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Pores Characteristics of Different Types of Shale in China

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1 Introduction

As the rapid development of the exploration of unconventional oil and gas resources, shale gas resources in China have been becoming the focus of unconventional oil and gas resources research with the characteristics of high resource potential and favorable geological setting. The exploration on the Paleozoic shale gas in southern Sichuan Basin and the Triassic shale gas in northern Sichuan Basin has already achieved important breakthrough and development, and had some initial understanding of evaluation on Ordos Basin and Songliao Basin (Zhou et al., 2011). Shale is characterized by low porosity and permeability, and its pore structure has influence on the occurrence of shale gas and also greatly affects the interaction between pores and gas molecules. A thorough understanding of the pore structure of shale, is the foundation for the reservoir physical properties, spatial structure, seepage characteristics of shale reservoir and the recoverability of shale gas, and also the important basis for reservoir effectiveness evaluation (Chalmers et al., 2012; Loucks et al., 2009; Nelson et al., 2009).

According to depositional environment, the shale with exploration potential in China can be divided into three types: marine shale, transitional shale and lacustrine shale. Marine shale with lower organic carbon content and higher thermal maturity is mainly distributed in the southern Yangtze Platform, North China Platform and Tarim area; transitional shale has moderate organic carbon content and thermal maturity, mostly exists in coal-bearing rock formations, such as the Carboniferous—Permian black-dark gray carbonaceous shale in Ordos Basin; lacustrine shale of Paleogene are widespread in Bohai Bay Basin, which is characterized by higher organic carbon content and lower thermal maturity (Zhou et al., 2010). We conducted the comparative analysis of the pores characteristics and controlling factors of these three types of shale, using the approaches of high pressure Hg injection and cryogenic adsorption, to evaluate the shale reservoir capacity and reveal the storage mechanism of shale gas.

2 Sampling and Methods

2.1 Samples

In this study, 30 core samples of three clastic types of shale were collected: 14 marine shale samples from the Silurian Longmaxi Formation in southern Sichuan Basin and 5 marine shale samples from Cambrian and the Lower Ordovician in Tarim Basin, with the organic matter content (TOC) between 0.102% to 4.73%, the maturity is about 1.8; 2 transitional shale samples from the Permian Shanxi formation in Ordos Basin and 4 transitional shale samples from Permian and Carboniferous in Tarim Basin, with the organic matter content (TOC) between 0.392% to 5.83%, the maturity between 1.59 to 1.72; 3 lacustrine shale samples from the Sahejie Formation in Bohai Bay Basin and 2 lacustrine shale samples from Jurassic in Tarim Basin, with the organic matter content (TOC) between 0.506% to 4.47%, the maturity between 0.53 to 0.8. The samples were tested and analysed at the Research Institute of Petroleum Exploration and Development, CNPC and the Beijing Centre for Physical & Chemical Analysis, Beijing, China separately.

2.2 Experimental methods

Unconventional reservoir primarily developed the nanoscale porosity-throat system while the mm scale to um scale pores were developed locally. Shale has complicated structure, wide-range pore diameter, and developed abundant nanoscale pores. No standardization of shale classification on pore types has been achieved to date (Zhou et al., 2010 and Yang et al., 2013). According to IUPAC classification, pores can be divided into three types based on pore diameter: micropores (<2nm),

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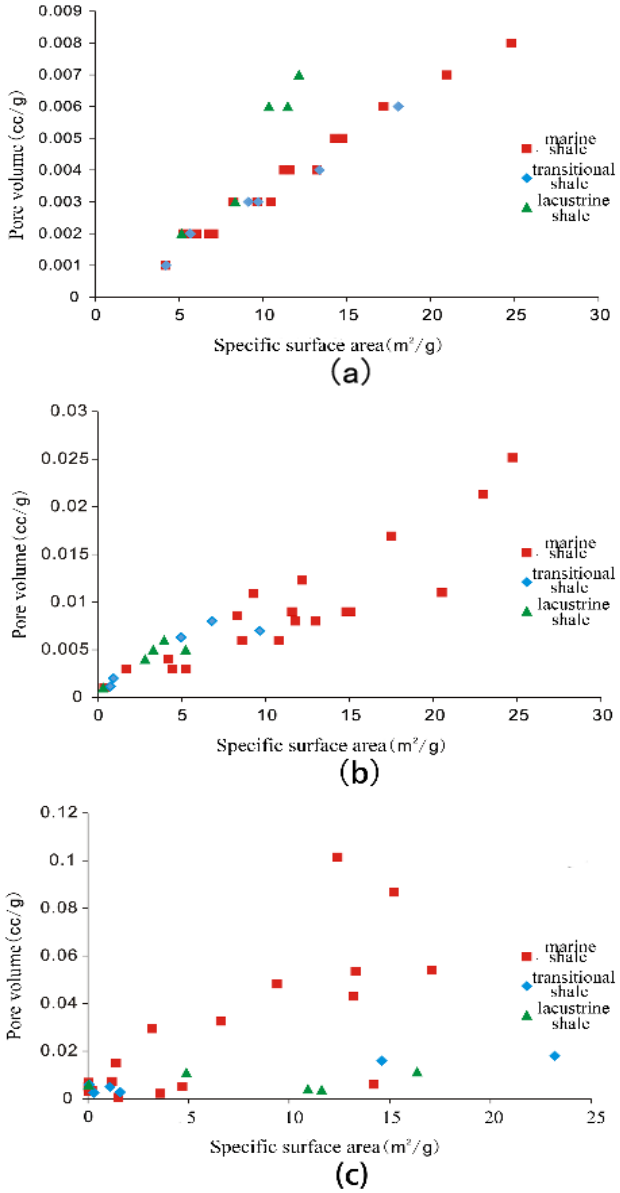

