Experimental Study of the Influence of Moisture Content on the Pore Structure and Permeability of Anthracite Treated by Liquid Nitrogen Freeze–Thaw

Changxing Li,* Baisheng Nie, Zhiwei Feng, Quanfei Wang, Huanying Yao, and Chunlian Cheng

ABSTRACT: The liquid nitrogen freeze–thaw (LN2-FT) method has been widely used to improve the coal permeability in the coalbed methane (CBM) production. However, the influence of moisture content on the permeability of coal treated by LN2-FT remains unclear, limiting the broad application of this technique. A novel seepage system was proposed to analyze the permeability evolution of anthracite coal samples treated by LN2-FT. Moreover, variations of the pore structure were analyzed using scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and low-field NMR. The results showed that pores and fractures appeared on the coal surface after the LN2-FT treatment. As the moisture content of the coal increased, more pores and fractures tended to be formed during the LN2-FT treatment. The total pore volume, porosity, and average pore diameter of the anthracite coal after the treatment were 1.77, 2.44, and 5.58 times higher, respectively, than that of the raw coal. The change in the specific surface area exhibited three trends as the moisture content of the coal samples increased: a slow descent, a steady increase, and a rapid descent. Moreover, it was found that the LN2-FT treatment increased the connections between pores and fractures, improving gas migration in the coal. Furthermore, the LN2-FT treatment significantly increased the permeability of the anthracite coal samples. The higher the coal moisture, the higher the permeability of the coal samples after the LN2-FT treatment. Hence, the LN2-FT technique can substantially improve the permeability of coal reservoirs, providing essential information for the efficient utilization of CBM.

1. INTRODUCTION

China is rich in coalbed methane (CBM) reserves, and shallow CBM resources within 2000 m depth comprise $36.7 \times 10^{12}$ m$^3$. The efficient extraction of CBM, an efficient and clean source, can substantially reduce China’s dependence on fossil energy.1–3 However, China’s CBM reservoirs usually are characterized by low permeability, which reduces the CBM extraction efficiency.4–7 Accordingly, the permeability improvement of coal seams to increase the CBM extraction efficiency is a hot research topic. Many scholars have proposed techniques for increasing the permeability of high-gas low-permeability coal seams.8–11 These techniques include the following types: protective layer mining, hydraulic techniques (hydraulic fracturing, hydraulic slotting, etc.), physical field excitation techniques (ultrasonic, microwave, etc.), and gas injection techniques (CO$_2$, N$_2$, etc.).12–18 Although these measures have achieved satisfactory results, they also have disadvantages, such as a small zone of influence, large quantities of products, water pollution, and uneven pressure relief.19,20 Therefore, it is urgent to develop new techniques to increase permeability and improve CBM mining efficiency. In 1997,
McDaniel et al.21 carried out a field test using liquid nitrogen to induce cracking in the San Juan CBM production area. The research showed that the thermal stress formed by a sudden drop in temperature after the injection of liquid nitrogen into the coal seam transformed the internal pore structure of the coal body and caused damage. Grundmann et al.22 found that the ultralow temperature of liquid nitrogen caused the tensile stress of the rock to exceed its tensile strength at the crack tip, leading to the failure of the rock fracture surface and the expansion and extension of the rock fracture. Subsequently, liquid nitrogen freeze−thaw (LN2-FT) fracturing has attracted extensive attention as an effective means to improve coal seam permeability.23−25 Liquid nitrogen has a very low temperature, stable chemical properties, low production costs, and is easy to obtain.26−28 The LN2-FT technique causes three types of damage to coal: in situ stress, expansion due to liquid water gasification, and freeze−thaw damage.29 Freeze−thaw damage is the primary failure mode of coal. When the coal contacts the injected liquid nitrogen, the temperature of the coal decreases sharply, resulting in rapid freezing shrinkage of the coal matrix.30 After liquid nitrogen injection, the coal absorbs the surrounding heat and melts. Thus, the liquid nitrogen cracking process consists of repeated freeze−thaw cycles of the coal seam. This process produces two types of failure forces: the expansion force of the gas−liquid and liquid−ice phase transition and uneven thermal stress of the coal due to low temperatures. The combined action of these two forces causes damage to the coal body, transforming the coal reservoir and improving its permeability. Multiple freeze−thaw cycles cause freeze shrinkage and tension fractures in the coal body, resulting in fatigue damage and propagation of internal fractures, which form a fracture network, thus improving the permeability.31−34

Studies have shown that the physical characteristics of coal, including the development degree and connections between pores and fractures, significantly affect the migration and utilization of CBM.35,36 Several scholars studied the effect of the LN2-FT treatment on the mechanical properties and permeability in detail. It was found that liquid nitrogen affects the pore structure at the microscale.37,38 When the low-temperature liquid nitrogen reaches the coal and rock, the water in the pores of the coal and rock rapidly condenses into ice due to the ultralow temperature. This phase change of the pore water can result in a 9% volumetric expansion inside the coal pores. Theoretically, this volumetric expansion can produce a stress of 207 MPa on the pore wall, exceeding the tensile strength of the coal and significantly expanding the pores.39 This response improves the pore connectivity and pore size distribution (PSD) and increases the coal pore volume, resulting in desorption and diffusion of CBM. Under standard conditions, the volumetric expansion of liquid nitrogen can reach 694 times, causing damage to the coal and propagating coal fractures. Such fractures usually have a complicated fracture network, thereby increasing the permeability of the coal seam.40 Further investigations have revealed that several parameters, including the frequency and duration of freeze−thaw cycles, and the injection pressure, affect the pore structure and permeability of coal. As the frequency and duration of the freeze−thaw cycles increase, the crack width on the coal surface increases. Meanwhile, as the frequency of the freeze−thaw cycles increases, the damage to the pore structure increases, the compressive strength of the coal decreases, and the mechanical properties of coal degrade.41−44 Moisture is an inherent part of coal and affects the ability to increase the permeability of LN2-FT cracked coal. In the field engineering of LN2-FT cracked coal, the water content in coal is different. However, the effects of moisture on the pore structure, freeze−thaw damage, and the migration characteristics of coal during LN2-FT cracking have been rarely investigated. The main target of the present research is to analyze the permeability evolution of anthracite coal with different moisture contents via a seepage experimental system. The pore structure of the samples is analyzed using scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and low-field NMR. This study is expected to provide insights into the mechanism and application of the LN2-FT technology in CBM development engineering use.

