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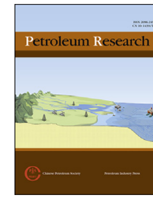

Pore evolution in hydrocarbon-generation simulation of organic matter-rich muddy shale

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For exploration and potential evaluation of deep shale reservoirs with high maturity, hydrocarbon generation and pore evolution of muddy shale in deep high evolution stage were investigated by the high-temperature high-pressure simulation experiment. Results indicated that under high pressure condition, nano-scale micropores in organic matter-rich muddy shale constantly increased as rise of temperature and pressure, leading to increase of shale porosity. However, in the high mature-overmature stage, shale porosity decreased with further increase of temperature and pressure. In contrast to micropores, micro-scale capillary pores and megapores in shale constantly decreased as rise of simulation temperature or pressure, indicating that deep-burial reservoirs was not favorable for free-gas storage; but significant increase of micropores and surface area during this stage could make up for a loss of adsorbed natural gas in shale due to decrease of adsorption capacity which was induced by increase of temperature and pressure, thus leading to high shale gas potential in deep layers. A large number of secondary micropores were developed in the simulated samples such as pyrite and dolomite, demonstrating that shale clasts and mineral matrix could also form abundant secondary micropores during the deep evolution stage; during the evolution process, shale as hydrocarbon source rock could generate a large amount of acidic fluid which was favorable for development of secondary porosity.

1. Introduction

Currently, thick and extensive Paleozoic deep marine high-evolution shale is the most potential target formation for shale gas exploration in China. Due to multi-period tectonic activities and deep-burial diagenesis evolution, not only organic matter in shale underwent in-depth degradation but also shale pores experienced complex transformation and destruction (Lin et al., 2014; Zhang et al., 2014), therefore correct assessment on the natural gas generating capability and pore characteristics of high-mature shale was an important part of shale gas potential evaluation. For demand of exploring Paleozoic deep high-mature shale with wide distribution over China, high-temperature and high-pressure simulation experiment was carried out to investigate gas-generating capability and pore evolution law of high-mature shale in an attempt to provide a basis for reservoir exploration and evaluation of deep high-mature gas-bearing shale in China.

The natural gas in shale reservoir primarily occurred in free or adsorbed state. The free gas was preserved in shale fractures and interparticle macropores, while the adsorbed gas was stored in surfaces of kerogen and clay micropore (Curtis, 2002; Ross and Bustin, 2007; Pu et al., 2010). Generally, the natural gas occurred in adsorbed state accounted for more than 50% of the total gas content (Lu et al., 1995), largely controlling enrichment and accumulation of natural gas in shale; while the adsorbed gas content depended on development degree of micropores in shale (Chalmers et al., 2009). The free gas was the main component of shale gas (Li and Zhu, 2013), especially when shale buried depth was over 4000 m, content of adsorbed natural gas decreased gradually with increase of temperature and pressure, then the adsorbed natural gas transformed into free gas and eventually became the main component of shale gas (Wang et al., 2013). Hence, when a large amount of adsorbed gas transforms into free gas, whether there was enough storage spaces in deep shale, i.e., whether there was enough macropores, capillary pores and

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microfractures in deep high-mature shale to storage excessive free gas, would directly influence gas-bearing potential of shale. During the high evolution stage, a large amount of pyrolysis gas was formed, and it further enhanced demand for macropores; free gas would be substantially lost in a case of no enough storage space, and then total shale gas content would not increase or might decrease.

Kerogen and clay mineral were normally regarded as the main factors controlling shale pore characteristics. Variation of pore characteristics in kerogen with formation and expulsion of hydrocarbons during shale thermal evolution, porosity evolution due to conversion of clay mineral type during clay mineral diagenesis and its influence on shale reservoir, had been systematically studied (Jarvie et al., 2007; Ross and Bustin, 2008; Cander, 2012; Ji et al., 2012). Generally, total organic carbon (TOC), kerogen type, clay mineral and thermal maturity (R_o) were main factors to control shale pore structure, especially influence of R_o was the most significant; when shale was in the over-mature stage, both specific surface area and pore volume decreased dramatically with increase of R_o, that was not favorable for natural gas accumulation (Liang et al., 2014).

Although researches on shale in different evolution stages could be used to invert natural evolution process of micropore, it was very difficult to obtain research samples with relative consistent mineral composition and TOC as well as representative of different continuous evolution stages from field sections and borehole; besides, as influence factors of shale were extremely complex during the long diagenetic evolution period, it was very difficult to exclude factors other than temperature and pressure which might influence pore change. Therefore, the simulation experiment was a good option for pore evolution researches. To quantitatively describe shale pore evolution characteristics during the deep burial process, a high-temperature high-pressure simulation experiment of organic matter-rich muddy shale was carried out to observe evolution laws of shale pore structure, pore size and porosity in hydrocarbon generation and expulsion process in details, so as to provide a basis to investigate occurrence status and potential evaluation of natural gas in deep high-evolution shale.

