Impacting Factors, Dynamic Process, and Correction of Adsorption Reduction in Shale Reservoir: A Case Study on Shale Samples from the Western Guizhou

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ABSTRACT: Adsorption reduction occurring during isothermal experiment leads to the failure of telling the true adsorption capacity of shale reservoir. A correct understanding of this will be helpful in improving the accuracy of resource estimation and economic evaluation of shale gas reserves. Six shale samples were collected from the Permian Longtan Formation in the western Guizhou Province, China. Volumetric methane isotherm adsorption experiment and data processing were conducted in this research. The study investigates the effect of free space volume reduction (FSVR), excess adsorption amount conversion (EAAC), and blank test correction (BTC) on adsorption reduction, the understanding of the dynamic process of adsorption reduction, and the evaluation of the way of weakening and correcting this phenomenon. The conclusions are as follows. (1) Adsorption reduction does exist in the shale sample. The adsorption process of methane in the shale sample can be divided into the strong adsorption stage, approximate saturation stage, and adsorption reduction stage. (2) Shale adsorbing methane has a positive effect on the experimental adsorption amount. Comparatively, free space volume, excess adsorption amount, and blank test have negative effects. Adsorption reduction is the result of combined influence of positive and negative effects above. (3) At the first two stages of methane adsorption, the positive effect is greater than the negative effect, resulting in the hidden of adsorption reduction, and the experimental adsorption amount increases with the growth of experimental pressure. While at the adsorption reduction stage, the former effect is smaller than the latter, and their difference increases as the experimental pressure increases. It leads to the occurrence of adsorption reduction, and the phenomenon becomes increasingly obvious. (4) FSVR has the strongest impact on the weakening of adsorption reduction, followed by EAAC and BTC. The adsorption reduction in shale reservoir can be corrected effectively by BTC and EAAC.

1. INTRODUCTION

Shale gas is an important unconventional natural gas resource that exists in shale reservoir and a significant compensation for conventional natural gas resource.1–4 Shale gas, both in adsorbed and free states, appears mainly in nanoscale pores and microcracks.5–8 Adsorption gas volume is one of key parameters for calculating shale gas reserves as it generally accounts for 20–85% of total gas volume in shale.9–12

The methane adsorption amount of shale samples is currently determined by isothermal adsorption experiment (MIAE) following the experimental technology of coal reservoir.13–20 Researchers have carried out a large number of MIAEs on coal and shale samples.21–27 They found that if the adsorption capacity of the sample is low, e.g., shale or low-rank coal, the adsorption amount will rise first and then decrease with the increase in experimental pressure. This is called adsorption reduction.28,29

Shale has a relatively low adsorption capacity (generally less than 2 cm³/g) compared with coal (generally above 10 cm³/g).
Ma et al. conducted a semiquantitative evaluation of the factors impacting the adsorption reduction. They demonstrated that adsorption amount during the MIAE is amplified, which leads to the occurrence of adsorption reduction. The testing result with adsorption reduction is of course not the true representation of adsorption capacity of shale reservoir. Therefore, clarifying this phenomenon will improve the accuracy of resource estimation and economic evaluation of shale gas.

Free space volume is one of the important parameters for calculating the experimental adsorption capacity volume. Helium is used in the determination. However, the diameter of helium molecule (0.26 nm) is smaller than that of methane (0.38 nm), and helium molecules can enter pores that methane molecules cannot. This causes the free space volume measured by helium to be larger than the true value. Therefore, the free space volume reduction (FSVR) can make the experimental adsorption amount closer to its true value. Based on MIAE, Tian et al. studied the adsorption reduction after eliminating the cumulative error of the experimental sample at a certain pressure minus the volume of blank test at that pressure, which is normally not zero but normally not. The adsorption amount of the shale capacity (such as steel balls), of which the testing result should be zero but normally not. This causes the free space volume measured by helium to be larger than the true value.

The result of MIAE, the adsorption amount, is called the excess adsorption amount (experimental adsorption amount also). The volume of methane in the adsorbed phase is not considered in its calculation process. Comparatively, the adsorption amount obtained by considering the volume of adsorbed-phase methane in the calculation is called the absolute adsorption amount. Therefore, it is necessary to convert the excess adsorption amount into the absolute adsorption amount. Using the improved calculation method of adsorption phase density of methane, Zhou et al. investigated the impact of excess adsorption amount conversion (EAAC) on adsorption reduction. Their results indicated that the essence of adsorption reduction is the excess adsorption of supercritical methane.

Blank test is the MIAE of materials that have no adsorption ability. The adsorption amount of the sample at a certain pressure minus the volume of blank test at the same pressure is called blank test correction (BTC). It can reduce the impact of systematic errors on the experimental adsorption amount. Through MIAE and numerical calculation, Ma et al. conducted a semiquantitative evaluation of the factors impacting the adsorption reduction. They demonstrated that after BTC, the adsorption reduction disappears gradually as the experimental pressure grows.

It is known from previous studies that main impacting factors on adsorption reduction of shale are FSVR, EAAC, and BTC. However, only qualitative and semiquantitative analyses of those factors affecting adsorption reduction have been carried out. A few people have studied the degree to which various factors impact adsorption reduction, and the mechanism of each factor causing adsorption reduction in the MIAE process is still unclear.

Based on the above discussion, in this paper, six shale samples were collected from the Permian Longtan Formation in the western Guizhou Province, China. Using volumetric MIAE and data calculation, the impact of FSVR, EAAC, and BTC on the experimental adsorption amount of shale samples and the dynamic process of adsorption reduction during MIAE was investigated. Then, the effect of the above three factors on the adsorption reduction was evaluated. Finally, the correction method of adsorption reduction was raised and tested.

## 2. SAMPLES, EXPERIMENTS, AND THEORIES

### 2.1. Samples

Six shale samples were selected from the Permian Longtan Formation in western Guizhou Province, China, and their basic properties are shown in Table 1.

According to the Chinese national standard for the determination of total organic carbon in sedimentary rocks (GB/T19145-2003), the total organic carbon content (TOC) was measured using a carbon-sulfur analyzer (multi-EA4000). True density (TRD) was measured following the Chinese national standard for industrial analysis (GB/T212-2008). Based on the conventional core analysis method (SY/T5336-2006), the porosity and permeability were measured by the ULTRA-PERM 200 permeability meter. An oil and gas display simulator (OG-2000 V) was used to determine the soluble hydrocarbon (C1), pyrolysis hydrocarbon (C2), and residual organic carbon (C3) content under the Chinese national standard for rock pyrolysis analysis (GB/T18602-2012).

### 2.2. Experiments

MIAE of shale mainly includes volumetric and gravimetric methods, and adsorption reduction exists in both of them. According to the principle of material conservation, volumetric MIAE calculates the adsorption amount by measuring the change in methane amount after methane adsorption. Meanwhile, gravimetric MIAE, based on the theory of mechanical equilibrium, obtains the adsorption amount by measuring the variation of sample weight after methane adsorption. The measuring principles of the two methods are different, and the influencing factors of the adsorption reduction also vary. At present, the most common application is the volumetric method. Therefore, we mainly study the adsorption reduction in volumetric MIAE in this research, and that in gravimetric MIAE can be compared subsequently.

