

Evaluation of coal swelling-controlled CO₂ diffusion processes

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Abstract: CO₂ sequestration in deep and unmineable coalbeds is regarded as a viable option for carbon storage. CO₂ diffusion is a key parameter determining the effectiveness of sealing CO₂ in coal seams. By conducting laboratory tests of coal CO₂ desorption and unsteady gas diffusion theory model calculations, the desorption dynamics of Yaojie coal were studied under the condition of constant temperature and varied balance pressures, and the CO₂ diffusion coefficient was obtained using the non-steady diffusion model at different times. The results show that the higher the balance pressure is, the greater the diffusion coefficient is under the same conditions. As the pressure drops, the CO₂ diffusion coefficient gradually decreases as time increases, and the mass fraction of desorbed CO₂ has a linear relationship with the diffusion coefficient. It was observed that under high pressures, the diffusion coefficient initially increases and then gradually decreases. The non-steady CO₂ diffusion in Yaojie coal is related to CO₂-induced swelling and to the effect of dissolved CO₂ on the coal's structures and properties, especially under high-pressure conditions. The glass transition of coal containing CO₂ may be the governing factor leading to the nonlinear diffusion of CO₂ in coal.

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Keywords: carbon dioxide; desorption; diffusion; swelling

Introduction

Carbon dioxide (CO₂) storage (CCS) in unmineable coal seams is regarded as one of the possible approaches to mitigate the rapidly increasing CO₂ concentration in the atmosphere that has resulted from human activities since the Industrial Revolution. The injection of CO₂ into unmineable coal seams not only provides a solution for the long-term storage of CO₂, it also provides the added advantage of enhancing coalbed methane recovery (ECBM). Experimental studies of CO₂ sequestration have been conducted in many countries. When CO₂ is

injected, gas flow in the coal seam consists of diffusion in the coal matrix and transport in coal cleats, and Fick's diffusion model and revised as Darcy's law can be used to describe these processes, respectively. In particular, it has been shown that coal swells as it adsorbs CO₂, and this may lead to reductions in permeability, which will cause difficulties in storing CO₂ in the coal. The amount of coal matrix swelling due to CO₂ adsorption clearly depends on the phase condition of the adsorbing CO₂, since super-critical CO₂ adsorption-induced swelling is about two times higher than sub-critical CO₂ adsorption-induced swelling.^{1,2} The diffusion coefficient controlled by the

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Received June 23, 2013; revised October 19, 2013; accepted October 28, 2013

Published online at Wiley Online Library (wileyonlinelibrary.com). DOI: 10.1002/ghg.1390

concentration of CO₂ is normally far less than that controlled by the pressure gradient. Hence, the time of transfusion is negligible when compared with the time of diffusion, and the diffusion flow is the dominant factor affecting the gas transport process in coal. The rate of CO₂ diffusion in a coal seam determines the effectiveness of sealing up CO₂ for safe storage. For this purpose, many scholars have conducted studies in the area of CO₂ adsorption and diffusion in coal.

The findings of many scholars indicate that the diffusion of gas in coal can be described by the bidisperse diffusion model^{3,4} by considering diffusion in the form of surface diffusion in micropores as well as pore diffusion in medium-sized or larger pores. Based on the bidisperse diffusion mechanism, Wei *et al.*⁵ adopted the diffusion theory of Maxwell-Stephen with numerical calculations and drew conclusions about the diffusion features of a mixed gas containing CO₂ and CH₄. Water has a notable influence on gas diffusion in coal; where there is more water in the coal, the diffusion coefficient decreases considerably.⁶ Based on the second law of Fick, the effective diffusion coefficient of CH₄ and CO₂ would increase when the adsorption temperature increases, and the effective diffusion coefficient has a u-shaped relationship with the coal rank.⁷ The expansion of coal caused by the absorption of CO₂ has been confirmed by many experiments, and it has been concluded that the interaction of CO₂ and coal in microcosmic conditions can change the physical and molecule structures of coal.⁸⁻¹¹ Studies of the influence of the diffusion of CO₂ in coal are still limited, and the diffusion of gas in coal is always assumed to occur in a steady state, without considering the influence of the interactions between the gas and the coal.

In light of coalbed CO₂ sequestration, this paper investigates the desorption diffusion characteristics of CO₂ in coal samples from Yaojie. Using the unstable diffusion model and adsorption method, the diffusion coefficient and the characteristics and mechanism of

CO₂ diffusion in coal samples under different pressures were studied.

