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Mathematical model for gas diffusion from non-homogeneous coal particles

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ABSTRACT
By establishing model and experimental verification, this paper aims to improve the accuracy and applicability of gas diffusion mathematical models from coal particles in engineering applications. Firstly, based on Fick's second law and the continuity theory of gas diffusion in porous media, a new constitutive model for gas diffusion from non-homogeneous coal particles with three-layer pore structure is constructed by considering the difference of characteristics in pore structure between soft coal and hard coal. Then, the analytical solution is derived from the new model, that is, the quantitative relationship between gas diffusion rate (Qt/Q∞) and diffusion time (t). The pore structure parameters of soft coal and hard coal from Juji coal mine are determined by using the mercury injection method. Gas desorption and diffusion rules of coal samples are numerically calculated and investigated by using physical simulation methods. Lastly, the applicability of the constitutive model is verified. The results show that the homogeneous model that is currently widely used only applies to the description of the gas diffusion process of the hard coal within the initial 10 minutes, while the new model can describe the gas diffusion law of different pore structure characteristics. The calculated results from the new model and the physical experimental results are nearly identical within the initial 30 minutes. The difference in the gas diffusion process between soft coal and hard coal can be effectively reflected by the parameters of pore structure in the new model.
KEYWORDS: soft coal and hard coal; gas desorption and diffusion rules; pore structure; mathematical models

1. INTRODUCTION

Gas diffusion laws and models from coal particles are the key theoretical bases for the determination of gas content in coal seams. At present, there are a couple of theoretical models to describe the law of gas diffusion from coal particles based on different perspectives. These models can be classified into two types, including homogeneous diffusion models (Qiluan and Youan, 1986; Nie, et al, 2001) and Bidispere diffusion models (Clarkson and Bustin, 1999; Ruckenstein, et al, 1971). However, when these models are applied to describe the gas diffusion laws of outburst prone soft coal, there are usually noticeable deviations that lead to not meeting the requirements of engineering (Liu, et al, 2015).

The conventional model commonly used is a transient mathematical model of gas diffusion based on uniform porous coal particles and the solution to Fick's second law for spherically symmetric flow (J. Crank, 1975). Its analytical solution is an infinite series function of diffusion rate vs. time, as shown in equation (1). Based on the numerical model calculations, Yang (Qiluan and Youan, 1986) found that the relationship between ln [1-(Qt/Q∞)2] and t is linear.

$$\frac{Q_t}{Q_\infty}=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-n^2Bt} \qquad (1)$$

Where, Qt is the total volume of the diffusing gas at time t, cm3/g; and Q∞ is the total diffusion volume cm3/g; t is the time of gas diffusion, s. B=π2D/a2, The value of B ranges from 6.5797×10^{-6} to 6.5797×10^{-3}. D is the diffusion coefficient of gas in coal particle, m2/s,

To verify the homogeneous model, the experiment concerning gas diffusion from soft coal and hard coal of Juji coal mine was performed. The experimental results showed that the relationship between ln [1-(Qt/Q∞)2] and t is not linear, as illustrated in Figure 1.

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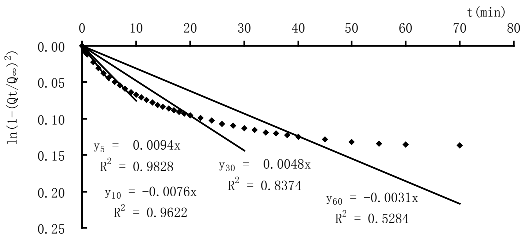
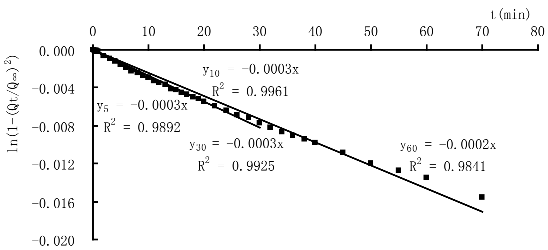


(a): Soft coal



(b): Hard coal

Figure 1: Fitting curves of Juji coal samples according to the unipore model.

Considering the mass transfer resistance of the surface of coal particles, Nie et al. (2001) adapted the unipore diffusion model based on the third kind boundary condition. Its analytical solution was obtained using the mathematical and physical methods. The simplification of the solution to the equation is similar to the empirical formula developed by Bolt and Innes (1959).

Bi-disperse diffusion models are based on the assumption that pore structure of coal merely consists of macro-porous and micro-porous.

