Nanopore Characteristics of Coal and Quantitative Analysis of Closed Holes in Coal

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ABSTRACT: Methane gas is mainly present in coal in two forms: free and adsorbed. There are a large number of closed pores inside the coal, which makes it difficult to measure the gas content of the coal. Therefore, studying the nanoscale closed pores of coal is of great importance for gas control. To study the pore structure characteristics of coal with different deformation degrees and to analyze the volume fraction of closed pores in coal, various coal samples were analyzed by the low-temperature liquid nitrogen adsorption method (LT-N2GA), the carbon dioxide adsorption method, and small-angle X-ray scattering (SAXS). The variation of parameters such as the pore size, pore volume, specific surface area, and degree of metamorphism was compared by using different methods to obtain the proportion of the closed pore volume of different coal samples. The results show that with the increase of the degree of coal metamorphism, the total pore volume and specific surface area of coal samples show a decreasing trend first and then an increasing trend, while the average pore diameter of coal samples gradually increases first and then decreases sharply. When the degree of deterioration of coal is low (volatile content > 20%), the closed pores of coal account for more than 48% of the open pores. When the degree of deterioration of coal samples is relatively high (volatile content <20%), the proportion of large pores in coal bodies decreased from 59.47 to 29.07%, and the proportion of pores in mesopores decreased from 12.15 to 11.09% and finally increased to 11.65%, and the proportion of micropore diameter increased from 28.38 to 59.28%. The volume fraction of the coal sample measured by the SAXS experiment shows that when the coal quality is high, the volume of the mesopores is large, which is consistent with the results of the low-temperature liquid nitrogen and CO2 adsorption experiments. Judging from the number of holes, the number of closed pores is 1 to 3 orders of magnitude greater than the number of open holes, and the number of closed holes of coal samples accounts for more than 94% of the total number of holes. It shows that the number of closed holes in the coal is far greater than the number of open holes, so the gas in the coal is mainly concentrated in the closed holes, and the formation of closed pores is partly because of the collapse of the internal structure and partly because of the volatilization of unstable substances. The research combined with LT-N2GA, the carbon dioxide adsorption method, and SAXS test methods can better analyze the number of closed pores of coal and characterize the nanopore fracture structure of coal. The novelties of this article are that this is a quantitative analysis performed using a scientific method of SAXS. The findings of this study can lead to a better understanding of the coal and gas outburst mechanism and the existence of gas to adopt better prevention measures.

1. INTRODUCTION

The coal reservoir is a discontinuous, nonhomogeneous, and anisotropic body, and it is a double-porosity medium composed of fissures and pores.1–3 Coal seam pores and closed pores are the main storage places for coal bed gas. The development characteristics of the coal pores and the number and volume of the closed pores are closely related to gas adsorption, desorption, diffusion, seepage, and so forth.4–6 Therefore, it is of great theoretical significance to study the nanoscale pore structure and closed pores of coal for coal gas occurrence and the gas migration mechanism.6–8

The nanopore structure of coal plays an important role in the occurrence of coal seam gas. To this end, many experts and scholars at home and abroad have studied the pore structure characteristics of coal and achieved many useful research results. For example, foreign scholar Hodot11 believes that the pores in coal can be divided into micropores (pore diameter <10 nm), transition pores (10–102 nm), mesopores (102–103 nm), and macropores (103–104 nm); Ju and Jiang et al.12 concluded that different types of structural coal nanopore size structures can be naturally classified, and the pore size structure can be divided into transition pores (15–100 nm),
micropores (5−15 nm), and submicropores (2.5−5 nm), and very micropores (2.5 nm). With the enhancement of structural deformation in the low coal rank deformation and metamorphic environment, the pore volume of transition pores of different types of structural coal is significantly reduced, and the pore volume of micropores and their lower pore diameter sections is significantly increased. The amplitude is reduced, but the submicropores increase faster; Chen et al.\textsuperscript{13} believe that the pores in coal are divided into three categories: category I is open-air permeable pores, including cylindrical pores and equal plate pores that are open on all four sides; category II is airtight holes closed at one end, including cylindrical holes, parallel plate holes, wedge holes, and tapered holes closed at one end. The third type is a special-shaped hole, that is, a narrow-necked bottle shape. According to the sealing of coal holes and cracks, it can also be divided into closed holes and semi-closed holes. Zhang et al\textsuperscript{14} proposed a composite model to investigate the pressure behavior and production performance of a multi-wing hydraulically fractured multiple fractured vertical wells in a coalbed gas reservoir with a stimulated reservoir volume. Kou and Mortez\textsuperscript{15} develop a mathematical model to simulate the transient performance of a multi-wing fractured well (MWFW) in a coal seam reservoir. Including the characteristics of initial pressure and pore structure of coal seam, the proposed model simultaneously considers the Langmuir isothermal adsorption, Knudson diffusion, and Darcy seepage in the coal seam matrix as well as the viscous flow in the fracture system. Zhao et al.\textsuperscript{16} found that the porosity of coal showed a high−low−high change law with the increase of the coal rank. The primary pores were rapidly compacted at low coal rank, which was the reason for the sharp decrease of porosity in the initial stage. The formation of thermally caused pores and cracked pores in the first grade makes the porosity increase after decreasing. Alexeev et al.\textsuperscript{17} determine the volume of closed pores in different types of coal through experiments, and believed that in most cases, the total porosity of closed pores contributes more than 60% to the total pores, for easily protruding coal, the closed pore volume tends to increase. Chen et al.\textsuperscript{18} believe that the pores of shale gas reservoirs in the Longmaxi Formation in southern Sichuan are mainly composed of micropores and have a certain amorphous structure. The internal pore structure of the particles has parallel-shaped slit-like pores and contains other pores in various forms; the pores are in an open shape and are mainly open holes such as cylindrical holes opened at both ends and parallel plate holes (cones, cylinders, flat plates, and ink bottle shapes) opened on four sides. Du\textsuperscript{19} believes that according to the openness of coal, the pores of coal can be divided into open pores, semipore pores, and closed pores. The open hole has a hysteretic ring for mercury intrusion, and the closed hole does not have a hysteretic ring because the mercury withdrawal pressure is equal to the mercury inlet pressure, but an inlet with an approximately closed pore, a narrow neck bottle hole, has a bottleneck different from the mercury withdrawal pressure of the bottle. It can also form a mercury drop curve with a sudden drop hysteresis loop. Niu\textsuperscript{20} concludes that there are two main reasons for the formation of closed pores during coal evolution: one is the formation of local uneven shrinkage of the matrix, and the other is the reduction of pore throat and local dislocation of pores caused by tectonic stress.

It can be seen from the above research and Figure 1 that many scholars are currently characterizing the microscopic open pore structure of coal, and there are few reports on the distribution of closed pores in coal. To this end, this article combines low-temperature liquid nitrogen adsorption (LT-N\textsubscript{2}GA), CO\textsubscript{2} adsorption and small-angle X-ray scattering (SAXS), and other experimental methods to study the internal pore characteristics of coal bodies of different metamorphic coal samples, focusing on exploring the structural characterization parameters such as the pore size distribution and specific surface area (SSA) of coal pore cracks at different scales. The distribution characteristics of the number and types of closed pores in the coal are analyzed to provide a basis for further improving the theory of coalbed methane mining and gas occurrence flow.

The novelties of this work are that this article gives a quantitative analysis of the closed pores of coal rather than just a qualitative analysis, which is performed by Du\textsuperscript{19} and uses the SAXS, which can evaluate the total number of pores in coal, combining the other two methods to estimate the number of closed holes in the coal, which is more reasonable than that reported in the study of Alexeev et al.\textsuperscript{17} because of the new testing method of SAXS. In this way, the findings of this study can help for a better understanding of the coal and gas outburst mechanism and the existence of gas to adopt better prevention measures.

