Experimental Study on the Effects of Different Heating Rates on Coalbed Methane Desorption and an Analysis of Desorption Kinetics

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ABSTRACT: Heat injection is an effective way to enhance coalbed methane (CBM) extraction. However, at present, the best way to inject that heat is not clear. To determine how the heating rate affects methane desorption, desorption tests at constant high (95 °C) and low (20 °C) temperatures and at three different heating rates (0.3, 0.6, and 0.9 °C/min to 95 °C) were conducted. The desorption content (the volume of gas desorbed per mass of coal) and the desorption rate under the constant 95 °C temperature were greater than those under the constant 20 °C temperature. For the heating rate tests, the total desorption contents under heating rates of 0.3, 0.6, and 0.9 °C/min were 1.322 times, 1.115 times, and 1.095 times that from the constant 95 °C temperature tests, respectively. The final desorption contents from the entire desorption process under heating rates of 0.3, 0.6, and 0.9 °C/min were 1.42 times, 1.30 times, and 1.20 times that from the constant 95 °C temperature tests, respectively. In the early parts of the heating stages, the desorption rates under the three heating rate tests were lower than those under the constant 95 °C temperature tests. When the heating stages ended, the desorption rates under the three heating rates were greater than those under the constant 95 °C temperature tests. After the heating ended, the desorption rates decreased rapidly. A higher heating rate was correlated with a faster decrease in the desorption rate. Kinetic analysis showed that heating coal to a high temperature before methane is desorbed did not suppress the diffusion coefficient decrease. Heating during desorption prevented the diffusion coefficient decrease. A lower heating rate is correlated with a slower diffusion coefficient decrease. Low heating rates were more effective for desorbing methane. The heat injection in the later stage of desorption had a more significant effect on promoting methane desorption than did the early desorption stage heat injection. An equation for calculating the optimal heat injection rate was proposed. These findings will offer significant references for the selection of a suitable way to inject heat to enhance CBM extraction.

1. INTRODUCTION

Coal seam gas, predominantly methane, is a major risk threatening coal mine safety. The gas can cause gas outbursts and explosions. It can also increase mine ventilation system energy requirements and costs. That being said, the gas is also an unconventional but relatively clean energy source.1,2 Pre-drainage of coal seam gas before coal extraction can be a double benefit by turning a hazardous material into a valuable asset. Unfortunately, many of the coal seams in Chinese mines that would benefit from gas drainage have low permeability and transmissivity. This means that in many mines, the gas extraction efficiency is low, and this makes it difficult for the mines to reach the National legal limit for methane in mine air. This can seriously restrict coal mine production.3,4 For these reasons, many methods to stimulate gas extraction have been proposed, methods that enhance gas desorption and improve gas extraction. These methods include hydraulic fracturing,5 mining protected coal seams, hydraulic seam cutting,6 gas injected for enhanced coalbed methane recovery (ECBM),7 electrochemical treatments,8 blasting vibration,9 and microwave irradiation.10 However, all these methods encounter both economic and environmental problems. For example, hydraulic fracturing is banned in some regions, owing to potential environmental problems, and CO₂-ECBM requires special geological conditions and is not suitable for some reservoirs.11,12

A heat injection is a technique that has been applied in the petroleum industry for years to inject heat into petroleum reservoirs to lower the viscosity of petroleum and to improve the output efficiency.13 Recently, this technique has been employed for the coalbed methane (CBM) extraction.14–16 A heat injection raises the temperature of the coal reservoir by importing hot liquid or steam via ways like steam flooding,17 cyclic steam stimulation,18 or steam-assisted gravity drainage.19

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The results of Salmachi showed that a hot water injection can increase gas production by 58%. Teng et al. found that according to a thermo-hydro-mechanical model, a heat injection can greatly improve coal’s permeability. The theoretical basis for heat injection-enhanced CBM recovery is the effect high temperatures have on methane adsorption and desorption. Concerning temperature’s effect on methane adsorption, many researchers have concluded that at constant adsorption pressure, coal’s gas adsorption capacity decreases as temperature increases. This has been confirmed by numerous experiments at adsorption pressures ranging from 0.1 to 8 MPa and at temperatures from 20 to 200 °C. In addition, Shi et al. investigated the temperature characteristics during spontaneous combustion of coal under temperature-programmed conditions by numerical simulation and studied the evolution of the oxygen consumption rates in multiple stages of coal oxidation and the changes in the temperature and reaction rate.24−26

Table 1. Experimental Conditions Used by Tang et al., Li et al., and Jiang et al.

| scholars   | adsorption temperature (°C) | adsorption equilibrium pressure (MPa) | desorption temperature (°C) | desorption time |
|-----------|-----------------------------|--------------------------------------|-----------------------------|-----------------|
| Tang et al. | 30                          | 1.5                                  | 30, 50, 60, 70, and 80      | 1800 s         |
| Li et al.  | 20                          | 0.5                                  | 20, 30, 40, 50, and 60      | 20 min         |
| Jiang et al. | 20.3                      | 1.5                                  | 20.3, 30, 40, 45, and 50    | about 300 min   |

Temperature affects not only gas adsorption but also desorption and diffusion. Several researchers have revealed that raising the temperature of coal seams can promote the desorption and diffusion of methane. Among these studies, those of Tang et al., Li et al., and Jiang et al. are the most cited. Their experimental conditions are shown in Table 1. All these experiments have shown that a higher constant desorption temperature was correlated with a greater desorption content. However, their research has only investigated the changes in the desorption content (the volume of gas desorbed per mass of coal, cm³/g) at several high temperatures under specific adsorption pressures.

