Pore Structure Characteristics and Adsorption and Desorption Capacity of Coal Rock after Exposure to Clean Fracturing Fluid

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ABSTRACT: In the hydraulic fracturing process, fracturing fluid contacts coal rock and physical and chemical reactions occur, which inevitably damage the pore structure of the coal rock and affect the adsorption and desorption capacity of the coal rock. In this paper, a low-temperature N₂ adsorption method and scanning electron microscopy (SEM) were used to characterize coal samples. Using gas adsorption/desorption tests, high-, medium-, and low-rank coal samples before and after the clean fracturing fluid treatment were systematically studied. According to the relationship between coal pore structure parameters and gas adsorption/desorption characteristics, a correlation between the microscopic pore structure and the macroscopic gas adsorption/desorption characteristics of coal was obtained. The results show that the number of closed pores in high-, medium-, and low-rank coal samples increased after the clean fracturing fluid treatment. The micropore volume increased by 0.0009, 0.00143, and 0.0035 mL/g, respectively, and the specific surface area increased by 4.87, 9.06, and 57.60%. The fractal dimension also increased compared with that of raw coal. SEM analysis indicated that the influence degree of clean fracturing fluid treatment on the pore structure of different-rank coal samples was Gengcun low-rank coal > Pingba middle-rank coal > Jiulishan high-rank coal. The experimental results of methane adsorption and desorption showed that the adsorption capacity of the coal samples after clean fracturing fluid treatment was enhanced, which is related to increases in the micropore proportion, micropore volume, and specific surface area of the coal. The desorption capacity of the coal samples was also enhanced. The desorption rate of medium- and high-rank coal samples increased after the clean fracturing fluid treatment but that of low-rank coal samples decreased. The main reason is the increase in the number of micropores in low-rank coal, which enhances the gas adsorption ability and makes gas desorption difficult. Therefore, clean fracturing fluid is suitable for medium- and high-grade metamorphic coalbed methane mines. These research results provide a theoretical basis for the application of clean fracturing fluid in different coalbed methane wells.

1. INTRODUCTION

China is rich in coalbed methane resources, ranking third in the world. As an efficient and low-pollution energy resource, it has a high utilization value. Due to the low-permeability characteristics of many coal reservoirs in China, in order to improve the mining efficiency of coalbed methane and improve the underground working environment, it is necessary to implement fracturing stimulation measures for coal reservoirs. At present, the main means of coal bed gas mining in China is hydraulic fracturing, which can effectively improve the flow environment of gas in coal seam and improve the gas production of coal seam. It is an important technology for coal seam gas mining. At the same time, with the continuous progress and improvement of coal seam hydraulic fracturing technology, more and more enterprises are using this technology to extract underground gas and prevent gas outburst. However, due to the heterogeneity and anisotropy of the coal seam itself, the foreign compounds are more sensitive. After the fracturing fluid is injected into the coal seam, the physical and chemical properties of the coal body are changed, so that the whole coal seam is damaged.¹ The fracturing fluid is an important part of the hydraulic fracturing stimulation. With the development of many years, the fracturing fluid system has experienced the development process of oil-based fracturing fluid, water-based fracturing fluid, clean fracturing fluid, and foam fracturing fluid. Due to its good viscosity, shear resistance, and rheological properties, clean fracturing fluid does not need cross-linking agents and gel breakers, causes little damage to the reservoir, forms no
Gradually increased. Kang and Li used external solution on small molecular compounds in coal. The study found that with the passage of time, the effect of external solution to soak Baode, Jincheng, and Hancheng coal samples. The study found that with the passage of time, the effect of external solution to soak Baode, Jincheng, and Hancheng coal samples.

Huang et al.12 found that on one hand, hydraulic fracturing affects the surface of coal samples, and the effect of different types of fracturing fluids on coal reservoirs is relatively less. In order to further explore the suitability of clean fracturing fluid in different coal seams, three coal samples with different coal ranks were selected to study the effects of clean fracturing fluid on the pore microstructure and adsorption/desorption characteristics of different coal rocks in various aspects and levels by the low-temperature N2 adsorption experiment, scanning electron microscopy (SEM) experiment, and methane adsorption/desorption experiment. On this basis, the correlation between the coal microscopic pore structure and macroscopic gas adsorption/desorption characteristics is further revealed, which provides a theoretical basis for the application of clean fracturing fluid in different coalbed methane wells.

