

Article

On Gas Desorption-Diffusion Regularity of Bituminous Coal with Different Particle Sizes and Its Influence on Outburst-Coal Breaking

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Abstract: Coal and gas outburst is an urgent and constantly perplexing problem with coal resource extraction, threatening coal mine safe and sustainable production severely. Its mechanism and the participation of gas in coal breaking are still unclear. To explore this problem, in this paper, gas desorption-diffusion regularity of bituminous coal with different particle sizes and its influence on outburst-coal breaking were investigated through mercury intrusion porosimetry (MIP) tests, isothermal adsorption tests, and desorption-diffusion tests for coal particles with different sizes. The results indicated that the cumulative diffusion amount (Q_t) and rate (Q_t/Q_∞), the effective diffusion coefficient (D'), and the kinetic diffusion parameter (v) decreased as particle size increased. That meant gas was easier to desorb and diffuse from the smaller coal blocks, consequently making coal break into more tiny particles and accelerating gas desorption. As a result, a positive feedback effect that coal breaks continuously and gas releases rapidly and abundantly was formed in a short time when outbursts started, which caused gas release in quantities and promoted the occurrence of outbursts. The findings of this study enhance our understanding of the mechanism of gas participating in coal fragmentation during outbursts, which are significantly conducive to the prevention and control of coal mine disasters and sustainable production of coal resources.

Keywords: mine disasters control; coal and gas outburst; gas desorption and diffusion; particle size; coal breaking



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1. Introduction

Coal and gas outburst and methane explosion are the urgent and constantly perplexing problems with coal resource extraction [1–4]. The former is a highly catastrophic and instantaneous dynamic disaster that is an outcome of the destruction and ejection of coal accompanied by massive gas at a working face [5,6], threatening coal mine safe production for nearly two hundred years [7,8]. The massive methane existing in coal seams will be released into mining space once its initial state changes, resulting in combustion and explosion when the methane concentration reaches a certain range, also causing severe damage and loss of life [9]. Successfully, lots of investigations have been carried out and numerous breakthroughs have been taken [4,9–13], the timely degassing from coal seams gradually becomes the main means of preventing outbursts and methane explosions. Moreover, the understanding that outburst is dependent on the physicommechanical properties of coal, in situ stresses, and gas adsorption has been commonly adopted. Wherein, the strong gas adsorptive property of coal is a significant factor affecting its occurrence [14,15], and gas is considered as the major energy contributor for triggering and sustaining outbursts [16]. Gas exists as adsorbed and free state in coal pore structure and keeps dynamic

equilibrium of two opposite physical processes of gas molecules gathering and escaping on the pore surface, i.e., adsorption equilibrium state [17]. Once the equilibrium state is disturbed, gas desorbs from pore surface and diffuses pass through pore network of coal. The desorption-diffusion process varies the coal structure and its mechanical properties and carries expansion energy, affecting outburst occurrence and coal breaking during outbursts [18,19]. However, the mechanism of gas participating in coal fragmentation during outbursts is still foggy since the complication of gas containing and migrating in coal structure. Thus, to investigate the influence of gas desorption-diffusion on outburst-coal breaking is of significance for clarifying outbursts mechanism.

Thus far, ongoing efforts intended to understand the regularity of gas desorption and diffusion have acquired great progress. A model of gas diffusing in coal and filtrating through the open pore-crack system was proposed by Alexeev et al. [20], then the effective diffusion coefficient of coal blocks containing closed pores filled with gas was derived. Meng et al. [21] experimentally studied the influence factors of gas diffusion such as coal ranks, gas pressure, temperature, and moisture et al. under methane conditions, and the relationships between the factors and diffusion coefficient were analyzed. Yan et al. [22] established a model similar to the Langmuir equation to investigate methane diffusion in coal, and found that the influence of moisture and coal molecular structure on gas diffusion varies with coal rank. Furthermore, the effect of particle size on gas desorption and diffusion in anthracite and meager coal was studied by Li et al. [23], they found that the initial methane diffusion rate was slowed with the particle size increased. Lu et al. [24] compared the gas desorption-diffusion characteristics between the high-rank intact coal and fractured coal, concluding that the gas molecules desorbed more easily from fractured coal than intact coal. In addition, findings of Nie et al. [25] indicated that the Knudsen number decreased with gas pressure and increased with temperature, and gas diffusion model went through Knudsen, transition, and Fick diffusion. Liu et al. [26] concluded that there existed an obvious scale effect for gas diffusion in coal, the effective diffusivity behaved differently when particle size was blow and above the critical value. In terms of theory, Li et al. [27,28] developed the model describing gas diffusion in columnar coal cores and the model dynamic diffusion coefficient considering the decay of diffusivity, and the experimental results using tectonic coal were analyzed based on these models.

Moreover, a quantity of investigations has been conducted to study the influence of gas desorption-diffusion on coal properties. He et al. [29–31] pointed out that gas adsorption often de-strengths coal body because the lubrication effect of free gas in coal pore structure will decrease the friction force and coefficient between coal pores when coal is subjected to shearing stress. Meanwhile, the uneven stress distribution will be intensified due to the tension provided by gas expanding at the weak point of cracks tip. Besides, high-pressure gas is equivalent to a wedge filled in a crack, which will split coal along the direction of crack propagation, ultimately expediting coal breaking as gas released and expanded. Liang et al. [32] suggested that the adsorption-desorption process can deteriorate the mechanical properties of coal under a composite effect of adsorbed and free gas, meaning it was a combined result of the gas pressure induced mechanical effects and the desorption induced non-mechanical effects on coal mass. While, it was explained as a result of the non-rigid attribute of coal body when gas desorbed and changed coal structure by Vandamme [33] and Nikoosokhan et al. [34]. Namely, coal becomes easier to be broken because the desorption induced structural alterations declines coal strength. Additionally, Peng et al. [35] explored the coupling mechanism of coal fracture and gas migration through experiments using gas-containing coal, and the results demonstrated that gas migration altered the mechanical properties of coal, reducing the strength of coal and accelerating its fracture process.

