Video Article

Experimental Study of the Relationship Between Particle Size and Methane Sorption Capacity in Shale

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Abstract

The amount of adsorbed shale gas is a key parameter used in shale gas resource evaluation and target area selection, and it is also an important standard for evaluating the mining value of shale gas. Currently, studies on the correlation between particle size and methane adsorption are controversial. In this study, an isothermal adsorption apparatus, the gravimetric sorption analyzer, is used to test the adsorption capacity of different particle sizes in shale to determine the relationship between the particle size and the adsorption capacity of shale. Thegravimetric method requires fewer parameters and produces better results in terms of accuracy and consistency than methods like the volumetric method. Gravimetric measurements are performed in four steps: a blank measurement, preprocessing, a buoyancy measurement, and adsorption and desorption measurements. Gravimetric measurement is presently considered to be a more scientific and accurate method of measuring the amount of adsorption; however, it is time-consuming and requires a strict measuring technique. A Magnetic Suspension Balance (MSB) is the key to verify the accuracy and consistency of this method. Our results show that adsorption capacity and particle size are correlated, but not a linear correlation, and the adsorptions in particles sieved into 40 - 60 and 60 - 80 meshes tend to be larger. We propose that the maximum adsorption corresponding to the particle size is approximately 250 µm (60 mesh) in the shale gas fracturing.

Video Link

The video component of this article can be found at https://www.jove.com/video/57705/

Introduction

Shale is a clay rock with a thin sheet of bedding structure, which serves as both a shale gas source rock and a reservoir. Shale has a strong anisotropy consisting of nano- and micron-scale pores, and graptolite fossils are commonly recognized[1,2,3].

Shale gas is commercially exploited in the Yangtze Plate, Southern China. As an unconventional gas system that serves as both a source rock and a reservoir for methane, shale gas is derived from the organic matter within the shale through biogenic and/or thermogenic processes[4,5]. Natural gas stores in reservoirs are in one of three forms: free gas in pores and fractures, adsorbed gas on the surface of organic matter or inorganic minerals, and dissolved gas in bitumen and water[6,7]. Previous studies suggest that adsorbed gas accounts for 20 - 85% of the total gas in shale formations[6]. Therefore, research on the adsorption capacity of shale and its controlling factors are significant to the exploration and development of shale gas resource.

The methane adsorption ability of shale has been widely recognized as significantly varying with temperature, pressure, humidity, maturity, mineral composition, organic matter, and specific surface area[1,4,5,6,7]; and previous studies have confirmed a larger and clearer correlation between external factors like temperature, pressure, and humidity and methane adsorption.

However, studies on the correlation between intrinsic factors like particle size and methane adsorption are controversial. Kang and Ji suggest that the methane adsorption capacity of the same shale samples increases with a decrease in particle size[8,14], whereas Rupple and Zhang believe the relevance between the particle size and adsorption is limited based on the isothermal adsorption curves[9,10,11]. In addition, without standards for a shale gas adsorption evaluation protocol, laboratories in China typically apply the coal adsorption evaluation protocols for evaluating shale gas adsorption. To clarify the relationship between particle size and adsorption,as well as investigate a prospective exploration zone, we obtained shale samples from the thick marine shale deposits of the Wuling Sag in the Upper Yangtze Plate. A gravimetric sorption analyzer was applied to conduct the isothermal adsorption experimentand obtain the relationship between the particle size and adsorption.

The volumetric and gravimetric methods are the main methods used to test the isothermal adsorption of shale. Volume is the key parameter of the volumetric method, which is easily affected by temperature and pressure[12,13,14]. Because of uncertainty in the error analysis, the cumulative propagation in direct measurements using the volumetric method for calculating adsorption amounts leads to a large error in the measurement results, which causes an abnormal adsorption isotherm[14,15]. Compared with the volumetric method, the gravimetric method requires fewer parameters and results in smaller errors: because the mass is conserved, the weight and mass of the gravimetric method are not affected by

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the temperature and pressure[12]. It is considered a more scientific and accurate method for measuring theadsorption amount of adsorption at present.

