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Research paper

Characterization of microscopic pore structures in Lower Silurian black shale(S_1l), southeastern Chongqing, China

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A B S T R A C T

Due to the large thickness and richness of organic matter in Longmaxi shale, southeastern Chongqing is considered as the most promising area for shale gas exploration and development and was a focus of numerous research interests in China. Characterization on the pore system of organic rich shale is significant for the reserve estimation and better understanding the production mechanism of shale gas plays. Shale composition, detected by X-ray diffraction, indicates that brittle minerals, especially quartz was the most prevalent component , with average contents of 41.72 wt.%. Pore types was classified by using a combination of argon-iron milling and field emission scanning electron microscopy (FESEM), and six types of pores were observed in rock images. High pressure mercury intrusion and low pressure N_2 adsorption were performed to extract the pore size distribution of Longmaxi shale. The results show that the nanopore was the major pore type in shale samples, which accounts for 95.6% of the pore volume. In the nanopore system, pore with diameters between 2 nm and 10 nm is the major component that contributes 76% of the total pore volume and 78% of the whole inner surface area. Furthermore, the dominant pore shape was interpreted from the adsorption-desorption hysteresis loop shape, and the typical slit-shaped pores were identified in the examined shale samples. Based on single factor analysis method, organic matter richness is the main controlling factor for the volume of nanopore and the specific surface area. No direct correlation between brittle minerals and nanopores, but high quartz and calcite content makes it much easier for the formation to generate natural fractures and to be hydraulically fractured. The study can inspire and guide shale gas exploration and exploitation southeastern Chongqing to some extent.

1. Introduction

Shale gas is formed by thermogenic, biogenic or combined biogenic-thermogenic process is featured by continuous distribution, subtle trapping mechanism, seals of variable lithology and relatively short hydrocarbon migration distances (Curtis, 2002). As an unconventional energy resource, shale gas can substitute conventional oil and gas to secure increasing energy demand and alleviate the environmental issues, and thus significant attention has been given to shale gas development worldwide, especially in China.

Recently, two wells, QJ1 and 2 were drilled by CNPC in the southeastern Chongqing and high gas content (2–4 m^3/t) has been achieved. The breakthrough discovery has made Lower Silurian Longmaxi shale in southeastern Chongqing a focus of attention and regarded as the next exploration target. Many studies have been carried to understand the sedimentary environments, large thickness and organic richness (Han et al., 2013; Zhang et al., 2008, 2012, 2013; Zeng et al., 2011; Zhao et al., 2012; Zou et al., 2010, 2011). However, these studies were based on outcrops and because of weathering, dissolution and erosion; the outcrops can't truly reflect the shale reservoir properties. This paper took advantage of cores from well QJ1 owned by CNPC and expected to give more details on shale reservoir characteristics, especially the microstructure.

Shale microstructure affect the most important properties,

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porosity and permeability (Cao et al., 2014; Ma et al., 2014; Nie et al., 2009; Roger and Neal, 2011). Porosity defines the amount of gas in place. In addition, as nanopore is the major component of pore system, surface area strongly affects the amount of adsorbed gas. The pore shapes will directly influence the structural integrity and how the pore space responds to changes in stress. Pore connectivity is quite significant to influence shale unfractured ability to deliver gas to the borehole. Permeability is also affected by pore connectivity.

Conventional scanning electron microscopy (SEM) usually fails to recognize mesopores and micropores, due to its low power of magnification (1000×) and the irregular surface topography of rock chip. Here, we treat the sample with argon-iron milling and use field emission scanning electron microscopy (FESEM) to detect the nanometer-scaled pore system of gas shales. The argon-iron milling technique is capable to remove topographic features and produce flat surfaces for high magnification FESEM observation. FESEM technique can be used to visualize the pore system that is too fine to observe by other methods of microscopy. And this approach was proven particular useful to observe micropores in shale system (e.g. Chalmers et al., 2009; Loucks et al., 2009; Wang and Reed, 2009; Ambrose et al., 2010; Curtis et al., 2010; Passey et al., 2010; Sondergeld et al., 2010). The macropore distribution was measured by mercury intrusion, while micropore and mecropore were defined by nitrogen adsorption. Qualitative analysis was done by FESEM. Pore types was documented, illustrated and classified by FESEM observation.

The purpose of this study is to provide both quantitative and visual qualitative analysis on pore system of shale gas reservoir in southeastern Chongqing. Quantitative analysis was completed to detect pore size distribution by using high pressure mercury intrusion and low pressure N_2 adsorption. Qualitative analysis was based on FESEM technique to define the pore types in shale system. The potential controlling factors of pore development were also discussed in this article.

