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Wei Li

National Engineering Research Center for Coal Gas control

Yuanping Cheng

National Engineering Research Center for Coal Gas control

Liguo Wang

National Engineering Research Center for Coal Gas control

Junhui Mo

National Engineering Research Center for Coal Gas control

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A STUDY OF COAL SWELLING-CONTROLLED CO₂ DIFFUSION PROCESSES

Wei Li^{1,2,3}, Yuanping Cheng^{1,2}, Ligu Wang^{1,2} and Junhui Mo^{1,2}

ABSTRACT: CO₂ sequestration in deep and unmineable coalbeds is regarded as a viable option for carbon storage. CO₂ diffusion is a key assessment parameter to effectively seal CO₂ in the coal seam. By conducting laboratory tests of coal CO₂ desorption and unsteady gas diffusion theory model calculation, the desorption dynamic characteristics of Yaojie coal was studied under the condition of constant temperature and different balance pressure, and the CO₂ diffusion coefficient was obtained through the non-steady diffusion model at different time. The results show that the higher the balance pressure, the greater the diffusion coefficient under the same condition. As the pressure drops, the CO₂ diffusion coefficient gradually decreases as time increases, and the CO₂ desorption mass fraction has a linear relationship with the diffusion coefficient. It is observed that under high pressures, the diffusion coefficient initially increases, then gently decreases. The non-steady CO₂ diffusion in Yaojie coal relates to the CO₂ swelling effect of the coal, especially in high pressure condition, the glass transition of coal with CO₂ maybe the governing factor leading to the nonlinear diffusion of CO₂ in coal.

INTRODUCTION

Carbon dioxide (CO₂) storage (CCS) in unmineable coal seams is regarded as one of the possible approaches to mitigate the ever increasing CO₂ concentration in the atmosphere resulting from human activities since the industrial Revolution. Injection of CO₂ into unmineable coal seams not only provides a solution for long term storage of CO₂ but also provides the added advantage of Enhancing Coalbed Methane Recovery (ECBM). Experimental studies of CO₂ sequestration were conducted in many countries. When CO₂ is injected, gas flow in the coal seam consists of the diffusion in coal matrix and the transport in coal cleat, of which the Fick diffusion model and Dracy's law can be used to describe these processes respectively. The diffusion coefficient controlled by concentration is normally far less than that controlled by pressure gradient, hence the time of transfusion is negligible when compared with the time of diffusion, the diffusion flow is the dominant coefficient of the gas transport process in the coal sample. The rate of CO₂ diffusion in the 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.

Findings by many scholars indicated that the diffusion of gas in coal could be adopted by the description of Bidisperse diffusion model(Cui, *et al.*, 2004; Shi, *et al.*, 2003), by considering the diffusion in the form of surface diffusion in micropore as well as the pore diffusion in middle or larger pores; Based on the diffusion mechanism of Bidisperse, Wei, *et al.*,(2007) adopted the diffusion theory of Maxwell-Stephen with numerical calculation, and draw conclusion of the diffusion feature of mixed gas CO₂ and CH₄; Pan, *et al.*, (2010) discovered the notable influence of water and gas diffusion in coal, with more water in coal the diffusion coefficient drops off remarkably; Based on the second law of Fick, Zhang, *et al.*,(2010) concluded that the effective diffusion coefficient of CH₄ and CO₂ would increase when the adsorption temperature goes up, and the effective diffusion coefficient has a relationship of "U" with the coal rank; the expansion of coal caused by the absorption of CO₂ was confirmed by many experiments, and it was concluded the interaction of CO₂ and coal in microcosmic, the physical and molecule structure could be changed by this interaction. Studies of the diffusion influence of CO₂ in coal are still limited, and the gas diffusion in coal is always regarded as the diffusion in steady state, without considering the influence of the diffusion of gas and coal interaction.

In view of the coal and CO₂ outburst hazard in Yaojie Mine, 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 was studied as well as the diffusion characteristics and mechanism of CO₂ in coal sample under different pressures.

¹ National Engineering Research Center for Coal Gas control, M: +86 (0)13952231131

² Faculty of Safety Engineering

³ The Key Laboratory of Coal-based CO₂ Capture and Geological Storage, China University of Mining and Technology, Xuzhou, Jiangsu 221116, China

SAMPLING AND ANALYTICAL PROCEDURES

Coal samples

In this study, Haishiwan coal was used as an adsorbent. The proximate and ultimate analyses for the Argonne premium coal samples are presented in Table 1.