First, the experimental sample collection is presented. Then, three experiments were performed with LT-N\textsubscript{2}GA, the carbon dioxide adsorption method, and the SAXS test method using eight samples, respectively. At last, the acquired data were compared.

2. EXPERIMENTAL SAMPLE COLLECTION

The experimental coal samples were taken from Ordos Coal Mine, Jiamusi Coal Mine, Matigou Coal Mine, Pingba Coal Mine, Pingbao Coal Mine, Haitian Coal Mine, Panxi Coal Mine, and Zhaozhuang Coal Mine. For the convenience of statistics and mapping, the coal sample of Erdos Mine is marked as 1, the coal sample of Jiamusi Mine is marked as 2,
the coal sample of Matigou Mine is marked as 3, the coal sample of Pingba Mine is marked as 4, the coal sample of Pingbao Mine is marked as 5, and the coal sample of Haitian Mine is marked as 6. The coal sample of Panxi Mine is marked as 7 and that of Zhaozhuang Mine is marked as 8.

We use the SDLA618 industrial analyzer, according to GB/T212-2008 “Coal Industrial Analysis Method”, to crush and screen 60−80 mesh (250−180 μm) dry coal samples to determine the coal quality, the composition ratio of moisture, ash, volatile matter, and fixed carbon. The measurement results are shown in Table 1.

### Table 1. Basic Information on the Test Coal Sample

| number | coal sample | coal quality | moisture % | ash % | volatile % | fixed carbon % |
|--------|-------------|--------------|------------|-------|------------|----------------|
| 1      | Ordos       | gas coal     | 4.77       | 3.3   | 32.24      | 60.81          |
| 2      | Jiamusi     | gas coal     | 0.81       | 14.9  | 28.05      | 56.59          |
| 3      | Matigou     | fat coal     | 9.5        | 8.37  | 25.38      | 58.12          |
| 4      | Pingba      | coking coal  | 0.67       | 16.21 | 20.49      | 62.88          |
| 5      | Pingbao     | lean coal    | 0.66       | 8.2   | 18.57      | 72.74          |
| 6      | Haitian     | lean coal    | 0.66       | 14.24 | 11.73      | 73.54          |
| 7      | Panxi       | lean coal    | 1.83       | 16.61 | 11.29      | 70.78          |
| 8      | Zhaozhuang   | anthracite   | 1.51       | 28.36 | 7.7        | 62.98          |

![Figure 2. Schematic diagram of the principle of the SAXS experiment.](https://dx.doi.org/10.1021/acsomega.0c03217)

3. EXPERIMENTAL METHOD AND PRINCIPLE

At present, domestic and foreign scholars have conducted a lot of research on the characterization of coal seam pore structure and formed two types of measurement and characterization methods mainly based on image analysis and fluid injection. Image analysis methods such as X-ray diffraction, scanning electron microscopy, and CT imaging can be used to directly observe the pore structure, morphology, and connectivity of the coal body. However, the obtained pore size distribution data are not representative in mathematical statistics and it is difficult to do quantitative analysis. The widely used fluid injection methods such as gas adsorption experiments and mercury intrusion experiments have the advantages of a wide measurement range and high accuracy, but such methods are limited by the test principle. The pore ranges of different experiments are different and can only characterize a certain scale. The pore distribution cannot fully reflect the pore structure characteristics of coal rock. Therefore, the author combined the two methods using low-temperature liquid nitrogen adsorption, CO₂ gas adsorption method, and small-angle X-ray to characterize the pore structure characteristics of the coal samples.

(1) Low-temperature liquid nitrogen adsorption method. In this test, the United States Kangta automatic SSA and pore size distribution analyzers were used to conduct experiments on the coal samples of the SY/T6154-1995 standard. First, the coal sample was degassed under vacuum for about 12 h, and the liquid nitrogen adsorption temperature was 77.35 K, and then at 1 standard atmospheric pressure, the low-temperature liquid nitrogen adsorption (LT-LN₂A)-related experimental data were obtained after about 3 h analysis. When a gas or vapor comes into contact with a solid, a part of the gas is captured by the solid. If the pressure is constant, its volume decreases. Therefore, the phenomenon of disappearing from the gas phase and adhering to the surface of the solid is called adsorption. The pore size of the coal sample pore structure is divided into a micropore, a mesopore, and a macropore. In liquid nitrogen isotherm adsorption experiments, Barrett–Joyner–Halenda (BJH) theory is commonly used to study mesopores and their distribution, DA theory to study the distribution of micropores, and density functional theory (DFT) theory to study the distribution of micropores and mesopores.

(2) CO₂ gas adsorption method. The test used an ultra-high-performance automatic gas adsorption instrument to perform isothermal adsorption of CO₂ with the method of gas adsorption static volume at 273.15 K to determine the pore structure parameters of different coal samples. The test pore size range is 0.3−1.5 nm hole. Based on the basic principles of the adsorption method (including BET theory, isothermal adsorption theory, DFT theory, DA theory, etc.), the SSA, pore volume, and pore size distribution of different coal samples can be analyzed to detect the micropores of the porous media structure.
(3) SAXS method. Guinier first proposed the small-angle scattering theory, which laid the initial theoretical foundation, Xu et al. applied it to the study of coal pore structure and affirmed the small-angle scattering technology. Compared with traditional research methods, the small-angle scattering technology has its superiority, and it can be used without destroying the coal samples. The experiment is carried out to obtain the pore structure characteristics of the sample, and it measures the total pores, including the closed pore problem that cannot be solved by adsorption.

The SAXS test instrument is the 1W2A SAXS instrument of Beijing Synchrotron Radiation Laboratory, the small-angle scattered experimental beam is emitted through the anode X-ray emitter, and enters the experimental channel through the synchrotron radiation device. In the case of a certain detector size and resolution, the shorter the distance, the larger the angular range of collection and the worse the angular resolution; the longer the distance, the smaller the angular range of collection and the better the angular resolution.

The schematic diagram of the experimental principle is shown in Figure 2.

4. TEST RESULTS AND ANALYSIS

4.1. Test Results of Low-Temperature Liquid Nitrogen Adsorption Method. Eight coal samples with different metamorphic degrees were subjected to low-temperature liquid nitrogen adsorption experiments, and the pore structure parameters of the coal samples were determined including their SSA, total pore volume, average pore size, DFT pore size, BJH mesopore size, DA micropore size and micropores, and the proportion of each aperture section of mesopores and large pores, and the relevant data results are shown in Table 2.

It can be seen from Table 2 that the total pore volume of coal samples is 0.00224–0.02689 cm$^3$/g, of which the total pore volume of the Pingbao coal sample is the smallest, which is 0.00224 cm$^3$/g, and the total pore volume of the Ordos coal sample is the largest, which is 0.02689 cm$^3$/g. The proportion of pore sections of each coal sample smaller than 10 nm ranges from 28.38 to 59.28%, among which the pore sections of the Pingbao coal sample less than 10 nm account for the least proportion, and the proportion of coal samples of Zhaozhuang smaller than 10 nm accounts for the most; the Pingbao coal sample has the largest proportion of large pores. It shows that the proportion of micropores in the pore size section of coal is relatively large, while the proportion of small pores and mesopores is relatively low. As shown in Figure 4, the relationship between the total pore volume and the degree of coal sample metamorphism is U-shaped, that is, as the volatile matter decreases, the total pore volume of the coal sample shows a decreasing trend first and then an increasing trend. The average pore size of the coal samples is 4.998–21.910 nm. Among them, the average pore size of the Zhaohuang coal sample is the smallest, which is 4.998 nm, and the average pore size of the coal sample of Matigou is the largest, which is 21.910 nm. As shown in Figure 3, the SSA of the coal samples is 0.4378–12.410 m$^2$/g, of which the SSA of the Pingbao coal sample is the smallest at 0.4378 m$^2$/g, and the SSA of the

