Insight into the Adsorption of Methane on Gas Shales and the Induced Shale Swelling

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ABSTRACT: Shale gas resources are highly abundant in the world. They can provide sustainable energy supply and have the potential to reduce energy prices. Therefore, shale gas has become one of the most important resources for oil and gas exploration and production, especially in North America today. Adsorption and desorption of methane gas are some of the important physical and chemical processes involved in the accumulation, transport, and production of shale gas. The shale matrix will shrink or swell due to the desorption or adsorption of methane gas, which will impact the recovery of shale gas reservoirs. The main purpose of this investigation is to quantitatively ascertain how the adsorption of methane gas affects the volumetric changes of the shale matrix. Based on the adsorption potential theory, a modified Dubinin−Astakhov (D−A) equation was employed to describe the adsorption of supercritical methane gas on shale. Then, a coupled adsorption−strain model was established to investigate the volumetric strain of shale induced by the combined effects of methane gas adsorption and stress compression. The methane adsorption and the induced shale swelling were measured on a black shale sample from the Sichuan Basin at 303.15 K and pressure up to 10 MPa, and the proposed models were employed to interpret the experimental data. The results demonstrate that the proposed models show good applicability and provide a reliable prediction. The swelling moduli of shale samples were obtained by fitting the experimental data using the coupled adsorption−strain model. The results indicate that the swelling modulus of shale in this study is generally greater than that of coal. The calculated ratios of Young’s modulus to the swelling modulus do not show great variation from shale to shale in this study, which is similar to coal. This study can be incorporated into the numerical simulation of the production process of shale gas reservoirs.

1. INTRODUCTION

In recent years, shale gas, as an unconventional fossil fuel with great potential, has become a hotspot in global energy exploration and development and is profoundly changing the energy consumption patterns.1−3 According to the reports provided by the U.S. Energy Information Administration (EIA), in the United States, natural gas production from shale gas and tight oil plays accounted for more than 80% of total U.S. dry natural gas production in 2019 (Annual Energy Outlook 2020), and based on the assessment of world shale oil and shale gas resources, the technically recoverable resources of world shale gas resources are about 7299 trillion cubic feet (World Shale Resource Assessments). Therefore, the efficient development of shale gas will greatly expand the worldwide energy supply and promote the rapid growth of the global economy.

Shale gas refers to self-generated and self-stored natural gas that accumulates within organic-rich shales or mudstones as a free gas phase or adsorbed gas. The adsorbed gas accounts for about 20−80% of total natural gas reserves.4−6 The shale matrix contains a large number of nanoscale micropores. Due to the extremely small pore size, they have a large specific surface area and are the main adsorption space for the adsorbed gas in shale gas reservoirs. At present, the conventional subcritical adsorption models, such as the Langmuir model, Langmuir–Freundlich model, and Brunauer–Emmett–Teller (BET) model, are widely used to study the adsorptive capacity of shale in engineering applications,6−8 but these studies do not consider that methane is in a supercritical state.

Both experimental and theoretical studies have shown that the adsorption fluid can exert tremendous pressure on the surface of the nanoporous material, causing its strain, resulting in the so-called adsorption-induced deformation.9 This phenomenon also has been found to manifest in petroleum engineering, e.g., swelling of shale and coal.10−12 Many scholars have studied the adsorption and desorption of methane on coal.13−15 It is believed that methane is desorbed when the pressure is decreased with the production of gas wells and the coal matrix shrinks because of the desorption of methane, which leads to the increase of the permeability and production. Several scholars also have suggested the potential important significances of...
adsorption-induced deformation on gas transport behavior for the recovery of shale gas.\textsuperscript{16–18}

Recently, a few workers have done some research on the swelling of shale caused by gas adsorption. They mainly conducted experimental measurements to obtain the adsorption isotherms of methane on shale and adsorption-induced strain. Heller et al.\textsuperscript{17} investigated the swelling of pure mineral samples that constitute shales caused by the adsorption of methane and carbon dioxide. However, the quantitative relationship between adsorption and swelling did not been studied. Chen et al. studied the swelling phenomenon of shale samples caused by the adsorption of different gas such as helium, nitrogen, methane, and carbon dioxide.\textsuperscript{10,19} They qualitatively discussed the adsorption and swelling did not been studied. Chen et al. studied carbon dioxide. However, the quantitative relationship between adsorption and swelling did not been studied.