Table 1 - Compositional analyses of Haishiwan coal samples

Proximate analysis				Maceral analysis				
moisture (wt %)	volatile (wt %)	ash (wt %)	fixed carbon (wt %)	vitrinite (wt %)	inertinite (wt %)	Exinite (wt %)	mineral (wt %)	vitrinite reflectance (%) R_{omax}
1.01	30.10	3.39	66.85	48.68	47.35	2.85	1.14	0.93

CO₂ desorption experiments

Experiments on the desorption of CO₂ gas were conducted in a desorption instrument 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. A certain amount of coal (50 g) for the adsorption experiment was weighed and then sealed in the coal canister. After verifying the air tightness of the canister, the samples were outgassed overnight in a 60°C thermostatic water bath under vacuum to a final pressure of 0.25 Pa. After these pretreatment steps, CO₂ with a purity of 99.99% was charged into the canister to a certain pressure, and then the canister was placed into a 30°C thermostatic water bath to reach adsorption equilibrium. After recording the equilibrium pressure, 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 two hours and the ambient and atmospheric pressures were also recorded. After two hours, the canister valve was tightened as quickly as possible to perform the residual gas content measurement. This measurement consists of placing the canister that undergone desorption for two hours into 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 there was no longer outgassing. Then, the total gas content was calculated as the sum of the two hours of desorbed gas and the residual gas.

DIFFUSION COEFFICIENTS MODEL

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. If the slack coal is assumed as spheroidal coal particle, and the gas concentration only depends 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: $C|_{t=0} = f(r) = C_1$,

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); r , the spherical coal particle radius(mm).

The diffusion model and diffusivity derivation of the three-dimensional sphere sample with radius of a can be seen in Jian, *et al.*, (2012).

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

where M_t is the mass of the spheroidal coal particles desorption of CO_2 at a given time (ml), M_∞ is the mass of spheroidal coal particles after complete desorption of CO_2 for a very long time(ml), a is the average radius of spheroidal coal particle(mm).

If D depends on time, then

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

Assume that; $x = \frac{\sqrt{\int_0^t D dt'}}{a}$, Eq. (3) is solved, then:

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

If $y = a^2 x^2$, then, the diffusion coefficients 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. The curve fitting formula and Eq. (4) are input into Eq. (5), we can obtain the D that changes with time t .

RESULTS AND DISCUSSIONS

CO_2 desorption

The balance pressures of desorption range from low (0.85 MPa, 1.74 MPa, 2.20 MPa) to high pressure (7.92 MPa) at 30°C , the dynamic curve of Yaojie coal desorption is shown in Figure 2.

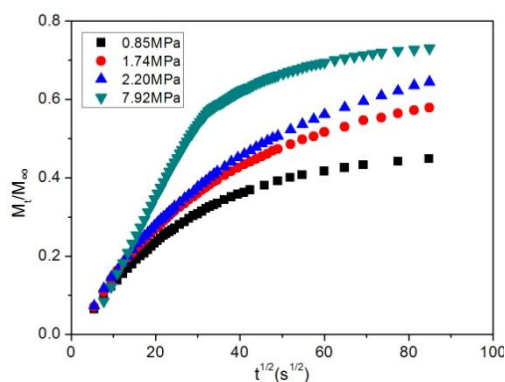


Figure 1 - Desorption kinetic curves of CO_2 at different pressures

As the balance pressure of adsorption increases, the CO_2 desorption becomes larger in 120 min, the curve of desorption could be divided into two phases, one is high desorption and the other in low desorption phase. The desorption curve at low pressure is relatively smooth, whilst two distinctive parts can be observed at the high pressure.

As explained in Section two, the migration process of gas molecule in coal can be expressed as:

$$F = \frac{M_t}{M_\infty} = k_1\sqrt{t} + k_2t \approx kt^n \tag{6}$$

where: K is constant; n is diffusion indexed number.

Ritger *et al.* (1987) provided a relationship of diffusion type and n in different coal geometrical characteristics, for sphere coal particle, when $n=0.43$, it follows Fick's diffusion model (Figure 2), when it was at low pressure, the Yaojie coal diffusion index number $n \approx 0.43$, which follows Fick's diffusion law; when it was in high pressure, the diffusion index number $n > 0.43$, it follows anomalous diffusion, indicating that the diffusion of CO_2 is not only determined by the concentration gradient, but also other influential coefficients at high CO_2 pressure.

