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Quantitative Studies on the Characterization and Evaluation of Adsorbed Gas and Free Gas in Deep Shale Reservoirs

Weijun Shen,* Luo Zuo, Tianran Ma, Cong Chen, Chaozhong Qin, Liu Yang, and Kun Xie

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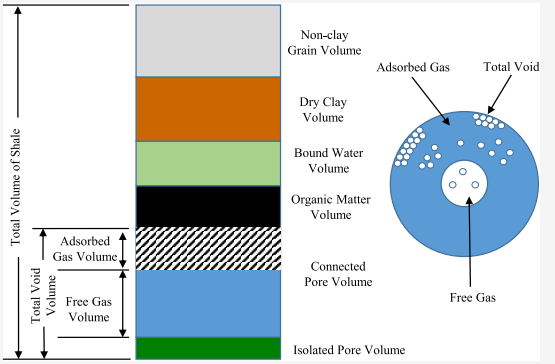
ABSTRACT: The quantitative characterization of adsorbed gas and free gas in shale reservoirs is a key issue in exploration and development of shale gas. Thus, the aforementioned topic is of great significance to the evaluation of reserves, the screening of favorable target areas, and the formulation of development plans. However, research on our current understanding of the quantities of adsorbed gas and free gas in deep shale gas reservoirs is still lacking. To address this problem, deep shales from the Longmaxi Formation in southern China were collected to conduct high-pressure isothermal adsorption experiments. The high-pressure isothermal adsorption model was used to describe the adsorption behavior of methane in deep shales, and the adsorbed gas and free gas in the deep shales were characterized quantitatively. The effects of temperature, pressure, and moisture on the adsorbed gas and the density of the free gas were analyzed. The results indicated that the excess adsorption isotherm curve for methane in deep shales increased and then decreased with the increase of pressure, and the modified Langmuir adsorption model may be used to describe the high-pressure adsorption behaviors. The adsorbed gas in shales decreases gradually with the increase of pressure, and the proportion of adsorbed gas and free gas is between 23 and 74% when the pressure reaches 50 MPa. The adsorbed gas in deep shales decreases with an increase of temperature, and the presence of water greatly reduces the adsorption capacity of the deep shale. The pore space occupied by the free gas in shale increased with the increase in the density of the free phase, and the ratio of the adsorbed gas to the free gas decreased. This research provides a useful reference for explaining how to best evaluate shale gas reservoirs, estimate the reserves in deep shales, and evaluate the adsorption and flow capacity of deep shale gas.



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1. INTRODUCTION

With breakthroughs in exploration and development for shale gas in Fuling, Changning, and Weiyuan and the increase in commercial development, the current exploration projects are gradually expanding to deep shale gas reservoirs (depths in excess of 3500 m).[1] It is estimated that deep shale gas resources are extensive in areas such as Jiao Shi Ba and Chuan Nan in the Sichuan basin. These deep shale gas resources have reached 4612 × 10^8 m^3 and are seen as having great prospects for exploration and development.[2,3] Given the rapid development of the national economy, the demand for natural gas in China continues to increase. The dependence on natural gas increased to 43% in 2021, and thus the security of energy supply is assuming increasing importance. Accelerating the development of deep shale gas resources is of strategic significance to alleviate the contradiction between natural gas supply and demand, guarantee national energy security, and optimize energy structure in the country.

Deep shale reservoirs are high-temperature and high-pressure environments, and the shale matrix consists of an excess of tight pores with low permeability and very small pore diameters and nanoscale pore throats.[4−6] Shale gas occurs in various physical states, including the free gas state, the adsorbed state, and a small amount of dissolved gas in the shale pore-fracture system. The volume of the adsorbed gas can reach 20−85% of the total volume of shale gas.[7,8] Due to the relatively small percentage of dissolved gas, this fraction is quite small when calculating the gas content of shale, and thus how to accurately quantify the adsorbed and free gas contents in shale reservoirs is the key to evaluating the shale resources.[9,10] The quantitative characterization and evaluation of the adsorbed and free gas in shale reservoirs is a difficult problem in exploration and is necessary to calculate the potential volume of the shale gas resource when screening favorable target areas and formulating development plans. This

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Table 1. Basic Physical Data for the Deep Shale Samples

Sample no.	Depth, m	Porosity, %	TOC, %	Surface area, m^2/g	Average pore size, nm	Mineral composition
SW-1	3873.92−3874.00	7.12	1.08	16.43	4.66	Quartz, pyrite, clay
SW-2	4028.75−4029.08	5.38	3.56	25.84	4.22	Quartz, plagioclase, pyrite, clay
SW-3	4035.81−4035.89	3.78	4.95	27.87	4.95	Quartz, illite, pyrite, clay
SW-4	4040.16−4040.26	4.52	2.56	20.00	2.56	Quartz, illite, calcite, pyrite, clay

