Experimental Study on Pore Structure and Gas Desorption Characteristics of a Low Rank Coal: Impact of Moisture

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Experimental study on pore structure and gas desorption characteristics of a Low rank coal: Impact of moisture

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Abstracts: Coal and gas outburst is one of the most serious disasters for underground coal mining. The water adsorbed on coal can lead to that the pore structure of moist coal is different from that of dry coal, thereby affecting methane desorption characteristics of coal for the outburst risk prediction. In this paper, the impact of moisture on pore structure and methane desorption performance were investigated. The analysis on low-temperature nitrogen gas adsorption tests show that the micropores (pore diameter < 10 nm) are most affected by the adsorbed water. In particular, for water-equilibrated coal sample at 98% relatively humidity, the micropores less than 4 nm analyzed by DFT pore size distributions almost disappear probably due to the blocking effect of the formed water clusters and capillary water. In this case, the micropores can still contribute most sites for gas adsorption. Furthermore, the fractal dimension at relative pressure of 0–0.5 ($D_1$) and 0.5–1 ($D_2$) calculated by the Frenkel-Halsey-Hill model indicates that, when moisture content is less than 4.74%, $D_1$ decreases rapidly while $D_2$ shows a slight change; whereas, further increases in moisture content results in that $D_2$ decreases significantly and $D_1$ remains at about 2.32. Further investigation shows that, below the equilibrium moisture content, the ultimate desorption volume ($A$) and initial desorption rate ($V_0$) are closely related to $D_1$, while the desorption constant ($K_t$) mainly depends on $D_2$. Therefore, the adsorbed moisture has significant negative impact on methane desorption performances by affecting characteristics of coal’s pores.

Keywords: Water adsorption; Pore structure; Fractal dimension; Methane desorption; Coal and gas outburst

1 Introduction

Currently, although the casualties caused by coal mine disasters have been effectively controlled, coal and gas outburst is still one of the most serious disasters associated with coal mine (Fu et al. 2020; Wang et al. 2014b; Zhai et al. 2016). A coal and gas outburst is closely related to the methane
desorption capacity of coal, and many methane desorption indices are used to predict the outburst risk
(Wang et al. 2020b; Xue et al. 2020). Therefore, understanding the methane desorption characteristics
of coal is critical for the prediction of coal and gas outburst. Coal is a porous medium with a highly
developed pore system (Cheng and Pan 2020; Lu et al. 2021). Water in coal can be divided into two
types: inherent moisture in coal matrix and free water in cleat system (Pan et al. 2010). The inherent
moisture mainly exists in the absorbed state, which can occupy the surface sites of coal pores due to the
physical adsorption and oxygen-containing functional group effects (Wang et al. 2021). Moreover, the
existing of oxygen-containing functional groups (e.g. carboxylic and hydroxyl groups) adsorption sites
are preferably occupied by water molecules (Li et al. 2019). Therefore, the adsorption advantage of
water molecules will weaken the capacity of coal adsorbing gas, thereby affecting desorption and
migration of methane gas in coal body.

Many scholars have long been concerned about moisture influences on gas adsorption and
desorption of coal through experimental, numerical simulation and mathematical theory methods. The
existence of water can significantly reduce the methane adsorption capacity of coal (Busch and
Gensterblum 2011; Nie et al. 2016), which is mainly due to the competitive adsorption of water and
methane and the advantage of coal adsorbing water molecules (Gensterblum et al. 2014; Xiang et al.
2014). It has been reported that 2% moisture content can result in an approximately 20% reduction in
both CH\textsubscript{4} and CO\textsubscript{2} adsorption capacity of moist coal (Clarkson and Bustin 2000). The impact of water
on methane adsorption capacity is also related to the metamorphic degree of coal. Dry coal shows a
trend of first falling and then rising with increasing coal rank, whereas the methane adsorption capacity
of the water-equilibrated coal increases slightly with coal rank (Laxminarayana and Crosdale 2002). It
is further found that the adsorbed water can induces the reduction in methane adsorption capacity of a
bituminous coal and the non-adsorbed water has no effect; in contrast, for anthracite coal, both the two
form of water have remarkably weaken on methane adsorption, which is considered to be related to the
difference in pore structure between the two coal samples (Wang et al. 2020a). Besides, water also has
great weakening impact on methane desorption and diffusion capacities of coal (Liu et al. 2019; Pan et
al. 2010). Combined with unipore, bidisperse and other diffusion models, it is observed that increasing
moisture content causes both micropores and macropores diffusion coefficients to decrease for different
rank coals (Guo et al. 2018; Wang et al. 2017). Other studies further show that increasing equilibrium
moisture content can induces the continual decreases in diffusivity for anthracite coal and the U-shaped
change in diffusivity for bituminous coal. This may be caused by the different moisture effects between
the reduction in adsorbed gas volume and the decrease of pore space for various rank coals (Wang et al.
2014a). Furthermore, increasing moisture content can also decreases the methane desorption volume
and velocity of coal, which has been widely accepted by scholars (Chen and Cheng 2015; Meng et al.
2020; Zhang et al. 2018).

