

2013

A fractal theory based Fractional diffusion model of methane in coal and experimental verification

Haina Jiang

National Engineering Research Center of Coal Gas Control

Yuanping Cheng

National Engineering Research Center of Coal Gas Control

Follow this and additional works at: <https://ro.uow.edu.au/coal>

Recommended Citation

Haina Jiang and Yuanping Cheng, A fractal theory based Fractional diffusion model of methane in coal and experimental verification, in Naj Aziz and Bob Kininmonth (eds.), Proceedings of the 2013 Coal Operators' Conference, Mining Engineering, University of Wollongong, 18-20 February 2019
<https://ro.uow.edu.au/coal/469>

A FRACTAL THEORY BASED FRACTIONAL DIFFUSION MODEL OF METHANE IN COAL AND EXPERIMENTAL VERIFICATION

Haina Jiang^{1,2} and Yuanping Cheng^{1,2}

ABSTRACT: Structure parameter θ that reflects the dynamic character of methane in coal and fractal dimension d_f that reflects the static structure of coal were introduced into Fick's model, and based on the assumption that the diffusion is memorable by introducing a parameter ν , a Fractional order of diffusion model was established (the FFD Model). Several adsorption and desorption experiments on anthracite coal with different grain sizes (0.2-0.25 mm, 1-3 mm) were performed under different equilibrium pressures (1 MPa, 4 MPa) to determine the parameters and to confirm the validity of the FFD Model. On that basis, further desorption experiment of pulverized coal was conducted to validate the applicability of the FFD Model on pulverised coal. The results showed that the desorption rate of the 0.045-0.075 mm grain size coal is seven times of the 0.106-0.25 mm grain size coal. The implications of the study are for the pulverising phenomenon during the coal and gas outburst. The desorption velocity will increase rapidly, resulting in the dramatic increase of expansion energy of methane, and this further accelerates the pulverising process - a positive feedback effect between desorption velocity and dusting process. This can be used to explain the phenomenon of the gas-solid two phases flow and the piston effect during the coal and gas outburst.

INTRODUCTION

Coal seam is a dual pore reservoir system that is composed of matrix pores and fractures (Warren and Root, 1963). The matrix pores in a coal seam can absorb 95 percent of the total amount of methane because of their large internal surface area (Gray, 1987). The size distribution of the matrix pores is within the nanometer to micrometer range (Cai, *et al.*, 2013). Fractures are the primary channels for gas migration, and their sizes are inconsistent, ranging from a few inches to several inches (Gan, *et al.*, 1972). Therefore, it can be stated that the pore structure of coal is heterogeneous, which suggests that the pore structure plays an important role in understanding the mechanism for the diffusion of methane in coal.

Because of the complexity of the coal pore structure, the migration of methane in coal is significantly different from its migration in traditional media. Researchers generally accept that the migration of methane in coal simultaneously exists in the following two states: laminar flow in the fracture, which can be described by Darcy's Law where pressure is the driving force, and movement through diffusion in the coal matrix, which can be described by Fick's diffusion law where the concentration gradient in the matrix is the driving force (Yi, *et al.*, 2009; Adler, *et al.*, 1990).

The diffusion model has received increasing attention following the development and utilization of coalbed methane (CBM) resources. Cui *et al.* (2004) reported that the diffusivity had an inverse relationship with the reservoir pressure based on the use of the dual diffusion resistance model to calculate the diffusivity of CH₄, CO₂, and N₂ under different pressures. Other researchers, including Busch *et al.* (2004), Pillalamarry *et al.* (2011), Saghafi *et al.* (2007) and Shi and Durucan (2003), conducted similar research on this topic. The single pore diffusion model, derived from Fick's second law, is widely used because of its simplicity and ease of use despite the low degree of fitting. Smith and William (1984) conducted experiments on six coal samples from the San Juan Basin to verify the applicability of the single pore diffusion model. Their results indicated that the single pore diffusion model is only suitable for the first 50% of the desorption gas.