Based on methane isothermal adsorption capacity test technology of shale (GB/T35210.1-2017), volumetric MIAE was carried out using an IS-100 high-pressure gas.
isothermal adsorption/desorption instrument (Figure 1). The experimental temperature was 303 K, and the error was within 0.2 K. The maximum experimental pressure was approximately 13 MPa, and the pressure accuracy was 3.51 kPa. The adsorption amount of methane was measured at eight experimental pressure values, i.e., 1, 2, 4, 5, 7, 9, 11, and 13 MPa. The adsorption equilibrium time of each experimental pressure value was longer than 2 h. Helium and methane were used as test gases for the free space volume and the experimental adsorption amount of methane, respectively. Their purity was both higher than 99.99%.

Samples were crushed to a size less than ~60 mesh and degassed at a temperature of 378.15 K in a high-vacuum container for more than 24 h to remove air, free water, and other gases. Then, the samples were loaded into the sample cylinder and the volume of samples was kept two-thirds larger than that of sample cylinder. After checking the air tightness of the instrument, the free space volume and methane adsorption amount were measured in sequence.

2.2.1. Free Space Volume. Free space volume refers to the space in the sample cylinder other than the sample particle volume. It includes the void space between sample particles, space remaining in the sample cylinder, and internal space of connecting the tube and valve. It is determined by two equilibria (Figure 1). Helium gas was used in this experiment.

For the first equilibrium, close valve 10 between the reference and sample cylinder. Then, open valve 8 of the helium cylinder and valve 9 between the reference and methane cylinder. After adjusting the pressure of reference cylinder to the first experimental pressure value (1 MPa), close valves 7 and 9 and record the pressure and temperature values of the two cylinders.

For the second equilibrium, open valve 10 between the sample and reference cylinders. After the pressure is balanced, record the pressures and temperatures of both cylinders.

According to the above-mentioned steps, the adsorption amount of methane was tested at eight pressure values, that is, 1, 2, 4, 5, 7, 9, 11, and 13 MPa. The calculation method is described in Section 2.3.2.

Blank test is the MIAE of materials that have no adsorption capacity (such as steel balls). All experimental conditions and steps are the same as those used for the MIAE.

2.3. Theories and Methodologies. According to the principle of matter conservation and MIAE data of shale samples, the equation of state of gas was used for the calculations. The free space volume, experimental adsorption amount, variation rate of adsorption amount, and absolute adsorption amount were obtained.

2.3.1. Free Space Volume. Free space volume can be calculated using the data of the helium isotherm adsorption experiment (refer to Section 2.2.1). According to the principle of matter conservation, the total mess of helium in the instrument is constant after the first and second equilibria (eq 1) (GB/T35210.1-2017).

\[ n_1 + n_2 = n_3 + n_4 \]  

where \( n_1 \) and \( n_2 \) are the helium mess in the reference cylinder after the first and second equilibria, respectively (mol), and \( n_3 \) and \( n_4 \) are the helium mess in the sample cylinder after the first and second equilibria, respectively (mol).

According to the equation of gas state, the helium mess \( n \) can be calculated based on the volume, compression factor, pressure, and temperature of helium (eq 2).

\[ n = PV/(ZRT) \]  

where \( n \) is the helium mess (mol), \( P \) is the experimental pressure (MPa), \( V \) is the volume of helium (cm\(^3\)), \( Z \) is the compression factor of helium, and \( T \) is the experimental temperature (303 K).

Free space volume \( V_f \) can be calculated (eq 3) by combining eqs 1 and 2.

\[ V_f = \frac{P_3/(Z_3T_3) - P_1/(Z_1T_1)}{P_2/(Z_2T_2) - P_1/(Z_4T_4)} V_i \]  

where \( V_i \) is the free space volume (cm\(^3\)), \( V_f \) is the volume of reference cylinder (cm\(^3\)), \( P_1 \) and \( P_3 \) are the pressure values of reference cylinder after the first and second equilibria (MPa), \( P_2 \) and \( P_4 \) are the pressure values of sample cylinder after the first and second equilibria (MPa), \( T_1 \) and \( T_2 \) are the experimental temperature values after the first and second equilibria (K), and \( Z_1 \) and \( Z_3 \) are the gas compression factors of reference cylinder after the first and second equilibria, and \( Z_2 \) and \( Z_4 \) are the gas compression factors of the sample cylinder after the first and second equilibria, respectively.

![Figure 1. Schematic diagram of volumetric methane isotherm adsorption instrument. Note: 1, methane cylinder; 2, helium cylinder; 3, booster pump; 4, vacuum pump; 5, reference cylinder; 6, sample cylinder; 7, methane cylinder valve; 8, helium cylinder valve; 9, reference cylinder valve; 10, sample cylinder valve; 11, incubator; P, pressure gauge; T, thermometer.](https://dx.doi.org/10.1021/acsomega.6b01286)
2.3.2. Adsorption Methane Volume. According to the principle of matter conservation, the increase in the adsorption methane mess $\Delta n_i$ at the $i$-th pressure value can be calculated from the change in the free methane mess obtained by the two equilibria (eq 4) (GB/T35210.1-2017). \(^4\)

$$\Delta n_i = n_i1 + n_{i2} - n_{i3} - n_{i4} \quad (i = 1, 2, ..., 8)$$ \hspace{1cm} (4)

where $\Delta n_i$ is the increase in the adsorption methane mess at the $i$-th pressure value (mol), $n_{i1}$ and $n_{i3}$ are the free methane mess in the reference cylinder at the $i$-th pressure value after the first and second equilibria (mol), and $n_{i2}$ and $n_{i4}$ are the free methane mess in the sample cylinder at the $i$-th pressure value after the first and second equilibria, respectively (mol).

By combining eqs 2 and 4, eq 5 is obtained.

$$\Delta n_i = \left( \frac{P_{i1}}{Z_{i1}T_{i1}} - \frac{P_{i3}}{Z_{i3}T_{i2}} \right) \frac{V_{i1}}{R} - \left( \frac{P_{i4}}{Z_{i4}T_{i2}} - \frac{P_{i2}}{Z_{i2}T_{i1}} \right) \frac{V_{i2}}{R} \quad \hspace{1cm} (i = 1, 2, ..., 8)$$ \hspace{1cm} (5)

where $P_{i1}$ and $P_{i3}$ are the pressure values of the reference cylinder at the $i$-th pressure value after the first and second equilibria (mol), $P_{i4}$ and $P_{i2}$ are the pressure values of the sample cylinder at the $i$-th pressure value after the first and second equilibria (mol), $T_{i1}$ and $T_{i2}$ are the experimental temperatures at the $i$-th pressure value after the first and second equilibria (K), $Z_{i1}$ and $Z_{i3}$ are the gas compression factors of the reference cylinder at the $i$-th pressure value after the first and second equilibria, $Z_{i2}$ and $Z_{i4}$ are the gas compression factors of the sample cylinder at the $i$-th pressure value after the first and second equilibria, respectively, $R$ has the same meaning as in eq 3, and $V_{i1}$ and $V_{i2}$ have the same meaning as in eq 3.

Total mess of adsorption methane $n_i$ at the $i$-th pressure value is shown in eq 6.

$$n_i = \sum_{j=1}^{i} \Delta n_j \quad (i = 1, 2, ..., 8)$$ \hspace{1cm} (6)

After standard state correction (273.15 K and 101.325 kPa) of total mess $n_i$, the experimental adsorption amount of unit mass sample at the $i$-th pressure value is obtained (eq 7).

$$V_{ai} = (n_i \times 22.4 \times 1000)/m_i \quad (i = 1, 2, ..., 8)$$ \hspace{1cm} (7)

where $V_{ai}$ is the experimental adsorption amount of unit mass sample at the $i$-th pressure value (cm$^3$/g), $n_i$ is the total mess of the adsorption methane at the $i$-th pressure value (mol), and $m_i$ is the quality of sample (g).

