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Pore structure characterization of Carboniferous shales from the eastern Qaidam Basin, China: Combining helium expansion with low-pressure adsorption and mercury intrusion

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ABSTRACT

Pore characteristics such as pore size distribution, pore geometry, and connectivity are key factors for evaluating shale reservoir capacities. In this study, multiple methods are used to characterize the pore structure of Carboniferous shales from the eastern Qaidam Basin, China. Low-pressure nitrogen and carbon dioxide adsorption (LPA) and high-pressure mercury intrusion (MICP) were applied to obtain pore size distributions (PSDs) of shale samples. X-ray diffraction (XRD) was used to obtain the mineral composition of the shale, while helium expansion using cylindrical shale samples was performed to obtain total porosity. In addition, field emission scanning electron microscopy (FESEM) was used to verify the results of the PSD analysis. Pores in the shale samples are generally under 10 μm in size. These micro- and mesopores, especially the mesopores, play a dominant role in PSDs. Bimodal PSDs are observed for micro- and mesopores, while unimodal or bimodal PSDs emerge in the macropore range. Total porosity was obtained by helium expansion, which provides relatively accurate porosity values when compared with the results of low-pressure adsorption and mercury intrusion. Total porosity and microporosity show an increasing trend with total organic carbon (TOC). Micro- and mesoporosities are found to significantly increase with total clay content, while macroporosity does not show any correlation with the latter. No correlation is found between porosity and quartz content. Surface area increases with total clay content as well as the proportions of micro- and mesopores, but no correlation between surface area and macroporosity is observed. This study suggests that a simple helium expansion experiment is sufficient to obtain reliable total porosity of shale samples. Pore characteristics obtained in this study provide useful information for the evaluation of shale reservoir capacity in the eastern Qaidam Basin.

1. Introduction

Shale gas is a clean and highly efficient energy source, whose resources total approximately 1.4 times those of conventional natural gas (Li et al., 2015). Pore size distribution and connectivity control storage and migration of shale gas; therefore, pore structure characterization is important for evaluating the potential of shale gas reservoirs. Numerous studies on pore classification exist. According to the classification of pores of the International Union of Pure and Applied Chemistry (IUPAC), which was developed by Rouquerol et al. (1994), pores can be divided into three categories: micropores (with pore diameters of less than 2 nm), mesopores (with pore diameters of 2–50 nm), and macropores (with pore diameters larger than 50 nm). Slatt and O'Brien (2011) reported that pores in the Barnett and Woodfort shales can be classified as inter-particle pores produced by flocculation, organoporosity produced during burial and maturation, intra-particle pores caused by organisms, fecal pellets, or fossil material, intra-particle pores within mineral grains, micro-channels in the shale matrix, and micro-fractures. Loucks et al. (2009, 2012) stated that there are four types of pores: (1) inter-particle pores between mineral crystals or grains, (2) intra-particle pores within mineral grains or biological particles, (3) organic pores, and (4) fracture pores.

In addition to many ultra-fine pores, shales are characterized by a wide pore size distribution, which necessitates the use of multiple techniques to investigate the full pore size range (Clarkson et al., 2013). Analysis of pores in shales can chiefly be divided into two techniques: microscopic studies, which include the direct observation of microscopic pores using various techniques such as field-emission scanning electron microscopy, and physical and chemical tests, which lead to an indirect calculation of pore size distribution by combining low pressure adsorption and mercury intrusion analysis. Although the characteristics of pores in shale such as geometry, pore size, connectivity, and

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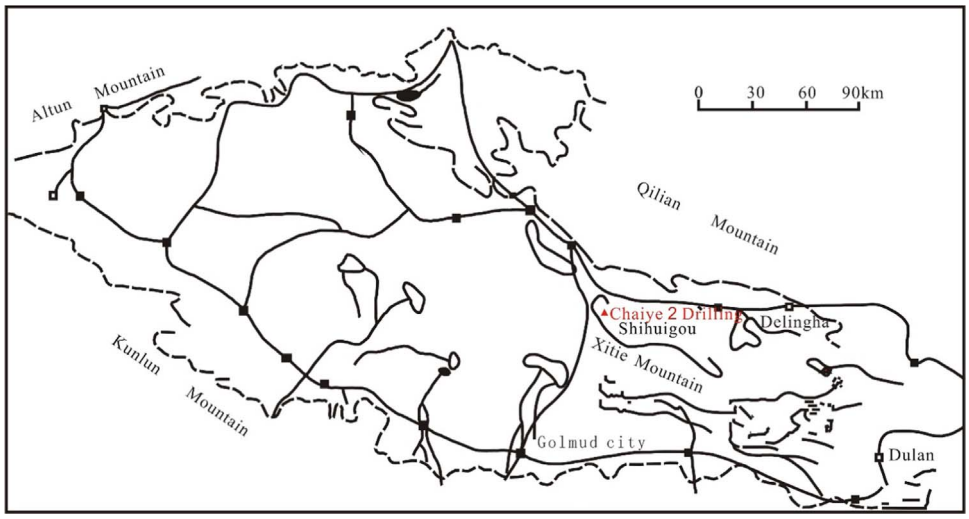

Fig. 1. Sampling location in the eastern Qaidam basin.

