Study on Temperature Variation and Pore Structure Evolution within Coal under the Effect of Liquid Nitrogen Mass Transfer

Bo Li,* Laisheng Huang, Xiaoquan Lv, and Yongjie Ren

ABSTRACT: Liquid nitrogen freezing, which is an effective permeability enhancement technology, has been applied to the extraction of oil, shale gas, and coalbed methane (CBM). This study is aimed at revealing the effect of liquid nitrogen mass transfer on the temperature variation and pore structure evolution within coal. To achieve this aim, first, temperature measurement tests under the action of liquid nitrogen freezing were conducted on saturated and dried coal samples, respectively. Next, the coal samples were subjected to nuclear magnetic resonance and computer tomography tests before and after liquid nitrogen cold soaking to further explore the mechanism of coal temperature variation from a microscopic perspective. The results show that the action of liquid nitrogen mass transfer can accelerate coal temperature variation through coal pore structure and pore water phase change. The thermal stress and frost heave force generated by liquid nitrogen cold soaking exceed the tensile strength of the coal sample, which directly causes crack initiation, expansion, and connection. The mass transfer of liquid nitrogen has a significant promoting effect on pore development. This study provides the technical support necessary for the efficient exploitation of CBM resources and the improvement of CBM extraction rate.

1. INTRODUCTION

Coalbed methane (CBM), an associated product in the process of coal formation, is not only an important factor affecting the safe and efficient production in mines but also a kind of high-quality clean energy. Several countries that possess abundant CBM reserves, including China, regard CBM as an important energy source.1,2 However, the compactness of coal reservoirs considerably restricts the exploitation of CBM. Hydraulic measures such as hydraulic slotting, hydraulic fracturing, hydraulic punching, and high-pressure water jet slitting are commonly adopted to enhance the permeability of coal reservoirs.3−5 Nevertheless, these measures require vast water resources and can hardly be applied in water-scarce areas. Liquid nitrogen cold soaking (LNCS) fracturing is an anhydrous seepage enhancement measure that can save water resources without inducing the water lock effect or environmental pollution. It has been applied to CBM extraction.6−8 Since liquid nitrogen is a kind of ultralow temperature medium, its contact with coal rock will directly change the temperature field distribution within coal rock, thus causing internal damage to coal rock and changing the permeability of it. Scholars have conducted extensive research on the temperature field evolution of coal rock under low-temperature freezing conditions. Park et al.9 experimentally studied factors influencing the thermophysical parameters of rock and their relationship with the temperature field. The results showed that as temperature decreased from 40 °C to −160 °C, the specific heat and thermal expansion coefficient of rock fell while the thermal conductivity did not change much. Watanabe et al.10 found that the migration of unfrozen water in porous media and the concentration of solutes in the water under freezing conditions directly affected temperature propagation. The research of Mottaghy and Rath considered the effect of latent heat of phase change on the temperature field.11 To reveal the heat transfer law of sandstone during freeze−thaw, Shen et al. and McDermott et al. monitored the temperature changes at different positions inside sandstone samples during freeze−thaw by embedding temperature sensors in the samples.12,13 Lunardini14 summarized the heat transfer law during freeze−thaw and established an important basic equation for the temperature field, which took the effects of heat flow and surface convection into account. Meanwhile, considering the effectiveness of heat conduction, Lunardini further divided the freeze−thaw process of rock and soil media into three regions. His study made a significant contribution to the research on temperature variation in frozen−thawed geotechnical soils.

Received: May 4, 2021
Accepted: July 16, 2021
Published: July 26, 2021
Tan et al.\textsuperscript{15} conducted numerical simulations and field measurements on the temperature field during freeze and thaw of rock and soil media, concluding that the latent heat of phase change could slow down the formation of ice and alter the temperature field of porous media. Guo and Liu\textsuperscript{16} arranged temperature sensors inside rock samples and investigated the temperature equilibrium law in the freeze−thaw environment through a combination of experiments and numerical analysis. In light of the heat transfer theory, Vitel et al.\textsuperscript{17} numerically simulated the effect of frozen pipes on the surrounding rock temperature. Tan et al. and Taron et al. divided the freezing process into the frozen region and the unfrozen region based on the location of the frozen peak surface.\textsuperscript{18,19} Additionally, they analyzed the temperature field by means of variable substitution. The above studies were conducive to disclosing the heat transfer law of coal rocks under low-temperature conditions. However, their analyses did not involve the law of temperature variation within coal rock and the effect of mass transfer of a low-temperature medium on temperature variation.