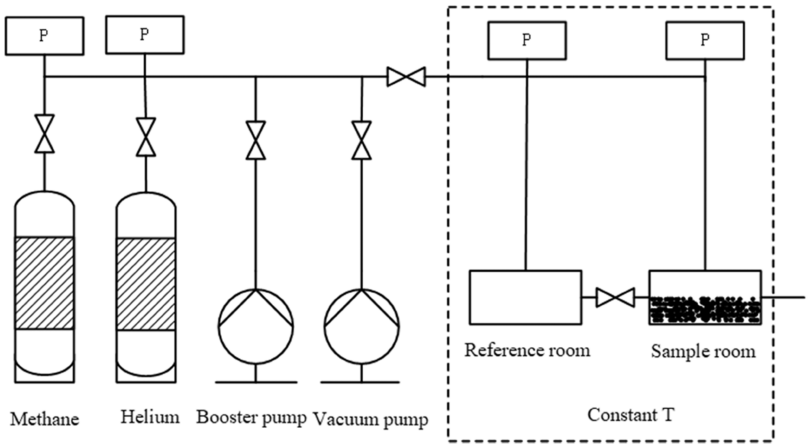

Figure 1. Schematic of the experimental setup for isothermal adsorption.

topic also underpins the basis for achieving scientific and efficient development of shale gas reservoirs.

Currently, many methods to characterize the gas content of shale are in use, including, for example, the field desorption method, logging measurements, molecular dynamics simulation, and the isothermal adsorption method.[10] The field desorption method cannot determine the amount of gas lost as a result of drilling and removal of the core, but a value can be estimated by mathematical computation.[11] The logging measurement needs to correct the empirical equation for the content of the adsorbed gas with respect to parameters such as temperature and pressure, and thus the accuracy is not high.[12] The accuracy of molecular dynamics simulation needs to be further verified, while isothermal adsorption is currently the most common method in use.[13] Isothermal adsorption is the main approach used to obtain the content of the adsorbed gas in shale under different temperatures and pressures.[14] Much experimental research has been carried out on the isothermal adsorption of shales. Li et al.[15] analyzed the effects of temperature and pressure on the content of the adsorbed gas in shales via isothermal adsorption and then used the Langmuir model to calculate the adsorbed gas for the reservoir conditions. Gasparik et al.[16] suggested that methane and water molecules share the same adsorption sites in shales, and their coexistence results in competitive adsorption, which will reduce the amount of adsorbed gas. Xiong et al.[17] proposed an improved Dubinin−Astakhov (D−A) model to calculate the volume of adsorbed gas by combining the characteristics of the D−A model and the isothermal adsorption curves. Li et al.[18] analyzed the adsorption characteristics of shale in the Songliao, Bohai Bay, and Ordos Basins and presented a comprehensive polynomial simulation to predict the adsorption pressure and volume of the Langmuir adsorptive layer, whose volume was influenced mainly by temperature and the shale properties. Duan et al.[19] conducted isothermal adsorption measurements under reservoir pressure conditions, established a high-pressure mathematical model for adsorption by shales, and proposed a modified method for calculating the content of shale gas. Rani et al.[20] pointed out that the adsorption of methane from water-bearing shales decreases and that organic-rich matter has a great effect on the adsorption of methane. Shi et al.[21] used comprehensive experimental methods such as isothermal adsorption and low-temperature nitrogen adsorption to perform comparative analysis of the high-pressure isothermal adsorption characteristics of shale and considered that the adsorbed gas of deep shale accounts for about 30% of the total gas. However, the above isothermal adsorption studies of shale gas are based mainly on its application to shales at depths shallower than 3500 m, where the experimental pressure is less than 40 MPa. In the high-pressure environment of a deep shale reservoir, the gas in the nano-limited space will exist in the form of a "solid-like dense accumulation" state, and the density would be much higher than that of free gas. The thermodynamic parameters of methane can change, and the phase characteristics of methane in the different shale pores vary greatly.[2,4] Quantitative studies concerning the characterization and evaluation of the adsorbed gas and free gas in deep shales are limited; hence, research aimed at quantifying the adsorbed gas and free gas in deep shales is necessary to optimize gas production in deep shale gas reservoirs.

In this study, the deep shales from the Longmaxi Formation in southern China were selected, and a high-pressure isothermal adsorption experiment of the deep shales was conducted. Then the high-pressure isothermal adsorption model was applied to describe the adsorption behavior of the deep shales and to characterize quantitatively the adsorbed and free gas in the deep shales. Moreover, a discussion of the effects of temperature, pressure, and water content, and the effects of the density of the free phase is given. The results provide a reference for interpreting and gaining a better understanding of the evaluation results for reservoirs, estimating the reserves of deep shales, and evaluating the adsorption capacity of deep shale gas.

