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Original research paper

Experimental study of the impact on methane adsorption capacity of continental shales with thermal evolution☆

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Abstract

In order to reveal the methane adsorption capacity influenced by the geological factors in the process of thermal evolution, a shale sample from Chang-7 Member of the Yanchang Formation in the southeastern part of the Ordos Basin was collected. Seven different samples were acquired to simulate burial depths through the thermal simulation experiment. The organic geochemical parameters, mineral composition, pore structure, and methane adsorption capacities were measured. According to this research, influence factors on methane adsorption capacity considering thermal evolution can be divided into three kinds: Physical factors such as specific surface area and pore diameter, organic geochemical factors such as *TOC* and thermal maturity, as well as mineral composition factors such as clay minerals and andreattite. Geological factors have intricate impacts on the methane adsorption capacity. Considering each factor was combined together, it may increase the significance of the adsorption amount and influence factors. Micro-pore is the most important factor, it has a positive correlation with the methane adsorption capacity. The adsorption quantity increases when *TOC* decreases due to the thermal evolution of organic produced micro-pores which increases the adsorption space. In addition, the adsorption capacity of shale has a negative correlation to the burial depth. The deeper it's buried the faster the adsorption capacity decreases.

Keywords: Thermal evolution; Methane adsorption; Influence factors; Continental shale; Ordos Basin

1. Introduction

Shale gas mainly exists in black shale through free and absorbed gases. Several studies show that absorbed gas is the main occurring state [1−3], accounting for more than 50% of shale gas content. Thus, it is critical to study the geological factors influencing the methane adsorption capacity in shale. To date, numerous scholars have conducted studies on the controlling factors of methane adsorption and have made significant accomplishments. Summarized factors that influence the methane adsorption capacity are the content of total organic carbon (*TOC*), the organic matter type, maturity, the mineral composition of shale, the pore size distribution, and the water content [4−15]. Chalmers et al. [16] found the *TOC* content has a positive relationship with adsorbed gas which makes it the primary factor controlling the methane adsorption in the lower Cretaceous shale, British Columbia, Canada. Zhang et al. [17] proved that the better the organic matter type

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is, the stronger adsorption capacity is; the difference in maturity has no obvious effect on methane adsorption capacity. Ross et al. [18] discovered that the methane adsorption capacity increases with the increase of the *TOC* content as well as micropore in the Mississippi shale, Western Canada sedimentary basin. Ji et al. [19,20] used a Scanning Electronic Microscope (SEM) to observe the different pore distribution characteristics of clay-rich rock samples which are composed of clay minerals (illite, smectite, kaolinite, andreattite, etc.). Combining this with the methane adsorption experiment, it was found that the clay mineral adsorption capacity has a positive relationship with porosity and specific surface area; the adsorption capacity of various clay minerals follows the order smectite >> andreattite > kaolinite > chlorite > illite.

However, previous researches were independent and dispersed which lacked comprehensive evaluations of various controlling factors associated with geological conditions. The related researches about the effect of kerogen's thermal maturity on shale adsorption capacity are few [21,22]. Our current study simulated the processes of thermal evolution of shale by hydrous pyrolysis, and it analyzed the changes of the various parameters and their effects on the methane absorption ability by conducting organic geochemistry, petrology, and adsorption test on the artificially matured. Lastly, results were summarized and factors were classified on how they control methane adsorption capacity.

2. Samples and experiment

2.1. Samples

The samples in this research were taken from Upper Triassic Chang 7 Member Zhangjiatan shale in an open-cut mine of Hejiafang area, southwest Ordos Basin. The samples were organic-rich, it possessed a *TOC* of 28.8%. The Rock-Eval pyrolysis presented a hydrocarbon index (I_H) of 631 mg/g_{TOC}, an oxygen index (I_O) of 2 mg/g_{TOC}, and a *T*-max of 438 °C. The values of S_1 (dissolved hydrocarbon) and S_2 (pyrolysed hydrocarbons) peak were 9.32 mg/g, 201.16 mg/g, respectively. The kerogen type for the experiment samples were TypeⅠ. The vitrinite reflectance (R_O) was about 0.53%. To avoid destroying the original pore structure, the 7 samples were placed in a ⌀25 mm cylinder. As a requirement of the pyrolysis, samples were drilled from a bulk core and were labeled HJF-0 to HJF-6. Data are plotted according to the geological conditions corresponding to the different buried depths, the simulated experiment conditions (temperature, pressure, time) as shown on Table 1.

2.2. Experiment condition

The pyrolysis experiments were conducted in the Lanzhou Institute of Geology, Chinese Academy of Sciences (LIG-CAS). Utilizing a WYMN-3 HTHP simulation instrument, this can imitate the lithostatic pressure and the hydrodynamic pressure by a hydraulic control system and deionized water. The equipment would maintain isothermal heating of samples with automatic pressure compensation and eventual expulsion of hydrocarbon right after the simulation temperature has reached the temperature point set in the first 2 h. Once the constant temperature time is over, the yields of the expelled oil, water, and gaseous hydrocarbon were collected and analyzed. Organic geochemistry, petrology, and Nitrogen adsorption measurement tests were conducted to evaluate the solid residues. All seven samples were collected from the same block to ensure freshness and to guarantee the consistency. In order to make the simulation experiment closer to the actual geological process we considered the hydrodynamic pressure of the geological evolution process and then designed the automatic pressure compensating device.

3. Results and discussion

The primary factors influencing the methane adsorption capacity are *TOC*, the organic matter type, maturity, mineral composition, and pore size distribution, all of which changed with the evolution of thermal maturity. In order to study concrete changes of the various geological factors as well as the effects on the methane adsorption capacity, the organic carbon content, the vitrinite reflectance (R_O), the whole rock analysis, clay minerals analysis with X-Ray diffraction (XRD), Scanning Electron Microscope (SEM), and nitrogen adsorption measurements were conducted on the original and thermal simulation samples after all the samples completed the experimental process of washing oil-out.

3.1. Organic geochemical and petrological experiment

The experimental results of *TOC* and maturity are shown in Table 2. The total organic content as a whole decreased with the increase of thermal maturity. The Ro value of HJF-0, whose original *R*o value was 0.53%, increased with the increase of temperature, pressure, and constant temperature. This caused the Ro value to reach its peak of 1.07%, which is consistent to the maturity stage of the organic matter evolution together with the decrease of the aliphatic chain structure of kerogen and the increase of aromatic structure. The increase of modeling temperature and thermal evolution degree caused the content of brittle mineral (quartz, feldspar and pyrite etc.) to change slightly (Fig. 1). The insignificant difference presented maybe caused by inhomogeneity of the original samples. The clay mineral compositions were mainly illite smectite mixed-layer and illite.

3.2. Distributions of pore size and specific surface area experiment

Nitrogen adsorption measurements were used to analyze the pore size and specific surface area. The measurements were carried out by an ASAP 2020 for the surface area, as well as a meso- and micro-pores analyzer. The working principle of the instrument was the isothermal physical adsorption static volumetric method. Prior to hydrous pyrolysis, shale samples were crushed and sieved to 40–60 mesh. The isothermal