Study the effect of temperature on methane desorption based on thermodynamics and kinetics

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Abstract:
Desorption hysteresis is important for primary gas production. Temperature may cause serious change in the methane adsorption/desorption behaviors. In order to study the mechanism of methane desorption and desorption hysteresis, three sets of samples of long flame coal, coking coal, and anthracite were collected, and experiments such as microscopic composition determination, liquid nitrogen adsorption, and isothermal adsorption/desorption were performed. From the perspectives of desorption kinetics, desorption thermodynamics and methane occurrence state, the differences in methane and methane desorption characteristics and the desorption hysteresis mechanism are discussed. The results show that at the same temperature, anthracite (SH3#) has the largest saturated adsorption capacity and residual adsorption capacity, followed by coking coal (SGZ11#), and long-flame coal (DFS4#) is the smallest. As the temperature rises, the theoretical desorption rate and residual adsorption capacity of anthracite (SH3#) and coking coal (SGZ11#) will increase first and then decrease. Temperature and methane desorption are not completely positive effects, and temperature may have a threshold for promoting methane desorption. It is necessary to comprehensively consider the influence of temperature on the activation of gas molecules and the pore structure of coal. Under the premise of a certain temperature, as the pressure increases, the desorption hysteresis rate changes in a logarithmic downward trend, and the methane desorption hysteresis rate in the low pressure stage (P<4MPa) is large, and the methane desorption hysteresis rate in the high-pressure stage (P>4MPa) is lower; During the isobaric adsorption process, the adsorption capacity of anthracite (SH3#) increases the fastest, followed by SGZ11#, and DFS4# is the smallest. In the low-pressure stage (P<4MPa), the adsorption capacity increases significantly with the increase of pressure, but in the high pressure stage (P>4MPa), the adsorption capacity does not change significantly with pressure, but gradually stabilizes. Under the same pressure, the molecular free path of methane increases with temperature. Under the premise of constant temperature, in the low-pressure stage (0<P<4MPa), when the pressure continues to decrease, the free path of methane molecules increases significantly, resulting in a decrease in the diffusion capacity. In the high-pressure stage (4<P<8MPa), when the pressure continues to decrease, the free path of methane molecules does not change significantly; DFS4#, SGZ11#, SH3# sample desorption process of three sets of samples, the intermediate adsorption heat is greater than the isometric adsorption heat during the adsorption process, indicating that the desorption process needs to continuously absorb heat from outside the system. The energy difference produced in the process of adsorption and desorption causes the desorption hysteresis effect. The greater the difference in the isometric heat value of adsorption, the more significant the hysteresis.

Keywords: adsorption/desorption, coalbed methane, desorption hysteresis, adsorption heat

1. Introduction
China's CBM resources account for roughly 1/3 of the low, medium, and high rank coals (Qin et al. 2018). The study of coalbed methane adsorption/desorption is of great significance to the development of coalbed methane. Experimental studies have shown that coalbed methane adsorption has many influencing factors including coal rank, temperature, pressure, particle size, moisture content and pore structure, etc. (Bing et al. 2014; Crosdale et al. 1998; Qiu et al. 2020). However, the current CBM desorption research and numerical simulation research mostly adopt the transient desorption model, and directly use the curve obtained by the adsorption experiment, without considering the desorption hysteresis effect. In engineering practice, the mining of coalbed methane is mainly a desorption process, so it is necessary to focus on the problem of coalbed methane desorption and the essence of desorption hysteresis. Among them, temperature is an important factor in the adsorption, desorption, and seepage of methane in coal reservoirs.