2. RESULTS AND DISCUSSION

2.1. SEM Results and Analysis. The pore structure of the raw coal samples and those subjected to the LN2-FT treatment were analyzed by a scanning electron microscope (Quanta 250, FEI Co.).45,46 The surface of the raw coal samples was relatively smooth and had no pores and fractures, as shown in Figure 1. In contrast, pores and fractures appeared on the surface of the samples with various moisture contents subjected to the LN2-FT treatment, and the surface was rough and broken, as shown in Figure 2. The likely reason is that the coal matrix is affected by the low temperature. During the freezing process, shrinkage stress appeared in the coal sample, resulting in shrinkage deformation of the coal matrix. During the thawing process, expansion stress appeared in the coal sample, resulting in expansion deformation of the coal matrix. The cyclic treatment process of shrinkage and expansion resulted in different degrees of damage in the coal sample and destroyed the pore structure. The shapes and sizes of the newly generated pore differed from the original pores. They were mostly irregular circles or ellipses with flat and narrow pores. The distribution pattern was variable; some pores occurred in groups, some occurred in zones, and some single pores were observed. In addition, under the same LN2-FT treatment conditions, the pores and fractures were more abundant in the samples with more moisture after the LN2-FT treatment. It was found that the corresponding width and length of the newly formed fractures in the coal increased with the water content of the coal, and small branch fractures also formed around the main fractures. In addition, the higher the moisture content, the more connected fractures were observed. When the liquid nitrogen contacted the coal, the water

![Figure 1. SEM image of the raw anthracite coal samples.](https://doi.org/10.1021/acsomega.1c06631)
in the pores rapidly froze, resulting in frost heave stress. The stress outstrips the tensile strength of the coal, thereby expanding the diameter and number of pores in the coal. Therefore, the more moisture in the coal, the greater the frost heave stress and more pores and fractures formed. These pores and fractures were conducive to gas desorption and migration, substantially enhancing the permeability of coal seams and increasing the rate of gas extraction rate.

Figure 2. SEM images of the anthracite coal samples with various moisture contents after the LN$_2$ -FT treatment: (a) 0.23%, (b) 0.95%, (c) 1.83%, (d) 2.97%, (e) 3.65%, (f) 5.12%.
2.2. MIP Results and Analysis. MIP is a common method for measuring coal porosity in a pore diameter within a range of 0.003–1000 μm. The pressurized mercury overcomes the surface tension and enters the coal pores. It should be noted that the amount of injected mercury depends on the pore size and PSD. The smaller the pore size, the greater the required pressure is. The pore characteristics of the coal, including the pore size, PSD, pore volume, and specific surface area, can be obtained.

Figure 3. PSD of the anthracite coal samples with different moisture contents: (a) 0.23%, (b) 0.95%, (c) 1.83%, (d) 2.97%, (e) 3.65%, (f) 5.12%.
through data analysis, calculation, and the mercury curve.\textsuperscript{47–49} Many pore classification methods for coal exist. This paper used the Hodort classification method with four levels, including macropores (i.e., $d > 1000$ nm), mesopores (i.e., $100 < d < 1000$ nm), transition pores (i.e., $10 < d < 100$ nm), and micropores (i.e., $d < 10$ nm).\textsuperscript{50–52} In this regard, a mercury intrusion porosimeter (PoreMaster-60, Quantachrome) with a working pressure of 0.1–60000 psi (0.0007–413.8 MPa) and a volume accuracy of fewer than 0.0001 mL was used.

Figure 3 illustrates the PSD of the coal samples with different moisture contents. The results indicate that the LN$_2$-FT treatment had a substantial impact on the PSD of the samples. Most of the pores can be classified as micropores and transition pores, which is consistent with the structure of middle-high rank coal. However, as the moisture content increased, the proportion of micropores and transition pores decreased, while the number of pores in the other classes of pores increased significantly. The micropores and transition pores are the primary locations for gas adsorption and storage, while the mesopores and macropores are the main channels for gas seepage.\textsuperscript{53} The PSD changed from complex before the LN$_2$-FT treatment to simple after the treatment. These changes in the pore structure are not conducive to gas adsorption but facilitate the desorption and migration of CBM.

Table 1 lists the values of the pore structure parameters after the LN$_2$-FT treatment. Figure 4 illustrates the increased amplitude of the pore parameters in the anthracite coal samples after LN$_2$-FT treatment: (a) total pore volume, (b) total porosity, (c) average pore diameter, and (d) total specific surface area.

| Sample | Moisture Content (%) | Raw Coal | LN$_2$-FT | Raw Coal | LN$_2$-FT | Raw Coal | LN$_2$-FT | Raw Coal | LN$_2$-FT |
|--------|----------------------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|
|        |                      | total pore volume ($10^{-4}$ cm$^3$/g) | total porosity (%) | average pore diameter (nm) | total specific surface area (m$^2$/g) |
| QJ     | 0.23                 | 229      | 261       | 5.21     | 6.43      | 5.25     | 7.61      | 15.23    | 13.32     |
|        | 0.95                 | 233      | 313       | 5.23     | 7.60      | 5.43     | 9.13      | 14.18    | 17.24     |
|        | 1.83                 | 242      | 357       | 5.26     | 8.99      | 5.51     | 13.34     | 16.08    | 17.56     |
|        | 2.97                 | 253      | 372       | 5.31     | 10.07     | 5.47     | 24.83     | 13.32    | 8.45      |
|        | 3.65                 | 245      | 391       | 5.28     | 12.83     | 5.34     | 29.27     | 14.24    | 5.81      |
|        | 5.12                 | 239      | 424       | 5.25     | 12.83     | 5.34     | 29.27     | 14.24    | 5.81      |

