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Experimental Research on the Shale Oil Reservoirs by Nuclear Magnetic Resonance (NMR) Technique

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Nanometer-scale pores exist in the shale, causing that shale has complex reservoir spaces, which results in a poor connectivity among various pores. In addition, because of the complex mineralogical compositions, there is a variety of fluid occurrence state in the pores of the shale, causing that it is difficult to do experimental research for shale. Nuclear magnetic resonance (NMR) is considered to be an important means for reservoir characterization, which has an advantage in characterizing the pore-structure, pore-size, etc [1]. Thus, the research of NMR experiment, as well as the investigation of the application of conventional NMR measurement method for shale has an important significance.

In this research, five shale samples were collected from exploration wells in the Upper Member 4 and the middle, lower part of Member 3 of Shahejie Formation, which are the main source rocks in the Dongying Depression of Bohaiwan Basin. The T_2 spectra of original samples were first measured with the low-field NMR method according to the Chinese petroleum industry standard specification for a normalization measurement of the core NMR parameters in the laboratory [2]. During the test process, the NMR spectrometer mainly detects the NMR signals of the hydrogen nucleus (^{1}H) from the water in the shale pores, and this produces the T_2 spectrum. After the T_2 spectra of the original samples were performed, the shale samples were placed into a vacuum chamber to soak in 100% distilled water for approximately 24 h to achieve water saturation. After removing the surface moisture, the shale samples were placed into the sample cell of the NMR to obtain the low-field NMR T_2 spectra of the water-saturated shale samples.

A MiniMR60 spectrometer was used with a fixed magnetic field of 0.53T and a frequency field of 23MHz for hydrogens. The temperature of the magnet and probe assembly was held constant at 32℃ and the room temperature was held constant at 24℃. The main NMR measurement parameter sets include the echo time (T_E) of 0.2 ms, the waiting time (T_W) of 3000 ms, the echo numbers of 5000 and the scanning numbers of 128. In addition, X-ray Diffraction (XRD), scanning electron microscope (SEM) and nitrogen adsorption experiments were employed to reveal mineralogical compositions (including compositions of the clay minerals), the reservoir spaces types and the pore size of the shale samples.

The results of the XRD experiment suggest that clay mineral (illite, mixed layer illite-semectic (I/S) and chlorite) contents of shale samples range from 39% to 58%, of which the swelling clay minerals (illite and mixed layer I/S) account for the main ingredients with the contents ranging from 38.13% to 53.36%. According to SEM photographs, the reservoir spaces types of the shale samples are mainly micro-cracks. The average width of the micro-cracks is approximately 37 nm with a range of 10 nm to 111 nm. The nitrogen adsorption experiment results demonstrate that the maximum pore size of the shale samples approximately ranges from 109 nm to 144.5 nm with an average of 36nm to 56 nm, which is consistent with that from SEM. The T_2 spectra of the original shale samples are showed in the Fig.1-a, which indicate that the T_2 spectra of the original shale samples all show as a single peak with the effective relaxation time ranging 0.04 ms to 2ms. However, after soaked in 100% distilled water for approximately 24 h, the state of the shale samples changed significantly, which resulted in the T_2 spectra changing to multi peaks (Fig.1-b). According to the distribution and magnitude of the T_2 spectra, it could be divided into two categories, which are the narrow distribution, less magnitude (type Ⅰ) and the wide distribution, more magnitude (type Ⅱ). It is consistent with the T_2 spectra, the state of the shale samples also can be divided into two