\subsection*{2. THEORY}

According to the classification for pores recommended by The International Union of Pure and Applied Chemistry (IUPAC), the pore diameter of a micropore is <2 nm, the pore diameter of a mesopore ranges from 2 to 50 nm, and the pore diameter of a macropore is >50 nm.\textsuperscript{21} Recent studies on the pore structure of shale have shown that the nanoscale pores are very abundant in shale and the pore types are mainly mesopores and micropores.\textsuperscript{22} The micropores provide substantial specific surface area and are the main adsorption sites for methane gas molecules. The dimension of the micropores is on the same order of magnitude as the diameter of methane gas molecules. According to the adsorption potential theory originally proposed by Polanyi,\textsuperscript{23} methane gas molecules residing within micropores are in proximity to the micropore walls and the micropore walls will provide an enhanced adsorption potential. Such adsorption potential field will exert a very strong adsorption force on methane gas molecules. Thus, once adsorption occurs, the micropores will be filled, causing micropore volume filling instead of a layering process because of the adsorption potential field encompassing the entire volume of micropores. Based on the Polanyi potential theory, Dubinin and his co-workers developed a micropore filling theory applicable to the description of adsorption equilibria in microporous solids.

The first basic equation of micropore filling theory is the Dubinin–Radushkevich (D–R) equation\textsuperscript{20}

\begin{equation}
    n = n_0 \exp \left(-\frac{A}{E_c}^2\right)
\end{equation}

where \( n \) is the amount adsorbed, mmol/g, \( n_0 \) is the maximum adsorption capacity, mmol/g, \( E_c \) is the characteristic energy, J/mol, and \( A \) is the adsorption potential, J/mol.

The adsorption potential \( A \) is the differential molar work of adsorption, expressed by

\begin{equation}
    A = RT \ln \left(\frac{P_0}{P}\right)
\end{equation}

where \( R \) is the universal gas constant, which is 8314 J/(kmol·K), \( T \) is the thermodynamic temperature, \( P_0 \) is the saturated vapor pressure, and \( P \) is the pressure.

The D–R equation is only suitable for describing a homogeneous microporous system. To describe a heterogeneous microporous system, Dubinin and Astakhov\textsuperscript{27} used Weibull’s distribution function to relate the amount adsorbed with the adsorption potential and then derived a more generalized adsorption curve equation. Because Weibull’s distribution function is a very flexible statistical function that can describe various probability distributions, the Dubinin–Astakhov (D–A) equation provides flexibility in allowing for the surface heterogeneity of the adsorbents. The D–A equation can be expressed as

\begin{equation}
    n = n_0 \exp \left(-\frac{A}{E_c}^m\right)
\end{equation}

where \( m \) is the heterogeneity parameter, which is a macroscopic measure of the sharpness of the micropore size distribution of the adsorbent. The D–R equation is a special case of the D–A equation. When \( m = 2 \), the D–A equation reduces to the D–R equation. If \( m < 2 \), the micropore structure of the adsorbent is generally recognized to be heterogeneous.

