Physical Simulation of Temperature and Pressure Evolvement in Coal by Different Refrigeration Modes for Freezing Coring

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ABSTRACT: Reduction of gas desorption capacity by cooling coal samples seems a feasible way to improve the accuracy of gas in place estimation. To find an efficient refrigeration mode for the freezing coring technology, the freezing tests for coal containing gas (at 0, 1.09, and 2.15 MPa) are separately conducted based on the precalculation of dry ice dose. The evolvement of coal temperature and gas pressure shows that under the catalysis of ethanol, the average cooling rate of coal gradually accelerates with the increased amount of ethanol (from 0 to 600 mL) in the early stage. Additionally when charging gas into the coal canister, the cooling rate of coal at each subzero temperature accelerates with the increased adsorption pressure of gas, and the low temperature preservation time (<0 °C) of coal is also prolonged. There is a good linear relationship between gas pressure and coal temperature, which indicates that the CH₄ adsorption and desorption in coal are basically reversible; but the desorption hysteresis is extensively observed, associated with the occurrence of numerous ink-bottle type micropores.

1. INTRODUCTION

As a substitute for conventional fossil fuels in electricity generation, coalbed gas (CBG) seems a promising solution for the energy crisis.¹ The estimated world CBG resources buried above 2000 m are around 240 Tm³ and China has 36.8 Tm³, ranking the third largest in the world after Russia and Canada.²,³ On the other hand, the accumulation of CBG in coalbed as the critical value of coal and gas outbursts.⁴ Thus, measuring the content of gas in place (GIP) is a crucial step not only for CBG resource estimation and exploitation, but also in evaluating the potential severity of gas disasters in new mines or in unmined areas of existing mines.

The underground direct measurement method of gas content, mainly developed by Bertard and Kissell et al.,⁵,⁶ is widely applied both in the United States and China. In the method, the total gas content of coal samples is subdivided into three parts: lost gas, measured desorbed gas from drill cuttings or coal sample, and residual gas desorbed from crushed coal in the lab.⁷ Among them, the lost gas is defined as the portion seeping from samples during their collection prior to being sealed into an airtight desorption canister, and thus cannot be measured directly. Despite the square-root-time method based on the work of Barrer always being recommended for the lost gas estimation,⁹ it’s accuracy is greatly affected by the sampling strategies. Collection drill cuttings from test boreholes is the simplest way to obtain coal samples in GIP, but these cuttings are generally mixed and too crushed, accelerating gas desorption before being sealed into canisters.¹² As a result, the gas contents evaluated by adopting drill cuttings should be considered as the minimum values. To solve the problem, a coring tube is recommended to collect intact samples in the preset place.⁶,⁸ Unfortunately, a fatal shortcoming is that the friction heat generated between the tube and hole wall accelerates gas transport from the samples due to increased gas kinetics,¹³ which results in a serious underestimation of the true loss content with the √t method, especially within a long exposure time. The results of heat distribution of twist drill pipes in rock drilling show that the endothermal coefficient of a workpiece has an effect on drilling temperature, and the most cutting energy will be converted into cutting heat, causing the temperature of the drill bit to rise rapidly.¹⁰−¹⁷ Friction heat can raise the bit temperature to about 500 °C, and the instantaneous temperature reaches 1000 °C. Devries¹⁸ considered the blockage of cuttings discharge as the main cause of temperature rise of drill tools, which is also affected by the lithology of the drilling site. Besides that, for a certain rotating speed of drill tools, the reduction of propelling speed will prolong the sampling time, inducing an increase in heat production.¹⁹,²⁰ The similar situations happen in lunar soil drilling. The conditions of vacuum and solar radiation make the drill bit reach a high temperature, and that can ruin the lunar samples.²¹ Wireline coring originated from oil drilling can quickly take out coal samples from the borehole bottom by winch hoisting, which greatly shortens the core-taking time.²² Nevertheless, if the depression angle of the borehole is not large enough, the salvager is hardly delivered to the bottom by its own weight. It also needs water to be pressed in and the operation is complicated. Hence, wireline coring is preferable in the reservoir geological exploration, but not for the underground gas content determination in the in-seam or upward cross-strata boreholes. Other coring methods (e.g., ejector sampling or reverse circulation drilling) create excessive...
or negative pressure conditions, differing from gas desorption in atmospheric pressure, and hence, also cause errors in the lost gas estimation.23,24 The reduction of gas desorption capacity and kinetics by cooling coal samples is probably a feasible way to improve the accuracy of lost gas estimation. Hence, the authors have proposed a freezing coring technology25 for gas content determination. Isothermal adsorption/desorption tests under low temperatures25−27 demonstrate that gas diffusion in the coal matrix is greatly inhibited, whereas the adsorption capacity enhanced below 273.15 K, and the mean isosteric adsorption heat can be used to evaluate the gas adsorption affinity of coal with different metamorphic ranks. In addition, the applications of artificial freezing technology in other related fields, such as sampling the frozen sediment from ice-covered lake,28 subsurface spawning gravel under shallow water,29 and land hydrates30,31 in particular, can also provide a reference for us. It is a priority to find a suitable refrigeration mode served in the underground coalbed sampling with the advantages of stable physical properties, no danger, rapid cooling performance, and long-running preservation of low temperature. In our study, based on the precalculation of the cryogen (dry ice) dose, the freezing tests of coking coal were conducted at different equilibrium pressures of gas adsorption to investigate the cooling performances of four kinds of refrigeration modes. The temperature and pressure evolvement in coal was monitored during the cooling and heating process, and the reasons behind these phenomena are also discussed. It provides a basis for the design and development of the freezing coring device used in the GIP evaluation.