Despite benefited from these achievements, the gas desorption-diffusion regularity affected by vary factors becomes more and more clear. Whereas, the regularity of bituminous coal with different particle sizes was still limited. Also, present investigations on gas desorption-diffusion gradually focuses on the computation of diffusion loss and the

establishment of models describing the process. The exploration of the influence of gas desorption-diffusion characteristics on coal breaking during a coal and gas outburst is rarely reported. However, it is important to clarify this influence for understanding how gas participating in coal breaking and outbursts occurrence. Therefore, in this paper, a series of desorption-diffusion tests using bituminous coal with different particle sizes were conducted to probe the desorption-diffusion regularity and further explore its influence on outburst-coal breaking. The findings will benefit gas disaster prevention and sustainable production of coal resources, further keeping energy security in the world.

2. Materials and Methods

2.1. Sample Preparation

The experimental coal samples were sourced from a fresh working face of coal seam No.5 in the Panzhihua coal mine located in western Guizhou in China. Coal seam No.5 is a bituminous seam, classified as an outburst-risk seam according to Chinese standard AQ 1024-2006 (Specification for Identification of Coal and Gas Outburst Mine) [36], belonging to the Longtan Formation (P₃l) of the Upper Permian unit. Large coal blocks were selected and sealed for sampling. The collected coal blocks were pulverized into powder and sieved in line with different sizes. Coal samples with a diameter of 3–6 mm were used for mercury intrusion porosimetry tests to determine the pore characteristics of coal. Coal particles ranging in size between 50 and 80 mesh (0.180–0.300 mm) were used for isothermal adsorption tests to determine the adsorption characteristics. Then, small particles with sizes of 70–120 mesh (0.125–0.212 mm) and 40–70 mesh (0.212–0.425 mm), larger particles with sizes of 10–18 mesh (1–2 mm), and large particles ranging 5–15 mm and 25–35 mm, which basically covers the common particle sizes of broken coal after an outburst accident, were used for the gas desorption-diffusion tests with different sizes of coal particles. Approximately 10 g of the coal samples (<80 mesh) were tested for proximate analysis in accordance with Chinese standard GB/T 212 2008 [37] using a 5E-MACIII infrared fast proximate analyzer, whose results were presented in Table 1. All coal samples were oven-dried at 353.15 K for 12 h before tests to minimize the influence of moisture on experimental results.

Table 1. Proximate analysis results for coal samples.

Coal Type	Visual Density (g/cm ³)	Real Density (g/cm ³)	A _{ad} (%)	V _{daf} (%)	M _{ad} (%)	FC _{ad} (%)
Bituminous coal	1.405	1.485	14.93	17.28	1.10	66.73

A_{ad} represents the ash content on air-dried basis, V_{daf} represents the volatile matter content on dry-ash-free basis, M_{ad} represents the moisture content on air-dried basis, and FC_{ad} represents the fixed carbon on air-dried basis.

2.2. Experimental Procedures

2.2.1. Mercury Intrusion Porosimetry (MIP) Tests

Coal is a kind of porous medium material with a well-developed pore structure and abundant pore-fracture network. The porous properties of coal can be measured by porosity, which refers to the ratio of the pores volume to the total volume of coal, expressed as a percentage

$$\varphi = \frac{V_p}{V_t} \times 100\% = \left(1 - \frac{V_s}{V_t}\right) \times 100\% = \left(1 - \frac{\rho_t}{\rho_s}\right) \times 100\% \quad (1)$$

where, φ represents the porosity of coal, V_p and V_t represent the pores volume and the total volume of coal, V_s denotes the volume of solid matrix in coal, ρ_s and ρ_t indicate the density of the solid matrix in coal and the density of the whole coal sample, i.e., the real density and visual density, respectively. Mercury intrusion porosimetry (MIP) is commonly used to measure the pore characteristics of coal. The pressurized liquid mercury is pressed into the coal pores by overcoming the surface tension from the pore surface. Then the amount of the intruded mercury can be calculated to determine the porosity, average pore size, and

pore size distribution of coal. Supposing that the pore is cylindrical-like, with a radius of r , in order to overcome surface tension and enter the interior of the pore, the applied mercury pressure at least meets the Washburn equation, formula as

$$P \cdot r = -2\gamma \cos \theta \quad (2)$$

where, P and r represent the applied mercury pressure and the pore radius, γ and θ refer to the surface tension of mercury and the contact angle between mercury and the surface of coal pores, respectively.

Therefore, the PoreMaster-33 automatic mercury intrusion instrument (see in Figure 1a) from the U.S. was used to conduct the MIP tests in this paper. The measurable pore distribution range (in diameter) of this instrument is 0.0064–950 μm . The mercury can be continuously or stepwise pressurized from a vacuum to 33,000 psi. The samples used for MIP tests are oven-dried coal particles with a mass of 0.831 g and a diameter of 3–6 mm.

