The pore size distribution and its relationship with shale gas capacity in organic-rich mudstone of Wufeng-Longmaxi Formations, Sichuan Basin, China

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Abstract

The pore size distribution for the 23 fresh outcrop shale samples collected from Shuanghe Town and Changning County, as well as the 14 core samples collected from the Qianqian 1 core well in southeast Chongqing, Sichuan Basin were investigated by means of low-pressure nitrogen adsorption. The main factors controlling pore development and gas accumulation in shales were discussed by integrating total organic carbon (TOC), mineralogy, and shale gas content. The results showed that open, slit-like, and parallel plate structure are major pore types that possess an average pore diameter of 3.76–8.53 nm; chiefly 2–30 nm for mesopores. The BET surface area and total pore volume are high in the Wufeng Formation and in the lower part of the Longmaxi Formation, and it’s a bit lower in the upper part of the Longmaxi Formation. Consistent with the trends of TOC, that organic matter is the key controlling factor in the shale pore development. In addition, samples with higher content of clay minerals, but comparative TOC content have a larger specific surface area where clay mineral hosted pores are present. The Wufeng Formation and lower part of the Longmaxi Formation in the Sichuan Basin are preferred layers of shale reservoir fracturing due to high TOC, high rock brittleness, and high gas content.

Keywords: Sichuan Basin; Shale nanopore; Nitrogen adsorption; Gas capacity; Specific surface area

1. Introduction

Shale gas is a natural gas produced from shale formations that typically functions as a self-contained source-reservoir system for the gas accumulation in situ [1–4]. The reservoir conditions of shales gas that is always characterized by serious heterogeneity and poor petrophysical properties (low porosity and low permeability) appeared to be essential for shale gas enrichment [5–8]. In the recent years, the application of focused ion beam milling in combination with field emission scanning electron microscopy and transmission electron microscopy has clarified the ambiguity of gas shale microstructure in unconventional petroleum system. Different types and scales of pores have been firstly and clearly shown to distribute in organic-rich shales, whereas so far no pore classification is universally accepted as a unified standard. Loucks et al. [9] proposed a pore classification on mudrocks consisting of three major matrix related pore types on the basis of their relationship to particles. The three pore types mentioned are the interparticle pores, intraparticle pores, and organic matter pores. In this study, it has been chosen to use the pore size standard of the International Union of Pure and Applied Chemistry (IUPAC), as developed by Rouquerol et al. [10].
According to this pore classification of IUPAC, pores in mudrocks are further subdivided into three basic categories as follows: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm).

The pore structure of gas shale reservoirs primarily depends on the combined processes of multiple geologic factors, including total organic carbon (TOC), mineral composition, the maturity of organic matter, etc. [3,11] Hence, characterizing the pore structure of gas shales is a feasible approach to establishing a relationship between these unconventional reservoir parameters such as TOC, mineral composition, the maturity of organic matter, and gas storage capacity of shales. In this research, the BET surface area and pore-size distribution of the Wufeng-Longmaxi shale samples in the Sichuan Basin, China were investigated using the low-pressure nitrogen adsorption method, coupled with TOC, mineralogy, and shale gas content, the main factors controlling nanometer pores development and gas accumulation in shales are discussed as follows. The objective of this study is to provide a theoretical basis for shale reservoir evaluation, gas content assessment, and shale gas exploration and development.

2. Materials and methods

2.1. Samples

23 shale samples from one fresh outcrop section located in the Upper Ordivician Wufeng Formation and Lower Silurian Longmaxi Formation, Shuanghe Town, Changning County, in Sichuan Basin, as well as the 14 core samples from the Qianqian 1 core well in the southeast of Chongqing City, were collected for experimental purposes according to the characteristic of TOC [12]. In the outcrop section, the Wufeng Formation is predominantly composed of carbonaceous and siliceous graptolite shale facies with a marlaceous shell facies and mixed facies deposit known as the Guanyinqiao Member (approximately 1 m thickness). The lower part of the Longmaxi Formation, conformably overlying the Wufeng Formation, is generally made up of black laminated graptolite shale with a small number of sandy mudstone and siltstone interbeds, which are brought about by frequent disseminated and nodular pyrite. From the bottom to the top, the Longmaxi Formation shales show a gradual increase of sandy content but a decrease of total organic carbon content. For the Qianqian 1 core well, as the color of the shales changes as it becomes shallow, the organic matter content and quartz content tends to decrease with the sandy content intensifying. Black carbonaceous shale facies, gray argillaceous siltite facies, and gray sandstone facies were deposited more commonly in the shallower parts of the layer.

