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Testing method and controlling factors of specific surface area of shales

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ABSTRACT

Shales contain abundant organic matter, and have complex mineral composition and developed nanopores. Shale porosity has large surface area and a strong gas adsorption capacity. The specific surface area (SSA) of shales is an important factor for the adsorption of shale gas, while there are several factors which can affect the test results of SSA. In this study, shales collected from Longmaxi formation in the south of Sichuan Basin were taken as the research object. A set of testing methods were established for determining shale SSA through low-pressure N_2 adsorption-desorption method. Following this, the key factors affecting shale SSA were investigated. The results show that particle size of shale samples has little effect on the SSA, and the recommended particle size for SSA measurement is about 3 mm. After 3-h heating treatment at 200 °C, most of adsorbed water and part of the interlayer water of clay minerals are removed, and the tested SSA is highest. Therefore, the recommended optimum degassing temperature is 200 °C. The content of total organic carbon and the SSA have positive linear relationship. The quartz content and the SSA show a good positive correlation. No positive correlation is found between the SSA and other mineral components. The SSA is of great significance for the evaluation of shale gas resources potential.

1. Introduction

The successful commercial development of shale gas in North America has enabled the recent boom in shale gas exploration and production worldwide. Shale gas is a kind of unconventional natural gas which mainly exists as adsorbed and free gas in shale sequences with abundant organic matter and nanopores (Kargbo et al., 2010).

Gas in shale reservoirs is stored both as free gas in natural fractures and matrix pores and as adsorbed gas on the surface of matrix particles. Moreover, unlike in conventional gas reservoirs where all the gas is stored in a free manner, a large fraction of gas present in shale gas reservoirs is stored by the adsorption mechanism (Song et al., 2011). Thus, to enhance adsorbed gas recovery is a key step for the long-term stability of shale gas wells. Nanopores in shale sections are abundant, characterized by large specific surface area (SSA), resulting in high adsorption capacity for gas. Therefore, investigating the SSA characteristics of nanopores in shale and factors of influence is of great significance for the evaluation of shale gas resource potential.

An important parameter for shale gas reservoirs is shale SSA, which has been studied for decades by scholars. For example, Wilcox (1990) thought that SSA is a key parameter for evaluating the wellbore stability of shale formations, which is closely related to the hydration characteristics, mechanical properties and water permeability of shale. SSA can be used to characterize shale hydration and clay expansion, and it is an important parameter for shale classification (Steiger, 1982). Adesida et al. (2011) discussed the effect of degassing temperature on shale SSA. The influence of organic matter content on shale SSA has been studied by several research groups (Nuttall et al., 2009; Wang and Reed, 2009; Ambrose et al., 2010). It has been reported that clay minerals can adsorb gas because of their internal structure, and the amount of adsorbed gas is dependent on clay type (Ross and Bustin, 2008; Ji et al., 2012; Wang et al., 2013).

The shale matrix is predominantly composed of micropores (pores less than 2 nm diameter) and mesopores (pores with 2–50 nm diameter) (Ross and Bustin, 2009). The Brunauer Emmett Teller (BET) method is widely used to measure the SSA of clay and shale dominated by micro- and mesopores (1–100 nm) at −197.3 °C and 1 atmosphere pressure (Kuila and Prasad, 2013). A limitation of this technique is that it fails to measure large pores

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(diameter >200 nm). Moreover, shales contain a large amount of clay minerals with various forms of water such as adsorbed water, interlayer water and structural water. The presence of water in these different states could exert some effects on the measurement of shale SSA. To the authors' knowledge, however, no studies have been conducted on how to evaluate or eliminate the effect of various forms of water on the determination of SSA of clay minerals and on shale micropore connectivity. In this work, Longmaxi formation shales collected from the south of Sichuan Basin were taken as the research object. The effects of various factors including particle diameter, degassing temperature on shale SSA were evaluated.

2. Materials and methods

2.1. Materials

Shale samples used in this study were collected from Longmaxi formation in the southern margin of Sichuan Basin (Changning-Weiyuan area), China. The mass of each sample was about 1 kg. These sheet- and block-shape shales mainly have black, gray with black and dark gray color, containing thin layers of muddy silt.

The Longmaxi formation is present with a range of 229.2–672.5 m in thickness in the southern Sichuan Basin. The lateral extent and thickness of the Longmaxi formation (stratigraphic) is stable, and the thickness ranges from 200 to 300 m on the basis of field investigation. The stratigraphy consists of black shale, black and dark/gray shale, dark gray shale, and silty mudstone, mainly comprising carbonaceous and clay shale. The bottom of the Longmaxi formation is rich in carbonaceous and various graptolites, and it has widely distributed dispersions and berry-like grains of pyrite, even if obvious stratification is spread on part of the layer (Chen et al., 2011).

