Experimental Study on Replacing Coal Seam CH₄ with CO₂ Gas

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ABSTRACT: In recent years, many studies have reported the mechanism of CH₄ stimulation by gas injection. However, the studies have focused only on monitoring CH₄ and CO₂ in the tail gas. Thus, it is difficult to distinguish the adsorbed and free gas in the coal and rock and accurately calculate the CO₂/CH₄ replacement ratio in the displacement process. The low-field NMR technology can effectively overcome the drawbacks of the traditional displacement experiments and distinguish the free and adsorbed gas in the coal and rock. In the present study, the NMR technology analyzed the T₂ spectrum for the CH₄ desorption amount and CO₂/CH₄ displacement efficiency in the replacement of methane with gaseous CO₂. The results suggested the following: (1) the process of CO₂ gas replacing CH₄ can be divided into three stages: the initial stage of competitive adsorption, the dominant stage of competitive adsorption, and the weakening stage of competitive adsorption. (2) The cumulative desorption of CH₄ gas increases with the increase in replacement time. With the increase in temperature, it first increases and then decreases, and the extreme value is obtained at about 40 °C. Additionally, the greater the CO₂ injection pressure is, the greater the cumulative desorption of CH₄ is. (3) The cumulative replacement ratio is positively correlated with the replacement time, and with the increase in replacement time, the increment in the cumulative replacement ratio decreases gradually and the upward trend tends to be stable. Overall, the cumulative displacement ratio would increase with an increase in the CO₂ injection pressure. With the increase in temperature, the maximum value of the cumulative replacement ratio first increases and then decreases, and the extreme value obtained is about 5.49 at 40 °C.

1. INTRODUCTION

China’s high-gas mines account for more than 40% of the total number of mines, and 95% of that are the low permeability coal seams.1,2 Therefore, permeability-modifying technologies, such as hydraulic fracturing and protective layer mining, are extensively used.3–5,30 Among these, inspired by the “gas displacement” technology of the petroleum system, carried out at the end of the 20th century, the experiment of injecting CO₂ into the coal seam to improve the CBM recovery (CO₂-ECBM) in the San Juan basin, United States, was successful, which explored a new technical way for the rapid gas drainage of low-permeability coal seam.6 CO₂ injection into a coal reservoir can realize CO₂ geological storage.7 It can also provide a high-pressure potential difference, effectively improving the gas production rate of the production hole, promoting the CH₄ desorption in the coal seam, and promoting gas drainage and outburst elimination.8,9 Therefore, the technology of using CO₂ gas displacement to replace coal seam CH₄ can not only realize mine safety production and protect the atmospheric environment but also help make full use of the underground resources and improve the mine’s economic benefits.

Many researchers have studied the mechanism of CH₄ stimulation by gas injection.10–15 Huo et al.16 observed that the increase in CO₂ injection pressure increases the CH₄ recovery and CO₂ storage rates. Sun et al.17 divided the enhanced production process into three stages: initial depressurization, medium-term CO₂ adsorption and replacement, and, finally, the CH₄ and CO₂ coproduction stage. COMSOL was used to simulate the process, and the study concluded that increasing the injection pressure could greatly improve the CO₂ storage and CH₄ gas production rate.18,19 Extensive research has been performed on the corresponding operating factors, such as the gas injection pressure, mode, and type, to optimize the gas injection displacement technology.5,20,21 Notably, all these studies believed that the experimental process is divided into two stages: seepage diffusion and competitive adsorption.22 Competitive adsorption mainly occurs between the adsorbed gases, and seepage diffusion mainly occurs between the free gases. However, all the above studies monitored CH₄ and CO₂ in the tail gas.23–25 Further, it is challenging to distinguish the adsorbed and free gas

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in the coal rock. In the traditional experiment of replacing CH₄ with CO₂ gas, the free CH₄ gas in the coal sample is often considered to be in the adsorbed state, leading to inaccurate calculations, and the CO₂/CH₄ replacement ratio in the displacement process cannot be calculated. The low-field nuclear magnetic resonance (NMR) technology can effectively overcome the drawbacks of traditional displacement experiments to distinguish the free and adsorbed gas in coal and rock. In addition, although a large number of scholars have applied the NMR technology to the experiment of coal adsorbing methane, no one has used the magnetic resonance imaging technology to carry out the experiment of CO₂ gas displacing CH₄ gas.