The ability of coal to adsorb methane is greatly affected by temperature. In recent years, many researchers have conducted studies on temperature-dependent adsorption, but still have not reached a comprehensive conclusion (Wang et al. 2019). It is basically agreed that the methane adsorption capacity in coal decreases with increasing temperature (Hao et al. 2014; Sakurovs et al. 2008; Wang et al. 2012; Zhu et al. 2020), but based on the temperature effect, there are few reports on analyzing the hysteresis of methane desorption from an energy perspective. Some researchers believe that the hysteresis of desorption is due to the fact that methane molecules enter the micropores with poor connectivity under high pressure and cause pore deformation. The methane molecules retained in the micropores cannot be desorbed from the pores due to the narrowing of the pore throat channels (Chen et al. 2016; Ma et al. 2012; Wang et al. 2014). In addition, the hysteresis of gas adsorption may also be due to gas molecules forming gas clusters in the mesopores (Romanov and Soong 2008). In addition, some researchers believe that the water in the pores of coal also plays an important role in preventing methane desorption (Li et al. 2017; Li et al. 2020; Tian et al. 2017). Predecessors have done a lot of work on the influencing factors of methane adsorption/desorption. However, based on the principle of thermodynamics, there are few reports on the study of temperature on the desorption mechanism and desorption hysteresis of methane.

In this paper, coal samples with different levels of metamorphism are the research objects, including long-flame coal (Dafosi 4# coal), coking coal (Shanggaozhai 11# coal) and anthracite (Sihe 3# coal). By studying the material composition, pore structure and adsorption/desorption characteristics of coal samples. Comprehensive analysis of the difference in adsorption/desorption characteristics and the desorption hysteresis effect from various aspects such as isotherm adsorption, isobaric adsorption, desorption kinetics, desorption thermodynamics, and methane occurrence state, etc. Trying to reveal the nature of desorption hysteresis from the energy point of view, hoping to provide a theoretical reference for coalbed methane development.

2. Samples and methods

2.1. Samples material composition

The samples were collected from the Dafosi coal mine in the southern Ordos Basin of China, the coal cores in the Shanggaozhai borehole in the eastern Ordos Basin of China, and the Sihe coal mine in the southern Qinshui Basin of China. Specifically, it is the No. 4 coal seam sample (DFS4#) directly collected from the 40105-working face of Dafosi Coal Mine, and the No. 11 coal sample (SGZ11#) taken from the coal core of the Shanggaozhai coal mine, and at the W2302-working face
of Sihe Coal Mine. No. 3 coal seam sample (SH3#) collected directly (Fig.1). The coal quality analysis was conducted in accordance with the coal industry standards of the People's Republic of China (GB/T 212-2008, GB/T 212-2008, GB/T 476-2001), and the results are listed in Table 1 and 2.

The sample is mainly used for methane adsorption/desorption measurement and cryogenic liquid nitrogen adsorption test. The original sample is placed in a pulverizer and crushed into powder with a particle size of 0.18-0.23mm. Then, part of the powder samples were placed in a vacuum drying at 50°C to completely dry to remove free moisture in the coal. Other samples were strictly made of samples with moisture balance according to the American Society for Testing and Materials (ASTM) standards (ASTM 1975).

2.2 Cryogenic liquid nitrogen adsorption experiment

Cryogenic liquid nitrogen adsorption experiment uses ASAP specific surface and pore size analyzer. The ASAP2020 specific surface and pore size analyzer produced by Beckman Coulter, USA, has a specific surface area measurement range of > 0.000 5m²/g and a pore size range of 0.35-500 nm. According to the decimal classification system of Hodot (1961), micropore (< 10 nm), transition pore (10-100 nm), mesopore(100-1000 nm), and macropore (> 1000 nm) for detailed analysis(Cai et al. 2013; Hodot 1966).

2.3 Isothermal adsorption/desorption measurements

The methane adsorption/desorption experiment was conducted using a volumetric method (Gruszkiewicz et al. 2009). The adsorption/desorption experiment instrument adopts the AST-2000 large sample coalbed methane isotherm adsorption/desorption simulation experiment instrument independently developed by Xi’an University of Science and Technology (Fig.2).

The experiment temperature is set at 5 temperature points, respectively 25°C, 30°C, 35°C, 40°C, 45°C. The maximum pressure of the experiment is 8MPa, and the adsorption/desorption equilibrium time is 12 hours.