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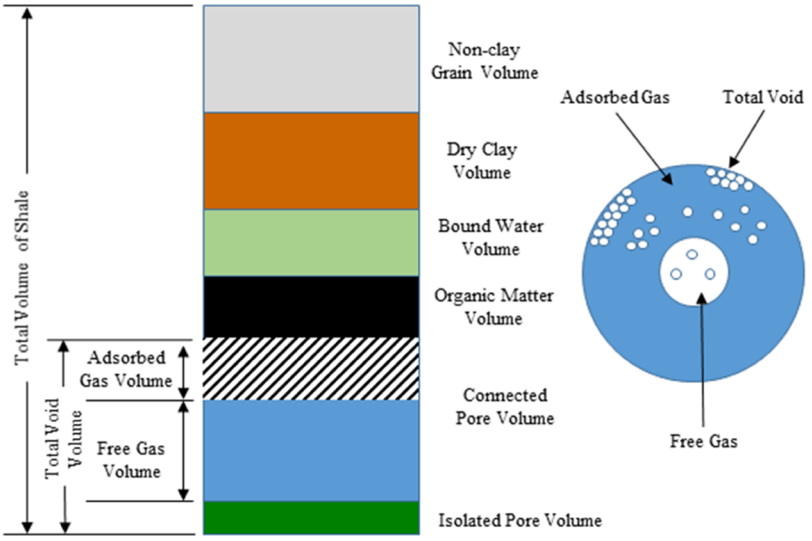

Figure 2. Schematic of the volumetric model for shale gas.

2. EXPERIMENTAL SAMPLES AND METHODS

2.1. Experimental Samples. Four deep shale samples at depths of 3873−4041 m were selected from the lower Silurian Longmaxi Formation of the Sichuan Basin, South China. Standard methods were used to measure the physical properties of the samples. The porosity was measured using an automated permeameter/porosimeter (Coretest Systems AP-608; CA), with values ranging from 3.78 to 7.12%. The total organic carbon (TOC) content was measured using a TOC analyzer (Shimadzu TOC-V; Kyoto, Japan). The TOC values ranged from 1.08 to 4.95% (measured using range settings of 2−6%). The specific surface area and pore size were measured using the low-temperature nitrogen method. The specific surface areas of the deep shales were between 16.43 and 27.84 m^2/g, and the average pore size was in the mesopore range, ranging from 2.56 to 4.95 nm. The mineral composition was measured by X-ray diffraction, and the results indicated that the mineral composition of the deep shales was dominated by quartz, pyrite, and clay minerals. The physical properties of the deep shales are specified in Table 1.

2.2. Experimental Methods. The high-pressure isothermal adsorption measurements of the deep shales were performed using a 3H-2000 PH high-pressure adsorption system (Beishide Instrument; Beijing, China). A schematic of the experimental setup is given in Figure 1. The system consisted of a gas adsorption station, a high-pressure booster pump, an air compressor, a constant temperature water bath, and a high-pressure gas cylinder. The adsorption capacity for the various samples was measured using the volumetric method.[22] The system was able to ensure a constant temperature of 20−80 °C and a maximum pressure of 69 MPa.

Adsorption studies on methane were carried out on crushed shale. Prior to isothermal adsorption measurement, ∼150 g of a crushed shale sample (60−80 mesh) was selected and dried at 105 °C for 24 h to remove water, followed by degassing under vacuum at 150 °C. In the high-pressure adsorption studies, the experiments were conducted using high-purity (99.99%) methane and the first pressure point was set to vacuum, and then the pressure of methane was adjusted continuously in the pressure range 1−50 MPa. The time to establish equilibrium for the adsorption was generally set to 6 h to ensure the complete adsorption of methane. The maximum pressure point was about 50 MPa, and the data points for adsorption were more than 10. After completion of the experiments, the shale samples were dried and degassed, and saturated K_2SO_4 solution was used to induce water adsorption by the deep shales. When the water adsorption by the shale samples had reached equilibrium, the isothermal adsorption experiment with methane was performed, and the methane adsorption characteristics of methane for the water-bearing shales were analyzed.

3. BASIC THEORY

3.1. High-Pressure Isothermal Adsorption Model. The critical temperature and critical pressure of methane are −82.5 °C and 4.59 MPa, respectively, and adsorption of methane in deep shales is supercritical under reservoir conditions.[22] The adsorption capacity for methane of deep shales under high-pressure conditions may be described using the terms excess adsorption and absolute adsorption.[3,23] In general, under low-pressure conditions, the volume of the adsorbed phase is relatively small, and the excess adsorption approximates to absolute adsorption. However, the volume of the adsorbed phase has a high value at the high-pressure stage, which cannot be neglected. The relationship between the excess adsorption volume and the absolute adsorption volume[23] can be expressed as

$$m_{exc} = m_{abs} \times \left(1-\frac{\rho_g}{\rho_a}\right) = m_L \frac{p}{p + p_L} \times \left(1-\frac{\rho_g}{\rho_a}\right) \quad (1)$$

where m_{exc} is the excess adsorption, m^3/t; m_{abs} is the absolute adsorption, m^3/t; m_L is the maximum amount adsorbed at the Langmuir pressure, and the Langmuir pressure is the pressure at which one-half of the Langmuir volume can be adsorbed; p_L is the Langmuir pressure, MPa; p is the pressure of gas adsorption, MPa; ρ_a is the gas density of the adsorbed methane, kg/m^3, and ρ_g is the free gas density of methane, kg/m^3.

