1 Introduction

There is a set of organic rich shale at E 2S4 2 sub-member in damintun sag. The organic material is typically type I. In recent years, breakthrough was obtained in shale oil exploration. The wettability of organic and inorganic pore is different. As a result, the mobility of oil in organic and inorganic pore is different. So it’s necessary to distinguish the organic and inorganic pore. While the ratio of organic and inorganic pore in oil-bearing shale is still not clear.

In this study, pore size distribution of shale samples before and after extraction is measured by N2 sorption experiment. At the same time, the kerogen is collected and pore size distribution of kerogen is measured. By comparison, the proportion of organic and inorganic pore and the oil-bearing pore size distribution are obtained.

2 Samples and Experiments

The sample A and B from Well Shen352 at E2S4 formation are selected, the depth is 3189.82m and 3317.29m respectively.

Shale samples are crushed into 80~100 mesh. Firstly, the total organic carbon content, the pyrolyzation, X-ray diffraction and pore size distribution of the crushed sample are measured. Secondly, the crushed sample is extracted by chloroform, and then the pore size distribution of the extracted samples are measured by N2 sorption experiment. Thirdly, the kerogen is collected from the crushed sample, and then the pore size distribution of kerogen is measured.

Total organic carbon content is measured by LECO CS230 Carbon/ Sulfur analytical instrument (according to GB/T 19145-2003). The pyrolyzation experiment is conducted by Rock-Eval 6 pyrolyzer (according to GB/T 18602-2012). X-ray diffraction experiment is conducted by Panalytical X’pert MPD Pro analytical instrument (according to SY/T 6210-1996). Pore size distribution is measured by ASAP2020 automatic gas adsorption instrument (according to GB/T 21650.2-2008).

3 Results

3.1 Geochemical experiment results

According to the geochemical experiment results, the TOC of sample A and sample B are very high. The S1 of sample A is obviously higher than that of sample B, the difference of S1 indicates that the oil content of E 2S4 2 I member is more than that of E 2S4 2 III member to a certain extent. Besides, the clay content of these two samples are almost equal.

3.2 N2 sorption experiment results

The pore structure characteristics can be distinguished from the types of N2 sorption (including adsorption and desorption) curves (Cao Taotao etc., 2015). The N2 sorption curves for sample A and B are almost reversed “S” shape, and it is approximately type IV sorption curve (Fig. 1). At the front end, the adsorption curves rise slowly until the relative pressure is close to 1.0, then the curves increase dramatically. The adsorption is not saturated at the relative pressure of 1.0, which indicates that the capillary condensation happened during the sorption process, and it can be inferred that there are mesopores and macropores in oil-bearing shale and kerogen. At high relative pressure, the adsorption and desorption curves are not overlapped, forming the hysteresis loop. The hysteresis loop of sample A and sample B are typically type H3 according to IUPAC, which indicates that there are many “slit” pores. When the relative pressure is close
to 1, the maximum adsorption amount of kerogen is much more than that of shale sample. For sample A, which is oil rich shale, the maximum adsorption amount of extracted sample is much more than that of original sample. For sample B, which is oil bare shale, the maximum adsorption amount of extracted sample is almost the same as that of original sample.

4 Discussion and Conclusion

4.1 The specific surface area and pore size distribution of shale

Both specific surface area and pore volume are relevant with the amount of pores. The more the small diameter pore are, the larger the specific surface area there is. The trends of BET specific surface area and the BJH desorption pore volume are almost the same according to the histogram (Fig. 2).

According to pyrolysis experiment results, the free hydrocarbon is 6.57mg/g, much more than that of sample B, which is just 1.31mg/g. The free hydrocarbon will occupy some pore space. Extraction process by chloroform will eliminate the free hydrocarbon from shale, while some of the chloroform may left in the pores, especially in the organic pores, it will also occupy some pore space. As a result, if there is enough free hydrocarbon in shale, such as sample A, the specific surface area and pore volume will increase after extraction (Fig. 2), since the amount of free hydrocarbon eliminated is more than that of organic solvent left during extraction process. If there is not so much free hydrocarbon, such as sample B,
the specific surface area and pore volume may decrease after extraction, since the amount of organic solvent left is more than that of free hydrocarbon eliminated during extraction process. However, the pore structure may be destroyed to some extent during the extraction process, while the mechanism and extent of the destruction are not so clear, it needs further study.

Both specific surface area and pore volume of keroger are bigger than that of original shale sample. Both specific surface area and pore volume of kerogen A is slightly bigger than that of kerogen B, which indicates that the amount of organic pore in E2S4 2 I member is more than that in E2S4 2 III member. Compare to kerogen of Dalong member in Sichuan basin, organic pores of sample A and sample B are much less. The reason lies in that the organic material of Dalong member in Sichuan basin is type II, while the type of sample A and B is type I, and the maturity of sample A and B is lower. The proportion of organic pore in shale is estimated using TOC content (Fig. 2 c). The organic pore proportion of sample A and B is 26.81% and 14.81% respectively, which is smaller than that of sample from Dalong member.

4.2 Pore size distribution of oil-bearing pore

According to the pore size distribution of samples that before and after extraction (Fig. 3), the pore diameter is mainly from 3 to 100 nm. At about 4nm, there is a narrow peak, which is formed because of the vanish of the hysteresis loop on desorption curve at low relative pressure. The appearance of the narrow peak dose not resort to the nature of the adsorbent. Ignore the “false peak”, the pore diameter of the main peak is from 4 to 6nm for both original sample sand extracted sample. The oil content of sample A is high, the pore volume with the diameter from 3 to 30 nm increased after extraction, which indicates that shale oil exist in the pores with the diameter from 3 to 30 nm. The oil content of sample B is low, in addition, the organic solvent may left in the pores after extraction, so the pore volume decrease after extraction, especially for the pore with the diameter from 5 to 11nm.

Acknowledgments

This study was funded by National Natural Science Foundation of China (41330313), National Natural Science Foundation of China (41172134), “the Fundamental Research Funds for the Central Universities” (13CX05013A), “the Fundamental Research Funds for the Central Universities” (15CX06013A), Postgraduate Innovation Project (YCX2015002) and Innovation Fund of CNPC(2011D-5006-0101).

References

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