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Petrophysical characterization of shale reservoir based on nuclear magnetic resonance (NMR) experiment: A case study of Lower Cambrian Qiongzhusi Formation in eastern Yunnan Province, South China

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ABSTRACT

In order to characterize the petrophysical properties of shale using NMR technique, eight shale samples from the Lower Cambrian Qiongzhusi Formation in the eastern Yunnan province were measured by porosity and permeability tests, field emission scanning electron microscopy (FE-SEM) and NMR experiment. Pore types were obtained from the shape and distribution of transverse relaxation time (T_2) spectrum. Residual porosity and movable porosity could be well estimated based on T_2 spectrum area fraction. On the basis of Coates model, we proposed a regional Coates model to calculate the NMR permeability of shale. A method for determining $T_{2cutoff}$ of shale samples was also expounded. Moreover, the specific surface area distributions and pore size distributions could be obtained based on the mathematical equation of T_2. Results show that T_2 spectrums of shale samples at water-saturated condition can be divided into unimodal and bimodal T_2 spectrums. Continuous bimodal T_2 spectrums reflect the samples with good connectivity between small pores and large pores, whereas discontinuous bimodal T_2 spectrums reflect that the connectivity between small pores and large pores is poor. Shale samples with higher bound water content have a greater $T_{2cutoff}$. The NMR permeability is close to gas log permeability, which proves the applicability of regional Coates model. In eight shale samples, transition pores account for the largest proportion, followed by mesopores, indicating that transition pores and mesopores are the major sites for the accumulation of shale gas.

1. Introduction

The large-scale commercial development of shale gas in North America has changed significantly the pattern of world oil and gas supply. A growing number of countries around the world have strengthened the exploration and development of this new energy (Bowker, 2007; Clarkson et al., 2012; Tang et al., 2014; Ding et al., 2015; Li et al., 2016). Shale as a reservoir of natural gas is characterized by low porosity, low permeability and strong heterogeneity. Reservoir quality has a significant influence on the accumulation of shale gas. As an important index for evaluating reservoir quality, shale pore structure has been widely studied by lots of scholars. Previous studies have indicated that pores in shale can be divided into four types on the basis of pore size: macropores (pore diameter > 1000 nm), mesopores (1000 nm < pore diameter > 100 nm), transition pores (100 nm > pore diameter > 10 nm), micropores (10 nm > pore diameter) (Zhong, 2012; Curtis, 2002; Caldwell, 2006). Shale gas existing in organic-rich shale is primarily in two states of free gas and adsorbed gas. Free gas is preserved in natural fractures and intergranular pores, and adsorbed gas is stored in the organic matter and clay particle surfaces (Curtis, 2002). There are a mass of nano-sized and micron-

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sized pores in shale reservoir which has complicated pore structure, and some qualitative and quantitative techniques have been used to characterize shale pores. For example, nano-CT imaging and field emission scanning electron microscopy (FE-SEM) have been utilized qualitatively to characterize the structure and morphology of shale pores (Heath et al., 2011; Curtis et al., 2012; Tiwari et al., 2013). Low-pressure nitrogen adsorption, small-angle neutron scattering, high-pressure mercury intrusion and nuclear magnetic resonance have proven to be effective methods to obtain the quantitative parameters such as surface area, pore volume and pore-size distribution (Ross and Bustin, 2007, 2009; Chalmers and Bustin, 2007; Clarkson et al., 2013; Li et al., 2016). However, some of these methods have certain limitations. For example, N_2 adsorption can not finely characterize parts of macropores and microfractures within shale. High-pressure mercury intrusion experiment is generally used to analyze mesopores and macropores. Besides, mercury intrusion may result in the damage of shale pore structure, thus affecting the reliability of measurement result. FE-SEM can only be used to observe the local pore characteristics of shale samples, but it cannot reflect the spatial distribution of pores and microfractures. Moreover, the primary structure of shale samples would be destroyed and a lot of pores and microfractures are produced artificially in the polishing process of rock section, which leads to great errors for the results. However, NMR has advantages in studying shale reservoirs with the characteristics of rapidity, undamage and accuracy. At present, a lot of scholars have extensively applied NMR technique to the evaluation of carbonate and sandstone reservoirs, but NMR experiments have not been used fully in the study of shale reservoirs (Yao et al., 2010a; Yu, 2013; Xu et al., 2015; Tan et al., 2015).

