Experimental Study on Desorption Hysteresis Characteristic for Shale Gas

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Abstract: Compared with the adsorption isotherms, desorption isotherms could evaluate accurately shale absorbed gas reserves in different pressure stage, the desorption hysteresis characteristics exists in shale gas formation. In order to discover the adsorption hysteresis phenomenon and the influence factor of adsorption hysteresis in high pressure range, The physical properties test and adsorption/ desorption test of shale gas were Carried out by shale outcrop samples from horse Creek group in Eastern Sichuan. The results show that the shale gas adsorption isotherm curve and desorption isotherm curve are not coincided. It has obvious adsorption hysteresis loop, which hysteresis degree relate to shale physical parameter. It shows that the worse shale gas physical property is, the more complicated pore structure is, the more hysteresis degree appears. Meanwhile, three theoretical models were used to fit the measured isotherm adsorption and desorption curves. The results show that comparing to the Langmuir-Freudlich equation and Freundlich equation, Langmuir equation fits the adsorption and desorption characteristic of shale gas betterly.

Keywords: Longmaxi formation, shale, desorption hysteresis.

1. INTRODUCTION

In 1950, Cosway Pierce [1] published a paper for the first time proposed adsorption hysteresis, the reason of which is attributed to capillary condensation. Since then, many researchers have studied the phenomenon of adsorption hysteresis [1-3], and some researchers used molecular modeling methods to study the phenomenon of adsorption hysteresis [4]. During this period, the researchers represented by A. Baile [5] attributed the reason of adsorption hysteresis to the complexity of porous media Structure. In 2004, He Yusheng [6] mentioned in the published article gas-solid adsorption hysteresis phenomenon, and analyzed its causes. Since then, our researchers began to pay more attention to the gas-solid adsorption phenomenon, the study of this phenomenon first concentrated on the adsorption hysteresis of coalbed methane, it is agreed that there is a significant adsorption hysteresis phenomenon in coalbed methane [7-9]. The main conclusion obtained through experiments is that during the process of desorption, with the decrease of pressure and the increase of coal rank, the characteristics of adsorption hysteresis are significant, The temperature increases the adsorption hysteresis phenomenon is not significant, the pore structure of coal led to the physical properties of coal, which is also the main reason for the adsorption hysteresis phenomenon. Until 2013, Yang Feng [10] conducted a methane adsorption-desorption experiment using nitrogen gas. Obvious desorption hysteresis was observed, but adsorption of nitrogen gas shale was below critical adsorption. In the same year, Guo Wei [11] concluded from the experiments of methane adsorption and desorption in shale that the adsorption hysteresis phenomenon between shale-methane was proved and different models of adsorption and desorption curves were fitted, but the disadvantage is that the experiment only studied the adsorption hysteresis phenomenon under the low pressure (less than 8MPa). Therefore, in order to reveal the adsorption hysteresis phenomenon of shale-methane supercritical adsorption under large pressure range, the characteristics of shale gas adsorption and desorption were studied by using outcrop core samples of Long maxi formation in east Sichuan and high purity methane as adsorbate, to further study of the adsorption hysteresis phenomenon and adsorption/desorption law.

2. EXPERIMENTAL DESIGN

2.1. Experimental Samples

The samples used for the experiment are shale gas outcrops of the Long maxi formation in *Eastern Sichuan*. Samples were taken at the provincial road of Shizhu County, Chongqing with latitude and longitude coordinates of N29°52.729'and E108° 17.108' at an altitude of 1231m. The outcrop section is nearly 20 m

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thick black carbonaceous shale, which is a part of a small anticline flank with a dip of about 70°. The foliation is extremely well-developed. The thickness of a single layer is between 2 and 10 cm and the thickness of the layer shows a certain rhythm.

In order to ensure the quality of the experiment after the rock sample is collected, the trial-produce experiment and demonstration of the sample preparation are carried out. The sample preparation is carried out in strict accordance with the experimental design and the sampling method and quality requirements of the experimental rock sample developed by SY/T 6437-2000. Standard shale samples were prepared by a wire cut method. The sample was a standard 2.5 cm diameter core and was subjected to high pressure oil washing and drying.