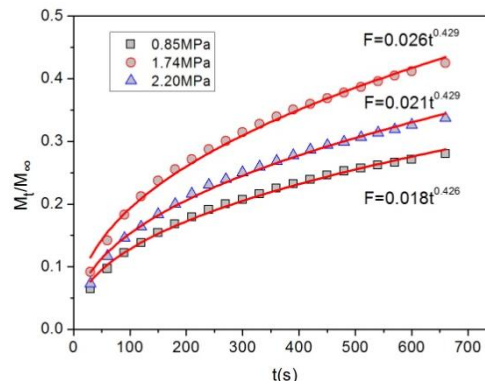


Figure 2 - Power relation equations of time versus CO_2 mass fraction (F)

Based on the calculation model of diffusion coefficient in section 1.3, the relationship of CO_2 diffusion time and diffusion coefficient in different pressures can be drawn as in Figure 3. Diffusion coefficient of CO_2 is $1.83 \times 10^{-6} - 9.08 \times 10^{-5} \text{ mm}^2/\text{s}$ in the low pressure, which is approximately the same result as reported by Zhang *et al.*(2010). As time increases, the value of diffusion coefficient D declines rapidly in the initial phase and then gradually flats out. The high pressure diffusion coefficient of CO_2 is $4.76 \times 10^{-6} - 1.91 \times 10^{-4} \text{ mm}^2/\text{s}$, the value of D in high pressure is one order of magnitude greater than that in low pressure.

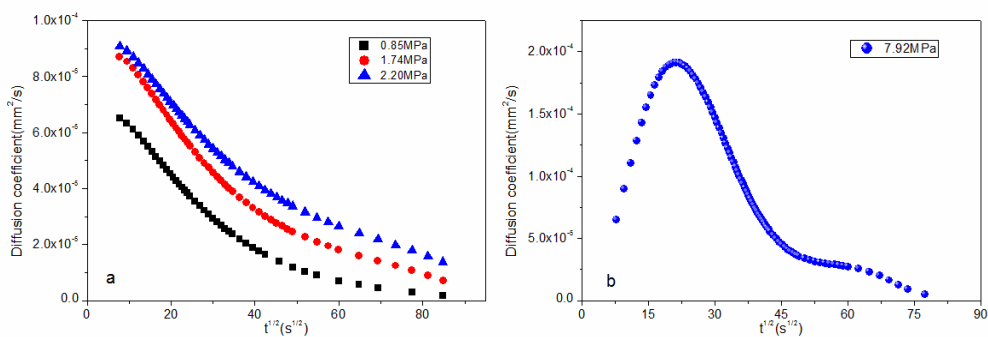


Figure 3 - Relation between CO_2 diffusivity and square root of time for different pressure

Figure 4 and Table 2 show a linear relationship between the mass fraction of CO_2 and diffusion coefficient D in low pressure. As CO_2 desorption takes place from coal, D drops gradually, and its variation rate also drops as the desorption equilibrium pressure increases. The adsorption of CO_2 would cause swelling of coal, and in high pressure, the numerical value of D with the mass coefficient of CO_2 desorption shows a near parabolic shape, which increases at first and then decreases with the increase of CO_2 desorption. Due to the high reaction rate of CO_2 with coal, such as the shape memory effect, the adsorption swelling effect etc, the interaction of coal with CO_2 appears to influence or even control CO_2 desorption from coal.

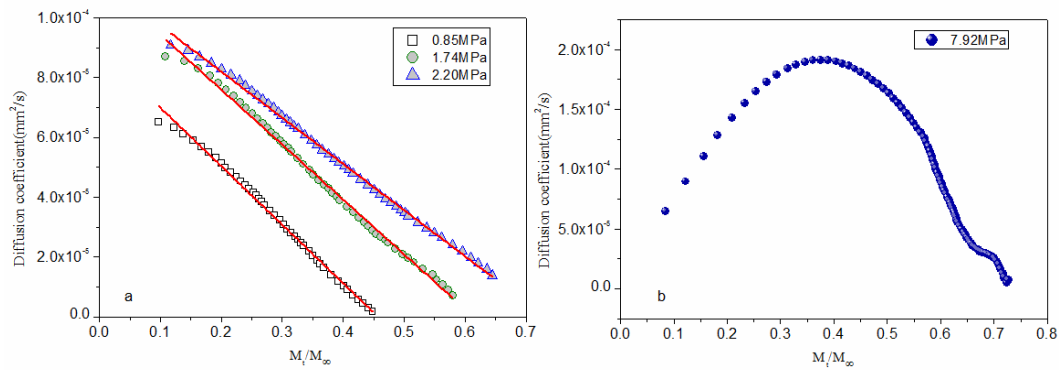


Figure 4 - Relation between diffusivity and mass fraction of CO₂ cumulative desorption in coal

Table 2 - Linear relation equations of D versus 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

Discussion of CO₂ diffusion mechanism

The transport of gas in coal may be influenced by temperature, pressure, moisture content, ash, coal rank, and maceral components (Mathews, *et al.*, 2011). The pore structure of coal directly influences gas diffusion. Considering the pore size and mean free path of gas molecule, the multi-disperse gas diffusion mechanisms in coal can be classified as self-diffusion, transition diffusion, Knudsen diffusion and surface diffusion (He, *et al.*, 2001; Zhang, *et al.*, 2011).