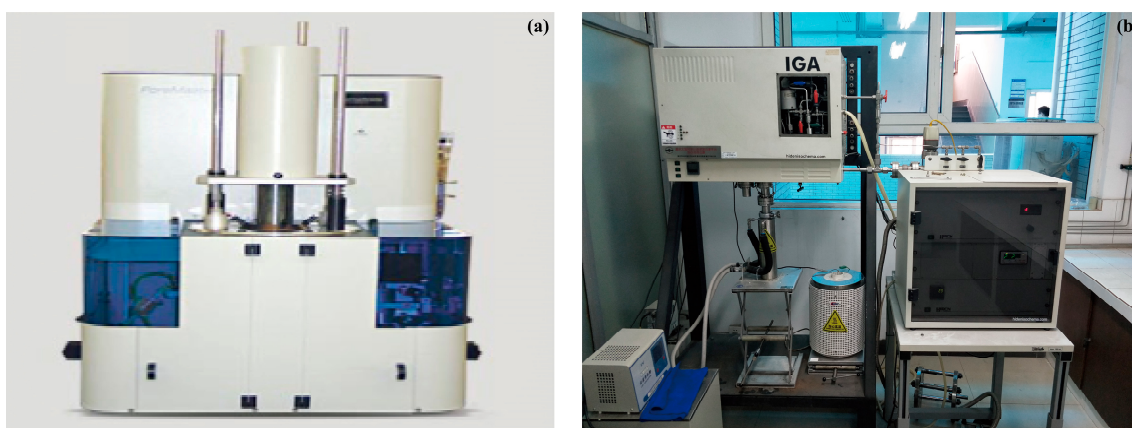


Figure 1. Test setups for Mercury intrusion porosimetry (MIP) tests and Isothermal adsorption tests. (a) PoreMaster-33 automatic MIP instrument; (b) IGA-100 automatic intelligent weight analyzer.

2.2.2. Isothermal Adsorption Tests

Coal performs strong adsorbability due to its well-developed pore structure. To study the adsorption characteristics of collected coal samples and obtain the key parameters for subsequent analysis, the isothermal adsorption tests were performed. The isothermal gas-adsorption process in porous medium could be described by the Langmuir theory, which suggests that the adsorption of gas in porous materials occurs on the pore surface, and is a dynamic equilibrium of two opposite physical processes of gas molecules gathering and escaping on the pore surface. That is, the gas in coal is in a dynamic equilibrium state of adsorption and desorption. The Langmuir equation describes the functional relationship between adsorption capacity and adsorption equilibrium pressure, and its common expression is

$$q = \frac{abp}{1 + bp} \quad (3)$$

where, q is the amount of gas adsorbed by the coal sample when arriving at isothermal adsorption equilibrium; p is the equilibrium pressure for adsorption; a is the Langmuir adsorption constant characterizing the maximum adsorption capacity of the coal sample at equilibrium pressure; b is the other adsorption constant quantifying the adsorption energy, valued as the reciprocal of the equilibrium pressure corresponding to the adsorption capacity reaching half the Langmuir volume, formula as $b = k_a/k_d$, in which k_a and k_d are the adsorption and desorption rate constant, respectively. Thus, the Langmuir adsorption constants a and b are usually used to judge the adsorbability of coal and used in correlative computation about ad/desorption.

Therefore, the isothermal adsorption tests of collected coal samples were conducted using an automatic intelligent weight analyzer (model IGA-100, see in Figure 1b) designed and manufactured by Hiden Company in the U.K., which measures the mass change of the sample using a magnetic suspension microbalance to determine the mass of adsorbed gas. This test system allowed testing samples with mass in the range of 0–200 mg, with a mass resolution of 0.1 μg . Thereby, 100 g coal particles sizing 50–80 mesh (0.180–0.300 mm) were picked up for isothermal adsorption tests. In order to minimize the contingency and guarantee the reliability of test results, three groups of isothermal adsorption tests were carried out. The experimental gas in this paper was selected as methane, which is common in coal and gas outburst accidents.

2.2.3. Desorption-Diffusion Tests for Coal Particles with Different Sizes

The desorption-diffusion tests for coal with different particle sizes were conducted using a self-developed setup at Chongqing University, China, as shown in Figure 2. The structure and function of this setup are similar to the most present gas desorption tests setups [38,39], consisting of an adsorption-desorption unit, a vacuum pumping unit, a high-pressure inflation unit, and a desorption-diffusion measurement unit. In detail, the adsorption-desorption unit comprises a coal sample tank and a reference tank in the material of stainless steel, of which the former provides an airtight environment for coal samples adsorbing gas sufficiently to a dynamic equilibrium state, and the latter functions as a gas-pressure conditioner and compensator. The vacuum pumping unit is controlled by a vacuum pump to exclude the influence of non-test gases. The high-pressure inflation unit is composed of a compressed gas cylinder and some pressure pipelines and valves, providing high-pressure experimental gas for tests. Furthermore, the desorption-diffusion measurement unit is comprised of a gas desorption instrument, some sensors, and a data monitoring system, measuring the gas desorption capacity and monitoring gas pressure and temperature changes using sensors and data acquisition terminal. However, this setup can be upgraded by using an automatic flow meter rather than a volumetric cylinder in the future.