3.2. Adsorption and Evaluation Method for the Free Gas. According to Ambrose et al.,[24] a simplified model of a physical shale matrix can be given as outlined in Figure 2, where the shale matrix consists of non-clay grain, dry clay, bound water, organic matter, and connected and isolated pores. In the case of the volumetric model for shale gas, the total volume of gas can be expressed as

$$G_{st} = G_f + G_a + G_{so} + G_{st} \quad (2)$$

where G_{st} is the total gas content of the shale, m^3/t; G_f and G_a are the free gas and adsorbed gas in the shale, m^3/t, respectively; and G_{so} and G_{sw} are the dissolved gases in the oil and water, m^3/t, respectively.

In the case of calculations for the content of industrial gases, the dissolved gas content in oil and water can be neglected.[24]

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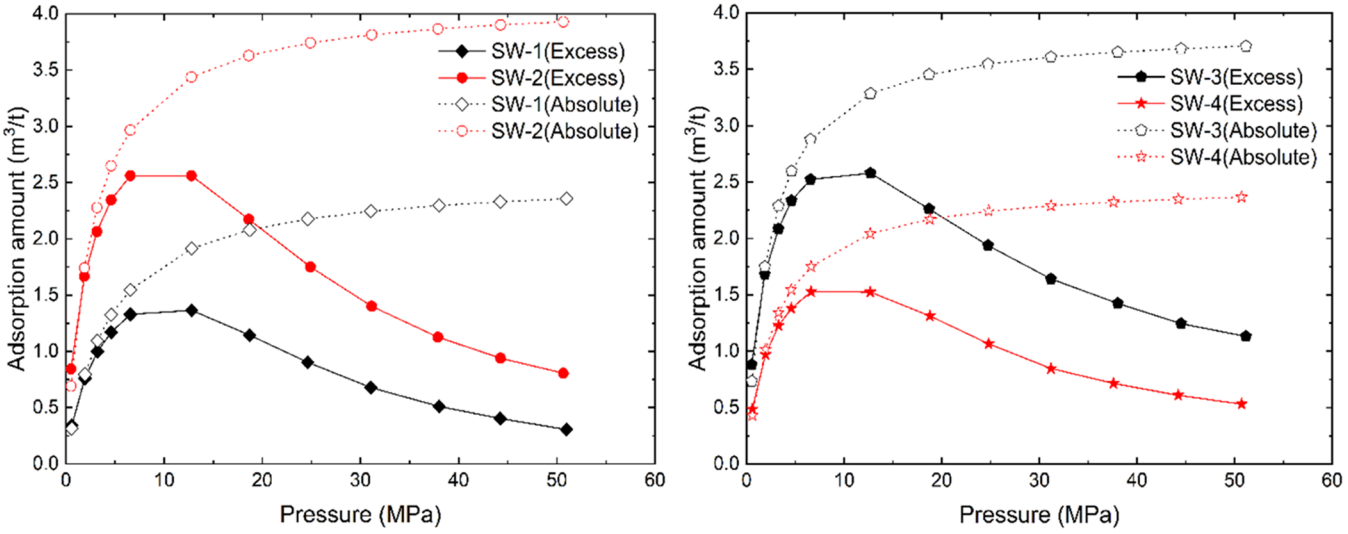

Figure 3. High-pressure isothermal adsorption curves for methane in deep shales.

The dissolved gas in oil and water and the adsorbed gas from organic matter can be determined precisely during the isothermal adsorption experiments. Therefore, the gas content of shale gas can be simplified as

$$G_{st} = G_f + G_a \tag{3}$$

Given that the adsorbed gas is adsorbed on the pore surface of the shale, the gas will occupy a certain amount of pore space in the shale. Also, assuming that the pore space in the shale occupied by the adsorbed gas is ϕ_a, the content of the free gas[25] can be expressed as

$$G_f = 32.0368 \frac{\phi(1 - S_w) - \phi_a}{\rho_b B_g} \tag{4}$$

For a system containing a single component, ϕ_a can be expressed as

$$\phi_a = 1.318 \times 10^{-6}\, M \frac{\rho_b}{\rho_s}(G_a) \tag{5}$$

where B_g is the gas volume coefficient, $B_g = Z\frac{273+T}{293}\frac{P_{sc}}{P}$; S_w is the saturated bound water content in shale; Z is the gas compression factor; T is the temperature, °C; P_{sc} is the gas pressure at standard conditions, MPa; and ρ_b and ρ_s are the densities for shale and the single component gas, t/m^3, respectively.

