RESEARCH ARTICLE

Study on the pore evolution law of anthracite coal under liquid nitrogen freeze-thaw cycles based on infrared thermal imaging and nuclear magnetic resonance

Yapei Chu1,2 | Dongming Zhang1,2

Abstract
The waterless fracturing method with liquid nitrogen (LN2) as the fracturing fluid has been proposed and successfully applied in coalbed methane (CBM) production in recent years. The temperature of the coal reservoir sharply decreases, causing damage to the pore structure of the coal reservoir due to the ultralow temperature of LN2 during fracturing. Thus, in this paper, infrared thermal imaging (ITI) and nuclear magnetic resonance (NMR) were used to measure the temperature distribution and pore evolution law of anthracite coal. The results demonstrate that the temperature of the coal sample after being frozen by LN2 was far less than 0°C, which causes the internal water of the coal sample to freeze and turn into ice and produce a frost-heave force. In addition, the temperature of the coal samples was not fixed but fluctuated, which led to the formation of a temperature gradient and induced thermal stress. The T2 spectra variation showed that LN2 freeze-thaw cycles can promote the development of pores in coal samples and enhance the connectivity of pores. Some of the micropores gradually connect and expand to form a large number of mesopores and macropores under the influence of frost-heave force and thermal stress. The total porosity, residual porosity, and effective porosity increase with the number of LN2 freeze-thaw cycles. The NMR imaging directly reflects the change characteristics of the internal pore structure before and after LN2 freeze-thaw, which provide a new way to reveal the pore evolution law of anthracite. These results show that LN2 freeze-thaw cycles can damage the pore structure of anthracite coal, and a large number of mesopores and macropores are formed to provide channels for CBM migration, which improves the efficiency of LN2 fracturing.

KEYWORDS
infrared thermal imaging, liquid nitrogen freeze-thaw cycles, nuclear magnetic resonance, pore evolution law
1 | INTRODUCTION

Coalbed methane (CBM), as an associated product of coal formation and metamorphism processes, has high calorific and efficient clean-burning characteristics, and mainly exists in coal seams in three states: the adsorbed state on the surface of the coal matrix, free state in the pores, and dissolved state in the water of the coal reservoir. Statistically, in China, CBM is known as a clean and alternative unconventional natural gas resource with vast reserves; the volume of CBM resources stored below a depth of 2000 m is approximately $36 \times 10^{12}$ m³, and the development of CBM resources has a great significance for reducing the occurrence of coal mine gas disasters and adjusting the energy structure, which has attracted interests by companies, experts, and scholars. However, in China, coal reservoirs are characterized by a low porosity, low permeability, low pressure, and high heterogeneity due to the influence of specific geological conditions; the permeability of coal reservoirs is $10^{-4}-10^{-2}$ mD, which is three orders of magnitude lower compared to the San Juan basin in the United States. The low permeability of the coal reservoirs seriously hinders the development of CBM in China. Hence, improving the permeability of coal reservoirs is a major challenge for the development of CBM. Currently, hydraulic fracturing (HF), which produces a larger number of fractures by injecting fracturing fluid at a high pressure, is commonly used for the development of CBM. Currently, hydraulic fracturing (HF), which produces a larger number of fractures by injecting fracturing fluid at a high pressure, is commonly used for the development of CBM. However, certain drawbacks, such as water pollution, high water consumption, and water lock effect, restrict the large-scale application in arid regions. Thus, a new technology is urgently needed that increases the permeability of coal reservoirs with low energy consumption, no pollution, and applicability under different geological conditions.