When samples containing fluid are in a uniform static magnetic field, the hydrogen protons in fluid are polarized to generate a magnetic vector. At this time, hydrogen protons are stimulated by frequency pulse to produce nuclear magnetic resonance phenomenon. After removing frequency pulse, we can obtain a signal whose amplitude attenuates with time. Two parameters can be used to measure the attenuation rate of nuclear magnetic signal: longitudinal relaxation time (T_1) and transverse relaxation time (T_2). Generally, transverse relaxation time spectrum is utilized to study sample characteristics because the measurement of transverse relaxation time is fast.

The major goals of this paper are to investigate the reservoir characteristics of the Lower Cambrian Qiongzhusi shale from the eastern Yunnan Province using NMR experiment. NMR T_2 response characteristics, pore types, porosity, permeability and pore structure parameters were analyzed based on NMR transverse relaxation time distributions. Then we compared the difference between NMR permeability and routine permeability. Meanwhile, we calculated the NMR T_2 cutoff value ($T_{2cutoff}$) according to the T_2 spectrums before and after centrifugation. The results could be helpful for the application of NMR technique in the study of shale reservoirs and provide a new way to characterize quantitatively the complicated pore structure of unconventional oil and gas reservoirs.

2. Materials and methods

2.1. Samples

Eight shale core samples from the Lower Cambrian Qiongzhusi Formation were collected in eastern Yunnan Province, located in the southwestern margin of the Yangtze plate (Fig. 1). The TOC content of shale samples ranges from 1.42% to 2.51% with an average of 2.09%. All shale samples are over-mature with the vitrinite reflectance R_o ranging from 2.16% to 3.32%. Mineralogically, quartz and clay minerals are the dominant minerals in shale samples. Quartz content is between 31.3% and 42.7%, with an average of 34.41%. Clay minerals content is in the range of 25.3%–36.4%, with a mean value of 31.44%. Lithologically, shale samples are dominated by silty shale based on the ternary diagram of mineral compositions (Fig. 2a). Moreover, the Lower Cambrian Qiongzhusi Formation was deposited in shallow-marine shelf, and quartz originated from terrigenous clast rather than siliceous organism. Therefore, TOC content has no apparent relationship with quartz content. Clay minerals mainly contain illite (average of 49.13%), illite/smectite mixed layer (average of 23%), chlorite (average of 20.5%) and a small amount of kaolinite (average of 7.38%). The parameters of eight samples are shown in Table 1. Several horizontal cylindrical core plugs with a diameter of 2.5 cm were prepared parallel to the bedding planes for each sample.

2.2. Porosity and permeability measurements

The porosity and permeability of shale samples were analyzed by SGS Unconventional Petroleum Technical Testing Co., Ltd. following the Chinese Oil and Gas Industry Standard SY/T5336-2006 “Method of core routine analysis”. A KXD-II porometer was used to measure the porosity of samples with a helium expansion method, and permeability measurements were carried out using dry nitrogen as the medium with an instrument of permeameter (QT-2). Porosity and permeability experiments utilized a pressure of 96.8 kPa and a temperature of 25 °C.

2.3. NMR core analyses

After porosity and permeability measurements, all eight samples were dried in the drying oven for 24 h and were vacuumed till the weight of samples no longer changed. Subsequently, samples were saturated in the 8% KCl solution and weighed at regular intervals. Shale samples were fully saturated when their weight was no longer increased. NMR analyses were performed by SGS Unconventional Petroleum Technical Testing Co., Ltd. using a RecCore-2500 instrument with a resonance frequency of 2.38 MHz and a magnetic field strength of 1200 G, and we obtained the T_2 spectrums of eight samples at water-saturated condition. The samples were centrifuged at a centrifuge pressure of 300Psi to reach a perfect irreducible water state, and then NMR experiments were conducted again to obtain the T_2 spectrums of all samples at irreducible water condition. The measurement parameters used in NMR experiments were as follows: echo spacing, 0.2 ms; waiting time, 6s; numbers of scans, 64; echo numbers, 1024; experiment temperature, 25 °C and humidity, 55%.

2.4. FE-SEM observation

The FE-SEM imaging of shale samples was performed using the Quanta 200F field emission scanning electron microscopy at the China University of Petroleum (Beijing). Before FE-SEM observation, one surface of each sample was polished using an argon-ion cross-section polisher “TechnoorgSC-100”. After polishing, the polishing surface was coated with gold film at a thickness of 10 nm to enhance the conductivity. Back-scattering electron model was chosen to observe the micromorphology of shale sample at various magnification scales.

3. Results

3.1. Porosity and permeability of shale

The porosity and permeability of eight shale samples are