A gravimetric sorption analyzer is used in this experiment, which has a maximum testing pressure of 70 MPa (700 bar) and temperature of 150 °C. The temperature and pressure generated by older apparatus are too low toaccurately simulate the temperature and pressure of the deep underground formation. The key to using a sorption analysis apparatus is reaching the magnetic suspension balance for accurately weighing the sample material, with an accuracy of 10 µg. The apparatus adopts a circulating oil bath heating mode and the temperature range can be controlled for a long time to within 0.2 °C. The accuracy of an old apparatus is low, and thus the error would be larger than that obtained with newer instruments. The experimental operations are performed with the software provided by the apparatus.The operating system will be updated regularly to ensure the analysis is close to the actual underground conditions[12].

A magnetic suspension balance (MSB) is used in the gravimetric method to test the methane isothermal adsorption of shale without direct contact between the sample and the equipment, in normal temperature and pressure. The sample is placed in the measuring pool, in which the weight of the sample can be transmitted to the balance through a non-contact suspension coupling mechanism[12,13]. Under the balance, there is a suspended magnet, controlled by a specially designed controller that allows the free suspension of the permanent magnet below. The permanent magnet connects the position sensor and the sample container with the coupling frame. The function of the coupling frame is to couple or decouple the sample container to the permanent magnet suspension rod[14,15,16].

Our measured samples are black organic-rich shales deposited in marine facies of the Long Maxi formation, Lower Silurian in the Daozhen, Guizhou province. The research area is in the Wuling Sag, upper Yangtze plate, which is bordered by the Sichuan Basin to the northwest and Xuefeng Mountain tectonic zone to the southwest[17]. The Wuling Sag is a structural transfer and transition zone between the Sichuan Basin and Xuefeng Mountain tectonic zone, which received shallow-deep sea shelf deposits, and marine black shale was widely developed during the early Silurian; the sag was then strongly superimposed by tectonic events like the Indo-China Movement, Yanshan Movement, and Himalayan Movement, which formed multistage folds, faults, and unconformities[18]. The marine black shale in the Wuling Sag has been significantly influenced by the complex geological conditions, which formed shale gas reserves. As a structural transfer zone, the sag is the sweet spot for shale gas exploration, which is characterized by a weaker deformation, better shale gas generation and preservation conditions, and a better natural fracture matching of the traps[19].

High-pressure sorption measurements are conducted based on a standardized procedure with the guidance of the isothermal adsorption apparatus protocol, which has been comprehensively elaborated on in several publications[10,11,12,13,14,15,16]. The isothermal adsorption experiments were completed in the Key Laboratory of Shale Oil and Gas Investigation and Evaluation of the Chinese Academy of Geosciences. A gravimetric measurement carried out with a magnetic suspension balance (MSB) is performed in four steps: a blank measurement, preprocessing, a buoyancy measurement, and an adsorption and desorption measurement (**Figure 1**, **Figure 2**).

Protocol

1. Sample Preparation

1. **Sample characterization**
    1. Measure the total organic carbon (TOC) using a TOC apparatus (see **Table of Materials**) at a temperature of 20 °C and a relative humidity of 65% (per standard GB/T 19145-2003).
    2. Perform a vitrinite reflectance measurement on polished sections of the shale using a photometer microscope (see **Table of Materials**).

2. **Sample cleaning and crushing**
NOTE: To avoid the influence of various internal and external factors as well as the inhomogeneity of shale as much as possible, select a large shale rock sample from the original horizontal bedding for this experiment.
    1. Select a large shale rock sample (about 20 cm long, 15 cm wide, and 2 cm high) from the original horizontal bedding.
    2. Clean the sample and crushing vessel with absorbent cotton, tweezers, and acetaldehyde.
    3. Smash the large original horizontal shale beddingsample into small pieces with a hammer, so that it can be placed into the residual gas tight grinder. The suitable crushing time (approximately 3 min) can be found through preliminary experiments.
    4. Then, sieve the sample into 20 - 40, 40 - 60, 60 - 80, 80 - 100, and 100 - 120 subsamples by first sieving particles through a 100 - 120 mesh, then a 80 - 100 mesh, 60 - 80 mesh, 40 - 60 mesh, and finally the 20 - 40 mesh.
    5. Discard any non-conforming shale particles. There will be a few discarded samples (approximately 5 g) when the crushing time is 3 min.
    6. Label each sample as 20-40-1, 40-60-1, 60-80-1, 80-100-1, and 100-120-1 (this is G1 in the **Representative Results**).
    7. Repeat the above-mentioned operation with another sample (about 20 cm long, 15 cm wide, and 2 cm high; use a different shale with a different composition or TOC) and create a set of repeat experiments for contrast. Label each sample as 20-40-2, 40-60-2, 60-80-2, 80-100-2, and 100-120-2 (G2 in the **Representative Results**).