Based on the NMR technology, the present study designed static experiments of the CO₂ displacement of CH₄ gas to investigate the displacement behavior between the adsorbed gases in this process.

2. EXPERIMENTAL DEVICE AND STEPS

2.1. Experimental Principle. NMR spectroscopy detects the hydrogen nuclei (H₁) in methane in coal pores and fissures. The signal amplitude of the NMR spectrum is directly proportional to the methane quality within the detection range. The gas quality of the coal and rock fracture in a single hole corresponds to the ordinate amplitude of the T₂ spectrum. The ordinate amplitude integral of the T₂ spectrum curve can be used to characterize the gas quantity of the coal and rock fracture hole. The existence of the coal rock porous medium structure makes the NMR transverse relaxation time of pore fissure methane much smaller than that of free-state methane. Different pore diameters in porous media correspond to different transverse relaxation times. Combined with the NMR spectrum characteristic test of free-state gas, micropores, medium—large pores, fractures, and unrestricted free space can be quantitatively divided in the NMR T₂ spectrum. Then, the adsorbed and free gas quantity can be obtained by integrating the ordinate of the T₂ spectrum.

According to the principle of nuclear magnetic resonance, the transverse relaxation time T₂ follows the following formula

\[ \frac{1}{T_2} \approx \rho_2 \left( \frac{S}{V} \right) + \frac{1}{T_{2B}} + \frac{D(\gamma GT_0)^2}{12} = F_2 \frac{\rho_2}{r} \]  
(1)

where T₂ is the gas relaxation time, given in milliseconds; \( \rho_2 \) is the transverse surface relaxation strength, given in micrometers per millisecond; S is the pore surface area of the coal measure shale, given in square centimeters; V is the pore volume of coal, given in cubic centimeters; D is the CH₄ diffusion coefficient, given in square micrometers per millisecond; G is the magnetic field gradient, given in gauss per centimeter; \( \gamma \) is the gyromagnetic ratio, given in radian per second per tesla; and \( T_0 \) is the echo interval, given in milliseconds.

Since the T₂ value is 2000~3000 ms, which is much greater than the T₁ value of gas in the coal sample, and the magnetic field uneveness of the NMR equipment is less than 35 ppm and the echo interval, the last two items in formula 1 can be ignored

\[ \frac{1}{T_2} \approx \rho_2 \left( \frac{S}{V} \right) \]  
(2)

The pore structure of the actual coal seam is extremely complex, and the specific surface area of coal pores has a nonlinear relationship with the pore diameter. For the convenience of analysis, it is assumed that all coal pores and roar channels have a columnar pore structure, which gives

\[ \rho_2 \left( \frac{S}{V} \right) = F_2 \frac{\rho_2}{r} \]  
(3)

\[ r = cT_2 \]  
(4)

where \( F_2 \) is the geometric factor, with \( F_2 = 2 \) for the columnar pore structure, and is dimensionless; \( r \) is the average pore radius, given in micrometers; A is the surface area, given in square micrometers; and C is the conversion coefficient, given in micrometers per millisecond.

According to formula 4, the value of the transverse relaxation time T₂ of gas NMR in the coal body corresponds to the pore radius r. The T₂ spectrum distribution can be used to evaluate the pore size and pore size distribution. The longer the transverse relaxation time is, the greater the pore fracture radius is. As a typical porous medium material, coal gas mainly exists in the pore structure, and the T₂ spectrum amplitude integral represents the total detectable gas signal. Therefore, the T₂ spectrum amplitude integral is used to represent the actual gas adsorption capacity of coal samples, and the gas adsorption law in the process of CO₂ replacing coal seam CH₄ is quantitatively studied in this paper.

