Study on the Evolution of Pore Structure of Anthracite Coal under Liquid-Nitrogen Freeze–Thaw Cycles

Junwei Yuan, Yao Wang,* and Xiangjun Chen

ABSTRACT: To analyze the evolution characteristics of the internal pore structure of anthracite by liquid-nitrogen (LN$_2$) freeze–thaw cycles, nuclear magnetic resonance was used to test the water-saturated samples, which were frozen–thawed with LN$_2$ for 0–9 exposure. The pore size distribution, development degree, and variation characteristics of different pores were examined from the changes of parameters related to $T_2$ spectra, which increased the macropore frequency: First, LN$_2$ freeze–thaw cycles are beneficial to the development of cracks and have the greatest promoting effect on macropores. Second, the crack development rate of coal samples decreased with the increase of the number of freeze–thaw cycles. The crack development rate was the fastest in the first freeze–thaw cycle, and the crack development did not increase significantly after the third freeze–thaw cycle. Third, the pore structure of anthracite is under the influences of thermal stress and frost heaving force (the force caused by the expansion of water as it freezes). Therefore, it can be determined that three times of LN$_2$ freeze–thaw cycles has the best effect in the LN$_2$ injection to increase coal permeability and recover coalbed methane. The results provide theoretical support for the field application of coal freezing cracking and antireflection promotion pumping.

1. INTRODUCTION

Coal bed storage features are generally characterized by “high reserves and low permeability” in China. The coal bed gas extraction is difficult, and the extraction rate is less than 30%, which leads to coal and gas outburst accidents causing economic losses and negative social impact.$^1$ A number of technical measures improve the coal seam permeability and promote the gas drainage. At present, the methods of enhanced gas extraction mainly include mining protective layers, hydraulic fracturing, hydraulic punching, deep hole presplitting blasting, etc. Mining a protective layer is the simplest, most effective, and most economical measure for regional outburst prevention and gas control in low permeability coal seam. However it is only applicable to coal seam group mining and not suitable for the single coal seam.$^{2,3}$ Hydraulic fracturing technology can significantly increase the permeability of coal seam, but the expansion of fracture is not controllable, and because of the complexity of the equipment, it is difficult to seal the hole, and the fracturing process has a certain risk.$^4,5$ The hydraulic punching technology is suitable for coal seams with flowing capacity.$^5,6$ In the process of punching, phenomena such as gushing hole and frequent overrun of gas will occur and present safety risks. Therefore, the existing measures for increasing permeability and promoting drainage of coal seams are limited by the storage of coal seams and other conditions, and there are still many shortcomings in economic and technical aspects. Therefore, it is urgent to find a new measure for increasing permeability and causing fracturing of coal seams to meet the requirements of enhancing gas extraction and ensuring the safe production of mines.

Inspired by the rock and soil mass failure caused by low-temperature freezing in high and cold regions, scholars have conducted a large number of studies on fractured rock mass cause by freeze–thaw cycles and then applied the research results to the field of oil and gas exploitation and gradually introduced them into the field of mine gas disaster prevention. Qin$^8$ and Yan$^9$ studied the distribution characteristics of coal pores caused by LN$_2$ freeze–thaw and found that LN$_2$ freeze–thaw was conducive to the enhancement of pore connectivity within all pore size ranges, the pore density generally increased, the distribution characteristics of coal pores became more complex, and the permeability of coal was effectively enhanced. Zhang$^{10,11}$ and Yuan$^{12}$ compared the pore development of coal samples of different ranks with LN$_2$ freezing and found that it...
significantly promoted the development of fractures in both high- and low-rank coal bodies, with the development of fractures in low-rank coal bodies being more extensive. Li13,14 and Lan15 studied the structural evolution of the damage zone of coal samples under the action of LN2. They found that when the action of LN2 lasted for 1 exposure, the porosity of coal samples increased relatively significantly and the damage effect was obvious. After multiple applications, the development, expansion, and penetration of micropores resulted in macroscopic cracks and damage of coal. Zhai16,17 and Sun18 used nuclear magnetic resonance (NMR) and strain monitoring technology to study the structure changes of coal and rock during LN2 freezing and found structural degradation of coal, and with the increase of the number of freeze—thaw cycles, the saturated mass and porosity of coal and rock increased. The use of LN2 freeze—thaw coal has three effects of cracking coal, increasing permeability and promoting pumping, and reducing gas pressure.