Previous research on the influence of temperature on methane desorption only considered desorption at high temperatures and did not investigate desorption under changing temperatures or the effects of heating rates. A preliminary study indicated that at a higher heating rate, more gas was desorbed from the coal. This shows that the rate of temperature increase had an effect on gas desorption, but this was only a preliminary and qualitative undertaking. Although the heat injection is considered to be an effective method for enhancing CBM extraction, additional research is required to find the most appropriate application procedures. Whether it is better to keep the coal seam at a high constant temperature or let the coal seam temperature fluctuate during the heat injection is a question that should be considered from both the performance and the energy usage points of view. Optimizing heat injection procedures can reduce heat consumption and save energy.

The aim of this study is to investigate the effect of heating rates on methane desorption from coal and to compare methane desorption under changing temperatures with desorption at a constant temperature. For this purpose, methane desorption experiments under different heating rates and constant temperatures using a self-developed, temperature-controlled experimental device have been carried out. Methane desorption rates and desorption kinetics under different heating rates are compared, and the ways in which heating enhances methane desorption are discussed. An optimum heating rate for enhancing methane desorption from coal is proposed.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1. Desorption Tests under Two Constant Temperatures. Isothermal desorption tests under high and low temperature (95 and 20 °C) were conducted to investigate the methane desorption at these two temperatures under three adsorption equilibrium pressures 0.9, 1.5, and 2.1 MPa. The desorption content–time curves from the tests are shown in Figure 1, and the desorption rate–time curves are shown in Figure 2. It can be seen from the figures that for the same adsorption equilibrium pressure, a higher desorption temperature is correlated with a greater desorption content and a higher desorption rate. At the same desorption temperature, a higher adsorption equilibrium pressure is correlated with a greater desorption content and a higher desorption rate. The average desorption rates under 0.9 MPa, CT-20 °C, 1.5 MPa, CT-20 °C, 2.1 MPa, CT-20 °C, 0.9 MPa, CT-95 °C, 1.5 MPa, CT-95 °C, and 2.1 MPa, CT-95 °C were 0.0229, 0.0312, 0.0349, and 0.0430 cm³/g min, respectively.

![Figure 1](https://doi.org/10.1021/acsomega.1c05562) Methane desorption content vs time for experiments run at 20 and 95 °C under adsorption equilibrium pressures of 0.9, 1.5, and 2.1 MPa.
pressures were 1.168 times, 1.10 times, and 1.076 times the desorption contents under the three adsorption equilibrium pressures. The heating stage time was 125 min and at that time, the desorption contents for the three adsorption tests (the average was 1.322 times). The HR-0.6 \( \times 10^3 \) \( ^{\circ} \text{C/min} \) heating tests, desorption contents are greater than those under the CT-20 \( ^{\circ} \text{C} \) tests but less than those under the CT-95 \( ^{\circ} \text{C} \) tests. After a certain amount of time, first the desorption content of the HR-0.9 \( ^{\circ} \text{C/min} \) test, then the desorption content of the HR-0.6 \( ^{\circ} \text{C/min} \) test, and finally the desorption content of the HR-0.3 \( ^{\circ} \text{C/min} \) test exceed that of the CT-95 \( ^{\circ} \text{C} \) tests. For the HR-0.9 \( ^{\circ} \text{C/min} \) heating rate tests at the adsorption equilibrium pressures of 0.9, 1.5, and 2.1 MPa, the experimental times at which HR-0.9 \( ^{\circ} \text{C/min} \) desorption exceeded those of the CT-95 \( ^{\circ} \text{C} \) tests were 60, 75, and 72 min, respectively. Similarly, the times at which HR-0.6 \( ^{\circ} \text{C/min} \) desorption at those same three adsorption pressures exceeded CT-95 \( ^{\circ} \text{C} \) desorption were 88, 104, and 103 min, respectively, and the correlative CT-95 \( ^{\circ} \text{C} \) "exceeding times" for the HR-0.3 \( ^{\circ} \text{C/min} \) tests were 112, 127, and 116 min, respectively. These "exceeding time" numbers indicate that for the same adsorption equilibrium pressure, the faster the heating rate, the shorter the time needed for the desorption content at that heating rate to exceed the desorption content from heating the coal at a constant high temperature.