Ruckenstein et al. (1971) developed the continuous bi-disperse diffusion model by considering the adsorbent to be a spherical particle (macrosphere) containing an assemblage of microspheres of uniform size. The Henry linear adsorption model and a step change in concentration of the adsorptive external to the particle are assumed in Ruckenstein's model. Smith and Williams (1984) adapted Ruckenstein's model and found that the bidisperse diffusion model better described the entire desorption rate curve than the unipore model for some coals. Crosdale et al. (1998) has verified successfully the bidisperse model by investigating Australian coal gravimetric transient adsorption data. In particular, it is believed that dull coal adsorption rate data are better a fit with the bidisperse model than with the unipore model when the whole process of diffusion from coal particles is described. Clarkson and Bustin (1999) developed an isothermal adsorption rate model based on Ruckenstein's model, considering variable pressure adsorption rate experiments as described by Mavor et al. (1990) and the adsorption isotherm that can be described by the Langmuir equation. They indicate that dull or banded coals have a more complicated pore structure, and are adequately modeled with diffusion models that incorporate a bidisperse pore volume distribution. However, it is inadequate to describe the gas diffusion process from soft coal.

2. THE DEVELOPMENT OF MODEL AND DISCUSSION

The current desorption model assumes a tridisperse pore structure for coal, as schematically shown in Figure 2, considering a macroporous particle which consists of uniform size mesoporous particles containing uniform microporous particles. The radius of the larger sphere is much more than that of the smaller sphere. Unlike the previous models, the current model takes into account the tridisperse pore structure based on the difference between soft coal and hard coal. It also assumes that there is no pressure gradients during intra-particle diffusion. The only driving force is the concentration of gas. In addition, the adsorption is occurring in both micropores and mesopores. The assumptions for the current model may be summarized as follows.

(1) Isothermal system.

(2) Applicable transport equation is Fick's second law.

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \cdot \frac{\partial}{\partial r}(r^2 \frac{\partial C}{\partial r}) = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right)$$

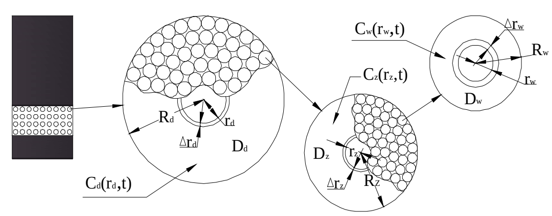


Figure 2: Conceptual model for tridisperse pore structure.

(3) Transport is the diffusion in both macro, meso and micropores.

(4) Significant adsorption occurs in both micro-, meso- and macroporosity and the adsorption isotherm can be described by Langmuir equation as follows.

$$C_s = a^{'} b^{'} C / \left(1 + b^{'} C\right)$$

Where, Cs is adsorption of gas concentration on the surface, mol/m3, C Free gas concentration in pore after desorption, mol/m3, stands for a gas concentration which is complete monolayer coverage of micropore of gas-solid surface, mol/m3, b langmuir constant, b'=bRT MPa-1 , R gas constant, R=8.314(cm^3.MPa)/(K.mol), T stands for the temperature, K;

(5) Pores are incompressible.

(6) Void volume is constant with time. No correction is made for void volume shrinkage during adsorption of gas.

(7) Coal particle is spherical in shape and uniform in size.

(8) The gas transport through pores complies with mass conservation and fluid continuity theorem.

The concentration field inside macropore satisfies the following equation (2).

$$D_d\phi_d\left(\frac{\partial^2 C_d}{\partial {r_d}^2}+\frac{2}{r_d}\frac{\partial C_d}{\partial r_d}\right)=a'b'S_d\frac{\partial}{\partial t}\left(\frac{C_d}{1+b'C_d}\right)+D_z\frac{3(1-\phi_d)}{R_z\phi_d}\frac{\partial C_z}{r_z}\Big|_{r_z=R_z} \quad (2)$$

Where the first term is due to variation of diffusional flux in the macropore, the second to accumulation in the macropore, and the third to the diffusional flux at the surface of mesospheres.