During the experiment, the following relationship exists for the CH₄ gas

\[ V_{\text{de}(CH_4)} = V_{\text{ads}(CH_4)} - V_{\text{ad}(CH_4)} \]  
(5)

\[ V_{\text{free}(CH_4)} = V_{\text{de}(CH_4)} + V_{\text{free}(CH_4)} \]  
(6)

where \( V_{\text{de}(CH_4)} \) is the desorption amount of CH₄, \( V_{\text{ads}(CH_4)} \) is the initial adsorption capacity of CH₄, \( V_{\text{ad}(CH_4)} \) is the amount of residual CH₄ adsorption at time \( t_i \), \( V_{\text{free}(CH_4)} \) is the free CH₄ gas volume at time \( t_i \), and \( V_{\text{free}(CH_4)} \) is the free CH₄ gas volume at the beginning of the experiment.

The partial pressure of free CH₄ gas at time \( t_i \) is as follows

\[ P_{\text{free}(CH_4)} = \frac{Zn_i(CH_4)RT}{V_{\text{free}(CH_4)}} \]  
(7)

where \( P_{\text{free}(CH_4)} \) is the partial pressure of CH₄ gas in the free state at time \( t_i \), \( Z \) is the compression factor of the mixture at the experimental temperature, \( R \) is the general gas constant, that is, 8.314 J/(mol·K), \( T \) is the temperature in kelvin, and \( V_0 \) is the volume of the free space.

According to Dalton’s partial pressure law, the partial pressure of CO₂ at time \( t_i \) can be obtained as follows

\[ P_{\text{free}(CO_2)} = P_i - P_{\text{free}(CH_4)} \]  
(8)

Therefore, the amount of free-state CO₂ at time \( t_i \) is

\[ V_{\text{free}(CO_2)} = \frac{Zn_i(CO_2)RT}{P_{\text{free}(CO_2)}} \]  
(9)

Moreover, the amount of adsorbed CO₂ is as follows

\[ V_{\text{ads}(CO_2)} = V_{0(CO_2)} - V_{\text{free}(CO_2)} \]  
(10)

2.2. Experimental Scheme and Steps. The conventional methods could destroy the primary pore fracture system of coal or produce some artificial secondary fracture in the sample preparation process, resulting in huge errors. The low-field NMR relaxation time analysis technology is a new detection technology, which can overcome these shortcomings. The analysis principle involves the quantitative characterization of the pore structure and fluid filling attributes of a hydrogen-
containing fluid (1H core) in coal seam through the relaxation time and signals’ amplitude.

The instrument used in the experiments is mainly composed of a low-field NMR detector, a coal sample container, pneumatic valves, a gas storage tank, a pressure control unit, a temperature sensor, a vacuum pump, and gas cylinders, as shown in Figure 1.

The present study used the long-flame coal of (9–15) 08 working face of the Liuhuanggou coal mine in Xinjiang as the samples for the experiments. Table 1 shows the industrial analysis of the coal sample. Before the experiment, the coal sample was crushed to 80 mesh and dried at 80 °C in the drying oven. After drying, CH₄ was replaced by gaseous CO₂ at 20–60 °C with an injection pressure of 0–6 MPa. The detailed experimental steps are as follows:

1. The pulverized coal was placed into the coal sample tank, and its quality was recorded. Then, valve 1 was closed, valves 2–6 were opened, and all the valves were closed after the vacuum treatment for 8 h.

2. According to the ISO 12213:2006 natural gas calculation of the compression factor, the compression factor for helium at different pressures (20–60 °C) was calculated. According to the equation of state \( PV = nRT \), the \( V_{\text{reference}} \) was calculated to be 44.87 mL and \( V_{\text{sample}} \) was calculated to be 33.39 mL.

3. Valves 1–4 were opened, and the CH₄ gas was continuously injected into the reference tank and the sample tank at 2.0 MPa pressure. After the pulverized coal adsorption for 12 h, the reference tank and sample bin pressures were recorded.

4. Valves 1 and 3 were closed, and valves 2, 4, and 5 were opened. The CH₄ gas-filled reference tank was emptied using the vacuum pump for 8 h.

5. Valve 5 was closed, and valves 1, 2, and 4 were opened. 2.0 MPa CO₂ was filled into the reference tank. Valve 1 was closed when it was stable, and valve 3 was opened to start the replacement of CH₄ gas with CO₂ gas. The experimental data were continuously recorded for 12 h.