The HR-0.3 \( ^{\circ} \text{C/min} \) heating stage time was 250 min and at that time, the desorption contents for the three adsorption equilibrium pressures tested were 1.302 times, 1.299 times, and 1.365 times the 250 min desorption content of the CT-95 \( ^{\circ} \text{C} \) tests (the average was 1.322 times). The HR-0.6 \( ^{\circ} \text{C/min} \) heating stage time was 125 min and at that time, the desorption contents under the three adsorption equilibrium pressures were 1.168 times, 1.10 times, and 1.076 times the 125 min desorption content of the CT-95 \( ^{\circ} \text{C} \) tests (the average was 1.115 times). For the HR-0.9 \( ^{\circ} \text{C/min} \) test, the heating stage was 83.3 min, and the multiples by which HR-0.9 \( ^{\circ} \text{C/min} \) desorption exceeded CT-95 \( ^{\circ} \text{C} \)’s 83.3 min desorption were 1.164 times, 1.05 times, and 1.07 times (average 1.095 times). These numbers show that the desorption contents at the end of the heating stages of the three heating rate tests exceeded the desorption contents of the constant high temperature tests for the same time.

Methane desorption rate—time curves for the heating stages of tests run at different heating rates under different adsorption equilibrium pressures are shown in Figure 4. For comparison, the desorption rate—time curves for the constant temperature tests are also shown. The desorption rates under the three heating rate tests were all higher than those under the low-temperature constant temperature tests (the CT-20 \( ^{\circ} \text{C} \) tests). In the initial desorption stages, the desorption rates under the three heating rate tests were lower than those under the high-temperature constant temperature tests (the CT-95 \( ^{\circ} \text{C} \) tests). During the CT-95 \( ^{\circ} \text{C} \) tests, as desorption progressed, the desorption rate decreased rapidly, but the desorption rates under the three heating rate tests decreased more slowly. At the end of their heating stages, the three heating test desorption rates were all higher than those observed in the high-temperature CT-95 \( ^{\circ} \text{C} \) constant temperature tests. At the same adsorption equilibrium pressure, the desorption rates increased, from HR-0.3 \( ^{\circ} \text{C/min} \) to HR-0.6 \( ^{\circ} \text{C/min} \) to HR-0.9 \( ^{\circ} \text{C/min} \). The desorption rates clearly increased at higher heating rates. These results showed that slower heating to the final temperature increased the rate at which methane is desorbed from coal, reduced the desorption rate decrease, and maintained a high desorption rate.

The results of this study showed that in the 20–95 \( ^{\circ} \text{C} \) temperature range, a higher heating rate was correlated with a higher average methane desorption rate, but the shorter duration of temperature increase is correlated with a smaller total desorption content. Conversely, a lower heating rate is correlated with a lower average methane desorption rate, but a longer duration of temperature increase is correlated with a greater total desorption content. For the 20–95 \( ^{\circ} \text{C} \) temperature range, since during the heat injection, the desorption rate is rapidly increased to save time, it is recommended that a higher heating rate is used. If total time is not an important consideration, it is recommended that a lower heating rate is used to obtain the best desorption content.

2.2. Desorption Tests at Different Heating Rates.

2.2.1. Desorption at Different Heating Rates. Methane desorption content—time curves for the heating stages of the tests run at different heating rates under different adsorption equilibrium pressures are shown in Figure 3. For comparison, the desorption content—time curves for the constant temperature tests are also shown. Figure 4 shows that for the same adsorption equilibrium pressure, in the initial stages of the heating rate tests, the desorption contents are greater than those under the CT-20 \( ^{\circ} \text{C} \) tests but less than those under the CT-95 \( ^{\circ} \text{C} \) tests. After a certain amount of time, first the desorption content of the HR-0.9 \( ^{\circ} \text{C/min} \) test, then the desorption content of the HR-0.6 \( ^{\circ} \text{C/min} \) test, and finally the desorption content of the HR-0.3 \( ^{\circ} \text{C/min} \) test exceed that of the CT-95 \( ^{\circ} \text{C} \) tests. For the HR-0.9 \( ^{\circ} \text{C/min} \) heating rate tests at the adsorption equilibrium pressures of 0.9, 1.5, and 2.1 MPa, the experimental times at which HR-0.9 \( ^{\circ} \text{C/min} \) desorption exceeded those of the CT-95 \( ^{\circ} \text{C} \) tests were 60, 75, and 72 min, respectively. Similarly, the times at which HR-0.6 \( ^{\circ} \text{C/min} \) desorption at those same three adsorption pressures exceeded CT-95 \( ^{\circ} \text{C} \) desorption were 88, 104, and 103 min, respectively, and the correlative CT-95 \( ^{\circ} \text{C} \) “exceeding times” for the HR-0.3 \( ^{\circ} \text{C/min} \) tests were 112, 127, and 116 min, respectively. These “exceeding time” numbers indicate that for the same adsorption equilibrium pressure, the faster the heating rate, the shorter the time needed for the desorption content at that heating rate to exceed the desorption content from heating the coal at a constant high temperature.

