INTRODUCTION

Coalbed methane (CBM), as an important unconventional natural gas resource with vast reserves around the world, mainly exists in the matrix, pores, and fractures of coal in both adsorbed and free state. To date, many countries have achieved large-scale CBM development. In China, the common characteristics of the special geological structure and burial conditions and the low permeability, low porosity, and high density of coal reservoirs hinder CBM development. Currently, hydraulic fracturing, which could produce a large number of fractures with a massive water pressure to improve the permeability of the coal seam, is commonly used in the development of CBM. However, conventional hydraulic fracturing can cause massive water consumption, water pollution, and reservoir sensitivity, which has limited the large-scale application of this process in CBM development. Therefore, waterless fracturing technology, which relies on liquid nitrogen (LN₂) or liquid carbon dioxide as a fracturing fluid, has been attracting the attention of many experts and scholars.

LN₂, which is an environment friendly cryogenic fluid, has a temperature of −196°C at normal temperature and atmospheric pressure (0.1 MPa). When LN₂ is injected into the reservoir rock, a temperature gradient is formed between the reservoir rock and the LN₂, which can cause the rock to undergo a freeze-thaw process. This process can enlarge the pore size, enhance the pore connectivity, and form a fracture network on the surface of coal samples, which increases the total porosity, residual porosity, effective porosity, and permeability. This study provides a theoretical value for LN₂ fracturing in the development of CBM.

KEYWORDS

liquid nitrogen freeze-thaw process, nuclear magnetic resonance (NMR), pore structure, scanning electron microscopy (SEM)
inner and outer rocks because of the extremely low temperature of LN₂, resulting in differential shrinkage of the rock and tensile stress on the rock surface. When the tensile stress exceeds the ultimate tensile strength of the rock, fractures will be generated on the rock surface. One cubic meter of liquid nitrogen can expand to 696 m³ of nitrogen at 21°C, thereby generating an extremely large expansion pressure. In addition, the volume of water expands by 9.1% when water in the fracture is frozen into ice by LN₂ and produces a frost heaving force of 210 MPa in the crack tip of the reservoir rock, resulting in fracture, propagation, and local damage of the pre-existing fracture. Moreover, the elimination of the frost heaving force and migration of water also leads to the damage of fractures.

Based on the above characteristics of LN₂, McDaniel et al. conducted a test with a LN₂ fracturing fluid to stimulate five CBM wells. Grundmann et al. treated a Devonian shale well with LN₂ and observed that the initial production rate was increased by 8% compared with those of other wells in which the traditional fracturing method was used. Cai et al. found that the LN₂ cooling process can cause damage and fracture failure in coal and promote the formation of fracture networks. Huang et al. studied the crack propagation and uniaxial compressive strength under LN₂ freeze-thaw cycles and found that the width of a crack in the coal increases with the number of freeze-thaw cycles and that the uniaxial compressive strength of the specimen decreases after the freeze-thaw cycles. Ren et al. analyzed the mechanism of the impact of LN₂ on coal and found that the wave velocity and amplitude of coal decreased greatly after LN₂ treatment.

The previous research mainly focused on changes in the coal strength and macroscopic characteristics using LN₂ freeze-thaw cycles and ignored the damage to the pore structure of the coal sample caused by the cryogenic effect of LN₂ under freeze-thaw cycles. Due to the temperature gradient formed in the coal samples by the ultralow temperature of LN₂, the coal sample undergoes a "shrinking-swelling" process during the freeze-thaw cycles, which might cause fatigue damage and damage to the pore structure. How to utilize the freeze-thaw effect generated during the LN₂ fracturing process is a relatively new research topic in need of comprehensive and systematic investigation. The CBM reservoirs in China are mostly high-rank coal (meager coal or anthracite) and high-rank coal often has higher degree of metamorphic and compaction, which result high-rank coal has the characteristics of strong adsorption capacity and high gas content. The previous research did not systematically study the damage to the pore structure of anthracite coal by LN₂ freeze-thaw, since the metamorphic degree and compaction degree of coal are different, the pore structure of different rank of coal has big difference. Based on the above characteristics, this study uses nuclear magnetic resonance (NMR) measurements and scanning electron microscopy (SEM) imaging to investigate the influence of LN₂ with different freezing times and different numbers of freeze-thaw cycles on the damage to the pore structure of anthracite. According to the $T_2$ spectra before and after the LN₂ freeze-thaw process, the porosity, $T_2$ cutoff value, pore connectivity, evolution of pores and fractures, and change in the permeability were analyzed. This study highlights theoretical and experimental techniques for the production of CBM by LN₂ freeze-thaw technology.

