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Methane adsorption behavior on shale matrix at in-situ pressure and temperature conditions: Measurement and modeling



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ABSTRACT

Adsorbed gas is a significant component of shale gas due to the abundant nanopores of organic matter in shales. Methane adsorption behavior on shale matrix is complex considering the geochemical properties, lithology, pore structure and pressure-temperature conditions. In this work, methane adsorption experiments were conducted through a gravimetric method for shale samples at reservoir pressure and temperature conditions. Meanwhile, total organic carbon (TOC), mineral contents and pore structure parameters of samples were measured, respectively. Experimental results show that (1) an excess adsorption phenomenon is obvious at high-pressure and high-temperature conditions; (2) methane adsorption capacity of shale tends to increase with an increase of TOC; (3) lithology and pore structure also affect the methane adsorption capacity of shales, inducing the different adsorption results of two samples with similar TOC; (4) a shale with a large TOC, a low illite content, a large specific area, a large pore volume and a small average diameter would have a strong methane adsorption capacity, nevertheless the effect of TOC is generally dominant. In order to further investigate the methane adsorption behavior on shales, a simplified local density adsorption model considering the cylindrical pore geometry is established, and is regressed and verified by the experimental data. The modeling results indicate that a sample with a large TOC would have a strong fluid-solid interaction energy and a large surface area of methane adsorption. At last, the mechanism of methane adsorption on shales at in-situ conditions is summarized. This work is beneficial for an accurate shale gas reservoir modeling.

1. Introduction

Gas shales are both the source rocks and the reservoirs. The organic-rich characteristic results in abundant nanopores developed in shale matrix, inducing a lot of hydrocarbons storing in shale gas reservoirs as a form of adsorbed gas. The significant role of adsorbed gas has been confirmed in shale gas development. The fraction of gas present as adsorbed gas in the five United States shale-gas systems developed in the 1990s takes an average of 20%–85% [1]. Especially for some shale-gas systems that have a relatively low reservoir pressure, the fraction of adsorbed gas is significant. For instance, the adsorbed gas in Antrim Shale, New Albany Shale and Lewis Shale account for 70%, 40%–60% and 60%–80% of the total gas content, respectively [2]. Therefore, reservoir modeling as well as economic development of shale gas would be limited without an intensive investigation of methane adsorption behavior on shales at in-situ high-pressure and high-temperature (HPHT) conditions.

The adsorption behavior of shale on methane is influenced by

several internal and external factors, such as geochemical properties, clay minerals, moisture content and pressure-temperature conditions. Lu et al. (1995) measured adsorption isotherms of Devonian shales on methane at various temperature and total organic carbon (TOC) conditions [3]. The results show that the adsorption capacity of shale samples becomes larger with a lower temperature and higher TOC. The methane adsorption experimental results of Zhang et al. (2012) show that the experimental data can be described by the Langmuir isothermal adsorption, and a shale-gas system with a higher thermal maturity and larger organic matter abundance would show a much stronger adsorption capacity [4]. However, the maximum pressure and temperature conditions of the experiments in current literatures are not high enough for the shale gas reservoirs. Therefore, those experimental results might not reveal the real adsorption behavior of shale gas at in-situ conditions.

A volumetric method has been the most commonly used adsorption experimental method by now [5,6], which indirectly measures the gas adsorption quantity of a sample through measuring the changes of bulk

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gas pressure. However, since a high-precision pressure transducer is difficult to have a wide enough measuring range, the volumetric method generally could not be used at a high-pressure condition, which is less than 20 MPa. Meanwhile, the required amount of sample used in the volumetric method should be much enough to meet the minimum resolution of the pressure transducer. However, for a gravimetric method, the changes of sample mass during gas adsorption experiment can be measured directly by a high-precision magnetic suspension balance, and then the adsorption quantity of samples can be obtained at different gas pressure. Compared with the volumetric method, the gravimetric method can measure the adsorption isotherm directly, so the experimental error caused by pressure measurement and indirect calculation in the volumetric method can be avoided. Meanwhile, the amount of sample in the gravimetric method is much less than that in the volumetric method. Therefore, the gravimetric method is more suitable for measuring adsorption isotherm of shale gas at the reservoir HPHT conditions.

The critical temperature and critical pressure of methane are $-82.6\text{ }^{\circ}\text{C}$ and 4.6 MPa , respectively. Therefore, the temperature and pressure of shale gas reservoirs are commonly much higher than the corresponding critical temperature and pressure. For example, the general depth of shale gas reservoirs in North America is $500\text{--}3000\text{ m}$, the formation temperature is generally not less than $35\text{ }^{\circ}\text{C}$, and the formation pressure is $5\text{--}30\text{ MPa}$. Therefore, shale gas adsorption belongs to the supercritical adsorption behavior. The supercritical fluid usually has the following two particular properties [7]: (1) its density is close to that of the liquid phase and its viscosity is close to that of the gas phase; (2) compared with the ideal gas, the actual volume of fluid is quite different, so the high-pressure physical parameters need to be amended. The adsorption behavior of supercritical fluid is quite different from that of the fluid at room temperature and pressure conditions [8–10]. First, there is not gas-liquid conversion, the saturated vapor pressure no longer exists, and the adsorption phase cannot be in the form of liquid. Second, the adsorption isotherm gradually increases from the form of type I [11] to the highest point. At last, the adsorption isotherm and the desorption isotherm are theoretically coincident. It should be noted that the characteristics above are aimed at the ideal conditions of an adsorbent and adsorbate. For a shale gas reservoir, its mineral composition and pore structure are much more complex than that of the ideal one, which induces the supercritical fluid adsorption behavior quite specific in a shale gas reservoir. Day et al. (2008) and Clarkson and Haghshenas (2013) studied methane adsorption behavior in porous media at supercritical conditions through Dubinin-Radushkevich model and showed that the experimental phenomenon that the measured adsorption isotherm rises first and then decreases with the increase of pressure is one of the typical characteristics of supercritical adsorption of shale gas under HPHT conditions [12,13].