The HR-0.3 \( ^{\circ} \text{C/min} \) heating stage time was 250 min and at that time, the desorption contents for the three adsorption equilibrium pressures tested were 1.302 times, 1.299 times, and 1.365 times the 250 min desorption content of the CT-95 \( ^{\circ} \text{C} \) tests (the average was 1.322 times). The HR-0.6 \( ^{\circ} \text{C/min} \) heating stage time was 125 min and at that time, the desorption contents under the three adsorption equilibrium pressures were 1.168 times, 1.10 times, and 1.076 times the 125 min desorption content of the CT-95 \( ^{\circ} \text{C} \) tests (the average was 1.115 times). For the HR-0.9 \( ^{\circ} \text{C/min} \) test, the heating stage was 83.3 min, and the multiples by which HR-0.9 \( ^{\circ} \text{C/min} \) desorption exceeded CT-95 \( ^{\circ} \text{C} \)’s 83.3 min desorption were 1.164 times, 1.05 times, and 1.07 times (average 1.095 times). These numbers show that the desorption contents at the end of the heating stages of the three heating rate tests exceeded the desorption contents of the constant high temperature tests for the same time.

Figure 5, showing methane desorption—time curves for the tests run at different heating rates, is the same as Figure 3 except the curves that have been extended to show the data from the subsequent heating stages, the data between the end of the temperature-rise stages and 360 min. Similarly, the methane desorption rate—time curves, as shown in Figure 6, are the same as those shown in Figure 4 except the curves that
have been extended to include the data from the subsequent heating stages.

As shown in Figures 5 and 6, in the isothermal desorption stages after the heating stages, methane continues to desorb, and the desorption content increases, but the desorption rates decrease to different degrees. The test that shows the most rapid desorption rate decrease is SCT-95 °C versus HR-0.9 °C/min. As shown in Figure 6a, at about 240 min, the three SCT-95 °C versus HR-0.9 °C/min desorption content curves converge, and the desorption contents for the three different heating rates are equal. At 360 min, however, the final desorption content of SCT-95 °C versus HR-0.3 °C/min is the largest, and it is 2.39 times the CT-20 °C desorption content and 1.42 times that of CT-95 °C. Figure 6a also shows that the SCT-95 versus HR-0.6 sample desorption content is 2.20 times that of CT-20 °C and 1.30 times that of CT-95 °C and that HR-0.9’s desorption content is 2.03 times that of CT-20 °C and 1.20 times CT-95 °C. It can be seen from these experimental results that in the 20−95 °C range, although the desorption rates at the high heating rates are high during the heating stages, they decrease rapidly after heating is discontinued. For the low heating rate, although the desorption rates are relatively low during the heating stages, they decrease more slowly after heating ends. The lowest heating rate results in the highest final desorption content. These results indicate that a low heating rate is the most effective rate for enhancing methane desorption.

Figure 3. Desorption content vs time during the heating stages for the three heating rate tests (Table 3) run under different adsorption equilibrium pressures: (a) 0.9; (b) 1.5; and (c) 2.1 MPa. The curves for the constant rate heating tests are also shown.
When a gas desorption program is initiated in a mine, it is commonly observed that in the early desorption stages, the desorption rate is relatively high because of the pressure difference, but as desorption continues, the desorption rate decreases rapidly. When the rate of desorption has decreased significantly, external intervention measures are needed to assist gas extraction. For this reason, the heat injection in the later stages of a desorption program enhances methane extraction more significantly than does the heat injection in the early stages.

3. REAL-TIME METHANE DESORPTION KINETICS

To study desorption further, a dynamic diffusion model was applied to assess the kinetics of methane desorption from coal.

3.1. Dynamic Diffusion Model. The unipore model is a classic model widely applied to represent methane desorption from coal. In this model, eq 1 is used to express the relationship between the desorption time and the quantity of desorbed methane.

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{r_0^2}\right)$$

Figure 4. Desorption rate vs time during the heating stages for the three heating rate tests (Table 3) run under different adsorption equilibrium pressures: (a) 0.9; (b) 1.5; and (c) 2.1 MPa. The curves for the constant rate heating tests are also shown.
where $D$ denotes the diffusion coefficient, cm$^2$/s; $r_0$ denotes the average radius of the coal particles, cm; $t$ denotes time, s; $Q_{\infty}$ denotes the total desorption amount of methane after infinite time, cm$^3$/g; and $Q_t$ denotes the cumulative desorption amount of methane in time $t$, cm$^3$/g. The variable $D$ in eq 1 is supposed to be a constant during desorption but, in fact, for methane−coal, it is not a constant. For methane−coal, the diffusion coefficient is time dependent due to the variations in the methane concentrations and the surface-to-volume ratios of coal granules. The diffusion coefficient in the unipore model cannot accurately reflect the actual methane diffusion.\textsuperscript{36,37}