**FIGURE 1** Classification and characterization of pore structure of coal reservoirs
2 | EXPERIMENTAL

2.1 | Nuclear magnetic resonance theory

The pore structure of coal involves the pore type, size, distribution, and connectivity of pores and fractures. The analysis method for determining pore structure can be divided into image method, fluid invasion, and nonfluid invasion. The image method includes SEM (scanning electron microscope), FE-SEM (field emission scanning electron microscope), TEM (transmission electron microscope), and AFM (atomic force microscope); the fluid invasion method includes SAXS/SANS (scattering/small-angle neutron scattering), μCT (micro computed tomography), and FIB-SEM (focused ion beam scanning electron microscopes); whereas the nonfluid invasion includes NMR, MIP (mercury intrusion porosimetry), nitrogen adsorption, and carbon dioxide adsorption. Figure 1 shows the classification and characterization of pore structure of coal reservoirs including SAXS/SANS (2-250 nm), μCT (60-10⁵ nm), NMR (0.1-10⁶ nm), MIP (3-10⁵ nm), nitrogen adsorption (1.5-360 nm), and carbon dioxide adsorption (0.4-500 nm). Some aforementioned methods for pore structure have certain limitations such as low efficiency, limited testing ranges, and damage to the original pore structure of coal.

The diameter of methane molecules is 0.38 nm, and most methane molecules exist in pores of coal with diameter of less than 100 nm as an adsorption state. Nuclear magnetic resonance is an advanced, fast, nondestructive, and convenient test method for analyzing the pore structure of coal reservoir and testing the largest range of pore size of coal reservoir. Therefore, the damage of pore structure of anthracite before and after freeze-thaw cycles was analyzed by MMR in this paper.

Theoretically, when fluids within a reservoir are in a low and uniform magnetic field, the spin magnetic moment of hydrogen atoms within fluids are changed; after removing the magnetic field, the spin magnetic moment is gradually restored to the original condition, generating an NMR signal. Generally, the transverse relaxation time is used to analyze the pore size distribution and connectivity. The relationship between the transverse relaxation time and the pore size can be expressed by the following equation:

\[
\frac{1}{T_2} = \rho_2 \left( \frac{S}{V} \right)_{\text{pore}} = F_S \rho_2 \frac{r_c}{r_p}
\]

where \(T_2\) is the transverse relaxation time (ms); \(\rho_2\) is a factor representing the relaxation surface strength (μm/ms), \((S/V)_{\text{pore}}\) is the ratio of the pore surface to volume (cm⁻¹), \(F_S\) is the shape factor, and \(r_p\) is the pore size.

According to Equation (1), the transverse relaxation time of fluid in pores is related to the pore size and shape; a smaller pore corresponds to a shorter \(T_2\) value, and a larger \(T_2\) value corresponds to a larger pore. Therefore, the \(T_2\) spectrum distribution can reflect the pore size distribution; for example, a higher area and amplitude of peak in the \(T_2\) spectrum distribution mirror the better development of pores or fractures in coal samples. In addition, the connection among the peaks in the \(T_2\) spectrum distribution reflects the connectivity between pores.

2.2 | Experimental samples

For this study, a large block of coal was collected from the Baijiao coal mine. The coal was elaborately wrapped with air-proof packaging and then immediately transported to the laboratory for the experiments. According to the Chinese Petroleum and Natural Gas Industry Standard Method SY/T 6490-2014, the coal was cut into cylinders with diameters of 25 mm and heights of 50 mm. To select coal samples with similar properties for the experiment, the density and ultrasonic characteristics of the coal samples were measured. The main properties of coal samples are shown in Table 1. Before the experiment, a proximate analysis of the coal was conducted using a 5E-MACIII Computer Ir Celerity Coal Analysis Instrument according to the British Standard ISO 17246-2005(E); the proximate analysis results and vitrinite reflectance of the coal sample are shown in Table 2.

