

## Multi-scale characterization of pores in shale by nitrogen adsorption and high pressure mercury methods

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**Abstract:** High pressure mercury and nitrogen adsorption had been conducted on outcrop and core samples for studying the pore structure characteristics about shale in eastern uplift of Liaohe depression. The results showed that: The pores mainly are nano-scale and irregular in size and arrangement. The nitrogen adsorption curves about shale are type II, and the adsorption loop can be divided into 3 types: type P1 represents the pores dominated by airtight pores with one end closed; type P2 demonstrates the pores dominated by ink-bottle pores and airtight pores with one end closed; type P3 represents the pores dominated by open pores and airtight pores with one end closed. The distribution of pores has two peaks that the pores' average diameter is 4nm and 6μm respectively. The mesoporous and macroporous pore volume accounted for 85% of all, and they provide the main place for free gas. The surface area of mesopore and micropore accounted for 97.86% of all, and they enhance the adsorption capacity of shale.

### Introduction

Shale gas is produced from organic-rich shales, and is continuously accumulated in shale nanometer pores with a typical character of self-generation and self-storage<sup>[1,2]</sup>. Shales in our country have a series of features: old ages, frequent transformations by multiphase tectonic activity, high evolutionary proportion. The previous studies have studied on reservoir forming and accumulation model, shale adsorption properties and gas preserving conditions on marine shale gas in South China. Compared to marine shales, continental shales have characteristics of thin thickness, low brittle mineral content, high clay mineral content and low pressure. With the help of CO<sub>2</sub>-fracturing technology, the deliverability building of demonstration plot for continental shale gas is steadily progressing. Nevertheless, the current study for transitional facies shale is still relatively little. Because of thin thickness, rapid changes of lithofacies in transitional facies shale, the potential of shale gas is controversial. Moreover, the kerogen types of marine shale in North American and South China are mainly Type I and Type II. The research about Type III source rock whether has a large potential for shale gas or not is less. The upper Carboniferous Taiyuan formation shale in the eastern uplift of Liaohe Depression is Type III source rock. Apparently, the study has practical and theoretical significance.

Shale gas in the study area is still during the exploration phase. The previous researches were mainly about shale geochemical characteristics, gas producing capacity, gas content and tectonic evaluation<sup>[3-7]</sup>. Economically, we need to transform the unconventional reservoir to be "man-made" conventional reservoir<sup>[8-11]</sup>. Therefore, the research about the upper Carboniferous Taiyuan Formation shale has great significance on developing shale gas efficiently.

## Geological Setting

Adjacent to Liaodong fold belt and Yanshan depression, Liaohe Depression lies in the east of North China Plate. Liaohe Depression is a Cenozoic basin located in central and northern region of Bohai Basin. Liaohe Depression presents a structural feature with three depressions and three uplifts which are western uplift, western depression, Damintun depression, central uplift, eastern depression and eastern uplift<sup>[5,7]</sup> (Fig.1). The eastern uplift locates on the east of Liaohe Depression and it is about 80km wide from north to south, 20km wide from east to west.