2. EXPERIMENTS AND METHODS

2.1. Preparation and Industrial Analysis of Coal Samples. Three coal samples with different coal ranks were selected for the experiment. The experimental coal samples were anthracite (high rank) from the Julishan mine, coking coal (middle rank) from the Pingba no. 8 mine, and long bituminous coal (low rank) from the Gengcun mine. The clean fracturing fluid was ionic surfactant +1% KCl solution. Ionic surfactants are widely available and have a low price; at very low concentrations, they can form a high-viscosity gel, which is a good raw material for viscoelastic fracturing fluids. KCl inhibits clay expansion, dissolves adsorbed macromolecules in coal samples, and reduces the surface tension of the solution, which is conducive to reflow and reduces the damage to the coal sample caused by the solution. Furthermore, KCl has good compatibility with coal.

After crushing and screening, the three selected coal samples were processed into particles ranging from 0.18 to 0.25 mm in size and dried in a vacuum drying box at 100 °C for 10 h. After cooling, the particles were sealed and preserved. A small amount of each dried coal sample was used for industrial analysis. The moisture, ash content, total volatile content, combustible volatile content, and fixed carbon content of the coal samples were determined. The results of industrial analysis are shown in Table 1. The coal classification is based on the “Chinese Classification of Coals” (GB/T 5751-2009).

2.2. Experimental Method. The three dried coal samples were weighed. The same mass of each sample was placed in a separate beaker; then, an identical concentration and mass of clean fracturing fluid was added to each beaker. After soaking

| coal sample     | moisture | ash   | total volatiles | combustible volatiles | fixed carbon | coal rank |
|-----------------|----------|-------|-----------------|-----------------------|--------------|-----------|
| Julishan mine   | 1.52     | 24.90 | 20.60           | 7.70                  | 52.98        | high      |
| Pingba mine     | 0.95     | 9.95  | 23.30           | 26.15                 | 65.80        | medium    |
| Gengcun mine    | 4.15     | 11.75 | 35.02           | 41.64                 | 49.08        | low       |
(a) Adsorption/desorption curves of Jiulishan high-rank coal before and after fracturing fluid treatment

(b) Adsorption/desorption curves of Pingba medium-rank coal before and after fracturing fluid treatment

(c) Adsorption/desorption curves of Gengcun low-rank coal before and after fracturing fluid treatment

Figure 1. Adsorption/desorption curves of the coal samples. (a) Adsorption/desorption curves of Jiulishan high-rank coal before and after fracturing fluid treatment. (b) Adsorption/desorption curves of Pingba medium-rank coal before and after fracturing fluid treatment. (c) Adsorption/desorption curves of Gengcun low-rank coal before and after fracturing fluid treatment.
for 24 h at room temperature, the coal samples were rinsed with deionized water until the solution became clear. Finally, the samples were dried in a vacuum drying oven at 100 °C for 15 h and used for experiments.

1) Low-temperature N\textsubscript{2} adsorption experiment: using a V-Sorb 2800 TP specific surface area and pore size analyzer produced by Beijing Jin’s spectrum company, the coal samples before and after fracturing treatment were put into the instrument. At constant temperature and pressure, the gas reached adsorption equilibrium on the solid surface, and the adsorption amount was a function of relative pressure. The adsorption/desorption curves can be obtained by measuring the adsorption amount under different relative pressures. The specific surface area is calculated according to the BET theoretical model, and the pore volume distribution is calculated using the BJH theoretical model.

2) SEM: SEM can more intuitively and clearly show the surface morphology and internal pore structure of solid particles. A FEI Quanta 250 FEG-SEM field-emission environmental scanning electron microscope (FEI-SEM) from FEI Corporation of the United States was used to magnify the coal samples before and after clean fracturing fluid treatment by 10,000 times to observe the surface morphology and pore characteristics.

3) Methane adsorption and desorption: the coal samples after nitrogen adsorption and desorption experiments were treated with equilibrium moisture, and the prepared coal samples with different coal ranks were loaded into a closed coal sample tank by using a self-developed high-temperature triaxial CBM desorption and seepage experimental device. A certain amount of methane was filled into the tank, and the adsorption equilibrium was achieved after a period of adsorption. The pressure values of buffer tanks before and after the adsorption equilibrium pressure balance of each group of

Figure 2. Coal sample pore volume distribution before and after clean fracturing fluid treatment. (a) Jiulishan high-rank coal. (b) Pingba middle-rank coal. (c) Gengcun low-rank coal.
experimental coal samples were recorded successively. After reaching the balance, the rapid pressure relief reduced the pressure gauge of the coal sample tank to 0, and the valve of the desorption instrument was immediately opened. The measured gas desorption amount at different time points was measured by the drainage gas collection method.