2.3 | Experimental procedures

After the coal samples were prepared, they were dried in a drying oven at 80°C for at least 24 hours. Next, the coal samples...
were placed into the water saturation device at a pressure of −0.1 MPa for 12 hours to reach the 100% water-saturated condition ($S_w$). The 100% water-saturated coal samples were first measured by NMR to obtain the $T_2$ spectrum distribution and porosity, and then, the coal samples were placed into a centrifuge machine for centrifugation at a pressure of 200 psi for 90 minutes to reach the irreducible condition ($S_{irr}$); the NMR test was then repeated to obtain another $T_2$ spectrum distribution and porosity. When the above steps were completed, the coal samples were used to test the damage to the pore structure caused by different LN$_2$ freezing times and number of freeze-thaw cycles. The freezing times were set as 60, 120, 180, 240, 300, and 360 minutes, and the freeze-thaw cycles were set as 2, 4, 6, 8, 10, and 12 cycles. Each freeze-thaw cycle included 30 minutes of freezing and 30 minutes of thawing at room temperature. After the coal sample freeze-thaw cycles were completed, the samples were resaturated with water, and then, the NMR measurements were repeated, followed by centrifugation for further NMR measurements. Since the high anisotropy of coals, for the repeatability of the experiment, the experimental coal samples in different LN$_2$ freezing times are the same coal samples, while the experimental coal samples in different LN$_2$ freeze-thaw cycles are the other same coal samples. In addition, the microscopic morphology of the coal samples after the freeze-thaw cycles was observed by SEM imaging. The experimental system and procedure are shown in Figure 2. The main NMR measurement parameters are as follows: the time interval of echoes (TE) was 0.1 ms, the waiting time (TW) was 1.5 seconds, the RF signal frequency was 12 MHz, the number of scans was 16, the number of echoes was 10 000, and the analyses were performed with magnets at 32°C.

### RESULTS AND DISCUSSION

#### 3.1 $T_2$ spectrum distribution analysis

According to the pore size, the $T_2$ spectrum distribution is divided into the following parts 33-35: The first peak located at a time of less than 1.7 ms corresponds to the micropores; the second peak located between 1.7 ms and 65 ms corresponds to the mesopores; and the third peak at a time greater than 65 ms corresponds to the macropores and microfractures. Cai et al$^{16}$ classified the micropores as adsorption pores, which provides storage space for CBM; the mesopores, macropores, and microfractures belong to seepage pores, which provide the pathways for CBM diffusion and seepage.

Figure 3 shows the $T_2$ spectrum distribution of the 100% water-saturated and irreducible condition BJ-1 and BJ-2 coal samples subjected to different LN$_2$ freezing times and different numbers of freeze-thaw cycles. As shown in Figure 3, before the freezing and freeze-thaw process by LN$_2$, the area and amplitude of the first peak were the largest; the second and third peaks were relatively small, implying that the pore structure of the coal was mainly occupied by micropores and that the mesopores and macropores were rarely developed. After 120 minutes of freezing and 4 freeze-thaw cycles, the areas and amplitudes of the three peaks in the $T_2$ spectrum distribution all increased, but the rate of increase was low; this result shows that, in the initial stage of freezing and freeze-thaw cycles, the micropores, mesopores, and macropores all expanded, but the extent of expansion is very small, and the degree of damage of pore structure is relatively weak during this stage. With increases in the time and number of cycles, the area and amplitude of the mesopore peak significantly increased; this result shows that the micropores undergo a large expansion and significantly increase the number of mesopores. When the intercommunicating mesopores reach a certain level, the change in the $T_2$ spectrum is mainly found in the macropore peak, the pore structure of coal samples is redistributed, and the micropores continue to develop, expand, and connect to generate a large number of macropores. After freezing for 360 minutes and undergoing 8 freeze-thaw cycles, the pore size and width of macropores are greatly increased, and fractures appear at the surface of the coal sample; this observation indicates that serious freeze-thaw damage occurred inside the coal samples. With the increase in the times and number of cycles, the width of the fractures gradually increases, and the fractures connect to form a fracture network, which is consistent with the results of SEM and macroscopic observations (as shown in Figures 8 and 9). This result suggests that the effect of the LN$_2$ ultralow temperature can accelerate the connection between pores, promote the formation of fractures, significantly increase the proportion of mesopores and macropores, and significantly increase the number of seepage pores. These seepage pores provide channels for CBM migration and diffusion.