It can be seen from eqs 5 to 7 that the calculation of the experimental adsorption amount contains free space volume, and thus, the change in free space volume can cause a variation in the experimental adsorption amount directly.

The variation rate of experimental adsorption amount $r$ refers to the ratio of the change in the corrected experimental adsorption amount to the original value. The former was adjusted by FSVR, EAAC, and BTC. Equation 8 presents its calculation. It can reflect the effect of varying conditions on the experimental adsorption amount. When this rate is greater than 0, it is called the growth rate, which means the increase in experimental adsorption amount; when this rate is less than 0, then it is called the decrease rate, which indicates the decrease in experimental adsorption amount. The magnitude of the absolute value of the rate indicates the magnitude of the change in the experimental adsorption amount.

$$r = (V_i - V_0)/V_0 \quad (8)$$

where $r$ is the variation rate of experimental adsorption amount (%), and $V_i$ and $V_0$ are the experimental adsorption amount values after changing conditions and the original value, respectively (cm$^3$/g).

2.3.3. Excess Adsorption Amount Conversion. During MIAE, the shale sample adsorbs methane molecules continuously, and part of methane molecules converts from the free phase to adsorbed phase, thereby reducing the methane molecules of the free phase. However, in the process of measuring the experimental adsorption amount, it is artificially assumed that the volume of methane of free phase is constant. This will lead to the overestimation of methane volume in the free phase and cause the experimental adsorption amount of sample to be smaller than the actual adsorption amount ultimately (eq 7).

Based on the experimental results of MIAE, the adsorption amount calculated by eq 7 is called the excess adsorption amount (experimental adsorption amount also). The volume of methane in the adsorbed phase is not considered in its calculation process. Comparatively, the adsorption amount obtained by considering the volume of adsorbed-phase methane in the calculation process is called the absolute adsorption amount. Since the reduction of free-phase methane volume is neglected, the excess adsorption amount is always smaller than the absolute adsorption amount. Therefore, it is necessary to convert the excess adsorption amount into the absolute adsorption amount. \(^4\)

According to the definition of Moffat and Weale, the excess adsorption amount $V_{ai}$ and the absolute adsorption amount $V_{as}$ of methane can be converted by eq 9.

$$V_{as} = V_{ai}/(1 - \rho_{free}/\rho_{ad}) \quad (i = 1, 2, ..., 8)$$ \hspace{1cm} (9)

where $V_{as}$ is the absolute adsorption amount of methane (cm$^3$/g), $V_{ai}$ is the excess adsorption amount (cm$^3$/g) and it is also the experimental adsorption amount and has the same meaning as in eq 7, and $\rho_{free}$ and $\rho_{ad}$ are the densities of methane in the free phase and adsorbed phase, respectively (g/cm$^3$).

The calculations for the density $\rho_{free}$ and mass $m_{free}$ of free-phase methane are shown in eqs 10 and 11, respectively.

$$\rho_{free} = m_{free}/V_{free} \quad (10)$$

$$m_{free} = n_{free}M \quad (11)$$

where $\rho_{free}$ is the density of free-phase methane (g/cm$^3$), $m_{free}$ is the mass of free-phase methane (g), $V_{free}$ is the volume of free-phase methane (cm$^3$), $n_{free}$ is the free-phase methane mess (mol), and $M$ is the relative molecular mass of methane (16.04 g/mol).

Equation 12 can be obtained by combining eqs 2, 10, and 11.

$$\rho_{free} = MP/(ZRT) \quad (12)$$

where $P$, $Z$, $R$, and $T$ have the same meaning as in eq 2, and $\rho_{free}$ and $M$ have the same meaning as in eqs 10 and 11, respectively.

The conversion eq 13 of excess adsorption amount and the absolute adsorption amount of methane can be obtained by combining eqs 9 and 12.
\[ V_{ab} = V_a/(1 - M/(ZRT_{PA})) \quad (i = 1, 2, ..., 8) \]  

where \( V_{ab} \) has the same meaning as in eq 9, \( V_a \) and \( M \) have the same meaning as in eqs 7 and 11, respectively, and \( P, Z, R, \) and \( T \) have the same meaning as in eq 2.

3. RESULTS AND DISCUSSION

Based on volumetric MIAE and calculation, the effect of FSVR, EAAC, and BTC on the adsorption amount and the adsorption reduction was discussed respectively. Moreover, the dynamic process and the correction of this phenomenon were explored and tested separately.

3.1. Adsorption Reduction of Shale Samples. The MIAE results of shale samples are shown in Figure 2. Those samples have different adsorption capacities, and their maximum experimental adsorption amount values are 0.78, 0.89, 1.55, 1.86, 2.36, and 2.88 cm\(^3\)/g. It can be seen from Figure 2 that the adsorption amount of shale samples increases first and then decreases as the experimental pressure grows. It is obvious that adsorption reduction does exist in all shale samples.

The experimental pressure corresponding to the maximum experimental adsorption amount of shale sample is defined as the pressure on the maximum adsorption amount (PMAA), which is different from the maximum experimental pressure (13 MPa). When the experimental pressure is less than the PMAA, the adsorption amount rises with the increase in pressure; however, when the experimental pressure is above the PMAA, the adsorption amount decreases with the increase in experimental pressure, resulting in the adsorption reduction. The PMAA values of six samples are 4, 4, 4, 4, 9, and 9 MPa separately (Figure 2).

Figure 2 shows that the adsorption amount has different variation trends at various experimental pressure ranges. Conventionally, the adsorption stage should be divided by the absolute adsorption curve, not by the experimental adsorption curve. However, to reflect the original characteristics of experimental adsorption curve and compare the effects of different correction methods on it, the experimental adsorption curve is used and divided into three stages.

At the first stage (strong adsorption stage), all the shale samples have strong adsorption on methane, and the adsorption amount rises rapidly with the increase in experimental pressure (Figure 2). The experimental pressure ranges of six shale samples at this stage are about 0−1, 0−1, 0−2, 0−2, 0−4, and 0−4 MPa.

At the second stage (approximate saturation stage), the adsorption of methane by the shale sample is gradually weakened, and the adsorption amount grows slowly with increasing experimental pressure (Figure 2). The experimental pressure ranges of six shale samples at this stage are about 0−1, 0−1, 0−2, 0−2, 0−4, and 0−4 MPa.

At the third stage (transition stage), the adsorption reduction effect on methane by the shale sample is further weakened, and the adsorption amount decreases with the increase in experimental pressure (Figure 2).
pressure ranges of samples at this stage are 1−4, 1−4, 2−4, 2−4, 4−9, and 4−9 MPa separately.

In addition, at the third stage (adsorption reduction stage), the adsorption amount decreases gradually with the increase in experimental pressure, indicating the occurrence of adsorption reduction. Meanwhile, the reduction of adsorption amount rises with the growing experimental pressure, which leads to the adsorption reduction becoming increasingly obvious (Figure 2). The experimental pressure ranges of samples at this stage are 4−13, 4−13, 4−13, 4−13, 9−13, and 9−13 MPa. It can be seen that methane is in a supercritical state during this stage (the critical temperature and pressure of methane are 190.15 K and 4.64 MPa, respectively).