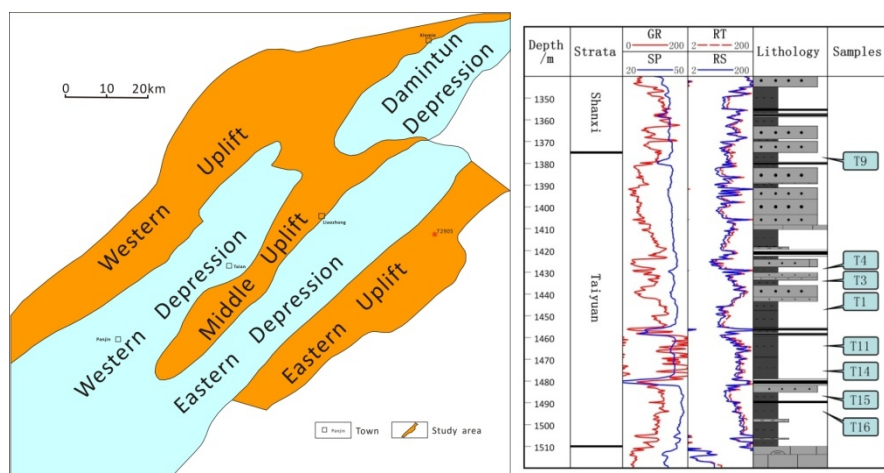


Fig.1 Location of T2905 core samples and eastern uplift in Liaohe basin

Depending on the drilling data, the thickness of Taiyuan formation in eastern uplift is 122.9m~171.3m and the shale thickness is 48m~87.4m. The core samples in this paper were chosen from Well 2905. The samples average TOC is 3%. The samples  $R_o$  is between 2.1% and 2.7%, which is in the phase of dry gas ( $R_o > 1.4\%$ ). The kerogen type is Type III and the vitrinite is nearly 77%.

The paper carried out high pressure mercury injection and  $N_2$  adsorption test on these samples. Based on Petroleum Industry Standard SY/T5346-2005, the high-pressure mercury injection was accomplished by Experimental Research Center of Wuxi Petroleum Geology Research Institute of PEPRIS. The machine is AutoPore IV 9520. Based on Petroleum Industry Standard SY/T6154-1995, the  $N_2$  adsorption was completed by CNPC Key Laboratory for unconventional oil and gas with machine Thermo SURFER (FCG-032). The conditions are 120°C and 5h for vacuum pumping under  $1.0 \times 10^{-3}$  Pa.

## Pore Characteristics

### Pore Morphology

Many scholars have carried out an amount of researches on pore of shale reservoir: pore of shale is mainly micron-nanometer sized pore. The accumulation space of shale is greatly related to the development of pore<sup>[12-14]</sup>. Depending on the pore size, shale pores are classified three types by Zou Caineng<sup>[15]</sup>: millimeter-level ( $>1\text{mm}$ ), micron-level ( $1\sim1000\mu\text{m}$ ) and nanometer-level ( $<1\mu\text{m}$ ). Furthermore, the IUPCU subdivides nanometer-level pore into macropore ( $>50\text{nm}$ ), mesopore ( $2\sim50\text{nm}$ ), micropore ( $<2\text{nm}$ )<sup>[16]</sup>.

According to the theory of adsorption and coagulation, the curve of adsorption and desorption measured by adsorption-desorption experiments on the solids with capillary pore may emerge overlap and separate. It will generate adsorption loop when the branches of adsorption and desorption separate, and the shape of adsorption loop is partly related to pore structure<sup>[17-19]</sup>.

The morphologies of  $N_2$  adsorption curves about different samples in this paper are different but similar (Fig.2), and all of the morphologies belong to Curve II that looks reverse "S"<sup>[17]</sup>. At low

pressure phase, the curve rises slowly with a slight-convex trend and it means the transition from monomolecular-layer adsorption to polymolecular-layer adsorption. The middle section of curve rises slowly with pressure and there is just polymolecular-layer adsorption for this phase. The adsorption curve goes up drastically at high pressure phase. Finally, the curve doesn't present a phenomenon of adsorption saturation with a pressure approaching to saturated vapor pressure, and it means the occurrence of capillary condensation which causes the drastic increase of adsorbance with the filling of macropore. Therefore the samples in this context contain a certain number of mesopore and macropore.