#### 3.2 The absolute and relative change rate of the $T_2$ spectra area

The peak areas in the $T_2$ spectra represent the number of pores with different pore size. To quantify the evaluated change in the number of coal pores under different freezing times and freeze-thaw cycles, this section analyzes the change rate of coal pores by determining the absolute and relative area change rate of peak area of $T_2$ spectra. The absolute area change rate is
FIGURE 2 Experimental system and procedure

![Experimental system and procedure](image)

The rate of total pores and adsorption pores was small relative to the seepage pores. The main reason for this phenomenon is that the average pore radius of coal samples increases greatly during the freezing and freeze-thaw process, and a large number of seepage pores were generated, which lead to the absolute area change rate of seepage pores much larger than that of total pores and adsorption pores. In addition, the absolute area change rate of total pores, adsorption pores, and seepage pores after freeze-thaw cycles is greater than those of total pores, adsorption pores, and seepage pores after freezing, it is clear that compared with a single freezing event, freeze-thaw cycle can promote the generation of pores with different pore size and transform the pore structure of coal samples more efficiently.

The relative area change rate of total pores, adsorption pores, and seepage pores can quantitatively analyze the area variation trend of coal samples after two adjacent freezing and freeze-thaw cycles. As shown in Figure 5, the relative area change rate of all pores was positive after the coal samples were frozen and freeze-thawed by using LN2, which means that freezing and freeze-thaw cycle can promote the generation of pores with different pore size of coal samples. The relative area change rate of the total pores exhibits a tendency for stable growth with increase in freezing time and freeze-thaw cycles, the relative area change rate of the adsorption pores shows a tendency for stable growth and then slowly decline during the freezing and freeze-thaw cycles processes, while the relative area change rate of the seepage pores exhibits a tendency for rapid growth. When the relative change rate of the T2 spectra for the adsorption pore is compared, the spectrum after a freezing time of 360 minutes and freeze-thaw cycles of 12 cycles could be divided into two stages based on the pore development. Those stages are stage I (before 180 minutes freezing and 6 freeze-thaw cycles) and stage II (after 180 minutes freezing and 6 freeze-thaw cycles) for adsorption pores.

In stage I, the adsorption pores develop rapidly, and the number of adsorption pores increases gradually. Therefore, the relative area change rate of adsorption pores gradually increases. In this stage, the number of total and seepage pores also increase under the tensile stress, expansion pressure, and frost heaving force, and the relative area change rate of total and seepage pores also increases. In stage II, the relative area change rate of adsorption pores gradually decreases as the
freezing time and number of freeze-thaw cycles increase. In this stage, the number of adsorption pores continuously increase, the newly developed and original adsorption pores begin to impinge on the seepage pores. The seepage pores as the natural weak surface of adsorption pores were continuously destroyed under the frost heaving force, resulting in a larger number of secondary pores, which were generated around the adsorption pores. Some secondary pores gradually expand and connect with adsorption pores to form seepage pores with large size when the number of secondary pores increases to a certain extent. Because some adsorption pores being transformed into seepage pores, the relative area change rate of adsorption pores slowly declines, and the expansion and communication speed of seepage pores were accelerated, which lead to continuous increase in the relative area change rate of seepage pores.