The diffusivity of methane in coal has also attracted the interest of many researchers (Cui, *et al.*, (2004); Busch, *et al.*, (2004); Pillalamarry, *et al.*, (2011); Saghafi, *et al.*, (2007); Shi and Durucan (2003); Charrière, *et al.*, (2010); Clarkson and Bustin, (1999); Nandi and Walker, (1970); Siemons, *et al.*, (2007)). Some conclusions have been obtained regarding the diffusivity of methane in coal, such as the adsorption kinetics under high and low pressures are related to the character of the gas, the moisture and the temperature. Based on Fick's classical diffusion model, Smith and William (1984) calculated the

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

² Faculty of Safety Engineering, China University of Mining and Technology, Xuzhou, Jiangsu 221116, China.

effective diffusion coefficient and concluded that the effective diffusion coefficient of the coal sample varied little with the depth of the coal sample. Nandi and Walker (1975) also examined coal samples from three regions of America to calculate the effective diffusion coefficient and concluded that diffusion coefficients of two of the samples will increase with the increase of the average diffusion concentration under high methane concentrations. Based on this result, Nandi and Walker (1975) believed that the concentration dependent diffusivity results follow a nonlinear adsorption process. However, Bielickiet and Perkins (1972) obtained the pressure dependent diffusivity, and based on this result, he believed that Fick's diffusion model was not suitable for coal because, from a theoretical perspective, the diffusivity in Fick's model is a constant that was not dependent on concentration and pressure. Smith and William (1984) reported that the causes of errors in Fick's diffusion model are due to the assumptions of sample homogeneity and isotropy. Smith and Keller (1985) studied the influence of nonlinear adsorption of a single medium on the diffusion and adsorption parameters and concluded that the magnitudes of the dynamic parameter in the linear and nonlinear adsorption models were different despite the similar adsorption rate curves. In addition, Smith and Keller (1985) also observed that the nonlinear adsorption behaviour is particularly obvious when the concentration significantly changes, especially during the gravimetric method experiment that was used to determine the adsorption rate.

The objectives of this paper are to solve the problems that exist in Fick's classical diffusion model, such as the inability of the model to describe heterogenous coal and the dynamic transport process of methane in coal. Therefore, in this paper, we introduce the fractal dimension (d_f), which can describe the heterogeneous nature of coal, and the structure parameter (θ), which can describe the dynamic transport of methane in coal into Fick's classical diffusion model. In addition, it is assumed that the transport process is memorable and can be described by a fractional partial differential equation of the time variable (t). Therefore, a fractal theory based Fractional diffusion model of methane in coal was established (FFD Model). To verify the validity of the FFD Model, three different types of coals from China were used in an adsorption and desorption experiment and other studies. The different relationships between the fractal dimensions, the structure parameter (θ), the grain size and pressure are also discussed.

EXPERIMENTAL METHODS

Physical property parameters of the coal

In this paper, three types of coal samples were collected, including long flame coal from Tie Fa, coking coal from Tun Lan, and anthracite from Da Nin. According to the Sample Preparation Method (GB 474-2008, 2008) standard, the coal sample was sieved in the laboratory to obtain samples with the grain sizes of 0.075-0.2 mm, 0.106-0.2, 0.2-0.25 mm, 1-3 mm, and 20-30 mm. The maceral and mineral contents and the vitrinite reflectance of the 0.2-0.25 mm grain size coal sample were determined using metallographic microscopes and micro-spectrophotometric methods (ZEISSaxio Imager M1 m) based on the Method of Determining Marcel Group Composition and Mineral Coal (GB/T8899-1998, 1998) and <Method of Determining Microscopically the Reflectance of Vitrinite in Coal (GB/T6948-2008, 2008) standards. Based on the Proximate Analysis of Coal (GB/T212-2008, 2008) standard, a fully automated industrial analyser (5E-6600) was used to perform the industrial analysis with the 0.074-0.2 mm grain size coal sample. The determination of the multipoint BET and average pore diameters with the 0.2-0.25 mm grain size coal samples is based on The Materials by mercury Porosimetry and Gas Adsorption - Part 2: Analysis of Micropores and Macropores by Gas adsorption (GB/T21650.2-2008, 2008) using the liquid nitrogen adsorption technique (77.35 K, 101.3 kPa) and the AUTOSORB-1 gas adsorption analyser. The experimental results from these analyses are presented in Table 1.