Substituting eq 5 into eq 4, the content of free gas in the shales can be expressed as

$$G_f = 32.0368 \frac{\phi(1 - S_w) - 1.318 \times 10^{-6}\, M \frac{\rho_b}{\rho_s}(G_a)}{\rho_b B_g} \tag{6}$$

For the adsorbed gas, the modified Langmuir model[25] can be used, and this can be expressed as

$$G_a = G_L \frac{p}{p + p_L} \times \left(1 - \frac{\rho_g}{\rho_a}\right) \tag{7}$$

Therefore, the total volume of gas in the shales can be expressed as

$$G_{st} = 32.0368 \frac{\phi(1 - S_w) - 1.318 \times 10^{-6}\, M \frac{\rho_b}{\rho_s}(G_a)}{\rho_b B_g} + G_L \frac{p}{p + p_L} \times \left(1 - \frac{\rho_g}{\rho_a}\right) \tag{8}$$

4. RESULTS AND DISCUSSION

4.1. High-Pressure Isothermal Adsorption Characteristics. The characteristics of the high-pressure adsorption curves for the different shales at 40 °C are plotted in Figure 3. From the results, it can be seen that the isothermal adsorption curves for excess methane in deep shales have similar characteristics. With the increase in pressure, the adsorption curves exhibit a rising and then a decreasing trend. At the low-pressure stage (less than 13 MPa), the adsorption curve rises rapidly and increases approximately linearly with the increase of pressure, whereas at high-pressure (greater than 13 MPa), the methane molecules in the adsorption layer gradually become saturated such that the excess adsorption decreases gradually with the increase of pressure. The amount of adsorption relates to the excess adsorption, not the absolute amount. With reference to eq 1, the excess adsorption can be converted into the absolute adsorption. In Figure 3, it can be seen that the absolute amount of adsorption in the deep shales also shows similar variation characteristics, and the trend is for a rapid increase and then a slow increase with an increase of pressure. According to IUPAC,[26] the absolute adsorption curves for these deep shales exhibit a type I isotherm response. At the low pressure stage (0−4 MPa), the absolute adsorption is almost equal to the excess adsorption, mainly because at low-pressure, the bulk density of the gas phase is relatively small and the volume of the adsorbed phase is negligible. As the pressure increases, the absolute amount of adsorption of methane increases slowly, while the excess amount gradually becomes parabolic and then decreases. Under low-, medium-, and high-pressure conditions, the excess adsorption in the deep shales increases rapidly, then reaches a peak, and finally decreases under high-pressure conditions.

The adsorption isotherm is the amount of adsorbed solute when the surface of a material (adsorbent) reaches equilibrium

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under specified temperatures when equilibrium is established.[27] To describe isothermal adsorption phenomena, various mathematical models for the adsorption have been proposed.[28−30] For the high-pressure adsorption behavior, a modified Langmuir adsorption model can be used for the description.[3,31] According to our results for the high-pressure adsorption of methane in deep shales, the modified Langmuir adsorption model was fitted, and the fitting results for the excess adsorption are illustrated in Figure 4. From the plots, it

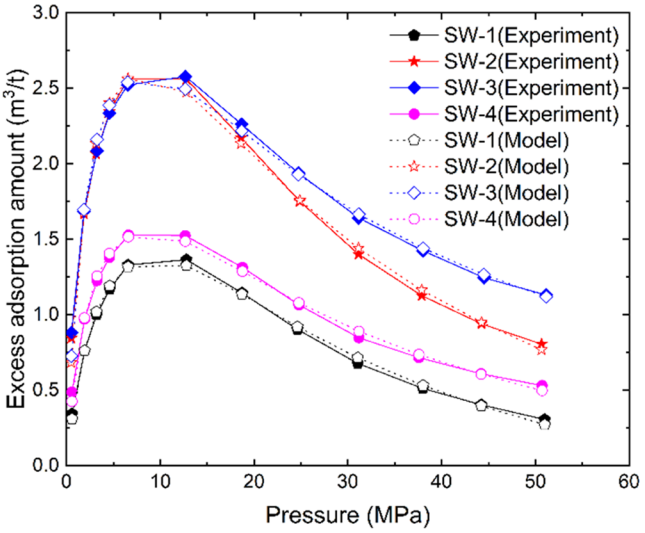

Figure 4. Excess sorption fitting results for the model in shales.

can be seen that the excess adsorption of methane can be well fitted by the modified Langmuir model throughout the pressure fitting section, and the correlation coefficient reaches 0.99. Therefore, the modified Langmuir adsorption model can be used to describe and predict the high-pressure isothermal sorption characteristics of methane in deep shales.