2.2. Experimental methods

Nitrogen adsorption experiments were accomplished using a surface areas and pore sizes analysis apparatus named HYA2010-C2 (Beijing Zhongke Huiyu Technology Co. Ltd.) at the Key Laboratory of Mineral Resources in Western China (Gansu Province). The outcrop and core samples after being washed and dried were pulverized to powder at 20–50 mesh and then homogenized. The powder samples prepared were heated at 110 °C for 12 h under relative vacuum conditions to remove rock water prior to the subsequent analysis. In the experiments, approximately 1.0 g duplicate powder samples weighed were loaded into two sample tubes for comparison purposes. Nitrogen with high purity (>99.999%) was used as the adsorbate, and the adsorption capacities at varying relative pressure conditions were measured at liquid nitrogen temperature (77 K) in further junctions of the experiment. Additionally, the bulk mineralogy of these samples from X-ray powder diffraction (XRD) analysis was performed using the PAN alytical X’pert PRO apparatus at the Analysis and Testing Center in the Lanzhou University.

The surface areas of the shale samples were calculated through the Brunauer–Emmett–Teller equation (BET equation) on the basis of the adsorption theory of multimolecular layers. Extensive details of the method were previously reported by Rouquerol et al. [13]. The pore size distribution was determined using the BJH model.

3. Experimental results

3.1. Adsorption–desorption isotherm

The actual testing of adsorption isotherms in the laboratory are regularly results of inter-combinations of six different types of standard isotherms shown in Fig. 1 (Type I–Type VI) [14]. The adsorbance of Type I isotherms increases rapidly at low relative pressures (P/P_0), and it slows down at moderate pressure, thus, revealing the adsorbent has micropore and mesopore. At low relative pressures, the adsorbance of Type II adsorption isotherm sharply increases, indicating the occurrence of micropore filling. As the pressure increases, the monolayer adsorption translates to multilayer, and due to well-developed macropore, the adsorbance sharply rises when the P/P_0 value is close to 1. The Type III adsorption isotherm shows the weak interaction of adsorbent and adsorbate. The hysteresis loop of Type IV reflects the connectivity of various sized pores, and the adsorbent develops considerable micropore and mesopore except non-macropore. The adsorbance of Type V adsorption isotherm increase slowly at the low relative pressures showing poorly developed micropore, then it sharply rises to which adsorption platform appears revealing large numbers of mesopores development and non-macropore. Type VI is rare and is not introduced here anymore. The shale samples measured in this article show similarity with Type II adsorption isotherm. It also presents an inverse ‘S’ shape (Fig. 2). Specifically, the adsorption curve rises with a slight convex at values for P/P_0 = 0–0.05, which reveals monolayer physical adsorption and micropore filling of nitrogen in the shale surface. The transition from monolayer to multilayer adsorption occur at a certain pressure range (P/ P_0 = 0.05–0.35); the adsorbance increases slowly at the moderate relative pressures between P/P_0 = 0.35–0.7, when the multilayer adsorption and condensation process occur;
then at the latter part of the adsorption curve ($P/P_0 = 0.35-0.7$), the sharp rising presents a concave shaped, not to mention, the adsorption saturation doesn't appear until it's near $P/P_0 = 1$, validating that the samples develop macropores and capillary condensates occur in the shale surface.

What described above indicates that the two groups of shale samples in this study have pore systems with micropores, mesopores, and macropores present.