The pore size distribution in the coal body has great influence on gas energy storage, strength, and permeability of the coal body and also affects the risk of gas outburst in the coal body. However, at present, the research on the modification of coal pore size structure after LN2 freeze—thaw cycles is not thorough enough, which affects the field popularization and application of this technology. In this paper, taking anthracite as the experimental object, NMR technology was used to study the pore structure modification characteristics of coal samples in the process of LN2 freeze—thaw cycle testing with different times, so as to provide theoretical support for the field application of the LN2 freeze-crack coal body and antireflection and promoting pumping technology.

2. THE PRINCIPLE OF NMR

The NMR technique has been widely used in the nondestructive determination of the microscopic pore structure of materials in many fields, such as geotechnical, materials, and mining. The coal belongs to multipore structure. In the low-intensity magnetic field, the $T_2$ spectral curve of the coal sample can be obtained by measuring the hydrogen atom nuclear magnetic signal in the liquid water in the pores, which can accurately judge the development of the pore fracture of the coal sample.

The relaxation time $T_2$ of water molecules in coal pores is proportional to the pore radius; that is, the larger the pore is, the longer the relaxation time is. On the contrary, the smaller the pore is, the shorter the relaxation time is. Only pores with the relaxation time longer than 0.01 ms are discussed in this paper because what we study is the change of permeability of coal before and after freezing and thawing.

There are three relaxation mechanisms for the fluids in the pores of coal samples, namely, free relaxation, surface relaxation, and diffusion relaxation. The relaxation time $T_{2f}$ of pore fluid can be expressed as eq 1, where $T_{2s}$ is the transverse free relaxation time; $T_{2s}$ is the transverse surface relaxation time; and $T_{2d}$ is the transverse diffusion relaxation time.

$$\frac{1}{T_2} = \frac{1}{T_{2f}} + \frac{1}{T_{2s}} + \frac{1}{T_{2d}}$$

Due to the nonmagnetism of the coal body and the nonviscosity of fluids between pores and fractures, the transverse free relaxation time can usually be ignored. Moreover, the magnetic field is uniform, the magnetic field gradient is small, and the transverse diffusion relaxation time can also be ignored.

Therefore, the time $T_2$ of the saturated water coal sample can be simplified as the surface relaxation between pore water and the coal body, as shown in eq 2, where $T_2$ is the surface relaxation time, $\rho$ is the transverse surface relaxation intensity, and $S/V$ is the pore surface area.

$$\frac{1}{T_2} = \rho \left( \frac{S}{V} \right)$$

It can be seen from eq 2 that the surface relaxation time of $T_2$ can reflect the size of the aperture. The longer the transverse relaxation time is, the larger the corresponding aperture is. Cai20 concluded that the $T_2$ relaxation time less than 10 ms represents small pores in the sample, between 10 and 100 ms represents medium pores, and larger than 100 ms represents large pores and cracks. The higher the amplitude of $T_2$ spectra is, the more pores there are.

3. EXPERIMENTAL SECTION

3.1. Coal Sample Preparation. The experimental coal sample is anthracite, which is taken from the open-cut of the 1606 working face of Guhanshan Coal Mine in Jiao Zhou. In the laboratory, it is cut into a Ø25 × 50 mm cylindrical coal core, upper and lower end face smooth, and perpendicular to the axis (Figure 1).