2. RESULTS AND DISCUSSION

2.1. Temperature Evolvement of Coal by Different Freezing Modes. 2.1.1. Cooling Performance. In order to achieve an optimal refrigeration effect in a short time, coal freezing tests by injecting different doses of ethanol (0, 200, 400, and 600 mL) as catalyst were conducted. The dry ice amount of 2 kg was adopted according to the calculation.
results and the molded coal samples without gas sorption were first selected here. The temperature variation caused by the Joule–Thomson effect\textsuperscript{27} can be neglected during the freezing test due to the large volume of the coal sample. The ambient temperature was kept $26 \pm 2 ^\circ C$.

Figure 1a–d shows that the temperature evolvement of the coal sample under different refrigeration modes presents a similar trend, which can be divided into three stages: rapid cooling in the early stage, low-temperature preservation in the mid-stage, and slow rising in the later stage. In the early stage, temperatures both of the coal center and the sidewall decrease fast, and the average cooling rates of the coal center gradually accelerate with the increased dose of injected ethanol (see Table 1), which are 0.34, 0.42, 0.51, and 0.66 $^\circ C/min$, respectively. For a regular amount of refrigeration, the increase of ethanol would promote more sublimation of dry ice, and thus accelerate the cooling rate in the early stage. Meanwhile, more dry ice is consumed with the increased ethanol injection, so that the low temperature preservation time ($<0 ^\circ C$) gets shorter and shorter: 548, 538, 454, and 409 min, respectively. The four refrigeration modes all can satisfy the time requirements of freezing coring from the perspective of low temperature duration. However, the mode by adding 600 mL ethanol as the catalyst can freeze the coal sample to $-40 ^\circ C$ in the shortest time, thereby inhibiting gas desorption as little as possible from coal during the freezing coring process.

2.1.2. Heat Transfer Model. A heat transfer model throughout the cooling and heating process was established with COMSOL multiphysics to explore the temperature distribution at each point in the coal sample. The refrigeration tank and coal canister are from the outside to the inside of the model, and the top and bottom surfaces are heat insulation. Coal is regarded as an isotropic material, and its thermal properties are replaced by equivalent thermal parameters. The heat of methane adsorption is neglected in the model. Thus, heat transfer can be described by the following equation.