The values of critical pressure and critical temperature of methane gas are 4.60 MPa and 190.56 K, respectively. Thus, methane gas exists as the supercritical state under shale reservoir conditions. The concept of saturated vapor pressure in the D–A equation loses its meaning under the supercritical conditions. However, the abrupt change will not occur when the adsorbed gas transitions from the subcritical state to the supercritical state in the adsorption process. Therefore, a concept of pseudosaturated vapor pressure was employed to apply the D–A isotherm equation to supercritical gases. Dubinin introduced an equation to calculate the pseudosaturated vapor pressure at any temperature above the critical temperature.\textsuperscript{28} The equation can be written as

\begin{equation}
    P_0 = P_c \left(\frac{T}{T_c}\right)^2
\end{equation}

where \( P_0 \) is the pseudosaturated vapor pressure, \( T_c \) is the critical temperature, and \( P_c \) is the critical pressure.

Substituting eq 4 for the saturated vapor pressure in eq 2 and then substituting eq 2 for the adsorption potential in eq 3, the obtained model can be applied to describe the supercritical adsorption of methane gas on shale.

The first theory to provide a quantitative explanation of adsorption-induced deformation may be Bangham’s law. Based on experimental measurements of swelling of charcoal when taking up sulfur dioxide, ammonia, and carbon dioxide,
Bangham et al.\textsuperscript{29} came up with a monotonic swelling theory that the percentage linear swelling is directly proportional to the surface free energy \( E_J \). Therefore, the linear strain \( \varepsilon_l \) can be expressed as follows

\[ \varepsilon_l = \lambda E_J \] (5)

where \( \lambda \) is a deformation constant depending on the elastic properties of the adsorbent.

Based on Bangham’s law, Liu et al.\textsuperscript{11} originally proposed a strain model to describe the swelling of coal induced by methane adsorption. This strain model relates the volumetric strain in the coal matrix to pressure and the calculated results by the strain model show excellent agreement with the laboratory volumetric strain data. Considering that the mechanisms of adsorption-induced deformation in shales and coals are very similar to some extent, this strain model can also be applied to shale. Following Liu’s approach, when assuming that the adsorbent has a homogeneous structure with long thin cylinders, the deformation constant \( \lambda \) can be given by eq 6, which is originally suggested by Maggs\textsuperscript{30}

\[ \lambda = \frac{\rho \sum E_A}{p} \] (6)

where \( \sum \) is the specific surface area of the adsorbent, \( \rho \) is the density of the adsorbent, and \( E_A \) is the swelling modulus of the adsorbent that differs from Young’s modulus.

For the case where gas adsorbs on the adsorbent, the adsorption equation of Gibbs becomes

\[ E_J = RT \int_0^p \Gamma d(\ln p) \] (7)

where \( \Gamma \) is the adsorption amount per specific surface area and can be written as follows

\[ \Gamma = \frac{n}{\sum} \] (8)

Combining eqs 5–8, the relationship between the adsorption-induced linear strain \( \varepsilon_l \) and the amount of adsorption \( n \) can be derived as

\[ \varepsilon_l = \frac{\rho RT}{E_A} \int_0^p \frac{n}{p} dp \] (9)

In addition to the strain caused by gas adsorption, stress compression due to the free gas also leads to the mechanical strain on shale. According to the rock mechanic theory, the linear mechanical strain \( \varepsilon_m \) caused by stress can be written as

\[ \varepsilon_m = \frac{1 - 2\nu}{E} \int_0^p dp \] (10)

where \( \nu \) is Poisson’s ratio and \( E \) is Young’s modulus.

On a matrix block scale, it is assumed that the elastic mechanical behavior of shale samples is isotropic\textsuperscript{14,31,32} and the strains caused by adsorption and stress are independent of each other. Therefore, the total volumetric strain \( \varepsilon_{Vt} \) of the shale sample is given as

\[ \varepsilon_{Vt} = \frac{3\rho RT}{E_A} \int_0^p n dp - \frac{3(1 - 2\nu)}{E} \int_0^p dp \] (11)

Substituting eq 3 in eq 11, the correlation between the total volumetric strain and pressure can be obtained. This sample-scale model can be used to describe the variation of the volumetric strain of shale samples.