Open pores, such as cylindrical pores, wedge-shaped pores, and parallel plate pores, which open at both ends or
around, especially thin bottleneck pores, can produce hysteresis. Nevertheless, closed pores can’t attribute to this phenomenon. Hysteresis is reasonably attributed to capillary condensation and evaporation at the region for $P/P_0 > 0.45$ in large pores ($d > ~4 \text{ nm}$) and Tensile Strength Effect (TSE) for small pores ($d < 4 \text{ nm}$) [15], the latter presents a sharp decrease of the desorption branch particularly around $P/P_0 = 0.45$ (for N$_2$ at 77 K), and it eventually leads to a forced closure of the hysteresis loop. There are mainly four pore types correlated with hysteresis loop (Type A – Type D; Fig. 2) [16]: Type A, featured by a strait loop, indicates a limited pore size distribution of the measured samples, and the adsorption and desorption branch is parallel to each other and perpendicular to the axis of pressure in a wide pressure range. The hysteresis loop of Type B is wide and the desorption curve is steeper than adsorption branch, showing that the samples have various distributions of pore types and pore diameter, which usually happens to slit-like pores and two parallel-plate cracks. The extreme adsorbance for adsorption and desorption branch of Type C doesn’t appear for it usually occurs with open-wedge pores. There is an inflection point for Type D for a sudden drop of desorption branch, which is associated with bottle neck pores. Overall, the measured samples have shown hystereses Type B, indicating that the shale reservoir's pore shapes for the Wufeng Formation and Longmaxi Formation in Sichuan Basin are entirely open, and the open slit-like pores in parallel plate structure are major pore types. Slatt et al. [17] suggested that the formation of “flocules”, which are clumps of electrostatically charged clay particles, have a strong compressive strength that protects the primary pore during early shale deposition. Through the sediments undergoing compaction, the interlamination of flocules can form plenty of micro-pores by dehydrating clay minerals. Obviously, the open slit-like pore, distributed widely in shale, is in favor of gas migration.

3.2. Pore size distribution (PSD)

Groen et al. [18] found that a strong artificial pores' peak, approximately 4 nm, results from TSE. Whenever the pore size distribution has been derived from the desorption branch of the isotherm the nitrogen isotherm is not a Type IV accompanied by a Type A hysteresis loop. Disappearance of the hysteresis loop in the critical range ($(P/P_0)_{\text{TSE}} = 0.41–0.48$) seems to be a result of instability of the hemispherical meniscus caused by an increased chemical potential of the pore walls during desorption in pores with critical diameters approximately 4 nm, and in according to what's mentioned, the tensile strength increases in the adsorbed phase as the pore size decreases. In addition, the appearance of an artificial peak may also be affected by pore network, various pore shape, and wide pore size distribution. Hence, we chose the adsorption branch and classical BJH calculation model to analyze shale samples' PSD since our samples are characterized by Type B hystereses and have a wide PSD, which is easy to have a critical situation.

As seen in Fig. 3, the shale samples’ PSD is complex and multimodal with the observation that pores less than 10 nm and between 20 and 30 nm in width are predominant, showing pores in these scales occupy an important proportion. Except for the samples CN-SH-07 and CN-SH-11, their PSD peaks are smaller than 10 nm and 70–80 nm regionally, while the sample QJ-15’s PSD peaks appear at 300 nm and less than 10 nm. The carbonate minerals content in the three samples above is higher than other samples. Pu et al. [19] observed many calcite dissolution pores of marine shale, developed in the south of Sichuan basin, and those pores have a large diameter and they come in various shapes resembling honeycomb or harbor and so on. All of the samples show a tailing phenomenon and they exemplify some macropores in their shales.

The BET specific surface area for the Changning shale samples with an average pore diameter of 3.76–8.53 nm ranges from 10.67 m$^2$/g to 35 m$^2$/g, which averaged 20.93 m$^2$/g. Their average total pore volume varies from 0.015 cm$^3$/g to 0.049 cm$^3$/g, which averaged 0.024 cm$^3$/g. For the Qianqian 1 core well shales, their BET specific surface area ranges between 10.67 and 35 m$^2$/g with an average 16.73 m$^2$/g. As for their total pore volume, it ranges from 0.006 cm$^3$/g to 0.028 cm$^3$/g, which averaged 0.015 cm$^3$/g. The average pore diameter of Qianqian 1’s core well samples is between 3.95 and 7.58 nm. Large specific surface area and pore volume are beneficial for gas adsorption and gas storage.