4.2. Adsorption and Evaluation of Free Gas. Gas is stored in shale mainly as adsorbed gas in the organic matter and clay minerals and as free gas in the fractures and other pores.[32,33] Therefore, understanding the characterization and evaluation of adsorbed gas and free gas is greatly significant in shale gas reservoir evaluations and estimating the original gas in place. In this study, the variation in the relationship between the adsorption of methane and the free gas in shale under different pressure conditions is illustrated in Figure 5. From the results, it can be seen that when the temperature is constant, the fraction of adsorbed gas in shale gradually decreases with the increase of pressure, while the free gas content gradually increases. When the pressure is low, the fraction of the adsorbed gas is larger than the content of the free gas. However, when the pressure exceeds a certain critical value, the adsorbed gas content in the shale is smaller than that of the free gas, and the amount of this change gradually increases with the increase of pressure. This is because when the adsorption enters the high-pressure stage, the adsorption force field of the methane molecules adsorbed at the wall surface does not change much with the increase of pressure, and the adsorbed molecules gradually increase and reach saturation, whereas the free methane molecules are only subject to the intermolecular forces of the gas. With an increase of pressure, the intermolecular forces of the methane molecules in the free states will keep increasing, which results in an increase in the

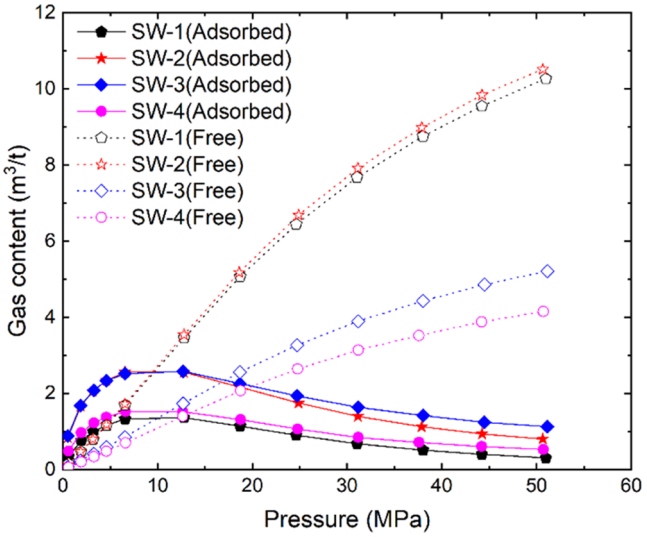

Figure 5. Relationship between the methane content of shale under different pressure conditions.

content of the free gas. When the pressure reaches 50 MPa, the amount of adsorbed gas in the deep shale is much smaller than the amount of free gas, and the ratio of adsorbed gas to free gas is in the range of 23−74%.

4.3. Effect of Pressure on Adsorbed and Free Gas. Gas adsorption depends on the chemical potential energy of the free gas as well as the composition of the shale surface, and the in situ high-pressure conditions play significant roles in the shale gas adsorption process.[34] Some previous studies have indicated that, in addition to the physicochemical properties of shale, external factors such as temperature and pressure have important effects on the methane adsorption capacity of shale.[35,36] To understand the effect of pressure on adsorption and the free gas content, the relationship between the ratio of the adsorbed gas and the free gas as a function of pressure is shown in Figure 6. From the results, it can be seen that the ratio of adsorbed gas to free gas in deep shales shows a rapid decrease and then tends to be constant as the pressure increases. When the pressure increases from 5 to 10 MPa, the ratio of the adsorbed gas to the free gas in shale decreases

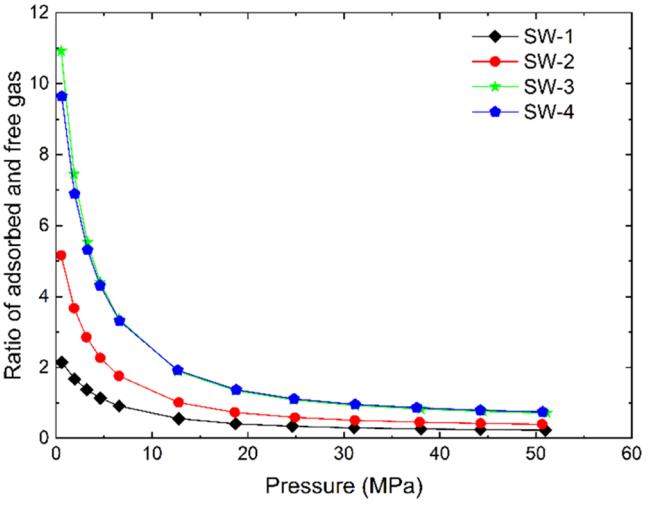

Figure 6. Ratio of the adsorbed gas to the free gas as a function of pressure.

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rapidly. When the pressure increases to nearly 20 MPa, the adsorbed gas content is approximately equal to the free gas content. As the pressure continues to increase, the growth rate in the content of the adsorbed gas becomes smaller than the growth rate of the free gas content, and this results in the ratio of the content of adsorbed gas to free gas in the shale decreasing slowly with the value eventually becoming constant.