3.2. Factors Impacting Adsorption Reduction. It can be seen from Section 1 that the adsorption reduction of shale is mainly affected by FSVR, EAAC, and BTC. Under the impact of one of these factors, the adsorption amount and PMAA will change to some extent, thereby affecting the adsorption reduction. The larger the increase in pressure on maximum adsorption amount (IPMAA) is, the more favorable this factor is to weaken the phenomenon. Therefore, the variation rate of adsorption amount and IPMAA were used to evaluate the effect of various factors on this phenomenon of shale.

3.2.1. Free Space Volume Reduction. Through experiments and calculations, Fang et al. found that the difference between free space volume measured by helium and the theoretical value of free space volume is about 0.1 cm³. Meanwhile, the allowable error for the determination of free space volume in the Chinese national standard for MIAE of the shale sample is also 0.1 cm³ (GB/T35210.1-2017). It is thus suggested that the maximum possible error of free space volume is 0.2 cm³. Tian et al. studied the effect of free space volume on the adsorption reduction and discovered that free space volume can affect the orientation of adsorption curve when it changes only in the range of 0.4−0.6 cm³. Therefore, 0.1, 0.2, 0.4, and 0.6 cm³ were set artificially as FSVR in this section. The variation rate of adsorption amount and IPMAA were used to study the impact of FSVR on the experimental adsorption amount and adsorption reduction (Figures 3 and 4 and Table 2).

After free space volume declines, the adsorption amount of shale samples at each pressure rises, and the variation rate increases as the experimental pressure grows (Figures 3 and 4). This indicates that the impact of free space volume on the adsorption reduction becomes increasingly obvious (Figure 2). The experimental pressure ranges of samples at this stage are 4−13, 4−13, 4−13, 4−13, 9−13, and 9−13 MPa. It can be seen that methane is in a supercritical state during this stage (the critical temperature and pressure of methane are 190.15 K and 4.64 MPa, respectively).

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Table 2. Pressure on the Maximum Adsorption Amount (PMAA) after the Reduction of Free Space Volume

| sample no. | V_max | P_br (MPa) | P_ar (MPa) | ΔP_r (MPa) | P_br (MPa) | P_ar (MPa) | ΔP_r (MPa) | P_br (MPa) | P_ar (MPa) | ΔP_r (MPa) |
|------------|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Y1         | 0.78  | 4          | 5          | 1          | 13         | 13         | 9*         | 13         | 9*         | 13         |
| Y2         | 0.89  | 4          | 4          | 0          | 9          | 5          | 13*        | 9*         | 13*        | |
| Y3         | 1.55  | 4          | 4          | 0          | 9          | 5          | 13*        | 9*         | 13*        | |
| Y4         | 1.86  | 4          | 4          | 0          | 7          | 3          | 13*        | 9*         | 13*        | |
| Y5         | 2.36  | 9          | 9          | 0          | 11         | 2          | 13*        | 4*         | 13*        | 4*         |
| Y6         | 2.88  | 9          | 9          | 0          | 13         | 4*         | 13*        | 4*         | 13*        | 4*         |

Note: V_max is the maximum experimental adsorption amount (cm³/g); P_br and P_ar are PMAA values before and after the reduction of free space volume, respectively (MPa); ΔP_r is the increase in PMAA after the reduction of free space volume (MPa); asterisk (*) indicates that the adsorption reduction has disappeared.
adsorption amount enhances gradually as the experimental pressure grows.

It can be seen from eqs 5 to 7 that the free space volume has a negative correlation with the adsorption amount. If the free space volume is reduced, then the calculation result of the experimental adsorption amount will inevitably increase, and this increment will be accumulated at each pressure. As a result, the variation rate of the experimental adsorption amount increases as the experimental pressure rises (Figures 3 and 4).

Furthermore, Figure 4 also shows that the effect of free space volume on the experimental adsorption amount differs in the three adsorption stages of shale reservoir. Sample Y4 is described as an example here (Figure 4d).

At the strong adsorption stage (experimental pressure is 0–2 MPa), the variation rate of adsorption amount is 3.33–5.79% after the free space volume is reduced by 0.2 cm³. This indicates that the free space volume has a weak impact on the adsorption amount and makes the volume increase slightly at this stage.

At the approximate saturation stage (experimental pressure is 2–4 MPa), the variation rate is 5.79–6.83%, indicating that the impact of FSVR on the adsorption amount is stronger than that at the strong adsorption stage.

In addition, at the adsorption reduction stage (experimental pressure is 4–13 MPa), the variation rate is 6.83–18.84%, which demonstrates that FSVR has the strongest effect on the adsorption amount at this stage.

Other samples have the similar feature as discussed above. Moreover, Figure 3 and Table 2 show that after FSVR, the adsorption amount and PMAA change, thereby causing the adsorption reduction to remain unchanged (IPMAA is 0 MPa), weaken, or disappear (IPMAA is larger than 0 MPa).

While FSVR is 0.1 cm³, the IPMAA of most samples is 0 (except for sample Y1), and adsorption reduction hardly changes. In addition, when FSVR is 0.2 cm³, the IPMAA of samples increases, indicating that the adsorption reduction has been weakened. Notably, the adsorption reduction in samples Y1 and Y6 disappears here. Furthermore, when FSVR is 0.4 and 0.6 cm³, respectively, the adsorption reduction phenomenon of all samples disappears (Table 2).

The above result shows that the larger the FSVR, the greater the IPMAA, and the easier it is for the adsorption reduction to weaken. There are two reasons. On the one hand, according to the equation for calculating the experimental adsorption amount (eqs 5–7), a decrease in the free space volume directly results in an increase in the experimental adsorption amount, and the larger the decrease, the greater the increase. On the other hand, due to the accumulation of calculations, the increase in the experimental adsorption amount will rise as the experimental pressure grows.

3.2.2. Excess Adsorption Amount Conversion. The discussion in Section 2.3.3 indicates that the volume of methane in the free phase is assumed to be constant, which leads to a deviation in the calculation of experimental adsorption amount. Therefore, it is necessary to convert the excess adsorption amount into the absolute adsorption amount using eq 13.

Previous studies have shown that the density can be calculated in various ways, and different results are obtained. The densities calculated by the ZGR (EOS) and the Ono–Kondo model are 0.345 and 0.354 g/cm³, respectively, while the density calculated by the volume element method of van

Figure 5. Adsorption amount of shale samples (a–f) after excess adsorption amount conversion.
der Waals is 0.374 g/cm$^3$.$^{51}$ In addition, Mavor et al. used the density at boiling point (0.422 g/cm$^3$) as the density of adsorbed-phase methane.$^{52}$

Zhou et al. considered that the applicability of the method setting the density of adsorbed-phase methane as a constant value was poor and proposed an improved method for the density, which successfully corrected adsorption reduction.$^{44}$ The writers believe that the classical densities are reasonable to some extent. Therefore, writers attempt to correct the adsorption reduction by other methods based on those classical densities, and the correction method will be discussed in Section 3.4.

Using the above four classical densities, the excess adsorption amount was converted into absolute adsorption amount in this section, and the impact of EAAC on the experimental adsorption amount and adsorption reduction of six shale samples was investigated. The calculation results are shown in Figures 5 and 6.

Figures 5 and 6 show that after EAAC, the adsorption amount of shale samples at each pressure value increases, and the variation rate of adsorption amount rises as the pressure grows. This indicates that the impact of EAAC on adsorption amount enhances gradually with the growing pressure.

It can be known from eq 9 that the density of free-phase methane is smaller than that of adsorbed-phase methane, and EAAC will inevitably cause an increase in excess adsorption amount. At the same time, the rise in pressure and excess adsorption amount will lead to an increase in calculation results, causing the variation rate of adsorption amount to rise with the growing pressure.