In this study of methane desorption under different heating rates, the process considered is increasing temperature. The equivalent diffusion coefficient $D_{eq}$ is commonly used to represent the diffusivity of gas when there are temperature variations during diffusion. In the light of the Arrhenius equation, the relationship between $D_{eq}$ and temperature is given by\textsuperscript{28}

$$D_{eq} = D_{\text{initial}} \exp \left(-\frac{E_0}{RT} - 1.5 \right)$$

where $D_{\text{initial}}$ denotes the initial value of $D_{eq}$ m$^2$/s; $T$ denotes the thermodynamic temperature, K; $R$ denotes the universal gas constant, kJ/mol K; and $E_0$ denotes the temperature-
independent activation energy, kJ/mol. From Eq. 2, it can be deduced that a higher temperature is correlated with a greater diffusion coefficient. Therefore, the unipore model is not suitable for representing the kinetics of methane desorption from coal that is being heated. A new diffusion model, called a dynamic diffusion model, was put forward in 2016 by Li et al.\textsuperscript{35} It is the model used in this work. In this new model, the diffusion coefficient is no longer regarded as a constant. Instead, it has a negative exponential relation with time, as shown in Eq. 3:\textsuperscript{35}

$$D(t) = D_0 \exp(-\beta t)$$

where $D_0$ denotes the initial value of the diffusion coefficient at $t = 0$, cm$^2$/s; $D(t)$ denotes the dynamic diffusion coefficient at time $t$, cm$^2$/s; $t$ denotes the time, s; and $\beta$ denotes the attenuation coefficient of $D(t)$, s$^{-1}$. The equation for the dynamic diffusion model is

$$Q_t = Q_\infty - \frac{6 \pi^2}{n^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_0}{r_0^2 \beta} \left(1 - e^{-\beta t}\right)\right)$$

In Eq. 4, the value of $r_0$ is 0.0375 cm, and the value of $Q_\infty$ is the difference between the adsorption amount, $Q_{eq}$, at an adsorption equilibrium pressure ($p = 0.9$, 1.5, or 2.1 MPa for

Figure 6. Desorption rate vs time for the three heating rate tests (Table 3) run under different adsorption equilibrium pressures: (a) 0.9; (b) 1.5; and (c) 2.1 MPa. The curves for the constant rate heating tests are also shown.
this work) and $Q_a$, the adsorption amount at atmospheric pressure. $Q_p$ and $Q_a$ can be calculated from eq 5\textsuperscript{35}

$$Q = \frac{abp}{1 + bp} \left( \frac{100 - A_{ad} - M_{ad}}{100(1 + 0.31M_{ad})} + \frac{10p\varphi 273}{\rho(273 + t_w)} \right)$$

where $t_w$ denotes the temperature of the saturated salt water, °C; $\varphi$ denotes the apparent relative density of the coal sample, g/cm$^3$; $\varphi$ denotes the porosity of the coal sample, %; $M_{ad}$ denotes the mass percent of moisture in the coal sample, %; $A_{ad}$ denotes the ash content of the coal sample, %; $p$ denotes the methane pressure at equilibrium, MPa; $b$ denotes the inverse of the Langmuir pressure, MPa$^{-1}$; $a$ denotes the Langmuir volume, cm$^3$/g; and $Q$ denotes the equilibrium adsorption amount of methane at a given pressure and temperature, cm$^3$/g.

3.2. Analysis of Methane Desorption Kinetics at Different Heating Rates Created. The desorption parameters in the dynamic diffusion model are acquired by carrying out nonlinear regressions. The curves created by means of these regressions and the curves from the experimental data are displayed in Figures 7–9; the regression parameters and determination coefficients can be seen in Table 2. It can be concluded from Figures 7–9 and Table 2 that the dynamic diffusion model fits the experimental data for both desorption tests under constant temperatures and those under different heating rates rather well. All determination coefficients for the regression curves exceed 0.98.

The equation for the dynamic diffusion coefficient $D(t)$ is obtained from $D_0$ and $\beta$, as listed in Table 2, and eq 3. Figure 10 shows graphs of the dynamic diffusion coefficients $D(t)$ versus time for the tests at the three adsorption equilibrium

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**Figure 7.** Curves showing experimental data and fitted data under an adsorption equilibrium pressure of 0.9 MPa at two constant temperatures and three increasing temperatures in °C/min: (a) constant 20 °C; (b) constant 95 °C; (c) increasing 0.9 °C; (d) increasing 0.6 °C; and (e) increasing 0.3 °C.
pressures. Figure 10 and Table 2 show that the $D_0$ and $\beta$ values behave in the same way under each of the adsorption equilibrium pressures. The $D_0$ value is the highest for CT-95 °C and the lowest for CT-20 °C. The $D_0$ values for the three heating rates are between those for CT-95 °C and CT-20 °C, and they decrease in order from HR-0.9 °C/min to HR-0.6 °C/min to HR-0.3 °C/min. This shows that the initial diffusion coefficients are closely related to the initial temperatures. The variate $\beta$ stands for a physical quantity that reflects the extent to which $D(t)$ decreases. A smaller value of $\beta$ is correlated with less decrease. It is worth noting that when the value of $\beta$ becomes negative, the value of $D(t)$ does not decrease but increases with time.

