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To cite this article: Zhongpei Ding *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **242** 052037

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# Study of High Pressure Isothermal Methane Adsorption on Shales

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**Abstract.** In order to research the problem that the Langmuir model cannot well described the experiment results of high pressure isotherm adsorption about shale gas, the Longmaxi formation shale samples which came from the CD-2 well in the Chengkou area, northeast of Chongqing were selected to the high pressure isothermal methane adsorption experiments under the reservoir temperature and pressure conditions, and used the liquid methane density under the atmospheric pressure boiling point as adsorption phase density to correct the excess adsorption capacity. The experiment results show that the excess adsorption capacity increase at the beginning and then decrease with the pressure rise and that's the characteristic of supercritical methane adsorption. Under the high pressure isothermal conditions, the excess adsorption capacity is different from the absolute adsorption capacity, the liquid methane density under the atmospheric pressure boiling point could be selected as adsorption phase density to calculate the absolute adsorption capacity. Langmuir model can be used to explain the absolute adsorption capacity of methane under the high pressure isotherm adsorption.

## 1. Introduction

In shale gas reservoirs, the occurrence state of natural gas mainly includes free state, adsorption state and dissolution state [1]. Among them, adsorption state is a special way that shale gas differs from conventional natural gas, and is also the main way of natural gas occurrence in shale gas reservoirs. Generally, the adsorption gas content in shale gas reservoirs is between 20% and 85% [2-3], so the study on the adsorption law of shale gas is of great significance for shale gas reserve assessment and efficient development.

Domestic and foreign scholars have conducted a large number of experimental studies on shale gas adsorption [4-9], but the experimental pressure is far lower than the pressure of shale gas reservoir in Longmaxi formation, Sichuan basin, China, which cannot reflect the law of shale gas adsorption under reservoir pressure and temperature. The adsorption capacity of shale directly measured in the laboratory is the excess adsorption capacity [10-11]. Under low pressure, the excess adsorption capacity is approximately equal to the absolute adsorption capacity. Langmuir model can be used to describe the isothermal adsorption law of shale gas. Under high pressure, the excess adsorption capacity is far less than the absolute adsorption capacity, so the Langmuir model cannot be directly used to describe the isothermal adsorption law of shale gas [12-13]. Therefore, how to calculate the



absolute adsorption capacity through the excess adsorption capacity measured in the experiment and establish the high pressure isothermal adsorption Langmuir model of shale gas has become a scientific problem that needs to be solved urgently.

## 2. Test method

### 2.1 Experimental sample

The experimental samples were taken from the black silty shale of the Silurian Longmaxi formation in the CD-2 well in Chengkou area of northeast Chongqing, with a depth of 1071.82 ~ 1074.53m. With reference to the technical standards [14], using vibration grinding mill to grind samples, shale powder between 60 ~ 80 meshes was selected, and dried 8 hours in the condition of 90°C, then removing water, placed in a vacuum dryer to cool to room temperature. Experimental gases are nitrogen (99.99% purity), helium (99.99% purity) and methane (99.99% purity).

### 2.2 Experimental equipment

The independently developed shale gas adsorption/desorption capacity tester is adopted, and the equipment flow is shown in figure 1. The experimental pressure range is 0 ~ 40MPa; the experimental temperature range is room temperature to 90°C, using digital water bath with temperature control precision of 0.1°C.

According to the temperature and pressure conditions of sample of formation, it was design that experiments stable temperature is 30°C, the highest test pressure is 30MPa, and the system pressure balance time is 24 h.

