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Fractal characteristics of shales from a shale gas reservoir in the Sichuan Basin, China

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HIGHLIGHTS

- Pore structure of shale was studied from fractal perspective.
- Shales samples with higher TOC have greater fractal dimension.
- Micropores have a greater impact on fractal dimension than mesopores and macropores.
- Shale samples with a higher fractal dimension have greater adsorption capacity.

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ABSTRACT

Nanopore structure greatly affects gas adsorption and transport in shales. Such structures in shale samples from the Lower Cambrian strata of the Sichuan Basin of China have been investigated using X-ray diffraction, total organic carbon content (TOC) tests, porosity and permeability tests, nitrogen adsorption, and methane adsorption experiments. Fractal dimensions were obtained from the nitrogen adsorption data using the Frenkel–Halsey–Hill method. The relationships between TOC, clay minerals, pore structure parameters and fractal dimension have been investigated. Based on the physical description of the fractal surfaces, the impact of fractal dimension on adsorption capacity has also been discussed. The results showed that the shale samples had fractal geometries with fractal dimensions ranging from 2.68 to 2.83. The organic matter is a controlling factor on fractal dimension, shown by positive correlation between TOC and fractal dimension. Fractal dimension increases with increasing surface area and pore volume, and also increases with decreasing pore diameter because of the complicated pore structure. Micropores have a greater impact on fractal dimension than mesopores and macropores. A negative correlation between fractal dimension and permeability was observed, especially for shales with high TOC and micropores counts. The fractal dimension can be used to evaluate adsorption capacity. Shale samples with larger fractal dimensions have higher methane adsorption capacity. Fractal analysis leads to a better understanding of the pore structure and adsorption capacity of a shale gas reservoir.

1. Introduction

Global energy shortages and high energy prices have led to much interest in shale gas [1,2]. Successful exploration and development of shale gas reservoirs has enabled the United States to ensure a predominantly domestic supply of gas for many years. China is also known to have relatively rich shale gas resources. The recoverable amount of shale gas in China is estimated to be approximately $26 \times 10^{12}\ m^3$, comparable to the quoted reserve of $28 \times 10^{12}\ m^3$ in the United States [3]. To reduce exploration risk and determine economic feasibility, considerable efforts are being undertaken to improve the knowledge of gas storage and transport mechanisms.

A shale gas reservoir is characterized as a self-contained source-reservoir system. Abundant gas can be stored as free gas in intergranular porosity and natural fractures, adsorbed in organic matter and clay particle surfaces or dissolved in kerogen and bitumen [1,4]. Pore structure in shale is complicated because of its wide pore-size distribution and abundant organic matter [5,6]. The pore-size spectrum of shale generally spans from micropore (pore diameter <2 nm) to mesopore (2 nm $\leqslant$ pore diameter $\leqslant$ 50 nm) and macropore (pore diameter > 50 nm), following the International Union of Pure and Applied Chemistry (IUPAC) classification [7]. Previous studies have provided useful information about the pore structure and adsorption capacity of shale [4,8,9]. Micropores

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play an important role in gas adsorption. A positive correlation exists between micropore volumes and the methane capacity of shales [5,8], which is akin to a coalbed methane reservoir [10]. The methane adsorption capacity also increases with the TOC content because of the high microporosity and surface area of the organic matter [8,9]. Clay minerals can adsorb gas because of their internal structure, the amount of which is dependent on clay type [10–12].

Various techniques or hybrid techniques are used for shale characterization. These methods include mercury intrusion [6,13], field emission scanning electron microscopy [5,13,14], transmission electron microscopy (TEM) [14], and gas adsorption analysis [6,8]. Gas adsorption analysis has proven to be an effective method to characterize nanopore structure, and gas adsorption data indicate that the porous materials have fractal geometries. Fractal methods have been widely used in material estimations. The textural properties of coals and activate carbons were investigated from a fractal perspective [15–17]. The composition of coals including carbon content, ash content, and coal rank has also been shown to be related to the fractal dimension [16,17]. However, there is no report of the fractal characterization of shale and its impact on adsorption capacity.

The major goals of this paper are to investigate the fractal characteristics of shales using a shale gas reservoir from the Sichuan Basin of China. The fractal dimension used to present the fractal characterization was calculated from nitrogen adsorption data with the fractal Frenkel–Halsey–Hill (FHH) method. Then the relationships between TOC, clay mineral content, pore structure parameters, and fractal dimension were characterized. Based on the physical significance of the fractal dimensions, their impact on the adsorption capacity of shales is also discussed.