Moreover, Figure 6 also shows that the effect of EAAC on the adsorption amount differs at the three adsorption stages. Sample Y4 is again used as an example to describe the process (Figure 6d).

At the strong adsorption stage, with EAAC using the density of 0.345 g/cm$^3$, the variation rate of the adsorption amount is 1.71−3.90%.

At the approximate saturation stage, the variation rate is 3.90−7.99%, concluding that the impact of EAAC on adsorption amount at this stage is stronger than that at the former stage.

While at the adsorption reduction stage, the variation rate is 7.99−32.12%, which demonstrates that EAAC has the strongest effect on the experimental adsorption amount among the three stages.

As can be seen from Table 3, the PMAA of shale samples increases after EAAC by different densities (except for sample Y6). It indicates that EAAC can weaken the adsorption reduction. There are two reasons. On the one hand, according to the conversion eq 9, EAAC can increase the adsorption amount, and the larger the excess adsorption amount is, the greater the absolute adsorption amount will be. On the other hand, the increase in adsorption amount caused by EAAC rises gradually with the growing pressure.

Notably, the value of adsorbed phase density cannot change this weakening effect on adsorption reduction. The reason is that the absolute adsorption amount calculated by different densities has little difference and will not cause the reversible change in the adsorption curve.

Figure 5 shows that adsorption reduction also appears in the absolute adsorption curve, which is similar to the results reached by Fang et al., Ma et al., and Zhou et al.$^{28,29,44}$ Methane is in a supercritical state at high pressure, and the experimental adsorption amount will decrease, which is the
essential characteristic of the supercritical fluid. However, according to the definition of absolute adsorption amount, the absolute adsorption curve should not show adsorption reduction.44 The absolute adsorption amount in this paper does decrease, which indicates that the experimental data should be corrected (the method of correction will be discussed in Section 3.4) before the conversion of the excess adsorption amount.

3.2.3. Blank Test Correction. The isothermal adsorption instrument consists of multiple cylinders, a series of sensors and valves, and a control system (Figure 1). They may become the sources of errors in the measurement of adsorption amount, such as the error of pressure sensor, error of state equation, error of gas purity, etc. Theoretically, the adsorption amount of materials without an adsorption capacity should be 0 cm$^3$/g at any condition. However, due to the impact of systematic errors, the isothermal adsorption curve of materials without any adsorption capacity is not a straight line with a value of zero. The adsorption curve obtained by blank test is a comprehensive reflection of these systematic errors.28

To investigate the effect of BTC on experimental adsorption amount and adsorption reduction of shale samples, blank test was carried out through an instrument mentioned in Section 2.2.1 with steel balls of which the diameter is 1 mm. As the six shale samples used the same set of sample and reference cylinders, the blank test results of these samples were the same. The blank test results and correction results are shown in Figures 7 and 8.

Table 3. Pressure of the Maximum Adsorption Amount (PMAA) after Conversion of Excess Adsorption Amount

| sample no. | $V_{\text{max}}$ (cm$^3$/g) | $P_{bc}$ (MPa) | $P_{ac}$ (MPa) | $\Delta P_{c}$ (MPa) | $P_{ac}$ (MPa) | $\Delta P_{c}$ (MPa) | $P_{ac}$ (MPa) | $\Delta P_{c}$ (MPa) |
|------------|----------------|---------------|---------------|----------------|---------------|----------------|---------------|----------------|
| Y1         | 0.78           | 4             | 9             | 5             | 9             | 5             | 9             | 5             |
| Y2         | 0.89           | 4             | 9             | 5             | 9             | 5             | 9             | 5             |
| Y3         | 1.55           | 4             | 9             | 5             | 9             | 5             | 9             | 5             |
| Y4         | 1.86           | 4             | 5             | 1             | 5             | 1             | 5             | 1             |
| Y5         | 2.36           | 9             | 11            | 2             | 11            | 2             | 11            | 2             |
| Y6         | 2.88           | 9             | 9             | 0             | 9             | 0             | 9             | 0             |

Note: $V_{\text{max}}$ is the maximum experimental adsorption amount (cm$^3$/g); $P_{bc}$ and $P_{ac}$ are the PMAA values before and after the conversion of excess adsorption amount, respectively (MPa); $\Delta P_{c}$ is the increase in PMAA after the conversion of excess adsorption amount, MPa.

Figure 7 shows that the maximum adsorption amount of the blank test does not exceed 0.22 cm$^3$/g, which is similar to the result (0.2 cm$^3$/g) of Ma et al.28 Blank test is a comprehensive...
reflection of systematic errors and is corrected by subtracting the adsorption amount of blank test from the experimental adsorption amount of shale samples. Systematic errors in the adsorption experiment of steel balls and shale samples may be different as the property and structure of steel ball and shale are diverse. However, there are no precise theories or instruments to calculate or measure these systematic errors. Therefore, this correction method is used temporarily to eliminate systematic errors as much as possible.

It can be seen from Figure 7 that when the experimental pressure is less or greater than 2 MPa, the adsorption amount of blank test increases and decreases, respectively. This is the comprehensive reflection of systematic errors. So, it is necessary to correct the blank test.

In addition, for Figure 8, when the experimental pressure is less than 4 MPa, the absolute value of the decrease rate of experimental adsorption amount reduces as the pressure grows. This indicates that the impact of BTC on the experimental adsorption amount diminishes gradually as the pressure increases at this pressure range. However, when the experimental pressure is equal to or greater than 4 MPa, the absolute value of decrease rate rises as the pressure grows. It demonstrates that the impact of BTC on the experimental adsorption amount enhances gradually as the pressure increases at this pressure stage.

Furthermore, as shown in Figure 8, the variation rate of adsorption amount at the same pressure declines as the adsorption capacity of shale samples enhances. The systematic error at the same pressure is considered to be constant, so the larger the adsorption amount at this pressure, the smaller the effect of the systematic error on the adsorption amount.

In addition, the effect of BTC on the experimental adsorption amount differs in three adsorption stages mentioned above. Here, the results for sample Y4 are still used to describe the process (Figure 8).

At the strong adsorption stage, the variation rate of experimental adsorption amount of sample Y4 reduces from 6.71 to −4.00%. This indicates that at this stage, BTC can decrease the experimental adsorption amount, and the reduction magnitude declines gradually.

At approximate saturation stage, the variation rate reduces from −4.00 to −2.18%, suggesting that BTC can only decrease the experimental adsorption amount slightly at this stage.

While at adsorption reduction stage, the variation rate increases from −2.18 to 14.86%, which demonstrates that at this stage, BTC can increase the experimental adsorption amount and the grown amplitude increases gradually with the rise in experimental pressure.

Figure 7 simultaneously shows that IPMAA values of six shale samples are 5, 5, 5, 1, 0 and 0 MPa. This indicates that BTC can weaken the adsorption reduction, and the larger the adsorption capacity of the shale sample is, the slighter the weakening effect will be. On the one hand, BTC can increase the experimental adsorption amount, and the correction value of BTC increases gradually with growing pressure, which can weaken the adsorption reduction phenomenon. On the other hand, the larger the experimental adsorption amount, the smaller the effect of BTC on it and the slighter the effect of BTC on adsorption reduction of shale samples with strong adsorption capacity.