Coal rock fracturing by LNCS is an innovative method to enhance the permeability. Relevant scholars have conducted in-depth investigations into the pore development of coal rock. McDaniels et al.\textsuperscript{20} pointed out that the violent temperature shock effect formed by injecting liquid nitrogen into the CBM reservoir caused physical changes in the fracture wall. Such an effect could not only prevent hydraulic fractures and thermally induced fractures from completely closing under the action of closure stress but also lead to the generation of thermally induced microfractures orthogonal to the hydraulic fractures. Cha et al.\textsuperscript{21} found that the temperature gradient generated by the action of liquid nitrogen could fracture the rock and alter the rock structure and that the low temperature of liquid nitrogen caused the rock skeleton to contract and rupture violently, resulting in a large number of microcracks. By performing scanning electron microscopy and nuclear magnetic resonance (NMR) tests, Cai et al. found that after liquid nitrogen freezing, the pore structure of rock mainly changed in three aspects, namely, reduction of pore volume, expansion of micropores, and growth of pore range.\textsuperscript{22−24} Wei et al.\textsuperscript{25} conducted an NMR test on coal before and after the liquid nitrogen freeze−thaw action. The results suggested that the pore diameter and the porosity both grew with the increase of water saturation degree, which proved the importance of pore water in coal. In addition, when the water saturation degree was higher, the coal sample was damaged more severely after the liquid nitrogen freeze−thaw action. Qin et al.\textsuperscript{26,27} obtained that the liquid nitrogen freeze−thaw action strengthened the growth of pore size and the formation of new pores and fractures, and that the rate of pore size growth was positively correlated with the time of liquid nitrogen freezing. The above studies indicate that liquid nitrogen freezing can promote coal pore development, but the influence of mass transfer of liquid nitrogen on coal pore development is rarely reported.

In summary, research on the temperature field of coal under the action of low temperatures is mostly focused on heat conduction and numerical simulation. However, there is a lack of discussion on the influence of mass transfer of liquid nitrogen on the temperature variation and pore structure within coal, which is the research purpose of this paper. Based on NMR and computer tomography (CT) tests, this paper presents an in-depth explanation to the temperature variation within coal from the perspective of a microscopic pore structure. The research results are expected to provide reference for the in-depth study on the temperature variation and pore structure evolution within coal rock subjected to LNCS.

2. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

2.1. Sample Preparation. The raw coal block in the test was anthracite taken from the No. II-1 coal seam in Jiulishan Coal Mine, Jiaozuo, China. Eight standard cylindrical coal samples with a size of $\Phi 50 \text{ mm} \times 100 \text{ mm}$ (error range ± 2 mm) were drilled from within the raw coal block in the laboratory, and both ends of each sample were polished smooth (error range ± 0.05 mm). To ensure test accuracy, all the samples were taken from the same large raw coal block under identical experimental conditions. In order to realize real-time measurement of the internal temperature of each sample by the temperature sensor, a borehole with a diameter of about 5 mm and depth of 50 ± 1 mm was drilled at the center of one end. The resolution of industrial CT scanning was related to the size of sample, and the smaller the size, the more accurate the CT scanning. Hence, four cylindrical coal samples with a size of $\Phi 25 \text{ mm} \times 25 \text{ mm}$ were prepared (Figure 1).

![Figure 1. Test coal samples. (a) Temperature measurement and NMR test samples; (b) CT scanning test samples.](image)

2.2. Experimental System. (1) The temperature measurement experiment on coal under LNCS was performed with the aid of a self-developed real-time temperature measurement system, which comprised a self-pressurized liquid nitrogen tank, a liquid nitrogen insulation container, a coal sample clamping device, a temperature sensor, and a real-time temperature acquisition device (Figure 2). The temperature measuring range and accuracy of the system were $-200$ to $200 \degree C$ and $\pm 0.1 \degree C$, respectively. The experiment adopted 99.99% pure liquid nitrogen whose boiling point was $-196 \degree C$ under 0.1 MPa pressure. Under such conditions, the system could achieve the goal of temperature measurement.

(2) The NMR test system adopted a MesoMR3-060H-1 low-field NMR analyzer produced by Suzhou Numag Electronic Technology Co., Ltd., China. The system could be used to conduct experiments on samples smaller than 60 mm in diameter (Figure 3). The main parameters involved in the NMR tests are as follows: the main magnetic field intensity was 0.24 T, the resonance frequency was 11.79 Hz, the magnet uniformity was 20.0 ppm, the pulse frequency was 1−60 MHz, the probe inner diameter was 38.0 mm, the maximum uniaxial gradient strength was 0.1 T/m, and the magnet temperature in the control box was $32 \pm 0.01 \degree C$.