2. Experimental Methods

1. **Laboratory set-up**
    1. Place the instruments in a quiet, vibration-free area of a clean laboratory with no electromagnetic interference.The temperature of the laboratory should be 10 - 40 °C.
    Note: The experiment will be conducted at room temperature for extended periods of time (multiple days).

2. Use alternating current at 230 V (±10%) and 50 Hz. Ensure every root power supply line has a current greater than 10 A and is safely handled with a ground lead. If the power grid is poor, an additional power supply should be used.
3. Use gas cylinders with high purity gas (not less than 99.999%). Fix all cylinders firmly.
4. If dangerous gas is used in the experiment, ensure that the laboratory has ventilation and exhaust facilities, along with a dangerous gas alarm device. Regularly use soap bubbles to detect any leaks from the pipe connections[12].
5. Avoid direct sunlight.

2. **Start the instrument**
   1. Power on the computer and start the main program.
   2. Open the cylinder and adjust it to the appropriate output pressure (adjust the outgassing pressure to 5 - 6 bar and the gas cylinder pressure to approximately 70 bar).
   3. Turn the instrument on. When the coupling controller has been powered on, the knob needs to remain in the OFF position. Open the oil bath and vacuum pump power.

3. **Blank measurement**
   1. Disassemble the sample pool, place the empty clean sample bucket inside, and install the metal guide sleeve. Check the ZP/MP coupling and adjust it to the appropriate state.
   2. Control the balance on the coupling controller and switch it to all positions in ZP/MP1/MP2. Observe the changes in the balance reading and confirm the reading is normal and stable. If the reading is incorrect or unstable, it is necessary to adjust the levels on all 4 feet of the flat head, based on the situation, or the high and low position of the support screw.
   3. Load the sample pool, temperature control oil bath jacket, and heat insulation cover.
   4. Move the coupling controller knob to the ZP position.
   5. Set it to the blank measurement program in the software.
      1. Click to configure the measurement, name a title, select gas 2 and other fluid, and select fluid bath.
      2. Set the sample temperature to 50 °C, the maximum pressure to 70 bar, the pressure step to 7, the pressure ramp to 2 bar/min, and the fluid therm to 50 °C.
         NOTE: For the blank test, use N_2 (recommended) or H_e at the appropriate pressure (0 - 70 bar). Weigh the empty bucket. When the temperature is consistent with the experimental temperature of adsorption, the boot program runs, which usually takes 7 - 8 h. Finally, the quality and volume of the empty bucket can be obtained manually when it is finished (see step 2.8.1).
         Caution: 6 sets of bolts on the sample pool flange are dismantled using the internal six-angle wrench and fixed wrench of the instrument.Notice that when the last group of bolts is removed, the sample pool needs to be held to avoid falling.

4. **Instrument balancing (if necessary)**
   NOTE: The instrument's operating motion must be a soft, uniform force.
   1. Do not strongly shake the balance support (otherwise, it may upset the balance) or move the position of the frame. When using a wrench, be careful not to knock the sensor traverse tube near the flange out of position.
   2. When the balance is confirmed, move the ZP to the OFF position.
   3. Check whether the O ring on the flange of the sample pool is installed. Replace the O ring if there is serious damage or deformation.
   4. Set up the sample pool vertically, so that the upper and lower flanges are connected, which will maintain the overall vertical state.
   5. Finally, install 6 groups of bolts.
      1. Use a wrench to fasten the bolts, using a symmetrical fastening method to ensure that the connection of the flange face is tight and not skewed. The fastening degree of the 6 groups of bolts should be as consistent as possible[13].
      2. Payattention to the spiral cap under the 6 groups of bolts to keep each edge out of the flange, to avoid difficulty when installing the rear oil bath jacket.
   6. If using electric heating, install insulation terracotta and fix it with a hoop ring without an outside insulation cotton package.
   7. If using oil bath heating, install the oil bath jacket from the bottom up to the sample pool, until the top and the upper flange are flat. Install three screws at the bottom to fix the oil bath jacket in place.
   8. Check whether the ZP/MP1/MP2 position and the balance reading are normal, then move the coupling controller knob to the ZP position.