Sampling and analytical procedures

Coal samples

The initial and final analyses for the Argonne premium coal samples are presented in Table 1. As samples of coal arrived, the initial analysis was performed with a Thermogravimeter (5EMAG6600, Changsha, China) following ASTM standards. The random vitrinite reflectance (R_o) measurements were performed using a microscope photometer (Zeiss, Oberkochen, Germany), according to international standards (ISO 7404-5, 1984). The maceral composition of the coals was determined by incident light microscopy and oil immersion according to international standards.¹²

CO₂ desorption experiments

Experiments on the desorption of CO₂ gas were conducted in a desorption instrument (Fig. 1) using the coal seam methane content from rapid determination equipment (FM4WP-1). All of the samples were prepared by grinding and sieving to a size range of 2 mm. For the adsorption experiment, 50 g of coal was weighed and then sealed in the coal canister. After verifying that the canister was airtight, the samples were outgassed overnight in a 60°C thermostatic water bath under vacuum to a final pressure of 0.25 Pa. After these pre-treatment steps, CO₂ with a purity of 99.99% was charged into the canister to a set pressure, and then the canister was placed in a 30°C thermostatic water bath to reach adsorption equilibrium. After the equilibrium pressure was recorded, the coal canister valve was opened as quickly as possible, and once the pressure reached zero, the canister was rapidly connected to the desorption apparatus. The amount of gas desorbed over 2 h and the ambient and atmospheric pressures were also recorded. After 2 h, the canister valve was tightened

Table 1. Compositional analyses of Yaojie coal samples

Initial analysis					Maceral analysis			
moisture (wt %)	volatile (wt %)	ash (wt %)	fixed carbon (wt %)	vitrinite (wt %)	inertinite (wt %)	Exinite (wt %)	mineral (wt %)	vitrinite reflectance (%)R _{o,max}
1.01	30.10	3.39	66.85	48.68	47.35	2.85	1.14	0.93

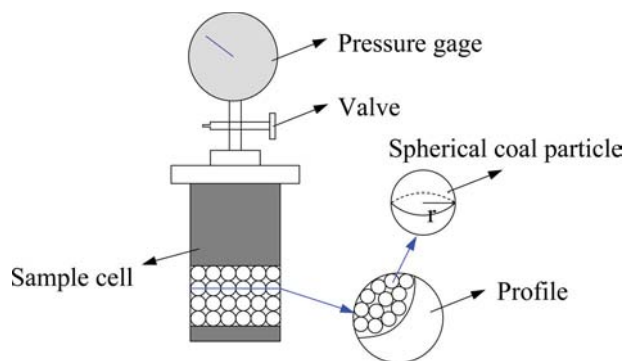


Figure 1. Model of coal particles and the parts of the experimental device.

as quickly as possible to perform the residual gas content measurement. This measurement consisted of placing the canister that underwent desorption for 2 h into a vacuum degassing pump in a 30°C bath. Gas chromatographs were then used to determine the components of the gas. After vacuum degasification, the sample in the vacuum canister was transferred into a ball-milling canister for a second grinding until the grain sizes of 80% of the coal sample were less than 0.25 mm. Then, the samples were outgassed and reground until outgassing no longer occurred. Then, the total gas content was calculated as the sum of the gas desorbed over 2 h and the residual gas.

Experimental method of adsorption

A volumetric system was used to measure adsorption isotherms. The volumes of the loading and adsorption cells are critical to the measurement of the adsorption capacity.^{13,14} The volumes of the two cells (loading and adsorption cells) and the free volume of the adsorption cell excluding coal were carefully measured using the helium expansion method. This volume was determined by the mass balance of compressed He between the loading and adsorption cells. Details of the method we employed have been published elsewhere.^{15,16}

Diffusion coefficient model

The process of gas diffusion in micropores, macropores, and fractures is controlled by various diffusion mechanisms. The pore size and pore structure of coal are related directly to the diffusion mechanisms and thus diffusivity. If slack coal is assumed to be a spheroidal coal particle and the gas concentration depends only on the spherical coal particle radius,

then the three-dimensional diffusion model can be expressed as follows:

$$\frac{\partial(rC)}{\partial t} = D \frac{\partial^2(rC)}{\partial r^2} \quad (1)$$

with the initial condition: $C|_{t=0} = f(r) = C_1$, and with the boundary condition: $C|_{r=a} = C_0$, where C is the gas concentration in the spheroidal coal particle (%); D is the diffusion coefficient (mm²/s); and r is the spherical coal particle radius (mm).

The diffusion model and diffusivity derivation of the three-dimensional sphere sample with a radius of a is as follows:¹⁷

$$F = \frac{M_t}{M_\infty} = 6 \frac{\sqrt{Dt}}{a\sqrt{\pi}} - 3 \frac{Dt}{a^2} \quad (2)$$

where M_t is the mass of desorbed CO₂ at a given time (ml), M_∞ is the total mass of CO₂ desorbed from spheroidal coal particles (ml), and a is the average radius of the spheroidal coal particles (mm).