With the rapid development of CBM exploration and production technology, waterless fracturing with liquid nitrogen (LN₂) as the fracturing fluid has been successfully applied since the 1990s. Compared with HF, LN₂ is a nonpolluting ultralow temperature fluid; the temperature of LN₂ is $-196{°}$C under atmospheric temperature and pressure conditions. LN₂ can greatly reduce the temperature of the reservoir after being injected into the coal reservoir, which promotes the original fissure expansion and generation of new fissures, and increases the fissure density of coal reservoirs and the degree of reservoir reconstruction. In addition, water in the coal reservoir freezes into ice and generates 210 MPa of frost-heave force when sufficient volumes of LN₂ are injected into the reservoir; when the frost-heave force exceeds the ultimate tensile strength of coal, the internal structure of the coal reservoir will be destroyed and fissures are generated. Moreover, LN₂ can generate a high gas pressure during the process of vaporization with a ratio of 1:696 at $21^\circ$C. Tran et al. found that secondary cracks may be created perpendicular to the main cracks during the injection of the cold fluid into a hot reservoir, and crack initiation, crack width, and crack length were discussed. Wang et al. analyzed the crack distribution, crack extension process, cracking mechanism, and propagation direction of the internal microcracks in coal by scanning electron microscopy (SEM) before and after the coal samples were subjected to thermal shock. Li et al. analyzed the law of crack propagation and evolution in coal samples at different temperatures after freezing occurred due to the injection of LN₂. Ren et al. found that the ultralow temperature of LN₂ can cause shrinkage of the coal matrix and produce frost-heave forces, which leads to the generation of local cracks and thermal stress cracking of coal samples, thereby improving the permeability of coal samples. Wei et al. analyzed the change in permeability and the development of microfractures in coal samples due to the temperature impact. Cai et al. measured the uniaxial compressive strength of coal samples before and after freezing due to LN₂ injection and found that the LN₂ freezing caused macrofractures on the surface of coal samples; the uniaxial compressive strength of coal decreased by 16.18%-33.74%.

The above research mainly focuses on the evolution of cracks and permeability of coal samples frozen due to the injection of LN₂. However, studies on the temperature distribution and pore evolution of coal samples under different LN₂ freeze-thaw cycles have not yet been systematically carried out. The temperature of coal samples will decrease sharply to form a temperature gradient and generate thermal stress when LN₂ comes into contact with the coal samples. In addition, water in the coal samples will be frozen into ice, which will generate a volume expansion of approximately 9.1%, while at the same time, frost-heave forces will cause the generation of local cracks in coal samples. The pore structure of coal samples will be destroyed under thermal stress effects and frost-heave forces during LN₂ freeze-thaw cycles. Thus, in this paper, the temperature of coal samples was monitored by infrared thermal imaging (ITI), and the pore size distribution and the change in porosity under different LN₂ freeze-thaw cycles were measured by nuclear magnetic resonance (NMR). Finally, the pore evolution law of coal samples was analyzed by the $T_2$ spectra under different LN₂ freeze-thaw cycles.

2 | EXPERIMENTAL

2.1 | Samples preparation

An experimental coal block was collected from the Baijiao Coal Mine, Sichuan Province, China, then carefully wrapped with preservative film, and immediately transported to the laboratory. The coal block was cut into cylindrical samples of 50 mm in height and 25 mm in diameter, and the end-surface nonparallelism error of the coal samples was less than 0.02 mm. Then,
the coal samples were dried under vacuum in an oven until the weight stopped changing or the weight change was less than 0.02 g between two sequential weighing. The proximate analysis and vitrinite reflectance data of the coal samples are shown in Table 1.

### 2.2 Experimental procedure

After the coal samples were prepared, they were placed into a vacuum water saturation device with a vacuum pressure of −0.1 MPa for 24 hours to reach the 100% water saturated condition. Then, the coal samples were first tested by NMR to record the T2 spectra under 100% water saturated conditions. Next, the fully water saturated coal samples were centrifuged at a pressure of 1.38 MPa for 90 minutes to remove the free fluid to reach the centrifuged condition, after which the centrifuged coal samples were again tested by NMR to obtain another set of T2 spectra. After the above steps were completed, freeze-thaw treatments were conducted on the coal samples for 2, 4, 6, 8, 10, and 12 cycles, in which a freeze-thaw cycle included 30 minutes of freezing and 30 minutes of thawing at room temperature. After being subjected to the LN2 freeze-thaw cycles, the coal samples were again analyzed by NMR under 100% water saturated and centrifuged conditions. In addition, the surface temperature of the coal samples was monitored by ITI to obtain the temperature distribution when the coal samples were being subjected to LN2 freeze-thaw cycles. The diagram of the experimental system and procedure is shown in Figure 1. In addition, the parameters of the equipment used in this experiment are as follows:

1. The main magnetic field strength of the NMR instrument (MacroMR 12-150H-I, Suzhou Niumag Corporation) was 0.3 T. The radio frequency (RF) pulses were in the range of 1.0-42 MHz, with a control accuracy of 0.01 Hz. The parameters of this NMR test were as follows: The signal frequency and frequency offset were 12 MHz and 683 909.4 Hz, respectively. The echo time $T_E$ and waiting time $T_W$ were set to 0.1 ms and 1.5 seconds, respectively. The scanning number was set to 16, and the magnet working temperature was 32°C.