The physical property test was carried out by using American core company PDP-200 pulse attenuation method permeability tester, and nitrogen was used as the test medium. A large number of shale core permeability tests were carried out. Three rock samples were selected according to the permeability, and the porosity and permeability parameters were shown in Table **1**.

2.2. Experimental Equipment and Methods

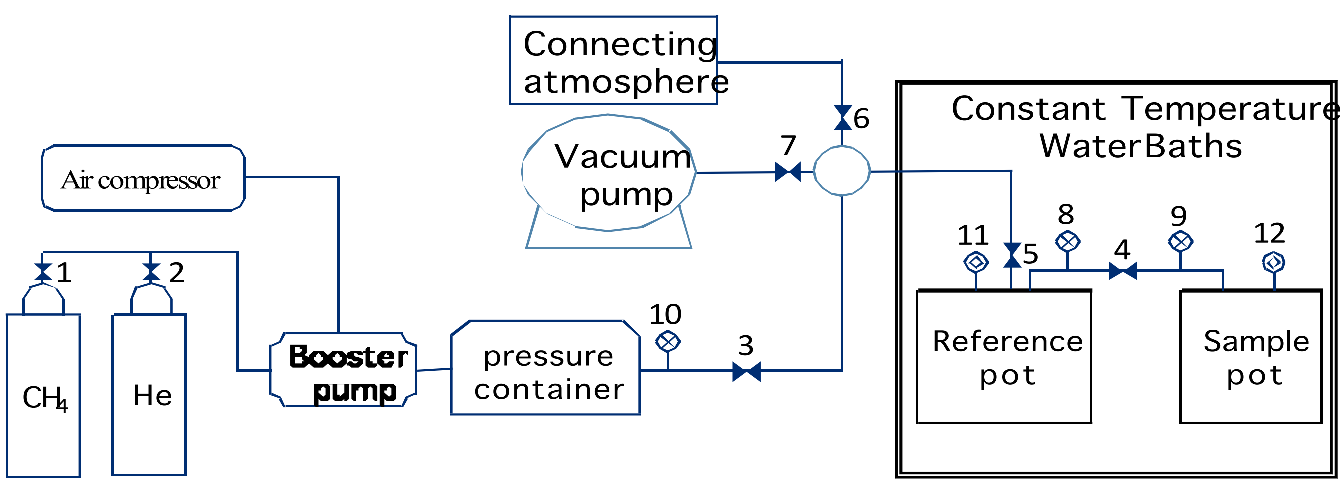
Experimental reference to GB/T 19560-2008 "experimental method of high pressure isothermal adsorption for coal" provisions of the experimental rules, the difference is that GB/T 19560-2008 uses crushed shale samples in the experiment.

This experimental sample is a standard columnar core, using PDP-200 to test the shale rock sample permeability, and Hubei Chuanglian Petroleum Technology Co., Ltd. CLDWXF-I isothermal adsorption analyzer is applied for the experiment, the instrument test pressure is 0 to 40MPa, the experiment temperature ranges 0 to 100 °C, with 99.99% high purity methane as shale adsorbate.

The diagram of connection device of CLDWXF-I isothermal adsorption tester is shown in Figure **1**. The experiment device collects the data of pressure and temperature automatically by computer. The experimental equipment mainly consists of air compressor, helium gas tank, methane tank, valve, booster pump, sample tank, reference tank, vent valve, vacuum pump, constant temperature oil bath, temperature sensor, pressure sensor and so on. Test

Table 1: Shale Rock Samples Test Data

Sample Number	Length, cm	Diameter, cm	Porosity, Decimal	Permeability $10^{-6}\mu m^2$	Sample Weight g
1	5.8	2.54	0.028	0.31	55.52
2	5.1	2.54	0.031	0.37	45.61
3	5.4	2.54	0.034	0.44	50.62



1_ 2_ 3_ 4_ 5_ 6_ 7- valve_ 8_ 9_ 10-Pressure sensor _ 11_ 12-Temperature sensor

Figure 1: Schematic diagram of high pressure isothermal adsorption experimental device for shale gas.