![Figure 1. (a) Raw coal sample and (b) experimental coal pillar. (Photograph courtesy of Yao Wang. Copyright 2021. the figure is free domain).](https://doi.org/10.1021/acsomega.1c06784)

3.2. NMR and LN2 Exposure. The experimental system consists of an NMR experimental system, vacuum water filling device, drying and weighing device, freezing and thawing cycle device, and other parts (Figure 2).

3.2.1. NMR. The low-field NMR experimental system MSEOMR23-060H-I produced by Suzhou Newmai Technology Co., Ltd. was adopted in the NMR experiment. The system was equipped with a coil of Ø25 mm.

3.2.2. Vacuum Water Filling Device. The vacuum water filling device mainly includes a vacuum pump and a water filling device. The vacuum pump model is 2XZ-4. The coal sample is treated with a vacuum water filling device, which is filled with distilled water under the vacuum condition below 10 Pa. The weight of coal samples was measured with a balance every 1 h after vacuum filling for 6 h. When the vacuum is filled with water for 8 h, the weight of the coal sample increases by less than 0.1 g compared with that at 7 h. At this time, the coal sample is considered to have been filled with water.

3.2.3. Drying and Weighing Device. The drying box is a GRX-9053A hot air disinfection box produced by Shanghai YiHeng Technology Co., Ltd. The temperature of the drying box is set at 105 °C. The electronic balance model is ME-T precision balance, its measuring range is 0–220 g, and the accuracy is 0.1 mg.
3.2.4. Freeze–Thaw Cycle Device. The freeze–thaw cycle experiment consists of an LN$_2$ barrel and thawing insulation barrel. The cold source used is LN$_2$. The temperature of LN$_2$ is $-196\,^\circ\text{C}$, and the experimental coal sample is immersed into LN$_2$ for 0.5 h to ensure that the coal sample can be frozen completely. The insulation bucket is made of double-layer stainless steel structure, which ensures that the coal sample is thawed at constant temperature and isolated to prevent moisture loss of the coal sample. Figure 5 shows the LN$_2$ barrel and thawed insulation barrel used in this experiment.

3.3. Experimental Sequence. In order to explore the pore evolution characteristics of anthracite coal under the condition of LN$_2$ freeze–thaw cycles, the experimental scheme of the following process was set:

1. The processed Ø25 × 50 mm anthracite sample is put into a drying oven for continuous drying for more than 48 h. The temperature of the drying oven is 105 °C. After drying, the sample is weighed.
2. The dried coal sample is placed in the vacuum water filling device. Under the condition of less than 10 Pa, the vacuum water filling is done for 24 h to ensure that the coal sample is completely filled with water. When filling the coal sample with vacuum water, the coal pillar shall be put into the beaker with distilled water to ensure that all the coal is covered. The beaker is put into the vacuum cover of the vacuum water filling device, and the switch of the vacuum water filling device is turned on for evacuating.
3. The water-saturated coal sample is taken out, and the outer surface water of coal is dried, and then, the $T_2$ spectrum of the original coal sample without freeze–thaw cycles by NMR is measured.
4. The coal sample after the NMR test is redried, and water is filled according to the requirements in step (2); the coal sample is taken out after full water, and the water on the outer surface is dried;
5. Coal is water-saturated and taken out, and the water on the surface is wiped, and then, it is placed in the freezing hole. The funnel is put in a bucket filled with LN$_2$, frozen for 30 min, taken out, put in the insulation bucket, and thawed naturally at room temperature, and no airflow is provided until it completely returns to room temperature, and a freeze–thaw cycle is completed.
6. The NMR test was carried out on the coal samples restored to room temperature.
7. Steps (4)–(6) are repeated, that is, the cycle of vacuum saturation—LN$_2$ freezing—restoring room temperature—NMR tests. The same coal sample was subjected to 9 freeze–thaw cycles.