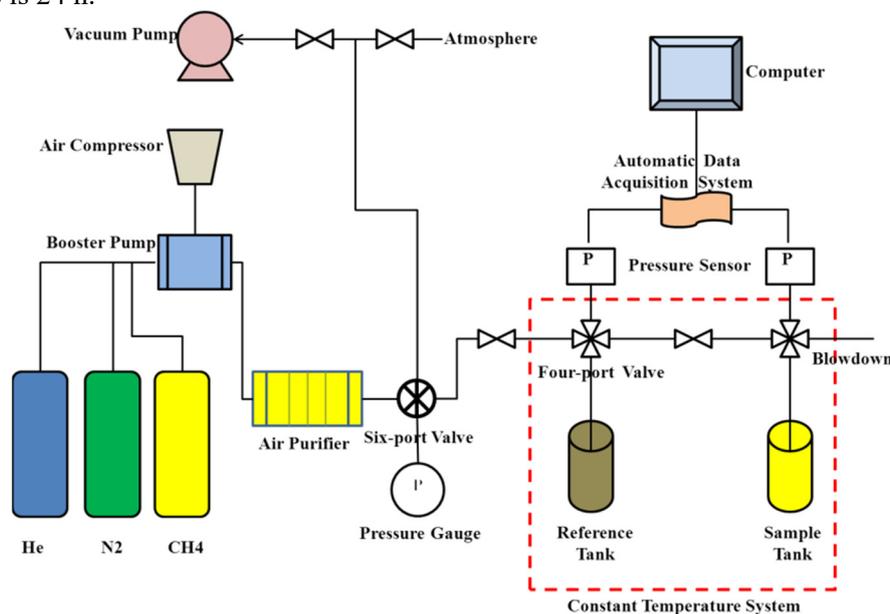


Figure 1. Flow chart of shale gas adsorption/desorption capacity test

### 2.3 Experimental procedure

Refer to "high pressure isothermal adsorption test method of coal: GB/T 19560-2008" to carry out the experiment. The specific experimental steps are as follows:

- a) Sealing inspection of equipment.
- b) Calibration of free volume of sample cylinder.
- c) Vacuuming the system and saturating the experimental gas.
- d) Adding temperature and pressure to the experimental conditions, stabilizing for 24 hours, and reaching the temperature balance and adsorption/desorption dynamic balance.

- e) Carrying out step-up adsorption, about 5MPa at a time, to 30MPa for a stable 24 hours.
- f) Recording the pressure before and after the system reaches dynamic equilibrium.
- g) Calculating the free gas volume, the adsorption gas volume and the gas adsorption quantity per unit mass of shale, according to the compression factor, the free volume of the sample cylinder and the pressure before and after the system reaches dynamic equilibrium.

### 2.4 Data processing

During the  $i$ th adsorption test, the difference between the free gas quantity in the system before pressure balance and the free gas quantity in the system after balance is the quantity of adsorbed gas.

The formula for calculating the total quantity of free gas  $n_i$  in the system before pressure balance in the  $i$ th adsorption process is as follows:

$$n_i = \frac{P_i V_1}{Z_i RT} \quad (1)$$

The formula for calculating the total quantity of free gas  $n_i'$  in the system after pressure balance in the  $i$ th adsorption process is as follows:

$$n_i' = \frac{P_i'(V_1 + V_f)}{Z_i' RT} \quad (2)$$

After the last adsorption test, the free gas quantity in the sample cylinder is:

$$n_{i\max}' = \frac{P_{i\max}'(V_1 + V_f)}{Z_{i\max}' RT} \quad (3)$$

During the  $i$ th adsorption test, the adsorption capacity is the amount of free gas quantity decreased before and after equilibrium, namely:

$$\Delta n_i = n_i - n_i' = \left[ \frac{P_i V_1}{Z_i} - \frac{P_i'(V_1 + V_f)}{Z_i'} \right] \cdot (RT)^{-1} \quad (4)$$

During the  $i$ th adsorption test, the adsorption gas quantity per unit mass of shale is:

$$V_i = \frac{\Delta n_i \times 22.4 \times 1000}{m} \quad (5)$$

The cumulative adsorption gas quantity is:

$$N_i = \sum_1^i \Delta n_i \quad (6)$$

The cumulative adsorption gas quantity per unit mass of shale is:

$$V_i = \frac{N_i \times 22.4 \times 1000}{m} \quad (7)$$

## 3. Experimental result and data analysis

### 3.1 Experimental result

Through shale gas high-pressure adsorption experiments, the adsorption data (table 1) and the adsorption curve (figure 2) of shale sample in 30°C are obtained. Under the condition of equilibrium

pressure of 25.75Mpa, the maximum adsorption capacity of shale gas is  $4.79 \text{ cm}^3 \cdot \text{g}^{-1}$ , indicating that the Longmaxi formation shale in CD-2 well has a high development potential. The high pressure isothermal adsorption curve of shale samples is different from that of low pressure isothermal adsorption curve, and the adsorption quantity appears "turning point" with the increase of pressure. With the increase of pressure, the adsorption isotherm rises rapidly, and the adsorption quantity reaches a maximum after reaching a certain pressure. After that, with the increase of pressure, the adsorption begins to decrease slowly.

