Original research paper

The influence of soluble organic matter on shale reservoir characterization☆

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Abstract

Shale with a maturity within the "oil window" contains a certain amount of residual soluble organic matter (SOM). This SOM have an important influence on characterization of shale reservoir. In this study, two shale samples were collected from the Upper Permian Dalong Formation in the northwestern boundary of Sichuan Basin. Their geochemistry, mineral composition, and pore structure (surface area and pore volume) were investigated before and after removing the SOM by means of extraction via dichloromethane or trichloromethane. The results show that the TOC, S_1, S_2, and I_H of the extracted samples decrease significantly, but the mineral composition has no evident change as compared with their raw samples. Thus, we can infer that the original pore structure is thought to be unaffected from the extraction. The SOM occupies pore volume and hinders pores connectivity. The extraction greatly increases the surface area and pore volume of the samples. The residual SOM in the shale samples occur mainly in the micropores and smaller mesopores, and their occupied pore size range seems being constrained by the maturity. For the lower mature shale samples, the SOM is mainly hosted in organic pores that are less than 5 nm in size. For the middle mature shale samples, the micropores and some mesopores ranging between 2 and 20 nm in size are the main storage space for the SOM.

1. Introduction

Most of the North American shales are in the middle and high mature stage ($1.2\% < R_O < 2.5\%$) [1−3]. Shales from various strata with various maturity levels are distributed extensively in China. The Lower Paleozoic shales in South China have relatively high maturity with EqR_O (equivalent vitrinite reflectance) value ranging from 2.0% to 4.0% [4−9]. The Upper Paleozoic shales are mainly in the middle and high mature stage ($1.5\% < R_O < 2.5\%$) [10−12], but some shales are still in relatively low mature stage ($R_O < 1.0\%$) [12,13]. The Lower Paleozoic shales in and around the Sichuan Basin were the focus of investigations and explorations in recent years [5−9], but the studies about reservoir properties in the Upper Paleozoic shales are comparatively few, especially shales with lower maturity. The studies about low mature coal have indicated that the SOM not only occupies a portion of porosity [14], but also has an important influence on methane adsorption [15]. The Soxhlet-extraction with dissimilar organic solvents have different product from shale [16], not to mention, the transformation of reservoir is also different [17]. The type and content of organic matter and the maturity of shale are the main factors in controlling pore structure [8,9,12,18−22]. The organic matter in shale is mainly composed of soluble organic matter and kerogen. For high mature shale, gas was generated and pyrobitumen formed by

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cracking the heavy hydrocarbons and light hydrocarbons in the maturation process [18,19]. Shale with a maturity within "oil window" contains a certain amount of residual SOM. The amount of SOM for the type I-IIa shales can reach 20%−30% of total organic matter in the peak period of hydrocarbon generation. The SOM has apparent influence on the quantitative characterization of shale reservoir [12,18] that calls for further study. In this paper, shale samples were collected from the Upper Permian Dalong Formation in the northwestern margin of the Sichuan Basin. The pore structures were investigated before and after removing SOM by the extraction with dichloromethane or trichloromethane. The primary objective is to reveal the main storage sites of SOM and its influence on shale reservoir characterization.

2. Sampling and methodology

2.1. Samples and preparation

In this study, two gray shale samples from the Upper Permian Dalong Formation were collected from Changjianggou area in the northwestern margin of the Sichuan Basin. The fresh samples were dried at 48 °C for 24 h to remove moisture. After being crushed and sieved, a size fraction of 80 and 120 mesh (180 and 120 μm) was obtained and divided into three groups, namely, A, B, and C.