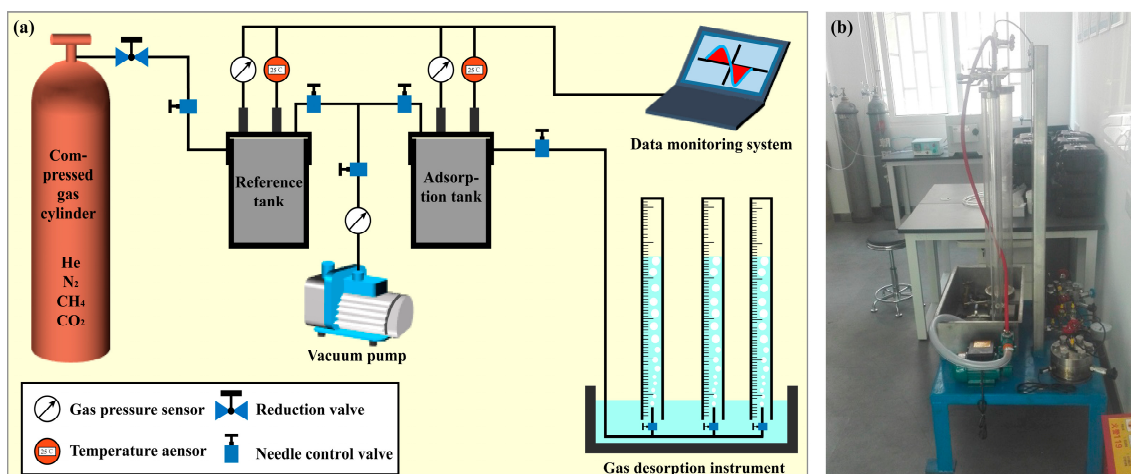


Figure 2. Desorption-diffusion tests apparatus for coal with different particle sizes. (a) Sketch of desorption-diffusion tests apparatus for coal with different particle sizes; (b) Physical picture of the apparatus.

After being pulverized, sieved, and oven-dried, different sizes of coal samples were selected for desorption-diffusion tests under the adsorption equilibrium pressure of 1.0 MPa to study the desorption-diffusion regularity of coal with different particle sizes. The experimental protocol is listed in Table 2 and the specific test steps are as follows:

1. Weigh a certain mass of oven-dried coal samples and fill them into the adsorption tank fully, reducing the influence of free space in the tank. Then the mass of tested

samples could be obtained by subtracting that of the remaining coal samples from the total.

2. Seal the test system and vacuum the reference tank and adsorption tank, minimizing the influence of non-test gases. Then close the valves and shut down the vacuum pump when the vacuum gauge reading -0.1 MPa.
3. Fill the test gas into the reference tank first using the high-pressure cylinder. Afterward, close the gas cylinder when the pressure of the reference tank reaches 1.2 times the adsorption equilibrium pressure set for the test.
4. Open the valve to connect the reference tank with the adsorption tank. Gas in the reference tank flows into the adsorption tank to get balance. Make coal samples adsorb sufficiently for at least 12 h to get adsorption equilibrium at the set pressure before closing the valve to make the adsorption tank independent.
5. Open the valve of the adsorption tank, releasing the free-space gas into the atmosphere. When the gas pressure in the adsorption tank drops to 1 atm, start timing and quickly pass the gas into the desorption-diffusion measurement unit to measure the volume of gas desorbed and diffused. The measurement time is 50 min.

Table 2. Experimental protocol of desorption-diffusion tests.

Sample	Sample Mass (g)	Particle Size (mm)	Average Particle Size (mm)	Test Gas	Test Temperature (K)	Adsorption Equilibrium Pressure (MPa)
1	107.66	0.125–0.212	0.168	CH ₄	298.15	1.0
2	120.30	0.212–0.425	0.319	CH ₄	298.15	1.0
3	49.69	1–2	1.5	CH ₄	298.15	1.0
4	101.12	5–15	10	CH ₄	298.15	1.0
5	60.00	25–35	30	CH ₄	298.15	1.0

The above experimental scheme is planned based on the control variate method. The only variate was set as the coal particle size, and other test conditions such as test gas, temperature and adsorption equilibrium pressure were fixed, benefitting clarifying the effect of particle size on desorption-diffusion regularity and further to explore its influence on outburst-coal breaking.

3. Results and Discussion

3.1. Pore Structure Characteristics of Coal Samples

The pore structure in coal is usually classified based on the pore diameter. The classification standard used in this study is proposed by Hodot, B.B. [5], according to which pores in coal are divided into micropores sizing below 10 nm, transitional pores sizing 10–100 nm, mesopores ranging 100–1000 nm, and macropores beyond 1000 nm. This classification method is widely used in coal rock pore structure characteristics analysis. Figure 3 shows the relationship between the mercury volume intruded into coal pores and the applied mercury pressure. The red segment as shown in Figure 3a indicates the mercury intrusion process, during which mercury first occupies the gaps between the particles and invades the visible and large pores in the coal particles under low-pressure conditions. After large pores are fully filled, as the pressure increases, mercury begins to enter mesopores and transition pores in sequence, and fills micropores when the pressure is higher at last. When micropores are filled fully, the mercury pressure is reduced and the mercury removal process begins, as shown in the blue segment in Figure 3a. With the decrease of pressure, the mercury intruded is sequentially removed from coal pores. However, the variation of the contact angle between mercury and the pore surface changes the surface tension. That means not all intruded mercury can be removed, resulting in some mercury remaining. Therefore, a hysteresis phenomenon occurs during the mercury removal process, where the mercury removal curve is higher than the mercury intrusion

curve. From Figure 3b,c, macropores beyond 1000 nm predominate in the tested coal samples, accounting for 55.9% of the total pore volume. Transitional pores and mesopores account for 22.3% and 16.2%, respectively. However, micropores occupy only about 5.6%, which is the result of the high surface tension of mercury, inducing most micropores to be difficult to detect owing to they are hard-intruded by mercury. By MIP testing, the total pores volume and the porosity of coal samples is $0.0652 \text{ cm}^3/\text{g}$ and 9.16%.