Table 1. The experiment results of high pressure isothermal adsorption on shale samples

Pre-equilibrium pressure(MPa)	Post-equilibrium pressure(MPa)	Amount of substance(mol)	Adsorption capacity( $\text{cm}^3 \cdot \text{g}^{-1}$ )
9.65	5.03	0.0107	1.8397
15.56	10.35	0.0171	2.9435
20.22	15.02	0.0231	3.9836
25.75	19.78	0.0278	4.7927
30.34	24.43	0.0274	4.7290
36.20	29.54	0.0275	4.4255

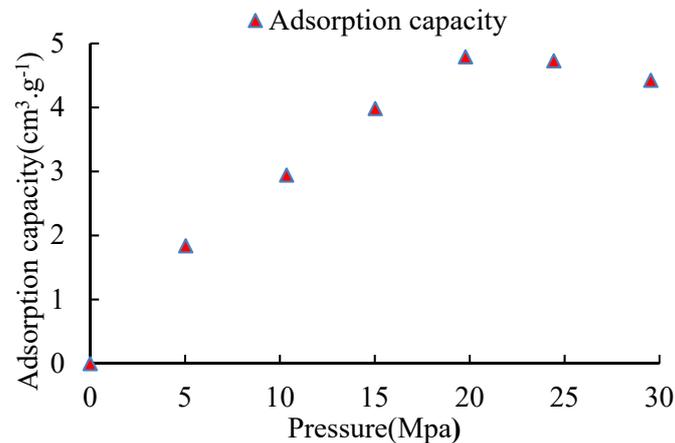


Figure 2. The experiment results of high pressure isothermal adsorption on shale samples

### 3.2 The calculation of absolute adsorption capacity

Under the conditions of experimental pressure and temperature, the adsorption of shale gas is supercritical [15]. Below the critical temperature, the gas is steam and has the ability of condensation, which can lead to multi-molecular layer adsorption, volume filling, capillary condensation and other phenomena on different types of adsorbents [12,16]. Above the critical temperature, the gas has only one type of adsorption isotherm on any adsorbent, that is, the initial part exhibits a type I isotherm characteristic, and after the maximum appears, decline phenomenon occurs, reflecting the essential characteristics of supercritical fluid [12,16].

When the adsorption phase volume is taken into account, the adsorption capacity measured in the experiment is the excess adsorption capacity, and the conversion relationship between the excess adsorption capacity and the absolute adsorption capacity is [17]:

$$m_{abs} = \frac{m_{ex}}{1 - \rho_g / \rho_a} \quad (8)$$

The density of liquid methane at atmospheric boiling point  $0.423 \text{ g} \cdot \text{cm}^{-3}$  was selected as the adsorption phase density [18-20], and the absolute adsorption capacity of methane was calculated according to equation (8) (table 2, figure 3). It can be seen that there is a big difference between the absolute adsorption capacity and the excess adsorption capacity under the conditions of high pressure.

In the process of studying the adsorption law and reserve evaluation of methane on shale, the excess adsorption capacity can no longer replace the absolute adsorption capacity. The absolute adsorption capacity increases with the increase of pressure, which accords with the theoretical understanding of adsorption.

Table 2. Calculation results of absolute adsorption capacity

Equilibrium pressure(MPa)	Excess adsorption capacity( $\text{cm}^3 \cdot \text{g}^{-1}$ )	Absolute adsorption capacity( $\text{cm}^3 \cdot \text{g}^{-1}$ )	Adsorption phase density( $\text{g} \cdot \text{cm}^{-3}$ )
5.03	1.8397	2.0033	0.423
10.35	2.9435	3.6000	0.423
15.02	3.9836	5.4711	0.423
19.78	4.7927	7.4381	0.423
24.43	4.7290	8.2321	0.423
29.54	4.4255	8.6265	0.423

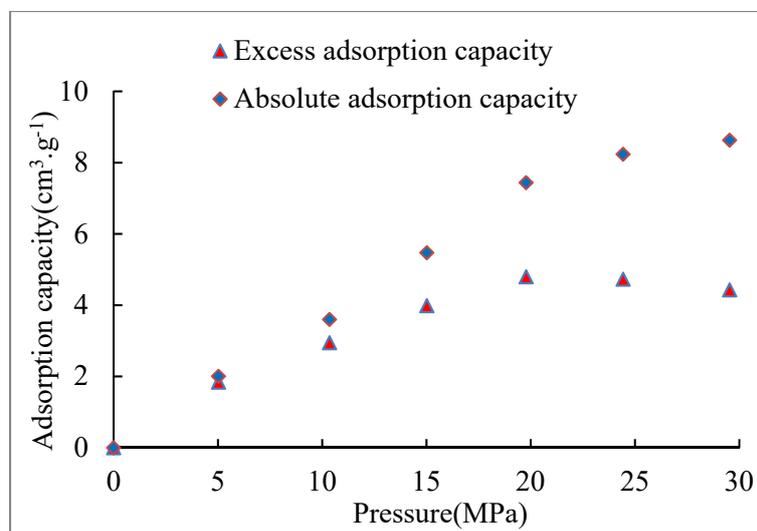


Figure 3. The comparison chart of excess adsorption capacity and absolute adsorption capacity