If D depends on time, then

$$F = \frac{6}{\sqrt{\pi}} \frac{\sqrt{\int_0^t D dt'}}{a} - 3 \frac{\int_0^t D dt'}{a^2} \quad (3)$$

If we assume that $x = \frac{\sqrt{\int_0^t D dt'}}{a}$, equation (3) is solved, and then we obtain:

$$x = \frac{1}{\sqrt{\pi}} - \sqrt{\frac{1}{\pi} - \frac{F}{3}} \quad (4)$$

If we assume that $y = a^2 x^2$, then, the diffusion coefficient D at a given time can be obtained as:

$$D = \frac{dy}{dt} = \frac{dy}{dx} \frac{dx}{dF} \frac{dF}{dt} \quad (5)$$

The relationship between t and F can be obtained by using polynomial fitting. Then, the curve fitting formula and Eqn (4) are inserted into Eqn (5), and we can obtain the D as a function of time t .

Results and discussion

The equilibrium pressure of desorption ranges from low (0.85 MPa, 1.74 MPa, 2.20 MPa) to high (7.92 MPa) at 30°C. The dynamic curve of Yaojie coal desorption is shown in Fig. 2.

As the balance pressure of adsorption increases, CO₂ desorption increases over 120 min. The desorption curve can be divided into two phases, one with high

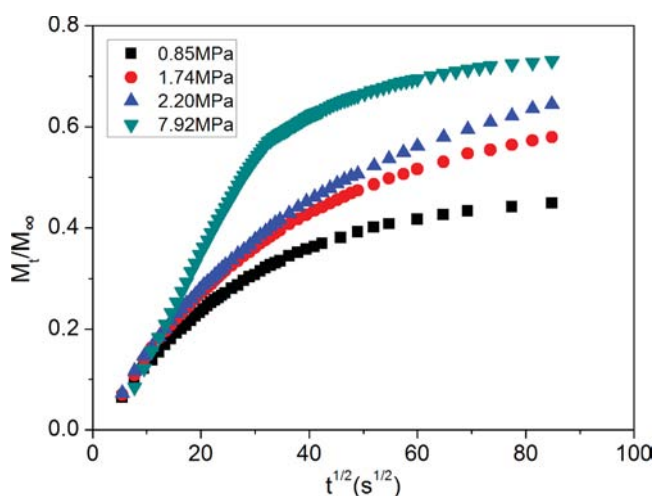


Figure 2. Desorption kinetics curves for CO₂ at different pressures.

desorption and the other with low desorption. The desorption curve at low pressure is relatively smooth, whereas two distinctive parts can be observed at high pressure.

The migration process of gas molecules in coal can be expressed as:¹⁸

$$F = \frac{M_t}{M_\infty} = k_1 \sqrt{t} + k_2 t \approx kt^n \quad (6)$$

where K is a constant and n is a diffusion index number.

Ritger *et al.*¹⁸ provided a relationship between the type of diffusion and the value of n for different coal geometrical characteristics. For spherical coal particles, when $n = 0.43$, this relationship follows Fick's diffusion model (Fig. 3), and when the coal particles are at low pressure, the Yaojie coal diffusion index number follows Fick's diffusion law. When the coal particles are at high pressure, the diffusion index number is $n > 0.43$, and the relationship follows anomalous diffusion, indicating that the diffusion of CO₂ is determined by not only the concentration gradient but also other influential coefficients at high CO₂ pressures.

Based on the calculation model for the diffusion coefficient, the relationship between the CO₂ diffusion time and the diffusion coefficient at different pressures can be drawn as shown in Fig. 4. The diffusion coefficient of CO₂ is $1.83 \times 10^{-6} - 9.08 \times 10^{-5} \text{ mm}^2/\text{s}$ at low pressure. As time increases, the value of the diffusion coefficient D declines rapidly in the initial phase and then gradually flattens out. The value of the

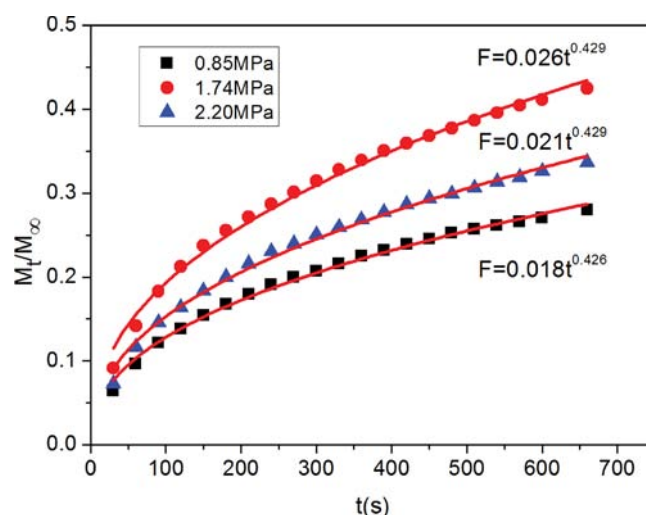


Figure 3. Power relation equations of time versus CO₂ mass fraction (F).