Figure 4. Increased amplitude of pore parameters in anthracite coal samples after LN$_2$-FT treatment: (a) total pore volume, (b) total porosity, (c) average pore diameter, and (d) total specific surface area.
The total pore volume of the coal samples with a moisture content of 5.12% before and after the LN$_2$-FT treatment was 239 $\times$ 10$^{-4}$ and 424 $\times$ 10$^{-4}$ cm$^3$/g, respectively, indicating an increase of 1.77 times. Similarly, as the moisture content increased, the porosity increased. The porosity of the coal samples after the treatment was 2.44 times that of the initial sample, indicating an improvement in the connectivity between the pores in the coal and is conducive to the gas migration.$^{54,55}$ The trend of the average pore diameter was consistent with that of the total pore volume and porosity. The average pore diameter was 5.42 nm before the treatment and 17.11 nm after the treatment, and the rate of increase in the average pore diameter increased with the moisture content. The average pore diameter of the sample with 5.12% moisture after the LN$_2$-FT treatment was 29.27 nm, which was 5.58 times that of the initial samples. Accordingly, it was inferred that the LN$_2$-FT treatment resulted in the expansion of the pores at all levels.

The change in the specific surface area of the samples with different moisture contents subjected to the LN$_2$-FT treatment was relatively complex. As the coal moisture content increased, the following three trends were observed:

1. **Slow descent:**
   At a low moisture content, the specific surface area exhibited a slow decline. The specific surface area of samples subjected to the LN$_2$-FT treatment was slightly lower than that of the initial samples, but the difference was relatively small. The reason is that the water in the coal preferentially occupies the micropores and transition pores. At a low moisture content, most of the water is in the micropores and transition pores. The expansion stress resulting from the freezing of the pore water due to the low-temperature liquid nitrogen mainly destroyed the micropores and transition pores, resulting in the expansion of some of the micropores and transition pores and a decrease in their volume. It was also observed in Figure 3a that the micropore volume of the coal sample treated with liquid nitrogen was lower than that of the raw coal when the moisture content was low. Because micropores and transition pores comprised the largest proportion of the specific surface area of coal, the total specific surface area decreased.

2. **Steady rising:**
   As the moisture content increased to 0.95 and 1.83%, the specific surface area exhibited a slow upward trend. Before the LN$_2$-FT treatment, the specific surface area of the sample increased from 14.18 to 17.56 m$^2$/g. The micropores and transition pores in the coal could not store all of the water; thus, some of the water occupied the mesopores. Since the frost heave force was stronger at a higher moisture content, some micropores expanded into transition pores and mesopores, and some transition pores changed into mesopores or macropores. Considering cyclic thermal stress of the coal, the ultralow temperature of the liquid nitrogen impacts the coal skeleton. However, the thermal conductivity of coal is low. When the internal temperature of the coal was uneven, the coal particles in the adjacent temperature zone deformed to varying degrees, leading to internal damages. Because of thermal stress and the freezing-induced expansion, the coal matrix opened due to repeated shrinkage and expansion. These changes increased the number of measurable micropores and the overall volume of the micropores in the coal.

3. **Rapid descent:**
   As the moisture content of samples continued to increase (>1.83%), water occupied all types of pores (including some macropores). When the coal contacted the liquid nitrogen, the water in the pores froze and solidified rapidly due to a large water volume. The expansion force was much greater than the thermal stress caused by the tensile strength and temperature change of the coal body. Therefore, most of the pores increased in volume. During this transformation, the increase in volume and number of newly formed micropores was smaller than the decrease caused by the transformation from micropores to larger pores, resulting in a reduction in the micropore volume and number. The increase in the number and volume of transition pores was attributed to the transformation of some micropores into transition pores. These changes resulted in the rapid reduction in the total specific surface area of the pores in coal. The decrease in the total specific surface area of the pores reduced the number of gas adsorption sites, which was not conducive to gas storage in coal.

Variation of the pore structure characteristics of the coal samples with increasing moisture content after LN$_2$-FT treatment indicated that LN$_2$-FT treatment increased the pore volume. It was found that as the moisture content increases, the corresponding effect is more pronounced so that the gas migration improves in the coal.

### 2.3. NMR Results and Analysis

A low-field NMR test is different from MIP. It measures the $T_2$ relaxation time of the fluid in the coal pores to obtain the pore distribution and connectivity and various physical parameters of the coal pores.$^{56,57}$ This method is fast and nondestructive, provides rich information, enables continuous detection, and has a wide measurement range. The correlation between the pore size and $T_2$ can be mathematically expressed in the form below:

$$\frac{1}{T_2} = \rho \times \frac{S}{V} = F_S \times \frac{\rho}{r}$$  \hspace{1cm} (1)

where $T_2$ represents the transverse relaxation time (ms), $\rho$ represents the transverse surface relaxation strength ($\mu$m/ms), $S$ represents the surface area of pore (cm$^2$), $V$ represents the volume of pore (cm$^3$), $F_S$ represents the pore shape coefficient (fracture, $F_S = 1$; cylindrical pore, $F_S = 2$, spherical pore, $F_S = 3$), and $r$ represents the pore diameter.

Equation 1 indicates that the pore radius $r$ of the coal is positively proportional to the transverse relaxation time $T_2$. Therefore, the NMR $T_2$ curve reflects the distribution of the pore diameter. The larger the $T_2$ value, the larger the pore diameter and vice versa. Three peaks typically occur in the $T_2$ spectrum. The value range of the micropores and transition pores is the interval of the first peak (the $T_2$ value is 0–10 ms), the value range of the mesopores and macropores is the interval of the second peak (the $T_2$ value is 10–100 ms), and the value range of the fractures is the interval of the third peak (the $T_2$ value is greater than 100 ms).$^{58,59}$ In addition, in the NMR $T_2$ curve, the magnitude of the amplitude is related to the number of pores. The greater the amplitude of the curve, the larger the number of pores corresponding to a particular pore diameter. In this paper, a Meso MR23-060H-I low-field NMR spectrometer was used to measure the pore parameters of the coal samples.
having various moisture contents before and after the LN2-FT treatment. The results are shown in Figure 5.