Generally, coal with $R_{o,max}$ less than 0.65% is classified as low-rank coal in China (Wang et al.
2017), which includes lignite and some long-flame coal. Low-rank coal generally features a higher
adsorbed water content than middle-high rank coals, because low-rank coal has a larger porosity,
specific surface area (SSA) and more oxygen-containing functional groups (Chen et al. 2018; Yu et al.
2013). Statistics show that in China, the moisture content of lignite is 10–28% and that of long-flame
coal mostly is 3–12% (Guo et al. 2015). Hence, more studies on the influence of adsorbed water on the
methane desorption characteristics of low-rank coal are needed.

In this paper, a typical long-flame coal was used to perform the following studies: (1) water
adsorption characteristics of coal and pore structure of water-equilibrated coal at different relatively
humidity, (2) the relationships between adsorbed moisture content and fractal dimension of coal pores, (3) the impact of adsorbed moisture on methane desorption performances and its relations with fractal dimension.

2 Experiment and method

2.1 Coal preparation and Basic parameters

2.1.1 Basic parameters

The low rank coal sample was selected from the No. 2 coal seam in the Yuanzigou coal mine, Baoji city, Shaanxi Province. The geological survey data show that the moisture content of the No. 2 coal seam on air dry basis is 3.60–11.28%. Several kilograms of fresh lump coal were collected from the working face, and various sizes of coal particles were prepared by crushing and screening. Following the ISO 17246:2010 standard, the coal sample with sizes of 0.074–0.20 mm was selected to perform the proximate analysis by an automatic proximate analyzer. The vitrinite reflectance of coal reflects the coalification degree, which was determined by following the ISO 7404–5:2009 standard. The ash content on air dry basis ($A_{ad}$), volatile matter on dry ash free basis ($V_{daf}$), fixed carbon on air dry basis ($FC_{ad}$), maximum vitrinite reflectance ($R_{o,max}$) are shown in Table 1.

| Sample       | $R_{o,max}$/% | $M_{ad}$/% | $A_{ad}$/% | $V_{daf}$/% | $FC_{ad}$/% |
|--------------|---------------|------------|------------|-------------|-------------|
| Long-flame coal | 0.65          | 6.33       | 26.59      | 40.53       | 39.90       |

2.1.2 Preparation of moist coal samples

First, the coal samples with particle sizes of 0.2–0.25 mm were placed in a vacuum drying oven at 378 K for at least 8 h to remove the original moisture. Eight saturated salt solutions were selected to prepare the water-equilibrated coal sample under a constant relatively humidity ($RH$) condition. The $RH$ was 11% for LiCl, 23% for CH₃COOK, 33% for MgCl₂, 43% for K₂CO₃, 57% for NaBr, 75% for NaCl, 85% for KCl, and 98% for K₂SO₄ at a room temperature of 293 K. Approximately 5 g of coal
sample was placed into glassware containing saturated salt solution, and the glassware was sealed with vacuum silica gel. A high-precision electronic balance (FA2204) was used to weigh the coal samples at 8 h intervals. When the quality of the sample remains steady, it was considered that the water adsorption equilibrium was achieved under the corresponding relative humidity (RH) conditions. Subsequently, the moisture content of the coal sample under different RH conditions was calculated by the following equation:

\[ M = \frac{(m_{\text{moist}} - m_{\text{dry}})}{m_{\text{dry}}} \]  

Where \( M \) is the moisture content, \%; \( m_{\text{moist}} \) is the weight of moist sample at a certain RH, g; and \( m_{\text{dry}} \) is the weight of dry sample, g. The water adsorption test was repeated twice and the mean values of moisture content at different relative humidity were determined for further study.

Furthermore, the water adsorption characteristic of the studied coal was analyzed by a modified Guggenheim–Anderson–de Boer (M-GAB) model. The M-GAB model is based on the BET and GAB model, which has been proved to be a good characterization of water vapor adsorption on porous materials (Zou et al. 2016). The M-GAB model, like GAB and M-Dent model (Duan and Li 2018), assumes water molecules adsorb on two sites: primary adsorption sites and secondary adsorption sites and one molecule occupies \( \alpha \) sites when being adsorbed. The M-GAB model can be described by the following equation:

\[ M = \frac{M_0 C + K x^\alpha}{(1-K x^\alpha)(1-K x^\alpha + C x^\alpha)} \]  

Where \( M_0 \) is the monolayer adsorption capacity, \( x \) is relative humidity, \( C \) and \( K \) are the adsorption constants related to primary sites and secondary sites, respectively, and \( \alpha \) represents the heterogeneity of the adsorption system. The water adsorption amounts of primary and secondary sites have the following relationships (Andrade et al., 2011):
\( M_1 = \frac{M_0 (C-1) + K \times x^a}{1 - K \times x^a + C \times K \times x^a} \)  \hspace{1cm} (3) \\

\( M_2 = \frac{M_0 K \times x^a}{1 - K \times x^a} \)  \hspace{1cm} (4)

### 2.2 Low-temperature nitrogen gas adsorption test

Low-temperature nitrogen gas adsorption (LN\(_2\)GA) was an important physical method to characterize the nanopores of porous media. In this study, the test instrument was an Autosorb-iQ2 analyzer (Quantachrome Ins, USA). The N\(_2\) ad/desorption isotherms at a \( P/P_0 \) of 0.001–0.995 of coal samples were measured. Before the LN\(_2\)GA tests, according to the moist coal sample preparation processes in Section 2.1.2, the coal samples with different water content were prepared. Then, the moist coal samples were placed in liquid N\(_2\) environments at a temperature of ~77 K for several minutes. Under these conditions, the moist samples were frozen so that the loss of pre-adsorbed water could be ignored. At the same time, the vacuum pumping step was omitted to avoid the loss of water in the tested samples.