high pressure diffusion coefficient of CO₂ is $4.76 \times 10^{-6} - 1.91 \times 10^{-4} \text{ mm}^2/\text{s}$, which is two orders of magnitude greater than that at low pressure.

Figure 5 and Table 2 show a linear relationship between the mass fraction of CO₂ and the diffusion coefficient D at low pressure. As CO₂ desorption from coal occurs, D drops gradually, and its variation rate also drops as the desorption equilibrium pressure increases. The adsorption of CO₂ would cause the coal to swell. At high pressure, the numerical value of D as a function of the mass coefficient of CO₂ desorption shows a near parabolic shape, which increases at first and then decreases with increases in CO₂ desorption. It is possible that the apparent concentration dependence of the diffusion coefficient is a response to coal swelling: the more the coal swells, the greater the number of relaxing volume elements becomes.

The transport of gas in coal may be influenced by temperature, pressure, moisture content, ash, coal rank, and maceral components.¹⁹ The pore structure of coal directly influences gas diffusion. Considering the pore size and mean free path of a gas molecule, the multi-disperse gas diffusion mechanisms in coal can be classified as self-diffusion, transition diffusion, Knudsen diffusion and surface diffusion^{7,20} Coal has greater affinity for CO₂ than for CH₄, thus leading to greater adsorption of CO₂ than CH₄ at the same pressure. The majority of CO₂ is thought to be adsorbed onto the surface of micropores in the coal matrix. However, the interactions between CO₂ and coal are considered to be complex. Pan and Connell²¹

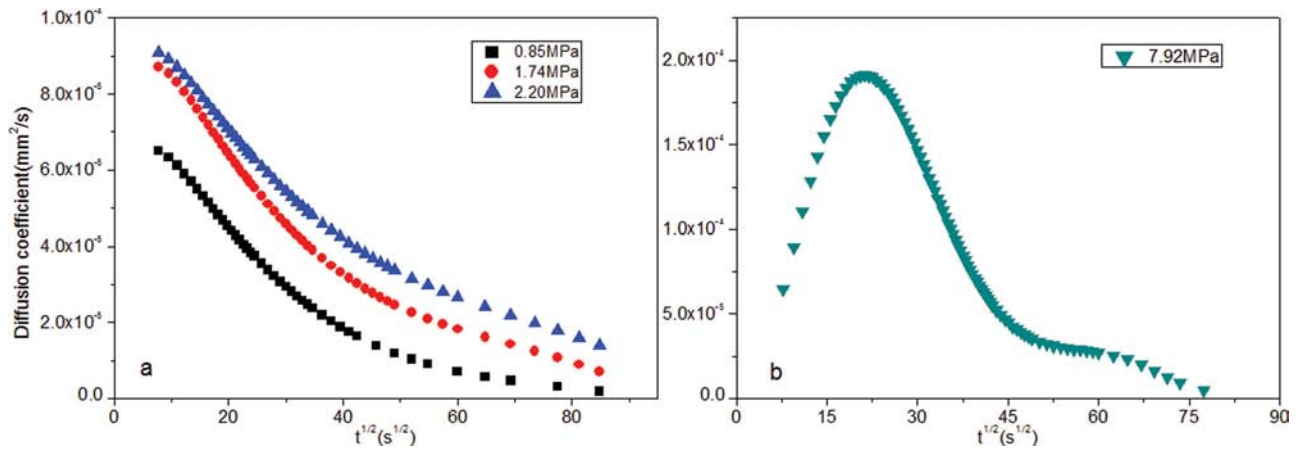


Figure 4. Relation between CO₂ diffusivity and square root of time for different pressures.

suggested that coal swells as a direct result of gas adsorption and gas pressure. Chemically, coal's structure, excluding anthracites and high rank coals that are graphitic, is generally viewed as a macro-molecular network of cross-linked (chemically bonded and physically entangled) chains or clusters of aromatic rings.^{22,23} A CO₂ molecule placed between the polymer chains of coal partly disrupts the original structure if the sorption takes place in locations where the available volume between the chains is smaller than the actual volume of the CO₂ molecule.²⁴