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p v \nabla T = \nabla \cdot (k \nabla T) + Q$$

where $\rho$ is coal density; $C_p$ is the specific heat capacity; $k$ is the thermal conductivity coefficient; $v$ is the flow velocity of gas; $\nabla T$ is the temperature gradient; and $Q$ is the heat-transfer capacity per volume. The thermal conductivity coefficient of coal can be expressed as follow\textsuperscript{36}

$$k_{\text{coal}} = 0.0018T + 0.2013$$

The gas flow in the gap between the sample canister and coal is regarded as the nonisothermal flow of incompressible fluid, so the governing equations are shown as follows

$$\frac{\partial \rho}{\partial t} + \rho \nabla \cdot v = 0$$

$$\frac{\partial v}{\partial t} + v \cdot \nabla v = -\nabla P + \nabla \cdot \mu \nabla v + \left( \nabla v \right)^T - \frac{2\mu}{3} \left( \nabla \cdot v \right)$$

$$\frac{\partial P}{\partial t} + \nabla \cdot (\rho v) = 0$$
where $\rho_g$ is gas density, $\rho_w = \frac{MP}{RT}$; $M$ is the molar mass of gas; $R$ is the gas constant, 8.314 J/(mol·K); $\mu$ is the gas kinetic viscosity; and $VP$ is the gas pressure gradient.

The refrigeration mode of 2 kg dry ice with 600 mL ethanol catalysis is taken here to show the evolution rules of coal temperature (Figure 2). The relationship between coal temperature and time can be fitted by the polynomial function (eq 5) as the heat boundary condition.

$$
\phi(t) = -1.04996t + 0.0134r^2 - 4.99886 \times 10^{-5}t^3 + 6.08483 \times 10^{-9}t^4 + 227.46205 K
$$

(5)

Initial condition: $T|_{t=0} = T_0 = 300.15 K$

Both the experimental and the modeling results indicate that the coal sample is frozen from the outside to the inside, and the temperature of the sidewall is lower than that of the coal center in the initial cooling stage. When the temperature of the coal center drops to the lowest, heat exchange between the whole refrigeration system is in a transient dynamic equilibrium state. Although with further consumption of dry ice in the later stage, the sample temperature slowly rises again, but the rising rate of the sidewall is slightly higher than that of the coal core. It is mainly attributed to the difference of thermal conductivity between the canister sidewall and coal center. The thermal conductivity of the sidewall is approximate to that of stainless steel, 40 W/m·K, but coal is a poor conductor with the thermal conductivity of about 0.25 W/m·K. The difference of thermal conductivity will affect the rate of heat transfer. The higher the thermal conductivity, the faster the heat transfer. Additionally, the canister sidewall is the earliest to exchange heat with the ambient, and then the heat transfer is from the sidewall to the center mainly by means of heat conduction. Therefore, both the cooling and heating rate of the sidewall are higher than that of the coal center at the same time.

2.2. Temperature Evolvement of Coal Containing Gas. Disturbed coal seams in China are generally developed by multistage tectonic movements, and thus, the pore structure of tectonic coal is very complex. A large amount of gas is adsorbed in disturbed coal. To study the influence of gas adsorption on the freezing performance of the coal sample, coal freezing tests, when charging different amounts of methane (the initial adsorption equilibrium pressure: 0, 1.09, and 2.15 MPa) were conducted at 23 °C ambient temperature. The refrigeration mode of 2 kg dry ice and injecting 600 mL ethanol were taken. The results are shown in Figure 3.

Figure 3 shows that in the early freezing stage, the average cooling rates of the coal sample accelerate with the increase of the equilibrium pressure of gas adsorption under the same conditions. When the temperature drops to 0 °C, the cooling time of the coal center under different gas pressures is 29, 14, and 10 min, respectively, and the cooling rates are 0.79, 1.64 and 2.3 °C/min, respectively. When the temperature drops to −30 °C, the cooling time of the coal center is 65, 58, and 48 min, respectively, and the cooling rates are 0.81, 0.91, and 1.1 °C/min, respectively (Table 2). In addition, the low temperature preservation time (below 0 °C) of the coal sample is prolonged by charging gas with a higher pressure, and it lasts for 409, 495, and 558 min, respectively, at 0, 1.09, and 2.15 MPa. It indicates that when coal fully adsorbs gas, the absorbed gas contributes to improve the refrigeration efficiency and the low temperature preservation time can also completely satisfy the requirements of underground freezing coring.