2.2. Experimental procedures

In this study, shale SSA was measured by the BET adsorption method with nitrogen gas using a Quantachrome surface area analyzer (NOVA 2000e, Quantachrome Instrument, Florida, FL, USA). The sample preparation and experimental procedures are as follows: First, shale samples collected at the same depth were processed to particles with diameters of 2, 3, 4 and 5 mm. Then the samples with different diameters were incubated for 3 h at room temperature (25 °C), 100 °C, 200 °C, 300 °C and 400 °C, respectively. After natural cooling and vacuum degassing, the SSA of samples was measured from the adsorption isotherms by the Quantachrome surface area analyzer based on the BET formula (Gregg and Sing, 1982):

$$\frac{1}{X[(P_0/P)-1)]} = \frac{1}{X_m C} + \frac{C-1}{X_m C}(P/P_0) \quad (1)$$

where X is the N_2 volume absorbed, X_m is the saturated N_2 volume of single molecular layer absorbed, P is the absolute N_2 equilibrium pressure, P_0 is the saturated vapour pressure of N_2 at −197.3 °C, C is a constant related to the strength of interaction between gas and solid, P/P_0 is the relative pressure of N_2 (0.05–0.35).

In a gas-adsorption experiment, a degassed shale sample was exposed to nitrogen gas at constant cryogenic liquid nitrogen temperature (−197.3 °C) at a series of precisely controlled pressures. The volume of adsorbed gas on the shale surface was determined at discrete pressures over the relative equilibrium adsorption pressure (P/P_0) range of 0.005–1.0 at a constant temperature, where P is the absolute N_2 equilibrium pressure and P_0 is the saturated vapour pressure of N_2 at laboratory conditions. The experiment was conducted by systematically increasing the pressure up to the condensation pressure (adsorption branch) followed by reduction of pressure from P_0 (desorption branch). The gas-adsorption isotherm is reported as the volume of N_2 adsorbed as a function of P/P_0. The pore size distribution of shale samples was calculated by the BJH (Barrett–Joyner–Halenda) method using the desorption branch of the isotherms according to the following equation (Gregg and Sing, 1982):

$$D = \frac{-4\gamma \cos\theta}{P} \quad (2)$$

where D is the pore diameter, γ is the surface tension, θ is the contact angle and P is the applied pressure. A contact angle of 130° and surface tension of 485 dyn/cm were used.

The mineral composition was analyzed by X-ray diffraction (XRD), carried out with a X-ray diffractometer (X'Pert Pro, PANalytical Co., Almelo, the Netherlands) with Cu K_α incident radiation. Total organic carbon (TOC) content was measured with a CNS-2000 analyzer (LECO Co., St. Joseph, MI, USA). The morphology was observed by scanning electron microscopy (SEM; QUANTA450, FEI Company, USA). Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo TGA 851 instrument (Mettler Toledo, Switzerland), heating a 5–10 mg sample at 10 °C/min from 25 to 400 °C. The three-dimensional microstructure was observed using a Zeiss NVision40 focused ion beam scanning electron microscopy (FIB-SEM) system (Carl Zeiss Inc. Thornwood, NY, USA) equipped with an energy dispersive X-ray spectroscopy unit.

3. Results and discussion

3.1. Composition analysis of shales

To obtain certain features of the Longmaxi shale mineral composition, this study utilized the XRD technique to qualitatively and quantitatively analyze 165 samples collected from the southern Sichuan Basin (Changning-Weiyuan area). The results are given in Table 1 and demonstrate a wide range in inorganic fraction compositions for this Longmaxi shale suite. The dominant minerals are quartz and clay, followed by calcite and plagioclase (Table 1). The other mineral compositions are potash feldspar, dolomite and pyrite, of which the average content is less than 7%. It was found that the Longmaxi shales collected from Changning-Xingwen area have lower clay (29.15%) and calcite (5.46%) content but higher quartz (53.39%) content compared to those shale samples used in the present study (Chen et al., 2011). But the overall mineral composition is similar between the two groups of Longmaxi shale suites. Clay minerals are favorable for the formation and development of shale gas reservoirs (Chen et al., 2011). In addition, pyrite abundance is closely related to the presence of organic matter (Chen et al., 2011).

Table 1
Mineral composition (%) of Longmaxi formation shales used in this study (n=165).

	Quartz	Potash feldspar	Plagioclase	Calcite	Dolomite	Pyrite	Clay
Range	11.4–70.1	0.4–10.2	1.6–30.9	2.4–41.1	0.5–59.2	0.7–8.1	6.7–64.2
Mean	31.8	2.3	8.2	10.5	6.9	2.6	37.6