In the process of methane adsorption, the experimental data is described by the Langmuir (Equation 1) equation (Langmuir 1918). Due to the hysteresis of desorption, the desorption process data is described by the desorption equation (Langmuir + c) (Equation 2) proposed by Ma et al. (Ma et al. 2011).

\[
V_a = \frac{abp}{1+bp} \quad (1)
\]

\[
V_d = \frac{abp}{1+bp} + c \quad (2)
\]

In the formula: \(V_a\)—the adsorption capacity under the coal reservoir pressure \(p\), cm³/g; \(V_d\)—the adsorption capacity of coalbed methane desorption to pressure \(p\), cm³/g; \(a\)—the limit adsorption capacity of the coal sample, cm³/g; \(b\)—the comprehensive parameters of adsorption and desorption rate and adsorption heat; \(c\)—constant or residual Adsorption capacity, cm³/g.

3. Results and discussions

3.1 Pore characteristics
The results of the liquid nitrogen adsorption experiment are shown in Table 3 and Fig.3. The specific surface area of DFS4# is the largest, SH3# is the second, and SGZ11# is the smallest, indicating that the coal rank increases, the specific surface area first decreases and then increases, like a "V" change trend.

Analyzing the characteristics of the liquid nitrogen adsorption/desorption curves of the three samples shows that the desorption curve of DFS4# coal is obviously higher than the adsorption curve, and the hysteresis loop is obvious. When the relative pressure is low (0<P/P₀<0.5), the adsorption curves and the desorption basically coincide, and the inflection point appears when the relative pressure P/P₀ is 0.5, indicating that there is a cylindrical hole with one end open and a certain amount of ink bottle holes. The adsorption and desorption curves of SGZ11# are close to parallel, the hysteresis loop is small, and there is no obvious inflection point when the relative pressure is 0.5, indicating that the pores are dominated by slit flat pores, which is beneficial to the desorption and diffusion of coalbed methane. The SH3# coal has an inflection point when the relative pressure (P/P₀) is 0.5, indicating that the ink bottle hole is developed, which is not conducive to methane desorption.

The FHH equation is used to indirectly calculate the fractal dimension of pores (Fu et al. 2017; Zhao et al. 2019), the formula is as follows:

\[
\ln\left(\frac{V}{V_0}\right) = A \times \ln(\ln(p_0 / p)) + B
\]

Where \( V \) is the volume of gas adsorbed at equilibrium pressure \( p \), cm³/g; \( V_0 \) is the volume of gas adsorbed by the monolayer, cm³/g; \( p_0 \) is the saturated vapor pressure of gas adsorption, MPa; \( p \) is the equilibrium pressure of gas adsorption, MPa; \( A \) is the slope under the relationship curve of \( \ln(V/V_0) \) and \( \ln(\ln(p_0/p)) \), which depends on the fractal dimension of the sample; \( B \) is a constant.

Fractal dimension:

\[
D = A + 3
\]

The calculation uses liquid nitrogen desorption data. Because the molar free energy change caused by desorption is smaller than the adsorption process, the adsorption state corresponding to the desorption process is more stable. In addition, the adsorption mechanism of methane in the micropores is different in different pressure sections. The low pressure section (0<P/P₀<0.5) nitrogen is adsorbed in the micropores. The force between gas molecules and coal molecules is mainly van der Waals force, while the high pressure section (0.5<P/P₀<1), nitrogen is mainly adsorbed in mesopores and macropores, mainly by capillary aggregation.

Therefore, in order to characterize different pore structures, it is necessary to calculate the fractal dimensions in sections, namely the low-pressure section (0<P/P₀<0.5) fractal dimension \( D_1 \) and the high-pressure section fractal dimension \( D_2 \) (Fig. 4 and Table 4). The pore fractal dimension \( D_1 \) values of low, medium and high coal rank samples are 2.29, 2.35, and 2.27, which change in an inverted “V” shape with the increase of coal rank. The \( D_2 \) values are 2.75, 2.65, and 2.89, respectively, which vary with coal rank. Contrary to \( D_1 \), during the process of surface coalification, the changes in coal pore surface properties and pore structure are not linear, but fluctuating.

### 3.2 Adsorption/desorption experiment results

The adsorption/desorption data at 5 temperature points of the three coal samples DFS4#, SGZ11# and SH3# are shown in Fig.5, and the fitting results are shown in Table 5. As the temperature increases, the saturated adsorption capacity of the three coal samples DFS4#, SGZ11#, and SH3# decreases significantly (Fig.6a), and the adsorption constants also show similar
characteristics (Fig. 6b), and have a good linear relationship. The degrees of fit are all greater than 0.9. Because the adsorption of methane gas molecules on the coal surface belongs to physical adsorption, heating up increases the activity of methane molecules, which promotes the transformation of methane molecules from an adsorbed state to a free state. In comparison, at the same temperature, the SH3# coal sample has the largest saturated adsorption capacity, followed by the SGZ11# coal sample, and the smallest is the DFS4# coal sample.