#### 4. The establishment of adsorption model

Domestic and foreign scholars have established many models for the adsorption characteristics of methane in shale, but compared with Langmuir adsorption model, these models are more complex and have poor applicability [4,21-24]. Langmuir adsorption model is still the most widely used at present[25]:

$$V = V_L \frac{bp}{1 + bp} \quad (9)$$

Equation (9) can be transformed into:

$$\frac{1}{V} = \frac{1}{V_L} + \frac{1}{bV_L} \frac{1}{p} \quad (10)$$

As can be seen from figure 3, when the equilibrium pressure reaches about 20MPa, the absolute adsorption capacity decreases with the increasing of the equilibrium pressure and becomes basically stable at about 25MPa. The curve pattern basically conforms to Langmuir adsorption law. According to equation(10), regression analysis on  $1/p$  is carried out for  $1/V$  (Figure 4),  $R^2=0.994$ , and  $V_L=36.9004$ ,  $b=0.0113$  are calculated. It can be seen that the correlation coefficient between  $1/V$  and  $1/p$  is large, indicating that Langmuir model can better describe the relationship between the absolute

adsorption capacity of methane on shale and the equilibrium pressure. According to the relationship between the coefficient of the regression equation and the parameters of equation(10), the Langmuir adsorption model of the sample can be calculated as  $V=0.4170P/(1+0.0113P)$ .

Furthermore, according to the Langmuir adsorption model obtained by regression, the adsorption capacity under experimental pressure was calculated, and the relative error between the predicted absolute adsorption capacity and the calculated absolute adsorption capacity was calculated (table 3). It can be seen that the relative error of the six data points was within 10%, and the forecast effect was good (figure 5).

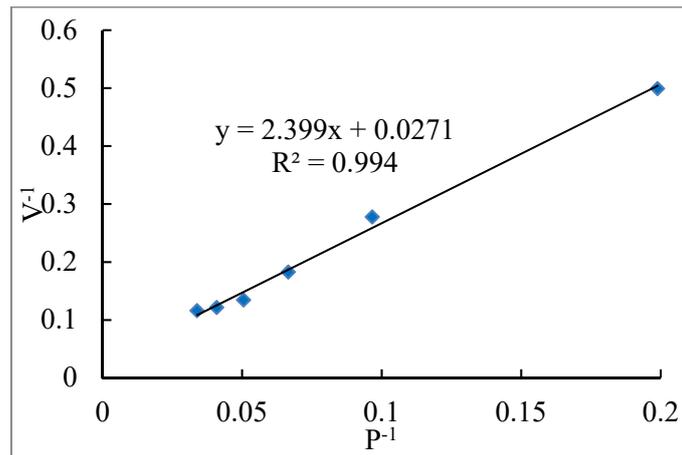


Figure 4. The regression results of  $1/V$  about  $1/p$

Table 3. The forecast results of Langmuir model

calculated absolute adsorption capacity ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	predicted absolute adsorption capacity ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	relative error (%)
2.0033	1.9846	0.93
3.6000	3.8638	-7.33
5.4711	5.3542	2.14
7.4381	6.7410	9.37
8.2321	7.9829	3.03
8.6265	9.2348	-7.05

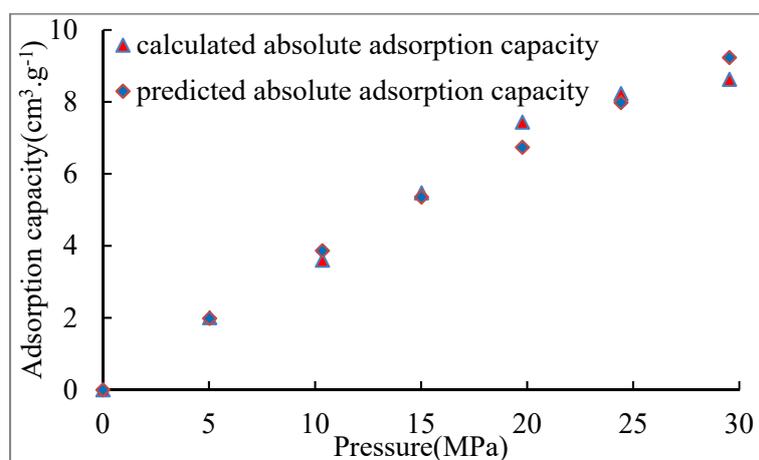


Figure 5. The forecast results of Langmuir model

## 5. Results discussion

The gas density in the supercritical state increases with the increase of pressure, and the difference between the adsorption phase density and the free phase density decreases continuously, which is manifested as the phenomenon that the adsorption capacity gradually reaches the maximum value and then decreases in the adsorption isotherm of the excess adsorption capacity. Methane under experimental conditions is in the supercritical state, the excess adsorption capacity of the Longmaxi formation shale in CD-2 well of methane has the trend that it increases gradually as pressure increases, and decreases after reaching a maximum, and absolute adsorption capacity increases with the rising of pressure and tends to saturation, which show the essential characteristics of supercritical state gas adsorption.