H_2O_2 or $NaClO$ treatments are commonly used methods in removing organic matter from shale. The methods not only remove the SOM and a part of kerogen, but it also changes the mineral components and destroys pores structure of the reservoir. The SOM can be effectively removed through Soxhlet-extraction preserving the pore structure of the reservoir. Therefore, the extraction with organic solvent is adopted to remove the SOM in this study. Approximately 40 g of each sample (Group B or C) was extracted for 72 h with dichloromethane and trichloromethane, respectively. The water bath temperature of dichloromethane extraction is 48 °C, and 80 °C for trichloromethane. The acquired filtrate was concentrated through rotary evaporation and was subsequently dried by nitrogen. The amount of SOM can be identified when its weight is constant in the drying box under room temperature. The extracted samples were dried at 90 °C in a vacuum for 24 h.

2.2. Experimental methods

The vitrinite reflectance (R_O) was determined on polished core samples using a 3Y-Leica DMR XP microphotometer. The instrument was calibrated using the sapphire standard ($R_O = 0.596\%$), and measurements were conducted in an oil medium using a 50×/0.85 oil lens with an optical fiber (d) of 0.6 mm. In each sample, 30−50 different vitrinite particles were randomly selected for measurements, and the average value represented the vitrinite reflectance [23].

The mineralogical composition analyses of the samples were carried out using a Bruker D8 Advance X-ray diffractometer at 40 kV and 30 mA. In a series of distinct stages, the scanning measurements were performed at a rate of 4°/min with a slit of 1 mm between 3° and 85° (2θ). The analogous mineral content was semi-quantitatively determined using peak area integration approach correlated for Lorentz Polarization [24].

The pore structure of the shale reservoir is dominated by nanometer-sized pores (i.e. micropores and mesopores). Organic matter is the main carrier of the pores, which provides the adsorption site and storage space altogether for the adsorption and free gas [18−21]. Nanometer-sized pores in low maturity shale are also the place where shale oil is stored [6]. Low-pressure N_2 adsorption is considered a standard and preferable method for surface area and pore volume measurement of porous materials [9,25]. In the modern day, CO_2 adsorption is one of the most operative methods to characterize the micropores [26,27]. Low-pressure gas adsorption has been widely used to characterize the pore structure of shale [16,18,19]. Prior the adsorption analysis, approximately 1−2 g dried samples (Groups A, B and C) were taken and degassed. Then the low-pressure N_2 and CO_2 adsorption experiments were carried out on an ASAP-2020 (Micromeritics Instruments). Supposedly the degassing treatment should not destroy the physical and chemical structure of shale [28], hence, for safety measures, a relatively low temperature (110 °C) under a vacuum condition and with longer degassing time (24 h) were adopted. Before moving the sample tube to the analysis station, the sample should be weighed again to determine the reduction. After the N_2 adsorption analysis, a second degassing (4 h) in situ was requested before CO_2 adsorption analysis.

N_2 adsorption−desorption isotherms were obtained at 77.4 K with pressure (P/P_o) ranging from 0.001 to 0.998. The adsorption branching was chosen for the calculation of surface area and pore volume [2,21]. The surface area was calculated using the BET equation [29,30]:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C_{BET}} + \frac{(C_{BET} - 1)}{V_m C_{BET}}\left(\frac{P}{P_o}\right) \tag{1}$$

where P is the equilibrium pressure, P_o is the saturated vapor pressure, V is the adsorbed volume, V_m is the monolayer volume, and C_{BET} is the BET constant whose value is positive. The BET surface area (S_{BET}) was calculated using the following equation [31]:

$$S_{BET} = \frac{0.001 \times V_m \times N \times A_{N_2}}{22.4} \tag{2}$$

where V_m is the monolayer volume, N is the Avogadro' number, and A_{N_2} is the atomic surface area of N_2 at 77.4 K (0.162 nm^2). The BJH model was used to characterize pore volume distribution with an effective range of 2−100 nm.

N_2 molecules are not completely entering the narrow micropores at low temperature (77.4 K) due to lack of sufficient energy [18,32]. Therefore, N_2 was replaced by CO_2 as an adsorbent for the micropores' analysis. CO_2 molecules with a cross-sectional area of 0.17 nm^2 have higher energy in ice water bath (273.1 K). The micropores' surface and pore