### 2.3 Tests and Analytical methods for methane desorption in coal

#### 2.3.1 Methane desorption tests

The bulk desorption method (Zhang 2008) was applied to perform the methane desorption test of coal samples with particle sizes of 0.2–0.25 mm. First, approximately 50 g of coal sample was put into a coal sample tank. To reduce the loss of water from the coal sample as much as possible, the vacuum pumping time was operated for no longer than 30 min. Then, the methane gas with a purity of 99.99% was pumped into the coal sample tank to a gas pressure, and the coal sample tank was put into a stable temperature water bath at 303.15 K. Subsequently, the gas pressure of the coal sample tank was adjusted to a predetermined pressure (1 MPa). When the pressure gauge remained constant for 8 h, it is deemed that the gas-containing coal sample has achieved the adsorption equilibrium state. Finally, the
free gas of the coal sample tank was removed, and then a methane desorption test of coal sample can be performed. The test time was conducted for 120 min, and the methane desorption volume of coal at regular intervals and the ultimate desorption volume \( Q_\infty \) were recorded. The moisture content of the test sample was measured by the weighing method after the methane desorption test.

2.3.2 Analytical methods of desorption data

Currently, numerous of mathematical equations have been proposed to describe the gas desorption law of coal particles (Cheng et al. 2010). Among them, the Airey-type and Winter-type equations are often used to analyze the law of underground coal seam gas desorption and emission.

Airey believed that the coal body could be regarded as a material composed of separated blocks containing fractures and proposing the following formula (Airey 1968):

\[
Q_t = A \left[ 1 - \exp \left\{ - \left( \frac{t}{t_0} \right)^n \right\} \right] \tag{5}
\]

where \( Q_t \) is the gas desorption volume at time \( t \), cm\(^3\)/g; \( A \) is the ultimate desorption volume, cm\(^3\)/g; \( t_0 \) is the desorption time constant; and \( n \) is a coefficient.

In Winter’s theory, when the gas pressure was removed, the change in the gas desorption rate with time can be described by the following power function (Winter and Janas 1975):

\[
V_t = V_a \left( \frac{t}{t_a} \right)^{-K_t} \tag{6}
\]

After mathematical integration, the relationship between methane desorption volume and time can be obtained, as shown in the following equation:

\[
Q_t = \frac{V_1}{1 - K_t} t^{1 - K_t} \tag{7}
\]

where \( Q_t \) is the cumulative desorption volume at time \( t \), cm\(^3\)/g; \( V_1 \) and \( V_a \) are the methane desorption rates at times \( t_1 \) and \( t_a \), respectively, cm\(^3\)/(g min); and \( K_t \) is a constant that reflects the degree of attenuation of the desorption rate (Banerjee 1988).
3 Experimental results

3.1 Water adsorption isotherms

The M-GAB model fitting for water adsorption data of the studied coal sample is shown in Figure 1. According to the International Union of Pure and Applied Chemistry (IUPAC) classification (Lowell et al. 2004), the adsorption curve belongs to type II isotherms. The M-GAB model has excellent fitting effect with a $R^2$ value of 0.9975. The water adsorption amount shows stage characteristics. Under the conditions of $RH < 0.2$ and $RH > 0.8$, the water adsorption amount increases rapidly. When $RH$ ranges from 0.2 to 0.8, the growth of water adsorption capacity is relatively gentle.

![Figure 1](image)

Figure 1 The M-GAB model fitting for water adsorption of the studied sample.

3.2 LN$_2$GA isotherms

The LN$_2$GA adsorption and desorption isotherms of coal samples are illustrated in Figure 2. The adsorption isotherms of dry and moist samples belong to type II of the IUPAC classification. With the moisture content increases, the slope of nitrogen adsorption curve decreases at the pressure range of 0.1 to 0.9. For the maximum nitrogen adsorption amount, the dry coal sample is 20.24 cm$^3$/g, whereas, that of water-equilibrated coal sample at 98% $RH$ ($M = 10.88\%$) is reduced by nearly 50%. In the low relative pressure range ($P/P_0 < 0.01$), the nitrogen adsorption capacity of coal samples generally
increases significantly, which is mainly related to the micropores filling effect caused by a large number of micropores in coal (Hong et al. 2019; Kondo et al. 2005). It can be observed that the nitrogen adsorption curves at $P/P_0 < 0.1$ become flatter with increasing moisture content, which reflects that the micropores filling effect is weakened for gas adsorption on moist coal samples. When the $P/P_0$ is close to 1.0, all adsorption curves increase sharply, which indicates that water has a weak impact on nitrogen gas adsorption in larger scale pores of coal.