3. ERROR ANALYSIS

To evaluate the accuracy of the regression analysis using the coupled model, the average relative error (ARE) was introduced to describe the fitting accuracy for the coupled model. The expression of ARE is

\[ \text{ARE} (\%) = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{x_{i,exp} - x_{i,cal}}{x_{i,exp}} \right| \times 100\% \] (12)

where \( N \) is the number of experimental data and \( x_{i,exp} \) and \( x_{i,cal} \) are the experimental value and the calculated value, respectively.

4. RESULTS AND DISCUSSION

4.1. Experimental Results. The methane gas adsorption isotherm of the shale sample from the Longmaxi Formation is shown in Figure 1a. The result of volumetric strain due to methane adsorption is presented in Figure 1b. Note that the strain as a function of pressure follows a trend very similar to that of the adsorption isotherm. Some researchers have found a linear relationship between the volumetric strain and the adsorption amount when studying the swelling of coal and shale.\textsuperscript{10,13,17} The relationship between the volumetric strain and the adsorption
amount of the experimental sample is plotted in Figure 2. The solid line is the result of linear regression, and the dotted line is the confidence bands. The confidence level for curves is 95%, and the correlation coefficient is 99.596%. It is apparent that the volumetric swelling of shale exhibits a good linear relationship with the adsorption amount, which is consistent with the results of previous studies.

4.2. Coal Samples from the Illinois Basin and the San Juan Basin. To date, the experimental data of the methane adsorption-induced swelling of shale have rarely been reported. However, numerous studies on the swelling of coal caused by the adsorption of methane gas have been reported in the literature, and some of these experimental data have been widely recognized. Considering the similarity of the adsorption and swelling mechanisms between shale and coal, the proposed model discussed above is verified using the published experimental data of the volumetric strain induced by the methane adsorption on coal first. Harpalani et al.13 measured the methane adsorption-induced volumetric strain on two coal samples taken from the Illinois Basin and the San Juan Basin. The experimental adsorption data were fitted using the modified D–A equation first. The fitting curves are shown in Figure 3, and the adsorption parameters are listed in Table 1. The saturation adsorption capacities of the San Juan sample and the Illinois sample are 0.6778 and 0.4340 mmol/g, respectively. The heterogeneity parameter of the Illinois sample is 1.57, which is lower than that of the San Juan sample (1.70). This may indicate that the degree of heterogeneity of the Illinois sample is greater than that of the San Juan sample. The ARE is 0.04% for the Illinois sample and 0.16% for the San Juan sample. The results demonstrate an excellent agreement between modeled and experimental data.

The experimental data of the volumetric strain induced by the adsorption of methane on coal samples were fitted by the coupled adsorption–strain model established above. The input parameters required include the density of coal samples, Young’s modulus, and Poisson’s ratio. The specific values are summarized in Table 1. These values are collected from Liu et al.11 and Harpalani et al.13, which are reasonable for the two coal samples. The fitting results are shown in Figure 4, and the ARE values are listed in Table 1. The ARE values between measured and calculated strain values are 6.69% for the Illinois Basin coal and 3.15% for the San Juan Basin coal, which indicates that the established coupled model can provide an accurate prediction for the adsorption-induced deformation. The ratio of Young’s modulus to swelling modulus is 2.47 for the San Juan Basin coal and 2.91 for the Illinois Basin coal. Maggs10 believed that the reasonable value of $E_A$ is smaller than $E$, and the ratio $E/E_A$ ranges from 2 to 11 for coal. The values of $E_A$ do not vary greatly from coal to coal. The results obtained above are consistent with Maggs,10 which verifies the correctness of the model proposed in this paper.