The $T_2$ spectrum of the coal sample showed peaks corresponding to micropores and transition pores and a peak corresponding to mesopores and macropores before the LN$_2$-FT treatment. The third peak corresponding to fractures was missing in the NMR $T_2$ spectrum of the coal samples with moisture contents of 0.23, 0.95, 2.97, and 5.12%. In contrast,
Figure 6. Permeability of the anthracite coal samples with different moisture contents: (a) before and (b) after the LN$_2$-FT treatment.

Figure 7. Increased amplitude of the permeability of the anthracite coal samples with different moisture contents after the LN$_2$-FT treatment: (a) 0.23%, (b) 0.95%, (c) 1.83%, (d) 2.97%, (e) 3.65%, (f) 5.12%.
there were three peaks in the T₂ spectrum of the coal samples with moisture contents of 1.83 and 3.65%. The signal amplitude of the peak indicated common characteristics. The signal amplitude of the first peak was the highest, followed by the second peak and the fracture peak. This result indicated that the micropores and transition pores of the raw anthracite were well developed, followed by the mesopores and macropores, whereas the fractures were not developed. The spectral peak amplitude differed for the coal samples because the coal is a multiporous and heterogeneous medium, and the PSD is different in different samples. The peaks indicating fractures in Figure 5c may have been caused by external factors during sample preparation.

Figure 5 reveals that the T₂ curves of different samples have different amplitudes of the peak after liquid nitrogen injection. It is observed that the number of micropores and transition pores in the coal samples decreased after the liquid nitrogen treatment. In contrast, the signal amplitude of the second peak of samples with different moisture contents was higher after the treatment, indicating that the micropores and transition pores expanded into mesopores and macropores, increasing the number of mesopores and macropores. A third peak occurred in all coal samples, indicating that the internal and surface pores of the anthracite coal samples formed a network, large fractures appeared, and the coal samples were broken. It was found that the higher the moisture content, the higher the signal amplitude of the third peak. This phenomenon may be attributed to damage of samples originating from the combined action of the frost heave force and thermal stress, increasing the compression degree. In addition, the continuity between the second and third peaks of the coal samples after the LN₂-FT treatment was good, supporting high connectivity between mesopores, macropores, and fractures, thereby desorbing the gas in coal. 60,61 The mesopores and macropores correspond to seepage pores, and the micropores and transition pores correspond to adsorption pores. The obtained results demonstrate that the corresponding gas diffusion in the coal improved as the number of seepage pores increased. An increase in the number of fractures provided channels for the migration and flow of gas in the coal. These changes were beneficial to the development of CBM.

2.4. Permeability Results and Analysis. Studies have shown that coal permeability is an important indicator of the difficulty of gas migration and largely depends on the pore size and connectivity. 60,62 Moreover, the freeze–thaw damage of the liquid nitrogen affects the permeability and the pore structure.

Figure 6 illustrates the influence of the LN₂-FT treatment on the permeability of the samples with different moisture contents, indicating that the LN₂-FT treatment significantly affected the permeability. It was found that the permeability curve changed to a V-shape as the gas pressure increased, i.e., a decrease followed by an increase. The gas pressure at the inflection point was about 1.0 MPa. This phenomenon is caused by the Klinkenberg effect. 63–65 As the gas pressure increased from 0.5 MPa to the inflection point, the amount of gas adsorbed by the coal samples increased. The adsorbed gas layer on the surface of the pores thickened, thereby enhancing the slip flow of the gas molecules on the pore fissure wall of the coal body. The effective seepage channel of gas was reduced, the migration resistance of gas molecules was increased, and the gas flow speed was significantly slower, resulting in the decline of permeability. When the gas pressure reached the inflection point, the gas adsorption speed was equal to the gas desorption speed, reaching the equilibrium limit. As the gas pressure exceeded the inflection point, the Klinkenberg effect gradually lost its dominant position in controlling the permeability of coal samples relative to the larger gas pressure, so the permeability began to rise. In addition, at the same gas pressure, the greater the moisture content of the samples before the LN₂-FT treatment, the lower the permeability. The reason is that water is preferentially adsorbed on the pore surface, blocking the gas flow channels. As the water content in samples increased, the corresponding gas flow resistance in the coal body increased, preventing the gas from escaping the samples. It was inferred that the LN₂-FT treatment increased the permeability of the coal samples. Due to the nitrogen-induced freeze–thaw damages during the LN₂-FT treatment, the pores in the coal samples were well developed, the cross-sectional area of the gas seepage channels was large, and gas migration occurred readily. The obtained results in this regard are presented in Figure 7. Compared to the initial samples, the average increase in permeability of the samples after LN₂-FT treatment with moisture contents of 0.23, 0.95, 1.83, 2.97, 3.65, and 5.12% was 69, 103, 141, 192, 268, and 362%, respectively. The higher the water content of the coal samples, the larger the freeze–thaw damage by the liquid nitrogen and the better the development of the pore channels in the coal body. Thus, the larger the cross-sectional area of the gas seepage channel, the higher the gas flow.

3. CONCLUSIONS
In this study, the effect of the moisture content on the evolution of the pore structure in anthracite coal samples subjected to the LN₂-FT treatment was investigated using SEM, MIP, and NMR. A gas seepage experimental device was utilized to analyze the influence of the moisture content on the permeability of the anthracite coal samples in the LN₂-FT treatment. The main conclusions of this paper were summarized as follows:

(1) The SEM results revealed that some pores and fractures appeared on the surface of the anthracite coal samples after the LN₂-FT treatment. As the moisture content increased, the size and width of the newly formed pores and fractures increased.

(2) The MIP and NMR results demonstrated that the proportion of micropores and transition pores was lower after the LN₂-FT treatment. The total pore volume, porosity, and average pore diameter of the anthracite coal samples after the LN₂-FT treatment were 1.77, 2.44, and 5.58 times larger, respectively, than those before the treatment. The change in the specific surface area with an increase in the moisture content of the coal was relatively complex. In addition, LN₂-FT treatment improved the connectivity between the pores and fractures. These changes were beneficial to the gas migration in the coal and critical for enhancing CBM recovery.