3.3 | Variation of coal porosity after the freeze-thaw process

In the coal reservoir, porosity is an important indicator for evaluating the permeability of coal reservoir, which
directly affects the desorption, diffusion, and seepage of CBM. The $T_2$ spectrum distribution under 100% water-saturated condition can be converted into the NMR total porosity; thus, the NMR total porosity includes the residual porosity corresponding to the bound fluid fraction and the effective porosity $\varphi_{NF}$ corresponding to the free fluid fraction. The residual porosity $\varphi_{NB}$ can be obtained by the $T_2$ spectrum under irreducible conditions, and the relationship between the porosities can be expressed by the following equations:

$$\varphi_{NB} = \varphi_N \times \text{BVI}/(\text{BVI} + \text{FFI})$$  \hspace{1cm} (6)

$$\varphi_{NF} = \varphi_N \times \text{FFI}/(\text{BVI} + \text{FFI})$$  \hspace{1cm} (7)

where $\varphi_{NB}$, $\varphi_{NF}$, and $\varphi_N$ are the residual porosity, effective porosity, and total porosity, respectively. FFI and BVI are free fluid index and bound fluid index, respectively. BVI + FFI represents the total fluid, which can be obtained from the area of the $T_2$ spectrum for the 100% water-saturated condition.

As shown in Figure 6, the total porosity, residual porosity, and effective porosity of coal samples are positively correlated with the freezing time. After the coal sample is frozen for 360 minutes, the total porosity of the coal samples increases by 1.92% with an increased ratio of 34.9%, the residual porosity increases by 0.88% with an increased ratio of 17.9%, and the effective porosity increases by 2.74 times; the results show that LN$_2$ freezing can damage the pore structure of the coal samples, resulting in increased porosity and enhanced pore connectivity. The reasons for this positive correlation are as follows: (a) because of the temperature gradient formed by the ultralow temperature of LN$_2$, the coefficient of expansion between the coal particles is different, and thermal expansion and contraction as
well as anisotropy cause the continuous weakening of the bonding surface between the particles, leading to the expansion of the original pores to form new pores, and (b) the water in the coal samples can be frozen into ice during the freezing process, with a 9.1% volume increase, which produces a frost heaving force in the crack tip, causing local damage inside the coal samples.

During the freeze-thaw process, as the number of LN\textsubscript{2} freeze-thaw cycles increases, the total porosity, residual porosity, and effective porosity positively correlate with the number of freeze-thaw cycles. After 4 freeze-thaw cycles, the total porosity, residual porosity, and effective porosity increase by 0.57%, 0.34%, and 0.23%, respectively. After 8 freeze-thaw cycles, the total porosity, residual porosity, and effective porosity of coal samples increase obviously, with the effective porosity increasing by 3.41 times; this result suggests that with increasing number of freeze-thaw cycles, the pore structure of the coal samples is continuously deteriorated and destroyed, the micropores continue to develop and expand to form mesopores and macropores, and the connectivity of pores and the effective porosity of coal samples significantly increase. After 12 freeze-thaw cycles, the trend of the porosity growth of the coal samples slows because the macropores gradually communicate to form a fracture on the surface of coal samples (as shown in Figure 9). Because the fracture cannot preserve water, the coal samples cannot reach the 100% water-saturated condition; as a result, the NMR porosity of coal sample is lower than the real porosity. It should be noted that the damage to the pore structure of the coal samples after the freeze-thaw cycles are more significant than that of coal samples subjected to a single freezing process. The reason for this observation is that after the temperature rises, the water of the coal samples melts after freezing. The melting of water causes the local damage to the pores to accelerate, resulting in the elimination of the frost heaving force and water migration; the process of initiation, development, expansion, and connection of the microfractures of the damage area results in macroscopic fractures and eventually produces a fracture network (as shown in Figure 9).