The theoretical desorption rate refers to the ratio of the amount of coalbed methane desorbed to the saturated adsorption amount when the pressure drops to the scarce pressure during the decompression desorption process. The formula is shown in 5.

\[ \zeta = \left( \frac{a - c}{a_a} \right) \times 100\% = (1 - \frac{c}{a_a}) \times 100\% \]  \hspace{1cm} (5)

In the formula:
- \( \zeta \) — theoretical desorption rate of coalbed methane, %;
- \( a_a \) — the saturated adsorption capacity of coalbed methane adsorption process, cm\(^3\)/g;
- \( c \) — Residual adsorption capacity under scarce pressure, cm\(^3\)/g.

It can be seen from Fig. 7 that the desorption rate of different types of coal samples at the same temperature can be sorted as follows: SGZ11#>DFS4#>SH3#. As the temperature increases, the theoretical desorption rate of coalbed methane decreases first, and then tends to rise, indicating that temperature is not completely positive for desorption, and temperature may have a critical value for promoting methane desorption. However, since the experimental temperature setting is limited to 5 temperature points, the specific temperature inflection point needs to be discussed.

The desorption hysteresis rate means that when the porous solid is used as the adsorbent, the adsorption curve of the adsorbate does not overlap with the desorption curve, and the desorption line is always on the left side of the adsorption line. This phenomenon is called desorption hysteresis (Li et al. 2018). According to the aforementioned Langmuir equation (Equation 3) and desorption equation (Equation 4), the desorption hysteresis rate \( (\delta) \) can be obtained, which is equation 6.

\[ \delta = \frac{V_d - V_a}{V_a} \times 100\% \]  \hspace{1cm} (6)

The change trend of the desorption hysteresis rate of coal samples of different metamorphism levels at the same temperature and different equilibrium pressures is shown in Fig. 8 above. The analysis shows that regardless of the coal sample type, as the pressure increases, the desorption hysteresis rate changes logarithmically, and the low-pressure hysteresis rate is large, and the high-pressure hysteresis rate is small. This is because the adsorbed methane is affected by the unit pressure drop, and its desorption is highly sensitive in the high-pressure stage, but weak in the low-pressure stage. In the high-pressure stage (which can be considered to be greater than the critical pressure of methane 4.62MPa), for every 1 MPa decrease in pressure, the adsorption value of the desorption process is close to that of the adsorption process, and the hysteresis is not obvious; In the low-pressure stage, the unit pressure drop is weakly sensitive to methane desorption, and the pressure decreases, and the adsorbed methane cannot be immediately desorbed from the surface of the coal matrix. In addition, the desorption hysteresis rate under the same temperature and pressure can be sorted as follows: SH3#, SGZ11#, DFS4#. Careful analysis reveals that the desorption hysteresis rates of coal samples with different metamorphic degrees are relatively small and similar in size at the high-pressure stage. In the low-pressure stage, the difference is relatively large, which
also reflects the difference in the desorption sensitivity of the unit pressure drop in different pressure stages.

Under the same pressure, the methane adsorption capacity of the same coal sample shows a linear decrease with the increase of temperature (Fig. 9), because the higher the temperature, the more violent the movement of methane molecules and the greater the molecular kinetic energy, which is not conducive to adsorption, and is conducive to the adsorption of methane. Desorbed from the pore surface into a free state. At the same temperature, the adsorption capacity and adsorption rate of samples of different coal ranks are significantly different. Taking 40°C as an example, the adsorption capacity of SH3# increases fastest during the adsorption process, followed by SGZ11#, and DFS4# is the smallest. In the low pressure stage (P < 4MPa), as the pressure increases, the adsorption capacity increases significantly and the adsorption rate is faster, but in the high pressure stage (P > 4MPa), the adsorption capacity increases slowly (Fig. 10). In other words, the temperature is constant and the pressure increases. When it reaches a certain value, the adsorption capacity tends to be stable and no longer increases.