6. At the end of the experiment, valves 2–5 were opened to drain.

7. Experimental steps 3–6 were repeated, and the CO₂ gas was injected at 3, 4, 5, and 6 MPa pressures in turn.

### 3. RESULTS AND DISCUSSION

Through the calibration experiment of coal adsorbing methane, the corresponding relationship between the mass of free methane and the signal amplitude can be obtained, as shown in Figure 2.

It can be seen from the figure that the mass of methane is directly proportional to the signal amplitude integral of the NMR \( T_2 \) spectrum. The greater the mass of CH₄ is, the greater

![Figure 2. Fitting curve between the free-state methane mass and the signal amplitude integral.](https://doi.org/10.1021/acsomega.1c06050)
the signal amplitude integral is, which conforms to the linear relationship, and the fitting coefficient $R^2$ is determined to be as high as 0.9999. Therefore, when we obtain the NMR $T_2$ spectrum of CH$_4$, we can use the fitting curve between the signal amplitude integral and CH$_4$ mass to calculate the amount of free CH$_4$ at different temperatures and pressures and then calculate the amount of adsorbed CH$_4$ and other parameters.

3.1. $T_2$ Spectrum Analysis. The NMR relaxation time analysis is one of the most important techniques in the industrial application of low-field NMR. In the coal reservoir, hydrogen nuclei exist in the coal matrix and reservoir fluid. There is a huge difference in the NMR characteristics of the hydrogen nucleus in these two environments. By selecting appropriate measurement parameters, signals related to pore fluid and independent of coal base block skeleton can be detected. The essence of the coal reservoir system research based on low-field NMR was to analyze the occurrence state of the multiphase fluid in the coal reservoir. It also included establishing the microscopic interaction mechanism between the coal reservoir and fluid using the surface relaxation and free relaxation characteristics of gas in the coal pores. The $T_2$ spectrum of CH$_4$ during the experiment is illustrated in Figures 3–5 below:

The $T_2$ relaxation time is associated with the binding force and degree of freedom of the hydrogen proton. Further, the binding degree of the hydrogen proton is closely related to the sample’s internal structure. Specifically, the smaller the pore size is, the more bound the methane in the pore will be, leading to a shorter relaxation time. Thus, it can be considered as the adsorption state. Longer relaxation time could indicate the free state. As shown in Figures 3 and 4, the amount of adsorbed CH$_4$...
decreased and the amount of free CH₄ gas increased with an increase in replacement time. After opening the connecting valve, the CO₂ gas could enter the coal sample tank under the pressure drive, which could have promoted the desorption of CH₄ gas in the coal sample through competitive adsorption, resulting in the adsorbed CH₄ gas amount decrease and free CH₄ gas amount increase in the coal sample.

3.2. Analysis of the Gas Change Law in the Replacement Process. 3.2.1. Effect of CO₂ Injection Pressure. 3.2.1.1. CH₄ Desorption by Stages. Low-field NMR (Mesomr12-060 h-i) software was used to analyze the T₂ spectrum adsorption peak area and free peak area. The amount of adsorbed CH₄ gas and free CH₄ gas at different times and under different CO₂ injection pressures can be measured. According to eqs 9 and 10, the amount of adsorbed CO₂ and free CO₂ and the displacement efficiency under various conditions can be calculated. The relationship between the stage desorption amount of CH₄ and the displacement time and pressure is shown in Figure 5.

Figure 5 indicates that in the P₁ stage (0−120 min), the staged desorption of CH₄ gas decreased rapidly, and in the P₂ stage (120−480 min), the staged desorption of CH₄ gas was increased steadily. At the P₃ stage (480−720 min), the staged desorption of CH₄ gas gradually decreased. The result could be because at the opening of the connecting valve in the P₁ stage, the gas pressure in the coal microcrack was increased when the CO₂ gas entered the coal sample tank. The increase in gas pressure hinders the desorption of CH₄. Thus, the staged desorption of CH₄ decreased rapidly. At the P₂ stage, the natural desorption of CH₄ was weakened, and the displacement of CO₂ gas dominated this stage. Although the staged desorption of CH₄ was continuously increasing, it tended to be stable. When it reached the P₃ stage, there was little residual adsorbed CH₄ in the coal, the replacement of adsorbed CH₄ by CO₂ gas became difficult, and the competitive adsorption was weakened, resulting in the continuous decline of the stage desorption capacity of CH₄ gas. Therefore, the process of replacing CH₄ with CO₂ can be divided into three stages: the initial stage of competitive adsorption, the dominant stage of competitive adsorption, and the weakening stage of competitive adsorption.