It can be obtained from Table 2 that the $\beta$ values are positive for the constant temperature tests, CT-20 °C and CT-95 °C, but negative for the three heating rate tests. The CT-95 °C $\beta$ values are larger than the CT-20 °C $\beta$ values. Accordingly, Figure 10 shows that although both the CT-20 °C and CT-95 °C diffusion coefficients decrease gradually with time, the diffusion coefficients for CT-95 °C decreases faster than those for CT-20 °C. These results show that under a constant high temperature, although the desorption content increases, diffusion coefficient decrease is not prevented; instead, it is accelerated. This means that heating coal to a high temperature, before methane is desorbed, cannot retard diffusion coefficient decrease; instead, it increases it.

As for the three heating rates, the $\beta$ values gradually increase from HR-0.3 °C/min to HR-0.6 °C/min and HR-0.9 °C/min. The dynamic diffusion coefficients increase gradually with time, and the heating rates increase in the ascending order from HR-0.9 °C/min to HR-0.6 °C/min to HR-0.3 °C/min. This shows that the heating can effectively prevent diffusion

Figure 8. Curves showing experimental data and fitted data under an adsorption equilibrium pressure of 1.5 MPa at two constant temperatures and three increasing temperatures in °C/min: (a) constant 20 °C; (b) constant 95 °C; (c) increasing 0.9 °C; (d) increasing 0.6 °C; and (e) increasing 0.3 °C.
coefficient decrease and that a lower heating rate is correlated with a slower decrease. Slow heating is more effective for methane desorption than fast heating.

4. DISCUSSION

Temperature has a significant effect on the adsorption and desorption of methane. Many research studies have indicated that coal’s methane adsorption ability is negatively related to temperature, but that methane desorption is positively correlated with temperature. In addition, higher temperature resulted in faster and more complete desorption of the methane.38,39 High temperatures can raise the kinetic energy of methane molecules adsorbed to the coal matrix. With more energy, the molecules are more likely to possess enough energy to surmount the adsorption potential energy barrier and to escape from the coal matrix. As a result, more methane is released under higher temperatures. In coal, methane desorption is endothermic, and increasing the coal’s temperature can supply energy to increase desorption.38

Different heating methods stimulate methane desorption in different ways. In this work, when methane is desorbed under a constant high temperature, the initial desorption rate and diffusion coefficient are high, but at the later stages, because of the reduction in the methane’s partial pressure in the coal, the force driving desorption is insufficient, and desorption slows. As desorption continues, the desorption rate goes down, and the rate of decrease in the desorption rate increases. Heating at a continuously increasing temperature can increase the kinetic energy of the adsorbed methane molecules and also increase the internal energy of those molecules considerably. The heat provides a persistent driving force for desorption so that the methane molecules can escape more easily. Longer heating
time, that is, a longer period in which the heat continues to be increased, is associated with a greater force driving the desorption in the later desorption stages and a slower decrease in the desorption rate. In the tests conducted for this study, the HR-0.3 °C/min heating time was the longest; therefore, the attenuation coefficient was the lowest, and the decrease in the desorption rate was also the lowest.

The heat calculation equation \( Q_H = mc(\Delta t) = mc(\Delta t) \) (\( Q_H \) denotes the amount of heat addition or heat rejection, kJ; \( m \) denotes the quality, kg; \( c \) denotes the specific heat, kJ/kg°C; \( t_1 \) denotes the initial temperature, °C; \( t_2 \) denotes the final temperature, °C; and \( \Delta t \) denotes the temperature difference, °C) means that the same mass of the same substance needs the same amount of heat to be added to increase its temperature from a lower temperature \( t_1 \) to a higher temperature \( t_2 \). Therefore, the amount of heat required to raise the temperatures of the samples of coal used in the three different heating tests is the same. In addition, considering the heat lost from keeping the coal samples at 95 °C, the heat lost by the 95 °C constant temperature tests, the CT-95 °C tests, is the largest because those samples were maintained at 95 °C for the longest time. The heat lost by the other tests were, in the descending order, HR-0.9 °C/min, HR-0.6 °C/min, and HR-0.3 °C/min (see Figure 12 for 95 °C retention times).