2. Sample and experiment

Although the temperature-pressure matching simulation condition was more suitable for actual strata burial process, in order to investigate effects of temperature and pressure controlling shale hydrocarbon generation-expulsion and pore evolution in deep strata condition, the representative organic matter-rich mudstone samples were selected for isobaric and isothermal high-temperature high-pressure hydrocarbon generation and expulsion simulation experiments separately; moreover, a semi-open system that was consistent with overpressure episodic hydrocarbon expulsion commonly in source rock burial process was adopted.

2.1. Sample

Two experimental samples were collected from Tarim Basin in China, one was carbonaceous mudstone of Jurassic Yangxia Formation (J_1y) at Kuqa depression, while the other was black shale of Ordovician Saergan Formation (O_2s) at the Dawangou outcrop in Keping. The sampe from Jurassic Yangxia Formation had TOC more than 10%, and contained abundant silt matter and plant debris which deposited in a lacustrine swampy environment; the sample from Ordovician Saergan Formation had TOC of 3.08%, and contained abundant imprint fossils of graptolite with pyrite which deposited in a typical still-water bay or relative deep slope. The Yangxia Formation mudstone had a low maturity ($R_o = 0.78\%$), but it evolved into the stage of massive liquid hydrocarbon generation (Table 1); the sample was selected for high-pressure simulation experiment to reveal diagenesis and hydrocarbon generation evolution characteristics of shallow-buried terrestrial organic matter-rich source rocks dominated by Type-III kerogen evolving into the sustained rapid deep burial stage. The Saergan Formation shale had a high maturity ($R_o = 1.6\%$) and entered into the gas generation peak period; the sample was chosen for the temperature-pressure simulation experiment to reflect evolution characteristics of deep-buried mature marine source rocks dominated by Type-I kerogen in the high mature-overmature stage to some extent.

2.2. Experimental condition

The simulation experiments were done on a WYMN-3 high-temperature high-pressure simulator developed by Sinopec Wuxi Research Institute of Petroleum Geology. The simulator-specific sample chamber was an open-ended stainless steel cylinder which was capable of withstanding high pressure, it was just fully filled with multiple stacked column samples, and left a certain clearance so that both ends of the chamber could be filled with circular metal strainers. Fresh lamellar shale samples from outcrops were drilled with a core drill in a direction perpendicular to bed plane to obtain a cylinder of 25 mm in diameter and 5–40 mm in length, and both ends of the cylinder were grinded flatly by fine-grained carborundum for later use.

Under high-pressure conditions, hydrocarbon-generation peak of simulated organic matter lagged behind obviously, and normally occurred at about 450 °C. To reveal as much as possible hydrocarbon-generation process and pore variation of deep-buried muddy shale in a high-pressure environment, isobaric and isothermal series of simulation experiments in semi-open systems were carried out at a fluid pressure of 90 MPa (equivalent to depth of 9000 m) and hydrocarbon-generation peak temperature of 450 °C respectively, and temperature and pressure conditions at each experimental point were shown in Table 2.

2.3. Experimental process

The sample chamber was put into the fixed chamber, and both ends were sealed with copper washers, then it was installed in the heating zone. Various pipelines were turned on for trial run till requirement was met, then the pressurization and heating began. The pressures in the sample chamber included lithostatic pressure and fluid pressure, of which the lithostatic pressure was controlled by the mechanical compression system applied to both ends of the sample chamber, and the fluid pressure was provided by a pipe connected to the sample chamber by high-pressure water injection. Through a temperature-pressure control system, the sample chamber was heated and pressurized to design temperature and pressure condition, and thereafter this temperature and pressure condition was kept for 72 h. With generation of oil and gas, the system fluid pressure kept rising during the experiment process; when the fluid pressure in the chamber exceeded 5 MPa over preset value, the sampling valve was opened automatically to collect effluent gaseous and liquid products; when the pressure was relieved to the preset value, the sampling valve was closed automatically, and the experiment would be continued; when the pressure rose again, and exceeded 5 MPa over the preset value, the sampling valve was opened again, hydrocarbon was expulsed again; this process could repeated for many times. After the simulation, the sampling valve was opened to collect the last effluent gaseous and liquid products. When the heating zone was cooled down completely, the sample chamber was opened to take

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