Fig. 1. The correlation of the specific surface area and the pore volume of the three types of shale.
(a) microres; (b) mesopores; (c) macropores.

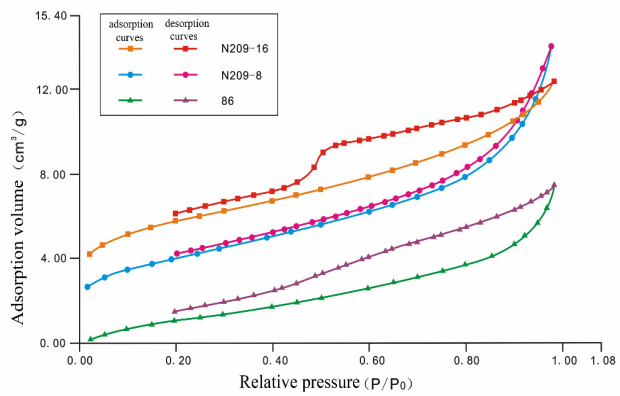

Fig. 2. N_2 absorption-desorption curves of shale samples.

mesopores (2nm-50nm) and macropores (>50nm). The pore volume, pore diameter and specific surface area of micropores and mesopores were measured by N_2 adsorption and CO_2 adsorption separately; the pores characteristics of macropores were measured by high pressure Hg injection, because it's hard for Hg to enter into pores and fractures form easily during Hg injection (Tian et al., 2012).

3 Results

3.1 Distribution characteristics of pore diameter

According to the data of average pore diameter of shale (Table.1), the BJH diagram of three types of shale have been made, using the approaches of cryogenic adsorption; high pressure Hg injection. They suggest that there exists difference in pore diameter distribution of three types of shale. Differences in formation mechanisms and regions can cause different pore diameter distribution in Tarim Basin and Sichuan Basin. The pore diameter of marine shale in Tarim Basin is about 1.2nm. Micropores were well-developed with a few mesopores and the distribution of macropores size has a change with multi-peak curve. Mesopores dominates in the marine shale in Sichuan Basin, with little micropores and the distribution curve of macropores size shows a huge peak. The peak has high attitude as well as width which indicates that microfractures were widely developed in the marine shale in Sichuan Basin. Compared with marine shale, the pores in lacustrine shale and transitional shale were poorly-developed, mainly are micropores and mesopores, rare microfractures. The micropores were better developed in lacustrine shale than transitional shale, which suggests that separate pores would merge into larger pores with the maturity increasing, and change the surface characteristics of pores, affecting its gas-storing capacity.

3.2 Pore volume and specific surface area

According to the correlation analysis of the pore volume of micropores, mesopores, macropores and the specific surface area (Fig. 1), it shows good correlation between the micropore volume and the specific surface area of three types of shale, revealing that the shale can avoid being influenced by microfractures, and its pore structure information can be better reflected. The micorpores with same pore volume in marine shale and transitional shale have similar specific surface area, larger than the micorpores with same pore volume in lacustrine shale. The correlation between the mesopores volume and the specific surface area of three types of shale with different deviation degree, indicates a certain amount of microfractures in shale. From the above is easy to see