4.3. Shale Sample from the Longmaxi Formation. Figure 5 shows the fitting curve of the adsorption data of the current experimental study in this paper. The maximum adsorption capacity, characteristic energy, heterogeneity parameter, and ARE are listed in Table 1. The calculated results are in excellent agreement with the experimental data. It can be seen from Figure 5 that the adsorption curve of the shale sample presents three stages: the adsorption amount increases sharply with the increase of pressure when it is less than 4000 kPa; the increase rate becomes small when the pressure is between 4000 and 8000 kPa, which can be regarded as a transition stage; and when the pressure is greater than 8000 kPa, the increase of the adsorption amount with the increase of pressure is stable, indicating that the adsorption of methane gas gradually becomes saturated.

The strain data of the sample were fitted using the established coupled model. The rock mechanical parameters of the sample are listed in Table 1. The fitting result is plotted in Figure 6. The ARE obtained by regression analysis is 3.11%. The fitting has achieved good results. The strain of the shale sample is the combined result of gas adsorption and stress compression due to free gas, which has opposite effects on the volumetric strain of the shale matrix. The overall trend of the volumetric strain is gradually increasing with increased pressure and gradually reaches a stable state when the pressure exceeds 10000 kPa. The swelling modulus of the shale sample obtained by regression analysis is 1590.11 MPa, which is greater than that of the coal samples. This indicates that the shale sample is less prone to deformation caused by adsorption compared with the coal sample. The ratio of Young’s modulus to the swelling modulus of the shale sample is 22.3, which is much larger than that of the coal sample.

4.4. Shale Samples from the Niutitang Formation. Chen et al.10 conducted experimental tests of methane gas adsorption and adsorption-induced strain on two shale samples collected from the lower Cambrian Niutitang Formation in Hunan Province, Southern China. Figure 7 presents the
adsorption isotherms of these two shale samples and the fitting results. The relevant fitting parameters are summarized in Table 1. The saturation adsorption capacity is 0.1544 mmol/g and the characteristic energy is 4570.53 J/mol for sample 1, and these are 0.1299 mmol/g and 5210.89 J/mol for sample 2. The ARE values are 5.43 and 4.76%, respectively. The heterogeneity parameter is considered to be an empirical parameter that can characterize the heterogeneity of the adsorbent. Activated carbon with a broad micropore size distribution is usually recognized to be strongly heterogeneous, and the heterogeneity

Table 1. Fitting Results and Input Parameters Required for Modeling

| samples       | maximum adsorption capacity, n₀ (mmol/g) | characteristic energy, E_c (J/mol) | heterogeneity parameter, m | ARE (%) | swelling modulus, Eₛ (MPa) | Young's modulus, E (MPa) | Poisson’s ratio, ν | ARE (%) |
|---------------|-----------------------------------------|------------------------------------|-----------------------------|---------|---------------------------|-----------------------|---------------------|---------|
| San Juan      | 0.6778                                  | 6353.48                            | 1.70                        | 0.16    | 1.40                      | 1395.99               | 0.37                | 3.15    |
| Illinois      | 0.4340                                  | 5474.71                            | 1.57                        | 0.04    | 1.40                      | 720.00                | 0.40                | 6.69    |
| Longmaxi      | 0.0556                                  | 5031.31                            | 1.52                        | 0.91    | 2.59                      | 1590.11               | 0.27                | 3.11    |
| Niutitang- S¹ | 0.1544                                  | 4570.53                            | 1.38                        | 5.43    | 2.35                      | 2419.35               | 0.28                | 2.39    |
| Niutitang- S² | 0.1299                                  | 5210.89                            | 1.55                        | 4.76    | 2.35                      | 2193.61               | 0.25                | 3.37    |
| illite        | 0.1209                                  | 5469.82                            | 1.53                        | 2.36    | 2.706                     | 8218.41               | 0.315               | 4.09    |
| kaolinite     | 0.0276                                  | 5273.15                            | 1.44                        | 4.32    | 2.444                     | 2691.27               | 0.319               | 4.13    |
| activated     | 6.240                                   | 5282.29                            | 1.19                        | 3.22    | 2.25                      | 62920.48              | 0.425               | 91.56   |
| carbon        |                                        |                                    |                             |         |                           |                       |                     |         |
| Barnett       | 0.0716                                  | 4911.75                            | 1.45                        | 10.08   | 2.25                      | 62920.48              | 0.425               | 91.56   |
| Marcellus     | 0.0261                                  | 5495.61                            | 1.65                        | 4.72    | 2.25                      | 62920.48              | 0.425               | 91.56   |
| Eagle Ford    | 0.0110                                  | 5548.18                            | 1.49                        | 4.38    | 2.25                      | 62920.48              | 0.425               | 91.56   |
| Montney       | 0.0392                                  | 4630.76                            | 1.23                        | 2.92    | 2.25                      | 62920.48              | 0.425               | 91.56   |