Table 1 - Basic physical property parameters of the coal samples

Maceral and mineral (vol.%)					Proximate analysis/%				Average Pore Diameter/ Å	Multipoint BET /(m ² /g)
Vitrinite	Intertinite	Liptinite	Mineral	Vitrinite reflectance	M_{ad}	A_d	V_{daf}	FC_d		
77.8	14.1	0	8.1	3.6	3.46	25.63	8.61	68.05	36.01	43.77

CO₂ adsorption isotherm analysis

Experiments on the adsorption of CO₂ gas were conducted in a HCA gas adsorption instrument using the high pressure volumetric analysis method. The laboratory procedure followed the Method of Determining Methane Adsorption Capacity in Coal Standard MT/T 752-1997 (1997). All of the samples were prepared

by grinding and sieving to a size range of 0.2~0.25 mm and 1~3 mm. Up to 50 g of the samples were weighed for the adsorption experiment, and the samples were then sealed in the coal canister. After verifying the air tightness of the coal canister, helium gas (He) was applied to determine the dead space 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, the coal samples were placed into a 30°C thermostatic water bath for the adsorption isotherm experiment. The tests were conducted under equilibrium pressures of 1 MPa and 4 MPa for all of the samples. The procedure for performing the test is as follows: a certain pressure of CO₂ was injected into a reference canister with a known volume. Then, the reference canister was connected to the coal canister after the pressure in the reference canister reached equilibrium. The connecting valve was then closed after the pressure in the coal canister reached the predetermined pressure, and the equilibrium pressure of the reference canister and the equilibrium adsorption pressure in the coal canister were recorded. The amount of adsorbed gas was then calculated as the difference of the amount of gas in the dead space of the coal canister from the amount of gas that moved from the reference canister to the coal canister.

Desorption experiments

Experiments examining the desorption of CH₄ 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 0.2~0.25 mm and 1~3 mm. A certain amount of coal (to fill the coal canister) for the adsorption experiment was weighed and then sealed in the coal canister. After verifying the air tightness of the coal 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, CH₄ with a purity of 99.99% was injected into the coal 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 graduate. 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 consisted of placing the canister that underwent desorption for two hours into vacuum degassing equipment in a 95°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 then 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.

ESTABLISHMENT OF THE FFD MODEL

Solution of FFD model

The adsorption processes are commonly interpreted by comparison with standard solutions of Fick's model. Fick's model (Zhao, 1991) used for Euclidean geometry is:

$$\frac{\partial c(r,t)}{\partial t} = \frac{D}{r^{d-1}} \frac{\partial}{\partial r} \left(r^{d-1} \frac{\partial c(r,t)}{\partial r} \right) \quad (1)$$

where c is the diffusion concentration of the components (kg/kg), d is the dimension for Euclidean geometry, D is the diffusivity (m²/s), r is the radius of the coal particles (m), and t is the time (s).

The pore structure is the primary factor that affects the diffusive transportation of methane in coal; however, Fick's classical diffusion model cannot describe the influence of the pore structure on the diffusive transport process. By considering the structures of the pores in the coal to be diffusive structures, the Euclidean dimension (d) in Eq.(1) was substituted with the fractal dimension, d_f . Based on simulations, Zhang *et al.* (2004) concluded the following: The diffusivity (D) in fractal structures is not a constant but rather a function of the position, r , in the form of $D = D_0 r^{-\theta}$, where D_0 is the pre-exponential coefficient and θ is a structure parameter that can describe the fractal dimensionality of the path of the diffusive component on the porous material and is related to the fractal dimension (d_f). In addition, it is assumed that the diffusive transport in fractal structures is memorable; therefore, the first-order partial

differential equation about time is changed into a ν fractional-order partial differential equation (Yi, *et al.*, 2009).

Through the above series substitution, the fractal theory based FFD model of methane in coal was established:

$$\frac{\partial c^\nu(r,t)}{\partial t^\nu} = \frac{D_0}{r^{d_f-1}} \frac{\partial}{\partial r} \left(r^{d_f-1-\theta} \frac{\partial c(r,t)}{\partial r} \right), \quad 0 < \nu \leq 1 \quad (2)$$

Where $c(r,t)$ is the concentration of the diffusion component; for coal particles, the concentration c_0 is at the adsorption equilibrium. Concentration gradients along the radii of the coal particles will appear after the coal particles have been exposed to atmospheric conditions because of the reduction of the concentration at the surface of the coal particles. The adsorbed gas becomes free gas, and the diffusion from the center of the coal particle to the surface occurred. The surface concentration is c_1 , and the initial and boundary conditions are:

$$c(r,t)|_{t=0} = c_0, \quad 0 \leq r < r_0 \quad (2a)$$

$$\frac{\partial c(r,t)}{\partial r} \Big|_{r=0} = 0, \quad t \geq 0 \quad (2b)$$

$$c(r,t)|_{r=r_0} = c_1, \quad t \geq 0 \quad (2c)$$

where c_0 is the initial concentration in an adsorbent, kg/m^3 and r_0 is the granule radius, m.