In general, SH3# has the largest residual adsorption capacity, SGZ11# is the second, and DFS4# is the smallest, indicating that the higher the coal rank, the more difficult it is to desorb methane and the greater the residual methane adsorption (Fig. 11). As the temperature rises, there are certain differences in the changes in the residual adsorption capacity of the three coal samples DFS4#, SGZ11# and SH3# (Fig. 11). The residual adsorption capacity of SH3# and SGZ11# increased first and then decreased, and the inflection point was 40°C, while the residual adsorption capacity of DFS4# was less affected by temperature. Comparing the relationship between temperature and saturated adsorption capacity and residual adsorption capacity, it is found that as temperature increases, the saturated adsorption capacity of different coal ranks shows a decreasing trend, but its influence on the residual adsorption capacity is more complicated. Temperature can not only affect the activity of gas molecules, but also change the pore structure and surface properties of coal (Ahamed et al. 2019; Cai et al. 2019). The change of residual adsorption capacity with temperature is actually the superposition of the above two effects, and the effect of temperature on the pore structure and surface properties of middle and high rank coals is more complicated than that of lower rank coals. In terms of residual adsorption capacity, when the temperature is low, the temperature-induced pore structure change effect of the medium and high rank coal ranks is dominated, and when the temperature is high, the molecular activity change effect caused by the temperature is the main effect. The strong-to-weak transition temperature is about 40°C. However, the effect of temperature on pore structure changes in low rank coal is limited.

3.3 Thermodynamic characteristics

Using the experimental data of isothermal adsorption and desorption, the isoestic heat of adsorption/desorption of coalbed methane can be calculated indirectly through the Clausius-Clapeyron equation (Skoczylas et al. 2020) (Wang et al. 2015), the formula is as follows:

$$\frac{d \ln f}{dT} = \frac{q^{st}}{RT}$$  \hspace{1cm} (7)

$$f = P \cdot Z$$  \hspace{1cm} (8)

According to the above relationship:

$$q^{st} = -R \cdot B$$  \hspace{1cm} (9)
In the formula, \( q^{st} \) is the isosteric heat of adsorption, KJ/mol; \( f \) is fugacity, Pa; \( T \) is temperature, K; \( R \) is the gas constant, take 8.314 J/(mol·K); \( B \) is the slope of linear fitting relationship; \( P \) is the balance pressure of gas adsorption, MPa; \( Z \) is the compression factor.

Set different adsorption capacity and calculate the corresponding isometric heat of adsorption during the pressure increase adsorption and decompression desorption process of DFS4#, SGZ11#, SH3# (Fig. 12). The results show that when the amount of adsorption is constant, the heat of adsorption released by the boost adsorption is less than the heat of adsorption desorption, indicating that there is an energy difference between the adsorption and desorption processes. From the energy point of view, the adsorption and desorption are not completely reversible. To desorb the same adsorbed amount of methane, energy must be absorbed from the external environment, which is the essential reason for the hysteresis of desorption.

As the amount of adsorption increases, the heat of isobaric adsorption increases linearly, indicating that adsorption is a continuous exothermic process. In the process of boosting pressure, SH3# isometric adsorption heating value is the largest, that is, the released heating value is the largest, and it is easier to adsorb methane, followed by DFS4# and SGZ11# the smallest. In the process of depressurization, SH3# isometric adsorption heat value is the largest, that is, absorption heat value is the largest, and desorption is the most difficult, followed by DFS4# and SGZ11# is the smallest.