Table 1 The average pore diameter of shale samples

Sample	Average pore diameter		
	CO_2 absorption (nm)	N_2 absorption (nm)	Hg injection (μm)
N209-2	1.484	4.13181	1.54
N209-3	1.091	3.409	0.85
N209-4	1.167	3.412	0.48
N209-5	1.136	3 .418	0.4
N209-6	1.127	3. 389	0.68
N209-8	1.13	3.426	0.77
N209-9	1.077	3.41	3.27
N209-10	1.068	3.403	1.12
N209-11	1.541	4.68674	23.74
N209-12	1.508	4.04213	4.23
N209-13	1.188	3.402	0.74
N209-14	1.467	3.86721	2.03
N209-16	1.559	3.70368	1.98
N209-17	1.283	4.07025	0.07
23	1.565	3.388	0.42
32	1.85	3.292	2.45
43	2.022	3.92	7.44
45	1.752	3.954	12.28
94	1.635	3.402	24.91
WL-01	1.665	5.07172	1.74
HS-4	1.845	6.09207	0.56
84	1.845	3.388	0.16
86	1.537	3.391	3.4
70	1.252	3.412	0.04
75	1.194	3.4	0.03
G2033-1	1.675	6.95247	0.01269
GS4-8	1.595	6.76523	0.02788
GS47-29	1.599	7.14353	0.0127
56	1.47	3.397	0.09
61	1.853	3.401	6.21

that marine shale is most heavily affected by microfractures. The Larger deviation of the correlation between the macropores volume and the specific surface area and some marine shale with small specific surface area but large pore volume, indicates a large number of microfractures in marine shale.

3.3 Pore structure types

The cryogenic N_2 absorption-desorption curves of three types of shale have the similar shape. Although little difference exists, the adsorption isotherms of various shale appear reverse S-shape with relative pressure increasing (Fig. 2). The adsorption isotherms of shale are typical IV isotherms, suggesting that the pores in shale range from molecular-level pores to whole continuous pore systems.

According to the pore structure and whether hysteretic loop can form, the pores types of shale were classified into three types. The type I is open pores, characterized by separated absorption and desorption curve with adsorption loop curve, including open tabular pores and both ends-opened cylindrical pores; the type II is one end-closed pores, characterized by overlapped absorption and desorption curve without adsorption loop curve, including one end-closed tabular pores, cylindrical pores and wedge-shaped pores; the type III is flask-shaped pores, characterized by absorption and desorption curve with hysteresis loop and an obvious flex point on the desorption curve (Yang et al., 2013).

The absorption and desorption curves of three types of shale rarely overlap. On the absorption-desorption curves of most samples, adsorption loop curves can form with the relative pressure between 0.4 and 1.0. Our studies show two shape types (Fig. 2). One type, as sample N209-16, is characterized by the overlap of absorption and desorption curves without adsorption loop curves ($0<P/P_0<0.4$), the relatively larger hysteretic loop ($0.4<P/P_0<1.0$) and an obvious flex point on the desorption curve indicating relatively larger pores (P/P_0~0.5). Above all indicates the type III of pores, that is, flask-shaped pores with well-developed micropores. Therefore, most pores in this sample belong to the type III. These pores are positive for larger shale gas adsorption but negative for shale gas desorption and diffusion. Another type, as sample 86, is characterized by the overlap of absorption and desorption curve ($0.4<P/P_0<1.0$), the relatively smaller larger hysteretic loop without an flex point ($0.4<P/P_0<1.0$) and the rapid increase of adsorption (P/P_0~1.0). Above all suggest the type I of pores: open tabular pores with good connectivity, well-developed micropores, mesopores and macropores, contributing to shale gas migration. Statistical analyses reveal that all three types of shale have complex pore systems, and both the type I and type III of pores can be found. The third type of pores dominates in marine shale while the first type of pores prevails in transitional and lacustrine shale.

4 Conclusions

(1) By the approaches of N_2 adsorption, CO_2 adsorption and high pressure Hg injection, t pore volume and the specific surface area was quantitative analysed, implying that marine shale has larger specific surface area and pore volume than transitional and lacustrine shale, and transitional shale has the same pore volume as lacustrine shale but larger specific surface area. Above all indicates the marine shale in China with large absorption gas and free gas storage space. There is positive correlation between the pore volume and the specific surface of the three types of shale. The specific surface area of the micropores and mesopores in three types of shale occupies a fairly large proportion, especially the micropores while the macropores give the greatest contribute to the pore volume, caused by nano-micro scale microfractures.

(2) According to the N_2 absorption-desorption curves, the analysis of different types of pores in three types of shale shows complex pore systems. Both the first type and the third type of pores can be found. The third type of

pores (flask-shaped pores) dominate in the marine shale, which is positive for shale gas absorption but negative for shale gas absorption and diffusion while the first type of pores (open tabular pores) prevail in transitional and lacustrine shale, with good connectivity, is conductive for shale gas migration.

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