2. Materials and experiments

Eleven shale samples were obtained from the Lower Cambrian Niutitang Formation in Sichuan Basin, located in Southwest China. The Sichuan Basin has abundant hydrocarbons and currently is the largest gas-producing region in China. Geological research shows that the Niutitang Formation formed in a neritic shelf with a stagnant and anaerobic marine sedimentary environment. The stratigraphy of the upper part of the Niutitang Formation consists of gray silty mudstone, siltstone and limestone, whereas the lower part of the Formation is mainly black shale. More detailed information on the stratigraphy, geology, and petroleum potential of these shales can be obtained in Refs. [11,18].

Core cuttings of all samples were assessed experimentally using X-ray diffraction (XRD) analysis, TOC content analysis, nitrogen adsorption, and methane adsorption. Helium porosity and pulse decay permeability tests were run on the core plugs.

The porosity and permeability of core plug samples were measured following the Chinese Oil and Gas Industry Standard (SY/T) 5336-1996. Porosity measurements were carried out with a ULTRAPORE-300 using a helium expansion method, whereas permeability measurements were conducted using a pulse-decay permeameter (TEMCO PDP-200) with dry nitrogen as the medium.

XRD analysis is a useful method for composition analysis. Shale samples were first ground into powder, and then XRD analysis was performed with a Rigaku D/max-2500PC.

The TOC content was determined by a LECO CS230 carbon/sulfur analyzer. Samples were crushed to a powder less than 100-mesh, then 1–2 g samples were pyrolyzed up to 540 °C.

Nitrogen adsorption experiments were conducted with a Quadrasorb™ SI Surface Area Analyzer and Pore Size Analyzer. All shale samples, weighing 200–500 mg, were prepared by sieving a maximum particle size of 0.2 mm and then outgassed at 423 K for 5 h, ensuring the removal of bound water adsorbed in the clays. Reagent grade nitrogen was used as adsorbent at 77 K, and adsorption–desorption isotherms were obtained under relative pressures ranging from 0.01 to 0.98.

High-pressure methane excess adsorption isotherms were collected using the manometric method described in Ref. [19]. Powdered samples were dried for 24 h at 105 °C before the methane adsorption experiments. All methane adsorption was measured at a consistent temperature of 35 °C and up to a consistent pressure of 12 MPa. The measured excess adsorption data were parametrized using Langmuir function, and the analytical results include Langmuir volume and Langmuir pressure.

3. Results

3.1. Compositional analysis and TOC

XRD analysis results are presented in Table 1. The shale samples contained abundant quartz and clay minerals. Quartz content averaged 35.2% and ranged from 17.6% to 55%, whereas carbonate mineral (calcite and dolomite) content averaged 16.6% and was between 0% and 36.6%, and clay mineral content averaged 26.9% with a range between 14.5% and 48%. The mineral composition of this formation was similar to the Barnett strata, for which the average values of quartz, carbonate and clay minerals are 34.3%, 21.1%, and 24.2%, respectively [2]. The TOC content of shale samples ranged from 0.16% to 9.15% with an average of 3.64% (Table 1).

3.2. Helium porosity, permeability and methane adsorption results

The helium porosity of the samples was between 1.3% and 10% with an average of 4.34% (Table 2). Their pulse-decay permeabilities are commonly < 1 μD, ranging from 0.32 to 0.89 μD. Permeabilities of these shales were similar to the Woodford shales, but lower than the Muskwa shales from Northeastern British Columbia [20].

The results of the methane adsorption analyses are shown in Table 2. The Langmuir volume of the dried samples was between 0.08 and 0.60 mmol/g, and the Langmuir pressure ranged from 2.5 to 12 MPa.

3.3. Pore structure from N_2 adsorption isotherms

The N_2 adsorption isotherms of the shale samples are illustrated in Fig. 1. According to the IUPAC classification, the N_2 adsorption isotherms of shale samples belong to Type IV [7]. All the shale samples showed hysteresis loops, which indicate that capillary condensation takes place in the mesopores [7]. When the relative pressure is less than 0.45, the adsorption isotherm is essentially coincident with the desorption branch, indicating that small pores are accessible via a single pore throat. As the relative pressure rises, the resulting hysteresis loop occurs can be attributed to the difference between the adsorption and desorption mechanism, corresponding to condensation and evaporation, respectively. Useful information on the pore structure can be obtained from the shape of hysteresis loop. The hysteresis loops that terminate at a relative pressure of about 0.45 mainly consist of two types: Type H2 (sample Y-6) and Type H3 (sample Y-10). Type H2 hysteresis is always observed in pores with narrow necks and wide bodies (referred as inkbottle-shaped pores), whereas Type H3 hysteresis occurs in aggregates of plate-like particles that give rise to slit-shaped pores. Shale samples (sample Y-10) that exhibit Type H3 hysteresis generally have slit-shaped pores, whereas Type H2 hysteresis (sample Y-6) is indicative of inkbottle-shaped pores or polymorphism pores [7]. A large proportion of the TOC shale samples displayed a wide