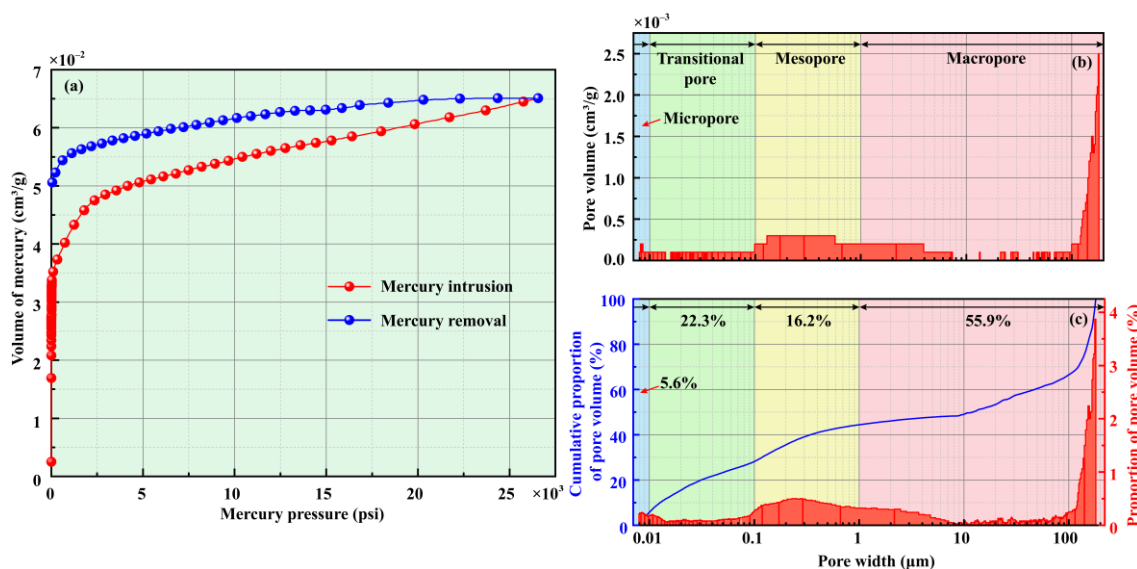


Figure 3. Results of mercury intrusion porosimetry (MIP) test. (a) MIP tests curve; (b) Pore size distribution; (c) Pore size proportion distribution.

3.2. Adsorption Characteristics of the Coal Samples

Coal is a typical dual-porosity structural medium with abundant pores, voids, cleats, and cracks, producing a large surface area for gas adsorption and giving rise to its strong adsorptive ability. Gas molecules are attracted by the Van Der Waals adsorptive potential to adhere to the coal pores surface within micropores, while gas is easier to occur the classical capillary condensation within mesopores and macropores. Gas adsorbing onto coal pores surface was most usually described by the Langmuir theory (monolayer adsorption theory) and the BET theory (Multilayer adsorption theory) [17]. The Langmuir theory suggests that gas molecules are adsorbed onto adsorption sites on coal pores surface in a single layer. Thus, it is well fit with the Type I isotherms classified by the IUPAC and often used to determine the key adsorption constants in practice. However, the BET theory thinks gas molecules adsorbed onto the pores surface also behave attraction to the free molecules, resulting in the multilayer adsorption, which is more commonly used in the determination of specific surface area in practice. Thereby, the Langmuir theory was used in this paper to fit with the experimental data. The results are shown in Figure 4, where it is the average result of the three groups of tests with methane and is plotted as the relationship between the adsorbed gas volumes and the adsorption equilibrium pressure. As shown in the figure, it can be recognized as a Type I isotherm. Under constant temperature conditions, with the increase of adsorption equilibrium pressure, the adsorption capacity of coal samples for CH_4 gradually increases and tends to reach a limit value. At the beginning of adsorption, the methane molecules were arrested by the specific adsorption sites to adhere. More methane molecules were adsorbed as the adsorption equilibrium pressure increases, inducing the adsorption capacity raises gradually. When the pressure is increased to a certain value, the adsorption sites were fully filled or the adsorbed methane molecules dynamically equals to those escaping from the sites, keeping an adsorption equilibrium state. Thereafter, according to Equation (3), the key adsorption parameters of tested coal

samples can be obtained from the fitting results, as listed in Table 3, where the maximum adsorption capacity of methane for the tested coal samples is $17.16 \text{ cm}^3/\text{g}$.

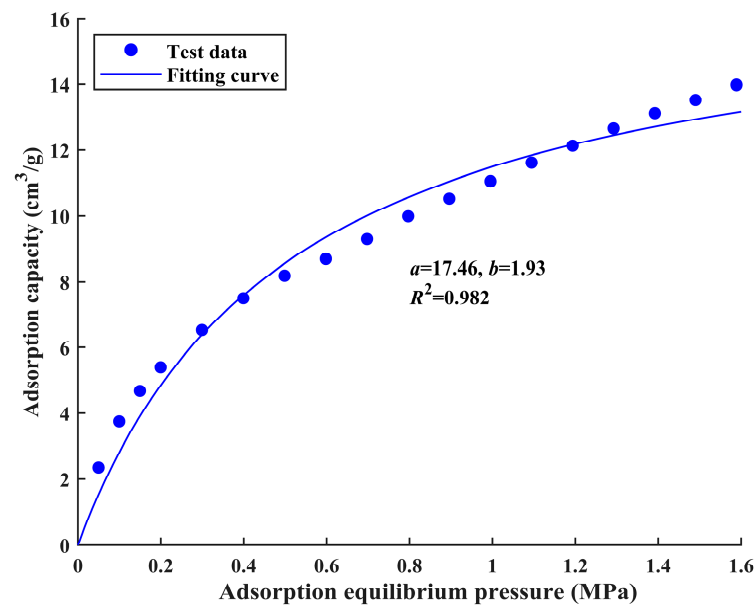


Figure 4. Adsorption isotherm curve of coal samples.

Table 3. Fitting parameters of Langmuir isothermal adsorption equation.