The mesopore (3) and micropore (4) transport equation used in the current study are thus.

$$D_z\phi_z\left(\frac{\partial^2 C_z}{\partial {r_z}^2}+\frac{2}{r_z}\frac{\partial C_z}{\partial r_z}\right)=a'b'S_z\frac{\partial}{\partial t}\left(\frac{C_z}{1+b'C_z}\right)+D_w\frac{3(1-\phi_{z.p})}{R_w\phi_{z.p}}\frac{\partial C_w}{r_w}\Big|_{r_w=R_w} \quad (3)$$

$$D_w\phi_w\left(\frac{\partial^2 C_w}{\partial r_w^2}+\frac{2}{r_w}\frac{\partial C_w}{\partial r_w}\right)=a'b'S_w\frac{\partial}{\partial t}\left(\frac{C_w}{1+b'C_w}\right) \quad (4)$$

With initial conditions:

$$C_d(0,\ r_d)=C_z(0\quad r_z)=C_w(0\quad r_w)=C_0 \quad (5)$$

And boundary conditions:

$$\frac{\partial C_d}{\partial r_d}=0,\ t\geq 0,\ r_d=0,\quad \frac{\partial C_z}{\partial r_z}=0\quad t\geq 0\quad r_z=0\quad \frac{\partial C_w}{\partial r_w}=0\quad t\geq 0\quad r_w=0 \quad (6)$$

$$C_d(t,\ R_d)=C_1$$

$$C_z(t,\ R_z)=C_d(t\quad r_d)\quad C_w(t\quad R_w)=C_z(t\quad r_z) \quad (7)$$

$$Q_t=\int_0^t -4\pi R_d^2 D_d\phi_d\frac{\partial C_d}{\partial r_d}\Big|_{r_d=R_d}dt,\ t\geq 0\quad r_d=R_d \quad (8)$$

Where, Dw is micropore diffusion coefficient, m2/s; Dz mesopore diffusion coefficient, m2/s; Dd macropore diffusion coefficient, m2/s; Cw micropore sorbate concentration, moles/m3; Cz mesopore sorbate concentration, moles/m3; Cd macropores sorbate concentration, moles/m3; C0 sorbate concentration at t=0, moles/m3; C1 sorbate concentration at r=Rd, moles/m3; rw the radius of small coal particle in spherical coordinate, m; rz the radius of medium coal particle in spherical coordinate, m; rd the radius of coal particle in spherical coordinate, m; Rw the radius of small coal particle, m; Rz the radius of medium coal particle, m; Rd the radius of coal particle, m. t is the time of diffusion, s; φw the average porosity of micropores; φzp the average porosity of mesopores and transition pores in a single coal particle, φz.p=φz/n m3/m3; n the number of the lower grade coal particle in unit volume, n=(1-φ)/(4πR3/3); φd the porosity of macropores, m3/m3(%); Sw the specific surface area of micropores, m2/m3; Sz the specific surface area of mesopores and transition pores, m2/m3; Sd the specific surface area of macropores, m2/m3; Qt total diffusion volume at time t, cm3/g.

At t=0, gas concentration is assumed to be equal in the macro, meso and micro-spheres (Eq. (5)). A no gas diffusion flow internal boundary condition is used for the macro, meso and micro-spheres (Eq. (6)). Eq.(7) states that the gas concentrations at micro and meso-spheres boundary are equal to the gas concentration in the meso and macro-porosity at rz and rd respectively, and the gas concentration at macro-spheres boundary is eternally equal to the constant C1. Eq. (8) is a balance statement which express that the change in mass of gas stored interparticle void space is equal to the mass flux of gas across all particle boundaries for t>0.

The initial and boundary conditions are substituted into Equations (2) - (4). After a series of derivations, the relationship between Qt and t is obtained. As shown in equation (9), the function is an exponential relation, and also a solution of infinite series. The infinite diffusion amount (Q_∞) is shown in Eq. (10). The relationship between Gas diffusion rate (Q_t/Q_∞) and time t is shown in Eq. (11).

$$Q_t=-16\pi^2\phi_d R_d^3 D_d(C_1-C_0)\varepsilon\sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{k^2\pi R_z^2\left(1-e^{\left(-\alpha\varepsilon\xi_{qk}^2 t\right)}\right)\delta}{\omega} \quad (9)$$

$$Q_\infty=-16\pi^2\phi_d R_d^3 D_d(C_1-C_0)\varepsilon\sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{k^2\pi R_z^2\delta}{\omega} \quad (10)$$

$$\frac{Q_t}{Q_\infty}=\frac{\sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{k^2\left(1-e^{\left(-\alpha\varepsilon\xi_{qk}^2 t\right)}\right)\delta}{\omega}}{\sum_{k=1}^{\infty}\sum_{q=1}^{\infty}\frac{k^2\delta}{\omega}} \quad (11)$$