Based on the theories of thermodynamics and gas kinetics, gas pressure is the interaction between gas molecules and the walls of the coal container. Coal is a poor conductor of heat with low thermal conductivity. However, after charging high-pressure gas, the adsorption system contains more gas molecules at the same ambient temperature. The increasing gas density makes the occurrence of gas molecules at the same place nearly equal, which weakens the difference in the kinetic energy of gas molecules caused by the temperature difference. Thus, the overall heat conductivity of coal containing gas is greater than that of coal without gas, resulting in the cooling rate increasing with gas pressure. Although the heat

![Figure 3. Temperature evolvement of coal center when charging gas.](image-url)

Table 2. Cooling Time of Coal by Charging Gas with Different Pressures

| temperature gradient (°C/min) | gas pressure 0 MPa | 1.09 MPa | 2.15 MPa |
|-------------------------------|-------------------|----------|----------|
| time (drop to 0 °C)/min       | 29                | 14       | 10       |
| time (drop to −10 °C)/min     | 37                | 22       | 17       |
| time (drop to −20 °C)/min     | 48                | 39       | 29       |
| time (drop to −30 °C)/min     | 65                | 58       | 48       |
| time (drop to −40 °C)/min     | 98                | 94       | 72       |
| low-T preservation time (<0 °C)/min | 409          | 495      | 558      |
| average freezing rate/°C/min  | 0.66              | 0.67     | 0.88     |
conductivity of coal is not constant, and it decreases with cooling.37−39 It reveals why the cooling rate is very fast in the initial freezing stage and then gradually decreases to the thermodynamic equilibrium state. Besides, the absorbed gas also provides a carrier for the system to absorb more cold energy, which makes the temperature of the coal center rise more slowly in the pick-up stage, and the re-desorbed gas also absorbs some heat. Consequently, the low temperature preservation time of coal containing high-pressure gas becomes longer than that of coal with no gas absorbed.

2.3. Response Characteristics of Gas Pressure to Temperature. 2.3.1. Gas Pressure Evolvement. The gas pressures in the freezing tests of coal containing gas were monitored. The initial adsorption equilibrium pressures in the coal canister are 1.09 and 2.15 MPa, and the ambient temperature was 23 °C. The results of pressure variation are shown in Figure 4a,b.

Figure 4a,b displays that the pressure variation in the coal canister is closely consistent with the temperature evolvement of the coal center. In the early stage, the gas pressure rapidly decreases with the cooling and finally tends to be stable for a while, which can be regarded as the end of cooling. The initial gas pressures of 1.09 and 2.15 MPa would reach the new adsorption equilibrium states of 0.52 and 1.25 MPa, respectively, at the lowest temperature of −40 °C. Subsequently, the coal temperature gradually rises again with the depletion of dry ice, and finally keeps the same with the ambient temperature. The gas pressure in the coal canister also picks up and eventually approaches the initial equilibrium pressure. The above results show that the processes of adsorption and desorption are basically reversible. Cooling can reduce the kinetic energy of gas molecules. When the molecular kinetic energy is lower than the adsorption barrier, the gas molecule is adsorbed on the coal surface. Conversely, heating accelerates the thermal movement of gas molecules, which frees the adsorbed gas molecules from the bondage of van der Waals force to diffuse from the surface of the coal matrix. This is the main reason why the pressure in the coal canister varies with the ambient temperature.

2.3.2. Desorption Hysteresis. Figure 5 shows that there is an obvious linear relationship between gas pressure and temperature below −10 °C. Whereas the gas pressures during cooling appear to cross the data during heating process in the range of 1.25−1.325 MPa in Figure 5b. It may be because for the whole refrigeration system, the ambient temperature changes all the time. When the coal temperature drops to the lowest, the heat exchange between the whole refrigeration system is in a transient dynamic equilibrium state. However, the adsorption of gas molecules on the coal surface never stops till equilibrium. Thus, the gas pressure drops sharply and does not keep the linear relation in the range of 1.25−1.325 MPa. Besides, the pressure at each temperature during cooling is higher than that during heating. It is mainly because, at the same temperature, the gas
Table 3. Distribution of the Specific Surface Area and Pore Volume of Coal

| pore size/nm | specific surface area (BET)/m²·g⁻¹ | proportion/% | pore volume/cm³·g⁻¹ | proportion/% |
|--------------|-----------------------------------|--------------|---------------------|--------------|
| micropore (<10) | 1.951                             | 70.36        | 0.002               | 18.73        |
| mesopore (10–100)  | 0.723                             | 26.07        | 0.006               | 46.85        |
| macropore (>100)   | 0.099                             | 3.57         | 0.004               | 34.42        |
| total             | 2.773                             | 100          | 0.012               | 100          |