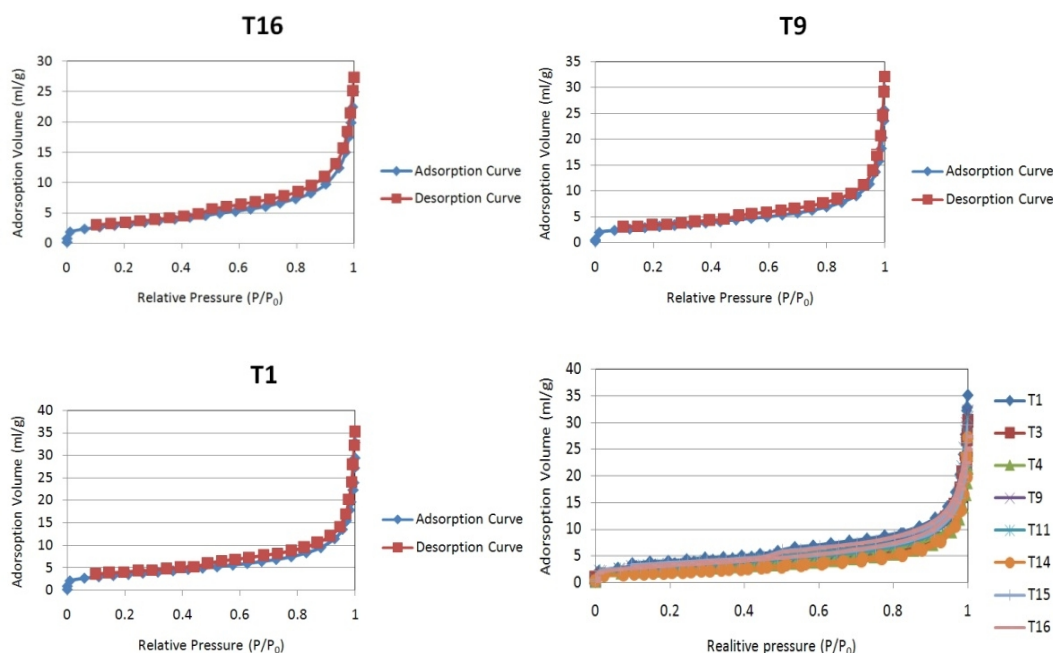


Fig.2 Adsorption isotherms of shale samples from eastern uplift of Liaohe depression

International pure chemistry and Applied Chemistry (IUPCU) divided the adsorption loop into 4 categories.  $H_1$  and  $H_4$  represent two kinds of extreme type.  $H_1$  adsorption, desorption branches in a wide range of adsorption pressure perpendicular to the axis and parallel to each other.  $H_4$  adsorption, desorption branch is horizontal in a wide range of pressure, and parallel to each other. The pores in size and arrangement are very regular often make  $H_1$ . The  $H_4$  loop is generated mainly by the micropores.  $H_2$ ,  $H_3$  is a moderate case. The  $H_2$  and  $H_3$  loops are mainly generated in the sample with littery pores [18].

Chen Ping [19] has divided the low temperature nitrogen adsorption loops into 3 types: Open pores, one end closed pores and Ink bottle pores. One end closed pores include cylindrical pore, parallel plate pore and wedge shaped pore. Because the relative pressure capillary condensate and evaporated is equivalent, one end closed pore' adsorption curve and desorption curves overlap and finally they don't have the adsorption loop. Open pores like four parallel sides plate pores can generate adsorption loops because of the different condensation and evaporation pressure. Ink bottle-shaped pores may have sharp decline adsorption loops on the condition of a sudden evaporation of condensed liquid.

The test samples desorption curves in the vicinity of the saturation vapor pressure is abrupt and is very flat at moderate pressure. These characteristics are similar with  $H_3$  and  $H_4$  curve recommended by IUPAC. It indicates that the shale pores are mainly micropores with complex structure, size and arrangement. Specific adsorption loops in the paper can be divided into three types: P1, P2, P3. P1: There is even no adsorption loop (Fig.2(a),(b),(c)). P1 illustrates the pores of shale mainly are one end closed pores include cylindrical pore, parallel plate pore and wedge shaped pore. P2: The adsorption loop is very small but has an inflection point (Fig.2(d), (e), (f)). The inflection point appears in the relative pressure of 0.5. In the low pressure, the adsorption loop and desorption curves is overlapped and a small adsorption loop appears in high pressure section. It reflects the pores mainly are Ink

bottle-shaped pores and one end closed pores. P3: The adsorption loop is obvious and has a Inflection point (Fig. 2(d),(e),(f). The inflection point is in the relative pressure of 0.5. In the low pressure section, the adsorption loop and desorption curves is overlapped. It reflects the pores mainly are open large pores, Ink bottle-shaped pores.