“Experimental data from Harpalani et al. ¹³” “Experimental data from this study.” “Experimental data from Chen et al. ¹⁰” “Experimental data from Heller et al. ¹⁷”

Figure 4. Fitting results of the volumetric strain data of two coal samples.

Figure 5. Fitting result of the experimental adsorption isotherm of the Longmaxi shale sample.

Figure 6. Fitting result of the volumetric strain data of the Longmaxi shale sample.

Figure 7. Fitting results of the adsorption isotherms of two shale samples from the Niutitang Formation.
parameter obtained for activated carbon generally ranges from 1.2 to 1.8. The values of the heterogeneity parameter of the two samples are 1.38 for sample 1 and 1.55 for sample 2, which indicates that the two samples are heterogeneous or have a broad micropore size distribution. Chen et al. also characterized the pore structure of the two shale samples using the nitrogen adsorption experiments and obtained the pore size distribution. The experimental results show that the pore size ranges from 1.69 to 58.11 nm for sample 1 and from 1.69 to 50.69 nm for sample 2. According to the classification for pore recommend by IUPAC, the two shale samples show a wide pore size distribution. The pore size distribution of sample 1 ranges from micropores to macropores and sample 2 is mainly micropores and mesopores. This may be the reason that the heterogeneity parameter of sample 2 obtained by the regression analysis is larger than that of sample 1.

Based on the adsorption parameters obtained by regression analysis, the strain data of these two shale samples were fitted. The fitting results are plotted in Figure 8. The relevant fitting parameters are listed in Table 1. The ARE obtained by regression analysis is 2.59% for sample 1 and 3.37% for sample 2, indicating that the proposed model achieved a good fitting result. The value of the swelling modulus obtained by regression analysis is 2419.35 MPa for sample 1 and 2193.61 MPa for sample 2. The ratio of Young’s modulus to swelling modulus is 19.2 for sample 1 and 20.1 for sample 2, respectively, which are close to that of the shale sample from the Longmaxi Formation. Compared with coal, the large ratios of Young’s modulus to swelling modulus for shale can be attributed to the high bulk modulus of shale. Shale is rigid; thus, the deformation of shale may be expected to be dominated by gas adsorption over stress compression exerted by free gas. The ratios of Young’s modulus to swelling modulus of these shale core samples do not vary greatly in this study, and to some extent, this is similar to coal core samples. This trend requires validation from more experimental data.

4.5. Shale Samples from the Barnett, Eagle Ford, Marcellus and Montney Reservoirs and Pure Mineral Samples. To better understand how the individual mineral compositions which constitute shales contribute to adsorption, Heller et al. conducted an experiment to test the adsorption capacity of pure mineral components and shale samples, and the adsorption-induced swelling of pure mineral samples was also studied. The shale samples were collected from different basins in the United States and had different characteristics. The pure mineral components included organic matter (using activated carbon instead), illite, and kaolinite. The experimental adsorption data are fitted using the modified D–A model. The fitting results are plotted in Figure 9, and the fitting parameters are listed in Table 1. The ARE values of the samples are all within 10.08%, indicating the successful fitting results. The adsorption capacities of shale samples are different, which can be ascribed to the contents of clay minerals and TOC of shale samples. For pure minerals, activated carbon exhibits a strong adsorption capacity. The adsorption capacity of kaolinite is relatively weaker than that of illite in clay minerals. The heterogeneity parameter of the activated carbon is about 1.19, indicating that the activated carbon has a very broad pore size distribution. The heterogeneity parameter of other shale samples and pure minerals is around 1.5 except for the Montney sample.