adsorption capacity of coal during cooling is less than that during heating. Some methane molecules adsorbed on the surface of the coal matrix during cooling cannot be desorbed from coal pores when heating to the same temperature, which is the desorption hysteresis. The descent trend of the initial pressure of 1.09 MPa during cooling can be fitted as follows: \( P = 0.0082T + 0.8588 \) \( (R^2 = 0.999) \), whereas the ascent curve during heating is \( P = 0.0078T + 0.8309 \) \( (R^2 = 0.996) \). For the initial pressure of 2.15 MPa, the pressure descent curve during cooling is fitted as follows: \( P = 0.0126T + 1.7871 \) \( (R^2 = 0.995) \), whereas the ascent curve during heating is \( P = 0.0119T + 1.7179 \) \( (R^2 = 0.999) \). Here, the hysteresis coefficient, \( H_c \) is defined as the difference between the intercepts of descent and ascent lines. Thus, \( H_c \) at different initial pressures is 0.0249 and 0.0692 MPa.

To investigate the contributing factors of desorption hysteresis, the pore structures of the coking coal samples were analyzed by the ASAP-2020 specific surface area analyzer (see Table 3). Based on the Brunauer–Emmett–Teller (BET) theory, the total specific surface area of coal ranges from 0.5319 to 8.098 m²/g (avg. 2.773), and micropores take up the largest proportion (70.36%), followed by mesopores (26.07%) and macropores (3.57%). The pore volume varies from 0.0016 to 8.098 m²/g (avg. 2.773) and is mainly dominated by mesopores and macropores, taking up 46.85 and 34.42%, respectively. Furthermore, the liquid N₂ adsorption/desorption results (Figure 6) indicate that when the partial pressure is greater than 0.8, the adsorption quantity of N₂ rises sharply, which means that the monolayer adsorption ends and the multilayer adsorption occurs, associated with capillary condensation. At the partial pressure of 0.50, a sudden yield point appears in the desorption isotherms, corresponding to a hysteresis loop. It is mainly caused by various ink-bottle type and narrow-slit pores, which are beneficial for gas adsorption, but bad for seepage.

To date, it is widely accepted that the pore structure of coal is heterogeneous, and the desorption hysteresis has been attributed to the ink-bottle type pore structure with narrow pore throats, which are smaller than the kinetic diameters of methane. These constricted micropores in the coking coal provide the main storage space for gas. When gas molecules enter and are absorbed into the ink-bottle micropores with the increase of gas pressure, the swelling of coal matrix would happen, which further narrows the pore throats. In the depressurization process, the absorbed gas molecules can still diffuse from the constricted pores through these narrowed pore throats, but it consumes more energy than that which enables them to enter the pores. Therefore, the number of gas molecules escaping from the constricted pores during desorption is less than that during adsorption at the same gas pressure, resulting in the desorption hysteresis.

3. CONCLUSIONS

To find an efficient refrigeration mode for the freezing coring technology used in GIP estimation, the freezing tests of coal containing gas are separately conducted by adding 2 kg of dry ice and injecting different amounts (0, 200, 400, and 600 mL) of ethanol as the catalyst. The article probes both the temperature and gas pressure evolvement in coal, and the following conclusions can be drawn from the test results:

1. The temperature evolvement of coal during freezing tests is divided into three stages: rapid cooling in the early stage, low-temperature preservation in the mid-stage, and slow rising in the later stage. Under the catalysis of ethanol, the average cooling rate of coal gradually accelerates with the increased dose of ethanol (from 0 to 600 mL) in the early stage.
2. When charging gas into the coal canister, the cooling rate of the coal center at each subzero temperature gradually accelerates with the increased gas pressure (from 0 to 2.15 MPa), and the low temperature preservation time of coal (< -6 °C) is also prolonged.
3. During the cooling stage, some free gas molecules are absorbed in coal, so the gas pressure continuously decreases until thermal equilibrium; then, it gradually picks up and eventually returns to the initial equilibrium pressure during the heating. There is a good linear relationship between gas pressure and coal temperature.
4. CH₄ adsorption and desorption are basically reversible, but the desorption hysteresis is extensively observed at different adsorption pressures, associated with the occurrence of numerous ink-bottle type micropores.