![Figure 2 Low-temperature nitrogen ad/desorption isotherms of coal samples.](image)

In addition, all coal samples show a prominent adsorption hysteresis characteristics, the features of the hysteresis loop correspond to types H3 and H4 in the IUPAC classification (Thommes et al. 2015), and its size tends to decrease with increasing moisture content. The coal samples with moisture content less than 7.14% (corresponding to $RH$ of 85%) exhibit an inflection point of the desorption curve at the $P/P_0$ around 0.45, which is considered to be related to the existence of ink-bottle pores (Liu et al. 2021; Qi et al. 2017). The desorption curve of coal sample around the inflection point gradually shrinks with moisture content increases. When the moisture content increases to the maximum equilibrium moisture content (10.88%), the inflection point of desorption curve almost disappears.

### 3.3 Methane desorption characteristics

For the methane desorption isotherms at gas pressure of 1 MPa, the fit curves of the Winter-type
and Airey-type equations are shown in Figure 3. The desorption process can be divided into rapid growth period (①), stable growth period (②) and slow growth period (③). It can be observed that the cumulative desorption amount shows a monotonous upward trend of the parabola with increasing desorption time. Besides, the cumulative desorption amount of coal samples decreases with the moisture content increases.

Figure 3 Methane desorption data and fit curves of coal samples at methane pressure of 1 MPa; (a) Airey-type fit; (b) Winter-type fit.

The fit results of the Airey-type and Winter-type equations are shown in Table 2. The correlation coefficient $R^2$ of the Airey-type equation is 0.9989–0.9998; for the Winter-type equation, it is 0.8670–0.9373. The Airey-type equation exhibits a higher fit accuracy than the Winter-type equation. The parameters $A$ and $V_1$ represent the ultimate methane desorption capacity and the initial rate of methane desorption, respectively (Chen et al. 2017; Guo et al. 2018). Obviously, increasing the moisture content can causes a significant reduction in methane desorption capacity.

| Moisture content /% | $A$ (cm$^3$/g) | $t_0$/min | $n$ | $R^2$ | $V_1$ (cm$^3$/g·min) | $k_1$ | $R^2$ |
|---------------------|----------------|------------|-----|-------|---------------------|-------|-------|
| 0                   | 6.460          | 1.406      | 0.387 | 0.9998 | 0.413               | 0.907 | 0.9373 |
| 2.01                | 5.225          | 1.530      | 0.463 | 0.9997 | 0.347               | 0.904 | 0.9013 |
| 3.98                | 3.504          | 1.901      | 0.554 | 0.9997 | 0.245               | 0.897 | 0.8670 |
| 5.02                | 2.392          | 3.329      | 0.446 | 0.9989 | 0.180               | 0.868 | 0.9290 |
| 6.90                | 1.934          | 3.175      | 0.484 | 0.9989 | 0.153               | 0.861 | 0.9139 |
Furthermore, the methane desorption amounts at different periods are illustrated in Table 3. The methane desorption volume of coal in the first minute ($Q_1$) and the third to fifth minute ($Q_{3-5}$) are two important parameters for predicting the risk of coal and gas outburst of a coal seam (Cheng et al. 2010).

The errors of parameter $A$ are 0.22–0.85% for methane pressure of 1 MPa, so parameter $A$ is very close to the measured value $Q_\infty$. Therefore, the Airey-type equation is more suitable to describe the methane desorption behavior of coal.

Table 3 Results of methane desorption amounts in different desorption periods.

| Moisture content (%| $Q_1$ (cm$^3$/g) | $Q_{3-5}$ (cm$^3$/g) | $Q_\infty$ (cm$^3$/g) | $\frac{A-Q_\infty}{Q_\infty}$ (%) |
|-------------------|-------------------|---------------------|----------------------|-------------------------------|
| 0                 | 3.791             | 0.413               | 6.406                | 0.85                          |
| 2.01              | 2.950             | 0.405               | 5.199                | 0.50                          |
| 3.98              | 1.778             | 0.325               | 3.496                | 0.22                          |
| 5.02              | 1.018             | 0.177               | 2.380                | 0.54                          |
| 6.90              | 0.857             | 0.172               | 1.922                | 0.63                          |

4 Analysis and Discussion

4.1 Water adsorption behavior of coal

The water adsorption isotherms of primary sites and secondary sites calculated by the M-GAB model for the studied coal sample are plotted in Figure 4. The initial water adsorption amount is mainly contributed by the primary sites, and the primary sites adsorption isotherms coincides with type I in the IUPAC classification (Lowell et al. 2004), which signifies that the primary sites adsorption is confined to a monolayer. With increasing relative humidity, the secondary sites adsorption becomes crucial, and the secondary sites adsorption corresponds to the type III isotherms associated with multilayer adsorption. An inflection point around $RH$ of 0.2 can be observed in the M-GAB fitting curve, indicating the completion of monolayer coverage and the beginning of multilayer adsorption (Thommes et al. 2015). When the $RH$ exceeds 0.5, the primary adsorption approach the dotted line representing the amount of saturated monolayer adsorption ($M_0$) calculated by the M-GAB model, and
then the water clusters gradually form (Charrière and Behra 2010). As the RH increases, the water uptake increases sharply at the region of RH > 0.8, which is related to the capillary condensation of water in pores.