5. **Preprocessing measurement**
   1. Disassemble the sample pool and place the sample into the sample barrel. Check the ZP/MP coupling and adjust them to the appropriate state.
   2. Load the sample pool and electric heat insulation cover.
   3. Move the coupling controller knob to the ZP position.
   4. The boot program will run automatically. Set the pretreatment program in the software. Click to configure the measurement, name a title, select the vacuum, select the electrical heater, set the sample temperature at 150 °C and the coupling temperature 20 °C, and set the duration at 600 min. This step usually takes 10 h.

6. **Buoyancy measurement**
   1. Dismantle the electric heating sheath and install the temperature control oil bath jacket and thermal insulation cover, which isadhesive.
   2. Start the buoyancy measurement program in the software, set the oil bath heating temperature at 50 °C, and heat for approximately 4 h. 7 pressure points will be divided under the maximum pressure of 70 bar. The boot program will run automatically.
      NOTE: The buoyancy measurement is the same as the blank measurement.
      Caution: Pull out the electric heat power supply joint before removing the temperature sensor joint at the bottom of the sample pool. After loading the sample, remember to check if the temperature sensor is inserted.

7. **Adsorption measurement**
   1. Set the sorption measurement program in the software. Start the program and it will run automatically.

2. If the desorption process is needed, set this up in the sorption measurement program, keep the fluid therm temperature at 50 °C, and set 19 pressure points (*e.g.*, 0, 10, 20, 40, 60, 80, 100, 150, 200, 250, 200, 150, 100, 80, 60, 40, 20, 10, and 0 bar). Then start the program, which will run automatically.
3. Set the pressure manually, using a pressurized pump, when the gas pressure cannot reach the set value automatically.
CAUTION: After the end of the experiment, the instrument will automatically exhaust and maintain the vacuum state for a period of time. The program will end automatically, and all the valves will be closed.

8. **Calculation**
1. The system can be selected to automatically correct the experimental results by using the following principles. The relationship between the weight reading, tray reading, sample buoyancy, and sorption buoyancy is as follows[10,11,12,13]:
$$m^A = \Delta m - m^{SC} - m^S + (V^{SC} + V^S + V^A) \times \rho$$
m^A: mass of adsorption gas; Δm: mass of balance reading; m^{SC}: mass of sample tray (obtained by Blank Measurement); m^S: mass of sample (obtained by Buoyancy Measurement); V^{SC}: volume of sample tray (obtained by Blank Measurement); V^S: volume of sample(obtained by Buoyancy Measurement); V^A: volume of sample adsorption gas (obtained by Adsorption Measurement); $\rho(p,T,y)$: density calculated from the Equation of State or determined through measurement.

9. **Completion**
1. Exit the program and close the computer. Close the experimental gas cylinder.
2. If only a short period of idling occurs, not more than 3 days, stop the power to the instrument, which is not needed to maintain the power state of each system. We suggest that the coupling controller knob is moved to the OFF position.
3. If the instrument needs to be stopped for a long time, the power of each system can be turned off. Before the coupling controller power is turned off, the knob first needs to be moved to the OFF position. Confirm that the OFF lamp lights are on and the other lights are out, and then close the controller power.

Representative Results

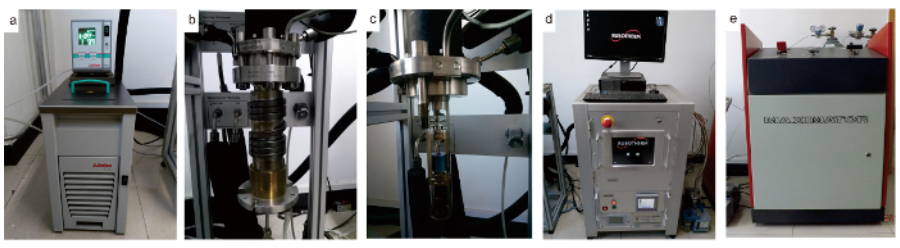

Figure 1: Experimental set-up for gravimetric gas adsorption at high temperatures and pressures. This figure shows the set-up for the isothermal adsorption experiment: (**a**) the oil bath heating device for the fluid bath; (**b**) the electrical heating device for the electrical heating; (**c**) the magnetic suspension balance - gravimetric sorption analyzers (**Figure 2**); (**d**) the operating system (the mainframe and monitor); and (**e**) the gas pumping and pressurization system. Please click here to view a larger version of this figure.