4. EXPERIMENTAL METHODOLOGY

4.1. Sample Preparation. The fresh coking coal samples used in this study were collected from no. 42207 longwall panel of Xingwu coalmine, Liulin, located in the Shansi
provinces of China, and then were sealed immediately to prevent oxidation. When using the coring tube in coalbed drilling, the obtained sample is more similar to molded coal than coal powder under compaction. Thus, coking coal specimens were first ground and sieved using 0.17–0.25 mm metal sifters, and evenly mixed with an appropriate amount of distilled water. Subsequently, they were placed into a mold and loaded with 60 kN pressure for 30 min. After molding and dehydration for 3 h at 105 °C, the prepared sample was stored in a dehydrator for later use (see Figure 7). The physical parameters of the coal specimen were evaluated using Chinese national standards (GB/T 212-2008, 217-2008, 6949-1998) shown in Table 4: ash content ($A_{ad}$), volatile matter ($V_{daf}$), moisture ($M_{ad}$), true relative density (TRD$_{20}$), apparent relative density (ARD$_{20}$), firmness ($f$), and porosity.

### 4.2. Freezing Test Procedure of Coal Specimen

In order to investigate freezing performances of different refrigeration modes on the coal specimen, temperature evolvement both of the coal center and sidewall are monitored by PT100 thermal resistance sensors (range: $-100$ to $200$ °C) during the freezing test. The physical experimental equipment consists of an airtight sample canister, the refrigeration system, vacuum degassing devices, a quantitative gas charging system, data acquisition system, and pipelines (Figure 8). The coal canister is made of stainless steel with the inner diameter of 6.00 cm, the wall thickness of 1.00 cm, the height of 18.2 cm, and the pressure resistance of 16 MPa. Two temperature sensors and a pressure sensor are separately arranged at the top and the pressure resistance of 16 MPa. Two temperature sensors and a pressure sensor are separately arranged at the top and the pressure resistance of 16 MPa.

The freezing test procedures of coal containing gas at 1.09 MPa pressure are shown as follows: (1) place the molded coal specimens into the freezing tank and simultaneously monitor the ambient temperature of 23 °C and pressure remains unchanged at the outside of the freezing tank. (2) Vacuum the coal canister below 10 Pa, and then charge a certain amount of methane into the canister via the reference canister into the freezing tank and simultaneously monitor the temperature equilibrium. By introducing the specimen into the freezing system, refrigeration, and ethanol under ideal conditions.

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### 4.3. Cryogen Dose Evaluation

There are three common refrigerants: freon, dry ice, and liquid nitrogen (LN$_2$). The freon method achieves the refrigeration effect mainly via the operation of a compressor, which is limited by the under-ground sampling conditions and only used in laboratory simulations. As an efficient cryogen, LN$_2$ is widely used in the biorefrigeration industry and its boiling point is 76.6 K. However, LN$_2$ can only be preserved in vacuum, and the storage container must have enough capacity of pressure resistance, presenting a big challenge for developing a portable LN$_2$ freezing coring tube. Thus, dry ice becomes the preferred choice when taking safety and cost into account. As shown in Figure 9, the 3-phase point parameters of CO$_2$ are about: temperature of 216 K and pressure of 0.52 MPa. When heated at atmospheric pressure, dry ice directly sublimates to the gaseous state. Moreover, the freezing point of ethanol (155.85 K) is much lower than that of dry ice (194.65 K), so that liquid ethanol can continue to provide heat to sublime more dry ice.