The meaningful attempts on the swelling of pure minerals were also made by Heller et al. However, this is a very challenging task. While we attempted to fit the strain data of pure minerals, a perfect match was not achieved. The fitting results are presented in Figure 10, and the ARE values are listed in Table 1. For illite and kaolinite, their effective elastic properties are from Wang et al. As can be seen, the ARE values of activated carbon and kaolinite between modeling results and experimental data are greater than 45%, showing a large fitting error. These errors may be related to two reasons. First, swelling and adsorption experiments were performed separately. Second, the swelling experiments were conducted at 25 °C, whereas the adsorption experiments were conducted at 40 °C. Despite these potential sources of error, an apparent trend is observed; that is, the swelling of clay and pure carbon both is approximately linearly proportional to the amount of adsorption, which is consistent with the results observed in shale samples.

5. CONCLUSIONS

To investigate the adsorption and swelling behavior of shale samples, a new coupled model was proposed and adsorption experiments were carried out. The experimental data of adsorption and strain of shale samples from different reservoirs were employed to validate the proposed model and shed light on the adsorption and swelling nature of shale. Based on the results and analysis of this work, the major conclusions can be summarized as follows:

1. The proposed modified D–A model is suitable for describing the adsorption behavior of the supercritical methane gas in shale. The modeling results are in good agreement with the experimental data, and the ARE between the predicted and observed data ranges from 0.04 to 10.08%, with an average of 3.61%.

2. The proposed coupled adsorption–strain model is a reliable predictive strain model for studying the swelling of shale induced by both methane gas adsorption and stress compression due to free gas. It can be used to accurately fit the volumetric strain data of shale samples with reasonable elastic properties of shale samples. Also, the swelling modulus of shale samples can be obtained by regression analysis. Generally, the swelling modulus of shale is greater than that of coal.

3. In this study, the calculated ratios of Young’s modulus to the swelling modulus for shale core samples range from 19.2 to 22.3, which do not show great variation. These
values are higher than that for coal core samples (about 2–11).

(4) The experimental study on swelling of pure mineral samples that constitute shales is necessary in future work for comprehensively understanding the adsorption-induced deformation of shale.

6. EXPERIMENTAL SECTION

6.1. Sample Preparation. In this paper, a black shale sample from the Longmaxi Formation of the Lower Silurian in the Sichuan Basin, which is located in Sichuan Province, China, was selected for the methane gas adsorption experiment and the corresponding swelling experiment. The mineral composition of the sample was analyzed by X-ray diffraction experiments, and the results are presented in Figure 11. The mineralogy of the shale sample is complex and mainly composed of quartz, feldspar (potassium feldspar, plagioclase, etc.), carbonate minerals (calcite, dolomite, etc.), and clay mineral composition, the contents of which are 42.2, 10.8, 12.1, and 32.6%, respectively. The clay minerals contained in the shale sample are mainly illite/smectite, illite, and a small amount of chlorite. The total organic carbon content (TOC) of the shale sample is 2.58%, indicating that the shale sample is rich in organic matter. The vitrinite reflectance ($R_o$) value of the shale sample is 3.17%, indicating that the shale sample is at the stage of over-maturation.