The hydrogen (1H) protons in the pore fluids were magnetized and generated a magnetization vector under the effect of an external magnetic field. At this time, the hydrogen (1H) protons were stimulated by a radio frequency field to produce an NMR phenomenon, which had a signal with an amplitude attenuation that decayed exponentially over time and could be obtained by removing the frequency field. Generally, the transverse relaxation time $T_2$ was used to describe the speed of signal attenuation. The intensity of the NMR signal is proportional to the number of hydrogen (1H) protons in the pore fluids; therefore, the magnitude of the relaxation time $T_2$ is proportional to the pore radius: A smaller pore size corresponds to a shorter relaxation time, a larger pore size has a longer relaxation time, and the area under the different peaks indicates the number of pores with different pore sizes. The relationship between the relaxation time and pore size can be expressed by Equation (1):

$$\frac{1}{T_2} = \rho \left( \frac{S}{V} \right)_{\text{pore}} = F_S \frac{\rho}{r}$$

where $T_2$ is the transverse relaxation time (ms), $\rho$ is the relaxation surface strength (c), $S$ and $V$ represent the pore surface area (cm²) and volume (cm³), respectively, $F_S$ is the shape factor of the pores, and $r$ is the pore radius, μm.

2. An ITI (FLIR T660) apparatus from the FLIR corporation, was used at an infrared resolution ratio of 680 × 480 pixels. The thermal sensitivity (the noise equivalent temperature difference) was less than 0.02°C, and the target temperature ranged from −60 to 2000°C, with a precision of 2%. The spectral range was from 7.5 to 14 μm. The imaging frequency was 30 Hz.

3. The proximate analysis of the coal samples was conducted by a 5E-MAC III Computer Ir Celerity Coal Analysis Instrument. The centrifuge used in the experiments was an Eppendorf 5430R, and the centrifuge radius was 10.5 cm, corresponding to a centrifugation of pressure of 1.38 MPa.

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Thermal imaging test

Temperature transfer would occur when the coal samples came into contact with LN2, which caused the temperature of the coal samples to sharply decrease. As shown in Figure 2, the coal samples exhibited a notable low temperature phenomenon. To investigate the influence of the ultralow temperature due to the LN2 on a coal sample during the cooling process, the surface of the coal sample was monitored by ITI. As shown in Figure 3, six monitoring lines on the end and lateral faces were chosen to study the temperature distribution of the coal sample. The surface temperature of the coal sample ranged from −10 to −30°C, and the interior temperature ranged from −30 to −60°C;

| $M_{\text{ad}}$/% | $A_{\text{ad}}$/% | $V_{\text{ad}}$/% | $F_{\text{ad}}$/% | $R_{\text{p}}$, max/% |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1.58            | 23.22           | 9.7             | 65.5            | 2.43            |
the temperature of the coal sample did not remain stable but fluctuated, which might be related to the anisotropic nature of coal as coal is composed of crystals, pores, joints, microfissures, cements, clays, and different mineral grains. The mineral grains have different coefficients of thermal expansion; the mineral grains could not freely be deformed under the action of the ultralow temperature due to LN$_2$, which caused the generation of stress between the mineral...
The $T_2$ spectra of the coal sample under 100% water saturated and centrifuged conditions after being subjected to LN$_2$ freeze-thaw cycles (2, 4, 6, 8, 10, and 12 cycles).

**Figure 4**

(A) 2 cycles

(B) 4 cycles

(C) 6 cycles

(D) 8 cycles

(E) 10 cycles

(F) 12 cycles

(G) $T_2$ spectra of anthracite at saturated water condition

(H) $T_2$ spectra of anthracite at centrifuged water condition
grains: The large mineral grains were compressed, and the small mineral grains were stretched. Thermal stress was generated in the coal sample due to the ultralow temperature. The thermal stress was usually concentrated at the boundary between mineral grains. When the thermal stress exceeded the ultimate tensile strength of the coal sample, fissures were generated at the mineral grain junctions, and as the temperature gradient increased, the fissures gradually developed and connected to form larger fissures, which eventually led to destruction of the pore structure of the coal sample. The temperature of the coal sample was far below 0°C, which resulted in the internal water of the coal sample freezing into ice with a 9.1% increase in volume, which produced a frost-heave force of 210 MPa that caused the pore walls to extrude. When the frost-heave force exceeded the ultimate tensile strength of the coal sample, the latter resulted in damage of the pore structure of the coal sample. In addition, ice wedges occurred in the coal sample along the fissures, and the fissures gradually extended under the recurring cycles of thermal stress and frost-heave force, which led to the extension of original fissures and formation of new fissures. Moreover, the coal samples underwent a shrinkage-expansion process during the freeze-thaw cycles, which might have caused fatigue damage to the coal samples. In addition, with the elimination of the frost-heave force and water migration, the degree of damage to the pore structure of the coal sample would be aggravated.