degree of filling, can be observed directly using a field emission scanning electron microscope (FESEM), pore size distribution details cannot be obtained. In addition, as the hardness of the shale surface can be quite variable, chemical–mechanical polishing (CMP) can cause nano- and irregular pores, which cannot be identified by FESEM. Therefore, complete and accurate information about the reservoir space characteristics of shale formations is difficult to obtain. High-pressure mercury intrusion (MICP) and low-pressure adsorption (LPA) using N_2 and CO_2 are two common methods that have been used for pore structure characterization of shale samples. Theoretically, mercury intrusion can be used to characterize pores with diameters > 2 nm, but some pore structure distortion may occur at the lower pore-size limit (~3 nm) due to compressibility effects (Bustin et al., 2008; Peng et al., 2012) because MICP requires tremendous injection pressure to access the finest pores. Furthermore, MICP requires drying of the samples, which may change the porosity and structure of shales with high clay content (Bustin et al., 2008). Therefore, MICP is often used to characterize macroporosity. Low-pressure adsorption of CO_2 is always used to characterize pores with pore diameters < 2 nm and LPA of N_2 can be used to characterize pores with pore diameters > 2 nm. In addition, the gas stored in shale gas reservoirs occurs as either free or adsorbed gas. Adsorbed gas is gas that is attached to the surface of clay minerals or organic material. Because of their small molecular sizes, CO_2 and N_2 can access these micropores and mesopores respectively (Clarkson et al., 2013; Labani et al., 2013;) to characterize pore structure, and some important parameters for adsorbed gas like surface area, pore volume and so on can be obtained. Accordingly, low-pressure adsorption may lead to a better understanding of the adsorbed gas capacity of a shale sample (Labani et al., 2013). According to Clarkson et al. (2011), LPA has an upper pore diameter limit of ~300 nm. Thus, an "overlapping" pore size region (3–300 nm) exists between MICP and LPA (Clarkson et al., 2013); therefore, comparisons between MICP and LPA are necessary to fully characterize the pore structure. In this study, LPA of N_2 is used to characterize pores with pore diameters of 2–50 nm (mesopores) while MICP is used to characterize pores with pore diameters > 50 nm (macropores) to eliminate this overlap.

Conventional gas expansion experiments commonly use crushed rock samples, which must be heated first to remove free water, gas, and any other hydrocarbons (Luffel and Guidry, 1992). With known sample mass and bulk density, the sample skeleton density and porosity can be determined (Cui et al., 2009). In this study, cylindrical rock samples instead of crushed samples were used. As a common experimental gas, helium was used in our experiments. Because the helium molecule is very small, helium can access extremely fine pores. In addition, helium is a gas that has no adsorptivity for shale. In our experiment, total porosity of the shale samples was obtained using the gas equation of state and the law of mass conservation.

In this study, we investigated the pore structure characteristics of several Carboniferous shale samples from the eastern Qaidam Basin using low-pressure adsorption and high-pressure mercury intrusion. A simple gas expansion experiment using helium as the experimental gas was conducted to obtain the total porosity of the shale samples. Pore size distribution (PSD) and porosity obtained by the various methods are compared and the relationship between pore size distribution and mineralogical composition of the shale samples is discussed.

2. Shale samples

The Qaidam Basin is located in northwestern China, in the northern part of the Qinghai–Tibet plateau. The basin contains Paleozoic, Mesozoic, and Cenozoic strata (Li et al., 2015). The Carboniferous of the eastern Qaidam basin underwent two periods of tectonic uplift and erosion during the late Hercynian–Indochina period. Deformation mainly consisted of thrust nappe formation as well as uplift and erosion, while the Aneymaqen ophiolite mélange zone in the north-eastern Qaidam basin was a ductile shear zone that was highly deformed and metamorphosed during the Indosinian orogeny. Shale can be dominated by terrestrial sources, marine sources or marine-terristial sources (Newport et al., 2016), Carboniferous shale of eastern Qaidam Basin is defined as marine shale. According to Li et al. (2015), the Carboniferous shale of the eastern Qaidam Basin is thick and widely distributed. Carboniferous shales reach their largest thickness of 400–800 m in the eastern Qaidam Basin. Average thickness is 600 m, with numerous high-angle fractures occurring throughout the shales. Recent studies have found that the Carboniferous rocks of the Qaidam Basin are unmetamorphosed and had formed under warm and humid climatic conditions in the sedimentary environment of a coastal platform facies. Several geological and geochemical analyses also indicate that this shale is a good hydrocarbon source (Liu et al., 2012).

All nine shale samples used in this study were taken from a core retrieved from borehole Chaiye 2 in the Shihui Trough, eastern Qaidam Basin. Fig. 1 shows the sample location in the study area. The Shihui Trough extends about 10.5 km from north to south and 7.6 km from east to west, covering an area of about 80 km^2. The elevation of the study area ranges from 2750 m to 3800 m above sea level, and the area is characterized by an arid climate typical for a continental plateau with alpine, arid, and windy conditions. The lithology log for borehole Chaiye 2 is shown in Fig. 2. Table 1 lists the X-ray diffraction (XRD) analysis results of the studied samples. Bulk mineralogy and clay