2. Geological setting

The study area is located in the passive margin fold belt of southern Yangtze Block, covering an area of 2×10^4 km^2 including Qianjiang County, Shizhu County, Pengshui County, Youyang County and Xiushan County. In study area, multiple phases of tectonic activities have created well-developed NE oriented ejective folds and trough-like folds. Major folds include Jinfoshan uplift fold belt to the west, Qiyaoshan uplift fold belt to the northeast, Qianjiang depression fold to the northeast and Xiushan uplift fold to the south (Fig. 1). Due to the uplift of the southeastern margin of the Yangtze platform from the late Silurian to the late Carboniferous, the Devonian, Carboniferous and part of the Silurian stratum were denuded along the elevated Yangtze platform (Liu et al., 1983; Shao et al., 1998). After the Yanshan and Indosinian orogenies, the NNE-trending Neocathaysian structural system finally formed (Ma et al., 2004; Liu et al., 2010). Depositional environment of Lower Silurian is mainly marine facies with stable distribution, large thickness and rich organic matter. The lithology of well QJ1 mainly consists of gray silty mudstone, gray black silty mudstone, gray black quartz siltstone, gray black crabon containing silty shale, black carbon containing silty shale, and black carbonaceous shale (Fig. 1).

3. Material and methods

Forty-five samples were collected from well QJ1 for lab test to analyze the pore system of shale interval in the study area (Fig. 1).

All samples from Well QJ1 were tested for mineral composition using X-ray diffractometer on the basis of the SY/T 5163-1995 standard. Crushed samples (<250 um) were mixed with ethanol, hand ground in a mortar and pestle and then smear mounted on glass slides for X-ray diffraction analysis. Results are presented in Table 1.

Eight samples from Well QJ1 in the interval between 711.8 m and 807.1 m were tested for total organic carbon (TOC) with a Leco carbon-sulfur measurement instrument by the recommended state standard of GB/T 19145-2003. The same samples were also taken for high pressure mercury intrusion and low pressure N_2 adsorption.

High pressure mercury intrusion test was carried out under GB/T 21650.1-2008/ISO 15901–1:2005 standard using Micromeritics™ Autopore IV 9520 series apparatus. Samples were crushed (2–4 mm) and dried in oven (110 °C) for 24 h, evacuated to 1×10^{-4} psia, and intruded with mercury from 1.5 to 60000 psia. The measured pressure ranges equates to the pore diameter range of 0.003–1000 μm. The minimal pore diameter limit of 3 nm is within the mesopore range, and the mercury porosimetry can't detect micropores within the pore system.

Low pressure N_2 adsorption experiments were using Quadrasorb SI following GB/T 19587-2004 standard. This technique was used to detect pores with diameter ranging from 0.35 to 400 nm. The smallest specific surface area measured by this equipment is 0.0005 m^2/g and the smallest volume tested is 0.1 m^3/g. Samples were crushed to grain size of less than 250 μm and in order to eliminate irreducible water and capillary water, all samples should be treated in vacuum-pumping at 300 °C for three hours. After that, nitrogen adsorption and desorption isotherms at different partial pressure were obtained.

Micropore scanning was using FEI Quanta 200F. The resolution of FEI Quanta 200F can reach 1.2 nm and the amplification factor of this equipment is 25–200000. The samples mounted to FESEM were 0.125 in (0.317 cm). Before scanning, samples should be polished using argon-iron beam to create a level surface. Then carbon was pasted and gold was coated to samples to provide a conductive surface layer.

4. Results and discussions

4.1. Petrologic characteristics

Qualitative and quantitative analyses by X-ray diffraction (XRD) were performed on 45 core samples of well QJ1 from the Lower Silurian Longmaxi shale in southeastern Chongqing, the results showed that components of the Longmaxi shale are composed of clay minerals, quartz, feldspar, calcite, dolomite and pyrite. As demonstrated by Fig. 1c, quartz and clay minerals were the major components with an average of 41.72 wt.% and 43.62 wt. % respectively. . The quartz content of shale reservoirs in North America is close to 45% (Li et al., 2007), while the quartz content in the study area varies greatly and unevenly distributed vertically. If taking 45% as the development boundary of quartz content, about 40 m of the bottom Longmaxi shale is ideal target. Feldspar is also a major component of brittle minerals, with an average of 9.57 wt. %. In addition, other mineral components include calcite, dolomite, and pyrite, with an average less than 5 wt. % for each mineral. Clay mineral compositions characterize a late diagenetic stage experienced by the Longmaxi shale, which corresponds to a mature or highly mature evolutionary stage of hydrocarbons. Further analyses of clay show that the mixed layer I/S is the main clay mineral, with a mean of 45.62 wt. %, and the mixed-layer ratio is in the range of 5 and 10%. The mean content of illite and chlorite are, respectively, 37.54 wt. % and 16.85 wt. %