3.2.1.2. CH₄ Cumulative Desorption. The relationship between the stage desorption amount of CH₄ and the displacement time and pressure is shown in Figure 6.

Figure 6 shows that the cumulative desorption amount of CH₄ gas increases with the replacement time, and the greater the CO₂ gas injection pressure is, the greater the cumulative desorption of CH₄ gas is. However, at an injection pressure higher than 5 MPa, the influence of CO₂ injection pressure on the cumulative desorption of CH₄ gas is weakened. This is because when the gas injection pressure of the microcracks in the coal is higher than 5 MPa, the gas pressure causes the micropores in the coal to reach their expansion extreme value, so they cannot accommodate more adsorption sites. If the gas pressure cannot enable its microcracks to continue to expand to accommodate more adsorption sites, the continuous increase in pressure will not have a great impact on the desorption capacity of CH₄ gas.

In order to more clearly observe the effect of CO₂ gas injection pressure on the cumulative desorption of CH₄ gas, the experimental time of 12 h is taken as an example, and the results are given in Table 2.

Table 2. Relationship between the Increase in CH₄ Cumulative Desorption and CO₂ Gas Injection Pressure

| CO₂ injection pressure (MPa) | increase in desorption capacity compared with the previous pressure point (%) |
|-----------------------------|----------------------------------------------------------------------------------|
| 3                           | 1.60                                                                              |
| 4                           | 12.99                                                                             |
| 5                           | 10.84                                                                             |
| 6                           | 8.15                                                                              |

At 4 MPa, the increase in CH₄ gas cumulative desorption reaches the extreme value. When the CO₂ injection pressure increases from 3 to 4 MPa, the increase in the CH₄ cumulative desorption amount reaches a maximum, which is 12.99%.

3.2.2. Effect of Temperature. 3.2.2.1. CH₄ Desorption by Stages. Taking the CO₂ injection pressure of 4 MPa as an example, the relationship between the stage desorption amount of CH₄ gas and temperature is shown in Figure 7.

Figure 7. Relationship between the stage desorption amount of CH₄ gas and temperature.
Figure 7 shows that the relationship between the stage desorption amount of CH₄ and the replacement time is consistent with the above conclusions. That is, the process of replacing CH₄ with CO₂ gas can be divided into three stages: the initial stage of competitive adsorption, the dominant stage of competitive adsorption, and the weakening stage of competitive adsorption. At the same time, it can be seen that under the influence of temperature, the stage desorption amount of CH₄ reaches the maximum at 40 °C. The order of the desorption amount of CH₄ at different temperatures from large to small is 40, 50, 60, 30, and 20 °C. This is because the desorption of methane in coal is an endothermic reaction. Desorption essentially means that the adsorption speed of adsorbate molecules on the adsorbent surface is less than its leaving speed. The formation of the interaction between the adsorbate and adsorbent needs to release energy, and the fracture of the weak bond between them also needs to absorb energy from the surrounding. Therefore, the increase in temperature is beneficial to the desorption. However, when the temperature exceeds 40 °C, the activity of free CH₄ gas increases and the partial pressure of CH₄ gas increases, which hinders the desorption of CH₄.

3.2.2.2. CH₄ Cumulative Desorption. The relationship between the CH₄ cumulative desorption and temperature is shown in Figure 8:

![Figure 8. Relationship between CH₄ cumulative desorption and temperature.](image)

The cumulative desorption of CH₄ increases with the increase in replacement time. Under the influence of temperature, the cumulative desorption of CH₄ gas reaches the maximum at 50 °C.

In order to more clearly see the effect of temperature on the cumulative desorption of CH₄, the case with the CO₂ injection pressure of 4 MPa and the experimental time of 600 min is taken as an example, and the results are given in Table 3.