| ID | BET SSA (m$^2$/g) | total pore volume (cm$^3$/g) | average pore size (nm) | DFT aperture (nm) | BJH medium hole diameter (nm) | DA pore size (nm) | Percentage of each aperture section/% | <10 nm | 10−10$^2$ nm | >10$^2$ nm |
|----|-------------------|-----------------------------|------------------------|-------------------|-------------------------------|------------------|----------------------------------------|--------|-------------|-------------|
| 1  | 1.6900            | 0.02689                     | 18.475                 | 6.079             | 3.412                         | 2.02             | 31.86                                  | 14.9   | 55.24       |
| 2  | 1.4385            | 0.01589                     | 20.650                 | 10.49             | 4.650                         | 2.00             | 31.42                                  | 10.97  | 57.61       |
| 3  | 1.4160            | 0.00776                     | 21.910                 | 12.35             | 12.400                        | 1.94             | 30.94                                  | 11.03  | 58.03       |
| 4  | 0.6643            | 0.00331                     | 20.910                 | 6.794             | 6.564                         | 1.98             | 29.21                                  | 11.88  | 58.91       |
| 5  | 0.4378            | 0.00224                     | 20.510                 | 12.55             | 4.640                         | 2.06             | 28.38                                  | 12.15  | 59.47       |
| 6  | 0.6982            | 0.00339                     | 20.580                 | 11.68             | 6.552                         | 2.04             | 43.73                                  | 11.11  | 45.16       |
| 7  | 1.2110            | 0.00619                     | 20.450                 | 7.032             | 4.640                         | 2.01             | 51.55                                  | 11.09  | 37.36       |
| 8  | 12.410            | 0.03202                     | 4.9980                 | 12.55             | 3.832                         | 1.94             | 59.28                                  | 11.65  | 29.07       |

Figure 3. Relationship between the SSA of the coal sample and volatile matter.

Figure 4. Relationship between the total pore volume, average pore size, and volatile matter of the coal samples.
Zhaozhuang coal sample is the largest at 12.410 m²/g. It can be seen that the relationship between the SSA and the degree of coal sample metamorphism is also U-shaped, that is, as the degree of metamorphism increases, the SSA of the coal sample decreases first and then increases. The DFT pore size range is 6.079−12.55 nm; the BJH mesopore size range is 3.412−12.4 nm; and the DA micropore size range is 1.94−2.06 nm.

It can be seen from Table 2, Figures 3, and 4 that as the degree of metamorphism increases, the SSA and total pore volume of the coal sample simultaneously decrease first and then increase sharply, and the average pore size generally shows an increasing trend first and then a decreasing trend sharply; among them, the coal sample of Zhaozhuang Mine, as the anthracite coal with the highest metamorphism degree, has the largest SSA and total pore volume and the smallest average pore diameter compared with other bituminous coal samples with medium and low metamorphism degrees, this indicates that the degree of coal metamorphism has a greater influence on the SSA, total pore volume, and average pore size of the coal samples.

As shown in Figure 5, the effect of micropore and mesopore diameters of different metamorphic coals on the adsorption volume can be obtained: layer 1 shows the pore size distribution of the DFT micromedium of coal samples with different metamorphisms with pore sizes between 0 and 80 nm; the BJH mesopore size range is 3.412−12.4 nm; and the DA micropore size range is 1.94−2.06 nm.

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Table 3. Related Data Results of CO₂ Adsorption Experiments

| ID | coal sample | BET SSA (m²/g) | microporous SSA (m²/g) | DA pore volume (cm³/g) | average pore size (nm) | DFT aperture (nm) | DA aperture (nm) |
|----|-------------|----------------|------------------------|-----------------------|-----------------------|------------------|------------------|
| 1  | Ordos       | 5.052          | 76.812                 | 0.028                 | 1.866                 | 0.785            | 1.72             |
| 2  | Jiamusi     | 3.743          | 40.033                 | 0.015                 | 1.956                 | 0.822            | 1.84             |
| 3  | Matigou     | 3.268          | 40.644                 | 0.015                 | 1.995                 | 0.627            | 1.7              |
| 4  | Pingba      | 2.824          | 36.889                 | 0.013                 | 2.078                 | 0.822            | 1.76             |
| 5  | Pingbao     | 2.175          | 34.815                 | 0.012                 | 2.110                 | 0.890            | 1.88             |
| 6  | Haitian     | 3.689          | 60.885                 | 0.020                 | 1.963                 | 0.822            | 1.740            |
| 7  | Panxi       | 9.342          | 95.229                 | 0.034                 | 1.824                 | 0.785            | 1.680            |
| 8  | Zhaozhuang  | 23.566         | 112.747                | 0.038                 | 1.436                 | 0.573            | 1.58             |
mesoporous, and the micropores take on the main task of adsorbing nitrogen. The DFT curves of other coal samples all have multiple peaks, concentrated in the micropore section and the mesopore section, indicating that the mesopores of bituminous coal are more developed than anthracite; at the same time, the ordinate axis shows the differential of volume to pore size. From the data, it can be seen that for the eight coal samples, as the degree of metamorphism changes from low to high, the dV (d) corresponding to the highest peak shows a decreasing trend first and then an increasing trend, and the peak ordinate corresponding to no. 8 anthracite is significantly higher than that of no. 1 gas coal. Comparative analysis of the coal samples shows that the micropores of highly metamorphic coal are more developed and the adsorption capacity is stronger than that of coals with low metamorphism and medium metamorphism, while the mesopores are the opposite.

4.2. Carbon Dioxide Adsorption Test Results. After adsorbing CO₂ on eight coal samples with different metamorphic degrees, combined with DFT theory and DA theory, the pore structure parameters are shown in Table 3: the range of mesopore SSA is 2.175–23.566 m²/g, of which the coal sample of Pingbao Mine has the smallest mesopore SSA and the Zhaozhuang coal sample has the largest mesopore SSA; the range of micropore SSA is 34.815–95.229 m²/g, of which the micropore SSA of the Pingbao coal sample is the smallest and the micropore SSA of the Zhaozhuang coal sample is the largest. The range of DA pore volume is 0.012–0.038 cm³/g, of which the coal sample of Pingbao Mine has the smallest DA pore volume, and the coal sample of Zhaozhuang Mine has the largest DA pore volume; the average pore size ranges from 1.436 to 2.11 nm, among which the average pore size of coal samples of Zhaozhuang Mine is the smallest, and the average pore size of the coal samples of Pingbao Mine is the largest; the range of DFT pore size is 0.573 to 0.890 nm, among which the DFT pore size of the coal samples of Zhaozhuang Mine is the smallest, the largest DFT pore size of coal samples is of Pingbao Mine; the range of DA pore size is 1.58–1.88 nm, among which the coal sample of Zhaozhuang Mine has the smallest DA pore size, and the coal sample of Pingbao Mine has the largest DA pore diameter. Combining the metamorphic degree of each coal sample in Table 3, that is, the size of the volatile matter, the relationship between the BET SSA, micropore SSA, and volatile matter Vdaf of the coal sample is shown in Figure 6, and the DA pore volume and the relationship between average pore diameter and volatile matter are shown in Figure 7.

It can be concluded from Table 3 and Figures 6 and 7 that with the increase of the coal sample metamorphism, after CO₂ adsorption, the measurement of BET SSA, micropore SSA, and DA pore volume of each coal sample showed a decrease and then increase trend. With the deepening of the metamorphism, the average pore size shows an increasing trend first and then a decreasing trend. That is, the coal with medium metamorphism has the smallest micropore SSA and pore volume, the largest average pore size and the micropore SSA, and pore capacity of high metamorphic coal is higher than that of low metamorphic coal, its average pore size is lower than that of low metamorphic coal. However, its DFT aperture and DA aperture generally did not change much. The no. 2 coal sample with low metamorphism contains a relatively small number of micropores and a large number of large and medium pores. In the no. 4 coking coal with a moderate degree of metamorphism, coali...
peak values of the DFT curves of other coal samples are concentrated in the 0.6—0.9 nm pore size segment, indicating that this pore size segment has a higher CO₂ adsorption capacity and a stronger adsorption capacity. In the 0.3—0.6 and 0.9—1.5 nm pore size sections, the adsorption capacity is basically zero, indicating that the adsorption capacity of the coal sample micropore section depends on the 0.6—0.9 nm pore size section.