3.2 | $T_2$ spectra

According to Yao, the $T_2$ spectra of coal samples when 100% water saturated reflect the characteristics of the pore size distribution. The first peak of the $T_2$ spectrum below 1.7 ms corresponded to micropores, the second peak of the $T_2$ spectrum range from 1.7 to 65 ms corresponded to the mesopores, and the third peak of the $T_2$ spectrum above 65 ms corresponded to the macropores or microfractures. According to Cai et al., the micropores are called adsorption pores, which have a large specific area and adsorption capacity, and provide space for CBM adsorption, whereas the mesopores, macropores, and microfractures belong to the seepage pores, which provide channels for CBM diffusion and seepage.

Figure 4 shows the $T_2$ spectra of coal samples under different LN$_2$ freeze-thaw cycles. As shown in Figure 4, after 4 freeze-thaw cycles, the amplitudes and areas of the micropore, mesopore, and macropore peaks of the $T_2$ spectrum of the coal sample all increased, which indicates that the number of micropores, mesopores, and macropores all increased; however, the change was small, indicating that the degree of damage to the pore structure of the coal sample was relatively small. After 8 freeze-thaw cycles, the mesopore peak changed significantly, which indicates that a larger number of micropores appeared in the coal sample, the pore size and volume of the micropores greatly increased under the influence of thermal stress and frost-heave force, and the micropores continuously developed and connected to form a larger number of mesopores. After 12 freeze-thaw cycles, the change in the $T_2$ spectrum of the coal sample was mainly concentrated on the peaks of the mesopores and macropores, and the results showed that the pore structure of the coal sample continuously deteriorated and was destroyed in this stage; the proportion of mesopores in the coal sample continued to increase, and mesopores continued to develop, expand, and connect. When the number of interconnected mesopores reached a certain level, macropores and microfractures were formed. After 12 freeze-thaw cycles, the area of adsorption and seepage pores in the $T_2$ spectrum of the coal sample increased 1.33 and 4.17 times, respectively; the results showed that LN$_2$ freeze-thaw cycles could promote the development of pores and the connection of microfractures and enhance the connectivity of pores. The proportion of mesopores, macropores, and microfractures in the coal sample significantly increased, providing channels for the flow and extraction of CBM.

3.3 | The change in $T_2$ cutoff values

There is a boundary value, namely the $T_2$ cutoff value, which could divide the $T_2$ spectrum of the coal sample under the 100% water saturated condition into two parts: free fluid (FFI, the free fluid index) and bound fluid (BVI, the bound fluid index), as shown in Figure 5. The fraction of the $T_2$ cutoff values is shown in Figure 5. The change in the BVI and FFI after LN$_2$ freeze-thaw cycles (pretest and posttest state).
The T2cutoff value was calculated based on the T2 spectra at 100% water saturated and centrifuged conditions. First, the T2 spectra at the 100% water saturated and the centrifuged conditions were accumulated sequentially to obtain the cumulative porosity curve. Second, a horizontal line was constructed at the maximum value of the cumulative porosity curve under the centrifuged condition that intersects the cumulative porosity curve under the 100% water saturated condition at one point. Lastly, a vertical line was constructed through the intersection point, and the T2 value at the intersection projected on the time axis was defined as the T2cutoff. Since the pore structure of anthracite is mainly occupied by micropores, the area and amplitude of micropores are largest; therefore, for the same T2 spectrum of anthracite coal, a large T2cutoff value indicated a larger volume of bound fluid and greater proportion of unconnected pores, while a small T2cutoff value indicated a larger volume of free fluid and greater connectivity of pores.

Figure 5 shows the variation in T2cutoff values of a coal sample in the pretest and posttest (12 LN2 freeze-thaw cycles) state. The pretest T2cutoff value was 7.317 ms, and the T2cutoff value after 12 LN2 freeze-thaw cycles was 11.097 ms. The T2cutoff value increased 3.78 ms with a decrement ratio of 34.1%. With the increase in the T2cutoff value, the proportion of BVI decreased while the proportion of FFI notably increased; the proportion of FFI increased by 3.16 times, and this result indicates that LN2 freeze-thaw cycles could promote the development of pores, increase the pore size and volume, and enhance the pore connectivity in the coal sample, which provides channels for the migration of CBM.