By comparing the conclusions of Ma et al.28 it is found that blank test results of different types of adsorption instruments are slightly different, but the impact of BTC on adsorption reduction of shale samples still conforms to the above rules. Therefore, BTC is required in MIAE, regardless of the type of adsorption instrument that is used in similar tests.

3.3. Impacting Factors Comparison and Dynamic Process Analysis. Through the discussion in Section 3.2, it is found that FSVR, EAAC, and BTC can all weaken the adsorption reduction of shale samples. Comparing the impact of various factors on the adsorption reduction is helpful in clarifying its dynamic process and mechanism. Therefore, the impact of various factors on adsorption reduction was compared by IPMAA (Table 4), and the dynamic process and mechanism of this phenomenon were analyzed here.

3.3.1. Factor Comparison. For shale samples with low and medium adsorption capacities (Y1 Y4, the maximum adsorption amount is less than 1.86 cm3/g), their IPMAA values under the impact of FSVR (0.2 MPa), ΔP0.374, ΔP0.354, and ΔP0.422 are the IPMAA values after excess adsorption amount conversion using the densities of 0.345, 0.354, 0.374, and 0.422 g/cm3, respectively (MPa); ΔP0 is the IPMAA after blank test correction (MPa); asterisk (*) indicates that the adsorption reduction has disappeared.

Table 4. Increase in Pressure on the Maximum Adsorption Amount (IPMAA) of Shale Samples under the Impact of Various Factors a

| sample no. | Vmax | ΔP0.11 | ΔP0.22 | ΔP0.34 | ΔP0.66 | ΔP0.345 | ΔP0.354 | ΔP0.374 | ΔP0.422 | blank test |
|------------|------|--------|--------|--------|--------|---------|---------|---------|---------|-----------|
| Y1         | 0.78 | 1      | 9*     | 9*     | 9*     | 5       | 5       | 5       | 5       | 5         |
| Y2         | 0.89 | 0      | 5      | 9*     | 9*     | 5       | 5       | 5       | 5       | 5         |
| Y3         | 1.55 | 0      | 5      | 9*     | 9*     | 5       | 5       | 5       | 5       | 5         |
| Y4         | 1.86 | 0      | 3      | 9*     | 9*     | 1       | 1       | 1       | 1       | 1         |
| Y5         | 2.36 | 0      | 2      | 4*     | 4*     | 2       | 2       | 2       | 2       | 0         |
| Y6         | 2.88 | 0      | 0      | 4*     | 4*     | 0       | 0       | 0       | 0       | 0         |

Note: Vmax is the maximum experimental adsorption amount (cm3/g); ΔP0.11, ΔP0.22, ΔP0.34, and ΔP0.66 are the IPMAA values after the free space volume is reduced by 0.1, 0.2, 0.4, and 0.6 cm3, respectively (MPa); ΔP0.345, ΔP0.354, ΔP0.374, and ΔP0.422 are the IPMAA values after excess adsorption amount conversion using the densities of 0.345, 0.354, 0.374, and 0.422 g/cm3, respectively (MPa); ΔP0 is the IPMAA after blank test correction (MPa); asterisk (*) indicates that the adsorption reduction has disappeared.
strongest weakening effect on it, followed by EAAC, while BTC has no impact. According to the classical gas adsorption theory, methane adsorption by shale belongs to the first type of isotherm adsorption curve. Its characteristic is that the adsorption amount increases rapidly with the rise in pressure, then grows slowly, and becomes stable eventually. There should be no adsorption reduction in this adsorption curve. However, the adsorption reduction does exist in MIAE.

Through the above analysis, it is believed that free space volume, excess adsorption amount, and blank test can all reduce the experimental adsorption amount in MIAE of the shale sample. They act on various methane adsorption stages of shale sample together and lead to the occurrence of adsorption reduction eventually (Figures 3−8).

3.3.2. Dynamic Process and Mechanism of Adsorption Reduction. The shale sample adsorbs methane continuously as the experimental pressure increases, which raises the experimental adsorption amount and has a positive effect on the experimental adsorption amount. Comparatively, free space volume, excess adsorption amount, and blank test have negative effects, resulting in a decrease in experimental adsorption amount. Adsorption reduction is the result of the combined influence of positive and negative effects above.

At the strong adsorption stage, methane in the shale sample is in an unsaturated adsorption state. Methane is adsorbed by the shale sample rapidly and the actual adsorption amount increases sharply. At this stage, free space volume, excess adsorption amount, and blank test have a weak effect on the reduction of experimental adsorption amount. The reduction of experimental adsorption amount caused by the three factors is far less than the increase in actual adsorption amount, and the negative effect of the three factors is therefore hidden by the latter. It leads to the experimental adsorption amount increasing rapidly as the experimental pressure rises and no adsorption reduction appears (Figures 3−8).

At the approximate saturation stage, methane adsorption of the shale sample reaches the state of saturation gradually and the actual adsorption amount grows slowly. At this stage, the impact of the three factors on the decrease in experimental adsorption amount heightens gradually as the experimental pressure increases. Then, compared with the first stage, the reduction of experimental adsorption amount caused by the three factors is only slightly less than or nearly equal to the rise in actual adsorption amount, and the negative effect is a little smaller than the positive effect. Eventually, it results in slightly hidden adsorption reduction and the experimental adsorption amount increasing slowly as the experimental pressure grows.

Moreover, at the adsorption reduction stage, methane adsorption of shale is in a supercritical and approximately saturated state, and the location where methane can be adsorbed is almost filled. At this stage, the impact of the three factors on the decrease in experimental adsorption amount still enhances as the experimental pressure grows. Then, the reduction of experimental adsorption amount caused by them is larger than the rise in actual adsorption amount, the negative effect is greater than the positive effect, and their difference increases as the experimental pressure grows. Finally, the experimental adsorption amount decreases as the experimental pressure rises, and the adsorption reduction appears and becomes increasingly obvious.

3.4. Adsorption Reduction Correction. Based on the analysis in Section 3.3, it is believed that free space volume, excess adsorption amount, and blank test lead to the
occurrence of adsorption reduction. Therefore, the correction of adsorption reduction should be the error adjustments of these three factors.

Blank test is corrected by subtracting the adsorption amount of blank test from the experimental adsorption amount of shale samples. There are no precise theories or instruments to calculate or measure these systematic errors. Therefore, this correction method is used temporarily to eliminate systematic errors as much as possible. The excess adsorption amount can be converted into absolute adsorption amount using eq 13, and it can eliminate the calculation error of experimental adsorption amount. Free space volume is measured by helium, and no better measurement technology has been found until now. In the future, it is possible to calculate the true free space volume by means of molecular simulation, and the free space volume is not corrected here.

According to the above discussion, the correction of adsorption reduction can be summarized as two steps. In the first step, the experimental adsorption amount should be corrected by blank test. Then, in the second step, the corrected experimental adsorption amount should be converted into the absolute adsorption amount. The calculation results are shown in Figure 9.

It can be seen from Figure 9 that after adsorption reduction correction, the PMAA of all shale samples becomes the maximum experimental pressure and all adsorption reduction disappears. It demonstrates that this correction method can effectively eliminate the adsorption reduction of shale reservoir.

Furthermore, as shown in Figure 9, adsorption stages in the experimental adsorption curve change after adsorption reduction correction. Sample Y4 is used as an example to describe it (Figure 9d). After the adsorption reduction correction, the experimental pressure range of strong adsorption stage does not change (0–2 MPa), while the range of approximate saturation stage is extended from 2–4 to 2–9 MPa. Notably, the adsorption reduction stage disappears and turns into the saturation stage, which is consistent with the traditional adsorption curve. Other samples have the similar feature as discussed above.