Table 2: Adsorption and Desorption Experiment Data of Different Samples at 60℃

1# Shale Sample				2# Shale Sample				3# Shale Sample			
Adsorption data		Desorption data		Adsorption data		Desorption data		Adsorption data		Desorption data	
P	adsorbance	P	adsorbance	P	adsorbance	P	adsorbance	P	adsorbance	P	adsorbance
MPa	cm^3/g	MPa	cm^3/g	MPa	cm^3/g	MPa	cm^3/g	MPa	cm^3/g	MPa	cm^3/g
0.00	0.000	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.83	0.613	0.89	0.732	0.94	0.75	0.83	0.68	0.79	0.59	0.94	0.73
2.65	1.199	2.61	1.535	2.79	1.35	2.65	1.52	2.07	1.10	2.79	1.52
5.30	1.688	5.02	2.093	5.55	1.81	5.30	2.10	4.25	1.63	5.55	2.06
8.77	2.134	8.65	2.489	9.20	2.21	8.77	2.46	6.88	2.02	9.20	2.42
12.48	2.462	11.01	2.622	13.02	2.49	12.48	2.66	9.00	2.26	13.02	2.63
15.81	2.669	13.76	2.746	16.55	2.69	15.81	2.78	11.26	2.45	16.55	2.75
19.10	2.814	16.91	2.847	19.92	2.82	19.10	2.86	13.66	2.58	19.92	2.83
22.38	2.913	20.43	2.928	23.253	2.909	22.38	2.926	16.13	2.69	23.25	2.89
25.89	2.978	23.26	2.978	26.793	2.978	25.89	2.977	18.68	2.77	26.79	2.94
30.11	3.039	26.99	3.029	29.830	3.019	30.11	3.025	21.61	2.85	29.83	2.97
35.26	3.094	30.11	3.063	34.230	3.056	35.26	3.069	24.95	2.90	34.23	3.01
38.98	3.132	35.00	3.105	39.460	3.096	39.46	3.096	28.10	2.96	39.12	3.04
		38.98	3.132					30.26	2.98		
								34.89	3.01		
								39.12	3.04		

pressure ranges 0 to 40MPa, accuracy is 0.0001MPa, experimental temperature is 0 to 150, accuracy is 0.1 degrees. Shale adsorption/desorption isotherms were tested at a pressure of 0 to 40MPa at a temperature of 60°C.

3. EXPERIMENTAL RESULTS AND DATA ANALYSIS

3.1. Analysis of Adsorption Hysteresis Phenomenon

Using the above instrument method and test procedure, three selected shale samples were tested for adsorption/desorption isotherms. The test results are shown in Table **2** and Figure **2-4**.

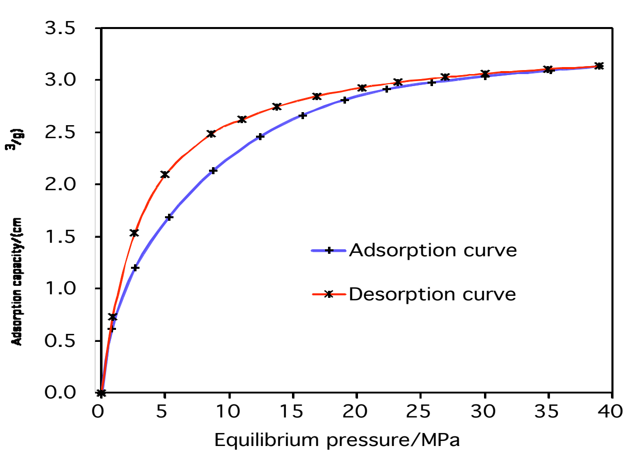


Figure 2: Adsorption/desorption isotherms of 1#shale samples at 60°C.