### 3.4 Porosity change

Porosity, as an important index for evaluating coal reservoirs, is mainly affected by the pore size, pore volume, and coal rank, which directly affects the adsorption, desorption, diffusion, and seepage of CBM. By accumulating and normalizing the T2 spectra, the T2 spectra under 100% water saturated and centrifuged conditions can be converted into porosity. The cumulative porosity curve at 100% water saturated could be regarded as the total porosity \( \varphi_r \), and the cumulative porosity curve at the centrifuged condition refers to the residual porosity \( \varphi_r \). As shown in Figure 6, \( \varphi_r \) and \( \varphi_r \) represent the cumulative porosity curves of 100% water saturated and the centrifuged conditions, respectively. The difference between the total porosity \( \varphi_r \) and residual porosity \( \varphi_r \) is the effective porosity \( \varphi_e \), which refers to the porosity of the interconnected pores of the coal sample and is an important factor for evaluating the permeability of coal reservoirs.

\[
\varphi_{ek} = \varphi_{rk} - \varphi_{rk} \quad (k = 0,2,4,6,8,10,12)
\]

where \( \varphi_{ek} \), \( \varphi_{rk} \), and \( \varphi_{rk} \) are the effective porosity, total porosity, and residual porosity, respectively. \( k = 0,2,4,6,8,10,12 \) represents the pretest and posttest state.

The change in the total porosity, residual porosity, and effective porosity of the coal sample is shown in Figure 6. The change in porosity could be divided into three stages based on the rate of increment in the porosity:

**Stage I**: In this stage, the rate of growth of the porosity exhibited a tendency of stable growth, and after 4 freeze-thaw cycles, the total porosity, residual porosity, and effective porosity of the coal sample increased by 0.57%, 0.34%, and 0.23%, respectively, with an increase ratio of 11.6%, 7.7%, and 47.9%, respectively. The change in the total porosity and residual porosity was relatively small, and the change in porosity was mainly concentrated on the effective porosity. The results show that the degree of damage to the pore structure of the coal sample was relatively small in this stage, and the LN2 freeze-thaw cycles could promote the development of pores in the coal sample and improve the proportion of connected pores.

**Stage II**: After 8 freeze-thaw cycles, the rate of growth of the porosity exhibited a tendency of rapid growth. Relative to stage I, the total porosity, residual porosity, and effective porosity increased by 1.84%, 0.91%, and 0.93%, respectively, with an increase ratio of 33.6%, 19.1% and...
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Freeze-thaw (0, 2, 4, 6, 8, 10, and 12 cycles) affects the characteristics of anthracite coal when mainly accounting for adsorption.

The number of micropores and macropores continued to increase due to the destruction of the pore structure of the coal sample, while mesopores and macropores continuously developed, expanded, and communicated to form microfissures, resulting in an increase in the total porosity and effective porosity. The number of micropores did not increase significantly during this stage; thus, the residual porosity did not change significantly during this stage.

Stage III: In this stage, the rate of growth of the total porosity and effective porosity exhibited a tendency of slow growth, during which the residual porosity remained stable and virtually did not change. After 12 freeze-thaw cycles, the proportion of micropores and macropores continuously developed and expanded, the volume and size of the micropores continuously increased to form a larger number of mesopores and macropores. The pore connectivity was continuously enhanced, which indicates that the pore structure of the coal sample was destroyed in this stage, resulting in a large increase in the porosity of the coal sample.

**3.5 The change in the pore size distribution**

As shown in Figure 7, the micropores accounted for the majority of the proportion of pores in the coal sample before the LN₂ freeze-thaw cycles, and mesopores and macropores were not well developed, which is consistent with the characteristics of anthracite coal when mainly accounting for adsorption pores. With an increase in the number of freeze-thaw cycles, the proportion of micropores gradually decreased, while the proportion of mesopores and macropores continued to increase. After 12 freeze-thaw cycles, the proportion of micropores decreased from 83.6% to 69.5% with a decrease ratio of 16.1%. While the proportion of mesopores increased from 11.6% to 17.1% with an increase ratio of 47.4%, the proportion of macropores increased from 4.8% to 13.4% with an increase ratio of 179.2%. This result indicates that the size and volume of the micropores continuously increased under the influence of thermal stress and frost-heave force during the LN₂ freeze-thaw cycles. Some of the micropores gradually connected and expanded to form a large number of mesopores and macropores, resulting in an increase in the proportion of mesopores and macropores, which provided channels for CBM diffusion and seepage.