The swelling of coal due to a penetrant can be referred to as an increase in the volume occupied by the coal as a result of the visco-elastic relaxation of its highly cross-linked macromolecular structure.²⁵ Although the macro-molecular network structure does not dissolve, the penetrant is almost universally

termed a solvent. Thus, a coal-coal hydrogen bond or any other weaker bond will be replaced by a coal-solvent bond only if the new coal solvent bond is thermodynamically favored. If intra-molecular bonding in the coal contributes significantly to its structural integrity, then strong coal-solvent bonding should disrupt such a structure, which results in coal swelling. Mastalerz *et al.*¹⁰ found that absorption bands at 2333 cm⁻¹ and at 657 cm⁻¹ increased in intensity as the CO₂ pressure increased (Fig. 7). The diffusion process is closely associated with the dynamic volumetric swelling of coal. The increase in volume of a coal sample is a function of time. Only the adsorbent that has diffused into the bulk structure induces coal swelling.

Figure 6 shows the results of the reproducibility tests of the CO₂ single-component desorption experiments.

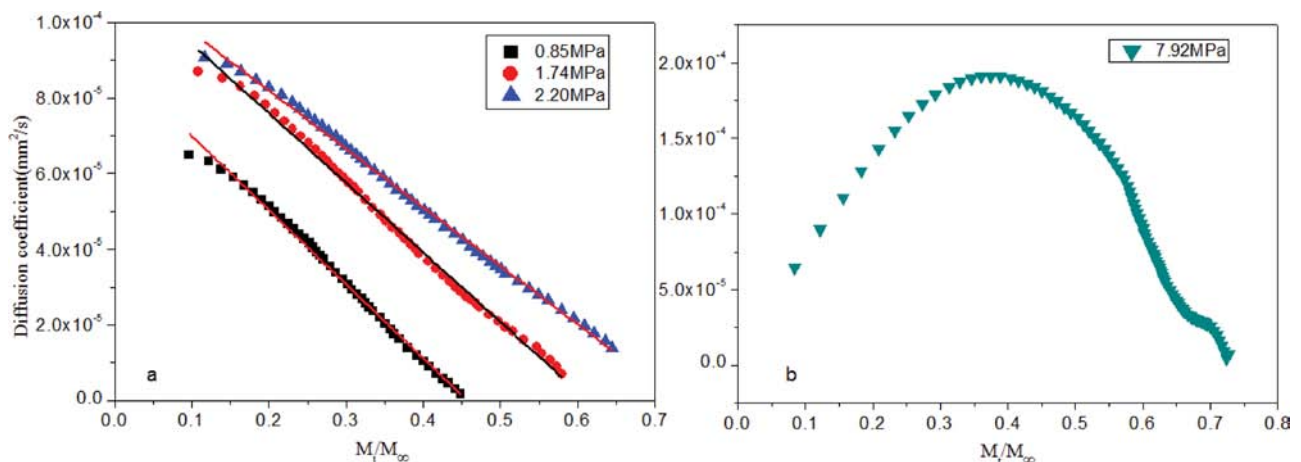


Figure 5. Relation between diffusivity and the cumulative mass fraction of desorbed CO₂ in coal.

Table 2. Linear equations for D as a function of the CO₂ mass fraction (F), and the correlation coefficient (R^2).

Experimental balance pressure (MPa)	Linear relation	R^2
0.85	$D = -1.95 \times 10^{-4}F + 8.95 \times 10^{-5}$	0.995
1.74	$D = -1.83 \times 10^{-4}F + 1.13 \times 10^{-4}$	0.996
2.20	$D = -1.54 \times 10^{-4}F + 1.13 \times 10^{-4}$	0.997

The tests were conducted three times on the same coal samples after thorough evacuation and removal of the adsorbed gas. It is obvious that for the follow-up experiments, slightly higher desorption values were achieved. Generally, follow-up experiments on the same sample resulted in desorption values of approximately 3–5% higher than in the first experiment (Fig. 6(a)). This phenomenon has also been observed by other tests.²⁶

At the pressures necessary for carbon dioxide sequestration, dissolution in coal can exceed adsorption. More CO₂ is dissolved as the coal rank decreases.⁸ Structural changes induced by this dissolution process include swelling, microcavity formation, and the phase transition from the glassy to the rubbery state, requiring rearrangement of the chain segments. Yaojie coal experiences different structural changes under the reproducibility after CO₂