The mineral constituents of these samples are characterized by high quartz, moderate clay, low feldspar, and a wide distribution of graptolite. The samples show a moisture content of less than 1%, based on the sample drying experiment. In addition, the TOC content of the sample is 4.2% (wt%). The reflectance of vitrinite Ro is approximately 2.5%, which remains in the maturity-over maturity stage. The mineral and reservoir physical characteristics are shown in **Table 1**.

	Composition (%)								
sample	clay	quartz	plagioclase	potassium feldspar	Toc (%)	Porosity (%)	Permeability (mD)	Mean Pore Diameter (μm)	Specific surface area (m^2/g)
G1	27	67	4	2	4.2	5.28	7.54E-03	0.03	12.13
G2	78	11	1	7	2.5	3.12	5.10E-03	0.02	4.49

Table 1. The relationship between shale parameters and methane isothermal adsorption.

When under the zero-point (ZP) state, the coupling box is decoupled to the position sensor; thereby, the quality of the sample and the sample container is not transmitted to the balance. When under the measuring-point (MP) state, the coupling box is coupled to the position sensor and the mass of the sample and the sample container is transmitted to the balance to measure the quality[12,13,14].

The regular automatic switching of ZP and MP can effectively remove the negative effect caused by the inherent zero drift of the electronic balance and offer a high-precision measurement. The principle structure can be seen in **Figure 2**.

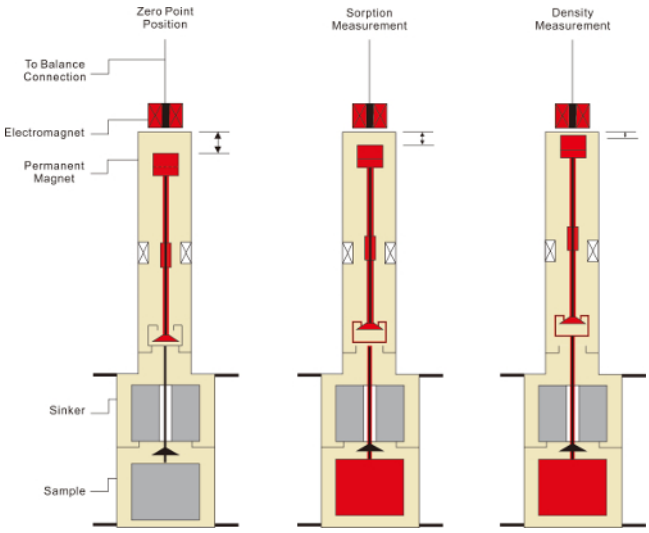

Figure 2: The heart of the sorption analysis instruments - the magnetic suspension balancer. The red sample is the sample cell with sample, and the blue sample is the sample cell without sample. The arrow above the sample is a hook, and the shrinking double-side arrow on the top right indicates that the magnetic force of the magnetic levitation balance increases, lifting weights and samples, resulting in the shortening of the distance. This figure has been modified from a report (experimental instrument operation report; private correspondence) by Gang Chen. Please click here to view a larger version of this figure.

The amount of adsorption linearly increased with the increase in pressure during the 0 ~ 60 bar, the low-pressure period. Afterward, the growth rate of adsorption gradually decreased to approximately 0.In addition, the absolute adsorption of shale reached a saturation state during the high-pressure period with a correction or decreased in the maximum uptake adsorption capacity without correction (**Figure 3**, **Table 2**).

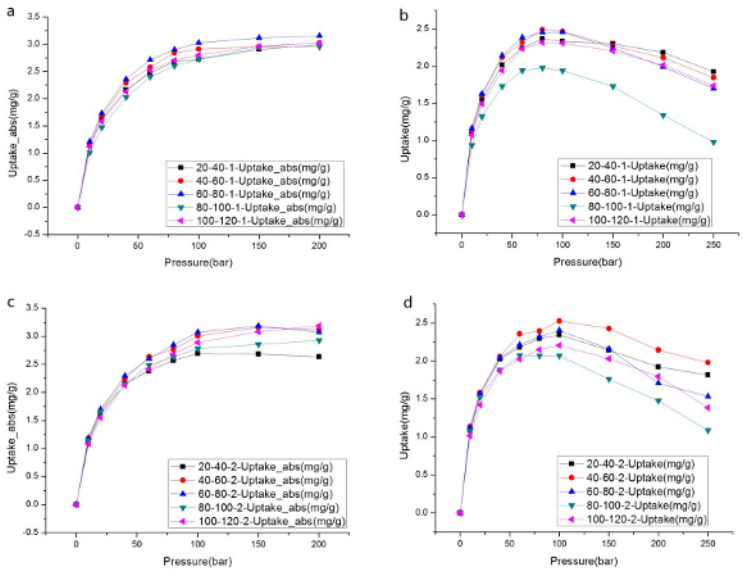

Figure 3: Methane isothermal adsorption experiment of different particle size. These panels show (**a**) the adsorption data of G1 with adjustment, (**b**) the adsorption data of G1 without adjustment, (**c**) the adsorption data of G2 with adjustment, and (**d**) the adsorption data of G2 without adjustment. Please click here to view a larger version of this figure.