4.3. Experimental Results of Small-Angle Scattering Method. The physical essence of small-angle scattering lies in the difference in electron cloud density between the scatterer and the surrounding medium. When analyzing results obtained for the coal samples, the difference observed in the scattering curve morphology was caused by the different pore structures of the coal sample. The comparison of the scattering curves of eight coal samples with different degrees of metamorphism is shown in Figure 9.

Because of the influence of the blocking sheet in front of the detector, the scattering curve in the extremely small-angle range cannot be obtained. Here, the small-angle range is extended using Guinier theory,⁴²,⁴³ to deduce a part of the small-angle scattering curve. Figure 9 shows the scattering curves of eight coal samples in a small-angle range. It can be seen from this that the trend of the scattering curves of coal samples with different metamorphic degrees is approximately the same, indicating that the coal pore structure has certain similarities. In the small-angle range, as the scattering angle increases, the scattering intensity of each coal sample gradually decreases, and as the coal sample metamorphism increases, the scattering intensity gradually increases, that is, the coal sample metamorphism degree in a small angle. It is proportional to the scattering intensity.⁴⁴

From the scattering curve in Figure 10, it can be seen that the coal sample in Jiamusi Mine has a relatively low degree of metamorphism. The pore shape in the coal particles is relatively rich, and the electron density fluctuations in the coal particles are obvious, resulting in a large scattering intensity. The downturn is caused by the micropores and smaller mesopores, indicating a larger SSA. The Panxi Mine
has a medium metamorphic bituminous coal. Because of the compaction and filling during coalification, the number of macropores and mesopores is reduced, and the fluctuation of electron density in the coal is relatively small, so the scattering intensity is low. When the degree of metamorphism reaches that of anthracite, a large number of micropores and mesopores are formed because of coalification, and the phenomenon of electron density fluctuations in the coal body is obvious, and the scattering intensity increases. The size of the SSA can be compared by the degree of downward bending of the second half of the image, that is, the greater the SSA, the greater the degree of downward bending.

The Guinier approximation formula was proposed by Guinier in 1939. It can be used to determine whether the pores are monodisperse or polydisperse, and to obtain the radius of gyration and pore radius of the pores of the monodisperse system within a small range of the scattering vector. The In(I(q)−q2) curve of the scattering system obeying Guinier’s law shows a linear relationship for the single scattering system of any scatterer when the scattering vector is close to zero. Rp can be obtained from the slope of the straight line because the scattering intensity of the through light part cannot be directly measured by experiment. It is generally believed that the Guinier theorem holds when Rp < 1. The Guinier curve that satisfies this scattering interval is shown in Figure 11 [45–47].

The following Table 4 lists the selection of the fitting range and the structural parameters of the scatterer corresponding to each fitting range by using the stepwise tangent method to estimate the pore size distribution of different coal samples. The histogram is used to visually characterize the pore size distribution of different characteristic pore size ranges of the coal samples, as shown in Figure 12. The volume fraction of the Jiamusi gas coal samples in the pore size range of less than 10 nm accounted for 39.1%, and the volume fraction of the Matigou coal samples in the pore size range of less than 10 nm accounted for 37.2%. The volume fraction of the Pingba Mine coking coal sample in the pore size range of less than 10 nm accounted for 32.9%, and the volume fraction of the Pingbao Mine thin coal sample in the pore size range of less than 10 nm accounted for 24.7%. The volume fraction of the poor coal sample in the Panxi Mine in the pore size range of less than 10 nm accounted for 32.9%, and the volume fraction of the anthracite coal sample in the Zhaozhuang Mine in the pore size range of less than 10 nm accounted for 33.4%. It shows the diversity of pore structures, and the coal samples with different metamorphic degrees have uneven pore size distribution, their metamorphic degree increases, and their pore development becomes more abundant.

It can be seen from Table 4 that in the same linear fitting range, the diameter of the no hypothetical scatterer is smaller than the diameter of the spherical scatterer. As the diameter of the scatterer increases, the volume fraction of the scatterer increases first and then decreases. As the degree of metamorphosis increases, the proportion of transition holes also increases.

The relevant parameters of the lognormal distribution function shown in Table 5 are mainly obtained based on the particle gyration radius Rp and Porod radius Rp. Where Kp is the Porod constant, Qh is the scale-invariant feature conversion, Rp is the radius of gyration, Rg is the radius of Porod, μ is the geometric mean of the particle size distribution, and σ is the standard deviation of the distribution.

### 4.4. Quantitative Analysis of Closed Pores in Coal

Because the carbon dioxide adsorption method and the liquid nitrogen adsorption method are limited by the test principle, the pore range of the experimental test is different. The carbon dioxide adsorption method can only test pores with a pore size in the range of 0.35–2 nm; the liquid nitrogen adsorption method can only test pores with a pore size in the range of 1.7–300 nm; while the small-angle scattering method measures the pore size in the range of 1–100 nm, and the number of open and closed pores of coal can be measured. Based on the small-angle scattering test range of 1–100 nm, the number of openings in the range of 1.7–10 nm measured by the liquid nitrogen adsorption method and the number of openings of 1–1.7 nm measured by carbon dioxide adsorption are estimated, to get the proportion of closed pores in the range of pore diameter 1–100 nm.

### 4.4.1. Estimation of the Number of Pores in Coal Based on the Liquid Nitrogen Test Results

The number of openings...
with a pore size in the range of 1.7−300 nm was obtained by the liquid nitrogen adsorption process, using the data shown in Table 2 where the total pore volume in each pore size section is below 10 nm to obtain the open pore volume in the range of 1.7−100 nm, the measured average pore diameter is then used to obtain the number of openings in the range of 1.7−100 nm. It is known from Table 2 that the total pore volume of the Ordos coal sample obtained by liquid nitrogen adsorption is 0.02689 cm³/g, the total pore volume of the Jiamusi coal sample is 0.01589 cm³/g, and the total pore volume of the Matigou coal sample is 0.00776 cm³/g. The total pore volume of coal samples in Pingba Mine is 0.00331 cm³/g, the total pore volume of coal samples in Pingbao Mine is 0.00224 cm³/g, the total pore volume of coal samples in Haitian Mine is 0.00359 cm³/g, the total pore volume of coal samples in Panxi Mine is 0.00619 cm³/g, and the total pore volume of the coal sample in Zhaozhuang Mine is 0.03202 cm³/g.

According to Table 2, the proportion of each pore size below 100 nm can be obtained. The pore volume of the Ordos coal sample with a pore diameter of less than 100 nm is 0.012573764 cm³/g, the pore volume of the Jiamusi coal sample is 0.006735771 cm³/g. The pore volume of the coal sample in Matigou is 0.003256872 cm³/g, and the pore volume of the coal sample in Pingba Mine is 0.001360079 cm³/g. The pore volume of the coal samples in Pingbao Mine is 0.000907872 cm³/g, the pore volume of the coal samples in Haitian Mine is 0.001968756 cm³/g, the pore volume of the coal samples in Panxi Mine is 0.003877416 cm³/g, and the pore volume of coal samples in Zhaozhuang Mine is 0.022711786 cm³/g. From Table 2, it can be seen that the average pore size of each coal body and the pore volume within a pore size of less than 100 nm, and then the number of open pores with a coal body pore size of less than 100 nm can be obtained. The relationship between the number of coal openings and the pore volume and average pore diameter is shown in formula 1

\[ N_i = \frac{3V}{4\pi R^3} \]  

In which, \( N_i \) is the number of openings per unit mass of coal with a pore size less than 100 nm; \( V \) is the pore volume of coal body with a pore diameter less than 100 nm, cm³/g; and \( R \) is the average pore radius of the coal body, nm.