Besides of a highly accurate methane adsorption experiment on shales at HPHT conditions, a suitable model to describe shale gas adsorption behavior is also indispensable. Sakurovs et al. (2007) modified the traditional Dubinin-Radushkevich model through the calculation of bulk gas density and adsorbed gas density [14]. Day et al. (2008) modified the traditional Dubinin-Radushkevich model through introducing a parameter related to the affinity of the sorbent for the gas [12]. Clarkson and Haghshenas (2013) investigated the supercritical fluid adsorption on shales and coals, and the results show that either the modified Langmuir model or Dubinin-Radushkevich model could be used [13]. In addition, other models such as simplified local density (SLD) model [15,16], 2D-EOS model [17], Ono-Kondo model [18], et al. have also been studied and been confirmed to be more suitable for an investigation of supercritical gas adsorption in porous media in the respect of microscale. Especially for the SLD model, it has been demonstrated to be suitable to describe gas adsorption on activated carbons, coals and shales [19]. Nevertheless, the traditional SLD model cannot be used for shale gas according to its reservoir characteristics. Therefore, a corresponding improvement of this model is made in this

study.

In this work, methane adsorption experiments were conducted for Longmaxi Shale through a gravimetric method to get the adsorption isotherms, the instrument of which is the Gravimetric Sorption Analyzer of ISOSORP-HP of Rubotherm. The experiments were conducted at in-situ pressure and temperature conditions. Experimental samples are several Longmaxi Shale samples with different TOC. In addition, X-ray diffraction (XRD) and low-pressure nitrogen adsorption measurement were performed to investigate the relationship between the methane adsorption capacity on shales and pore structure/lithology of shale samples. In order to further study shale gas adsorption behavior, a modified SLD model considering the cylindrical pore geometry other than traditional slit geometry is established. Then the model is used to regress and analyze the experimental data. Combining measurement and modeling results, the mechanism of methane adsorption behavior on shales at in-situ HPHT conditions are summarized at last.

2. Shale samples and experimental methods

2.1. Experimental samples

Samples in this work are from a Longmaxi formation on the southeast of the Sichuan Basin in China. The Longmaxi Shale has been the most successfully developed shale gas reservoir in China [20]. Samples are selected from the depth between $2343\text{ and }2407\text{ m}$. The sampling target temperature and pressure are about $82\text{ }^{\circ}\text{C}$ and 38 MPa , respectively. The formation pressure coefficient is calculated to be 1.56 , so it is an abnormal high-pressure gas reservoir. The in-situ testing result of shale gas content shows that the adsorbed gas takes an average of $40\%\text{--}50\%$.

Two geochemical parameters, TOC and vitrinite reflectance (R_o), were measured for over one hundred samples. TOC was measured by the Carbon and Sulfur Analyzer of CS230SH of Leco. R_o was measured by the Polarizing Microscope of DM4500P of Leica and Microscopic Spectrophotometer of QDI302 of Leica. The results show that (1) TOC of the samples are between 0.5% and 4.97% with an average of 3.09% ; (2) R_o of the samples takes an average of 2.89% . Boyer and Droser (2007) presented that a shale formation with a TOC larger than 2% generally had a good economic development potential [21]. Meanwhile, R_o of the samples are relatively larger than that of the five US shale-gas systems developed in the 1990s [1]. Therefore, the above measurement results indicate that samples in this work belong to the over-matured and organic-rich shale, which is conducive to gas adsorption.

Twenty-one samples from different target depth were selected to measure the mineral contents through XRD System of X'Pert MPD PRO. Results of the total mineral contents are shown in Fig. 1a). It is indicated that the main minerals are quartz and clay minerals. Also, the pyrite is relatively rich, the average content of which is 3.82% . For the relative contents of clay minerals, the measurement results are shown in Fig. 1b). It is indicated that illite plays a dominant role with an average relative content of 64.93% in the total clay minerals. Other two kinds of clay minerals are interstratified illite-smectite and chlorite with an average relative content of 20.73% and 14.34% in the total clay minerals, respectively. The measurement results show that there isn't smectite and kaolinite in the samples.

Since shale matrix is dominated by nanopores, the low-pressure nitrogen adsorption measurements were conducted for thirty-one samples to get the pore diameter, pore surface area and pore volume through the Gas Sorption Surface Area and Pore Size Analyzer of Quantachrome of NOVA2000e. The measurement results are shown in Fig. 2. It is indicated that the pore diameter is characterized by a unimodal distribution and the main peak is $3\text{--}4\text{ nm}$ as shown in Fig. 2a). Also, a sample with a higher TOC would show a larger percentage of pore diameter distribution that is smaller than $3\text{--}4\text{ nm}$. The specific surface area of the samples is between $8.08\text{--}22.06\text{ m}^2/\text{g}$ with an

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