Test Gas	Adsorption Constant a (cm^3/g)	Adsorption Constant b (MPa^{-1})	Fitting Correlation Coefficient R^2
CH_4	17.46	1.93	0.982

3.3. The Desorption-Diffusion Characteristics

Gas escaping from the coal structure is a complex series-parallel process of desorption, diffusion, and seepage [40,41]. When the adsorption equilibrium state of coal is disrupted by external disturbances or gas pressure differences, the adsorbed gas generally undergoes instantaneous desorption [42]. However, for overcoming the resistance of the developed pore network, gas in fact needs a certain amount of time to pass through the coal matrix to free [43]. That is, only free gas and the gas desorbed from coal surface and open pores surface could immediately free, while gas in micropores and mesopores must experience diffusion and seepage process after desorption. The desorption-diffusion process is discussed in this study to explore their influence on coal breaking during coal and gas outburst. To date, scholars at home and abroad unanimously agree that the gas diffusion in the initial stage of desorption follows Fick's law, formulated as

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (4)$$

where, C is the gas concentration, D represents diffusion coefficient. Chinese scholar Yang Q. and Wang Y. [43] solved the above expression under the first type of boundary conditions in 1980s, and obtained its series solution as

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 D' t) \quad (5)$$

where, Q_t and Q_∞ indicates the cumulative amount of diffused gas after time t and the ultimate gas diffusion amount when time t approaching infinity, D' represents the effective

diffusion coefficient, characterizing the speed of gas emitting from coal. Thereafter, the classical Fick's law in Equation (4) was updated by Li Z. et al. [28] based on the understanding that the diffusion coefficient is decayed over time rather than a constant. The dynamic diffusion coefficient expressed as a negative exponential function was proposed, as formula

$$D(t) = D_0 \exp(-\beta t) \quad (6)$$

where, $D(t)$ represents the dynamic diffusion coefficient, D_0 represents the initial diffusion coefficient at $t = 0$, β is the decay coefficient of D_0 . That means, gas containing in macropores first diffuses due to the weak resistance. As time goes on, the reduction of gas in macropores promotes the diffusion of gas in mesopores and micropores, where the resistance increases and the diffusion coefficient decays. Based on this, Equation (5) is rewrite as

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_0}{r_0^2 \beta} (1 - e^{-\beta t})\right) \quad (7)$$

which is more suitable for describing the process of gas desorbing and diffusing from the outburst-broken coal.

Therefore, Equation (7) was applied to fit with the data measured from the desorption-diffusion tests for coal particles of different sizes. The results were shown in Figure 5, drawing into the variation of the gas diffusion rate of coal particles over time, where Q_t/Q_∞ is the accumulated gas diffusion rate. Under the testing conditions,

$$Q_\infty = Q - Q_0 \quad (8)$$

where, Q represents the total gas content in coal samples. It can be computed by the following equation, in which the influence of moisture was ignored because of the dried coal samples.

$$Q = \frac{\phi V_m}{\rho RT} p + \frac{100 - A}{100} \cdot \frac{abp}{1 + bp} \quad (9)$$

where, the first term indicates the free gas content per unit mass of coal and the second term reveals the adsorbed gas content per unit mass of coal. Besides, ϕ is the porosity detected by the MIP tests, V_m represents the molar volume of gas valued at 22.4 L/mol, ρ and A represent the visual density and ash content of coal samples listed in Table 1, R and T mean the gas constant and the absolute temperature under test conditions, a and b are the adsorption constant in Table 3, p represents the adsorption equilibrium pressure. Furthermore, the value of Q_0 in Equation (8) could be obtained by substituting $p = p_0$ into Equation (9), meaning the gas content under atmospheric pressure conditions.

From the fitting results in Figure 5 and the specific fitting parameters shown in Table 4, the correlation coefficient indicates that Equation (7) has a good fitting effect on the experimental data. However, it is found that the initial diffusion coefficient of the tested coal samples does not decay significantly over time. As shown in Figure 5, as time goes on, the accumulated gas diffusion rate of coal samples with different particle sizes all increases gradually and the growth rate decreased, tending to a certain level at last. Adsorbed gas escapes from the pore surface of coal as long as the gas pressure is released, then it overcomes the resistance of coal structures to diffuse through the pores network to the atmosphere. As time goes by, more adsorbed gas desorbs and diffuses from coal, increasing the accumulated gas diffusion rate regarding that the ultimate gas diffusion amount Q_∞ is a constant for a certain mass of coal samples under a certain adsorption equilibrium pressure. Thereby, the accumulated gas diffusion rate will tend to one and the cumulative gas diffusion amount will tend to the ultimate gas diffusion amount when time t approaching infinity, reaching the ideal state where there is no gas remaining in coal.

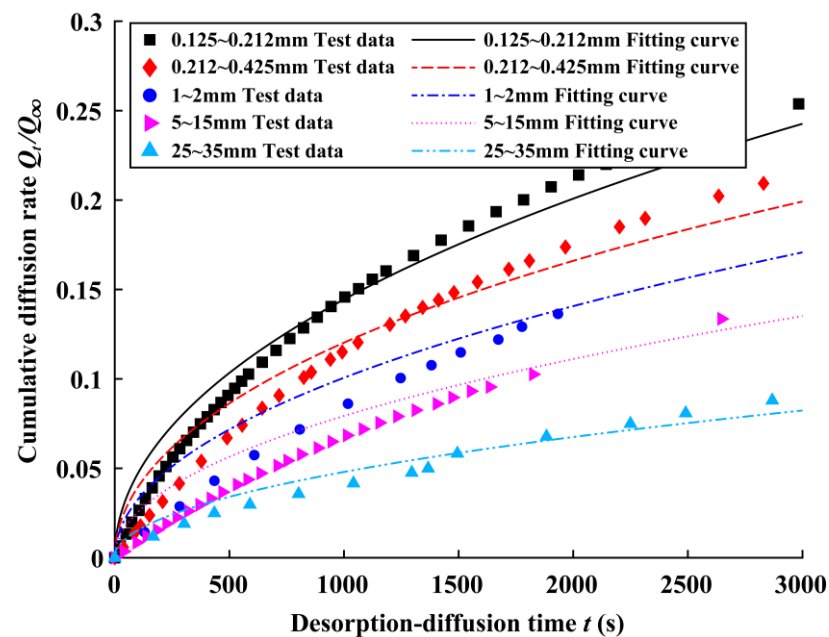


Figure 5. Desorption-diffusion characteristics of coal samples with different particle sizes.