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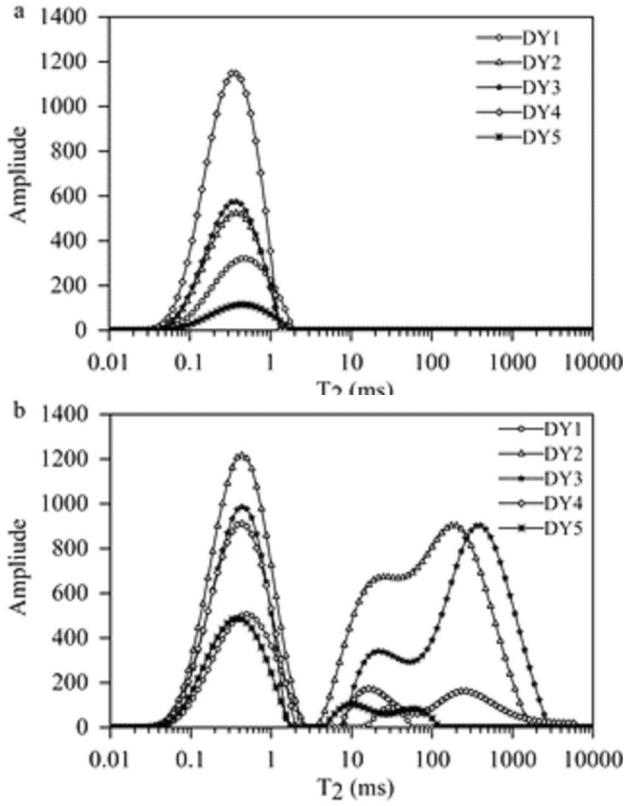

Fig. 1 The T_2 spectra of the shale samples

(a) the T_2 spectra of the original shale samples; (b) the T_2 spectra of the water-saturated shale samples

categories, one is kept well, and the other is badly broken. The T_2 spectra of type Ⅰ (DY1 and DY 5) show discontinuous bimodal or three peaks, the magnitude of the left peak is significantly more than that of the right peak, and the distribution of the left peak is similar to the T_2 spectrum of the original samples, but the magnitude of the peak is increased. The effective relaxation time of the right peak is approximately 5 ms-100 ms with narrow distribution and less magnitude. Compared with the T_2 spectra of type I, it can be observed that, the T_2 spectra of the type Ⅱ (DY2, DY3 and DY4) show as three peaks and the right bimodal peaks are continuous distribution, which is discontinuous with the left peak. The left peak is similar to the T_2 spectra of the original samples, which is consistent with the type I, while the effective relaxation time of the right peaks is approximately 4 ms-3000 ms with wide distribution and large magnitude, and the magnitude of the right peaks is significantly larger than that of the type I.

After soaked in 100% distilled water for approximately 24 h, severe hydration occurred, resulting in a serious breakage of shale samples. When shale samples were placed in 100% distilled water, the swelling clay minerals (illite and mixed layer I/S) would soak distilled water and hydrate, which caused that a large number of micro-cracks generated in the shale samples, leading to the changes in microscopic pore-structure even macroscopic breakage [3]. The T_2 spectra of the shale samples are consistent with integrity of the cores, which indicate that the shale samples show T_2 spectra of the type Ⅱ suffered serious hydration, and formed a large number of micro-cracks, resulting in the changes in microscopic pore-structure and macroscopic breakage. Compared with the shale samples show T_2 spectra of the type Ⅱ, it can be observed that the contents of the clay minerals and the swelling clay minerals of shale samples show T_2 spectra of the type Ⅰ are much less than that of the type Ⅱ. The contents of the clay minerals and the swelling clay minerals of the two shale samples (type Ⅰ) are 41% and 39%, 38.13% and 36.66% respectively, while the shale samples (type Ⅱ) are all more than 50%. According to the results of the nitrogen adsorption and the SEM experiments, the Nanometer-scale pores are the main pores in the shale samples, which suggests that the difference of the T_2 spectra of the shale samples soaked in 100% distilled water for approximately 24 h, is caused by hydration. It follows that the T_2 spectra of the water-saturated shale samples may be produced by the relaxation signals of water both in the original pores (cracks) and pores (cracks) generated by hydration. Therefore, compared with the conventional sand reservoirs and the tight sand reservoirs, the original pore-structure and pore-size cannot be correctly reflected by the T_2 spectra of the water-saturated shale samples due to the hydration. As the conventional NMR measurement method is not suitable for shale, a new NMR measurement method applied to shale should be established, aiming at providing technical support for the accurate measurement of shale.

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