Besides, in the M-GAB model, C relates to adsorption energies of water molecules on primary sites, while K associates with adsorption energies of the interaction between water molecules and adsorbed water molecules at secondary sites (Zou et al. 2016). For the studied coal sample, the value of C is far larger than that of K, which is mainly due to that the weak interactions of coal-water molecules need more energy than the strong interactions of water-water molecules (Duan and Li 2018; Charrière and Behra 2010).

![Figure 4. Amount of water adsorption on primary sites and secondary sites.](image)

4.2 Impact of water on pore structure of coal

4.2.1 N$_2$-SSA and N$_2$-PV

The pore size classification method proposed by B.B. ХОДОТ has widely used, and coal pores are divided into five categories (Chen et al. 2015; Jiang et al. 2016). Among them, micropores ($d<10$ nm) constitutes gas adsorption volume of coal, transition pores ($10<d<100$ nm) is the gas diffusion space,
The pore diameter of 100 nm is always considered to be a cut point for gas diffusion and seepage (Chen et al., 2017), and mesopores (100<d<1000 nm) forms a slow seepage space. In this paper, after integrating the pore parameters from the QSDFT model (1–10 nm) and BJH model (10–300 nm), the specific surface area (SSA), pore volume (PV) of different scales pores (micropores, transition pores, mesopores) are calculated, as illustrated in Table 4. When the moisture content increases to the equilibrium moisture content of 2.02% (corresponding to RH of 11%), the total SSA can be decreased by about 39.3%. With increasing moisture content, both the total SSA and total PV tend to decrease, whereas the average pore diameter (PD) shows an increase tendency. For the water-equilibrated coal sample at 98% RH (M = 10.88%), the total SSA and total PV were reduced to 16.31% and 53.47%, respectively. That indicates that the adsorbed water can leads to a significant reduction in the SSA of coal.

### Table 5 Pore parameters of coal samples from LN:eGA tests.

| Sample no. | Mean moisture content (%) | SSA (m²/g) | PV (×10⁻³ cm³/g) | PD (nm) |
|------------|--------------------------|------------|------------------|--------|
|            |                          | S1 S2 S3   | Total V1 V2 V3 | Total  |
| YZG1       | 0                        | 16.44 1.12 | 0.096 17.66 18.79 4.83 | 30.82 5.66 |
| YZG2       | 2.02                     | 9.59 1.02 | 0.101 10.71 12.52 6.86 4.91 | 24.28 7.51 |
| YZG3       | 3.99                     | 8.72 1.03 | 0.096 9.85 11.75 6.98 5.09 | 23.82 7.97 |
| YZG4       | 4.32                     | 9.47 1.01 | 0.098 10.57 12.52 6.76 4.84 | 24.12 7.29 |
| YZG5       | 4.74                     | 7.68 1.01 | 0.24 8.93 10.53 7.26 13.50 | 31.29 11.63 |
| YZG6       | 5.46                     | 6.80 0.96 | 0.094 7.85 9.55 6.50 4.74 | 20.79 8.88 |
| YZG7       | 6.25                     | 6.23 0.99 | 0.21 7.43 8.91 7.33 10.98 | 27.23 12.38 |
| YZG8       | 7.14                     | 5.65 0.96 | 0.13 6.73 8.20 6.84 6.80 | 21.84 10.81 |
| YZG9       | 10.88                    | 1.95 0.79 | 0.14 2.87 3.35 5.94 7.19 | 16.48 20.50 |

Note: Si (Vi) represents the SSA and PV of micropores, transition pores and mesopores, respectively, where i= 1, 2, 3.
The percentages of SSA and PV of different scale pores (micropores, transition pores, mesopores) are shown in Figure 5. The micropores SSA of sample YZG1 accounts for 93.11%, which indicates that the micropores play a key role in gas adsorption at dry condition. The percentage of micropores SSA shows a decreasing trend with increasing moisture content, and that of sample YZG9 decreased to the lowest value (67.71%). This means that the micropores can still contribute most sites for nitrogen adsorption on water-equilibrated coal samples. For pore volume, with increasing moisture content, the percentage of micropores volume also shows a decreasing trend, and 60.97% is for sample YZG1 at dry condition and only 20.33% is for sample YZG9 that is attained at water-equilibrated condition of 98% RH. In contrast, the percentage of SSA and PV of both transition pores and mesopores show an increasing trend. Therefore, water can significantly reduce the SSA and PV of coal pores. In particular, the micropores ($d<10$ nm) are most significantly weakened owing to the existence of water.