#### 4.3.1. Calculation of Dry Ice Volume under Ideal Conditions

Taking the coal sample and the refrigeration system as a whole, when the cooling temperature of the whole system reaches equilibrium, the total amount of heat absorbed by dry ice sublimation is equal to the sum of the freezing capacity needed by the coal specimen, sample canister, refrigeration tank, and ethanol under ideal conditions. Thus, the freezing capacity provided by dry ice is calculated based on the energy conservation law

$$Q_i = Q_{coal} + Q_{tank} + Q_{refrigeration} + Q_{ethanol} \tag{6}$$

where $Q_i$ is the freezing capacity provided by dry ice under ideal conditions; and $Q_{coal}$, $Q_{tank}$, $Q_{refrigeration}$, and $Q_{ethanol}$ are the freezing capacity absorbed by the coal sample, sample canister, refrigeration tank, and ethanol, respectively, when the system reaches temperature equilibrium. By introducing the specific heat capacity equation into eq 6, the volume form can be written as follows

$$q_v V_i = \Delta T \cdot (C_{coal} \cdot V_{coal} + C_{tank} \cdot V_{tank} + C_{refrigeration} \cdot V_{refrigeration} + C_{ethanol} \cdot V_{ethanol}) \tag{7}$$

where $q_v$ is the volume sublimation heat of dry ice; $V_i$ is the required dry ice volume under ideal conditions; $\Delta T$ is the temperature difference of the freezing system; $C_{coal}$, $C_{tank}$, $C_{refrigeration}$, and $C_{ethanol}$ are the volumetric specific heat capacity of the coal sample, sample canister, refrigeration tank, and ethanol, respectively; and $V_{coal}$, $V_{tank}$, $V_{refrigeration}$, and $V_{ethanol}$ are the volume of the coal sample, canister, refrigeration tank, and ethanol, respectively.

The above physical parameters are shown in Table 5. $q_v$ is $9.91 \times 10^8$ J/m$^2$ and $\Delta T$ is 65 K here. By substituting these values into eq 7, the dry ice weight required by injecting

### Table 4. Physical Parameters of Coal Samples

| sampling location | $A_{ad}$/% | $V_{daf}$/% | $M_{ad}$/% | $f$ | porosity/% | TRD$_{20}$/g·cm$^{-3}$ | ARD$_{20}$/g·cm$^{-3}$ |
|-------------------|------------|-------------|------------|-----|------------|-------------------|-------------------|
| Xingwu coalmine   | 6.66       | 19.40       | 2.64       | 0.42| 9.26       | 1.38              | 1.25              |

Figure 7. Preparation of molded coal specimens.
different amounts of ethanol under ideal conditions ($M_1$) can be evaluated as listed in Table 6.

### 4.3.2. Dry Ice Loss during Freezing Test.

The outside surface of the freezing tank is wrapped around with a flexible nitrile rubber−polyvinyl chloride insulation layer of 0.01 m, which can form multiple barriers to water vapor molecules due to low heat conductivity. However, there will still be some inevitable heat exchange with the ambient during the cooling process. According to "Codes for Design of Insulation Engineering for Industrial Equipment and Pipeline" the loss of the cooling capacity of cylindrical single-layer insulator is calculated by eq 8

$$Q_0 = \frac{\Delta T}{D_1 \ln \frac{D_1}{D_2} + \frac{1}{\alpha}}$$

(8)

where $Q_0$ is heat loss on per unit area of the insulation layer surface; $D_1$ is the external diameter of the insulation layer, 0.182 m; $D_2$ is the internal diameter of the insulation layer, 0.180 m; $\Delta T$ is the heat conductivity of the insulator, 0.034 W/(m·K); and $\alpha$ is the surface heat transfer coefficient, 11.63 W/(m²·K). Thus, $Q_0$ of 562.48 W/m² is obtained here by inputting the parameters.

Successively, the total freezing capacity loss of dry ice during test ($Q_2$) can be evaluated by eq 9

$$Q_2 = Q_0 ST = Q_0 \pi D_1 H t$$

(9)

and $V_2 = Q_2/\rho_i$,

(10)

where $S$ is the surface area of the insulation layer; $t$ is the holding time, 2.5 h; $H$ is the height of the insulation layer, 0.21 m; and $V_2$ is the loss volume of dry ice in the test. Consequently, the loss amount of dry ice in the test ($M_2$) is about 0.95 kg by fitting the parameters.

### 4.3.3. Gas Absorption Heat in Freezing Process.

For a gas−solid sorption system, the adsorption equilibrium will be broken by the temperature change. Previous tests indicated that cooling can largely reduce kinetic energy of gas molecules, and more gas molecules will be adsorbed on the surface of the coal matrix when the kinetic energy of gas molecules is lower than the adsorption barrier. The readsorption heat of gas molecules in the freezing process could be evaluated as follows.