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 Connell (2007) suggested that coal swells as a direct result of gas adsorption and gas pressure. Chemically, coal structure, excluding anthracites and the high rank coals that are graphitic in their nature, is generally viewed as a macromolecular network of cross-linked (chemically bonded and physically entangled) chains or clusters of aromatic rings (Romanov, 2007; Li and Zhou, 2001). A CO₂ molecule placed between the polymer chains of coal disrupts partly 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 (Mazumder, *et al.*, 2011).

The swelling of coal by 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 (Suuberg, 1997). Although the macro molecular network structure does not dissolve, the penetrant is almost universally termed as 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 favoured. 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 (Larsen, 2004). Mastalerz *et al.* (2012) found that these absorption bands increased in intensity as CO₂ pressure increased (Figure 5), The diffusion process is closely interlinked to 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.

Unswollen coal is in a glassy state (not in the lowest energy state) under typical reservoir conditions. The temperature required to cause a transition from glass to rubber is the glass transition temperature (Mackinnon and Hall, 1996). High-pressure CO₂ on the macromolecular structure of coal shows that the glass transition temperature of coal decreases with CO₂ pressure significantly (Larsen, 2004; Day, *et al.*, 2008), 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 are 395.1 K and 349.2 K at various CO₂ pressures of 0 MPa and 3 MPa

(Mirzaeian and Hall, 2006), respectively. Structural changes induced during this process include swelling, microcavity formation and primary phase transition requiring rearrangements of each chain segments. As compared to the glassy state of coal, in the rubbery state the crosslink polymeric chains can move separately and rapidly by a process involving rotation of main chain bonds so that the equilibrium is obtained almost instantaneously. Thus, the initial penetrant volume will be less than the equilibrium volume fraction, CO₂ diffusion coefficient in rubber state is faster than that in the glass state of coal (Govindjee and Simo, 1993; Mazumder, *et al.*, 2011).

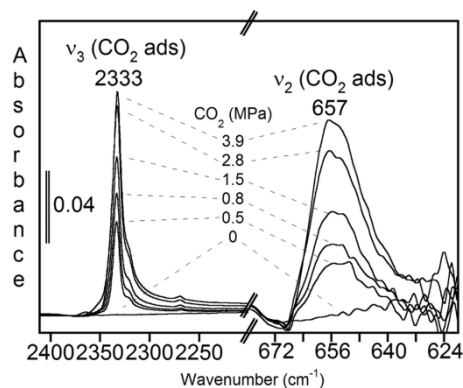


Figure 5 - Graph of *in situ* ATR-FTIR spectra of sorbed CO₂ on vitrain lithotype from Lower Block (LB) as a function of increasing CO₂ pressure (0.5, 0.8, 1.5, 2.8, and 3.9 MPa). (Mastalerz, *et al.*, 2012)

If the diffusion is controlled by the volume fraction gradient between the centre and the outside of the glass state coal matrix, the diffusion mechanism is Fickian. CO₂ diffusion coefficient linearly decreases as coal matrix shrinking after CO₂ desorbing at low pressure. High pressure CO₂ saturated coal can develop into rubber state on a lower glass transition temperature easily. 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 part free volume is frozen with the CO₂ desorption and reduction at high pressure, coal transform into glass state once again, CO₂ diffusion coefficient linearly decreases with time, and which is higher than diffusion coefficient at lower pressure. Simultaneously, 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 for a mechanism of CO₂ diffusion in the coal.

CONCLUSIONS

The CO₂ diffusion coefficient (D) is of un-steady state for coal samples from Yaojie. Under identical conditions, the higher the desorption equilibrium pressure, the larger the diffusion coefficient. The value of D is 1.83×10^{-6} - 9.08×10^{-5} mm²/s at low pressure, and 4.76×10^{-6} - 1.91×10^{-4} mm²/s at high pressure, which is one order of magnitude larger than that in low pressure. As desorption time increases, the value of D reduces rapidly in the initial phase, and then it levels off gradually. The CO₂ mass fraction desorption and the diffusion coefficient has a linear relationship under low pressure and parabolic relationship at high pressure respectively. The un-steady gas diffusion in Yaojie coal is a result of CO₂ adsorption swelling, particularly at high pressures, the coal containing CO₂ undergoes glass transition to high-elastic state, which is probably the governing factor lead to the abnormal and non-linear gas diffusion.

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