4.2.2 Pore size distribution

Thommes et al. (2015) indicated that the BJH method is more suitable for pore size analysis of mesopores and larger pores (>10 nm), and the DFT method can provide a reasonably reliable assessment of the nanopore size distributions. In this paper, both DFT and BJH models are employed to investigate the PSDs (pore size distributions) of pores with the size of 1–300 nm. The BJH-PSDs...
curves of the coal samples are illustrated in Figure 6. All samples show multi-peak distribution characteristics, and there are a large number of nanopores in the size range of 3–300 nm. With increasing moisture content, the dV(d) value of coal samples gradually approach the X-axis, especially for micropores (d<10 nm). The DFT-PSDs curves of coal samples are shown in Figure 7. The DFT dV(d) plots of coal samples with moisture content less than 7.14% mainly exhibit bi-peak values at ~1.1 nm and ~5.0 nm, whereas, that of sample YZG9 (M= 10.88%) shows an uni-peak at ~5.6 nm. The DFT dV(d) value tends to decrease with increasing moisture content, and when the moisture content reaches 10.88%, the peak value of dV(d) approaches 0 at ~1.1 nm, thereby indicating that pores less than 4 nm almost disappear for water-equilibrated coal sample YZG9. For both DFT-PSDs and BJH-PSDs curves, there is no significant difference in the PSDs of pores greater than 10 nm for coal samples with different moisture content. Therefore, water mainly has a significant impact on micropores (d< 10 nm) of coal, which can be attributed to the adsorption of water on coal surface. Under the condition of low moisture content, the effective sites for CH₄ or N₂ molecules are decreased by the preferential adsorption of water molecules (Gensterblum et al. 2014; Gensterblum et al. 2013). With a further increase in moisture content, the multilayer adsorption will occurs and the thickness of water molecule layers becomes significant. The process can results in the formation of water clusters (Do and Do, 2009; Charrière and Behra, 2010). And further the growth of water clusters and the capillary condensation will fill up some small pores. With a further increase in RH, the adsorbed moisture content of coal is enhanced (Figure 1). Especially for the water-equilibrated coal sample YZG9 at 98% RH, some pore throats can be blocked by the adsorbed water, thereby hindering the intrusion of gas molecules into the micropores. Thus the available nanopores for methane molecules adsorption on the water-equilibrated coal at 98% RH are mainly larger-scale pores (pore diameter > 4
4.3 Fractal characteristics of coal pores under moist condition

Based on the LN$_2$GA data, the fractal dimension can be determined by the fractal Frenkel-Halsey-Hill (FHH) equation (Ni et al. 2020; Si et al. 2021; Liu and Nie 2016). It can be described by the following expression:

$$\ln V = A \left[ \ln \left( \frac{P_0}{P} \right) \right] + B$$

(8)

Where $V$ is the gas adsorption amount at adsorption equilibrium pressure $P$; $P_0$ is the saturated gas pressure; $A$ is the slope of the fitting line, which is linear with the fractal dimension $D$, and there are two mathematical expressions for $A$ and $D$, namely, $A=D-3$ and $A=(D-3)/3$; and $B$ is a constant.
fractal dimension, $D$ ranges from 2 to 3, which can reflect the irregularity of coal pores. The closer $D$ is to 2, the smoother the pore surface is; and the closer $D$ is to 3, the more complex the pore surface is.

Low-temperature nitrogen desorption isotherms is generally used to calculate the fractal dimension, because the corresponding adsorption state is more stable (Li et al. 2015). In the region of $P/P_0 < 0.5$, the adsorption and desorption curves essentially parallel and even coincide, while in the region of $P/P_0 > 0.5$, there is significant adsorption hysteresis. This phenomenon suggests that the mechanisms of coal adsorbing gas are different for the two pressure regions. The fractal dimension of the two regions is always calculated with the relative pressure of 0.5 as the dividing point (Yao et al. 2008). The results of the fractal dimension $D$ calculated by the FHH equation are illustrated in Table 5.

The calculation results obtained by the equation ‘$A = D - 3$‘ are between 2 and 3, which is more reasonable than the calculation from the equation ‘$A = (D - 3)/3$‘. It can be seen that $D_1$ is 2.296–2.534 and $D_2$ is 2.651–2.912.

Table 5 The fractal dimensions calculated by FHH model for low-temperature nitrogen desorption isotherms.

| Sample no. | Mean moisture content/% | $A_1$ | $D_1=A_1+3A_1$ | $R^2$ | $A_2$ | $D_2=A_2+3A_2$ | $R^2$ |
|------------|------------------------|-------|----------------|------|-------|----------------|------|
| YZG1       | 0                      | -0.466| 2.534          | 1.602| 0.9533| 2.912          | 2.737| 0.9769        |
| YZG2       | 2.02                   | -0.617| 2.383          | 1.149| 0.9594| 2.877          | 2.632| 0.9604        |
| YZG3       | 3.99                   | -0.687| 2.313          | 0.938| 0.9543| 2.866          | 2.599| 0.9695        |
| YZG4       | 4.32                   | -0.704| 2.296          | 0.888| 0.9649| 2.873          | 2.619| 0.9737        |
| YZG5       | 4.74                   | -0.667| 2.333          | 0.998| 0.9605| 2.807          | 2.421| 0.9586        |
| YZG6       | 5.46                   | -0.666| 2.335          | 1.004| 0.9561| 2.853          | 2.558| 0.9575        |
| YZG7       | 6.25                   | -0.677| 2.323          | 0.970| 0.9629| 2.784          | 2.351| 0.9638        |
| YZG8       | 7.14                   | -0.694| 2.306          | 0.919| 0.9826| 2.804          | 2.412| 0.9471        |
| YZG9       | 10.88                  | -0.666| 2.334          | 1.003| 0.9914| 2.651          | 1.952| 0.9360        |