Table 4. Fitting parameters for desorption-diffusion of coal samples with different particle sizes.

Coal Particle Size $2r(\text{mm})$	Initial Diffusion Coefficient $D_0 (\times 10^{-9} \text{cm}^2/\text{s})$	Decay Coefficient $\beta (\text{s}^{-1})$	Correlation Coefficient R^2
0.125~0.212	0.140	1.83×10^{-10}	0.9677
0.212~0.425	0.349	4.29×10^{-5}	0.9890
1~2	5.253	2.33×10^{-13}	0.9388
5~15	143.17	4.07×10^{-14}	0.8907
25~35	463.99	1.72×10^{-8}	0.9496

Additionally, with the increase in coal particle size, the accumulated gas diffusion rate gradually decreases, resulting in the cumulative gas diffusion amount during the same time also decreasing. That means, it is more difficult for gas to desorb and diffuse because of the more complex pore structure and longer and more tortuous diffusion route in bigger coal particles. Moreover, based on the test results, the parameters characterizing the desorption-diffusion capacity were computed. Specifically, the effective diffusion coefficient D' reflects the speed of gas emitting from coal particles. And the kinetic diffusion parameter ν reveals the difficulty for gas molecules desorbing from coal structure [43,44].

The calculation results were figured in Figure 6. Combined with Table 4, it can be revealed that the larger the particle size of coal samples, the greater its initial gas diffusion coefficient, while its effective diffusion coefficient and kinetic diffusion parameters are smaller. This is because the gas diffusion coefficient is closely related to the size of the diffusion area. As the coal particle size decreases, its specific surface area and average pore size become smaller, inducing a decrease in effective diffusion area. What's more, the smaller coal particles mean a shorter and more simple diffusion route. Thus, its initial gas diffusion coefficient is smaller. In the same way, these reasons also lead to gas molecules desorbing and diffusing out of coal particles more easily and quickly, meaning a greater effective diffusion coefficient and kinetic diffusion parameter. Therefore, as shown in Figure 6, it further validated that as the particle size of the coal samples increases, the gas molecules in the coal particles become more difficult to desorb from the pore surface, and the desorbed gas molecules diffuse slower in the pore throats of coal particles. Also, the

similar results that the effective diffusivity and diffusion amount of crushed coal particles is commonly larger than that of a coal core have been obtained in Bowen Basin (Australia) bituminous coal [45,46]. Thus, conclusions drawn based on the results of desorption-diffusion tests in this study may be used in guiding production and management in similar coal mines in other regions of the world after amending the difference of the geological conditions and coal seam characteristics.

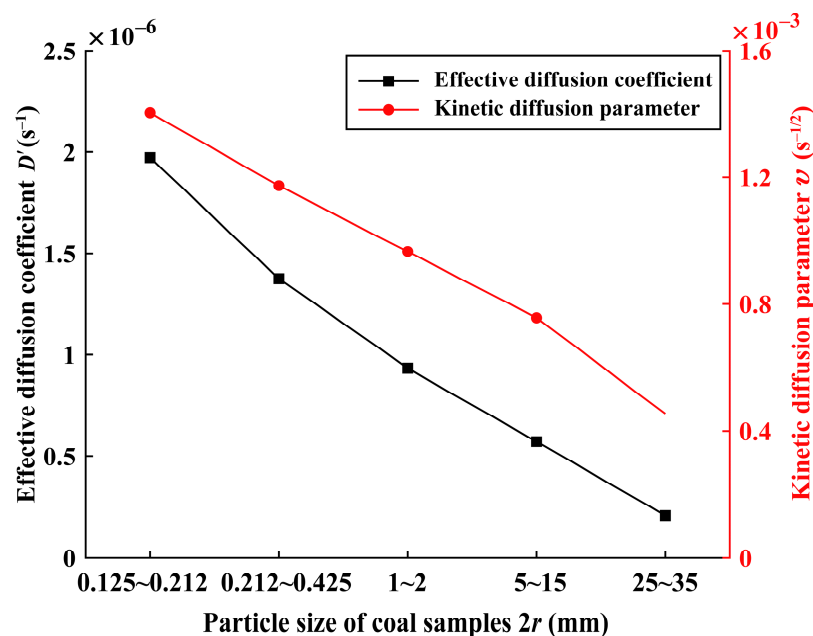


Figure 6. Characteristic parameters for desorption-diffusion of coal samples with different particle sizes.