Assume that the total adsorption space contains $N$ independent gas molecules, which are in two states: free state and adsorbed state. The potential energy of gas molecules in the free/adsorbed state is $\epsilon_f$, $\epsilon_a$ and the molecular number is $N_f$, $N_a$, respectively. Regardless of the interaction between gas molecules, the adsorption heat of a single gas molecule can be expressed as

$$\Delta \epsilon = \epsilon_a - \epsilon_f$$

(11)

When the system equilibrates again at the temperature of $T$, gas molecules obey the Boltzmann distribution

$$N_i = e^{\alpha - \beta \epsilon_i}, \quad N_f = e^{\alpha - \beta \epsilon_f}$$

(12)

where $\alpha = \mu/kT$, $\beta = 1/kT$, and $k$ is the Boltzmann constant. From $N_f + N_i = N_0$, eq 12 can be rewritten in the following form by logarithm of both members.

| material          | volume/m³ | density/kg·m⁻³ | $C_f$/kg⁻¹·K⁻¹ | $C_r$/J·m⁻³·K⁻¹ |
|-------------------|-----------|----------------|----------------|----------------|
| coal sample       | 0.20 × 10⁻³ | 1380          | 1260           | 1.73 × 10⁶     |
| coal canister     | 0.63 × 10⁻³ | 7930          | 500            | 3.97 × 10⁶     |
| refri-tank        | 1.72 × 10⁻³ | 7930          | 500            | 3.97 × 10⁶     |
| ethanol           | 0.2–0.6 × 10⁻³ | 800           | 2400           | 1.92 × 10⁶     |
\[ e_f = \frac{\alpha - \ln N_f}{\beta}, \quad e_s = \frac{\alpha - \ln N_s}{\beta} \]  
\[ \Delta e = kT \ln \frac{N_f}{N_s} \]  

Then, the total adsorption heat of free gas molecules can be obtained as follow:

\[ Q_3 = N_f kT \ln \frac{N_f}{N_s} = n_fRT \ln \frac{n_f}{n_s} \]  

where \( \frac{N_f}{N_s} = n_f/n_s = R/k = N_A \), \( R \) is the molar gas constant; \( n_f \) is the total gas amount; \( n_s \) is the amount of free gas, and \( N_A \) is the Avogadro constant. As the absorbed gas is dominant in coal, owing to the lower potential energy than free gas (\( N_f < N_s \)), the adsorption is an exothermic process.

Because of the total gas mass conservation before and after freezing, the absorbed gas amount, \( n_a \), can be calculated based on the ideal gas state equation

\[ n_a = n - n_f = \frac{\Delta P V_{\text{cell}}}{ZRT} - \frac{P_2 V_f}{ZRT} \]  

where \( \Delta P \) is pressure difference of the reference cell when the sorption system first reaches equilibrium at the setting pressure, \( V_{\text{cell}} \) is the volume of reference cell (here the gas reduction in reference cell is actually the total amount of charging gas into coal canister); \( P_2 \) is the gas pressure when coal is frozen at the temperature of \( T_f \); \( V_f \) is the volume of free gas in coal canister; \( T_f \) is the ambient temperature; \( Z, Z_f \) are gas compressibility factors at the relevant temperature and pressure, respectively, derived by the Redlich–Kwong equation; and \( R \) is the gas constant.

Therefore, the volume of dry ice consumed by the absorption heat \( (V_s) \) is evaluated as follows

\[ V_s = \frac{Q_3}{q_v} \]  

As the dry ice weight consumed by the absorption heat is quite small (\(<0.01 \text{ kg})\), it is neglected in the tests. It is identical with previous conclusions \(^{33} \) that gas molecules are physically absorbed in coal and the adsorption heat is often less than 30 \( \text{kJ/mol} \). Additionally, the consumption of dry ice is not much different when injecting different amounts of ethanol, and thus the following tests were conducted with the amount of dry ice of 2 kg (the sum of \( M_1 \) and \( M_2 \)) for the sake of uniform measurement.

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**Notes**
The authors declare no competing financial interest.

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