The relationships between the fractal dimensions $D_1$, $D_2$ and moisture content are shown in Figure 8. When the moisture content is less than 4.74% (corresponding to RH of 43%), $D_1$ decreases rapidly, whereas $D_2$ reduces from 2.91 to 2.87, showing a slight change. When the moisture content increases from 4.74% to 10.88% (corresponding to RH of 98%), $D_2$ decreases significantly, while $D_1$ remains at
Water sorption on coal is gradually divided into the following stages (Liu et al. 2020): primary adsorption, secondary and even multilayer adsorption, the formation of water clusters, and capillary condensation of water. As illustrated in the section 4.1, when the RH is lower than 43% (corresponding of equilibrium moisture content of 4.74%), the adsorbed water content shows a Langmuir-type trend with an increase in RH, indicating that the water adsorption on coal mainly occurs on the primary sites, i.e., oxygen-containing functional groups (Charrière and Behra 2010; Švábová et al. 2011). In this process, water molecules are preferentially adsorbed on the surface of micropores, which can result in that the homogeneity of surface of micropores is enhanced for the water-equilibrated coal. This should be responsible for the significant reduction of fractal dimension $D_1$. As the relative humidity increases $(RH > 43%)$, the secondary sites adsorption gradually turns into the main behavior. In this process, the formed water clusters grow continuously and capillary condensation will occurs. As shown in Figures 6 and 7, the PSDs curves of micropores shrinks close to the X-axis, while these of larger scale pores (pore diameter > 10 nm) is basically unchanged. This shows that the water molecules adsorbing on the
larger scale pores fails to cause a significant variation in the nitrogen molecules on the surface of larger scale pores. However, the formed water clusters and capillary water will occupy the pore space and even fill some small pores and throat, thereby improving the homogeneity of pores structure. These should be responsible for the reduction in fractal dimension $D_2$ at high equilibrium moisture content ($M > 4.74\%$). However, in the same stage, the fractal dimension $D_1$ is basically unchanged, which may be related to (i) the completion of saturated monolayer adsorption of water molecules on micropores; and (ii) the inability of gas molecules to pass through the pores and throat blocked by the adsorbed water.

4.4 Impact of moisture on methane desorption performances

4.4.1 Methane desorption characteristics of moist coals

The parameters $K_1$, $\Delta h_2$ are always selected as the methane desorption indices to predict the outburst risk of mining coal seams (Cheng et al. 2010). The two indices reflect the methane desorption performances of coal samples in the first minute ($Q_1$) and the third to fifth minutes ($Q_{3.5}$) (Chen and Cheng 2015; Jiang et al. 2015). The relationships between the initial desorption amounts $Q_1$ and $Q_{3.5}$ and moisture content are shown in Figure 9. The two desorption parameters decrease with moisture content in negative exponential form. In the range of the studied moisture content, the parameters $Q_1$ and $Q_{3.5}$ are reduced by 77.39% and 58.35%. Namely, each 1% increase in moisture content can leads to about 11% reduction in $Q_1$ and about 8% reduction in $Q_{3.5}$, respectively. Therefore, moisture has a weakening effect on the initial methane desorption capacity of coal, and $Q_1$ (corresponding to $K_1$ index) is more significantly affected than $Q_{3.5}$ (corresponding to $\Delta h_2$ index).
Figure 9 Relationships between $Q_1$, $Q_{3.5}$ and moisture content.

As shown in Figure 10, the relationships between methane desorption parameters ($V_1$, $A$, $K_t$) and moisture content at methane pressure of 1 MPa are further studied. Below the studied moisture content, the ultimate desorption amount ($A$) is decreased by about 0.66 cm$^3$/g for each 1% increase in moisture content. For the initial desorption rate ($V_1$), each 1% increase in moisture content can leads to a reduction of about 0.04 cm$^3$/(g·min). Water molecules have more adsorption advantages than methane molecules and can seize some adsorption spaces of gas molecules (Gensterblum et al. 2013; Gensterblum et al. 2014), thereby reducing the saturated adsorption capacity of moist coal.

Furthermore, the reduction in gas adsorption capacity can decreases the concentration gradient of the desorbed gas and gas desorption amount (Liu et al. 2015; Xu et al. 2015), which should be responsible for that the initial desorption rate of low moisture content coal is higher than that of high moisture content coal. Besides, the desorption constant $K_t$ shows a different change trend from the parameters $V_1$ and $A$. When the moisture content is less than 3.98%, the parameter $K_t$ decreases slightly, while it reduces significantly at the range of 3.98–6.9%. As analyzed in the sections 4.3.2, this can be attributed to the fact that the constant $K_t$ is mainly related to the fractal dimension $D_2$ representing the fractal
structural characteristics of larger scale pores.

Figure 10 Changes in methane desorption parameters with moisture content.

4.4.2 Relationship between fractal dimension and desorption parameters

Many researchers have indicated that the methane desorption performances of coal is related to pore structure of coal under dry condition (Chen et al. 2017; Liu et al. 2022). In this paper, the Pearson product-moment correlation coefficient ($\gamma$) is selected to further analyze the above relationship under moist condition. If the random variable $X = \{x_1, x_2, x_3, \ldots, x_n\}$, $Y = \{y_1, y_2, y_3, \ldots, y_n\}$, the Pearson correlation coefficient ($\gamma$) for the two variables is defined as

$$\gamma = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{n \sum x_i^2 - (\sum x_i)^2} \sqrt{n \sum y_i^2 - (\sum y_i)^2}}$$  \hspace{1cm} (9)

where $n$ is the sequence length of the random variable, and $\gamma$ ranges from -1 to +1. When $\gamma$ is 0, the two variables are independent; when $\gamma$ is [-1, 0], the two variables are negatively correlated; and when $\gamma$ is [0, +1], the two variables are positively correlated. The absolute value of $\gamma$ is close to 1 suggesting a higher correlation degree.