Where

$$\alpha=\frac{D_wR_z^2\frac{abS_z}{\phi_z}}{D_zR_w^2\frac{abS_w}{\phi_w}}=\frac{D_wR_z^2S_z\phi_w}{D_zR_w^2S_w\phi_z}$$

$$\varepsilon=\frac{D_dR_z^2\frac{abS_z}{\phi z}}{D_zR_d^2\frac{abS_d}{\phi_d}}=\frac{D_dR_z^2S_z\phi_d}{D_zR_d^2S_d\phi z}\qquad \beta=\frac{3D_wR_z^2(1-\phi_d-\phi_z)}{D_zR_w^2\phi_z}$$

$$\eta=\frac{3D_dR_z^2(1-\phi_d)}{D_zR_d^2\phi_d}\qquad \delta=\sqrt{\alpha\xi_{qk}^2-\xi_{qk}\cot(\xi_{qk})\beta+\beta}$$

ξ_{qk} is the root of transcendental Eq. (12)

$$\alpha\xi_{qk}^2-\eta\sqrt{\alpha\xi_{qk}^2-\xi_{qk}\cot(\xi_{qk})\beta+\beta}\cdot\cot\sqrt{\xi_{qk}\cot(\xi_{qk})\beta+\beta}+\eta=\varepsilon k^2\pi^2$$

(12)

3. EXPERIMENTAL VERIFICATION

The soft coal and hard coal samples were collected from Juji coal mine in China, and the physical parameters that reflect their characteristics were determined. As shown in Table 1, these parameters show the differences between soft coal and hard coal in hardness, industry analysis, adsorption constants, and porosity. Then, these samples were dried, sieved, and classified. The porous structure parameters needed to be provided when calculating according to the new model, and were determined by mercury porosimetry method, as shown in Table 2.

The above data and the intermediate parameters shown in Table 3 were substituted into equation (12). The theoretical curves of (Qt/Q∞) vs. t are plotted, as shown in Figure 4. Meanwhile, the effective diffusivity (D/R2) was determined by fitting experimental data according to unipore analytical solution (equation (2)).

Dynamic process tests of gas diffusion from coal particles were carried out on specially prepared coal samples 1-3mm in diameter by the experimental system shown in Figure 3. The experimental process can be classified as having 4 stages: firstly, vacuums pumping of the air-proof system bearing samples is performed until the gas pressure becomes stable at 10±0.1 Pa. Then, methane is gradually charged into the samples until the adsorption achieves equilibrium at 0.74 ±0.01 MPa. The third step is to release the free gas in void space until the pressure becomes 0. This step takes about 10 seconds. Lastly, the data of desorption volume and corresponding time are measured. The experimental temperature is kept at 298 K by constant temperature bath across the process.

As shown in Figure 4, the dots are experimental data, and the curves are the theoretical values from the analytical solution. A comparison of experimental rate curves for hard and soft coal samples with theoretical curves gives some indications of the process of gas diffusion from coal particles. Experimental results show that the numerical calculation results by the new model are almost identical to the experimental data within the first 30 minutes, although there are increasing deviations between the two types of results after 30 minutes. The main reasons for this finding may be the truncation error of infinite series solution and that the values of k and q in the series general solution are taken as 100, as well as the determination error of porous parameters.

Table 1: Physical properties of soft coal and hard coal from Juji coal mine.

Samples	Firmness coefficient *f*	Industry analysis/%			Adsorption constants		Porosity /%	Apparent density /(t-1·m3)
		Mad	Aad	Vdaf	a/m3·t-1	b/MPa-1		
Hard coal	0.85	0.89	10.08	10.00	36.117	0.668	4.0793	1.41
Soft coal	0.15	0.92	9.92	8.64	32.654	0.930	6.1406	1.43

Table 2: porous structure parameters by mercury intrusion porosimetry method.

Samples	Vdaf /%	Pore specific surface area/(m2·g -1)				Ratio of pore volume /%			Connectivity /%
		Sw	Sz	Sd	St	φw	φz	φd	
Hard coal	10.00	10.00	3.922	1.428	0.002	22.32	26.91	50.76	26
Soft coal	8.64	8.64	4.167	1.807	0.014	15.31	37.78	46.92	39