(3) The performed experiment revealed that the permeability of the anthracite samples was significantly higher after than before the LN₂-FT treatment under the same experimental conditions. The higher the moisture content in the coal, the higher the permeability of the coal samples was after the LN₂-FT treatment. Hence, the moisture is conducive to improving the permeability of the anthracite samples during LN₂-FT treatment.

(4) The performed analyses demonstrate that the LN₂-FT treatment improved the pore structure and permeability of coal reservoirs, which is conducive to CBM exploitation.
4. EXPERIMENT SECTION

4.1. Sample Preparation. To perform the experiments, anthracite samples were prepared from Qianjin coal mine, Bijie coalfield, Guizhou, China. To this end, large coal samples were packed in a cling film and quickly transferred to the laboratory for processing and analysis. A large coal block was selected as the sampling material, and its structure was not damaged during sampling. The $\Phi 50 \times 100$ mm standard coal samples were drilled and cut using an automatic drilling and coring machine, and both ends of the prepared samples were ground to obtain a smooth surface. The height of the coal samples was compatible with the stratification direction to ensure that the liquid nitrogen was injected in the horizontal stratification direction of the coal seam. An HTGF-9000 automatic industrial analyzer was used for the elemental analysis of the coal samples on the basis of the "Chinese national standards GB/T 212-2008" and "GB/T 476-2001". A Leica DM4500P polarizing microscope was used to analyze the vitrinite reflectance of the coal samples on the basis of the "Chinese national standard GB/T 6948-2008". The properties of the coal samples are summarized in Table 2, and the mineral types and contents of the coal samples are presented in Table 3.

In the present study, samples were prepared as follows:

1. Six groups of cylindrical standard coal samples (a−f) were prepared.
2. Using a vacuum drying oven for drying treatment, the dry weight $m_d$ of the coal samples was obtained using a scale.
3. The dried coal samples were placed in a vacuum saturation machine for 48 h to ensure water saturation of the samples. The weight of the saturated coal samples $m_s$ was obtained.
4. The saturated coal samples were dried at 105 °C. The heating times of different groups of samples were set to 1, 2, 4, 6, 8, and 10 h, respectively. Subsequently, the weight $m_w$ of coal samples was acquired. The moisture content $w$ of the samples was calculated as follows

$$w = \frac{m_w - m_d}{m_d}$$

4.2. Test Setup. All experiments were carried out in a custom-made coal and rock triaxial seepage experimental device, consisting of a gas cylinder, a vacuum pump, a coal sample gripper, a constant-temperature control device, a servo press, a digital gas flowmeter, and a precision pressure gauge. The gripper containing the coal sample consists of fluororubber inner and stainless-steel outer layers and holds the coal sample. The outer layer was a sleeve that had an air inlet, air outlet, and inlet holes for the liquid. During the experiment, a hydraulic oil pump was used to inject hydraulic oil around the inner rubber sleeve through the inlet hole for confining pressure loading. The confining pressure range was 0−30 MPa and the axial pressure was provided using a servo press. The axial pressure loading setting was controlled by a computer connected to the servo press. The axial pressure range was 0−70 MPa. All experiments were conducted in a vacuum environment. To this end, the gas

| sample | coal rank | $R_{\text{max}}$ | $M_{\text{d}}$ | $A_{\text{d}}$ | $V_{\text{daf}}$ | $F_{\text{daf}}$ | $O_{\text{ad}}$ | $C_{\text{ad}}$ | $H_{\text{ad}}$ | $N_{\text{ad}}$ |
|--------|-----------|------------------|----------------|--------------|----------------|----------------|--------------|--------------|--------------|--------------|
| QJ     | anthracite| 3.03             | 2.32           | 16.17        | 6.44           | 75.07          | 2.96         | 92.63        | 3.09         | 1.32         |

| sample | coal rank | kaolinite | calcite | pyrite | quartz | ankerite | marcasite | plaster |
|--------|-----------|-----------|---------|--------|--------|----------|-----------|---------|
| QJ     | anthracite| 11.32     | 3.61    | 2.44   | 1.65   | 0.96     | 0.63      | 1.32    |

Figure 8. Configuration of the experimental seepage system.

Table 2. Properties of the Coal Samples

Table 3. Mineral Type and Content of the Coal Samples
was extracted to reach the desired vacuum level using a vacuum pump. A high-pressure gas cylinder was installed at the inlet port to inject gas into the gripper, and the air outlet on the coal sample gripper was connected to a digital gas flowmeter to measure the airflow at the air outlet. The working principle of the seepage experiment is illustrated in Figure 8.

4.3. Experimental Process. The flowchart in Figure 9 shows the experimental process. The coal samples were subjected to the LN₂-FT treatment consisting of a cycle of cold immersion for 30 min and recovery at room temperature for 1 h. Some of the coal samples from each group were placed into the vacuum LN₂ cup, quickly pouring the LN₂ over the samples to immerse them and covering them with thermal insulation. The temperature of the coal body rapidly decreased from the surface to the inside, reaching −195.8 °C. After the designated cold-soaking period, the vacuum LN₂ cup was opened to let the samples reach room temperature. The permeability of the samples was tested as follows:

1. The coal samples were placed in the holder and the gas cylinder was connected. After ensuring that all valves in the system were closed, the valve on the He gas storage bottle was opened to fill the system with 3 MPa high-purity He, and let it sit for 24 h. If the pressure gauge was stable, the airtightness of the system was adequate.

2. The temperature of the constant-temperature water bath system was set to 30 °C. After the system reached this temperature, the predetermined axial pressure and confining pressure were applied using the liquid injection pressure servo machine and hydraulic oil pump. To prevent gas leakage during the experiment, the confining pressure should exceed the gas pressure.

3. The vacuum pump was started and ran for 12 h to ensure vacuum in the pipeline. Gas was injected from the gas cylinder into the experimental system. The injection pressure reached the predetermined value and remained stable for 12 h. The pressure changes of the gas adsorbed by the coal samples were observed through the pressure gauge. If the pressure decreased, the gas cylinder was opened to increase the gas adsorption pressure. This process continued until the pressure did not decrease within 30 min, indicating that the coal sample had reached the adsorption limit.