According to formula 1, the number of openings per unit mass of coal with a pore diameter of less than 100 nm is obtained. The number of openings of the coal samples in Ordos is \( 3.808144 \times 10^{12} \), the number of openings of the Jiamusi coal sample is \( 1.460927 \times 10^{12} \), the number of openings in the coal sample of Matigou is \( 5.913913 \times 10^{11} \), the number of openings of the coal samples in Pingba Mine is

| coal sample | \( q^2 \) linear fitting range | \[ q^2 \] minimum value/nm | \[ q^2 \] maximum/nm | no hypothetical scatterer diameter/nm | the diameter of the hypothetical spherical scatterer/nm | normalized scatterer volume fraction/% |
|-------------|-------------------------------|--------------------------|------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| Ordos       | 0.47                          | 0.228                    | 4.61             | 11.9                                | 0.315                               |
|             | 0.165                         | 0.084                    | 8.99             | 23.22                               | 0.277                               |
|             | 0.084                         | 0.007                    | 17.35            | 44.79                               | 0.408                               |
|             | 0.47                          | 0.228                    | 4.61             | 11.9                                | 0.315                               |
| Jiamusi     | 0.165                         | 0.081                    | 8.22             | 21.23                               | 0.253                               |
|             | 0.061                         | 0.034                    | 15.62            | 40.33                               | 0.288                               |
|             | 0.034                         | 0.007                    | 27.41            | 70.76                               | 0.459                               |
|             | 0.165                         | 0.081                    | 8.22             | 21.23                               | 0.253                               |
| Matigou     | 0.35                          | 0.167                    | 5.43             | 14.01                               | 0.263                               |
|             | 0.13                          | 0.065                    | 10.8             | 27.89                               | 0.284                               |
|             | 0.065                         | 0.007                    | 19.83            | 51.21                               | 0.452                               |
|             | 0.35                          | 0.167                    | 5.43             | 14.01                               | 0.263                               |
| Pingba      | 0.19                          | 0.096                    | 7.65             | 19.76                               | 0.242                               |
|             | 0.068                         | 0.038                    | 14.91            | 38.49                               | 0.297                               |
|             | 0.038                         | 0.007                    | 27.53            | 71.08                               | 0.461                               |
|             | 0.19                          | 0.096                    | 7.65             | 19.76                               | 0.242                               |
| Pingbao     | 0.21                          | 0.105                    | 7.17             | 18.51                               | 0.236                               |
|             | 0.078                         | 0.043                    | 13.6             | 35.12                               | 0.287                               |
|             | 0.043                         | 0.007                    | 24.07            | 62.14                               | 0.477                               |
|             | 0.21                          | 0.105                    | 7.17             | 18.51                               | 0.236                               |
| Haitian     | 0.3                           | 0.145                    | 5.88             | 15.19                               | 0.178                               |
|             | 0.11                          | 0.04                     | 11.6             | 29.95                               | 0.242                               |
|             | 0.037                         | 0.007                    | 21.92            | 56.59                               | 0.356                               |
|             | 0.007                         | 0.007                    | 36.22            | 93.52                               | 0.224                               |
| Panxi       | 0.21                          | 0.105                    | 6.99             | 18.04                               | 0.249                               |
|             | 0.082                         | 0.044                    | 13.71            | 35.39                               | 0.298                               |
|             | 0.044                         | 0.007                    | 24.95            | 64.42                               | 0.453                               |
|             | 0.21                          | 0.105                    | 6.99             | 18.04                               | 0.249                               |
| Zhaozhuang  | 0.242                         | 0.124                    | 6.48             | 16.73                               | 0.257                               |
|             | 0.097                         | 0.052                    | 12.45            | 32.15                               | 0.294                               |
|             | 0.052                         | 0.007                    | 21.98            | 56.75                               | 0.449                               |
|             | 0.242                         | 0.124                    | 6.48             | 16.73                               | 0.257                               |
2.841211 \times 10^{11}$, the number of openings of the coal samples in Pingbao Mine is $2.009689 \times 10^{11}$, the number of openings of the coal samples in Haitian Mine is $4.313772 \times 10^{11}$, the number of openings of the coal samples in Panxi Mine is $8.658922 \times 10^{11}$, and the number of openings of the coal samples in Zhaozhuang Mine is $3.474273 \times 10^{14}$.

4.4.2. Estimation of the Number of Pores in Coal Based on the CO$_2$ Test Results. The pore size of the CO$_2$ test is

![Aperture distribution of the stepwise tangent method.](image)

(a) Ordos coal sample, (b) Jiamusi coal sample, (c) Matigou coal sample, (d) Pingba coal sample, (e) Pingbao coal sample, (f) Haitian coal sample, (g) Panxi coal sample, and (h) Zhaozhuang coal sample.
Table 5. Related Parameters of a Lognormal Distribution Function

| K_μ/\text{nm}^3 | Q_μ/\text{nm}^3 | R_{\min}/\text{nm} | R_{\max}/\text{nm} | \mu/\text{nm} | \sigma |
|----------------|----------------|-------------------|-------------------|-------------|-------|
| 1              | 26.6598        | 1.0622            | 54.82             | 0.04        | 11.02 | 0.07481 |
| 2              | 129.0809       | 1195.926          | 10.77             | 9.20        | 19.15 | 0.03744 |
| 3              | 13.1795        | 44.8599           | 24.77             | 3.25        | 13.47 | 0.10174 |
| 4              | 1.4548         | 12.1707           | 8.92              | 7.99        | 18.97 | 0.04085 |
| 5              | 0.0048         | 0.3189            | 27.70             | 63.83       | 22.33 | 0.04202 |
| 6              | 24.1736        | 133.1367          | 5.58              | 5.26        | 19.78 | 0.05877 |
| 7              | 0.0542         | 0.8795            | 25.87             | 15.50       | 17.13 | 0.04901 |
| 8              | 10.3704        | 54.6849           | 5.62              | 5.04        | 15.19 | 0.06408 |

The true density of the coal samples of Ordos Mine is 1.31 g/cm³, the true density of the coal samples of Jiamusi Mine is 1.31 g/cm³, the true density of the coal samples of Matigou Mine is 1.3 g/cm³, and the true density of coal samples of Pingbao Mine is 1.31 g/cm³. The true density of coal samples of Panxi Mine is 1.32 g/cm³, the true density of coal samples of Haitian Mine is 1.4 g/cm³, the true density of coal samples of Panxi Mine is 1.43 g/cm³, and the true density of coal samples of Zhaozhuang Mine is 1.52 g/cm³. The relationship between the volume SSA and mass SSA is shown in formula 3

\[ S_m = \frac{S_v}{\rho} \]  

In which, \( S_m \) is the mass SSA, m²/g; \( S_v \) is the volume SSA, m²/cm³; \( \rho \) is the density, g/cm³.

Therefore, the mass SSA of the coal samples of Ordos Mine is 5008.507252 m²/g, the mass SSA of the Jiamusi coal sample is 19.12419847 m²/g, the mass SSA of the Matigou coal sample is 30.399 m²/g, and the mass SSA of the Pingbao coal sample is 18.34053435 m²/g, the mass SSA of the coal samples of Haitian Mine is 9.85242424 m²/g, the mass SSA of the coal samples of Panxi Mine is 34.33492857 m²/g, and the mass SSA of the coal samples of Panxi Mine is 16.60405594 m²/g, the mass SSA of the coal samples of Zhaozhuang Mine is 36.92671053 m²/g.