### Pore Size and Distribution

Nitrogen adsorption method mainly measures the mesopores and micropores. High-pressure mercury injection method mainly tests the macropores or even large<sup>[20]</sup>. Based on the research of pore morphology, the pores of the Taiyuan formation shale in the eastern uplift in Liaohe depression mainly are nano-scale pores. The author combined the nitrogen adsorption and high-pressure mercury injection for characterizing the pore size and distribution quantitatively.

The results of N<sub>2</sub> adsorption show that the pores' BJH volume distribution presents bimodal phenomenon. The two peaks are at 4nm and 100nm (Fig.3). And the BET pore specific surface only has one peak at 4nm. The two phenomenon indicate that macropores and mesopores mainly provide the most gas accumulation space and the micropores mainly contribute the specific surface.

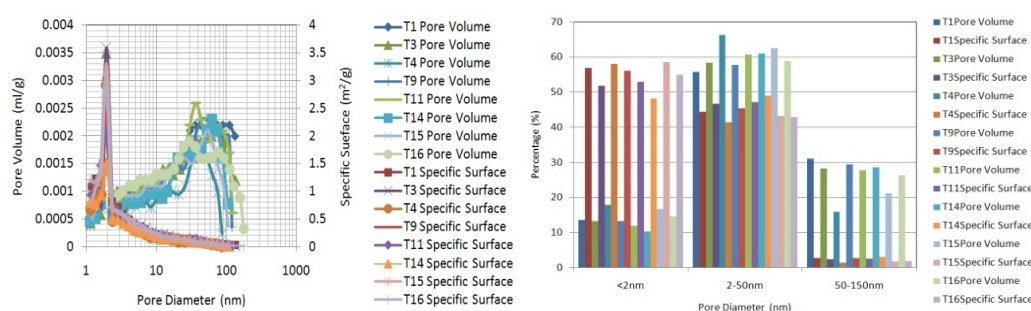


Fig.3 Pore size distribution of shale samples tested by N<sub>2</sub> adsorption

Based on the test data (table 1), the average pore diameter is 44.62nm. The specific surface ranges from 6.37m<sup>2</sup>/g to 12.55m<sup>2</sup>/g, and the average is 9.56m<sup>2</sup>/g. The BET specific surface of micropores, mesopores and macropores account for 54.85%、45.58%、2.14% respectively. The micropores and mesopores specific surface account for 97.86% and they enhance the adsorption capacity of shale. The pore volume ranges from 0.0234ml/g to 0.0527ml/g, and the average is 0.0414ml/g. The BJH pore volume of micropores, mesopores and macropores account for 14.6%、62.4%、23.5% respectively. The macropores and mesopores volume account for 85% and they provide most gas accumulation space.

Table1 Pore size distribution of shale samples tested by N<sub>2</sub> adsorption