**3.6 Nuclear magnetic resonance imaging analysis**

The hydrogen (¹H) protons in the pore fluids of coal samples were magnetized and generated an electromagnetic wave under an external gradient magnetic field, and then, they were spatially localized by a gradient pulse sequence. The N x N data matrix was formed by phase and frequency encoding, and finally, the cross-sectional image was formed by image reconstruction. The deeper the color of the pixel indicates the larger development of pores and fractures. The NMR imaging can directly reflect the distribution of the pores and fractures of coal samples.

Figure 8 shows typical proton density-weighted images of cross and longitudinal sections of coal samples subjected to different freeze-thaw cycles. The color bar shows the relative strength range of the hydrogen (¹H) protons in the pore and fracture fluids of coal samples. The black is the imaging background and does not have an imaging signal. The red shows the relatively strong signal of hydrogen (¹H) protons, indicating the development of pores and fractures. As shown in Figure 8A, before the freeze-thaw cycles by LN₂, the area of proton clusters of coal samples is not developed, indicating that the pores and fractures of coal samples are not developed, and thus, the NMR signal is weak. As shown in Figure 8B, after 4 freeze-thaw cycles, the number and brightness of the blue proton clusters of coal samples were significantly enhanced to form a high-proton-density area, indicating that the size and volume of micropores gradually increased under the thermal stress and frost-heave force, and the micropores gradually expand and connect to form mesopores. At this stage, the high-proton areas are small and isolated. As shown in Figure 8C, after 8 freeze-thaw cycles, a large number of blue and green proton clusters appear, and tiny high-proton areas merge together to form a large region, which indicates that the number of mesopores of coal samples increases significantly after 8 freeze-thaw cycles. As shown in Figure 8D, after 12 freeze-thaw cycles, the number of bright green proton clusters is significantly increased, and red proton clusters appeared. The appearance of the red proton clusters is mainly due to the
connection and coalescence of microfractures, which indicates that the pore structure of coal samples was redistributed, the pore size and width of the mesopores were greatly increased to form macropores and microfractures, and the microfractures gradually interconnected to form the fracture network.

In this paper, the temperature distribution, the change in porosity, and the pore evolution law of coal samples were analyzed by ITI and NMR, and some significant results were obtained, which provides the theoretical and experimental technique for LN₂ fracturing. However, there are still some limitations in this paper. For example, different moisture contents, different temperatures of coal samples, and different coal ranks have not been considered. Thus, further research will need to be carried out on these parameters in future investigations to improve the LN₂ fracturing technology.

4 | CONCLUSION

In this study, the pore evolution law of anthracite coal under LN₂ freeze-thaw cycles was investigated by ITI and NMR. The following conclusions can be obtained based on the results:

1. After the coal samples were frozen by LN₂, the coal samples displayed an obvious low temperature phenomenon, and the temperature of the coal samples was far below 0°C, which resulted in the water of the coal samples freezing into ice and generating frost-heave force which extruded the pore walls. In addition, the temperature of the coal samples did not remain stable but fluctuated, which led to the formation of a temperature gradient and induced thermal stress.

2. According to the analysis of the T₂ spectra, as a result of the succession of different freeze-thaw cycles, the size and volume of micropores gradually increased and enlarged to form a larger number of mesopores. With an increase in the number of freeze-thaw cycles, the pore structure of the coal sample continuously deteriorated and was destroyed, while the mesopores continuously developed, expanded, and connected. When the number of interconnected mesopores reached a certain level, macropores and fissures were formed.

3. As the number of freeze-thaw cycles increased, the T₂cutoff value gradually increased while the proportion of FFI notably increased. The change in porosity of the coal sample was divided into three stages with an increase in the number of freeze-thaw cycles. The total porosity, residual porosity, and effective porosity increased with the number of freeze-thaw cycles, which indicates that LN₂ freeze-thaw cycles could promote the development of pores in coal samples and enhance the connectivity of pores.

4. With an increase in the number of freeze-thaw cycles, the proportion of micropores gradually decreased, while the proportion of mesopores and macropores continuously increased. After 12 freeze-thaw cycles, the proportion of micropores decreased by 14.1%, while the number of mesopores and macropores increased by 5.5% and 8.6%, respectively. This result indicates that some of the micropores gradually connected and expanded to form a large number of mesopores and macropores under thermal stress and frost-heave force during the freeze-thaw cycles.