6.2. Experimental Apparatus and Procedure. The schematic of the experimental apparatus for the study is presented in Figure 12. The experimental apparatus is mainly composed of a high-pressure injection system, a high-pressure adsorption chamber, an evacuation system, a temperature control system, a pressure control system, a strain testing system, and a data detection and recording system. The high-pressure injection system is mainly composed of an ISCO pump. The ISCO pump can precisely control the injection pressure and detect the fluid injection. The temperature control system mainly includes an air bath with a constant temperature. The high-pressure adsorption chamber is placed in the air bath to ensure that the temperature remains constant during the experiment. The strain testing system is mainly composed of the strain data acquisition instrument. After polishing the sample to remove the debris on the surface of the sample, the strain sensors are mounted on the surface of the sample. Then, the sample is quickly transferred to the high-pressure adsorption chamber and connected to the strain test device for the experiment. The data detection and recording system mainly consists of sensors and high-performance computers. The gas source used in the experiment includes helium with purity $\geq 99.999\%$ and methane gas with purity $\geq 99.99\%$. The experiments were carried out at 303.15 K and pressure up to 10 MPa.

The airtightness of the experimental apparatus is a key factor affecting the reliability of the experimental results. Therefore, the air pressure test for the tightness of the whole system is first carried out before the experiment begins. The entire experimental setup is connected, and then, helium gas is injected into the experimental system to increase the system...
pressure slightly above the required experimental pressure. If the system pressure is stable within 24 h, the experimental system can be considered to be airtight. If the pressure fluctuates or falls, the leak point should be found and the experimental setup should be adjusted until the airtightness of the experimental system meets the experimental requirements.

Prior to the adsorption experiment, the void volume of the experimental system should be determined. Helium is generally considered to be a nonadsorbed gas; that is, the amount adsorbed can be neglected at a certain temperature and pressure. Therefore, it is possible to determine the void volume using helium. First, the experimental system is evacuated, then a certain amount of helium is injected, and the equilibrium pressure is recorded. The void volume can be calculated by

![Figure 10](image1.png)

**Figure 10.** Fitting results of the experimental data of the volumetric strain: (a) activated carbon, (b) illite, and (c) kaolinite.

![Figure 11](image2.png)

**Figure 11.** Mineralogy data of the shale sample from Sichuan Basin: (a) mineralogical composition and (b) clay mineral composition.

![Figure 12](image3.png)

**Figure 12.** Schematic of the experimental apparatus.
applying the equation of state and the mass conservation equation. Once the void volume is determined, measuring the adsorption isotherms of the shale sample can be started. The experimental system is first evacuated and then injected with a quantity of methane gas. After the adsorption reaches equilibrium under the desired pressure, an appropriate amount of methane gas is continuously injected into the high-pressure adsorption chamber to determine the next adsorption equilibrium pressure. The above experimental procedure is repeated until a complete adsorption isothermal is determined. The adsorption amount of methane gas is calculated using the equation of state and the mass conservation equation. During the adsorption experiment, the data of the volumetric strain of the shale sample is continuously detected and recorded.

6.3. Absolute Adsorption Amount. The experimental measurements of adsorption isotherms only provide excess adsorption amount, which ignores the volume occupied by the adsorbed phase. However, the absolute adsorption amount (that is the real adsorption amount) is used in the D—A equation. Therefore, it is necessary to estimate the absolute adsorption amount from the excess adsorption amount. In this study, the conversion method between the excess adsorption amount and the absolute adsorption amount introduced by Sudibandriyo and Pan35 is used. The equation can be expressed as

\[ n_{\text{ads}}^{\text{absolute}} = n_{\text{ads}}^{\text{excess}} \left( \frac{\rho_{\text{ads}}}{\rho_{\text{ads}} - \rho_{\text{gas}}} \right) \]  

(13)

where \( n_{\text{ads}}^{\text{absolute}} \) and \( n_{\text{ads}}^{\text{excess}} \) are the absolute adsorption amount and the excess adsorption amount, respectively, \( \rho_{\text{ads}} \) is the density of the adsorbed gas, which is assumed to be the liquid density at the atmospheric pressure boiling point for CH\(_4\), and \( \rho_{\text{gas}} \) is the density of the free gas, which is calculated from the NIST Standard Reference Database.37

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Notes

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