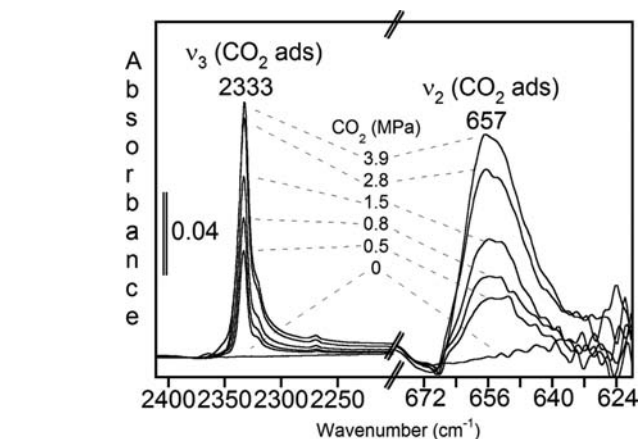
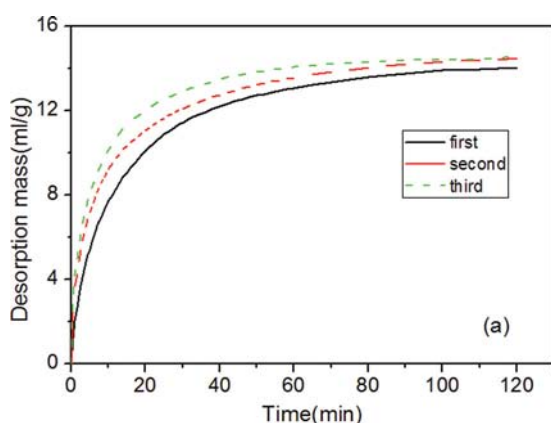


Figure 7. Graph of *in situ* ATR-FTIR spectra of sorbed CO₂ on a vitrain lithotype from Lower Block (LB) as a function of increasing CO₂ pressure (0.5, 0.8, 1.5, 2.8, and 3.9 MPa).

desorption, which could be attributable to increases in adsorption sites or slower dissolution CO₂ desorption. However, the high-pressure CO₂ sorption isotherms appear to have two peaks. A similar result was obtained in RWTH Aachen University experimental and NETL tests (Fig. 6(b)).^{13,27} In the standard excess sorption isotherms that assume a constant void volume, the effects of the free volume may reveal themselves in the form of local maxima and minima. There is a dramatic decrease in the coal softening

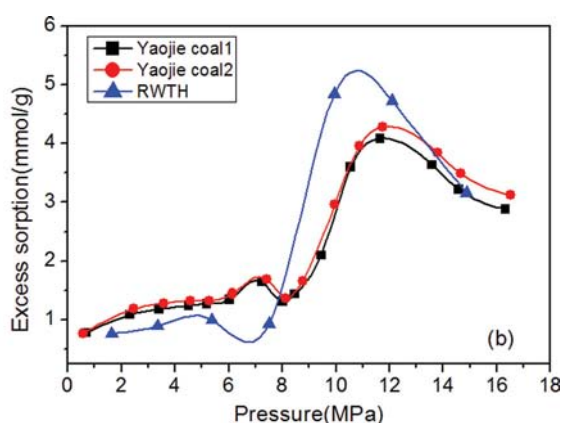


Figure 6. (a) CO₂ reproducibility test performed on Yaojie coal. The same coal powder was used for a follow-up test after evacuation for 36 h at 60 °C. (b) The RWTH laboratory measured CO₂ excess sorption isotherms for moisture-equilibrated Argonne coal at 55 °C and pressures up to 15 MPa using manometric equipment. The data from the RWTH laboratory also show an increase in excess sorption up to 8 MPa. After 8 MPa, the excess sorption for RWTH laboratory increases sharply and then begins to decrease after 12 MPa. Effects of coal volume changes on sorption capacity under supercritical CO₂ conditions for Yaojie coal and Pocahontas No. 3 coal.

temperature under supercritical CO₂, and changes in the solubility of CO₂ in coal due to density fluctuations near the critical isochore could play a role in either sorption or excess volume changes.^{28,29} The structural changes and phase transition of coal lead to anomalous CO₂ desorption and adsorption from Yaojie coal.

Unswollen coal is in a glassy state (not in the lowest energy state) under typical reservoir conditions. The temperature required to cause a transition in coal from the glassy to rubbery state is the glass transition temperature.²⁹ Analysis of the effects of high-pressure CO₂ on the macromolecular structure of coal shows that the glass transition temperature of coal decreases significantly with CO₂ pressure,^{8,30} indicating that high-pressure CO₂ diffuses through the coal matrix, causing significant plasticization effects and changes in the macromolecular structure of coal. The glass transition temperature of Wyodak coal is 395.1 K and 349.2 K at CO₂ pressures of 0 MPa and 3 MPa³¹, respectively. The structural changes induced during this process include swelling, microcavity formation and primary phase transition requiring rearrangements of each chain segment. Compared to the glassy state of coal, in the rubbery state, the crosslinked polymeric chains can move separately and rapidly by a process involving the rotation of main chain bonds so that equilibrium is obtained almost instantaneously. Thus, the initial penetrant volume will be less than the equilibrium volume fraction. CO₂ diffusion in the rubber state is faster than that in the glass state of coal.^{24,32}