4.4. Effect of Temperature on the Adsorbed Gas. Temperature is one of the most important factors impacting the methane adsorption capacity of shale; previous studies have shown that temperature will reduce the adsorbed gas in shale.[36] Due to the exothermic nature of physical adsorption, less adsorbed gas is expected in the high-temperature shale gas reservoirs. In this study, the absolute adsorption capacity of shale as a function of temperature is presented in Figure 7.

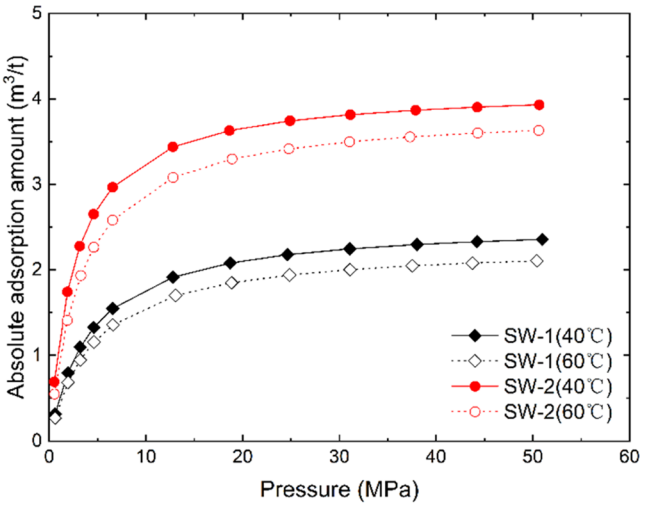

Figure 7. Relationship between the pressure and the absolute adsorption capacity for methane in shale at different temperatures.

From the results, it can be seen that when the pressure is constant, the adsorbed gas content of the deep shales decreases with the increase of temperature; for temperature increases from 40 to 60 °C, the gas content decreases by 7−10% on average. The reason for this trend is that the adsorption of methane is an exothermic process. As the temperature increases, the capacity of adsorption of the shale gas becomes smaller than the capacity of desorption, and this eventually leads to a decrease in the adsorption capacity of the shale. When the pressure increases from 0 to 10 MPa, the volume of the adsorbed gas increases faster. Once the pressure is higher than 10 MPa, the increment in the volume of the adsorbed gas becomes smaller as the pressure continues to increase; when the pressure increases from 10 to 50 MPa, the adsorbed gas content of the shale increases by about 20%.

4.5. Effect of Water Content on the Adsorption of Methane. The presence of water content has a large impact on the gas adsorption capacity of shale and the evaluation of shale gas content, which is due to the fact that adsorbed water molecules will occupy the adsorption sites and block pores in the shales.[3,37] The variation in the relationship of the adsorption isotherm for shale due to differences in the water content is illustrated in Figure 8. As can be seen, when the temperature is constant, the adsorption of water-bearing shale under the same pressure conditions decreases significantly, and the adsorption isotherm on the whole shifts in a downward

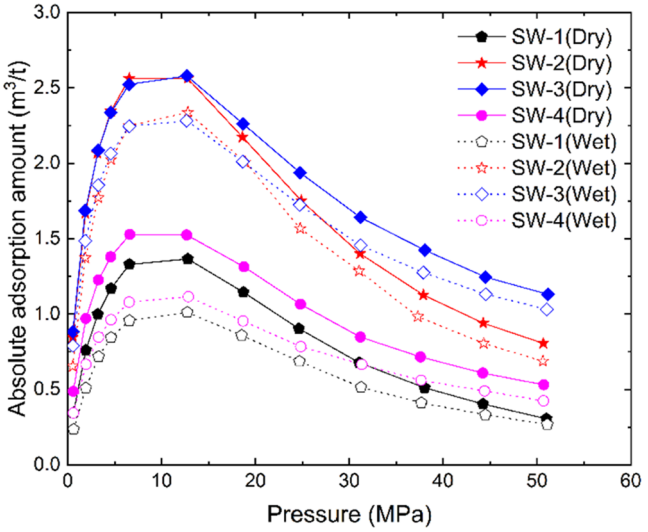

Figure 8. High-pressure isothermal adsorption of deep shales in dry and wet conditions.

direction. At low pressure, the isothermal adsorption curve rises rapidly, and the growth is approximately linear. Once the adsorption reaches the high-pressure stage (greater than 13 MPa), the methane molecules in the adsorbed layer gradually increase and attain saturation, and the excess adsorption gradually decreases as the pressure increases. The water content of the shale will cause a significant reduction in the adsorption of methane molecules, due mainly to the fact that the water molecules will occupy a large number of adsorption sites on the surface layers of the shale. Thus, the adsorption sites available for the adsorption of methane molecules are significantly reduced, and the adsorption capacity of the water-bearing shale is reduced substantially.