Table 2. Experimental Conditions for the Heating Rate Experiments and Regression Parameters for the Regression Curves, as Shown in Figures 7–9

| Adsorption equilibrium pressure | Experimental condition | \( D_0 \) \((10^{-3} \text{ cm}^2/\text{s})\) | \( \beta \) \((\text{s}^{-1})\) | Determination coefficient \( R^2 \) |
|--------------------------------|------------------------|---------------------------------|-----------------|---------------------|
| 0.9 MPa                        | CT-20 °C               | 1.62                            | 0.00009020      | 0.9950              |
|                                 | CT-95 °C               | 9.45                            | 0.00009159      | 0.9989              |
|                                 | HR-0.3 °C/min          | 4.53                            | -0.00012209     | 0.9978              |
|                                 | HR-0.6 °C/min          | 5.32                            | -0.00010908     | 0.9891              |
|                                 | HR-0.9 °C/min          | 7.98                            | -0.00004723     | 0.9819              |
| 1.5 MPa                        | CT-20 °C               | 3.48                            | 0.00014608      | 0.9973              |
|                                 | CT-95 °C               | 12.70                           | 0.00014932      | 0.9984              |
|                                 | HR-0.3 °C/min          | 4.84                            | -0.00009670     | 0.9987              |
|                                 | HR-0.6 °C/min          | 6.04                            | -0.00007554     | 0.9849              |
|                                 | HR-0.9 °C/min          | 7.63                            | -0.00003348     | 0.9836              |
| 2.1 MPa                        | CT-20 °C               | 3.71                            | 0.00015465      | 0.9905              |
|                                 | CT-95 °C               | 11.32                           | 0.00017563      | 0.9999              |
|                                 | HR-0.3 °C/min          | 4.47                            | -0.00009050     | 0.9997              |
|                                 | HR-0.6 °C/min          | 5.51                            | -0.00004989     | 0.9959              |
|                                 | HR-0.9 °C/min          | 6.98                            | -0.00001587     | 0.9873              |

Figure 10. Dynamic diffusion coefficients \( D(t) \) vs time for two constant temperatures and three increasing temperatures at different adsorption equilibrium pressures: (a) 0.9; (b) 1.5; and (c) 2.1 MPa.
HR-0.6 °C/min, and HR-0.3 °C/min. Presumably, this is a benefit of using a slowly increasing temperature.

To summarize, in the 20–95 °C temperature range, desorbing methane from coal using a constant high temperature produces the least satisfactory result. Overall, methane desorption using heating to cause a continuous temperature increase is better than maintaining a constant high temperature. A lower heating rate correlates with better desorption. This study finds that a 0.3 °C/min heating rate is optimal. In the tests conducted for this study, a heating time of 250 min consumed approximately two-thirds of the total desorption time of 360 min. Considering the amount of methane produced by this heating rate and the limited desorption time, it is suggested that when this desorption technique is used, the heating time should be two-thirds of the allowed desorption time. In the remaining desorption time, high desorption will continue, owing to the inertial force of the desorption caused by continuous heating. At the same time, it ensures a larger desorption content in the early stage. Therefore, the recommended optimal heating rate is

\[
\text{optimal heating rate} = \frac{2}{3} \times \frac{\text{high temperature} - \text{low temperature}}{\text{allowed desorption time}}
\]

5. CONCLUSIONS

For the same adsorption equilibrium pressure, both the desorption content and the desorption rate under a constant high temperature are greater than those under a constant low temperature.

In the early parts of the heating stages, the desorption contents and desorption rates under the three heating rate tests are all greater than the desorption contents and rates under the low constant temperature tests but less than those under the high constant temperature tests. At the end of the three heating stages, however, the total desorption contents and desorption rates during the heating stages are greater than those of the high constant temperature tests. The total desorption content under the heating rate is on average 1.18 times that from the constant 95 °C temperature tests. The total desorption contents and desorption rates under the three heating rate tests exceed that from the high constant temperature tests. A lower heating rate is correlated with a slower decrease. Low heating rates desorb methane more effectively. The heat injection in the later stage of desorption has a more significant performance on enhancing methane desorption than the early desorption stage heat injection. An equation for calculating the optimal heat injection rate is proposed.

6. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

6.1. Sample Preparation. The coal samples for this study were taken from the two coal seams of the Julishan coal mine, Jiaozuo City, Henan province, China. The samples used in the experiments, with high gas adsorption and low permeability coal, were collected from a single site and then ground into powder in the laboratory and sieved with a metal sieve to produce specimens with a particle size of 0.5–1 mm. The specimens were then dried using a drying oven. After drying, the prepared specimens were kept in a dry environment. To make the results of different experiments comparable, fresh portions with the same quality of the dried coal sample were employed in each experiment. A GF-A2000 automatic proximate analyzer was used for physical analysis, and the results were as follows: ash 12.40%; moisture 2.1%; and volatile matter 8.62%. The isothermal tests were conducted using the volumetric method. The Langmuir adsorption constant \( a \) was 37.62 cm³/g, and the Langmuir adsorption constant \( b \) was 1.69 MPa⁻¹.

