi-disperse diffusion model [46–48], pore structure apparently influences the gas diffusion process and diffusivity, as mentioned above.

The sorption and desorption process may alter the pore structure of coal, and influence the sorption capacity of coal and gas diffusivity. Busch et al. [31] carried out experiments on the same coal, and found that the sorption capacity of the given coal increases slightly.

3.4 Applications

It is common to apply the techniques of releasing gas regularly and injecting water to prevent coal outbursts [58]. Before using these methods, the sorption and diffusion properties of coal seams should be considered. Coal outbursts may be regarded as another type of gas-driven eruption [1], in addition to explosive volcanic, lake, and possible ocean eruptions. This study is helpful for investigating the mechanism of coal outbursts.

There are many examples of CO_2 geologic sequestration in coal seams and CO_2 -enhanced coalbed methane recovery (CO_2 -ECBM). 760 t CO_2 gas has been injected into coal seams of Silesian basin in Poland, RECOPOL Program [6] of European Union. 10^5 t CO_2 gas has been injected into Fruitland coal seams of San Juan basin since 1996 [59]. Kronimus et al. [7] estimated that 1.6×10^8 t CO_2 gas could be sequestrated in 37.5 Gt coal in Munster basin, in Germany. The "Allison Unit CO_2 -ECBM Pilot" Program was carried out successfully in San Juan basin in the United States in 1995 [60].

Hence, this study also demonstrates that coal can adsorb much CO_2 gas. Based on the sorption isotherms, the coal mine geological setting and basic properties of coal seams, the CO_2 sequestration capacity of the given unminable coal seams could be evaluated. The new diffusivity model that we obtain can be applied to quantify how rapidly injected CO_2 in an unminable coal seams wound disperse. The CO_2 diffusivity can facilitate technological studies of enhancing coalbed methane recovery.

4 Conclusions

(1) CO₂ sorption isotherms for coal samples from Dashucun, Wutongzhuang and Jinhuagong coalmines are consistent with the monolayer sorption model (Langmuir model), and are represented as nonstandard hyperbola curves. The Langmuir volume $V_{\rm L}$ and Langmuir pressure $P_{\rm L}$ of coal samples from Dashucun, Wutongzhuang and Jinhuagong Mines are 31.72, 25.73, 24.74 cc/g; 0.82, 0.46, 0.72 MPa, respectively.

(2) CO_2 sorption capacity of coal tends to increase with the increasing vitrinite content, and coal in low and high rank can adsorb more CO_2 gas, whereas the medium rank coal has the least capacity.

(3) CO₂ diffusivity in coal is not constant, but increases linearly with the mass fraction of CO₂ (or CO₂ partial pressure) in coal for CO₂ mass fraction greater than 1%. CO₂ diffusivity in coal ranges from 10^{-4} to 10^{-2} mm²/s. Specifically, the diffusivity ranges in coals from Dashucun, Wutongzhuang and Jinhuagong Mines are $3 \times 10^{-4} - 8 \times 10^{-3}$, $2 \times 10^{-4} - 4 \times 10^{-3}$, $2 \times 10^{-4} - 4 \times 10^{-3}$ mm²/s, respectively.

(4) The results in this work can be applied to understand coal and gas outbursts. In addition, they also help to evaluate the feasibility of CO_2 geological sequestration in unminable coal seams and to enhance coalbed methane recovery (CO₂-ECBM).

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- 1 Guan P, Wang H Y, Zhang Y X. Mechanism of instantaneous coal outbursts. Geology, 2009, 37: 915–918
- 2 Bodziony J, Lama R D. Sudden outbursts of gas and coal in underground coal mines. Australian Coal Association Research Program Report C4034, 1996. 677
- 3 Zhou S N, Lin B Q. Coal Seams Gas Sorption and Flow Theory (in Chinese). Beijing: Coal Industry Press, 1997
- 4 Gunter W D, Wong S, Cheel D B, et al. Large CO₂ sinks: Their role in the mitigation of greenhouse gases from an international, national (Canadian) and provincial (Alberta) perspective. Appl Energ, 1998, 61: 209–227
- 5 Gentzis T. Subsurface sequestration of carbon dioxide—An overview from an Alberta (Canada) perspective. Int J Coal Geol, 2000, 43: 287–305
- 6 Van Bergen F, Pagnier H, Krzystolik P. Field experiments of enhanced coalbed methane-CO₂ in the upper Silesian basin of Poland. Environ Geosci, 2006, 13: 201–224
- 7 Kronimus A, Busch A, Alles S, et al. A preliminary evaluation of the CO₂ storage potential in unminable coal seams of the Munster Creta-