4. Subsequently, the valve was opened at the outlet of the gripper. After the gas outflow at the outlet was stable, the digital flowmeter software automatically acquired the flow data.

5. The gas pressure (pressures of 0.5, 0.8, 1.0, 1.2, and 1.5 MPa were used in the experiment) was changed and steps (3) and (4) were repeated.

6. Steps (1)–(5) were repeated using the remaining samples.

4.4. Analysis Method. Coal is an extremely complex porous medium with many pores, and the PSD ranges from the millimeter to the nanometer scale. Pores with different sizes affect the gas adsorption and desorption, gas diffusion, and gas seepage behavior, thereby affecting the permeability of the coal seam. Numerous researchers investigated the pore structure for coal using image observations and fluid injection. Image observation methods include using image slices to obtain quantitative statistics on holes and fractures in a small field of view using electron microscope imaging techniques such as SEM, atomic force microscopy (AFM), and transmission electron microscopy (TEM). It is worth noting that measuring accuracy is substantially affected by the mode of handling, field of view, and device resolution. The image observation method is typically used for the qualitative observation and analysis of pores. Fluid injection is mainly used for the quantitative measurements of the pore structure of open pores in coal. Common methods include MIP, gas adsorption methods (N₂ and CO₂), and NMR spectroscopy. These methods have superior advantages such as a wide measurement range and high precision, but they do not provide information on closed pores. The ranges of pore sizes that can be obtained from different methods are variable, as shown in Figure 10. Accordingly, it is challenging to determine the properties of the coal pore structure using a single characterization method.
Therefore, SEM, MIP, and NMR were applied to analyze the pore structure of anthracite samples before and after the LN2-FT treatment.

Coal permeability is a crucial index of gas flow in coal. In this regard, Darcy’s seepage law was applied to calculate the coal permeability and determine the treatment effect on the seepage performance. The permeability $K$ was calculated according to the difference between gas pressure $P_1$ at the inlet and gas pressure $P_2$ at the outlet of the coal sample, atmospheric pressure $P_0$, gas viscosity $\mu$, stable gas flow $q_0$, length $L$, and cross-sectional area $A$. It was calculated as follows:

$$K = \frac{2q_0 \mu L}{A(P_1 - P_2)}$$ (3)