3. ANALYSIS OF EXPERIMENTAL RESULTS

3.1. Results of Nitrogen Adsorption Analysis of Coal Samples. 3.1.1. Analysis of Adsorption Isotherms and Pore Shape of Coal Samples. According to the hysteresis loop type of the adsorption isotherm, coal pores can be divided into five types: cylindrical (A), slit (B), wedge (C, D), and ink bottle (E). According to their connectivity, pores can be divided into four types: connected pores, internal connected pores, dead end pores, and closed pores. Since the first three types of pores are connected, they are called openings and greatly affect the adsorption and desorption ability of coal.

The nitrogen adsorption isotherms of different-rank coal samples after clean fracturing fluid treatment are shown in Figure 1.

Figure 1a shows the adsorption/desorption curves of high-rank coal from Jiulishan. The adsorption/desorption curves are between 0 and 1; the two curves are always separated and do not intersect when the relative pressure is 0–0.2. This phenomenon shows that there are more micropores than other pores in Jiulishan high-rank coal and the pore connectivity is poor. Nitrogen is not easily desorbed after being adsorbed, so there are more cylindrical micropores with one closed end than other pore shapes in Jiulishan high-rank coal.

Figure 1b shows the adsorption/desorption curves of medium-rank coal from the Pingba no. 8 coal mine. The adsorption/desorption curves are between 0 and 1, and the two curves basically coincide. The results show that the medium-rank coal from Pingba is mainly composed of pores with a closed cylinder at one end and an open slit on four sides. The relative pressures required for this pore structure in the adsorption and desorption processes are basically equal, so the two curves are minimally separated.

Figure 1c shows the adsorption/desorption curves of the Gengcun low-rank coal. The adsorption/desorption curves are basically coincident at relative pressures of 0–0.5 and 0.9–1.0, which indicates that there are many open and semiclosed pores in Gengcun low-rank coal. However, when the relative pressure is 0.5, the curves show an obvious inflection point that corresponds to ink bottle pores.

Figure 1 shows that although the adsorption isotherms of the three different-rank coal samples belong to different types, the adsorption isotherms of the coal samples after soaking in clean fracturing fluid are all of the same type. The adsorption isotherms of the three different-rank coal samples in Figure 1 show that the treated coal samples have a larger nitrogen adsorption volume at the highest relative pressure and smaller hysteresis loops than the raw coal, which indicates a larger proportion of closed holes in coal samples treated with clean fracturing fluid.12

3.1.2. Pore Size Distribution of Coal Samples. The volume distribution of micropores, minipores, and mesopores in the coal samples before and after the clean fracturing fluid treatment is shown in Figure 2.

Figure 2 shows that after clean fracturing fluid treatment, the micropore volume of high-rank coal increased from 0.0015 to 0.0028 mL/g, that of medium-rank coal increased from 0.0013 to 0.0025 mL/g, and that of low-rank coal increased from 0.0012 to 0.0047 mL/g. The proportions of micropores, minipores, and mesopores in coal samples will increase compared with those in raw coal after the treatment with clean fracturing fluid for high-, medium-, and low-rank coal. When acidic clean fracturing fluid contacts an immersed coal sample, it will continuously corrode small molecules on the coal surface and form more micropores. When CH2−NH2− groups in coal and rock contact clean fracturing fluid, three processes occur: physical adsorption, chemical adsorption, and chemical reactions, which greatly change the chemical bonds of the groups. When the old chemical bonds are broken, new chemical bonds are generated. Simultaneously, inorganic substances in coal and rock will react with the clean fracturing fluid, which increases the number of micropores, minipores, and mesopores in coal samples. The clean fracturing fluid had the greatest impact on the pore structure of the low-rank coal from Gengcun, followed by the medium-rank coal from the Pingba coal mine and the high-rank coal from Jiulishan.

3.1.3. Specific Surface Area of Coal Samples. The change in the specific surface area of different coal samples before and after the fracturing fluid treatment is shown in Table 2.