The open and closed holes of coal in the coal body are formed during coal formation, and their morphology should be relatively close. From the small-angle scattering experiment, the pore size of each coal sample cannot be directly obtained. The BJH mesopore data measured by the liquid nitrogen adsorption experiment can best reflect the pore size distribution of 1–100 nm. Therefore, the BJH mesopore diameter obtained from the liquid nitrogen adsorption experiment is used to estimate the total number of pores in each coal sample (including closed pores and open pores). The relationship between the number of closed pores of coal body, the SSA, and the unit pore surface area is shown in formula 4

\[ N = \frac{S_1}{4\pi R^2} \]  

Table 6. Summary of the Number of Closed and Open Holes in Coal

| sample number | number of openings | number of closed cells | total number of holes | proportion of closed holes (%) |
|---------------|--------------------|-----------------------|----------------------|-------------------------------|
| 1             | 1.05175 x 10^10    | 1.36933 x 10^20       | 1.36943 x 10^20      | 99.99                         |
| 2             | 4.60020 x 10^10    | 2.76932 x 10^17       | 2.81532 x 10^17      | 98.37                         |
| 3             | 5.83163 x 10^10    | 9.85030 x 10^10       | 1.04335 x 10^10      | 94.41                         |
| 4             | 4.55443 x 10^10    | 1.30941 x 10^10       | 1.35496 x 10^10      | 96.64                         |
| 5             | 3.44933 x 10^10    | 1.42216 x 10^10       | 1.45666 x 10^10      | 97.63                         |
| 6             | 7.25119 x 10^10    | 2.47337 x 10^10       | 2.54588 x 10^10      | 97.15                         |
| 7             | 1.36956 x 10^10    | 2.31791 x 10^10       | 2.45487 x 10^10      | 94.42                         |
| 8             | 1.87473 x 10^10    | 7.81713 x 10^10       | 8.00460 x 10^10      | 97.66                         |
In which, \( N \) is the number of closed holes in coal per unit mass; \( S_1 \) is the SSA of the closed pores of coal, \( m^2/g \); and \( R \) is the closed pore radius of the coal body, nm.

From Table 2, the BJH mesopore diameter of each coal sample can be obtained and substituted into eq 4: the total number of holes in the Ordos coal sample per unit mass of coal is \( 1.36943 \times 10^{17} \), the total number of holes in the Jiamusi coal sample is \( 2.81532 \times 10^{17} \), the total number of holes in the Matigou coal sample is \( 1.04335 \times 10^{17} \), the total number of holes in the Pingba coal Mine sample is \( 1.35496 \times 10^{17} \), the total number of holes in the Pingbao Mine sample is \( 1.45666 \times 10^{17} \), the total number of holes in the Haitian Mine sample is \( 2.54588 \times 10^{17} \), the total number of holes in the Panxi Mine sample is \( 2.45487 \times 10^{17} \), and the total number of holes in the Zhaozhuang Mine sample is \( 8.00460 \times 10^{17} \).

4.4.4. Estimation of the Number of Closed Pores in Coal. In summary, it is estimated that the total number of open pores of each coal sample in the range of pore diameter less than 100 nm and the number of open and closed pores obtained by small-angle scattering are shown in Table 6, and the proportion of closed pores of each coal sample can be obtained. The closed pores of the Ordos coal samples accounted for 99.99%, the closed pores of the Jiamusi coal samples accounted for 98.37%, the closed pores of the Matigou coal samples accounted for 94.41%, and the closed pores of the Pingba coal Mine samples accounted for 96.64%. The closed pores of the coal samples of Pingbao Mine accounted for 97.63%, the closed pores of the coal samples of Haitian Mine accounted for 97.15%, the closed pores of the coal samples of Panxi Mine accounted for 94.42%, and the closed pores of the coal samples of Zhaozhuang Mine accounted for 97.66%.

5. DISCUSSION

In this article, the low-temperature liquid nitrogen adsorption method, carbon dioxide adsorption method, and small-angle scattering method are used to study the nanopore structure and closed pore conditions of eight different metamorphic coals. The results of low-temperature liquid nitrogen adsorption indicate that as the coal sample metamorphism increases, the mesopore SSA and micropore pore volume of the coal decrease first and then increase, but the average pore size is different, which shows that the degree of coal metamorphism has a great influence on the SSA of pores and the pore volume of micropores. For coal with a high degree of metamorphism (volatile content < 18%), the pore size of mesopores generally shows an increasing trend first and then a decreasing trend, but the proportion of the pore size segments shows the opposite trend. At the same time, the overall pore size of micropores gradually decreases, while the proportion of micropore diameter segments has been increasing and the proportion of macropore diameter segments is not. The reason is that the polycondensation of coal macromolecules during coalification is not obvious at the beginning of coalification. However, as the degree of coalification increases, the coal body polycondensation gradually appears, and the coal structure shrinks. The number and pore size of pores and macropores decrease, and micropores and microcracks further develop. This is consistent with the results of liquid nitrogen adsorption reported in this article. Wang et al. believed that with the increase of the coal rank, the pore type of the coal reservoirs changed from open air-permeable pores to one-end air-permeable pores and ink bottle-shaped pores; the percentage of micropores in the total pore volume shows an increasing trend as a whole; the pore volume and BET SSA show a high—low—high change law with the increase of the coal rank, and the lowest value appears between the bituminous coal and anthracite coal ranks.

The \( \text{CO}_2 \) adsorption experiment results show that the mesopore SSA, micropore SSA, and average pore size of the coal sample decrease first and then increase as the degree of metamorphism increases, which is the same as the low-temperature liquid nitrogen adsorption experiment results. For highly metamorphic coal (volatile content < 18%), the average pore size, DFT pore size, and DA pore size of the coal samples decrease with the increase of metamorphism. They are one order of magnitude smaller than those obtained using the liquid nitrogen adsorption experiment. Pore size changes are caused by coalification, which is the condensation of coal molecules. Jan believed that under the same humidity and pressure conditions, the \( \text{CO}_2 \) adsorption capacity of the coal body increases with the increase of the content of its vitrinite component, while the adsorption capacity of the medium coal rank coal sample is the smallest. This is consistent with the results of liquid nitrogen adsorption reported in this article.

From the results of the small-angle scattering experiments based on the stepwise tangent method, the volume fraction of the coal samples in the pore size range of less than 10 nm showed a decreasing trend first and then an increasing trend as the coal sample metamorphism increased. However, because the step-by-step tangent method requires manually selecting the aperture range with the same slope every time, the volume fraction ratio within a certain range is not accurate and may have errors.

Based on the lognormal distribution function method, the geometric mean value of its particle size distribution, except for the Jiamusi coal sample, showed an increasing trend first and then a decreasing trend. Although the principle is different from the stepwise tangent method, the results obtained by the lognormal distribution function method are more accurate, which may be related to the error caused by manual operation. Zhao and Peng reported based on the maximum entropy probability method of small-angle scattering that the average pore size of the coal sample showed a decreasing trend as the degree of coal metamorphism increased. The results in this article are different, which may be because of the different methods of the processing data. There are many methods for processing the small-angle scattering data. Different processing methods for processing small-angle scattering data will have a certain range of differences in the coal pore size distribution and fractal characteristics. Therefore, in future research, different processing methods should be used to analyze the data to compare the difference of the results obtained.

There are many types of pores in the openings of coal bodies, such as cylindrical holes, crack-shaped holes, wedge-shaped holes, and ink bottle holes. Therefore, the shape of the closed hole inside the coal body should also include the above types, and this article considers that the shape of the closed hole inside the coal body is only spherical. In the future research, the types of closed pores should be gradually processed to further study the characteristics of closed pores in coal. However, the article proposes a method for estimating the closed pores of coal, which has certain significance for further study of the closed pores of coal. Judging from the estimation results of closed pores in coal samples, there are a large number of closed pores in coal samples, this will provide a theoretical basis for further understanding the nanopore
structure of the coal body, exploring the occurrence of gas in the coal seam, and explaining the dynamic disaster of coal and gas.