This indicates that the experimental adsorption amount obtained directly from MIAE is not an actual reflection of adsorption capacity, and it needs adsorption reduction correction. The correction method has a weak influence during the strong adsorption stage but has a strong impact during the approximate saturation and adsorption reduction stages. The reason is that at the strong adsorption stage, the influence of the adsorption reduction correction is masked by the rapidly increasing experimental adsorption amount. At the approximate saturation and adsorption reduction stages, the experimental adsorption amount increases slowly, while the correction value increases faster, so that the influence of the correction on the experimental adsorption amount enhances gradually.

The above experiments and calculation results suggest that the correction method can effectively eliminate the adsorption reduction of shale reservoir. However, the correction of adsorption reduction in shale reservoir still requires deployment for specific experimental equipment and technologies.

4. CONCLUSIONS

By conducting volumetric MIAE and data processing, adsorption reduction of shale samples during MIAE was investigated, the impact of FSVR, EAAC, and BTC on adsorption reduction of shale samples was evaluated, and the dynamic process and correction method of adsorption reduction were explored and tested, respectively. The conclusions are as follows:

1. Adsorption reduction does exist while conducting MIAE on the shale sample. In the process, the positive effect caused by adsorption and the negative effect aroused by free space volume, excess adsorption amount, and blank test act together on the experimental adsorption amount and lead to adsorption reduction.

2. At the first two stages of methane adsorption, the positive effect is greater than the negative effect, resulting in the hidden adsorption reduction. While at the adsorption reduction stage, methane adsorption of shale is in a supercritical and approximately saturated state, the positive effect is smaller than the negative effect, and their difference increases as the experimental pressure grows. Subsequently, adsorption reduction occurs and becomes increasingly obvious.

3. FSVR, EAAC, and BTC can cause the weakening or even disappearance of adsorption reduction, and their effect enhances with the increasing experimental pressure. FSVR has the strongest impact on the weakening of adsorption reduction, followed by EAAC and BTC.

4. For the adsorption reduction correction, it is necessary to carry out BTC on the experimental adsorption amount and then convert the corrected volume into the absolute adsorption amount. This correction method can effectively eliminate the phenomenon of shale reservoir. In addition, the above work is helpful in improving the accuracy of resource estimation and economic evaluation of shale gas.

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**ABBREVIATION**

MIAE  methane isotherm adsorption experiment  
FSVR  free space volume reduction  
EAAC  excess adsorption amount conversion  
BTC  blank test correction  
PMAA  pressure on the maximum adsorption amount  
IPMAA  increase in pressure on maximum adsorption amount

**REFERENCES**

(1) Liu, H.; Hu, X.; Guo, Y.; Ma, X.; Wang, F.; Chen, Q. Fracture characterization using flowback water transients from hydraulically fractured shale gas wells. *ACS Omega* 2019, 4, 14688−14698.

(2) Sun, H.; Zhao, H.; Qi, N.; Li, Y. Effects of surface composition on the microbehaviors of CH4 and CO2 in slit-nanopores: a simulation exploration. *ACS Omega* 2017, 2, 7600−7608.

(3) Moore, T. A.; Mares, T. E.; Amijaya, D. H. Introduction to the special issue of papers from the 2015 annual meeting of the society for organic petrology, Yogyakarta, Indonesia. *Int. J. Coal Geol.* 2016, 166, 1.

(4) Hu, K.; Mischo, H. Modeling high-pressure methane adsorption on shales with a simplified local density model. *ACS Omega* 2020, 5048.

(5) Curtis, J. B. Fractured shale-gas systems. *AAPG Bull.* 2002, 86, 1921−1938.

(6) Tao, S.; Tang, D.; Xu, H.; Liang, J.; Shi, X. Organic geochemistry and elements distribution in Daungangshan oil shale, southern Junggar Basin: Origin of organic matter and depositional environment. *Int. J. Coal Geol.* 2013, 115, 41−51.

(7) Yu, S.; Bo, J.; Pei, S.; Jiahao, W. Matrix compression and multifractal characterization for tectonically deformed coals by Hg porosimetry. *Fuel* 2018, 211, 661−675.

(8) Feng, X.; Liao, X. Study on well spacing optimization in a tight sandstone gas reservoir based on dynamic analysis. *ACS Omega* 2020, 3755.

(9) Nie, H. K.; Zhang, J. C. Shale gas accumulation conditions and gas content calculation: a case study of Sichuan basin and its periphery in the lower Paleozoic. *Acta. Geol. Sin.* 2012, 86, 349−361.

(10) Tang, X.; Ripepi, N.; Stadie, N. P.; Yu, L.; Hall, M. R. A dual-site Langmuir equation for accurate estimation of high pressure deep shale gas resources. *Fuel* 2016, 185, 10−17.

(11) Tang, X.; Ripepi, N.; Stadie, N. P.; Yu, L. Thermodynamic analysis of high pressure methane adsorption in Longmaxi shale. *Fuel* 2017, 193, 411−418.

(12) Li, Z.; Wu, X.; Han, G.; Ma, G.; Zhang, L.; Wang, B.; Shi, S. Transient pressure analysis of volume-fractured horizontal wells considering complex fracture networks and stress sensitivity in tight reservoirs. *ACS Omega* 2019, 4, 14466−14477.

(13) Nie, H.; Zhang, J.; Ma, X.; Bian, R. A preliminary study of negative adsorption phenomena of shale adsorption gas content by isothermal adsorption. *Earth Sci. Front.* 2013, 20, 282−288.

(14) Chang, M.; Zhao, Y.; Yang, Q.; Liu, D. Microporous metal–organic frameworks with hydrophilic and hydrophobic pores for efficient separation of CH4/N2 mixture. *ACS Omega* 2019, 4, 14511−14516.

(15) Yu, S.; Bo, J.; Jie-gang, L. Nanopore structural characteristics and their impact on methane adsorption and diffusion in low to medium tectonically deformed coals: case study in the Huabei coal field. *Energy Fuels* 2017, 31, 6711−6723.

(16) Liu, H.; Sang, S.; Liu, S.; Wu, H.; Lan, T.; Xu, H.; Ren, B. Supercritical-CO2 adsorption quantification and modeling for a deep coaled methane reservoir in the southern Qinshui basin, China. *ACS Omega* 2019, 4, 11685−11700.

(17) Meng, J.; Li, S.; Niu, J. Crystallite structure characteristics and its influence on methane adsorption for different rank coals. *ACS Omega* 2019, 4, 20762−20772.

(18) Yu, S.; Bo, J.; Meijun, Q. Molecular dynamic simulation of self-and transport diffusion for CO2/CH4/N2 in low-rank coal vitrinite. *Energy Fuels* 2018, 32, 3085−3096.

(19) Yu, S.; Bo, J.; Wu, L. Molecular simulation of CH4/CO2/H2O competitive adsorption on low rank coal vitrinite. *Phys. Chem. Chem. Phys.* 2017, 19, 17773−17788.

(20) Goodarzi, F.; Gentzis, T.; Sanei, H.; Pedersen, P. K. Elemental composition and organic petrology of a lower carboniferous-age freshwater oil shale in nova scotia, Canada. *ACS Omega* 2019, 4, 20773−20786.

(21) Zhang, J.; Wei, C.; Zhao, J.; Ju, W.; Chen, Y.; Tamehe, L. S. Comparative evaluation of the compressibility of middle and high rank coals by different experimental methods. *Fuel* 2019, 245, 39−51.