In order to obtain the absolute adsorption capacity of methane in shale under high pressure and better evaluate the adsorption capacity of shale reservoir, the excess adsorption capacity obtained by experimental test should be corrected. The correction of excess adsorption capacity in this study is based on two assumptions. First, the shale volume remains constant under different conditions (free volume does not change). Second, the adsorption phase density remains unchanged under different conditions (the adsorption phase density is  $0.423\text{g}\cdot\text{cm}^{-3}$  of liquid methane at atmospheric boiling point), and then the absolute adsorption capacity was corrected according to the conversion relationship between the absolute adsorption capacity and the excess adsorption capacity.

For methane of shale in the supercritical state, its initial part of the adsorption isotherm shows the I type adsorption isotherm characteristics of IUPAC classification, and the Langmuir adsorption model is applied widely as the classic adsorption model. Langmuir adsorption model was used to fit the absolute adsorption capacity, and a good fitting effect was obtained.

## 6. Conclusion

The excess adsorption capacity of Longmaxi formation shale in CD-2 well of methane showed a trend of increasing first and then decreasing with the increase of equilibrium pressure, and the absolute adsorption capacity showed a trend of increasing first and then tending to equilibrium with the increase of equilibrium pressure. The high pressure isothermal adsorption law of methane on shale shows typical characteristics of supercritical fluid adsorption.

Under high pressure and isothermal conditions, the excess adsorption capacity of methane on shale is quite different from the absolute adsorption capacity, so it can no longer be approximately replaced. The density of liquid methane at atmospheric boiling point  $0.423\text{g}\cdot\text{cm}^{-3}$  can be selected as the adsorption phase density, and the absolute adsorption capacity can be converted according to the relationship between the absolute adsorption capacity and the excess adsorption capacity.

There is a strong linear correlation between the reciprocal of absolute adsorption capacity of

methane on shale and the reciprocal of equilibrium pressure. Langmuir model can better describe the change law of absolute adsorption capacity of methane on shale with equilibrium pressure under high pressure and isothermal conditions.

### Appendix

$P_i$  — the pressure of the gas in reference tank before the equilibrium of the  $i$ th adsorption process, MPa;

$P_i'$  — the pressure of the gas in the system after the equilibrium of the  $i$ th adsorption process, MPa;

$P_{i\max}'$  — the pressure of the gas in the system after the equilibrium of the last adsorption process, MPa;

$V_i$  — the free gas volume of reference tank,  $\text{cm}^3$ ;

$V_f$  — the free gas volume of sample tank after the equilibrium,  $\text{cm}^3$ ;

$Z_i$  — the gas compression factor when the pressure is  $P_i$ , dimensionless;

$Z_i'$  — the gas compression factor when the pressure is  $P_i'$ , dimensionless;

$Z_{i\max}'$  — the gas compression factor when the pressure is  $P_{i\max}'$ , dimensionless;

$R$  — gas constant,  $8.314\text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$ ;

$T$  — the temperature of the gas in the system before the pressure equilibrium, K;

$m$  — the sample mass of shale, g;

$m_{\text{abs}}$  — the absolute adsorption capacity,  $\text{cm}^3\cdot\text{g}^{-1}$ ;

$m_{\text{ex}}$  — the excess adsorption capacity,  $\text{cm}^3\cdot\text{g}^{-1}$ ;

$\rho_g$  — the methane density at different equilibrium pressure points,  $\text{g}\cdot\text{cm}^{-3}$ ;

$\rho_a$  — the adsorption phase density of methane,  $\text{g}\cdot\text{cm}^{-3}$ ;

$V$  — the adsorption capacity at pressure equilibrium,  $\text{cm}^3\cdot\text{g}^{-1}$ ;

$V_L$  — the saturated adsorption capacity,  $\text{cm}^3\cdot\text{g}^{-1}$ ;

$b$  — Langmuir coefficient,  $\text{MPa}^{-1}$ ;

$p$  — the equilibrium pressure, MPa.

### Acknowledgements

The thesis is funded by the basic science and frontier technology research project (NO. cstc2017jcyj0290) of Chongqing Science and Technology Commission.

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