### ACKNOWLEDGMENTS

The authors are grateful to the partial financial support from the National Natural Science Foundation of China (51574316) and the Science and Technology Program of Guizhou ([2019] 2876). They also thank the Science and Technology Program for Youth Scholar of Guizhou ([2022]122), the Science and Technology Cooperation Program of Bijie (G[2019]23), and the National College Students’ Innovation Project (20201068907).
desorption and seepage characteristics of shale gas. J Pet. Sci. Eng. 2021, 200, No. 108418.
(16) Hu, G.; He, W.; Sun, M. Enhancing coal seam gas using liquid CO2 phase-transition blasting with cross-measure borehole. J. Nat. Gas Sci. Eng. 2018, 60, 164–173.
(17) Lin, J.; Ren, T.; Cheng, Y.; Nemeck, J.; Wang, G. Cyclic N2 injection for enhanced coal seam gas recovery: A laboratory study. Energy 2019, 188, No. 116115.
(18) Li, Y.; Wang, J.; Wang, Z.; Pan, Z. Variation in permeability during CO2-CH4 Displacement in Coal Seams. Part 2: Modeling and Simulation. ACS Omega 2020, S, 18432–18440.
(19) Zhou, J.; Jin, Y.; Zhan, M. Experimental investigation of hydraulic fracturing in random naturally fractured blocks. Int. J. Rock Mech. Min. Sci. 2010, 47, 1193–1199.
(20) Liang, L.; Li, J.; Xue, J.; Zhang, C.; Fang, X. Experimental studies on the changing characteristics of the gas flow capacity on bituminous coal in CO2-ECBM and N2-ECBM. Fuel 2021, 291, No. 120115.
(21) McDaniel, B.; Grundmann, S.; Kendrick, W. Field Applications of Cryogenic Nitrogen as a Hydraulic Fracturing Fluid. J. Pet. Technol. 1998, 50, 38–39.
(22) Grundmann, S.; Redvelt, G.; Dials, G.; Allen, R. In Cryogenic Nitrogen as a Hydraulic Fracturing Fluid in the Devonian Shale, SPE Eastern Regional Meeting; OnePetro, 1998; pp 1–6.
(23) Yin, G.; Shang, D.; Li, M.; Huang, J.; Gong, T.; Song, Z.; Deng, B.; Liu, C.; Xie, Z. Permeability evolution and mesoscopic cracking behaviors of liquid nitrogen cryogenic freeze fracturing in low permeable and heterogeneous coal. Powder Technol. 2018, 325, 234–246.
(24) Li, B.; Zhang, L.; Wei, J.; Ren, Y. Pore Damage Properties and Permeability Change of Coal Caused by Freeze-Thaw Action of Liquid Nitrogen. Adv. Civ. Eng. 2018, No. S076391.
(25) Xu, J.; Zhao, C.; Liu, S.; Qin, L.; Wu, S. Pore variation of three different metamorphic coals by multiple freezing-thawing cycles of liquid CO2 injection for coalesced methane. Fuel 2017, 208, 41–51.
(26) Cha, M.; Yi, J.; Kneafsey, T.; Johanson, B.; Alqahtani, N.; Mushinsims, J.; Patterson, T.; Wu, Y. Cryogenic fracturing for reservoir stimulation-Laboratory studies. J. Pet. Sci. Eng. 2014, 124, 436–450.
(27) Cai, C.; Li, G.; Huang, Z.; Shen, Z.; Wang, H.; Tian, S.; Wei, J. Experiment study of rock porous structure damage under cryogenic nitrogen freezing. Rock Soil Mech. 2014, 35, 965–971.
(28) Zhang, S.; Huang, Z.; Huang, P.; Wu, X.; Xiong, C.; Zhang, C. Numerical and experimental analysis of high pressure liquid nitrogen freezing with high-pressure abrasive liquid nitrogen jet. J. Pet. Sci. Eng. 2018, 163, 156–165.
(29) Wei, J.; Zhang, L.; Li, B.; Wen, Z. Non-uniformity of coal damage caused by liquid nitrogen freeze-thaw. J. Nat. Gas Sci. Eng. 2019, 69, No. 102946.
(30) Li, C.; Yao, H.; Xin, C.; Li, H.; Liu, Y.; et al. Changes in pore structure and permeability of middle-high rank coal subjected to liquid nitrogen freeze-thaw. Energy Fuels 2021, 35, 226–236.
(31) Cai, C.; Li, G.; Huang, Z.; Tian, S.; Shen, Z.; Fu, X. Experiment of coal damage due to super-cooling with liquid nitrogen. J. Nat. Gas Sci. Eng. 2015, 22, 42–48.
(32) Lin, H.; Li, J.; Yan, M.; Li, S.; Qin, L.; Zhang, Y. Damage caused by freeze-thaw treatment with liquid nitrogen on pore and fracture structures in a water-bearing coal mass. Energy Sci. Eng. 2020, 8, 1667–1680.
(33) Zhai, C.; Qin, L.; Liu, S.; Xu, J.; Tang, Z.; Wu, S. Pore Structure in Coal: Pore evolution after cryogenic freezing with cyclic liquid nitrogen injection and its implication on coals heating extraction. Energy Fuels 2016, 30, 6009–6020.
(34) Chu, Y.; Zhang, D. Study on the pore evolution law of anthracite coal under liquid nitrogen freeze-thaw cycles based on infrared thermal imaging and nuclear magnetic resonance. Energy. Sci. Eng. 2019, 7, 3344–3354.
(35) Akhondzadeh, H.; Keshavarz, A.; Al-Yaseria, A.; Ali, M.; Awan, F.; Wang, X.; Yang, Y.; Lglauer, S.; Lebedev, M. Pore-scale analysis of coal cleat network evolution through liquid nitrogen treatment: A Micro-Computed Tomography investigation. Int. J. Coal Geol. 2020, 219, No. 103370.
(36) Yan, H.; Tian, L.; Feng, R.; Mitri, H.; Chen, J.; Zhang, B. Fracture evolution in coalesced methane reservoirs subjected to liquid nitrogen thermal shocking. J. Cent. South Univ. 2020, 27, 1846–1860.
(37) Du, M.; Gao, F.; Cai, C.; Su, S.; Wang, Z. Study on the surface crack propagation mechanism of coal and sandstone subjected to cryogenic cooling with liquid nitrogen. J. Nat. Gas Sci. Eng. 2020, 81, No. 103436.
(38) Akhondzadeh, H.; Keshavarz, A.; Awan, F.; Ali, M.; Al-Yaseria, A.; Liu, C.; Yang, Y.; Lglauer, S.; Gurevich, B.; Lebedev, M. Liquid nitrogen fracturing efficiency as a function of coal rank: A multi-scale tomographic study. J. Nat. Gas Sci. Eng. 2021, 95, No. 104177.
(39) Chen, S.; Zhang, L.; Zhang, C.; Huang, M. Experimental study on the seepage characteristics of bituminous coal under the conditions of liquid nitrogen fracturing. Energy Sci. Eng. 2019, 7, 2138–2154.
(40) Zhang, L.; Liu, S.; Zhang, C.; Chen, S. Effect of cyclic cold/hot shock treatment on the permeability characteristics of bituminous coal under different temperature gradients. J. Nat. Gas Sci. Eng. 2020, 75, No. 103121.
(41) Qin, L.; Zhai, C.; Liu, S.; Xu, J. Factors controlling the mechanical properties degradation and permeability of coal subjected to liquid nitrogen freeze-thaw. Sci. Rep. 2017, 7, No. 3675.
(42) Liu, J.; Li, X.; Wang, D. Numerical simulation of the coal temperature field evolution under the liquid nitrogen cold soaking. Arab. J. Geosci. 2020, 13, No. 1215.
(43) Zhao, D.; Wang, Q.; Li, D.; Feng, Z. Experimental study on infiltration and freeze-thaw damage of water-bearing coal samples with cryogenic liquid nitrogen. J. Nat. Gas Sci. Eng. 2018, 60, 24–31.