NO.	Diameter (μm)	Mesh	Max Adsorption		NO.	Diameter (μm)	Mesh	Max Adsorption	
			M_{abs} (mg/g)	P_L (bar)				M_{exc} (mg/g)	P_L (bar)
G_1	425-850	20-40	2.99	200	G_1	425-850	20-40	2.37	80
	250-425	40-60	3.03	200		250-425	40-60	2.49	80
	180-250	60-80	3.16	200		180-250	60-80	2.46	80
	150-180	80-100	2.95	200		150-180	80-100	1.98	80
	125-150	100-120	3.01	200		125-150	100-120	2.32	80
G_2	425-850	20-40	2.51	200	G_2	425-850	20-40	2.34	100
	250-425	40-60	3.11	200		250-425	40-60	2.53	100
	180-250	60-80	3.1	200		180-250	60-80	2.4	100
	150-180	80-100	2.93	200		150-180	80-100	2.07	100
	125-150	100-120	3.18	200		125-150	100-120	2.21	100

Table 2. Methane isothermal maximum adsorption experiment data of different particle size.

The maximum absolute adsorptions (M_{abs}) of sample G1 were 2.99 mg/g, 3.03 mg/g, 3.16 mg/g, 2.95 mg/g, and 3.01 mg/g; in order of the particle sample meshes from 20 - 40 to 100 - 120; when they reached the saturation state (**Figure 3a**). In addition, the maximum excess adsorptions (M_{exc}) of sample G1 were 2.37 mg/g, 2.49 mg/g, 2.46 mg/g, 1.98 mg/g, and 2.32 mg/g; in order (**Figure 3b**). In addition, the maximum absolute adsorptions (M_{abs}) of sample G2 were 2.51 mg/g, 3.11 mg/g, 3.10 mg/g, 2.93 mg/g, and 3.18 mg/g; in order; when they reached the saturation state (**Figure 3c**). Lastly, the maximum excess adsorptions (M_{exc}) of sample G1 were 2.34 mg/g, 2.53 mg/g, 2.40 mg/g, 2.07 mg/g, and 2.21 mg/g; in order (**Figure 3d**).

Discussion

The materials used in this experiment are shown in the **Table of Materials**. Before the sample pool is removed, it must be confirmed that the temperature and pressure in the sample pool are at normal pressure and normal temperature; otherwise, there is a danger of injury. If the temperature is too high, wait for the temperature to drop and then removethe sample pool. If the pressure is too high or too low, manually set the air pressure on the software and use an inert gas[13,14,15]. Do not disassemble the sample pool during the experiment. After the experiment is finished, the instrument is in a standby state. The coupling controller should display as ZP or the OFF position. The circulating oil bath is in the OFF state. Remove the 3 screws that are fixed at the bottom of the oil bath jacket, hold the metal clamping sleeve down vertically, and place the jacket to the left of the fixed support. In this process, pay attention to the protection of the electric wire and tubing connected to the jacket. Do not bend or twist too much, so as not to break the line.

MSB guarantees the application of a gravimetric isothermal adsorption apparatus to any kind of texts gases (*e.g.*, corrosive, explosive, and toxic) in any type of extreme environment (*e.g.*, vacuum and high pressure)[20,21]. Even under extreme conditions, such as a high-pressure or toxic atmosphere, the adsorption capacity of the samples in a closed chamber can be analyzed with the maximum accuracy by the equipment[22,23,24,25,26]. The mass of the sample and the density of the reaction medium can be measured at the same time in a single experiment, which could save a good deal of time[24,25,26]. The equipment and method can guarantee long-endurance high-precision measurement experiments with no baseline drift or accuracy loss.The separation and isolation of the experimentation area (sample) and the weighing area (balance) avoids the damage or pollution of the balance by the reaction medium or the experimental conditions and manages to weigh the mass in the high intensity sealed reaction chamber[26].