Table 2 shows that the specific surface area of the high-rank coal after treatment increased by 0.17 m2/g, that is, an increase of 4.9%. The specific surface area of the middle-rank coal after treatment increased by 0.0062 m2/g, that is, an increase of 9.1%. The specific surface area of the low-rank coal after treatment increased by 0.936 m2/g, that is, an increase of 57.6%. Thus, regardless of the rank of the coal samples, after the clean fracturing fluid treatment, the specific surface area increased relative to that of the raw coal samples. The Gengcun low-rank coal showed the largest increase in the specific surface area, followed by the Pingba middle-rank coal and finally the Jiulishan high-rank coal. After the acidic clean fracturing fluid contacts a coal sample, the surface of the coal sample is corroded, and the number of micropores, minipores, and mesopores in the coal sample increases, which increases the total specific surface area of micropores, minipores, and mesopores in the coal sample. Therefore, the coal samples treated with clean fracturing fluid had a larger specific surface area than the untreated coal samples. With the deterioration
degree of coal samples from low to high, more complete pore development corresponds to less damage caused by clean fracturing fluid to the pore structure. Moreover, due to the increase in the pore volume of the coal samples after fracturing fluid treatment, especially the increase in the micropore volume, the surface area increased. Therefore, the low-rank coal from Gengcun showed the largest increase in the specific surface area, followed by the medium-rank coal from the Pingba mine and finally the high-rank coal from Jiulishan.

3.1.4. Coal Surface Fractal Analysis. Coal has a complex pore structure, the analysis of which is also complex. Fractal geometry is the most effective method to describe the pore structure of coal. At present, the Frenkel–Halsey–Hill (FHH) model is commonly used.\(^\text{16,17}\) It can be described as follows

\[
\ln(V/V_m) = C + S \ln(\ln(p/p_s)) \tag{1}
\]

where \(V\) is the volume of adsorbed gas at equilibrium pressure \(p\), \(V_m\) is the volume of monolayer adsorbed gas, \(p_s\) is the saturated pressure, and \(C\) and \(S\) are related constants.

When \(p\) is small, the adsorption interface is affected by van der Waals forces.

\[
S = \frac{D - 3}{3} \tag{2}
\]

When the coverage is high, the adsorption interface is affected by the surface tension.

\[
D = S + 3 \tag{3}
\]

For a smooth plane, \(D = 2\); greater roughness of the plane corresponds to higher values of \(D\).\(^\text{18,19}\)

Fractal analysis of the coal samples with different ranks before and after the clean fracturing fluid treatment was performed according to FHH fractal theory. Taking the Pingba middle-rank coal as an example, the fractal analysis diagram of the coal samples is shown in Figure 3.

According to the isothermal adsorption curve obtained from the low-temperature \(N_2\) adsorption experiment, \(\ln V\) was used to plot \(\ln(\ln(p/p_s))\), where \(S\) is the slope; then, \(D\) was obtained according to \(S\). Generally, the range of \(D\) is 2–3. When \(-1 < S < -1/3\), eq 3 should be selected. When \(-1/3 < S < 0\), eq 2 should be selected.\(^\text{17–19}\)

The classification results of the coal samples before and after clean fracturing fluid treatment are shown in Figure 3 and Table 3. Table 3 shows that the surface fractal dimensions of all coal samples were between 2 and 3, regardless of the coal rank and whether treatment with clean fracturing fluid was performed; the coal samples treated with clean fracturing fluid generally had larger surface fractal dimensions than the raw coal, increasing is in the following order: Gengcun low-rank coal > medium-rank coal from the Pingba coal mine > high-rank coal from Jiulishan. These calculated results are consistent with the results of the pore specific surface area analysis. After the clean fracturing fluid treatment, the number of internal pores, the specific surface area, and the surface fractal dimension of the coal samples increased.

To further verify the above low-temperature liquid nitrogen experimental results, coal samples before and after the clean fracturing fluid treatment were observed by SEM, as shown in Figure 4.

![Fractal analysis of a coal sample. (a) Pingba middle-rank coal before treatment. (b) Pingba middle-rank coal after treatment.](https://doi.org/10.1021/acsomega.2c00436)

![Fractal analysis of a coal sample. (a) Pingba middle-rank coal before treatment. (b) Pingba middle-rank coal after treatment.](https://doi.org/10.1021/acsomega.2c00436)