3.4. Influence of Coal Desorption-Diffusion on Outburst-Coal Breaking

Coal breaking and structural instability are the prerequisites for outbursts happening. The participation of gas in breaking coal during outburst occurrence is mainly manifested in two aspects. On the one hand, its desorption-diffusion may change the mechanical properties of the coal body owing to the adsorption expansion and desorption contraction effects during the incubation and trigger stages of outbursts [18,19,32,47]. On the other hand, its release and expansion may break coal again or affect coal breaking as a medium providing and transmitting energy when coal is thrown out, thereby affecting the occurrence of outbursts. Thus, gas desorption and diffusion are key factors affecting the occurrence of the coal and gas outburst. According to the abovementioned second aspect of gas participating outburst-coal breaking, the energy dissipation during gas desorption-diffusion could be analyzed. The viewpoint that it is a polytropic process near an isothermal one for gas releasing and expanding to do work when outbursts occur has been widely adopted [48,49]. Thus, the expansion energy done by one molar of ideal gas experiencing a polytropic process is formulated as

$$W = \frac{RT}{n-1} \left[1 - \left(\frac{p_1}{p} \right)^{\frac{n-1}{n}} \right] \quad (10)$$

where, p is the initial gas pressure, p_1 is the expanded gas pressure, R and T are the gas constant and the initial gas temperature, n represents the polytropic index, $n \approx 1$.

Thereafter, the expansion work done by a certain volume of gas during its desorption and diffusion could be calculated through the formula

$$W = \frac{V \cdot RT}{V_m(n-1)} \left[1 - \left(\frac{p_1}{p} \right)^{\frac{n-1}{n}} \right] \quad (11)$$

where, V_m represents the molar volume of gas valued at 22.4 L/mol. From Equation (11), it is easy to find that the expansion work done by gas desorbing and diffusing from coal is linear with the gas volume, i.e., the cumulative amount of diffused gas. That means the more gas desorbs and diffuses from coal particles, the more energy it carries for breaking coal. Consequently, as the particle size of coal decreases, the cumulative gas diffusion amount increases, and gas expansion energy thereto increases, which induces coal particles more easily to be further broken, in turn, making coal particle size smaller and gas diffusion amount larger, forming a closed cycle where coal breaking and gas release is stimulated at last.

To sum up, as shown in Figure 7, the fragmentation of coal during outbursts will accelerate the desorption and diffusion of gas in coal. And the higher the degree of coal fragmentation, the smaller the particle size of coal after breaking. Thus, it is easier for gas to desorb from coal particles, and the desorbed gas diffuses faster, resulting in more gas emitted from the coal body in a short time. Accordingly, when a coal and gas outburst occurs, coal will be broken into different particle sizes, the cumulative gas diffusion amount will increase in a short period of time, and the diffusion rate will also rapidly increase, this kind of promotional effect of desorption and diffusion will be more significant with the coal destruction increases. As a result, when outbursts occur, with the release of gas pressure and the instantaneous destruction of coal structures, a large amount of gas will be rapidly released into the pore-crack network in the coal body, forming a high-speed gas flow, further expanding the degree of coal fragmentation, and even pulverizing coal. As the degree of fragmentation enlarges, the gas stored in the coal particles will quickly and heavily desorb and diffuse, supplementing the gas to be released in the pore-crack network. In this way, a positive feedback effect of continuous coal fragmentation and rapid and abundant gas release in coal is formed in a short time. This positive feedback effect may be the reason for the gas released in quantities in outbursts and often exceeding the original gas content of coal seams, which promotes the occurrence and development of outbursts to a certain extent, whereas threatens the coal mine safe production and coal resources sustainable production.

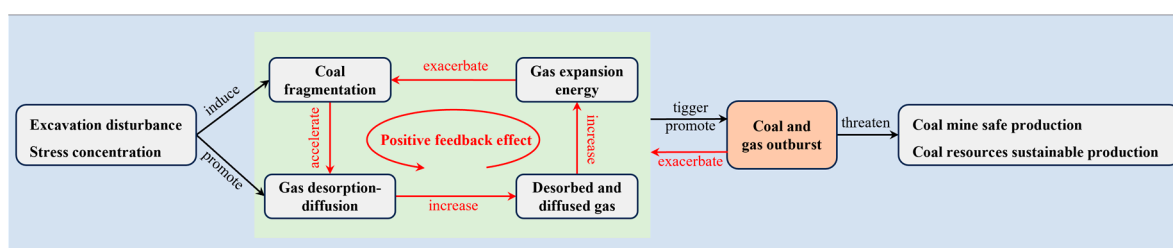


Figure 7. Positive feedback effect of desorption-diffusion on outburst-coal breaking.

4. Conclusions

In this paper, tests were carried out to study the gas desorption-diffusion regularity of coal with different particle sizes and its influence on outburst-coal breaking. The mercury intrusion porosimetry (MIP) tests and isothermal adsorption tests were conducted to determine the porosity and the isothermal characteristics of coal samples. Then, the desorption-diffusion tests were performed to analyze the desorption-diffusion regularity of coal with different particle sizes. Finally, the desorption-diffusion characteristics of coal varied with particle sizes and its influence on outburst-coal breaking was discussed. According to the results, the main conclusions were summarized as follows:

1. As time goes on, the accumulated gas diffusion rate of coal samples with different particle sizes all increases gradually and the growth rate decreased, tending to a certain level at last.
2. With the increase in coal particle size, the cumulative gas diffusion rate and amount decrease. That means, it is more difficult for gas to desorb and diffuse from larger coal particles, due to its more complex pore structure and longer and more tortuous diffusion route.
3. The larger the particle size of coal samples, the smaller the effective diffusion coefficient and kinetic diffusion parameter, demonstrating that larger particle size increases the difficulty for gas molecules desorbing from the pore surface and slows the desorbed gas diffusing out of the pore throats of coal particles.
4. When outbursts occur, a positive feedback effect that coal breaks continuously and gas releases rapidly and abundantly is formed in a short time. This positive feedback effect may be the reason for the gas released in quantities in outbursts and often exceeding the original gas content of coal seams, which promotes the occurrence and development of outbursts to a certain extent. This finding will make sense in coal mine disaster prevention and sustainable production of coal resources. In the future, further research on the micro-mechanism of desorption-diffusion promoting outburst-coal breaking will be carried out.

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