ceous Basin, Germany. Int J Greenh Gas Con, 2008, 2: 329-341

- 8 White C M, Smith D H, Jones K L, et al. Sequestration of carbon dioxide in coal with enhanced coalbed methane recovery—A review. Energ Fuel, 2005, 19: 659–724
- 9 Wang E Y, He X Q, Lin H Y. adsorption statement of gas in coal (in Chinese). Coal Eng, 1996, 5: 12–16
- 10 Zhang L, He X Q, Wang E Y, et al. Study of absorptive characteristics of coal (in Chinese). J Taiyuan Univ Tech, 2001, 32: 449–451
- Xie J L, Guo Y Y, Wu S Y. Study of adsorption of methane on coal at normal temperature (in Chinese). J Taiyuan Univ Tech, 2004, 35: 562–564
- 12 Sang S X, Zhu Y M, Zhang J, et al. The mechanism of gas adsorption in coal (II)—the physical process and theory model (in Chinese). Nat Gas Ind, 2005, 25: 16–18
- 13 Jiang W P, Cui Y J, Zhong L W, et al. Quantum chemical study on coal surface interacting with CH_4 and H_2O (in Chinese). Nat Gas Geosci, 2007, 18: 576–579
- 14 Zhang S Y, Sang S X, Yang Z G. Mechanism analysis on the effect of liquid water on coal adsorbing methane (in Chinese). J Chin Univ Min Tech, 2009, 38: 707–712
- 15 Jiang W P. Microscopic mechanism study on the influence of coal rank on adsorption capacity (in Chinese). Chin Coalbed Methane, 2009, 6: 19–22
- 16 Sang S X, Zhu Y M, Zhang J, et al. Influence of liquid water on coalbed methane adsorption: An experimental research on coal reservoirs in the south of Qingshui Basin. Chin Sci Bull, 2005, 50(Suppl.1): 79–85
- 17 Zhang L P, Su X B, Zeng R S. Discussion on the controlling effects of coal properties on coal adsorption capacity (in Chinese). Acta Geol Sin, 2006, 80: 910–915
- 18 Zhang S Y, Sang S X. Mechanism of liquid water influencing on methane adsorption of coals with different ranks (in Chinese). Acta Geol Sin, 2008, 82: 1350–1354
- 19 Tang S H, Tang D Z, Yang Q. Binary-component gas adsorption isotherm experiments and their significance to exploitation of coalbed methane (in Chinese). J Chin Univ Geosci, 2004, 29: 219–223
- 20 Tang S H, Han D X. Exploitation potential evaluation to coalbed methane based on multi-component gas adsorption isotherms (in Chinese). J Chin Univ Min Tech, 2002, 31: 630–633
- 21 Tang S H, Yang Q, Tang D Z. Comparison between the experiment data of binary-component gas adsorption isotherms and the calculating results with extended-Langmuir equation (in Chinese). Geol Sci Technol Inf, 2003, 22: 68–70
- 22 Zhou S N. Mechanism of gas flow in coal seams (in Chinese). J Chin Coal Soc, 1990, 15: 15–24
- 23 Wu S Y. Preliminary approach on the low of gas diffusion and permeation on coal seams (in Chinese). J Taiyuan Univ Tech, 1994, 12: 259–263
- 24 Duan S M, Nie B S. The preliminary study on diffusion and permeation regularity of coal gas (in Chinese). J Taiyuan Univ Tech, 1998, 29: 413–416
- 25 Nie B S, He X Q, Wang E Y. Mechanism and modes of gas diffusion in coal seams (in Chinese). Chin Safety Sci J, 2000, 10: 24–28
- 26 Nie B S, Guo Y Y, Wu S Y, et al. Theoretical model of gas diffusion through coal particles and its analytical solution (in Chinese). J Chin Univ Min Tech, 2001, 30: 19–22
- 27 Nandi S P, Walker P L. Activated diffusion of methane in coal. Fuel, 1970, 49: 309–323
- 28 Harpalani S, Ouyang S. A new laboratory technique to estimate gas diffusion characteristics of coal. Int Coalbed Methane Symposium, May 3–7, 1999, Tuscaloosa, Alabama, 141–152
- 29 Saghafi A, Faiz M, Roberts D. CO₂ storage and gas diffusivity properties of coals from sydney basin, australia. Int J Coal Geol, 2007, 70: 240–254
- 30 Saghafi A, Pinetown K L, Grobler P G, et al. CO₂ storage potential of south african coals and gas entrapment enhancement due to igneous intrusions. Int J Coal Geol, 2008, 73: 74–87
- 31 Busch A, Gensterblum Y, Krooss B M. Methane and CO₂ sorption and desorption measurements on dry argonne premium coals: Pure