3.4 Pore Structure analysis

Studies have shown that the ink bottle-shaped holes have the strongest adsorption capacity for methane, followed by slit flat holes, cylindrical holes and wedge-shaped holes (Song et al. 2018). It is difficult for supercritical gas to physically adsorb on the surface of mesoporous or macroporous adsorbents. In microporous adsorbents, due to the superposition of the adsorption potential energy of adjacent pore walls, the interaction between gas and solid molecules in the micropores is enhanced, and a large amount of gas accumulates in the micropores. The interaction between molecules and gas molecules has also been enhanced (Kaneko and Murata 1997). The pore characteristics of coal directly affect the adsorption/desorption capacity of coal. The main reason is the pore throat structure. Due to the small pore throat and strong adsorption capacity of the ink bottle, the difficulty of desorption increases. SH3# has more ink bottle holes. Compared with SGZ11# and DFS4#, it has the largest adsorption capacity and a larger desorption hysteresis. And the D_2 of SH3# is the largest, indicating that its pore structure is more complicated and it also increases the difficulty of desorption. Relatively speaking, DFS4# develops open pores, so the adsorption capacity is poor, but the desorption is easier and the hysteresis is small. And DFS4# fractal dimension D_2 value is small, indicating that the pore structure is relatively simple, which is beneficial to desorption.

3.5 Desorption kinetic analysis

The kinetic process of methane desorption is a process of desorption-diffusion-percolation. The diffusion of methane in the coal matrix complies with Fick's law. The essence of diffusion is the result of the irregular movement of gas molecules, and the speed of gas molecule diffusion can be expressed by the mean free path. The formula for the molecular mean free path is as follows:

\[
\lambda = \frac{kT}{\sqrt{2\pi d^3}p}
\]

(10)
Among them: \(k\) is Boltzmann's constant, \(1.38 \times 10^{-23} \text{ J/K}\); \(T\) is the absolute temperature, \(\text{K}\); \(\pi\) is 3.14; \(d\) is the methane molecular diameter, 0.414 nm; \(p\) is the gas pressure, MPa.

Under the same pressure, the molecular free path of methane increases with temperature. Under the premise of constant temperature, in the low pressure stage (0<P<4MPa), when the pressure continues to decrease, the free path of methane molecules increases significantly, which leads to a decrease in the diffusion capacity; in the high pressure stage (4<P<8MPa), when the pressure continues to decrease, the free path of methane molecules does not change significantly (Fig.13).

The large and medium pores of methane are mainly laminar or turbulent flow, transition pores or small pores are mainly diffusion or adsorption, and micropores are mainly adsorption. The desorption of methane is the reverse process of adsorption. The desorption of methane starts from macropores, mesopores, small pores, and micropores. The coal matrix is a porous body, and the methane molecules in the micropores are finally desorbed. At this time, the pressure is low, which makes the methane diffuse in the micropores for a long time. This causes the methane in the high-rank coal matrix with highly developed micropores to be very high. It is difficult to desorb, and both the desorption hysteresis ratio and residual adsorption capacity can be reflected. Therefore, it comprehensively shows that the desorption hysteresis of high-rank coal is relatively large.

3.6 Desorption thermodynamic analysis

Due to metamorphism, medium and low-rank coals are mainly small-micropores (10-100 nm), and high-rank coals are mainly micropores (less than 10 nm), so the ability to adsorb methane is different (Hou et al. 2020; Xin et al. 2019). With the generation of adsorption during the adsorption process, the coal-CH4 adsorption equilibrium system becomes more stable. The methane molecules adsorbed on the inner surface of the coal need to absorb more energy to get rid of the van der Waals force with the coal surface during desorption. The experimental results show that the increase in temperature inhibits the adsorption. As the temperature increases, the activation energy of CH4 increases, so the saturated adsorption capacity of the coal becomes smaller, the adsorption capacity decreases, and the desorption capacity increases. The methane process is an exothermic process, and the desorption process is an endothermic process. The isometric heat of adsorption in the desorption process is greater than that in the adsorption process, indicating that the energy released by adsorption is less than the energy required for desorption. From the perspective of thermodynamics, it shows that the adsorption and desorption of methane in coal are not completely reversible, and the result will inevitably cause desorption hysteresis. Some researchers studied the temperature change during the adsorption/desorption process of methane in granular coal, and the results showed that the temperature of the test chamber increased when the pressure was increased, and the temperature of the test chamber decreased when the pressure was decompressed. However, the temperature dropped during desorption is lower than the temperature increased during adsorption, indicating that the same amount of methane needs to be desorbed to absorb more heat from the external environment(Xie et al. 2019; Yang and Nie 2015). Therefore, it comprehensively shows that methane desorption has a desorption hysteresis, and the energy difference between before and after adsorption and desorption will cause desorption hysteresis.