5. With an increasing number of freeze-thaw cycles, the number and brightness of proton clusters in the NMR imaging of coal samples gradually increased, and after several freeze-thaw cycles, the connection and coalescence occurred among the microfractures. The NMR imaging can directly reflect the variation characteristics of the pore structure of coal samples before and after freeze-thaw cycles.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.
REFERENCES

1. Moore TA. Coalbed methane: a review. Int J Coal Geol. 2012;101:36-81.
2. Qin Y, Moore TA, Shen J, Yang Z, Shen Y, Wang G. Resources and geology of coalbed methane in China: a review. Int Geol Rev. 2018;60(5-6):777-812.
3. Liu A, Fu X, Wang K, An H, Wang G. Investigation of coalbed methane potential in low-rank coal reservoirs - free and soluble gas contents. Fuel. 2013;112:14-22.
4. Xu J, Zhai C, Liu S, Qin L, Dong R. Investigation of temperature effects from LCO2 with different cycle parameters on the coal pore variation based on infrared thermal imagery and low-field nuclear magnetic resonance. Fuel. 2018;215:528-540.
5. Xu J, Zhai C, Qin L. Mechanism and application of pulse hydraulic fracturing in improving drainage of coalbed methane. J Nat Gas Sci Eng. 2017;40:79-90.
6. Cai Y, Liu D, Pan Z, Yao Y, Li J, Qiu Y. Pore structure and its impact on CH4 adsorption capacity and flow capability of bituminous and subbituminous coals from Northeast China. Fuel. 2013;103:258-268.
7. Karacan CO, Ruiz FA, Cote M, Phipps S. Coal mine methane: a review of capture and utilization practices with benefits to mining safety and to greenhouse gas reduction. Int J Coal Geol. 2011;86(2-3):121-156.
8. Liang Y, Sheng X. Defining outburst-free zones in protective mining with seam gas content-method and application. J Chin Coal Soc. 2014;39(9):1786-1791.
9. Christopher M, Michael G. Evaluating the risk of coal bursts in underground coal mines. Int J Min Sci Technol. 2016;26(1):47-52.
10. Jia C, Zheng M, Zhang Y. Unconventional hydrocarbon resources in China and the prospect of exploration and development. Petrol Explor Develop. 2012;39(2):139-146.
11. Zhang Q, Feng SL, Yang XL. Basic reservoir characteristics and development strategy of coalbed methane resource in China. J Chin Coal Soc. 2001;26(3):230-235.
12. Xu J, Zhai C, Liu S, Qin L, Sun Y. Feasibility investigation of cryogenic effect from liquid carbon dioxide multi cycle fracturing technology in coalbed methane recovery. Fuel. 2017;206:371-380.
13. Tang Z, Yang S, Xu G, Sharifzadeh M, Zhai C. Investigation of the effect of low-temperature oxidation on extraction efficiency and capacity of coalbed methane. Process Saf Environ Prot. 2018;117:573-581.
14. Xu J, Zhai C, Liu S, Qin L, Wu S. Pore variation of three different metamorphic coals by multiple freezing-thawing cycles of liquid CO2 injection for coalbed methane recovery. Fuel. 2017;208:41-51.
15. Mohammad BK, Robert H. Processing of measurement while drilling data for rock mass characterization. Int J Min Sci Technol. 2016;26(6):989-994.
16. Yin G, Wenpu LI, Jiang XU, et al. Development and application of fracturing and seepage experimental system for multi-physical field and multiphase coupling of porous media. Chin J Rock Mech Eng. 2016;35(81):2853-2861.
17. Yin GZ, Jiang CB, Hu J, Peng SJ, Li WP. Experimental study of thermo-fluid-solid coupling seepage of coal containing gas. J Chin Coal Soc. 2011;36(9):1495-1500.
18. Yang XL, Ren CZ, Zhang YL, Guo RN. Numerical simulation of the coupled thermal-fluid-solid mathematical models during extracting methane in low-permeability coal bed by heat injection. J Chin Coal Soc. 2013;38(6):1044-1049.
19. Li H, Lau HC, Huang S. China's coalbed methane development: a review of the challenges and opportunities in subsurface and surface engineering. J Petrol Sci Eng. 2018;166:621-635.
20. Liu J, Yao Y, Liu D, et al. Experimental simulation of the hydraulic fracture propagation in an anthracite coal reservoir in the southern Qinshui basin. China. J Petrol Sci Eng. 2018;168:400-408.
21. Orem W, Tatu C, Varonka M, et al. Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale. Int J Coal Geol. 2014;126:20-31.