(3) The micro-CT scanning equipment used in this experiment (Figure 4) was from the State Key Laboratory of Gas Geology and Gas Control of Henan Polytechnic
The formula for the coal sample saturation water content is as follows:

\[ \rho \times (w - m_0) = \rho \times \frac{S}{V} = F_2 \times \frac{\rho}{r} \]

where \( \rho \) is the shape parameter; \( r \) is the pore radius.

The relationship between \( T_2 \) and pore size can be expressed as \( 30,31 \)

\[ r = T_2F_2\rho \]

The transverse relaxation characteristics of pores and fractures in the coal rock can be probed into through the distribution curve of the transverse relaxation time \( T_2 \) in the NMR test. \( 28,29 \)

The NMR technology, which is based on the hydrogen nucleus spin as well as the resonance relaxation phenomenon between the hydrogen nuclei and the external magnetic field when a superimposed magnetic field is applied, can be used to study the relaxation characteristics of the hydrogen-containing nuclear fluid in coal pores. The distribution characteristics of pores and fractures in the coal rock can be probed into through the distribution curve of the transverse relaxation time \( T_2 \) in the NMR test. \( 28,29 \)

The distribution curve of dried and saturated coal samples over LNCS was obtained by real-time temperature measurement under LNCS, an experiment that was performed on the temperature variation within coal under LNCS and further explored the mechanism of temperature variation within both kinds of coal samples exhibits a threestage distribution. In Stage I, the rate of temperature variation was approximately linear at a stable rate approximately linear, while they are only about 180 and 120 min under the condition of mass transfer, respectively. The former is about three times longer than the latter. Moreover, under the condition of mass transfer, the temperature variation within both kinds of coal samples exhibits a three-stage distribution. In Stage I, the rate of temperature variation was approximately linear at a stable rate approximately linear.

In order to disclose the effect of liquid nitrogen mass transfer on the temperature variation of coal and further explore the mechanism of temperature variation within coal under LNCS, an experiment was performed on the temperature variation within coal under LNCS. Based on the experimental results, the temperature change curves of dried and saturated coal samples over LNCS time under the same experimental conditions were obtained.

As can be seen from Figure 6, the times required for the temperature within the dried and saturated coal samples to reach equilibrium are about 500 and 400 min under the condition of no mass transfer, while they are only about 180 and 120 min under the condition of mass transfer, respectively. The former is about three times longer than the latter. Moreover, under the condition of mass transfer, the temperature variation within both kinds of coal samples exhibits a three-stage distribution. In Stage I, the rate of temperature change gradually increases from zero. In Stage II, the temperature changes approximately linearly at a stable rate approximately linear.
with the passage of time (the section marked by dashed lines in Figures 6 and 7). In Stage III, the rate of temperature change gradually decreases until the temperature remains constant.

As shown in Figures 6a and 7a, the temperature change curves of the dried coal samples D3 and D4 show a sharp change in the area marked by the arrow. The main reason is that liquid nitrogen and low-temperature gas nitrogen produced by liquid nitrogen evaporation under the condition of mass transfer reaches the temperature measuring point within the coal sample, which accelerates temperature reduction. It can be seen that the above immersion effect under the condition of mass transfer can accelerate temperature variation within the coal sample, thus shortening the time required for the coal temperature to reach equilibrium. The following analysis is made from the perspective of pore development. When the coal sample comes into contact with liquid nitrogen, its temperature at the contact surface plummets to produce a large temperature gradient. Affected by the low temperature, part of the grains at the contact surface experiences volume contraction. Thus, the local thermal stress formed between these grains and the internal grains becomes

Table 1. Details of Coal Sample Grouping Number

| sample | test                                    | height (mm) | saturated water content (wt %) | TRD (g·cm⁻³) | ARD (g·cm⁻³) | Mₐd | Aₐd | Vₐdaf |
|--------|-----------------------------------------|-------------|-------------------------------|--------------|--------------|------|-----|-------|
| D₁     | temperature measurement and NMR test    | 100.00      | 8.79                          | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| D₂     |                                         | 99.90       | 8.75                          | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| D₃     |                                         | 100.37      | 9.06                          | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| D₄     |                                         | 100.11      | 8.70                          | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| S₁     |                                         | 100.20      | 7.96                          | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| S₂     |                                         | 100.57      | 9.42                          | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| S₃     |                                         | 100.43      | 8.56                          | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| S₄     |                                         | 100.61      | 8.84                          | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| D₅     | micro-CT scanning test                  | 25.20       | /                             | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| D₆     |                                         | 24.86       | /                             | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| S₅     |                                         | 25.34       | /                             | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |
| S₆     |                                         | 25.46       | /                             | 1.49         | 1.43         | 0.44 | 8.13| 10.58 |