By performing the transform of $u(r,t) = c(r,t) - c_1$, Eq. (2) becomes,

$$\frac{\partial u^\nu(r,t)}{\partial t^\nu} = \frac{D_0}{r^{d_f-1}} \frac{\partial}{\partial r} \left(r^{d_f-1-\theta} \frac{\partial u(r,t)}{\partial r} \right), \quad 0 < \nu \leq 1 \quad (3)$$

$$u(r,t)|_{t=0} = c_0 - c_1, \quad 0 \leq r < r_0 \quad (3a)$$

$$\frac{\partial u(r,t)}{\partial r} \Big|_{r=0} = 0, \quad t \geq 0 \quad (3b)$$

$$u(r,t)|_{r=r_0} = 0, \quad t \geq 0 \quad (3c)$$

The solution of the Eq. (3) is:

$$\frac{c_0 - c(r,t)}{c_0 - c_1} = 1 - \sum_{n=1}^{\infty} \frac{2}{\mu_n J_{1-\alpha}(\mu_n)} \left(\frac{r}{r_0} \right)^{\frac{d_w - d_f}{2}} \cdot J_{-\alpha} \left[\mu_n \left(\frac{r}{r_0} \right)^{\frac{d_w}{2}} \right] \cdot e^{-D_0 \left(\frac{\mu_n d_w}{2 r_0^{d_w/2}} \right)^2 t^\nu} \quad (4)$$

The cumulative diffusion amount at time t was expressed in Q_t and the limiting diffusion amount when $t \rightarrow \infty$ was expressed as Q_∞ :

$$\frac{Q_t}{Q_\infty} = \frac{c_0 - \overline{c(r,t)}}{c_0 - c_1} = 1 - \sum_{n=1}^{\infty} \frac{4d_f}{d_w \mu_n^2} e^{-\left(\frac{\mu_n d_w}{2} \right)^2 \frac{D_0}{r_0^{d_w}} t^\nu} \quad (5)$$

where

$$\overline{c(r,t)} = \frac{d_f}{r_0^{d_f}} \int_0^{r_0} c(r,t) r^{d_f-1} dr \tag{6}$$

when the parameters in Eq. (4)、Eq. (5) change into the following values: $d_f = 3$, $\theta = 0$,

correspondingly, $d_w = 2$, $D_0 = D$, $\alpha = -0.5$, $\mu_n = n\pi$, $J_{0.5}(\frac{n\pi r}{r_0}) = \sqrt{\frac{2r_0}{n\pi^2 r}} \sin(\frac{n\pi r}{r_0})$,

$$J_{1.5}(n\pi) = \sqrt{\frac{2}{n\pi^2}} (-1)^{n+1}$$

Eq. (4) and Eq. (5) were changed into:

$$\frac{c_0 - c(r,t)}{c_0 - c_1} = 1 - \frac{2r_0}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \cdot \sin(\frac{n\pi r}{r_0}) \cdot e^{-D_0 (\frac{n\pi}{r_0})^2 t} \tag{7}$$

$$\frac{Q_t}{Q_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6}{(n\pi)^2} e^{-\frac{(n\pi)^2 D_0}{r_0^2} t} \tag{8}$$

This result is the solution of Fick's diffusion model. From this solution, it can be seen that Fick's model is a special condition of the FFD Model; therefore, the validity of the FFD Model is confirmed (Qilin, 2004; Society, 1986).

Determination of the parameters

In this paper, the fractal dimension is determined from an analysis of multiplayer adsorption to a fractal surface according to the FHH equation (Radiński, *et al.*, 2009; Triolo and Child, 1984; Allen, *et al.*, 1985; Yao, *et al.*, 2009; Machnikowski, *et al.*, 2004; Wang, *et al.*, 2011). The structure parameter (θ) was calculated using the exact-enumeration method (Gorenflo, *et al.*, 2007; Turk, *et al.*, 1987; Xin, 1997). The diffusivity (D) was obtained through its definition (Donghui, 2004), the calculated results are shown in Table 2:

Table 2 - The calculated results of the diffusivity

Pressure/MPa	Grain size/mm	$D_{avr}/(m^2/s)$	d_f	θ	$D_0/(m^2/s)$
1	0.2-0.25	4.05689E-11	2.5841	1.7036	2.59166E-18
	1-3	4.24814E-10	2.5185	1.6165	2.15161E-15
4	0.2-0.25	4.05742E-11	2.7149	1.8772	4.83959E-19
	1-3	4.2487E-10	2.6266	1.7600	7.35474E-16