22. Clarkson CR. Production data analysis of unconventional gas wells: review of theory and best practices. Int J Coal Geol. 2013;109:101-146.
23. Aguilera RF, Ripple RD, Aguilera R. Link between endowments, economics and environment in conventional and unconventional gas reservoirs. Fuel. 2014;126:224-238.
24. Boudet H, Clarke C, Bugden D, Maibach E, Roser-Renouf C, Leiserowitz A. “Fracking” controversy and communication: using national survey data to understand public perceptions of hydraulic fracturing. Energy Pol. 2014;65:55-67.
25. Jackson RE, Gorody AW, Mayer B, Roy JW, Ryan MC, Van Stempvoort DR. Groundwater protection and unconventional gas extraction: the critical need for field-based hydrogeological research. Ground Water. 2013;51(4):488-510.
26. Liu Q, Guo Y, An F, Lin L, Lai Y. Water blocking effect caused by the use of hydraulic methods for permeability enhancement in coal seams and methods for its removal. Int J Min Sci Technol. 2016;26(4):615-621.
27. Cha M, Yin X, Knaefsey T, et al. Cryogenic fracturing for reservoir stimulation - laboratory studies. J Petrol Sci Eng. 2014;124:436-450.
28. Grundmann S, Rodvelt G, Dials G, Allen R. Cryogenic nitrogen as a hydraulic fracturing fluid in the Devonian shale. In: SPE Eastern Regional Meeting; 1998.
29. McDaniel B, Grundmann S, Kendrick W, Wilson D, Jordan S. Field applications of cryogenic nitrogen as a hydraulic-fracturing fluid. J Pet Technol. 1998;50(3):38-39.
30. Mueller M, Amro M, Haefner F, Hossain MM. Stimulation of tight gas reservoir using coupled hydraulic and CO2 cold-frac technology. In: Asia Pacific Oil and Gas Conference and Exhibition; 2012.
31. Zhang XX, Wang JG, Gao F, Ju Y. Impact of water, nitrogen and CO2 fracturing fluids on fracturing initiation pressure and flow pattern in anisotropic shale reservoirs. J Nat Gas Sci Eng. 2018;168:291-306.
32. Kim M, Kemeny J. Effect of thermal shock and rapid unloading on mechanical rock properties. Rock Mech Rock Eng. 2009;47(6):2005-2019.
33. Winkler EM. Frost damage to stone and concrete - geological considerations. Eng Geol. 1968;2(5):315-323.
34. Tran D, Settari A, Nghiem L. Initiation and propagation of secondary cracks in thermo-poroelastic media. In: 46th US Rock
35. Wang D, Zhang P, Pu H, et al. Experimental research on cracking process of coal under temperature variation with industrial micro-CT. Chin J Rock Mech Eng. 2018;37(10):2243-2252.
36. Wang D, Sun L, Wei J. Microstructure and fracture mechanism of coal under thermal shock. Rock Soil Mech. 2019;40(2):1-12.
37. He-Wan LI, Wang LG, Niu FM, Liu WF, Zhang CH. Study on effect of freeze-thaw cycle with liquid nitrogen on crack extension of coal at different initial temperatures. Chin Saf Sci J. 2015;25(10):121-126.
38. Ren S, Fan Z, Liang Z, Yong Y, Luo J, Hang C. Mechanisms and experimental study of thermal-shock effect on coal-rock using liquid nitrogen. Chin J Rock Mech Eng. 2013;32:3790-3794.
39. Wei J, Sun L, Wang D, Bo LI, Ming P, Liu S. Change law of permeability of coal under temperature impact and the mechanism of increasing permeability. J Chin Coal Soc. 2017;42(8):1919-1925.
40. 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.
41. 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.
42. Yao Y, Liu D, Cai Y, Li J. Advanced characterization of pores and fractures in coals by nuclear magnetic resonance and X-ray computed tomography. Sci Chin-Earth Sci. 2010;53(6):854-862.
43. Yao Y, Liu D. Comparison of low-field NMR and mercury intrusion porosimetry in characterizing pore size distributions of coals. Fuel. 2012;95(1):152-158.
44. Kleinberg RL. Pore size distributions, pore coupling, and transverse relaxation spectra of porous rocks. Magn Reson Imaging. 1994;12(2):271-274.
45. Yao Y, Liu D, Che Y, Tang D, Tang S, Huang W. Petrophysical characterization of coals by low-field nuclear magnetic resonance (NMR). Fuel. 2010;89(7):1371-1380.
46. Zheng S, Yao Y, Liu D, Cai Y, Liu Y. Characterizations of full-scale pore size distribution, porosity and permeability of coals: a novel methodology by nuclear magnetic resonance and fractal analysis theory. Int J Coal Geol. 2018;196:148-158.

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