### 3.4 $T_{2cutoff}$ value change

By definition, a relaxation time boundary exists, referred to as the $T_{2cutoff}$ value, which divides the $T_2$ spectrum of coal samples in the 100% water-saturated condition into bound fluid and free fluid regions. The volume less than the $T_{2cutoff}$ value in the $T_2$ spectrum represents the volume of bound fluid, whereas the volume larger than the $T_{2cutoff}$ value corresponds to the volume of free fluid. Since the pore structure of anthracite is mainly occupied by micropores, the area and amplitude of micropores are largest; therefore, for the same $T_2$ spectrum of anthracite coal, a greater $T_{2cutoff}$ value corresponds to greater volume the bound fluid; the higher bound fluid index is, the greater the proportion of unconnected pores and the greater the residual porosity. A smaller $T_{2cutoff}$ value indicates a larger proportion of free fluid; the higher the free fluid index is, the greater the connectivity among pores and the greater the effective porosity. The details of the calculation of the $T_{2cutoff}$ value can be found in the work of Yao et al\textsuperscript{39} and Qin et al.\textsuperscript{40} As shown in Figure 7, the initial $T_{2cutoff}$ value of the coal sample before being frozen by LN\textsubscript{2} is 6.368 ms, and the $T_{2cutoff}$ value after being frozen for 360 minutes is 9.011 ms; the $T_{2cutoff}$ value increases 2.643 ms with an increased ratio of 29.3%; the $T_{2cutoff}$ value of the coal sample before the LN\textsubscript{2} freeze-thaw cycles is 7.317 ms, and the value after 12 freeze-thaw cycles changes to 11.097 ms with a 34.1% increase. The free fluid index increases with increases in the freezing time and the number of freeze-thaw cycles; the free fluid index of the coal sample before frozen by LN\textsubscript{2} is 10.7% (pretest state), and the value is 21.9% after the sample is frozen for 360 minutes, with an increased ratio of 104.7%. The free fluid index of the coal sample before LN\textsubscript{2} freeze-thaw cycles is 9.8% (pretest state), and the value is 25.4% after 12 freeze-thaw cycles, with an increased ratio of 159.1%; that is, as both the freezing time and the number of freeze-thaw cycles increase, the $T_{2cutoff}$ value gradually increases. This implies that micropores continuously expand and then connect to form a large number of mesopores, macropores, and fractures under the tensile stress, expansion pressure, and frost heaving force, indicating that LN\textsubscript{2} freeze-thaw cycles can enlarge the pore size and enhance pore connectivity, thereby providing a pathway for fluid to flow and the corresponding increase in the free fluid index as well as the effective porosity.

### 3.5 Fracture evolution analysis

To intuitively characterize the fracture evolution of the coal sample subjected to different numbers of LN\textsubscript{2} freeze-thaw cycles, the image and SEM images of the BJ-2 after freeze-thaw cycles by LN\textsubscript{2} shown in Figures 8 and 9 were studied. As shown in Figure 8, the surface of coal sample is smooth before the LN\textsubscript{2} freeze-thaw cycles. After 4 freeze-thaw cycles, some fractures are generated on the surface of the coal sample under the frost heaving force and tensile stress. After 8 freeze-thaw cycles, the original fractures are expanded, which destroys the pore structure of the coal sample, and some secondary fractures are formed near the weakened location along the original fracture. After 12 freeze-thaw cycles, the secondary fractures gradually expand and connect to form a fracture network throughout the whole coal sample surface, thereby providing the pathway for CBM diffusion and seepage.
Figure 9 shows SEM images of the BJ-2 before and after being subjected to different numbers of LN2 freeze-thaw cycles, and the local temperature of the coal sample decreases sharply after freeze-thaw by LN2, with each coal particle shrinking violently via the ultralow temperature of LN2. Before freeze-thaw cycles, an original slender-type fracture with widths ranging from 1.47 μm to 1.96 μm already exist on the surfaces of the coal samples, with some particles spalling off the coal surface and filling into the fracture; such particles act as the propping agent to prevent the fracture from closing. After 12 freeze-thaw cycles, the original fracture gradually expands, and the width and depth of the fracture obviously increase. The secondary fracture along the main fracture is formed with a width of 0.85 μm, forming a “Y”-type fracture that provides the pathway for CBM migration and diffusion.

3.6 Analysis of the change in the coal permeability

Permeability, as an important index for evaluating the fluid to flow through the porous media, is a key property for evaluating the production performance of coal reservoirs. Permeability mainly depends on the pore size, connectivity of the pores, and effective porosity.41-44 Although NMR
cannot directly measure permeability, it can be calculated by the porosity, FFI, BVI, and geometric mean reflected by the $T_2$ spectrum. The known calculated NMR permeability models are the SDR model (also called the mean $T_2$ model), the Timur-Coates model (also called the free fluid mode), and the producible porosity (PP) model. The Timur-Coates model and PP model are not suitable for a medium with low porosity and permeability, as error between the NMR permeability and matrix permeability of coal is larger. In addition, the PP model requires a large amount of sample data to calculate the NMR permeability. Thus, in this study, the SDR model was used to study the permeability changes of coal samples treated with different freezing times and different numbers of freeze-thaw cycles.