4. RESULTS AND DISCUSSION

4.1. Analysis of the $T_2$ Chromatogram of Original Unfreeze–Thaw Coal Samples. The transverse relaxation time $T_2$ can quantitatively represent the relaxation characteristics of water molecules. In this experiment, the coal sample is filled with saturated water, and its internal pores and fractures are considered to be filled with water. The $T_2$ spectra of NMR test results can reflect the distribution of pore and fissure structure of the coal body. The relaxation time is shorter, so the $T_2$ value is smaller.

According to the classification basis of Cai and other scholars, the $T_2$ spectrum of the coal sample is divided into three areas I, II, and III, namely, $T_2 < 10$, $10 < T_2 < 100$, and $T_2 > 100$ ms, respectively, represent micropores, mesopores, macropores, and fractures. The area of the representative area is the number of the corresponding aperture. The higher the amplitude of $T_2$, the larger the area and the larger the number of corresponding apertures. The $T_2$ spectrum of the original coal sample without freezing and thawing is shown in Figure 3. The area of each region of the $T_2$ graph in Figure 3 can be obtained by analyzing and integrating the graph. As is seen from Figure 3, the $T_2$ spectrum of the coal sample shows a bimodal distribution with a total area of 17621.64. The area of the first peak is 17561.87, accounting for 99.661%. The area of the second peak is 59.771, accounting for 0.339%. The first peak is all distributed in region I, and the second peak is distributed in region III, and the second peak is rarely distributed in region II, which indicates that the micropores in...
The $T_2$ spectral analysis of the coal samples in Figures 4 and 5 shows that the number of pores in the coal samples increases continuously after the LN$_2$ freeze–thaw cycle. Therefore, the freeze–thaw cycle can transform the pore structure of the coal body, and the freezing cracking effect is obvious.

According to the analysis of Figures 4 and 5 and Tables 1 and 2, the following can be seen:

4.2.1. Analysis of $T_2$ Spectra of Coal Samples after 0–3 Freeze–Thaw Cycles. The $T_2$ spectrum of the coal sample still shows a bimodal distribution. After three freeze–thaw cycles, the area of $T_2$ spectra increases by 32.09% compared with the original coal sample, and the area of the second peak increases by 18 times, and it is distributed in the II and III regions. This indicates that the number of mesopores, macropores, and cracks of the coal sample increases greatly after three LN$_2$ freeze–thaw cycles.

After three freeze–thaw cycles, the $T_2$ spectra of the coal sample shifted upward to the right, and the maximum relaxation time increased, indicating that the freeze–thaw cycles promoted the initiation, expansion and communication of pores in the coal sample, and the further development of mesopores, macropores, and microcracks, and the number of pores above mesopores increased greatly. By analyzing the growth rate of $T_2$ spectral area of coal samples after 0–3 freeze–thaw cycles, it can be seen that the crack development of coal samples is the fastest in the first freeze–thaw cycle.

4.2.2. Analysis of $T_2$ Spectra of Coal Samples after 4–6 Freeze–Thaw Cycles. After four freeze–thaw cycles, the $T_2$ spectra of the coal sample changed to a three-peak distribution, and the area increase of $T_2$ spectra decreased significantly compared with that of the third freeze–thaw cycle, and the area increases only 2.61% compared with that of the third freeze–thaw cycle, indicating that after three freeze–thaw cycles, with the increase of the number of freeze–thaw cycles, the crack effect caused by freeze–thaw cycles began to weaken.

After three freeze–thaw cycles, the number of internal pores in the coal sample continues to increase for three more freeze–thaw cycles, but the increase gradually decreases. The growth rate of $T_2$ spectral area was 2.61% for the fourth freeze–thaw cycles and 1.83 and 1.64% for the fifth and sixth cycles, respectively. This shows that after four freeze–thaw cycles, with the increase of the number of freeze–thaw cycles, the reformation effect of freezing cracking on the pore structure of the coal body is rapidly weakened.