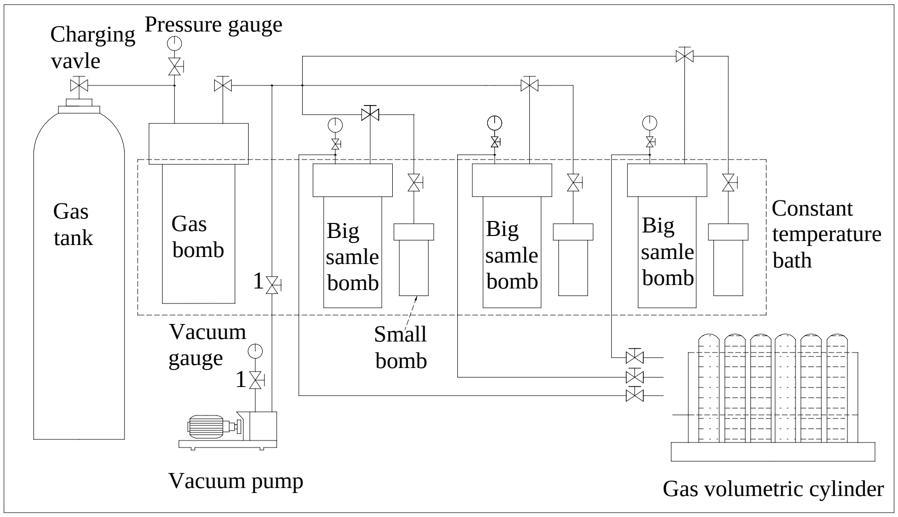
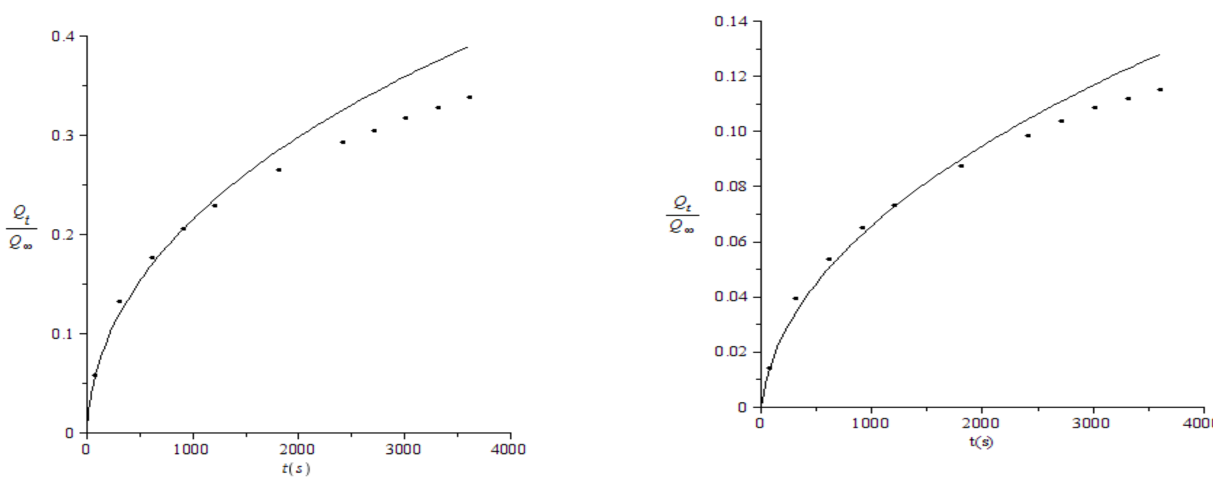


Figure 3: Experimental set up.

Table 3: Results of gas diffusion parameters according to the new model

Samples	α	ε	β	η	β/α	η/ε	Dd/R2d	Dz/R2z	Dw/R2w
Hard coal	0.256	315.0	220.0	302.6	860.0	0.96	1.57E-04	8.00E-05	5.50E-05
Soft coal	9.62E-03	4.23E+04	3.52707	10526.85	9.62E-03	0.25			



(a) Verification of soft coal

(b) Verification of hard coal

Figure 4: Experimental verification of the new model.

4. CONCLUSIONS

(1) Due to the different porous structure between soft coal and hard coal, there is a noticeable distinction of transient gas desorption rules. The previous models are inadequate to describe the transient process from soft coal.

(2) A model for transient desorption from coal particles, which shows the influence of competing effects of macropore, mesopore and micropore diffusion has been developed. Compared to previous models, the new model considers the effect of the mesopore based on the difference between soft coal

and hard coal, and the gas adsorption equation of coal as Langmuir equation.

(3) The general solution of infinite series of the new model is theoretically derived. The relationship of the rate of diffusion with time is an exponential function. The results of experimental verification show that the new model precisely describes the gas diffusion process from coal particles within the first 30 minutes.

(4) The new model should be optimized and simplified in the future to be satisfactory for field application.

5. ACKNOWLEDGEMENTS

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