Note: D represents dry; S represents saturated water; mass transfer of liquid nitrogen: D₃, D₄, S₃, S₄, D₆, S₆; no mass transfer of liquid nitrogen: D₁, D₂, S₁, S₂, D₅, S₅; TRD represents true density; ARD represents apparent density; Mₐd represents moisture, air-drying base; Aₐd represents ash yield, air-drying base; Vₐdaf represents volatile matter dry ash-free basis.

Figure 5. Experimental flowchart.

Figure 6. Temperature change curves of measuring points within coal samples: (a) dried and (b) saturated.
rather large. When the local thermal stress exceeds the limit of coal strength, new pores come into being and primary pores expand and connect. For the saturated coal sample, when it is exposed to liquid nitrogen, the pore water within it will freeze quickly. The water-ice phase transformation will result in about 9% volume expansion, which can generate up to 207 MPa frost heave force theoretically.\textsuperscript{32} When the frost heave force exceeds the limit of coal strength, new pores are generated and primary pores expand and connect as well. These pores and fractures then become channels for liquid nitrogen and low-temperature gas nitrogen to infiltrate into the interior of the coal sample, thus accelerating temperature variation there.

As can be observed from Figure 7, under the conditions of both mass transfer and no mass transfer, the time required for the temperature field within the saturated coal sample to reach equilibrium is shorter than that of the dried one. Hence, it can be concluded that moisture plays a role in promoting temperature variation during coal freezing. The following analysis is made from the perspective of ice-water phase transformation. After the coal sample comes into contact with the cold source, its temperature drop will cause the internal pore water to freeze. Due to the difference in the thermal conductivities of ice and water, the temperature variation within coal is affected. By summarizing previous experiments, Hobbs drew the following conclusion concerning the thermal conductivity of ice in 1958. The thermal conductivity of ice at 0 °C is 2.2 W/m °C, which is about 4 times that of liquid water at the same temperature ($\lambda_{\text{water}} = 0.58$ W/m °C), and as the temperature decreases, the thermal conductivity of ice will continue to increase.\textsuperscript{33} Since the temperature of liquid nitrogen is extremely low (about −196 °C), when the pore water phase within the coal sample turns into ice, its thermal conductivity will continue to increase, thereby accelerating temperature variation within the coal sample. Moreover, the pore water phase within the coal sample becomes ice whose volume expands to fill the pores. As a result, the voids are relatively reduced, and the ice inside the pores is directly exposed to the coal matrix for heat conduction, further accelerating temperature variation within the coal sample.

As shown in Figure 7a, no sharp change occurs in the curves of temperature change rates of saturated coal samples, due to the frozen zone formed by the contact between coal and the cold source. The transformation of the pore water phase into ice and the resultant filling effect lowers coal permeability, so that liquid nitrogen and low-temperature gas nitrogen generated by liquid nitrogen evaporation can hardly infiltrate into the frozen zone. Therefore, when the coal sample is in contact with the cold source, it gradually freezes as the temperature propagates and can be divided into three zones,\textsuperscript{34,35} i.e., frozen zone, freezing zone, and unfrozen zone (Figure 8).

![Figure 7. Temperature change rate curves of measuring points within coal samples: (a) mass transfer and (b) no mass transfer.](image)

![Figure 8. Diagram of the three zones.](image)