It can be seen from Table 2 that the fractal dimension (d_f) of the long flame coal from TieFa is between 2.4~2.55; and within the experimental pressure range (1 MPa-4 MPa), the fractal dimension (d_f) will increase with pressure because the surface structure was damaged and becomes more complex with increasing pressure. The fractal dimension (d_f) will increase with the decreasing grain size of the coal because the large and medium pores disappeared and the micropore porosity relatively increased, which caused the coal structure to become complex. θ is a parameter that can reflect the dynamic walk process in the porous media; therefore, it is consistent with the fractal dimension (d_f). The structure parameter (θ) for the long flame coal from TieFa is between 1.5~1.9. The magnitudes of the pre-exponential coefficient (D_0) are between 10^{-19} ~ 10^{-15} and the average diffusivity (D_{avr}) rate is between 10^{-12} ~ 10^{-10} ; this result is consistent with the results of previous researchers (Busch, *et al.*, 2004; Pillalamarri, *et al.*, 2011; Saghafi, *et al.*, 2007; Shi and Durucan, 2003). Furthermore, from Table 2 also it can be observed that the diffusivity in the FFD Model has little variance with the pressure and can be

basically considered to remain constant with pressure. The diffusivity in the FFD Model will increase with the grain size and first increase then decrease with the coal types.

A COMPARATIVE ANALYSIS OF FICK'S MODEL AND THE FFD MODEL

By substituting d_f , θ , and D_0 into Eq. (8) and applying the positive zero of the Bessel function, the relative desorption amounts of the different coal samples (three coal types and two grain sizes) can be calculated for CH₄ at 273 K with time at different initial pressures (1 MPa and 4 MPa). The results from the FFD Model and Fick's model for comparison with experimental data are shown in Figure 1a and Figure 1b. In addition, the parameter ν was obtained by fitting the FFD Model with the experimental data, and it represents the trend of the desorption curve. The gradient of the curve will increase with the increase of ν , especially during the initial stage of the desorption curve.

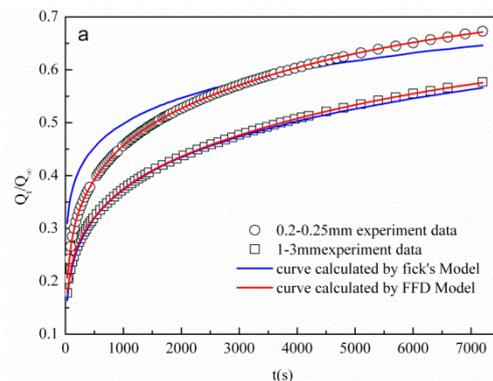


Figure 1a - The desorption curve of anthracite from DaNing at different pressures (a: 1 MPa)

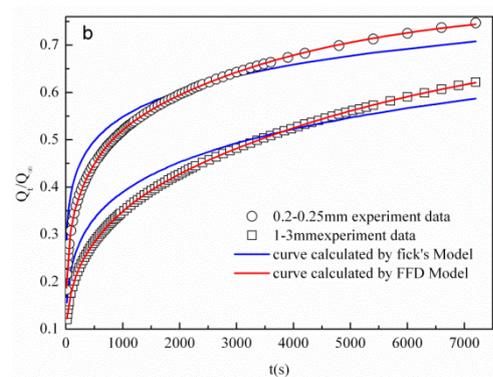


Figure 1b - The desorption curve of anthracite from DaNing at different pressures (b: 4 MPa)

It can be seen from Figure 1a and Figure 1b that the trend of the relative desorption curve has basically similar pattern, i.e., the desorption rate is fast initially. The influence of the microstructure pore will be apparent with the increase of diffusion time, and the difference between the FFD Model and Fick's model becomes more obvious. The diffusion channel will be regular when the d_f , θ are small, and the calculated relative adsorption volume will also be small.