In this article, we just estimated the closed pores in coal. Because the pore size within 1–100 nm cannot be directly measured from the small-angle scattering experiments, the BJH mesopore diameter obtained from the liquid nitrogen adsorption experiment data was used to replace the mesopore diameter from the small-angle scattering experiment. Then, the total number of open and closed pores in the coal sample can be estimated.

For the shape of open and closed holes in coal, this article assumes a spherical shape for calculation convenience. In theory, there are other types of pores such as: parallelogram, prismatic, conical, cylindrical, and so forth. These pore types have not been studied, and in the future these should also be studied separately by pore type. In this article, the number of holes is obtained from the obtained hole diameter, which cannot distinguish the number of holes of different sizes, which is different from the actual one. In the future, the hole diameter and related parameters can be measured in stages to obtain the number of holes of different sizes.

6. SUMMARY AND CONCLUSIONS

In this article, low-temperature liquid nitrogen adsorption, CO₂ adsorption experiments, and small-angle scattering are used to study and analyze the coal nanopore cracks. By comparing the pore volume of the coal body obtained by the experiment, the closed pores in the coal body are analyzed, and the results are as follows:

1. As the coal rank increases, the SSA and total pore volume of the coal sample decrease slowly at first and increase sharply in the end, while the average pore diameter increases slowly at first, then decreases slightly, and finally decreases sharply.

2. Coal samples with metamorphism ranging from 12 to 25% have a lower SSA and a total pore volume. This is because coalification deforms the internal structure of the coal body, causing part of the pore fissures to be filled or covered by the material generated by coalification.

3. According to the pore volume data measured by the low-temperature liquid nitrogen adsorption method, carbon dioxide adsorption method, and small-angle scattering method, the number of closed pores in the coal body ranges from 1 to 2 orders of magnitude larger than the semiclosed pores and open pores.

4. For high-metamorphic coal samples, small-angle scattering SAXS shows that the volume fraction of pores between 10 and 30 nm accounts for 60 to 70% of the total volume, indicating that the volume of mesopores is relatively large, which is consistent with the results of low-temperature liquid nitrogen and CO₂ adsorption experiments.

5. The number of closed holes of coal accounts for more than 94% of the total number of holes of the eight coal samples.

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Notes
The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This work was financially supported by the Natural Science Foundation of Beijing Municipality (grant no. 8192036), the Fundamental Research Foundation for the Central Universities (grant no. 2009QZ09), Youth Foundation of Social Science and Humanity, Ministry of Education of China (grant no. 19YJCZH087), the National Key Research and Development Program of China (grant no. 2018YFC0808301), the State Key Laboratory Cultivation Base for Gas Geology and Gas Control (Henan Polytechnic University) (grant no. WS2018B04), and National Natural Science Foundation of China (grant no. 51974127). The authors greatly acknowledge the editor and reviewers for their valuable comments.

# NOMENCLATURE

Alphabetic Letters:
- LT-N₂GA, low-temperature liquid nitrogen adsorption method
- SAXS, small-angle X-ray scattering
- BJH, Barrett–Joyner–Halenda
- DFT, density functional theory
- SSA, specific surface area

Greek Letters
- Qᵥ, scale-invariant feature conversion
- Rᵥ, radius of gyration
- Rᵥ, radius of Porod
- µ, geometric mean of the particle size distribution
- σ, standard deviation of the distribution
- Nᵥ, number of openings per unit mass of coal with a pore size less than 100 nm;
$V$, pore volume of coal body with pore diameter less than 100 nm, cm$^3$/g;
$R_p$, average pore radius of the coal body, nm
$N_p$, number of openings per unit mass of coal;
$V_c$, DA pore volume of coal sample, cm$^3$/g;
$S_m$, mass specific surface area, m$^2$/g;
$S_0$, volume specific surface area, m$^2$/cm$^3$;
$\rho$, density, g/cm$^3$;
$N_h$, number of closed holes in coal per unit mass;
$S_s$, specific surface area of the closed pores of coal, m$^2$/g