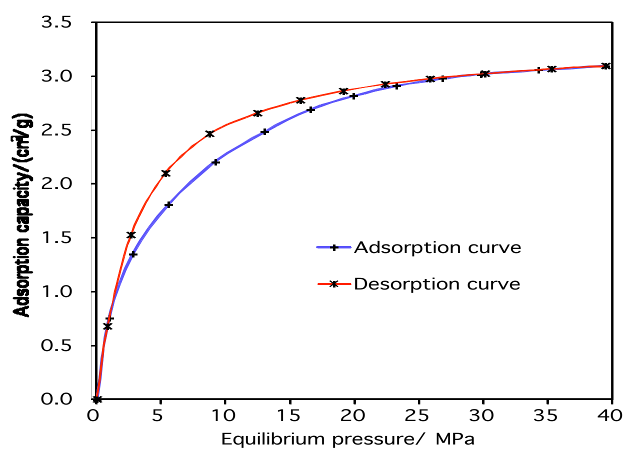


Figure 3: Adsorption/desorption isotherms of 2#shale samples at 60°C.

It can be seen from Table **2** and Figure **2-4** that the adsorption hysteresis exists in the three shale samples, but the adsorption hysteresis degree of the three shale samples is different, the adsorption hysteresis loop of 1#rock is the largest, and the adsorption hysteresis loop of 3#rock is the smallest. As can be seen from Table **1**, the physical properties of 1#rock are the worst, and the 3#rock are the best. Obviously, the differences of physical properties cause the differences of adsorption hysteresis. However, the complexity of pore structure determines the rock physical properties, the more complex the rock pore structure is, the worse the physical property is, the more serious adsorption hysteresis is, which is recognized by most researchers on adsorption hysteresis phenomenon.

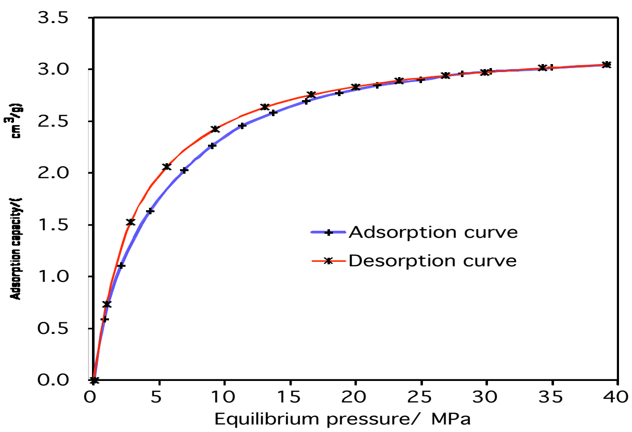


Figure 4: Adsorption/desorption isotherms of 3#shale samples at 60°C.

3.2. Isothermal Adsorption Equation Fitting

Many adsorption models have been established by scholars both at home and abroad, and the adsorption model of shale is mainly fitted by Langmuir equation, Freundlich equation [12] and Langmuir-Freundlich equation [13]. The experimental adsorption isotherms were fitted by using Origin Lab Origin Pro software. The results show that the Langmuir equation of the three equations has the highest fitting accuracy for shale gas adsorption isotherms.

It is proved that the adsorption of multi-molecular layer will not occur, when the adsorption temperature is higher than the critical temperature above 10 degrees, and the adsorption of shale gas is completely consistent with this condition. At this time, the Langmuir equation based on the single molecule layer theory can be used to describe the adsorption isotherm of shale gas. The Langmuir equation takes into account the heterogeneous nature of the adsorbent surface and the interaction between the adsorbed molecules. Its expression is shown in equation (1), and the Langmuir equation has 2 parameters.

$$V = \frac{abP}{1+bP} \quad (1)$$

where V is the amount of adsorption, cm^3/g; P is the equilibrium pressure, MPa; a is the maximum adsorption capacity, cm^3/g; b is Langmuir constant, dimensionless.