6.2. Methane Desorption and Measurement Equipment (the “Experimental Device”). The self-developed testing system or experimental device for methane desorption was composed of a gas adsorption and desorption canister, a temperature-controlled water bath, a temperature measuring unit, gas supply and measuring units, a cooling water bath, and a vacuum pump (Figure 11). The temperature-controlled water bath was manufactured by Shanghai Laboratory Instrument Works Co., Ltd.; it can maintain any temperature between 5 and 95 °C with a temperature fluctuation of ±0.05 °C. High purity 99.99% CH₄ was used as the adsorption gas. The gas supply unit comprised a gas cylinder, a precision pressure gauge, a buffer tank, a reducing valve, and a pipeline. The gas measuring unit gathered and measured the desorbed gas by means of the water displacement method. To ensure the temperature of the desorbed gas was close to room temperature before it was measured, the pipeline passed through a cooling water bath to reduce the temperature of the desorbed gas. The temperature measuring unit was composed...
of a digital temperature display regulator, a thermocouple, and a filter capacitor. The thermocouple was a WRC-T-type thermocouple with a precision of ±0.5 °C and was manufactured by Anhui Huilun Instrument Co., LTD.

6.3. Testing Procedures. For this study, two types of desorption tests were conducted, desorption tests under constant temperatures and desorption tests at different heating rates. Constant temperature desorption tests were conducted at two temperatures, room temperature (20 °C) and 95 °C. These desorption tests were designated as CT-20 °C and CT-95 °C, and the test conditions are shown in Figure 12a. The different heating rate tests were carried out at three different heating rates, namely, 0.3, 0.6, and 0.9 °C/min to a final temperature of 95 °C. These desorption tests were called HR-0.3 °C/min, HR-0.6 °C/min, and HR-0.9 °C/min, and the test conditions are shown in Figure 12b. The heating rates were set according to the experimental requirements. First, the relationship of integer multiples among the three heating rates made it easy to compare the experimental results. Second, most of the temperature-rise times (250, 125, and 83.3 min) under 0.3, 0.6, and 0.9 °C/min were between 1/4 and 2/3 of the total desorption time (360 min), which was conducive to analyzing the change in desorption characteristics during the heating stages and the post-heating stages. The methane adsorption stage preceding each experiment was carried out under the same pressure and at room temperature (20 °C).

All the desorption tests included pre-adsorption degassing, methane adsorption, and then desorption testing, and all test conditions, except for desorption temperatures, were the same. The detailed experimental conditions are listed in Table 3 and are summarized below.

1. Degassing. Before starting each experiment, the testing system was checked to ensure no seals were leaking. A dried specimen was then placed in the adsorption−desorption canister. Then, valve 16, as shown in Figure 11, was opened, and the specimen was degassed through the vacuum pump for not less than 6 h.

2. Adsorption. After the coal sample was degassed, valve 16 was closed, and valve 15 was linked to the methane supply unit and opened. The adsorption−desorption canister was filled with 99.99% methane and kept at 20 °C for about 24 h until equilibrium was attained. Generally, the gas pressure in the coal sample tank decreased by 0.02 MPa within 1 h, and it was considered that the coal sample had attained the adsorption equilibrium. All adsorptions were carried out at 20 °C.

3. Desorption. After equilibrium was attained, valve 15 was shut, and valve 17 was opened. The adsorption−desorption canister was connected with the atmosphere, and the free methane in the canister was quickly discharged. Once the pressure of the canister reduced to atmospheric pressure, valve 17 was shut, and valve 18 was immediately opened. Since the canister was

Table 3. Experimental Conditions for the Constant Temperature and Different Heating Rates of Methane Desorption Experiments

| test type                          | desorption temperature | duration of temperature conditions (min) | duration at 95 °C (min) | adsorption equilibrium pressure (MPa) | room temperature (°C) | desorption time (min) |
|-----------------------------------|------------------------|------------------------------------------|-------------------------|---------------------------------------|-----------------------|-----------------------|
| desorption tests under constant temperature | CT-20 °C | 360                                         | no                      | 0.9                                   | 20                    | 360                   |
|                                   | CT-95 °C  | 360                                         | 360                     | 0.9                                   | 20                    | 360                   |
| desorption tests under different heating rates | HR-0.3 °C/min | 250                                         | 110                     | 0.9                                   | 20                    | 360                   |
|                                   | HR-0.6 °C/min  | 125                                         | 235                     | 0.9                                   | 20                    | 360                   |
|                                   | HR-0.9 °C/min  | 83.3                                         | 276.7                   | 0.9                                   | 20                    | 360                   |

Figure 12. Time−temperature conditions for the desorption tests: (a) constant temperatures tests and (b) heating rate tests.
connected with the methane measurement cylinder, the methane desorption volume could be measured. The methane desorption volume versus time was recorded. For the first 120 min, the data recording interval was 10 s, and after 120 min, the data recording interval was 30 s. The desorption rate (cm$^3$/g/min) was calculated as the ratio of desorption volume increment to time increment. The duration of each methane desorption experiment was 6 h. Desorption temperatures, as shown in Figure 12, were controlled by the temperature-controlled water bath. For the constant temperature (95 °C) experiment, after adsorption equilibrium at 20 °C, the coal sample temperature was slowly increased to 95 °C for about 25 h.

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Z.W. conceived and designed the study, analyzed the data, discussed the results, and wrote the manuscript text. Z.Z. performed the experiments, analyzed the data, and prepared figures and tables.

Notes
The authors declare no competing financial interest.

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