Combined with the interpolation method, the values of $\gamma$ between methane desorption parameters ($V_1$, $A$, $K_t$) and fractal dimensions ($D_1$ and $D_2$) at gas pressure of 1 MPa are calculated by SPSS software, as shown in Figure 9. The values of $\gamma$ for the correlations of $A$ and $D_1$ or $V_1$ and $D_1$ are larger
than 0.8, which are slightly higher than that for the correlations of $A$ and $D_2$ or $V_1$ and $D_2$. Conversely, the value of $\gamma$ for the correlation of $D_2$ and $K_t$ is 0.780, which is greater than that for the correlation of $D_1$ and $K_t$. Therefore, the parameters $A$ and $V_1$ are more closely related to the fractal dimension $D_1$, whereas the desorption constant $K_t$ is more dependent on the fractal dimension $D_2$. This is mainly due to that the fractal dimension $D_1$ and $D_2$ represents the surface fractal characteristic of micropores and the structural fractal characteristic of larger scale pores, respectively (Yao et al. 2008; Li et al. 2015).

The methane desorption parameters $A$ and $V_1$ reflect the ultimate and initial methane desorption capacities, which depend on the methane adsorption amount of coal (Liu et al. 2015). The micropores of coal plays a key role on methane adsorption capacity (An et al. 2013; Song et al. 2020), which provides an explanation for the close relationships between $D_1$ and $A$, $V_1$. Besides, the parameter $K_t$ characterizes the ratio between the gas desorption volume in the macropores and micro-fractures in the first minute after methane gas is relieved (Guo et al. 2014). Chen et al. (2017) further suggested that the methane desorption constant $K_t$ is associated with macropores volumes. Obviously, for both dry coal and water-equilibrated coal, the constant $K_t$ is closely related to $D_2$ representing fractal dimension of larger scale pores.

### Table 6: Correlation coefficients between fractal dimension and desorption parameters.

| Variables | $A$   | $V_1$ | $K_t$ |
|-----------|-------|-------|-------|
| $D_1$     | 0.854** | 0.847** | 0.684** |
| $D_2$     | 0.727** | 0.729** | 0.780** |

Note: ** significance level $\alpha=0.01$.

Moreover, in the prevention and control of coal mine gas disasters, many desorption parameters are applied to assess the risk of coal and gas outburst. For example, for the desorption indices $\Delta h_2$ and $K_1$, the outburst critical values of moist coal ($\Delta h_2 = 160$ Pa, $K_1=0.4$ cm$^3$/(g·min$^{0.5}$)) are provided by some industrial standards (Cheng et al. 2010; Cheng et al. 2016). However, the loss and fluctuation of the adsorbed moisture in low-rank coal will affect the methane adsorption capacity of coal and...
sequentially lead to the variation in critical values of the desorption indices for outburst prediction. It’s necessary to study the quantitative relationship between methane desorption indices and moisture content, and further put forward a reasonable method to determine the critical value of methane desorption indices of in-situ coal seam. Another revelation is that developing new engineering technologies to reduce the water content of low-rank coal is also necessary to improve gas migration in the development of coalbed methane (CBM) (Guo et al. 2018).

5 Conclusions

(1) Both N$_2$-SSA and N$_2$-PV decrease significantly with equilibrium moisture content increases, and the adsorbed moisture has greater influence on coal’s micropores with pore diameter less than 10 nm. In particular, when the adsorbed moisture content increases to 10.88% that is attained at 98% relatively humidity, the micropores less than 4 nm almost disappear in the DFT-PSDs probably due to the blocking effect of the formed water clusters and capillary water. However, the N$_2$-SSA of micropores (pore diameter < 10 nm) shows that it can still contributes most sites for gas adsorption on water-equilibrated coal at 98% relatively humidity.

(2) The fractal characteristics analyzed by the FHH model shows that, when the equilibrium moisture content is less than 4.74% (corresponding to a RH of 43%), $D_1$ decreases rapidly while $D_2$ shows a slight change, which is mainly due to the water adsorption on coal mainly occurs on the surface of micropores. Whereas, at high equilibrium moisture content ($M > 4.74\%$), the $D_2$ decreases significantly and $D_1$ remains at about 2.32 with moisture content increases. The phenomenon can be attributed to the completion of monolayer adsorption of water molecules on micropores, and the pore-filling and pore-blocking effects of the adsorbed water in some pores and throat.

(3) The adsorbed moisture has significant negative impact on methane desorption capacity, and
each 1% increase in moisture content can lead to about 11% reduction in $Q_1$ and about 8% reduction in $Q_{3.5}$. The analysis on the Pearson’s correlation coefficient ($\gamma$) shows that, below the studied equilibrium moisture content, the ultimate methane desorption capacity ($A$) and initial desorption rate ($V_1$) are closely related to $D_1$, while the desorption constant $K_t$ mainly depends on $D_2$.

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