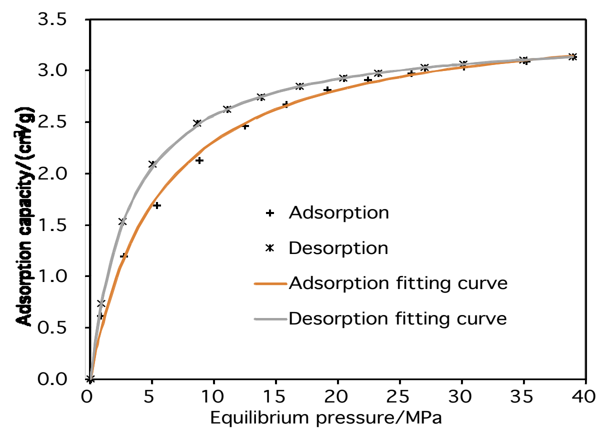


Figure 5: Langmuir model fitting curves of adsorption/desorption isotherms of 1#shale samples.

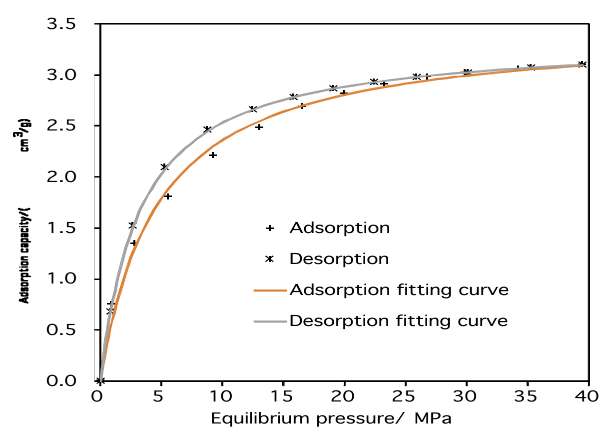


Figure 6: Langmuir model fitting curves of adsorption/desorption isotherms of 2#shale samples.

Table 3: Fitting Value of Adsorption and Desorption Equation of Three Samples

Sample number	Adsorption isotherm fitting			Desorption isotherm fitting		
	a	b	R^2	a	b	R^2
1#	3.589	0.181	0.969	3.392	0.309	0.989
2#	3.455	0.215	0.954	3.352	0.307	0.989
3#	3.412	0.224	0.981	3.301	0.303	0.989

The fitting results of adsorption/desorption isotherms of three shale samples by Langmuir equation are shown in Figure **5-7**, and the fitting parameters are shown in Table **3**. From Figure **5-7** and Table **3**, it can be seen that the adsorption/desorption isotherms of three shale samples are more in line with the Langmuir adsorption theory model.

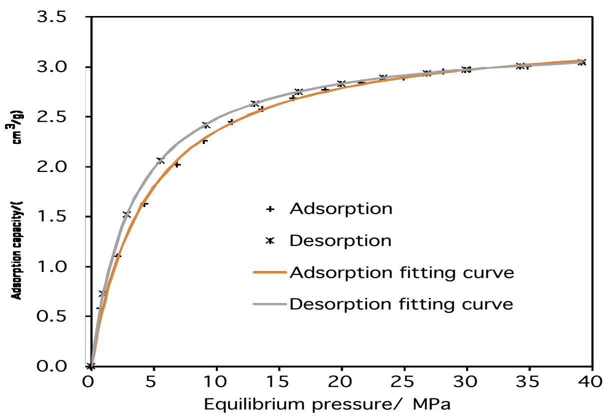


Figure 7: LANGMUIR model fitting curves of adsorption/desorption isotherms of 3#shale samples.

CONCLUSIONS

(1) The adsorption isotherms and desorption isotherms of Longmaxi shale in east Sichuan are not coincident with each other, and there is a clear adsorption hysteresis phenomenon.

(2) The size of the desorption hysteresis loop of the adsorption/desorption isotherms of the Longmaxi formation in east Sichuan is controlled by the physical properties of the shale. That is, the pore structure affects the degree of adsorption hysteresis. The worse the physical properties of the shale are, the more complicated the pore structure is and the bigger the adsorption hysteresis loop appears.

(3) The adsorption/desorption isotherms of the Longmaxi formation in the east Sichuan all fit the Langmuir adsorption model.

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