### 3.2. Effect of Liquid Nitrogen Mass Transfer on Pore Structure Evolution

Coal belongs to a dual porosity medium whose matrix contains a developed cleat system and meso/micropores.\textsuperscript{36,37} When the coal sample is subjected to LNCS, the difference in heat conduction coefficients of different minerals in it will bring about uneven thermal stress. Meanwhile, the ice-water phase transformation of saturated coal will produce frost heave force. The above two effects will both promote the generation of new pores and the expansion and connection of primary pores and fractures. The analysis on coal temperature variation experimental results has revealed that the evolution of pore structure can affect the rate of temperature variation within the coal sample. In the hope of more intuitively exploring the influence of liquid nitrogen mass transfer on the evolution of coal pore structure, the pore structures of the coal samples before and after temperature variation experiments were characterized through NMR tests in this study. The test results are illustrated in Figure 9 and Table 2.
Figure 9. $T_1$ Distributions obtained by NMR tests before and after temperature measurement experiments: (a) sample D1; (b) sample D2; (c) sample D3; (d) sample D4; (e) sample S1; (f) sample S2; (g) sample S3; (h) sample S4.
According to the study of Zheng et al., the transverse surface relaxation strength of anthracite (high-rank coal) can be taken as 1.6 μm/s. From eq 2, the first, second, and third peaks in the T2 spectrum correspond to pores with radii of below 0.1 μm, 0.1–1 μm, and over 1 μm, respectively. According to the previous studies on the classification of coal pore size, the first peak in Figure 8 corresponds to micropores, which belong to adsorption pores. The second peak corresponds to mesopores, and the third peak corresponds to macropores and fractures. The pores corresponding to the second and third peaks belong to seepage pores. Clearly, pores with sizes below 0.1 μm are dominant in the coal samples because the area of the first peak accounts for more than 90% of the total peak area, which indicates that micropores are well developed in the coal samples.

Figure 9 shows the T2 spectra from the NMR test of the coal samples. The NMR results show that the first peak in the T2 spectrum has the largest area followed by the second peak, and the third peak has the smallest area. This demonstrates that micropores in the coal sample are well developed, while mesopores, macropores, and fractures are relatively poorly developed. The start–stop relaxation time interval of each peak becomes wider, and the amplitude of the T2 curve increases after the coal undergoes LNCS, indicating that a greater number of pores with different sizes appear after the coal sample undergoes LNCS. As displayed in Table 2, after the dried coal samples D1, D2, D3, and D4 are subjected to LNCS, their T2 spectral areas of adsorption pores increase by 775.48, 691.34, 1130.31, and 881.44, with the growth rates being 15.26, 15.89, 25.60, and 26.41%, respectively. The T2 spectral areas of seepage pores grow by 24.38, 24.88, 26.64, and 28.65, with the growth rates being 11.45, 11.41, 36.01, and 25.90%, respectively. After the saturated coal samples S1, S2, S3, and S4 are subjected to LNCS, their T2 spectral areas of adsorption pores surge by 2510.21, 2249.89, 2666.54, and 2785.59, with the growth rates being 51.42, 49.11, 51.66, and 63.53%, respectively. The T2 spectral areas of seepage pores jump by 274.67, 304.11, 391.20, and 405.89, with the growth rates being 126.92, 125.60, 186.47, and 191.68%, respectively. The pore size increases and new pores and cracks are produced in the coal samples after LNCS. Moreover, the condition of mass transfer induces greater increases in peak amplitude and peak area than the condition of no mass transfer, suggesting that mass transfer of liquid nitrogen can promote pore extension and microcrack growth.

The coal samples D5, D6, S5, and S6 experience LNCS under the condition of mass transfer, while the coal samples D7, D8, S7, and S8 experience LNCS under the condition of no mass transfer. Through a comparison between the dried and saturated coal samples under the same experimental conditions, it can be concluded that the pores in coal develop more vigorously under the condition of mass transfer. For the dried coal samples D1 and D2, the start value of the first peak relaxation time shifts leftward more significantly and the T2 spectral area corresponding to micropores and mesopores increases more notably, compared with those of the dried coal samples D3 and D4. The reason for this phenomenon is that the mass transfer of liquid nitrogen leads to a greater temperature gradient inside the coal sample. The coal undergoes complex geomechanics and thermodynamic and chemical processes, which in turn creates complex internal heterogeneity structural features. The coal with a complex internal structure exhibits non-uniformity and anisotropy after being subjected to LNCS. Because of differences in expansion and contraction of the components in the coal under the temperature impact, the mutual restraint cannot be deformed freely, and thermal stress is generated between the mineral crystal grains. The expansion of solid particles and the thermal cracking of the solid skeleton jointly cause the constant change of pore space within the coal. As a result, new pores are generated, expanded, and bifurcated to form a new pore network.

### 3.3. Analysis on Micro-CT Scanning Test Results

Although the NMR test can reflect the promotion of coal pore structure variation by LNCS, it fails to characterize the expansion and connection of the internal pore structure spatially. CT technology can be used to observe the spatial distribution of the internal microstructure of a coal sample before and after LNCS on a mesoscale. In this section, the promotion of internal pore microstructures of coal samples by LNCS is investigated based on the results of micro-CT scanning tests before and after LNCS.