If diffusion is controlled by the volume fraction gradient between the center and the outside of the glassy state coal matrix, the diffusion mechanism is Fickian. The CO₂ diffusion coefficient linearly decreases as the coal matrix shrinks after CO₂ desorption occurs at low pressure. High-pressure CO₂-saturated coal can easily develop into a rubbery state at a lower glass transition temperature. If the transport is controlled by a stress gradient induced by the penetration of molecules, the diffusion mechanism is anomalous. At this early stage, CO₂ diffusion speed increases quickly with time. The partly free volume is frozen with CO₂ desorption and reduction at high pressure, and the coal transforms into the glassy state once again. The CO₂ diffusion coefficient decreases linearly with time, and is greater than the diffusion coefficient at lower pressure. The interactions of coal with CO₂ concerning the mechanisms of diffusion, the strength

of interactions, and the irreversibility of uptake for the permanent disposal of CO₂ into coal fields are complicated. Further research is needed to determine the mechanism of CO₂ diffusion in coal.

Conclusions

The CO₂ diffusion coefficient (D) was investigated under unsteady state conditions using coal samples from Yaojie. Under identical conditions, the diffusion coefficient increases with the desorption equilibrium pressure. The value of D is $1.83 \times 10^{-6} - 9.08 \times 10^{-5} \text{ mm}^2/\text{s}$ at low pressure and $4.76 \times 10^{-6} - 1.91 \times 10^{-4} \text{ mm}^2/\text{s}$ at high pressure, which is two orders of magnitude larger than that at low pressure. As the desorption time increases, the value of D decreases rapidly in the initial phase, and then it levels off gradually. The mass fraction of desorbed CO₂ and the diffusion coefficient have a linear relationship at low pressure and a parabolic relationship at high pressure. The unsteady gas diffusion in Yaojie coal is a result of CO₂ adsorption swelling, particularly at high pressures. Coal containing CO₂ undergoes the glass transition to form a high-elastic state, which is most likely the governing factor leading to abnormal and non-linear gas diffusion. The structural changes and phase transition of coal lead to CO₂ desorption and anomalous adsorption from Yaojie coal.

Acknowledgements

This research was financially supported by the Natural Science Foundation for the Youth of China (No. 41202118) and the Fundamental Research Funds for the Central Universities (No. 2012QNB03) and the open fund of The Key Laboratory of Coal-based CO₂ Capture and Geological Storage, Jiangsu Province (2011KF04).

References

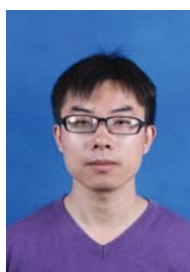
1. Jasinge D, Ranjith PG, Choi SK and Fernando J, Investigation of the influence of coal swelling on permeability characteristics using natural brown coal and reconstituted brown coal specimens. *Energy* **39**(1):303–309 (2012).
2. Perera MSA, Ranjith PG, Choi SK and Airey D, The effects of sub-critical and super-critical carbon dioxide adsorption-induced coal matrix swelling on the permeability of naturally fractured black coal. *Energy* **36**(11): 6442–6450 (2011).
3. Cui XJ, Bustin RM and Dipple G, Selective transport of CO₂, CH₄, and N₂ in coals: insights from modelling of experimental gas adsorption data. *Fuel* **83**(3): 293–303 (2004).