| type of coal sample          | specific surface area \(A/(m^2 \cdot g^{-1})\) | \(S\)     | fractal dimension \(D\) | increase in fractal dimension/% | \(R^2\)  |
|------------------------------|---------------------------------------------|-----------|------------------------|-------------------------------|---------|
| Jiulishan high-rank coal     | 3.49                                        | -0.365    | 2.635                  | 1.82                          | 0.9615  |
| Jiulishan high-rank coal     | 3.66                                        | -0.317    | 2.683                  | 1.82                          | 0.9583  |
| Pingba middle-rank coal      | 0.684                                       | -0.5897   | 2.4103                 | 1.82                          | 0.9488  |
| Pingba middle-rank coal      | 0.746                                       | -0.5114   | 2.4857                 | 1.82                          | 0.9908  |
| Gengcun low-rank coal        | 1.625                                       | -0.6581   | 2.3419                 | 1.82                          | 0.9891  |
| Gengcun low-rank coal        | 2.561                                       | -0.5465   | 2.4535                 | 1.82                          | 0.9523  |
The SEM results showed that after soaking in the clean fracturing fluid, the surface roughness of coal and rock increased, there were obvious corrosion marks on the surface, and the cracks on the surface of the coal samples significantly increased. The immersion of coal samples in clean fracturing fluid corrodes the surface of coal and rock, dissolves small molecular substances on the surface of the coal, and forms new cracks, causing the surface of coal samples treated with clean fracturing fluid to appear pitted. The SEM results are consistent with the results of the previous pore structure analysis.

### 3.2. Results of Methane Adsorption and Desorption Capacity Analysis of Coal Samples

#### 3.2.1. Analysis of Adsorption Results

Methane isothermal adsorption experiments were performed at 30 °C on raw coal samples and coal samples treated with clean fracturing fluid. The experimental results are shown in Table 4.

Table 4 shows that under an adsorption equilibrium pressure of 0.5 MPa, the adsorption capacity of high-, medium-, and low-rank coal for methane was 2.58, 1.55, and 0.85 mL/g, respectively. After the clean fracturing fluid treatment, the methane adsorption capacity of coal samples significantly increased compared with that before the treatment: the methane adsorption capacity of high-, medium-, and low-rank coal increased by 0.28 mL/g (10.9%), 0.53 mL/g (34.2%), and 0.87 mL/g (102.4%), respectively. The clean fracturing fluid treatment had the greatest influence on the methane adsorption capacity of the low-rank coal, followed by...
the medium-rank coal, and finally the high-rank coal. The reason for this finding is that after clean fracturing fluid soaks a coal sample, physical and chemical reactions occur with the compounds in the coal, which change the pore structure inside the coal, increase the number of micropores in the coal, and increase the specific surface area of coal samples with different coal ranks. The increase in the specific surface area increases the adsorption area of methane gas, which increases the amount of methane gas adsorption. Based on the measured methane adsorption capacity, micropore volume, micropore volume ratio, and specific surface area, Figure 5 shows the relationship between the coal sample adsorption capacity and micropore proportion of coal samples.

Figure 5, Relationship between adsorption capacity and micropore proportion of coal samples.

From Figure 5, it can be seen that the adsorption capacity of experimental coal samples increases linearly with the proportion of micropores, which is mainly due to the fact that micropores largely determine the gas adsorption capacity of coal.20 The pore size of micropores is small, and the potential energy field formed between the pore walls is superimposed, which enhances the interaction energy of the coal pore surface and methane molecules, thus enhancing the gas adsorption capacity. This is also the reason why gas adsorption is mostly concentrated on the surface of micropores. It can be seen from Figure 6 that the increase in adsorption capacity of coal samples is positively correlated with the increase in the micropore volume and specific surface area. The specific surface area of coal is mainly contributed by micropores, and the greater the specific surface area of coal, the greater the adsorption capacity of gas. The gas adsorption capacity of coal samples with pore volume in each pore section is mainly affected by the pore volume. The main reason is that the potential energy field formed between the pore walls of the micropores enhances the interaction energy between the coal pore surface and the methane molecule. At the same time, some microporous pore surfaces are not only filled with molecular layers but also filled with methane molecules. Therefore, the specific surface area and micropore volume of coal samples are the main factors for the increase in adsorption capacity. After clean fracturing fluid treatment, the micropore volume, micropore proportion, and specific surface area of coal samples all increased, among which the increase in Gengcun low-rank coal was the most obvious and the increase in methane adsorption was also the most obvious.

3.2.2. Analysis of Desorption Experimental Results. Methane desorption was performed under a pressure of 0.5 MPa for coal samples at adsorption equilibrium, and the test results are shown in Figure 7. Figure 7 shows that in the process of methane desorption from coal, the amount of methane desorbed rapidly increased in the first 5 min and subsequently tended to be stable. Compared with the raw coal results, the desorption amount of coal samples being treated with clean fracturing fluid was greatly improved. The recorded data were imported into Origin software for fitting analysis using formula $Q = a(1 - b^t)$, and the maximum desorption amount of methane was obtained as shown in Table 5.