3.3. Characteristics of pore structure, organic matter, and minerals

The TOC is high in the Wufeng Formation and in the lower part of the Longmaxi Formation. However, TOC is somewhat lower in the upper part of the Longmaxi Formation. Vertical variation of main mineral compositions can be observed in Fig. 4. For Changning’s fresh outcrop shale samples, the TOC and quartz contents range from 1.02% to 7.28% with an average of 3.04%, and from 14.58% to 76.09% with an average of 41.94%, respectively. Both of the aforementioned variables have a positive correlation with each other (Fig. 4a). This relationship may correlate with the shale state of organic matter concomitant with silica in this area [20], also biological siliceous deposition is principal in marine shale. Authigenic quartz crystallite accompanied with organic matter was previously observed in kerogen microscopic figures [21]. For Qianqian 1’s core well samples, the TOC value varies from 0.15% to 6.09% with an average of 2.2%, and the quartz content ranges from 11.45% to 77.1% with an average of 37.94%. No obvious correlation was found between TOC and quartz content (Fig. 4b). This difference from Changning may be attributed to the fact that the Qianjiang area is located at the southeast edge of the eastern Sichuan depositional center, which is close to provenance. Therefore, the input of large numbers of terrigenous detrital minerals caused a disturbance. This interpretation needs to be further verified by analyzing more samples from the Shizhu County in the depocenter of eastern Sichuan. The average clay mineral contents are
10.13% for Changning shale, and 16.91% for Qianqian 1 core well shale. The content of clay minerals is lower in the Wufeng Formation and lower part of the Longmaxi Formation. In comparison, there's a higher value within the narrow range in the upper part of the Longmaxi, while carbonate minerals contents are rather unpredictable it also show opposite growth and a decline in trend in terms of the clay mineral. In general, the Wufeng Formation and lower part of the Longmaxi Formation in the Sichuan Basin have higher quartz and TOC content while clay minerals are lower, but it shows an increase in the upper part of the Longmaxi Formation, indicating that the lower part of the Longmaxi Formation are preferred layers of shale reservoir fracturing because of high TOC and high brittle minerals, which are good for microcrack formation.

The BET surface area, total pore volume, micropore volume, and mesopore volume fluctuates but are generally high in the Wufeng Formation and the lower part of the Longmaxi Formation. On the other hand, they’re lower in the upper part of the Longmaxi Formation; consistent with the trends of TOC, which may be related to organic matter hosted pores. The macropore volume of Changning samples does not present an evident constantly changing trend except it’s much bigger at the boundary of Wufeng Formation and Longmaxi Formation. Nevertheless, macropore volume changes accordingly with carbonate minerals in 20 m at the bottom of Qianqian section, which is consistent with the clay minerals content. These observations suggest that the vital controlling factor on the shale pore development of the Wufeng Formation-Longmaxi Formation in Sichuan Basin is complex and not only restricted by a single factor.

4. Discussions

4.1. Controls of pore development in organic-rich shale

Loucks et al. [22] found that most nanopores develop within organic matter from researches on Barnett shale pore characteristic and honeycomb-like organic micropores are extremely widespread when oil is cracking in the high maturity stage [9]. The organic matter (OM) pores’ formation are closely connected with convertible organic carbon content (namely activated carbon) [23] and attributed to OM type [3] and the cracking of retained oil in shales. Studies have shown that shale can gain a 4.9% net increase in effective porosity assuming the loss 35% of organic carbon in the pyrolysis process [1]. As shown in Fig. 5a, b, d, e, TOC has a positive relationship with total pore volume and BET specific surface area. Specifically, the coefficients $R^2$ are 0.565 and 0.807, respectively when the TOC is less than 2%, meanwhile, the $R^2$ are 0.476 and 0.736 when the TOC is greater than 2% for the Changning samples. In comparison, the Qianqian 1 core well shale has the coefficients $R^2$ up to the range between 0.885 and 0.853. The shale of the Longmaxi Formation in the Sichuan Basin has experienced high thermal maturity stage and the thermal maturity ranges from 2.4% to 3.6%. Meanwhile, Type I and Type II of organic matter are dominating [12]. All of these illustrate that a good number of nanopores which are mainly composed of micropores and mesopores develop within an organic matter of Lower Silurian Longmaxi Formation. Organic matter is a significant controlling factor on the shale pore development and reservoir properties.