Data samples	Pore diameter [nm]	Specific surface [m <sup>2</sup> /g]	Pore volume [ml/g]	Pore volume proportion [%]			Specific surface proportion [%]		
				<2nm	2-50nm	50-150nm	<2nm	2-50nm	50-150nm
T1	59.3454	12.5473	0.0527	13.699	55.842	31.206	56.993	44.543	2.746
T3	46.7672	8.5802	0.0466	13.322	58.415	28.325	51.855	46.76	2.529
T4	30.1151	8.1101	0.0311	17.872	66.297	16.052	58.105	41.53	1.445
T9	60.1385	10.7762	0.0474	13.362	57.838	29.561	56.131	45.4	2.79
T11	54.0789	10.7667	0.0463	11.943	60.73	27.791	52.966	47.191	2.689
T14	68.7560	6.5099	0.0394	10.377	61.086	28.609	48.271	49.078	3.091
T15	38.9129	11.1711	0.0428	16.879	62.665	21.244	58.595	43.33	1.885
T16	27.1690	11.2335	0.0425	14.704	59.013	26.294	55.038	43.015	1.964
WC1	16.2793	6.3737	0.0234	19.656	79.689	2.076	55.76	49.391	0.186
Average	44.6180	9.56319	0.04136	14.646	62.39722	23.462	54.85711	45.582	2.147222

According to high-pressure mercury injection, the large pores can be measured exactly (Fig.4). The capillary pressure curve can be divided into three stages: initial ascending stage, middle flat stage and terminal ascending stage.

Initial ascending stage: with the increasing pressure, the mercury injection saturation increases gradually. Middle gental stage: with the increasing relative pressure, the mercury saturation increased slowly. It represents the mercury saturation improved slowly during this pressure stage. Terminal ascending atage: with the pressure further increasing, the saturation of mercury increased rapidly. The stage of terminal major mercury is flat and long. It indicates the most mercury is injected in this pressure and in another word the pores gather in small diameter range. The high pressure of injection illustrates pores diameter is tiny like nano-scale pores.

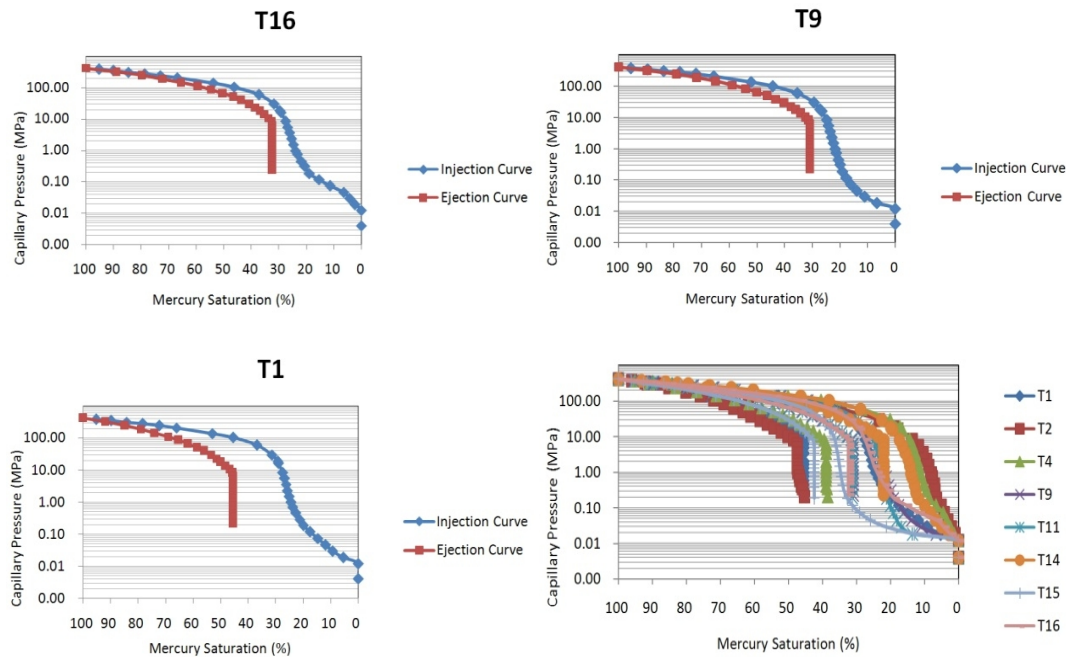


Fig.4 Capillary pressure curve of shale samples from eastern uplift of Liaohe depression

The conclusion from this research on the quantitative characteristics of capillary pressure curve (table 2): the average displacement pressure of different samples is 41.03MPa. The displacement pressure represents the lowest pressure that mercury begin to enter the shale pores. The displacement pressure refers to the capillary pressure of the largest pore among the injected pores. The displaced pressure can be calculated by the capillary pressure curve. The average connected radius is 30nm. The average mercury withdrawal efficiency is 64.85%. The average mercury withdrawal efficiency and connected radius shows the pores mostly are open and connected. The pores are beneficial to shale gas development.