Table 5 shows that the methane desorption amount of the high-rank coal was 1.96 and 2.64 mL/g before and after the clean fracturing fluid treatment, respectively, which corresponds to an increase of 0.68 mL/g (34.7%). The desorption amount of methane in medium-rank coal was 1.14 mL/g but increased to 1.75 mL/g after the clean fracturing fluid treatment, which corresponds to an increase of 0.61 mL/g (53.5%). The methane desorption amount of low-rank coal was 0.63 mL/g and increased to approximately 1.06 mL/g after the clean fracturing fluid treatment, which corresponds to an increase of 0.43 mL/g (68.3%). The adsorption of coal to clean fracturing fluid is stronger than that of methane. When the clean fracturing fluid enters the coal rock, a part of methane adsorbed on the coal surface is displaced. At the same time, after the coal sample is treated with the clean fracturing fluid, the large pores and cracks in the coal increase and the methane migration channel increases, resulting in a certain enhancement of the desorption ability of coal to methane. However, the effect of clean fracturing fluid on desorption capacity of different-rank coal samples is different. From Table 5, it can be seen that the effect of clean fracturing fluid on methane desorption capacity of low-rank coal is the largest, followed by medium rank coal, and the effect on high-rank coal is the smallest. The reason is that the number of closed pores of high-order coal increases after clean fracturing fluid treatment. From the adsorption/desorption curve of liquid nitrogen in Figure 1, it can be seen that after clean fracturing fluid...
treatment, the adsorption loop of coal samples with different coal ranks becomes smaller, and the change in the adsorption loop of high-order coal is more obvious than that of medium- and low-order coal, indicating that the number of closed pores becomes more, the pore connectivity becomes worse, and the desorption ability of methane is also relatively reduced.

3.2.3. Analysis of the Desorption Ratios of Coal Samples.

After the fracturing fluid treatment of the three kinds of coal samples, the amount of methane desorption increased, but this increase cannot directly reflect the increase in desorption capacity because the desorption amount simultaneously increases the adsorption amount. Therefore, one should consider the coal sample desorption rate to determine the real impact of fracturing fluid on the coal sample desorption capacity. The desorption ratios of different coal samples are shown in Table 6.

Table 6 shows that the desorption rates of the high- and medium-rank coal after the fracturing fluid treatment increased after the treatment, indicating that the clean fracturing fluid enhanced the desorption capacity of the medium- and high-rank coal. However, the desorption rate of the low-rank coal decreased after the fracturing fluid treatment, indicating that the clean fracturing fluid treatment weakened the desorption capacity of the low-rank coal. The reason for this finding may be that the number of micropores and the specific surface area of low-rank coal increase after fracturing fluid treatment and the methane adsorption capacity of coal rock is strengthened, resulting in difficult desorption. Therefore, clean fracturing fluid is suitable for coalbed methane wells with a high metamorphic degree.

4. CONCLUSIONS

(1) The adsorption isotherms of high-, medium-, and low-rank coal after the clean fracturing fluid treatment and
those of raw coal were of the same type, but the coal samples treated with the clean fracturing fluid showed smaller adsorption isotherms than the raw coal samples, which indicates that the proportion of closed pores in the coal samples increased after the clean fracturing fluid treatment.

(2) After the clean fracturing fluid treatment, the pore structures of the high-, medium-, and low-rank coal samples changed. The micropore volume increased by 0.0009, 0.00143, and 0.0035 mL/g, and the specific surface area increased by 4.87, 9.06, and 57.60%, respectively. The fractal dimension also increased compared with that of raw coal. SEM experiments showed that the clean fracturing fluid had the greatest impact on the low-rank coal, followed by the medium-rank coal and finally the high-rank coal.

(3) The experimental results of methane adsorption and desorption showed that the adsorption capacity of the coal samples after the clean fracturing fluid treatment was enhanced, which was positively correlated with the increases in the micropore proportion, micropore volume, and specific surface area of the coal samples. Moreover, the desorption capacity of the coal samples was enhanced.

(4) After the clean fracturing fluid treatment, the desorption rates of the medium- and high-rank coal samples increased, while the desorption rate of the low-rank coal decreased. The main reason for this finding is the increase in the number of micropores of the low-order coal, which enhanced its ability to absorb gas and made gas desorption more difficult. Therefore, clean fracturing fluid is suitable for coalbed methane mines with a high metamorphic degree.

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**Notes**

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