As Fig. 5c and f have shown, samples with higher content of clay minerals but similar TOC content have larger specific surface area and the positive correlation coefficients $R^2$ between BET surface area and clay minerals are 0.709 and 0.713. The main mineral compositions are illite/chlorite accompanied with mixed illite/smectite layer of the Lower Silurian Longmaxi Formation by X-ray diffraction (XRD) analysis [24], and the weak adsorption ability of illite/chlorite can still adsorb little OM and the clay minerals layer structure can benefit in the micropores’ formation. Tian et al. [24] found that micropores develop in schistose illite from the observation via FE-SEM imaging. Visibly, the shale nanopores development is affected by TOC and clay minerals at different degrees.

4.2. Relationship between pore development and shale gas content

The abundant nanopores developed in shale are introduced in complex structures, extensive pore size distribution, and large numbers of micropores and mesopores, and also this helps determine the gas occurrence, storage, and transport mechanism. As seen in Fig. 6a, the total shale gas content and desorbed gas content do not change much when TOC is less than 2% while they rise significantly when TOC is higher than
Fig. 4. Vertical variation of TOC, pore volume, and mineral composition of the Wufeng-Longmaxi Formation shale.
2%. Generally, high TOC corresponds to high shale gas content with the coefficients $R^2$ reaching up to 0.863 and 0.839, respectively. The organic matter influence shale gas accumulation mainly in two aspects. High OM contents can produce more gas and provide source material and be consistent with large pore volume, on the other hand, be a key controlling factor of nanopores development in shale gas reservoirs. The total pore volume has a positive relationship with total gas content and adsorbed gas content as seen in Fig. 6b. The lower part of Lower Silurian Longmaxi Formation is favorable to shale gas formation and accumulation due to its high TOC, high gas capacity, and vast OM pores.

The abundance of micropores and mesopores within OM has large specific surface area and OM-hosted pores which provide sites for gas adsorption [25]. The main pores are mesopores where the gas molecule is affected interactively by intra-molecular force and molecule-pore wall force [26]. Gas storage primarily adsorbs gas and free gas, while pore structure determines the preserved mode and exploiting features of shale gas. Therefore, the Upper Ordovician Wufeng Formation and lower part of the Lower Silurian Longmaxi Formation in the Sichuan Basin are preferred layers of shale reservoir fracturing due to its high porosity [27], high rock brittleness, and high gas content.

5. Conclusions

(1) The gas shale reservoirs in the Upper Ordovician Wufeng Formation and Lower Silurian Longmaxi Formation in the Sichuan Basin have mainly developed open slit-like pores with parallel plate structure resulting in good pore connectivity, which is beneficial for both gas preservation and migration.

(2) An extensive pore size distribution, dominated by micropores and mesopores, exists in the Wufeng and Longmaxi Formations' shales in the Sichuan Basin. A positive correlation between the total pore volume and micropore volume with the TOC values reveal that OM pores are primarily composed of micropores and mesopores, and OM acts as a key controlling factor in shale gas reservoir evaluation.

(3) The clay mineral hosted pores are also present in the studied shale. This showed that samples with higher content of clay minerals with similar TOC content have larger specific surface area.

(4) The nanopores' complicated structure determines the storage and exploiting features of shale gas. The Lower Silurian Longmaxi Formation in the Sichuan Basin is favorable layers of shale reservoir fracturing due to high TOC, high rock brittleness value, and high gas content.
References