Compared with that at 20 °C, the cumulative desorption of CH₄ measured at 50 °C increased the most, about 54.54%. This is because the desorption of CH₄ is an endothermic process. When the temperature increases to 40–50 °C, the increase in temperature provides energy for the desorption of CH₄ and promotes the desorption of CH₄. When the temperature is higher than 50 °C, due to the increase in the amount of free CH₄ and the coal having not been discharged in time, the increase in temperature will reduce the density of CH₄ in the coal and increase the gas partial pressure, which hinders the desorption of CH₄.

### 3.3. Replacement Efficiency Analysis.

The stage displacement ratio and cumulative displacement ratio were introduced to characterize the relationship between CO₂ adsorption and CH₄ desorption. According to Avogadro’s law, any gas with the same volume at a certain temperature and pressure contains the same number of molecules. It also suggests that the gas volume ratio must be equal to the number of molecules at the same temperature and pressure. The relationship between different gases at the same temperature and pressure can be obtained as

\[
\frac{n_1}{n_2} = \frac{V_1}{V_2}
\]

Therefore, the stage replacement ratio can be defined as the ratio of CO₂ staged adsorption to CH₄ staged desorption, as given in eq 11.

\[
S = \frac{A_1}{D_1}
\]  

Here, S is the stage replacement ratio, \(A_1\) is the staged adsorption capacity of CO₂ in mole, and \(D_1\) is the staged desorption of CH₄ in mole.

The cumulative displacement ratio is defined as the ratio of cumulative CO₂ adsorption to cumulative CH₄ desorption, as shown in eq 12.

\[
C = \frac{A_2}{D_2}
\]

C is the cumulative replacement ratio, \(A_2\) is the cumulative adsorption capacity of CO₂ in mole, and \(D_2\) is the cumulative desorption of CH₄ in mole.

Figure 9 shows that the stage replacement ratio of CO₂/CH₄ increased with an increase in the replacement time. The stage replacement ratio shows a rapid growth trend before 120 min, a relatively stable state between 120 and 480 min, and a rapid upward trend after 480 min. This may be because in the initial S1 stage (before 120 min), CO₂ gas quickly occupies the remaining adsorption site after entering the coal. Moreover, because part of CH₄ gas is replaced by competitive adsorption, this stage includes not only the natural adsorption of CO₂ gas but also the competitive adsorption of CO₂ and CH₄, resulting in the fact that the stage adsorption amount of CO₂ is much greater than the stage desorption amount of CH₄. Therefore, the stage replacement ratio increases rapidly. With further progress of the experiment, competitive adsorption dominates in the S2 stage (120–480 min), resulting in the steady growth of the stage replacement ratio in this stage. With the increase in experimental time, the reduction of the residual adsorbed CH₄ in coal makes CH₄ desorption more challenging. However, the competitive adsorption of CO₂ and CH₄ increases the adsorbed CO₂ amount in coal. Thus, the stage replacement ratio increases rapidly in the S3 stage.

| Temperature (°C) | Increase of CH₄ cumulative desorption (relative to 20 °C) (%) |
|-----------------|-------------------------------------------------------------|
| 30              | 52.67                                                       |
| 40              | 39.26                                                       |
| 50              | 54.54                                                       |
| 60              | 48.31                                                       |

Table 3. Effect of Temperature on the Cumulative Desorption of CH₄
At the same time, it can be seen that the stage replacement ratio of the coal sample increases with the increase in CO$_2$ injection pressure, but this law is not very obvious. The reason may be that the stage adsorption amount of CO$_2$ and stage desorption amount of CH$_4$ are not only related to the injection pressure of CO$_2$ gas but also related to the parameters such as micropore expansion, permeability, and the diffusion rate of coal.