4.2.3. Analysis of $T_2$ Spectra of Coal Samples after 7–9 Freeze–Thaw Cycles. After 7–9 freeze–thaw cycles, the $T_2$ spectrum of coal samples still maintains a three-peak distribution, and the area growth rate of $T_2$ spectra decreases gradually, indicating that the effect of 7–9 freeze–thaw cycles on improving the pore structure of the coal body is no longer obvious.

After 7–9 cycles of freezing–thawing, the number of pores in coal samples still shows an increasing trend. According to $T_2$ spectral analysis of coal samples, the growth rates of $T_2$ spectral area are 1.59, 1.56, and 1.53%, respectively, after the 7th, 8th, and 9th cycles of freezing–thawing; that is, the development rate of pores in coal samples gradually decreases and tends to be stable.

Figure 6 shows the curve of the increase of $T_2$ spectral area with the number of freeze–thaw cycles after 1–9 LN$_2$ freeze–thaw cycles for coal samples. It can be seen from Figure 6 that, as the number of freeze–thaw cycles increases, the evolution effect of freeze–thaw cycles on the pore structure of coal samples
gradually decreases, and the trend is consistent with that in Figures 4 and 5, as well as Tables 1 and 2. Generally, with the increase of freezing and thawing times, the growth rate of $T_2$ spectral area showed a decreasing trend. After the third freeze-thaw cycle, the area of $T_2$ spectra increased by 32.09% compared with the original coal sample, which enhanced the pore development of the coal body and improved the gas extraction conditions of the coal body effectively. After the fourth freeze-thaw cycle, the growth rate of $T_2$ spectral area is less than 3%, and the growth rate of pore development in the coal sample is very low. Therefore, considering the technical feasibility and economic rationality comprehensively, when the LN2 freezing cracking technology is applied to the coal field, four times of nitrogen injection to freeze anthracite can achieve a better result.

5. ANALYSIS OF THE MECHANISM

From the experiment results, the anthracite after many LN2 freezing and thawing cycle, the pore structure of coal sample change presents the obvious regularity, namely the anthracite coal sample after repeated freezing and thawing cycles, after the internal pore structure of coal is further initiated and propagated, $T_2$ spectral area increased, and the coal sample damage is more serious. In this paper, combining the previous research results and the results of this experiment, the mechanical mechanism of pore expansion in coal samples under freeze-thaw cycles is analyzed from two aspects of thermal stress and frost heave force.

5.1. The Thermal Stress. When the coal sample at room temperature is placed in low-temperature LN2, a temperature field will be generated on the surface and inside of the coal body,
En T in the freezing process of LN₂, which is greater than the fracture toughness of coal, so the pores and cracks in the generated by water-ice phase transformation and volume pores and cracks of the coal body. The frost heaving force the coal skeleton will restrain the water phase in the pores and water phase turns into ice and the volume increases. However, the temperature of coal samples drops to the freezing point, the temperature di range is not an increase significantly.

5.2 Frost Heaving Force. The water exists in an adsorbed state in the pores and cracks of coal samples. When the temperature of coal samples drops to the freezing point, the water phase turns into ice and the volume increases. However, the coal skeleton will restrain the water phase in the pores and cracks to turn into ice and produce frost heaving pressure in the pores and cracks of the coal body. The frost heaving force generated by water-ice phase transformation and volume expansion of saturated fractures is the fundamental driving force of rock fracture initiation and expansion under freezing–thawing cycles and the leading factor inducing damage and failure of rock mass engineering.22

The water frost heaving pressure in cracks is affected by internal and external factors. The internal factors mainly include mechanical properties of the coal matrix, while the external factors include freezing temperature, freezing time, and water content of the coal sample. The lower the freezing temperature is, the greater the temperature gradient is, the faster the freezing rate is, and the greater the frost heaving force is.