Figure 10 shows the CT results of coal samples before and after LNCS, in which coal samples D3 and S3 are treated under no mass transfer, and coal samples D6 and S6 are treated under mass transfer. From a 3D perspective, Figure 10 clearly shows the structural characteristics of internal microcracks in coal samples before and after LNCS. The crack volumes of coal samples D5, D6, S5, and S6 before liquid nitrogen treatment were 68.48, 22.71, 48.03, and 25.95 mm³, respectively. After liquid nitrogen treatment, the crack volumes increase to 142.60, 61.63, 175.32, and 108.52 mm³ by 108.24, 171.38, 265.02, and 318.19%, respectively. Compared with the dried coal samples, the saturated coal samples experience a more evident increase in crack volume. While new pores are generated, primary cracks become connected to form a crack network (Figure 10c,d). In contrast, the dried coal samples are...
mainly dominated by the generation of new pores. Under the condition of mass transfer, the increase in the crack volume is even more obvious, and the number of new pores grows more vigorously (Figure 10b,d). This result agrees with the results of the NMR test.

Figure 10. 3D views of coal samples: (a) sample D₅ (no mass transfer); (b) sample D₆ (no mass transfer); (c) sample S₅ (mass transfer); (d) sample S₆ (mass transfer).

To further study crack evolution under the influence of LNCS, the micro-CT scanning images of transverse and longitudinal sections of the coal samples and the reconstructed 3D crack model are compared. Considering the limited space, this paper only shows the micro-CT scanning test results of the S₆ coal sample before and after LNCS and expounds the crack characteristics (Figure 11). As can be observed from the images in Figure 11, the cracks extend along the primary main cracks after LNCS, thus forming a crack network spatially. The thermal stress caused by temperature gradient and the frost heaving force caused by ice-water phase transformation are greater than the tensile strength of the coal sample, so that the primary cracks expand and new cracks are generated. When the cracks grow to a certain extent, they become connected to form a crack network, which significantly enhanced the permeability of the coal sample.

4. CONCLUSIONS

In this paper, the effect of liquid nitrogen mass transfer on the temperature variation within coal was studied with the aid of a real-time temperature measurement system. Furthermore, the pore structures of the coal samples before and after temperature variation experiments were characterized through NMR and micro-CT scanning tests. In this way, the influence mechanism of pore structure change on the temperature variation within coal was explained from a microscopic perspective. The following conclusions were drawn.

(1) Under the same experimental conditions, the mass transfer of liquid nitrogen drastically shortens the time required for the temperature within coal to reach equilibrium during the freezing process. Specifically, it is shortened to about one-third of the time required under the condition of no mass transfer. In other words, the mass transfer can accelerate temperature variation within coal.

(2) Compared with dried coal, the temperature varies faster within saturated coal during LNCS. The pore water phase within saturated coal turns into ice whose thermal conductivity is much larger than that of water, and the lower the temperature, the larger the thermal conductivity of ice. In addition, the volume expansion resulting from the transformation of the pore water phase into ice can also increase the contact area between ice and the coal matrix. Thus, the water-ice phase transformation accelerates temperature variation within coal.

Figure 11. Micro-CT scanning images of the S₆ coal sample (a) Before LNCS and (b) after LNCS.
(3) Under the action of liquid nitrogen mass transfer, the $T_2$ spectral areas of adsorption pores and seepage pores of dried and saturated coal both increase significantly, and that of seepage pores surges more notably. This indicates that the mass transfer of liquid nitrogen has a significant promoting effect on pore development.

(4) The results of NMR and micro-CT scanning tests show that both dried and saturated coal samples experience pore structure variations after the treatment of LNCS, but the pore expansion and connection is more obvious for the saturated coal samples. That is, the transformation of pore water phase into ice plays a superior role in promoting the pore development of coal, compared with the thermal stress generated by the temperature gradient.

(5) The results of NMR and micro-CT scanning tests show that LNCS results in the volume expansion of adsorption pores and seepage pores. Accordingly, new pores are formed and macropores expand and connect into a crack network, which considerably promotes the channel of gas migration and enhance the permeability of coal.

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#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors would like to thank the financial support from the National Natural Science Foundation of China (51874125, 51974109, and 51704099), the project of youth talent promotion in Henan Province (2020HYTP020), the Outstanding Youth Fund in Henan Polytechnic University in 2020 (J2020-4), and the Young Key Teachers in Henan Polytechnic University (2019XQG-10).

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