From Figure 1a, Figure 1b, it can also be observed that at the initial stage, the relative adsorption curve for the FFD Model is lower than Fick's model because at the initial time, the influence of the structure parameter θ is not obvious but the fractal dimension d_f is smaller than in Fick's model. With the increase in time, the influence of the structure parameter θ becomes obvious, but there is no structure parameter θ in Fick's model; therefore, Fick's model cannot be used to describe the dynamic movement process of gas in the porous coal, and consequently, the growth rate of the relative adsorption curve of Fick's model is less than the FFD Model, the relative adsorption curve in the FFD Model will intercept the curve of Fick's model. A comparison of the two models is as shown in Table 3:

Table 3 - A comparison of the FFD Model and Fick's model results

Pressure/MPa	Grain size/mm	ν	D_F /(m^2/s)	Correlation coefficient in Fick's model	Correlation coefficient in FFD Model
1	0.2-0.25	0.32	1.11E-11	0.97253	0.99475
	1-3	0.52	5.01E-10	0.98531	0.99325
4	0.2-0.25	0.34	1.37E-11	0.96515	0.99482
	1-3	0.7	5.50E-10	0.97568	0.99475

It can be seen from Table 3 that the degree of curve-fitting for the FFD Model is higher than that of Fick's model. Furthermore, Fick's model is not suitable for the desorption of small grain sized coal, as well as for describing the desorption process under high pressure.

SUITABILITY OF THE FFD MODEL FOR PULVERISED COAL

During coal and gas outburst, the coal that were ejected can be transported by the gas, and the high pressure gas in ejected coal has the explosive characteristics, and this can break the outburst coal further, resulting in the accumulation of large volumes of pulverised coal in the outburst solids.

The quick desorption of the pulverized coal will then further speed up the dusting process - a positive feedback effect between desorption velocity of pulverized coal and dusting process. Based on this observation, additional desorption experiments were conducted using the pulverized coal to study its effect on coal and gas outburst and the suitability of the FFD Model on pulverised coal.

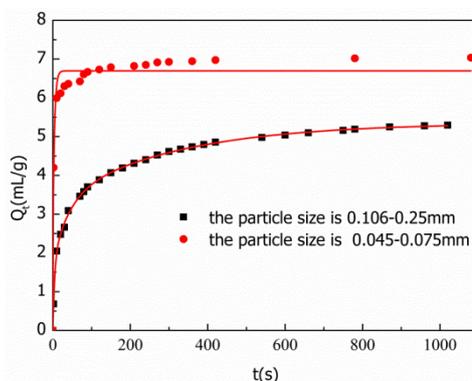


Figure 2 - Desorption isotherm of methane in pulverised coal

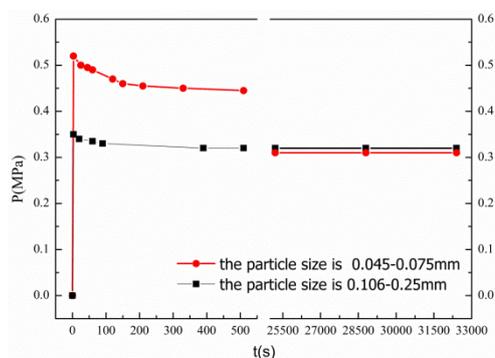


Figure 3 - The adsorption rate curves on 0.045-0.075 mm and 0.106-0.25 mm grain size coal

When the coal was crushed into a certain size, the pore in it will be damaged, and in this case, the coal can be considered to be isotropy, thus it can be assumed that $d_f = 3$, correspondingly, $\theta = 0$, take the value of d_f and θ into the Eq. (8), the average diffusivity D_{avt} and memorable parameter ν were obtained, the results are shown in Table 4.

Table 4 - The fitting result of FFD Model on 0.045-0.075 mm and 0.106-0.25 mm grain size coal

Grain size/mm	Equilibrium pressure/MPa	ν	d_f	θ	Correlation coefficient
0.045-0.075	0.32	0.19	3	0	0.9551
0.106-0.25	0.31	0.21	3	0	0.9998

From the Figure 2 and Table 4, it can be observed that the fitting degree of 0.106-0.25 mm grain size coal is higher than the 0.045-0.075 mm grain size coal. This indicates that the FFD Model is not suitable for the pulverized coal, and another model should be used.

CONCLUSIONS

The fractal dimension, d_f , of the long flame coal from TieFa, is between 2.4~2.55; within the experimental pressure range (1-4 MPa), the fractal dimension, d_f , will increase with pressure due to the damage of the surface structure. The fractal dimension, d_f , will increase with the decreasing grain size of the coal because of the reduction of the large and medium pores and the increase in micropore porosity, causing the coal structure to become more complex. The structure parameter θ is a parameter that can reflect the dynamic adsorption process in the porous media and is consistent with the fractal dimension, d_f . The structure parameter θ for the long flame coal from TieFa is between 1.5~1.9. The magnitudes of the average diffusivity D_{avr} in the FFD Model are between 10^{-12} ~ 10^{-10} , and this parameter can be basically considered to remain constant with pressure. The magnitudes of the pre-exponential coefficient D_0 are between 10^{-19} ~ 10^{-15} . This result is consistent with the results of other researchers. The diffusivity in the FFD Model increases with the grain size.