3.7 Analysis of methane occurrence state

The occurrence state of methane in coal reservoirs is mainly adsorption state and free state. For the methane in the adsorption state, it is reflected from the perspective of thermodynamics that the isometric heat of adsorption during desorption is greater than the equivalent heat of adsorption during adsorption. Because the sample used in the isotherm adsorption experiment is 60-80 mesh
coal, the original pore-fracture structure of the coal reservoir was destroyed by the external force during the process of making the experimental sample. During this process, part of the pores were blocked and it was similar to the original coal reservoir. Compared with, the granular coal in the sample produced more tiny holes and cracks. For methane in the free state, the isothermal adsorption experiment is pressure-boosted adsorption, so the free methane molecules can enter the micropores under high pressure. Some closed pores will cause the pore structure to deform (the pore throat becomes narrower) after inhaling methane. The adsorbed methane is restricted by narrow pore channels and cannot be desorbed from the pores (Wang et al. 2016). In actual production, due to drainage, pressure reduction and fracturing, the original pore and fracture structure of coal reservoirs are also destroyed, and some methane desorption channels are blocked, resulting in desorption hysteresis.

The author attributed the desorption hysteresis effect to two points. First, the isometric heat of adsorption (absorption energy) required for desorption of methane in the adsorbed state is greater than the isometric heat of adsorption (release energy) during adsorption. When the methane in the adsorbed state changes to a free state, it needs to absorb energy from the external environment. Second, the methane in the free state enters the tiny pores under high pressure, which causes deformation of the coal matrix and changes in the pore structure, resulting in limited methane desorption, resulting in desorption hysteresis. At this time, a large pressure difference (energy) is required to desorb the blocked methane.

4. Conclusion

Major conclusions in this work can be summarized as follows:

(1) As the degree of coal metamorphism increases, the ability of coal to adsorb methane is significantly enhanced. At the same temperature, the saturated adsorption capacity, desorption hysteresis rate and residual adsorption capacity of SH3# are the largest, followed by SGZ11#, and the smallest is the DFS4#. As the temperature increases, the theoretical desorption rate and residual adsorption capacity of SH3# and SGZ11# show a trend of first rising and then falling. Temperature and methane desorption are not completely positive effects. Temperature may have a critical value for promoting methane desorption. The effect of temperature on the activation of gas molecules and the pore structure of coal should be considered comprehensively. As the pressure increases, the desorption hysteresis rate changes in a logarithmic downward trend, and the methane desorption hysteresis rate in the low-pressure stage (P<4MPa) is large, and the methane desorption hysteresis rate in the high-pressure stage (P>4MPa) is lower.

(2) In the isobaric adsorption process, the adsorption capacity of SH3# increased the fastest, SGZ11# followed, and DFS4# was the smallest. In the low pressure stage (P<4MPa), with the increase of pressure, the adsorption capacity increases significantly, but in the high pressure stage (P>4MPa), the adsorption capacity does not change significantly with pressure and gradually stabilizes. Under the same pressure, the molecular free path of methane increases with temperature. Under the premise of constant temperature, in the low pressure stage (0<P<4MPa), when the pressure continues to decrease, the free path of methane molecules increases significantly, which leads to a decrease in the diffusion capacity; In the high pressure stage (4<P<8MPa), when the pressure continues to decrease, the free path of methane molecules does not change significantly;

(3) DFS4#, SGZ11#, SH3# three coal samples, the intermediate adsorption heat in the desorption process is greater than the isometric adsorption heat in the adsorption process, indicating
that the desorption process needs to continuously absorb heat from outside the system. The energy
difference produced in the process of adsorption and desorption causes the desorption hysteresis
effect. The greater the difference in the isometric heat value of adsorption, the more significant the
hysteresis.

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Authors’ contributions
ZG conducted literature analysis and drafted the manuscript. DM and YC guided the
interpretation of the corresponding results, edited and improved the manuscript. JT and CZ were
major contributors in structuring and revising the manuscript. All authors read and approved the
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Availability of data and materials
The datasets used and/or analyzed during the current study are available from the
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Competing interests
The authors declare no competing financial interest.

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