The stage replacement ratio of coal samples first increased and then decreased with the increase in temperature, and it reached the peak at 40 $^\circ$C. The reason is that the formation of the interaction between the adsorbate and adsorbent needs to release energy, and the fracture of the weak bond between them also needs to absorb energy from the surrounding. The adsorption of CO$_2$ by coal is an exothermic reaction, while the desorption of CH$_4$ gas is an endothermic reaction. The higher the temperature is, the more conducive it is to the desorption of CH$_4$ gas but not to the adsorption of CO$_2$ gas. Therefore, after 40 $^\circ$C, with the increase in temperature, the stage adsorption amount of CO$_2$ decreases and the stage desorption amount of CH$_4$ increases, resulting in the decrease of the stage replacement ratio.

Figure 9. Staged replacement ratio of CO$_2$/CH$_4$.

Figure 10 shows that the cumulative replacement ratio is positively correlated with the replacement time, and with the increase in replacement time, the cumulative replacement ratio increases rapidly at first and then tends to become stable gradually. This is because when the replacement time is less than 60−120 min, after opening the connecting valve, CO$_2$ gas will first quickly occupy the remaining adsorption position in the coal sample, and then replace CH$_4$ in the coal due to competitive adsorption. From the previous analysis of CH$_4$ desorption capacity, the CH$_4$ desorption capacity is less at this stage, while the CO$_2$ adsorption capacity increases rapidly. It can be seen that the increment of CO$_2$ adsorption capacity is much greater than that of CH$_4$ desorption capacity. Therefore, in the P1 stage, the cumulative replacement ratio of the three coal samples increases rapidly. In the 60−600 min period, it can be seen from the above analysis that in this stage, CO$_2$ gas has filled the remaining adsorption sites. At this time, the competitive adsorption of CO$_2$ gas and CH$_4$ gas occupies the dominant position, so the cumulative replacement ratio in this stage shows a slow upward trend. When the experimental time exceeds 600 min, the adsorbed CO$_2$ has reached saturation, there is little residual adsorbed CH$_4$ in the coal sample, and the CH$_4$ gas that can be replaced is also decreasing. Therefore, the cumulative
replacement ratio of CO₂/CH₄ tends to be stable in the later stage of the experiment. In addition, there is no obvious change law between the cumulative replacement ratio and the increase in CO₂ injection pressure.

Table 4 shows that at 2 and 6 MPa CO₂ injection pressures, the maximum cumulative displacement ratios were about 3.61 and 4.25, respectively. Overall, the cumulative displacement ratio increases with an increase in the CO₂ injection pressure. With the increase in temperature, the maximum value of the cumulative replacement ratio first increases and then decreases, and the extreme value is about 5.49 at 40 °C.

4. CONCLUSIONS

Based on nuclear the NMR technology, the stage desorption amount, cumulative desorption amount, stage replacement ratio, and cumulative replacement ratio of CH₄ under different CO₂ injection pressures and temperatures are deeply analyzed. The effects of CO₂ injection pressure and experimental temperature were studied. The main conclusions are as follows:

(1) Through the study of the change law of CH₄ gas in the replacement process, it is concluded that the stage desorption amount of CH₄ increases with the increase in CO₂ injection pressure. Under the influence of temperature, the stage desorption amount of CH₄ first increases and then decreases, reaching the maximum at 40 °C. According to the variation law of the stage desorption amount of CH₄ with replacement time, the process of CO₂ gas replacing CH₄ can be divided into three stages: the initial stage of competitive adsorption, the dominant stage of competitive adsorption, and the weakening stage of competitive adsorption.

(2) Variation law of the cumulative desorption of CH₄ gas: the cumulative desorption of CH₄ gas increases with the increase in replacement time. With the increase in temperature, it first increases and then decreases, and the extreme value is obtained at about 40 °C. Additionally, the greater the CO₂ injection pressure is, the greater the cumulative desorption of CH₄ gas is. However, when the CO₂ injection pressure is higher than 4 MPa, the effect of CO₂ injection pressure on the cumulative desorption of CH₄ gas is weakened.

(3) The cumulative replacement ratio is positively correlated with the replacement time, and with the increase in replacement time, the increment in the cumulative replacement ratio decreases gradually, and the upward trend tends to be stable. Overall, the cumulative displacement ratio increases with an increase in the CO₂ injection pressure. With the increase in temperature, the maximum value of the cumulative replacement ratio first increases and then decreases, and the extreme value is about 5.49 at 40 °C.

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