components and mixtures. Int J Coal Geol, 2003, 55: 205-224

- 32 Busch A, Gensterblum Y, Krooss B M, et al. Methane and carbon dioxide adsorption-diffusion experiments on coal: Upscaling and modeling. Int J Coal Geol, 2004, 60: 151–168
- 33 Mazumder S, Van Hemert P, Busch A, et al. Flue gas and pure CO₂ sorption properties of coal: A comparative study. Int J Coal Geol, 2006, 67: 267–279
- 34 Siemons N, Busch A. Measurement and interpretation of supercritical CO₂ sorption on various coals. Int J Coal Geol, 2007, 69: 229–242
- 35 Zhang Y X. Geochemical Kinetics. Boston: Princeton University Press, 2008. 224–227, 284–298, 418–434
- 36 Harpalani S, Chen G L. Estimation of changes in fracture porosity of coal with gas emission. Fuel, 1995, 74: 1491–1498
- 37 Harpalani S, Chen G. Influence of gas production induced volumetric strain on permeability of coal. Geotechnol Geol Eng, 1997, 15: 303– 325
- 38 Van Bergen F, Spiers C, Floor G, et al. Strain development in unconfined coals exposed to CO₂, CH₄ and Ar: Effect of moisture. Int J Coal Geol, 2009, 77: 43–53
- 39 Majewska Z, Ceglarska-Stefanska G, Majewski S, et al. Binary gas sorption/desorption experiments on a bituminous coal: Simultaneous measurements on sorption kinetics, volumetric strain and acoustic emission. Int J Coal Geol, 2009, 77: 90–102
- 40 Larsen J W. The effects of dissolved CO₂ on coal structure and properties. Int J Coal Geol, 2004, 57: 63–70
- 41 International Union of Pure and Applied Chemistry (IUPAC) Manual of Symbols and Terminology for Physico Chemical Quantities and Units. Butterworth: London, U.K., 1972
- 42 Dutta P, Harpalani S, Prusty B. Modeling of CO₂ sorption on coal. Fuel, 2008, 87: 2023–2036
- 43 Harpalani S, Prusty B, Dutta P. Methane/CO₂ sorption modeling for coalbed methane production and CO₂ sequestration. Energy Fuels, 2006, 20: 1591–1599
- 44 Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc, 1918, 40: 1361–1403
- 45 Zhang T J, Xu H J, Li S G, et al. The effect of temperature on adsorbing capacity of coal (in Chinese). J Chin Coal Soc, 2009, 34: 802–805
- 46 Ruckenstein E, Vaidyanathan A S, Youngquist G R. Sorption by solids with bidisperse pore structures. Chem Eng Sci, 1971, 26: 1305– 1318.
- 47 Clarkson C R, Bustin R M. The effect of pore structure and gas pres-

sure upon the transport properties of coal: A laboratory and modeling study. 2. adsorption rate modeling. Fuel, 1999, 78: 1345–1362

- 48 Shi J Q, Durucan S. A bidisperse pore diffusion model for methane displacement desorption in coal by CO₂ injection. Fuel, 2003, 82: 1219–1229
- 49 Cui X, Bustin R M, Dipple G. Selective transport of CO₂, CH₄, and N₂ in coals: Insights from modeling of experimental gas adsorption data. Fuel, 2004, 83: 293–303
- 50 Karacan C O, Mitchell G D. Behavior and effect of different coal microlithotypes during gas transport for carbon dioxide sequestration into coal seams. Int J Coal Geol, 2003, 53: 201–217
- 51 Hildenbrand A, Krooss B M, Busch A, et al. Evolution of methane sorption capacity of coal seams as a function of burial history—A case study from the Campine Basin, NE Belgium. Int J Coal Geol, 2006, 66: 179–203
- 52 Radlinski A P, Busbridge T L, Gray E, et al. Small angle X-ray scattering mapping and kinetics study of sub-critical CO₂ sorption by two Australian coals. Int J Coal Geol, 2009, 77: 80–89
- 53 Kelemen S R, Kwiatek L M. Physical properties of selected block argonne premium bituminous coal related to CO₂, CH₄, and N₂ adsorption. Int J Coal Geol, 2009, 77: 2–9
- 54 Suuberg E M, Otake Y, Yun Y, et al. Role of moisture in coal structure and the effect of drying upon the accessibility of coal structure. Energy Fuels 1993, 7: 384–392
- 55 Thimons E D, Kissell F N. Diffusion of methane through coal. Fuel, 1973, 52: 274–280
- 56 Gruszkiewicz M S, Naney M T, Blencoe J G, et al. Adsorption kinetics of CO₂, CH₄, and their equimolar mixture on coal from the black warrior basin, west-central alabama. Int J Coal Geol, 2009, 77: 23–33
- 57 Siemons N, Wolf K, Bruining J. Interpretation of carbon dioxide diffusion behavior in coals. Int J Coal Geol, 2007, 72: 315–324
- 58 Hua F M. Prevention of coal and gas outbursts (in Chinese). Min Ind Sec Environ Prot, 2002, 29: 58–61
- 59 Stevens S H, Kuuskraa V A, Spector D, et al. CO₂ sequestration in deep coal seams: Pilot results and worldwide potential. In: Riemer P, Eliasson B, Wokaun A, eds. Greenhouse Gas Control Technologies. Oxford: Elsevier, 1999. 175–180
- 60 Stevens S H, Spector D, Riemer P. Enhanced coalbed methane recovery using CO₂ injection: Worldwide resource and CO₂ sequestration potential. In: Proceedings of the International Oil & Gas Conference and Exhibition of the Society of Petroleum Engineers, 1998, November 2–6, Beijing, China, SPE Paper No. 48881, 489