In the saturated coal sample, the frost heave force caused by the change of the internal water phase into ice is the main reason for the cracking of coal mass in the LN₂ freeze–thaw cycle. In the ideal state, that is, without considering the elastic deformation of the crack wall and ice, the frost heave force \( P_f \) generated by the water phase in the coal body turning into ice can be expressed as eq 4.12 In the equation, \( E \) and \( \nu \) are the elastic modulus and Poisson’s ratio of ice, \( n \) is the porosity, \( \beta \) is the expansion coefficient of the water phase into ice, \( \Delta T \) is the temperature difference, and \( \alpha \) is the thermal volume expansion coefficient.

\[
P_f = \frac{E[\beta n \Delta T - T\alpha(1-\nu)]}{3(1-2\nu)}
\]  

The porosity of the anthracite sample is 5.14%, the elastic modulus of ice is 600 MPa, Poisson’s ratio is 0.3, and the expansion coefficient is 9%. Substituting into eq 4, the frost heaving force of coal samples is 2.012 MPa, respectively, which exceeds the tensile strength of anthracite by 0.71 MPa, indicating that the freezing of LN₂ will cause damage to coal.

6. CONCLUSIONS

Based on the above research, the following three conclusions can be drawn:

1. The freeze–thaw cycle of anthracite with LN₂ is helpful to promote the development of pores and fissures in the coal body and increase both the number of pores in the coal body and the fissure scale effectively. By analyzing the growth trends of each peak area, the LN₂ freezing has the most obvious promotion effect on the development of macropores, and the least promotion effect on the development of micropores. After one freeze–thaw cycle, the pores of the coal body develop the fastest. With the increase of the number of freeze–thaw cycles, the reformation effect of freeze-crack on the pores of the coal body shows a decreasing trend. This is consistent with the research results of other scholars.

2. After the third time of LN₂ freezing, the cracking effect did not increase significantly. During the third freeze–thaw cycles, the absolute growth rate of \( T_2 \) spectral area of the sample reached 32.09%, which effectively enhanced the development degree of fissure between coal bodies, and effectively improved the gas extraction conditions of coal bodies, and then ensured the smooth development of gas extraction work. Therefore, in the actual production, the more number of LN₂ freeze–thaw cycles is not the better for coal seam. Considering the technical feasibility and economic rationality, the number of freeze–thaw cycles should not exceed 3 when the LN₂ freeze-crack technology is applied in the coal mine site.

3. Under the freezing action of LN₂, the thermal strength factor of the experimental coal sample is larger than the fracture toughness of the coal body, so the thermal stress is conducive to

![Figure 6. Area growth rate curve of \( T_2 \) spectra of the coal sample.](image-url)

![Figure 7. Schematic diagram of coal internal crack.](image-url)
the pore structure development of the coal sample. In the frozen state, the water phase in the saturated coal sample changes into ice, and the frost heaving force is generated in the pores and cracks of the coal body, and the frost heaving force is greater than the tensile strength of the coal body, which is conducive to the expansion of the coal body cracks.

In the field practice, the damage of low-temperature cracking technology to coal includes in situ stress, confining pressure, gas and other factors. Due to the limitations of experimental conditions, there is no constraint on the coal sample in the experimental process, and the influence of coal gas on the damage of coal in the freezing-thawing cycle is not considered. These factors will be taken into account in the further study.

**AUTHOR INFORMATION**

**Corresponding Author**

Yao Wang — School of Safety Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China; orcid.org/0000-0001-7247-4019; Email: 1446732686@qq.com

**Authors**

Junwei Yuan — School of Safety Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China; MOE Engineering Research Center of Coal Mine Disaster Prevention and Emergency Rescue, Jiaozuo 454000, China; Collaborative Innovation Center of Coal Work Safety and Clean High Efficiency Utilization, Jiaozuo 454000, China

Xiangjun Chen — School of Safety Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China; MOE Engineering Research Center of Coal Mine Disaster Prevention and Emergency Rescue, Jiaozuo 454000, China; Collaborative Innovation Center of Coal Work Safety and Clean High Efficiency Utilization, Jiaozuo 454000, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06784

**Notes**

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