The main limit of the technique is, firstly, that it requires a lot of time: 1 sample to be totally completed usually takes 2 - 4 days. Secondly, the balance and stability of the magnetic levitation balance need to be regularly corrected with continuous use; otherwise, it is difficult to achieve a balance, which will consume more time. Additionally, the experimental process comes with certain risks (*e.g.*, high temperature, high pressure, and flammable and explosive gas)[12,13,14].

Fortunately, the existing instruments have a good stability, good safety, high accuracy, and high precision. In addition, there is no particular requirement for the species of the sample, as long as it is a porous powder[20,21,22]. In the future, this method will be more time-saving, efficient, and safe and accurate, and suit more kinds of samples.

The sample process protocol used in previous studies was generally used for coalbed gas. Coal is a massive, structurally isotropic rock consisting of carbon, whereas shale is a layered, structurally, vertical anisotropic rock consisting of multiple clay minerals[23,24,25,26]. When crushing and screening the coal samples, particles in different meshes still show similar physical properties. When dealing with shale, particles of different sizes may show different physical properties, such as adsorption. The reason is that when dealing with shale rock, the complicated mineral composition and layering structure may enlarge the anisotropy among different meshes[27,28,29,30].

The Langmuir model is usually used to fit the isothermal adsorption. The Langmuir model includes adsorption characteristics from the study of a solid surface that occurred in 1916, completed by the French chemist Langmuir; this model began from the standpoint of dynamics, in which the monolayer state equation is presented, for a nonporous solid[31]. The basic assumption is that the surface of the adsorbent is even and smooth, and the energy of the solid surface is uniform, forming only single molecule layer. There is no interaction between the adsorbed gas molecules, and the adsorption is in a dynamic equilibrium[25,26]. From this point of view, the Langmuir model is not suitable for shale gas adsorption,and thus, the formula is not used here.

When testing shallow buried shale gas and coal with low pressure, there is little difference between the excess adsorption capacity and absolute adsorption capacity. However, with the increase in pressure, the excess adsorption capacity and absolute adsorption capacity will become increasingly larger. Because of the deep burial and high pressure of shale, the adsorption capacity is relatively weak. If not adjusted, the shale adsorption capacity will be largely underestimated[30,31,32]. Thus, a combination of various correction methods is used, which are obtained by the system. In addition, the adjustment will automatically omit the last point (**Figure 3a** and **3c**). However, the adjustment also decreases the difference in the amount of adsorption between the samples (**Figure 3**).

Micropores and mesopores in the shale control the adsorption by dominating the specific surface area[32,33]. Liang and Zhang both suggested that an intense shale fragmentation reduces the number of micropores and mesopores and increases the amount of macropores[8,33]. A shale gas well fracturing or structural movement may crush the integral shale rock into pieces (large particles) to generate microfractures (small particles), which increases the specific surface area, and thereby, the adsorption is increased. However, during the experiment, as the fracturing or structural movement continued, shale rock was crushed into smaller particles; and the micropores and mesopores in the shale developed and connected to each other to form mesopores and macropores; therefore, the total specific surface area and adsorption of the shale decreased (**Figure 3b** and **3d**). In conclusion, the amount of adsorption does not increase with the decrease in particle size monotonically and there must be a maximum value or interval.

It is suggested that the variation rule between the adsorption capacity and particle size is not a linear correlation, whether referring to an absolute adsorption with adjustment or to an excessive adsorption without adjustment. Therefore, it is of great significance to figure out the maximum value for determining the particle size in the process of fracturing in shale. The adsorption capacity does reach a maximum at the pressure of 80 - 100 bar and the number of adsorptions in meshes 40 - 60 and 60 - 80 is larger. Considering samples from the study area, the maximum adsorption is approximately 250 µm (60 - 80 mesh), the values of samples from different regions and strata may be different (**Figure 3**, **Table 2**).

The gravimetric and volumetric methods are widely used in shale gas adsorption experiments; the differences are large between their respective corresponding experimental apparatuses, but the common feature of both is to destroy the natural pore structure of the sample. The sample particle size on the adsorption quantity has some influence, and the pore structure without the broken rock of adsorption experiments can reflect the real formation of shale gas in the adsorption capacity[30,31,32,33], but its main disadvantage is that it requires a lot of time to complete.

Disclosures

The authors have nothing to disclose.

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