(22) Lu, G.; Wei, C.; Wang, J.; Yan, G.; Zhang, J.; Song, Y. Methane adsorption characteristics and adsorption model applicability of tectonically deformed coals in the Huabei coalfield. *Energy Fuels* 2018, 32, 7485−7496.

(23) Xia, P.; Li, K.; Zeng, F.; Xiao, X.; Zhang, J.; Xiang, J.; Sun, B. Pyrolysis characteristic of coals with different metamorphic grades and its instruction to coalbed methane development. *World J. Eng.* 2017, 14, 423−432.

(24) Yuan, J.; Zhang, H.; Guo, Y.; Cai, N. Thermodynamic properties of high-rank tectonically deformed coals during isothermal adsorption. *Arabian J. Geosci.* 2017, 10, 278.

(25) Ozkaymak, M.; Ceylan, M. A.; Okutan, H.; Atakul, H.; Berrin, E.; Coşkun, T.; Inanç, Ö. CO2 emission during the combustion of Orhaneli lignite coal. *World J. Eng.* 2017, 14, 27−34.

(26) Yang, W.; Hu, S.; Ma, S. The relationship of palaeontology, palaeobotany and coal thickness of Taiyuan Formation, Late Carboniferous-Early Permian in Shanxi Province. *World J. Eng.* 2017, 14, 139−144.

(27) Yingbin, G.; Xinghen, W.; Shengwen, G. An initial study of the risk of coal-rove water flow based on the “three maps two predictions” method. *World J. Eng.* 2017, 14, 121−126.

(28) Ma, X.−z.; Li, S.-b.; Jiang, L.; Tian, H.; Hao, J.−q. Quantitative analysis on affecting factors of gas adsorption capacity measurement on the shale. *Nat. Gas Geosci.* 2016, 27, 488−493.

(29) Fang, F.; Sun, C.; Shu, X.; Zhu, Z.; Fang, Z. Problems of methane isothermal adsorption calculation in shale and method improvement. *Pet. Geol. Exp.* 2018, 40, 71−77.

(30) Moore, T. A.; Pearce, S. Hydrogen from coal. *Int. J. Coal Geol.* 2006, 65, 171−172.

(31) Luo, F.; Li, G.; Zhang, H. Mechanical behavior and damage mechanism of loaded coal and rock. *World J. Eng.* 2017, 14, 200−207.

(32) Yang, Y.; Zhao, Q. Analysis of aromatic hydrocarbon in medium-to-high-sulfur coals from Fexin, Shanxi Province. *World J. Eng.* 2018, 15, 786−791.

(33) Hou, Y.; Wang, D.; Dong, G. The net primary productivity of early Permian peatland and their control factors: evidenced by the no. 6 coal seam of Jungar coalfield in North China. *World J. Eng.* 2019, 16, 582−591.

(34) Ma, X.; Song, Y.; Liu, S.; Jiang, L.; Hong, F. Quantitative research on adsorption capacity evolution of middle-high rank coal reservoirs in geological history: a case study from Hancheng area in Ordos Basin. *Acta. Pet. Sin.* 2014, 35, 1080−1086.

(35) Wang, G.; Yang, L.; Zhang, Y. S. Modularized design of coalmine paste filling station based on fuzzy theory. *World J. Eng.* 2018, 15, 743−750.

(36) Quan, F.; Wei, C.; Zhang, J.; Feng, S.; Hao, S.; Lu, G.; Hu, Y. Study on desorption and diffusion dynamics of coal reservoir through step-by-step depressurization simulation—an experimental simulation study based on LF-NMR technology. *J. Nat. Gas Sci. Eng.* 2020, 103149.

(37) Lu, G.; Wei, C.; Wang, J.; Zhang, J.; Quan, F.; Tamehe, L. S. Variation of Surface Free Energy in the Process of Methane Adsorption in the Nanopores of Tectonically Deformed Coals: A
Case Study of Middle-Rank Tectonically Deformed Coals in the Huaibei Coalfield. *Energy Fuels* **2019**, *33*, 7155–7165.
(38) Zhou, S.; Li, Q.; Xue, H.; Guo, W.; Li, X.; Lu, B. Comparative study on the volumetric and gravimetric method for isothermal adsorption experiment of shale. *Chem. Ind. Eng. Prog.* **2017**, *36*, 1690–1697.
(39) Ross, D. J. K.; Bustin, R. M. Impact of mass balance calculations on adsorption capacities in microporous shale gas reservoirs. *Fuel* **2007**, *86*, 2696–2706.
(40) Tian, W.; Deng, Z.; Wang, H.; Liu, H.; Li, G.; Liu, X.; Chen, Z.; Chen, H.; Li, Y. Negative adsorption in the isotherm adsorption experiments of low-adsorption coal and shale. *Nat. Gas Ind.* **2018**, *38*, 19–26.
(41) Jian, X.; Xiangjun, L.; Lixi, L. Improved Dubinin-Astakhov model for shale-gas supercritical adsorption. *Acta Pet. Sin.* **2015**, *36*, 849–857.
(42) Zhang, C.; Xu, J.; Peng, S.; Li, Q.; Yan, F. Experimental study of drainage radius considering borehole interaction based on 3D monitoring of gas pressure in coal. *Fuel* **2019**, *239*, 955–963.
(43) Lu, G.; Wang, J.; Wei, C.; Song, Y.; Yan, G.; Zhang, J.; Chen, G. Pore fractal model applicability and fractal characteristics of seepage and adsorption pores in middle rank tectonic deformed coals from the Huaibei coal field. *J. Pet. Sci. Eng.* **2018**, *171*, 808–817.
(44) Zhou, S.; Wang, H.; Xue, H.; Guo, W.; Lu, B. Difference between excess and absolute adsorption capacity of shale and a new shale gas reserve calculation method. *Nat. Gas Ind.* **2016**, *36*, 12–20.
(45) Xu, G. J.; Gao, Y.; Dong, S. H.; Wang, D. L. GB/T 19145-2003, Determination of total organic carbon in sedimentary rock; Standards Press of China: 2003.
(46) GB/T212-2008, Proximate analysis of coal; China National Coal Association: 2008.
(47) SY/T5124-2012, Method of determining microscopically the reflectance of vitrinite in sedimentary; China National Energy Administration: 2012.
(48) GB/T18602-2012, Rock pyrolysis analysis; China Petroleum and Natural Gas Standardization Technical Committee: 2012.
(49) GB/T35210.1-2017, Determination methods of methane isothermal adsorption in shale; China National Standardization Administration: 2017.
(50) Moffat, D. H.; Weale, K. E. Sorption by coal of methane at high pressures. *Fuel* **1955**, *34*, 449–462.
(51) Sudibandriyo, M.; Pan, Z.; Fitzgerald, J. E.; Robinson, R. L.; Gasem, K. A. M. Adsorption of methane, nitrogen, carbon dioxide, and their binary mixtures on dry activated carbon at 318.2 k and pressures up to 13.6 MPa. *Langmuir* **2003**, *19*, 5323–5331.
(52) Mavor, M. J.; Hartman, C.; Pratt, T. J. Uncertainty in sorption isotherm measurements, paper 411. In *Proceedings 2004 international coalbed methane symposium*; University of Alabama: Tuscaloosa, May 2004.
(53) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.
(54) Fu, X. H.; Qin, Y.; Wei, C. T. *Coalbed methane geology*; China University of Mining and Technology Press: Xu Zhou, 2007.