4.6. Effect of the Free Phase Density on the Adsorption of the Free Gas. The hydrocarbons contained in shale pores are mainly adsorbed gas and free gas, and accurately understanding the reservoir free phase density can assist in evaluating the reservoir parameters and gas transport in shale gas reservoirs.[38,39] Adsorbed gas exists mainly in organic pores and is adsorbed onto the pore walls of a reservoir, whereas free gas is freely distributed in the pores of the reservoir.[40] In terms of their physical properties, the free phase density is lower than the adsorbed phase density. In this study, the relationship between the ratio of the adsorbed gas to the free gas and the free phase density is shown in Figure 9. From the results, it can be seen that the ratio of the adsorbed gas to the free gas in deep shales decreases with the increase of the free phase density. This trend is mainly due to the fact that as the free phase density increases, the pore spaces occupied by the methane molecules in the adsorbed phase decrease, and consequently the corresponding pore spaces occupied by the free gas increase. Thus, as the free gas content of the shale reservoir increases, the ratio of the adsorbed gas to the free gas decreases.

5. CONCLUSIONS

In this study, deep shale samples from the Longmaxi Formation in southern China were collected, and high-pressure isothermal adsorption measurements of the deep shale were performed. The high-pressure adsorption model was used to describe the adsorption behavior of deep shales, and the

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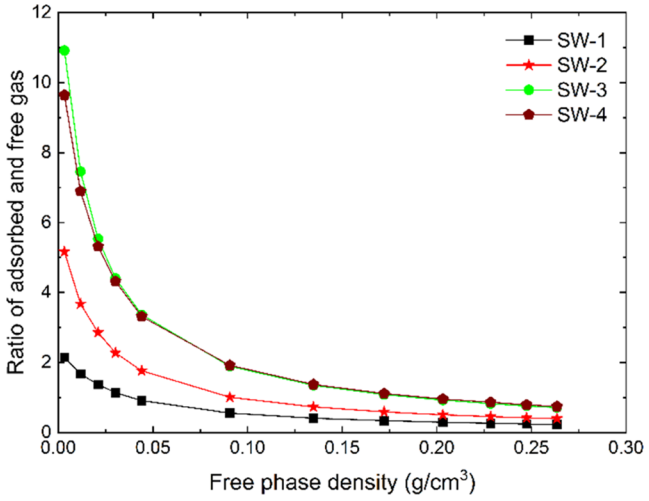

Figure 9. Ratio of the adsorbed gas to the free gas as a function of the free phase density.

adsorbed gas and free gas in deep shales were characterized quantitatively. The effects of temperature, pressure, water content, and free phase density on the adsorbed gas in the shales were evaluated. The main conclusions were as follows:

(1) The excess isothermal sorption curves of deep shales exhibited similar trends in terms of the variation in key characteristics, which revealed an increasing and then a decreasing trend with the increase of pressure. The modified Langmuir adsorption model can fit well the excess adsorption of methane in shale, with the correlation coefficient reaching 0.99. Therefore, the modified Langmuir model can be used to describe and predict the high-pressure isothermal adsorption characteristics of deep shales.

(2) When the temperature is constant, the adsorbed gas content of deep shales gradually decreases with increasing pressure, while the corresponding free gas content gradually increases. Once the pressure exceeds a certain critical value, the amount of adsorbed gas becomes smaller than the amount of free gas, and the amount of this change gradually increases with the increase of pressure. When the pressure reaches 50 MPa, the amount of adsorbed gas in deep shales is much smaller than the amount of free gas, and the ratio of the contents of adsorbed gas to free gas is in the range 23−74%.

(3) When the pressure is constant, the volume of the adsorbed gas in deep shales decreases with the increase of temperature. If the temperature is constant, the increment of the adsorbed gas in the shale starts to slow down as the pressure continues to increase. As the pressure increases, the ratio of adsorbed gas to free gas decreases. The excess adsorption capacity of water-bearing shale under the same pressure conditions is significantly lower, mainly because water molecules will occupy the adsorption sites in the pore space of the shale and reduce the available adsorption sites for the adsorption of methane molecules. As the free phase density increases, the pore space in the shales occupied by the free gas will increase, resulting in a decrease in the ratio of the content of adsorbed gas to free gas.

AUTHOR INFORMATION

Corresponding Author

Weijun Shen − *Key Laboratory for Mechanics in Fluid Solid Coupling Systems, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China; School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China;* orcid.org/0000-0003-3658-8670; Email: wjshen763@imech.ac.cn

Authors

Luo Zuo − *Sinopec Research Institute of Petroleum Engineering, Beijing 100101, China*

Tianran Ma − *School of Mechanics and Civil Engineering, China University of Mining and Technology, Jiangsu 221116, China*

Cong Chen − *Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian 116024, China;* orcid.org/0000-0001-5035-1026

Chaozhong Qin − *State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China*

Liu Yang − *State Key Laboratory for Geomechanics and Deep Underground Engineering, China University of Mining and Technology, Beijing 100083, China*

Kun Xie − *Laboratory of Enhanced Oil Recovery of Education Ministry, Northeast Petroleum University College of Petroleum Engineering, Daqing 163318, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.2c04261

Notes

The authors declare no competing financial interest.

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