**REFERENCES**

(1) Moore, T. A. Coalbed methane: A review. *Int. J. Coal Geol.* 2012, 101, 36–81.
(2) White, C. M.; Smith, D. H.; Jones, K. L.; Goodman, A. L.; Jikich, S. A.; LaCount, R. B.; DuBose, S. B.; Ozdemir, E.; Morsi, B. I.; Schroeder, K. T. Sequestration of carbon dioxide in coal with enhanced coalbed methane recovery - A review. *Energy Fuels* 2005, 19, 659–724.
(3) Yu, J.; Tahmasebi, A.; Han, Y.; Yin, F.; Li, X. A review on water effects on coal utilization. *Chin. J. Rock Mech. Eng.* 2013, 32, 2065–2071.
(4) Zhao, J.-L.; Jiang, B.; Wang, J.; Li, M. Study of Nanopores of Tectonically Deformed Coal Based on Low Nitrogen Adsorption at Low-temperatures. *J. Nanosci. Nanotechnol.* 2017, 17, 6566–6575.
(5) Zhao, Y. G.; Jiao, Y. Q.; Li, D. Study on adsorption characteristics and fractal properties of nano-scale pores at low-temperature coal. *J. Nanol. Technol. Univ., Nat. Sci.* 2016, 35, 141–148.
(6) Chen, Y. Q.; Fu, L. B.; Hao, M. Q. Derivation and application of gas adsorption equation and desorption equation. *China Offshore Oil Gas* 2018, 30, 85–89.
(7) Jiang, W.-P.; Song, Z.-X.; Zhong, L.-W. Research on the pore characteristics and fractal properties of nano-scale pores at low-temperature coal. *Int. J. Coal Geol.* 2012, 116, 208–214.
(8) Wang, M. S.; Tang, D. Z.; Zhang, S. H. Research activity and significance of pore in coal reservoir. *China Coal Meth.* 2004, 2, 9–11.
(9) Qiu, X.; Tan, S. P.; Dejam, M.; Adidharma, H.; Dejam, P. Isothermal analysis of the amount of pure fluid in bulk and nanoporous media using differential scanning calorimetry. *Phys. Chem. Chem. Phys.* 2020, 22, 7048–7057.
(10) Qiu, X.; Tan, S. P.; Dejam, M.; Adidharma, H. Experimental Study on the Criticality of a Methane/Thane Mixture Confined in Nanoporous Media. *Langmuir* 2019, 35, 11635–11642.
(11) Hodot, B. B. *Coal and Gas Outburst*; China Industry Press: Beijing; 1966; pp 1–5.
(12) Ju, Y.; Jiang, B.; Hou, Q.; Wang, G. Structural evolution of nano-scale pores of tectonic coals in southern China and its mechanism. *Acta Geol. Sin.* 2005, 79, 269–285.
(13) Chen, P.; Tang, X. The research on the adsorption of nitrogen in low-temperature and micro-pore properties in coal. *J. China Coal Soc.* 2001, 26, 552–556.
(14) Zhang, L.; Kou, Z.; Wang, H.; Zhao, Y.; Dejam, M.; Guo, J.; Du, J. Performance analysis for a model of a multi-wing hydraulically fractured vertical well in a coalbed methane gas reservoir. *J. Pet. Sci. Eng.* 2018, 166, 104–120.
(15) Kou, Z. H.; Morteza, D. A mathematical model for a hydraulically fractured well in a coal seam reservoir by considering desorption, viscous flow, and diffusion. *71st Annual Meeting of the APS (American Physical Society) Division of Fluid Dynamics, Atlanta, Georgia, USA*, 2018; pp 18–20.
(16) Zhao, X.-L.; Tang, D.-Z.; Xu, H.; Tao, S. Effect of coal metamorphic process on pore system of coal reservoirs. *J. China Coal Soc.* 2010, 35, 1506–1511.
(17) Alexeev, A. D.; Vasilenko, T. A.; Ulyanova, E. V. Closed porosity in fossil coals. *Fuel* 1999, 78, 635–638.
(18) Chen, S.-B.; Zhu, Y.-M.; Wang, G.-Y.; Liu, H.-L. Structure characteristics and accumulation significance of nanopores in Longmaxi shale gas reservoir in the southern Sichuan Basin. *J. China Coal Soc.* 2012, 37, 438–444.
(19) Du, Y. E. *The Affect about Pore Characteristics of Coal to the Coal-Bed Methane Desorption*; Xi’an University of Science and Technology, 2010.
(20) Niu, Q. H. *Study on the Evolution Mechanism and Formation Mechanism of Closed Pores in Tectonically Deformed Coal*; Henan Polytechnic University, 2016.
(21) Li, Y.; Zhang, Y. G.; Zhang, L. Characterization on pore structure of tectonic coals based on the method of mercury intrusion, carbon dioxide adsorption. *J. China Coal Soc.* 2019, 44, 1188.
(22) Wu, Z.; Jiang, B.; Wang, J.; Li, M. Study of Nanopores of Tectonically Deformed Coal Based on Liquid Nitrogen Adsorption at Low-temperatures. *J. Nanosci. Nanotechnol.* 2017, 17, 6566–6575.
(23) Zhang, Y. G.; Jiao, Y. Q.; Lei, D. Study on adsorption characteristics and fractal properties of nano-scale pores at low-temperature coal. *J. Nanol. Technol. Univ., Nat. Sci.* 2016, 35, 141–148.
(24) Chen, Y. Q.; Fu, L. B.; Hao, M. Q. Derivation and application of gas adsorption equation and desorption equation. *China Offshore Oil Gas* 2018, 30, 85–89.
(25) Han, S.; Sang, S.; Jiang, J.; Zhang, J. Supercritical CO2 adsorption in a simulated deep coal reservoir environment, implications for geological storage of CO2 in deep coals in the southern Qinshui Basin, China. *Energy Sci. Eng.* 2019, 7, 488–503.
(26) Cui, Y. J.; Zhang, Q.; Zhang, H. Adsorption of different rank coals to single component gas. *Nat. Gas Ind.* 2005, 23, 61–65.
(27) Song, X.-X.; Tang, Y.-G.; Li, W.; Zeng, F.-G. Pore structure in tectonically deformed coals by small-angle X-ray scattering. *J. China Coal Soc.* 2014, 39, 719–724.
(28) Setek, M.; Wagenfeld, H. K.; Stacy, W. O.; Kiss, L. T. Determination of microporosity of brown coal. Small-angle x-ray scattering. *Fuel* 1983, 62, 480–482.
(29) Benedetti, A.; Ciccariello, S. Coal Rank and Shape of the Small-Angle X-Ray Intensity. *J. Phys.* 1996, 6, 1479–1487.
(30) André, G.; Gérard, F.; Walker, C. B. Small-Angle Scattering of X-Rays. *Phys. Today* 1955, 9, 38–39.
(31) Xu, Y.; Koga, Y.; Watkinson, A. P. Pore size distribution of coals and chars from western Canada. *Fuel* 1994, 73, 1797–1801.
(32) Lin, J. S.; Hendricks, R. W.; Harris, L. A.; Yust, C. S. Microporosity and micromeritology of vitrinite in a bituminous coal. *J. Appl. Crystallogr.* 1978, 11, 621–625.
(33) Melnichenko, Y. B.; He, L.; Sakurovs, R.; Kholodenko, A. I.; Blach, T.; Mastalerz, M.; Radlinski, A. P.; Cheng, G.; Mildner, D. F. R. Accessibility of pores in coal to methane and carbon dioxide. *Fuel* 2012, 91, 200–208.
(34) Zhang, L. Construction and application study of X-ray small-angle scattering system. *J. Electron. Meas. Instrum.* 2013, 27, 289–297.
(35) Beeman, W. W. Small-Angle Scattering of X-Rays. *J. Am. Chem. Soc.* 1956, 78, 3231–3232.
(36) Xu, H.; Chu, W.; Huang, X.; Sun, W.; Jiang, C.; Liu, Z. CO2 adsorption-assisted CH4 desorption on carbon models of coal surface: A DFT study. *Appl. Surf. Sci.* 2016, 375, 196–206.
(37) Huang, M. C. Recent developments in density functional theory. *Prog. Phys.* 2000, 20, 199.
(38) Hou, J. X.; Wang, B. J.; Zhang, Y. G. Evolution characteristics of micropore and mesopore of different rank coal and cause of their formation. *Coal Geol. Explor.* 2017, 45, 79–85.
(39) Zhang, Q. Influence of metamorphic grade on gas adsorption/desorption characteristics of outburst coal. *China Univ. Min. Technol.* 2018, 64–66.
(40) Si, S.-J.; Wang, X.-j. Coal Particle Size Influence on the pore structure of fat coal and gas coal. *Saf. Coal Mines* 2012, 4, 26–29.
(41) Liu, G.; Zhang, Z.; Zhang, X.; Lu, R. Pore distribution regularity and adsorption-desorption characteristics of gas coal and coking coal. *Chin. J. Rock Mech. Eng.* 2009, 28, 1587–1592.
(42) Meng, Q.-R.; Zhao, Y.-S.; Hu, Y.-Q.; Zengchao, F. Experimental study on pore structure and pore shape of coking coal. *J. China Coal Soc.* 2011, 36, 487–490.
(43) Wang, W.; Chen, X.; Cai, Q.; Mo, G. SAXS1.0—a program for small-angle X-ray scattering data analysis. *Nucl. Technol.* **2007**, *30*, 571–575.

(44) Amenitsch, H.; Rappolt, M.; Kriechbaum, M.; Mio, H.; Laggner, P.; Bernstorff, S. First performance assessment of the small-angle X-ray scattering beamline at ELETTRA. *J. Synchrotron Radiat.* **1998**, *5*, 506–508.

(45) Xie, F.; Li, D.; Li, Z.; Li, Z.; Mo, G.; Lv, B. Small-angle X-ray scattering study on the fractal structure of solid products of bituminous coal at different carbonization temperatures. *Philos. Mag. Lett.* **2019**, *99*, 95–101.

(46) Bragg, S. L. X-ray crystallography. *Sci. Am.* **1968**, *219*, 58.

(47) Guinier, A.; Lorrain, P.; Lorrain, D. S. M.; Gillis, J. X-Ray diffraction in crystals, imperfect crystals, and amorphous bodies. *Phys. Today* **1964**, *17*, 70–72.

(48) Zhang, X. B.; Zhang, Z. M.; Zhang, Y. G. Mechanochemical action and deformed coal structure. *Coal Geol. China.* **2009**, *21*, 10–14.

(49) Chen, S.-B.; Zhu, Y.-M.; Wang, G.-Y.; Liu, H.-L. Structure characteristics and accumulation significance of nanopores in Longmaxi shale gas reservoir in the southern Sichuan Basin. *J. China Coal Soc.* **2012**, *37*, 438–444.

(50) Wang, L.; Tang, D. Z.; Xu, H. Influence of metamorphism on micropores in coal seams based on nitrogen adsorption experiment. *Coal Sci. Technol.* **2014**, *42*, 256–260.

(51) Jan, X.; Guan, F.; Zhang, W. Adsorption and diffusion of CO$_2$ in coal: experiment and modeling. *Sci. China: Earth Sci.* **2012**, *04*, 26–38.

(52) Zhao, Y.; Peng, L. Investigation on the size and fractal dimension of nano-pore in coals by synchrotron small-angle X-ray scattering. *Chin. Sci. Bull.* **2017**, *62*, 2416–2427.