The relative adsorption curve of the FFD Model is initially lower than that of Fick's model because at the initial stage, the influence of the structure parameter θ is not obvious but the fractal dimension d_f is smaller than that in Fick's model. As time increases, the influence of the structure parameter θ becomes evident. As there is no structure parameter θ in Fick's model, it therefore cannot be used to describe the dynamic movement process of gas in the porous coal. The growth rate of the relative adsorption curve of Fick's model is lower than the FFD Model, and that the relative adsorption curve in the FFD Model will eventually intersect that of Fick's model.

The fitting degree of the FFD Model is higher than Fick's model. Furthermore, Fick's model is neither suitable for describing the desorption of gas in small grain sized coal, and nor for describing the desorption process under high pressure. Equally, the FFD Model is not suitable for the pulverized coal.

REFERENCES

- Adler, P M, Jacquin, C G and Quiblier, J A, 1990. Flow in simulated porous media. *International Journal of Multiphase Flow*, 16(4):691-712.
- Allen, M, Brown, G J and Miles, N J, 1995. Measurement of boundary fractal dimensions: review of current techniques. *Powder Technology*, 84(1):1-14.
- Busch, A, Gensterblum, Y, Krooss, B M and Littke, R, 2004. Methane and carbon dioxide adsorption-diffusion experiments on coal: upscaling and modelling. *International Journal of Coal Geology*, 60(2-4):151-168.
- Bielicki, R J and Perkins, J H, 1972. Methane diffusion parameters for sized coal particles: a measuring apparatus and some preliminary results. United States. Bureau of Mines. p12.
- Charrière, D, Pokryszka, Z and Behra, P, 2010. Effect of pressure and temperature on diffusion of CO₂ and CH₄ into coal from the Lorraine basin (France). *International Journal of Coal Geology*, 81(4):373-380.
- Clarkson, C R and Bustin, R M, 1999. The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modelling study. 2. Adsorption rate modelling. *Fuel*, 78(11):1345-1362.