(44) Cai, C.; Gao, F.; Li, G.; Huang, Z.; Hou, P. Evaluation of coal damage and cracking characteristics due to liquid nitrogen cooling on the basis of the energy evolution laws. J. Nat. Gas Sci. Eng. 2016, 29, 30–36.
(45) Klaver, J.; Desbois, G.; Urai, J.; Littke, R. BIB-SEM study of the pore space morphology in early mature Posidonia Shale from the Hills area, Germany. Int. J. Coal Geol. 2012, 103, 12–25.
(46) Neupane, B.; Ju, Y.; Huang, C. Micro/nano-pore structure characterization of western and central nepal coals using scanning electron microscopy and gas adsorption. J. Nanosci. Nanotechnol. 2017, 17, 6836–6842.
(47) Wang, B.; Qin, Y.; Shen, J.; Zhang, Q.; Wang, G. Pore structure characteristics of low- and medium-rank coals and their differential adsorption and desorption effects. J. Pet. Sci. Eng. 2018, 165, 1–12.
(48) Friesen, W.; Ogunsola, O. Mercury porosimetry of upgraded western Canadian coals. Fuel 1995, 74, 604–609.
(49) Chalmers, G.; Bustin, R. On the effects of petrographic composition on coaled methane sorption. Int. J. Coal Geol. 2007, 69, 288–304.
(50) Li, Y.; Zhang, C.; Tang, D.; Gan, Q.; Niu, X.; Wang, K.; Shen, R. Coal pore size distributions controlled by the coalification process: An experimental study of coals from the Junggar, Ordos and Qinshui basins in China. Fuel 2017, 206, 352–363.
(51) Li, Y.; Song, D.; Liu, S.; Ji, X.; Hao, H. Evaluation of pore properties in coal through compressibility correction based on mercury intrusion porosimetry: A practical approach. Fuel 2021, 291, 120–130.
(52) Okolo, G.; Everson, R.; Neomagus, H.; Roberts, M.; Sakurovs, R. Comparing the porosity and surface areas of coal as measured by gas adsorption, mercury intrusion and SAXS techniques. Fuel 2015, 141, 293–304.
(53) Zhang, L.; Li, Z.; Yang, Y.; Zhou, Y.; Kong, B.; Li, J.; Li, L. Effect of acid treatment on the characteristics and structures of high-sulfur bituminous coal. Fuel 2016, 184, 418–429.
(54) Chalmers, G.; Bustin, R. On the effects of petrographic composition on coaled methane sorption. Int. J. Coal Geol. 2007, 69, 288–304.
(55) Chen, Y.; Tang, D.; Xu, H.; Tao, S.; Li, S.; Yang, G.; Yu, J. Pore and fracture characteristics of different rank coals in the eastern margin of the Ordos Basin, China. J. Nat. Gas Sci. Eng. 2015, 26, 1264–1277.
(56) Ghomeshi, S.; Kryuchkov, S.; Kantzas, A. An investigation into the effects of pore connectivity on T2 NMR relaxation. J. Magn. Reson. 2018, 289, 79–91.
(57) Li, Z.; Liu, D.; Cai, Y.; Wang, Y.; Si, G. Evaluation of coal petrophysics incorporating fractal characteristics by mercury intrusion porosimetry and low-field NMR. Fuel 2020, 263, No. 116802.
(58) Moroeng, O.; Wagner, N.; Brand, D.; Roberts, R. A Nuclear Magnetic Resonance study: Implications for coal formation in the Witbank Coalfield, South Africa. Int. J. Coal Geol. 2018, 188, 145–155.
(59) Saidian, M.; Prasad, M. Effect of mineralogy on nuclear magnetic resonance surface relaxivity: A case study of Middle Bakken and Three Forks formations. Fuel 2015, 161, 197–206.
(60) Zhang, X.; Lin, B.; Zhu, C.; Yan, F.; Liu, T.; Liu, T.; Li, Y. Petrophysical variation of coal treated by cyclic high-voltage electrical pulse for coalbed methane recovery. J. Pet. Sci. Eng. 2019, 178, 795–804.
(61) Liang, Y.; Tan, Y.; Wang, F.; Luo, Y.; Zhao, Z. Improving permeability of coal seams by freeze-fracturing method: The characterization of pore structure changes under low-field NMR. Energy Rep. 2020, 6, 550–561.
(62) Meng, Z.; Li, G. Experimental research on the permeability of high-rank coal under a varying stress and its influencing factors. Eng. Geol. 2013, 162, 108–117.
(63) Liu, T.; Lin, B.; Wang, Y.; Zhai, C.; Liu, T. Coal permeability evolution and gas migration under non-equilibrium state. Transp. Porous Media 2017, 118, 393–416.
(64) Yan, F.; Xu, J.; Lin, B.; Peng, S.; Zou, Q.; Zhang, X. Changes in pore structure and permeability of anthracite coal before and after high-voltage electrical pulses treatment. Powder Technol. 2019, 343, 560–567.
(65) Wei, J.; Wang, D.; Wei, L. Comparison of permeability between two kinds of loaded coal containing gas samples. J. China Coal Soc. 2013, 38, 93–99.
(66) Fu, H.; Wang, X.; Zhang, L.; Gao, R.; Li, Z.; Xu, T.; Zhu, X.; Xu, W.; Li, Q. Investigation of the factors that control the development of pore structure in lacustrine shale: A case study of block X in the Ordos Basin, China. J. Nat. Gas Sci. Eng. 2015, 26, 1422–1432.
(67) Zhu, H.; Zhang, Y.; Qi, B.; Liao, Q.; Wang, H.; Gao, R. Thermodynamic characteristics of methane adsorption about coking coal molecular with different sulfur components: Considering the influence of moisture contents. J. Nat. Gas Sci. Eng. 2021, 94, No. 104053.
(68) Ren, J.; Song, Z.; Li, B.; Liu, J.; Lv, R.; Liu, G. Structure feature and evolution mechanism of pores in different metamorphism and deformation coals. Fuel 2021, 283, No. 119292.
(69) Giffin, S.; Littke, R.; Klaver, J.; Urai, J. Application of BIB-SEM technology to characterize macropore morphology in coal. Int. J. Coal Geol. 2013, 114, 85–95.
(70) Kwiecińska, B.; Pusz, S.; Valentine, B. Application of electron microscopy tem and sem for analysis of coals, organic-rich shales and carbonate matter. Int. J. Coal Geol. 2019, 211, No. 103203.
(71) Li, Y.; Yang, J.; Pan, Z.; Tong, W. Nanoscale pore structure and mechanical property analysis of coal: An insight combining AFM and SEM images. Fuel 2020, 260, No. 116352.
(72) Clarkson, C.; Wood, J.; Burgis, S.; Aquino, S.; Freeman, M. Nanopore-structure analysis and permeability predictions for a tight gas siltstone reservoir by use of low-pressure adsorption and mercury-intrusion techniques. SPE Reservoir Eval. Eng. 2012, 15, 648–661.
(73) Jiang, J.; Yang, W.; Cheng, Y.; Zhao, K.; Zheng, S. Pore structure characterization of coal particles via MIP, N2 and CO2 adsorption: Effect of coalification on nanopores evolution. Powder Technol. 2019, 354, 136–148.
(74) Wang, Z.; Cheng, Y.; Qi, Y.; Wang, R.; Wang, L.; Jiang, J. Experimental study of pore structure and fractal characteristics of pulverized intact coal and tectonic coal by low temperature nitrogen adsorption. Powder Technol. 2019, 350, 15–25.
(75) Lin, J.; Ren, T.; Wang, G.; Booth, P.; Nemcik, J. Experimental investigation of N2 injection to enhance gas drainage in CO2-rich low permeable seam. Fuel 2018, 215, 665–674.