The SDR model and its regression equations for calculating permeability can be described by the following equation:

\[
K_{SDR} = a q_n (T_{2gm}^{\text{regression}}) ^{m} \rightarrow K_{SDR} = 0.0224(T_{2gm}^{\text{regression}})^{1.534}(T_{2gm}^{b})^{0.182} \quad (8)
\]

where $a$ and $m$ are the constants related to the characteristic rock-coal masses, and $T_{2gm}^{a}$ and $T_{2gm}^{b}$ (ms) represent the geometric mean of the $T_2$ distribution of coal samples at water-saturated and irreducible water conditions, respectively.

The calculated $K_{SDR}$ permeability change in coal samples at different freezing times and with different numbers of freeze-thaw cycles is shown in Figure 10. The $K_{SDR}$ permeability of the coal sample before being frozen by LN$_2$ is initially 0.01495 mD, and the permeability gradually increases with the freezing time. The $K_{SDR}$ permeability of the coal sample increases to 0.2697 mD (after freezing for 360 minutes), with an increased ratio of 79.2%. The $K_{SDR}$ permeability

**FIGURE 9** SEM images of the surface of BJ-2 before and after freeze-thaw cycles by LN2 (A. The original fracture of coal sample. B. The enlarged view of original fracture. C. The fracture of coal samples after freeze-thaw at the same scan domain. D. The enlarged view of secondary fracture.)

**FIGURE 10** Variation in the $K_{SDR}$ permeability of BJ-1 and BJ-2 for different freeze-thaw times and cycles
of the coal sample before LN$_2$ freeze-thaw cycles is initially 0.01169 mD, and the values are 0.01533 mD (after 4 cycles), 0.02633 mD (after 8 cycles), and 0.03065 mD (after 12 cycles). Before the 4 freeze-thaw cycles, the permeability of coal samples increases slowly, and after 4 freeze-thaw cycles, the values all increase significantly. After 12 freeze-thaw cycles, the permeability of the coal sample increases to 0.01896 mD, with an increased ratio of 162%, that is, an increase in the number of freeze-thaw cycles can cause more accumulated damage to the pore structure of coal samples, thereby inducing more mesopores, macropores, and fractures to form. As a result, the volume and size of the pores are enlarged, causing an increase in the effective porosity. These variations all indicate that the LN$_2$ freeze-thaw cycles can enhance the $K_{SDR}$ permeability by generating a larger number of mesopores and macropores as well as enhancing the connectivity of pores.

4 | CONCLUSIONS

In this study, NMR analysis and SEM have been conducted on the anthracite after treatment by LN$_2$ with different freezing times and different numbers of freeze-thaw cycles. Several conclusions were made based on this work:

1. With an increase in the LN$_2$ freezing time and number of freeze-thaw cycles, the micropores gradually develop and expand, the volume and size of the pores gradually increase, and the connectivity between the pores was enhanced to form a large number of mesopores and macropores under the tensile stress, expansion pressure, and frost heaving force.

2. The total porosity, residual porosity, and effective porosity of coal samples were positively correlated with the freezing time and number of freeze-thaw cycles. The results show that LN$_2$ freezing and freezing-thawing can damage the pore structure of the coal sample. Although the freezing time was same, the damage to the pore structure of the coal sample after freeze-thaw is more significant than that to coal samples subjected to a single freezing.

3. As the pore structure of the coal samples continuously deteriorated and destroyed, fractures were generated on the surface of coal samples. With the increase in times and cycles, the fracture gradually expanded, and the width and depth of the fracture obviously increased. Some secondary fractures were formed along the original fracture and connected to form a fracture network.

4. The number of seepage pores increased with the increase in freezing time and number of freeze-thaw cycles, which suggested that LN$_2$ freezing-thawing could enlarge the pore size and enhance the pore connectivity, which provides the pathway for fluid to flow leading to the increase in the free fluid index and permeability.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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