- Coal science research institute of coal analysis laboratory, 2008. Yunnan coalfield geological exploration company 143 team, proximate analysis of coal. In *GB/T 212-2008*, General Administration of Quality Supervision: 2008.
- Cui, X, Bustin, R M and Dipple, G, 2004. Selective transport of CO₂, CH₄, and N₂ in coals: insights from modelling of experimental gas adsorption data. *Fuel*, 83(3):293-303.
- Cai, Y, Liu, D, Pan, Z, Yao, Y, Li, J and Qiu, Y, 2013. Pore structure and its impact on CH₄ adsorption capacity and flow capability of bituminous and subbituminous coals from Northeast China. *Fuel*, 103:258-268.
- Donghui, Z, Mingheng, S and Jin Feng, Y H, 2004. Diffusion characteristic in fractal porous media(I). *Journal of engineering thermophysics*, 25(5):822-824. (in Chinese).
- Fushun Branch, China Coal Science Research Institute, 1997. Determine method of methane adsorption capacity in coal. In *MT/T 752-1997*, Industry standard - coal: 1997.
- Gan, H, Nandi, S P and Walker Jr, P L, 1972. Nature of the porosity in American coals. *Fuel*, 51(4):272-277.
- Gorenflo, R, Mainardi, F and Vivoli, A, 2007. Continuous-time random walk and parametric subordination in fractional diffusion. *Chaos, Solitons & Fractals*, 34(1):87-103.
- Gray, I, 1987. Reservoir engineering in coal seams: Part 1 - The physical process of gas storage and movement in coal seams. *SPE Reservoir Engineering*, 2(1):28-34.
- Laboratory of Coal Science Research Institute, 2008. National Coal Quality Supervision center, sample preparation method. In *GB 474-2008*, General Administration of Quality Supervision: 2008.
- Machnikowski, J, Grzyb, B, Weber, J V, Frackowiak, E, Rouzaud, J N and Béguin, F, 2004. Structural and electrochemical characterisation of nitrogen enriched carbons produced by the co-pyrolysis of coal-tar pitch with polyacrylonitrile. *Electrochimica Acta*, 49(3):423-432.
- Nandi, S P and Walker Jr, P L, 1970. Activated diffusion of methane in coal. *Fuel*, 49(3):309-323.
- Nandi, S P and Walker Jr, P L, 1975. Activated diffusion of methane from coals at elevated pressures. *Fuel*, 54(2):81-86.
- Pillalamarri, M, Harpalani, S and Liu, S, 2011. Gas diffusion behavior of coal and its impact on production from coalbed methane reservoirs. *International Journal of Coal Geology*, 86(4):342-348.
- Qilin, Y, 2004. *Mathematical physics equation and the special function*. Tsinghua University Press, p6.
- Society, J O C C, 1986. Theory of methane diffusion from coal cuttings and its application. *Journal of China coal society*, (3):87-94.
- Radliński, A P, Busbridge, T L, Gray, E M A, Blach, T P and Cookson, D J, 2009. Small angle X-ray scattering mapping and kinetics study of sub-critical CO₂ sorption by two Australian coals. *International Journal of Coal Geology*, 77(1-2):80-89.
- Saghafi, A, Faiz, M and Roberts, D, 2007. CO₂ storage and gas diffusivity properties of coals from Sydney Basin, Australia. *International Journal of Coal Geology*, 70(1-3):240-254.
- Shi, J Q and Durucan, S, 2003. A bidisperse pore diffusion model for methane displacement desorption in coal by CO₂ injection. *Fuel*, 82(10):1219-1229.
- Siemons, N, Wolf, K A A and Bruining, J, 2007. Interpretation of carbon dioxide diffusion behavior in coals. *International Journal of Coal Geology*, 72(3-4):315-324.
- Smith, D M and Williams, F L, 1984. Diffusion models for gas production from coals: Application to methane content determination. *Fuel*, 63(2):251-255.
- Smith, D M and Keller, J F, 1985. Nonlinear sorption effects on the determination of diffusion/sorption parameters. *Industrial & Engineering Chemistry Fundamentals*, 24(4):497-499.
- The Chinese academy of sciences institute of process engineering, 2008. The physical and chemical analysis and test center, the materials by mercury porosimetry and gas adsorption - Part 2: Analysis of mesopores and macropores by gas adsorption. In *GB/T 21650.2-2008*, General Administration of Quality Supervision.
- Triolo, R and Child, H R, 1984. Small-angle neutron scattering study of coal extract solutions in pyridine. *Fuel*, 63(2):274-279.
- Turk, G A, Cobb, T B, Jankowski, D J, Wolsky, A M and Sparrow, F T, 1987. CO₂ Transport: A new application of the assignment problem. *Energy*, 12(2):123-130.
- Wang, S, Yu, B, Zheng, Q, Duan, Y and Fang, Q, 2011. A fractal model for the starting pressure gradient for Bingham fluids in porous media embedded with randomly distributed fractal-like tree networks. *Advances in Water Resources*, 34(12):1574-1580.
- Warren, J and Root, P, 1963. The behaviour of naturally fractured reservoirs. *society of petroleum engineers journal*, 426:245-255.
- Xian branch, 1998. Coal scientific research institute, method of determining marcel group composition and mineral coal. In *GB/T 8899-1998*, General Administration of Quality Supervision.
- Xian branch, 2008. Coal scientific research institute, Method of determining microscopically the reflectance of vitrinite in coal. In *GB/T 6948-2008*, General Administration of Quality Supervision.

- Xin, Hw, 1997. Reaction kinetics in fractal media. Shanghai Scientific and Technological Education Press: Shanghai.
- Yi, J, Akkutlu, I Y, Karacan, C Ö and Clarkson, C R, 2009. Gas sorption and transport in coals: A poroelastic medium approach. *International Journal of Coal Geology*, 77(1-2):137-144.
- Yao, Y, Liu, D, Tang, D, Tang, S, Huang, W, Liu, Z and Che, Y, 2009. Fractal characterisation of seepage-pores of coals from China: An investigation on permeability of coals. *Computers and amp; Geosciences*, 35(6):1159-1166.
- Zhao, X, 1991. An experimental study of methane diffusion in coal using transient approach. Ph.D Dissertation. University of Arizona.
- Zhang, D, Mingheng, S and Jin Feng, Y H, 2004. Diffusion characteristic in fractal porous media (α). *Journal of engineering thermophysics*, 25(5):825-827. (in Chinese).