4. Shi SQ and Durucan S, A bidisperse pore diffusion model for methane displacement desorption in coal by CO₂ injection. *Fuel* **82(10)**:1219–1229 (2003).
5. Wei XR, Wang GX and Massarotto P, Numerical simulation of multicomponent gas diffusion and flow in coals for CO₂ enhanced coalbed methane recovery. *Chem Eng Sci* **62(16)**:4193–4203 (2007).
6. Pan ZJ, Connell LD and Camilleri M, Effects of matrix moisture on gas diffusion and flow in coal. *Fuel* **89(11)**:3207–3217 (2010).
7. Zhang DF, Cui YJ and Li SG, Adsorption and diffusion behaviours of methane and carbon dioxide on various rank coals. *Journal of China Coal Society* **36(10)**:1693–1698 (2011).
8. Larsen JW, The effects of dissolved CO₂ on coal structure and properties. *Int J Coal Geol* **57(1)**:63–70 (2004).
9. Goodman AL, Favors RN and John WL, Argonne coal structure rearrangement caused by sorption of CO₂. *Energ Fuel* **20(6)**:2537–2543 (2006).
10. Mastalerz M, Goodman A and Chirdon D, Coal litho types before, during, and after Exposure to CO₂: Insights from Direct Fourier Transform Infrared Investigation. *Energ Fuel* **26(6)**:3586–3591 (2012).
11. Peppas NA, Swelling and dissolution of the macromolecular structure of bituminous Coals. *Polymer* **38(13)**:3425–3427 (1997).
12. Taylor GH, Teichmuller M, Davis A, Diessel CFK, Littke R and Robert P, *Organic petrology*. Gebruder Borntraeger, Berlin, 704 pp (1998).
13. Romanov V, Soong Y and Schroeder K, Volumetric effects in coal sorption capacity measurements. *Chem Eng Technol* **29(3)**:368–374 (2006).
14. Sakurovs R, Day S and Weir S, Causes and consequences of errors in determining sorption capacity of coals for carbon dioxide at high pressure. *Int J Coal Geol* **77(1)**:16–22 (2009).
15. Fitzgerald JE, Pan Z, Sudibandriyo M, Robinson JrRL, Gasem KAM and Reeves S, Adsorption of methane, nitrogen, carbon dioxide and their mixtures on wet Tiffany coal. *Fuel* **84(18)**:2351–2363 (2005).
16. Busch A and Gensterblum Y, CBM and CO₂-ECBM related sorption processes in coal: a review. *Int J Coal Geol* **87(2)**:49–71 (2011).
17. Jian X, Guan P and Zhang W, Carbon dioxide sorption and diffusion in coals: Experimental investigation and modelling. *Science China Earth Science* **55(4)**:633–643 (2012).
18. Ritger PL and Peppas NA, Transport of penetrants in the macromolecular structure of coals. *Fuel* **66(6)**:815–826 (1987).
19. Mathews JP, Van duin ACT and Chaffee AL, The utility of coal molecular models. *Fuel Process Technol* **92(4)**:718–728 (2011).
20. He XQ and Nie BS, Diffusion mechanism of porous gases in coal seams. *Journal of China University of Mining and Technology* **30(1)**:1–4 (2001).
21. Pan Z and Connell LD, A theoretical model for gas adsorption-induced coal swelling. *Int J Coal Geol* **69(4)**:243–252 (2007).
22. Romanov V, Coal chemistry for mechanical engineers: from macromolecular thermodynamics to reservoir simulation. *Energ Fuel* **21(3)**:1646–1654 (2007).
23. Li KS and Zhou AN, Progress of coal-base material researches. *Poly Mat Sci Eng* **17(4)**:19–22 (2001).
24. Mazumder S, Vermolen F and Bruining J, Analysis of a model for anomalous-diffusion behaviour of CO₂ in the macromolecular-network structure of coal. *SPE Journal* **16(5)**:856–863 (2011).
25. Suuberg EM, Comments regarding the use of coal swelling to count hydrogen-bond cross-links in coals. *Energ Fuel* **11(5)**:1103–1104 (1997).
26. Busch A, Gensterblum Y and Krooss BM, Methane and CO₂ sorption and desorption measurements on dry Argonne premium coals: pure components and mixtures. *Int J Coal Geol* **55(4)**: 205–224 (2003).
27. Goodman AL, Busch A, Bustin RM, Chikatamarla L, Day S, Duffy GJ *et al.*, Inter-laboratory comparison II: CO₂ isotherms measured on moisture-equilibrated Argonne premium coals at 55 degrees C and up to 15 MPa[J]. *Int J Coal Geol* **72(3)**:153–164 (2007).
28. Romanov VN, Goodman AL and Larsen JW, Errors in CO₂ adsorption measurements caused by coal swelling. *Energ Fuel* **20(1)**: 415–416 (2006).
29. Mackinnon AJ and Hall PJ, Observation of first- and second-order transitions during the heating of argonne premium coals. *Energ Fuel* **9(1)**:25–32 (1996).
30. Day S, Fry R and Sakurovs R, Swelling of Australian coals in supercritical CO₂. *Int J Coal Geol* **74(1)**:41–52 (2008).
31. Mirzaeian M and Hall PJ, The Interactions of coal with CO₂ and Its effects on coal structure. *Energ Fuel* **20(5)**:2022–2027 (2006).
32. Govindjee S and Simo JC, Coupled stress-diffusion: Case II. *J Mech Phys Solids* **41(5)**:863–887 (1993).



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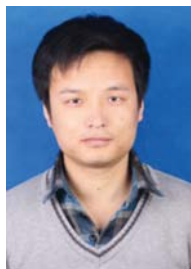
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