Table2 High pressure mercury injection characteristic parameters of Taiyuan formation samples

Data Samples	Displacement pressure (MPa)	Connected radius ( $\mu\text{m}$ )	Average pressure (MPa)	Average diameter ( $\mu\text{m}$ )	Mercury Saturation (%)	Residual saturation (%)	Ejection efficiency (%)
T1	53.25669	0.013801	123.3005	0.005961	100	45.44427	54.55573
T2	24.07091	0.030535	99.5688	0.007382	100	45.3444	54.6556
T4	37.79729	0.019446	137.3208	0.005352	100	38.46313	61.53687
T9	53.27746	0.013796	127.7273	0.005754	100	31.03269	68.96731
T15	48.06381	0.015292	87.69488	0.008381	100	42.42424	57.57576
T16	53.28251	0.013794	120.1871	0.006115	100	32.39362	67.60638
T11	53.26795	0.013798	125.5626	0.005854	100	31.25196	68.74804
T14	53.26465	0.013799	154.8728	0.004746	100	22.08751	77.91249
Average	47.03515	0.016783	122.0293	0.006193	100	36.05523	63.94477

Data of the high-pressure mercury injection shows shale pores' volume distribution presents bimodal phenomenon (which is consistent with nitrogen adsorption). The two peaks are at  $6\mu\text{m}$  and



4nm in pore size. The macropores and mesopores volume account for 85% and they provide most gas accumulation space. The bimodal phenomenon has advantages in shale gas development: The macropores maintain the high productivity in early process. The micropores may prolong the high productivity time in later development.

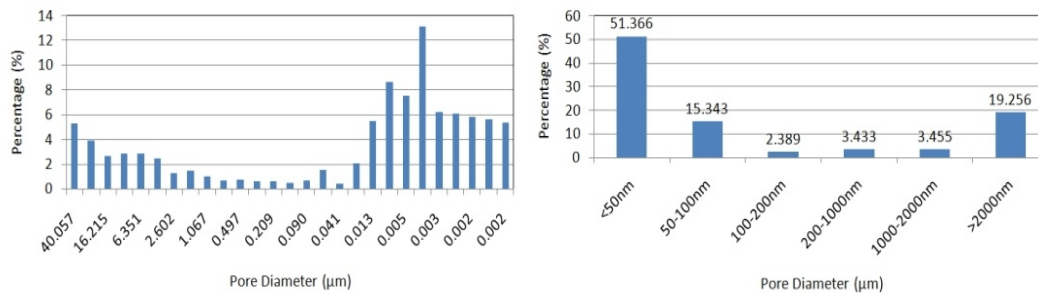


Fig.5 Pore size distribution of shale sample T1 tested by high pressure mercury injection

## Conclusion

Based on the  $N_2$  adsorption and high-pressure mercury injection, there are some views about the marine-continental transitional shale of the upper Carboniferous Taiyuan Formation in eastern uplift of Liaohe depression:

(1) The shale pores mainly are nano-scale. The pores are complicated in structure, and arrange irregularly.

(2) The  $N_2$  adsorption curve is type II. The adsorption loops are three types: P1 illustrates the pores of shale mainly are one end closed pores include cylindrical pore, parallel plate pore and wedge shaped pore. P2 reflects the pores mainly are Ink bottle-shaped pores and one end closed pores. P3 reflects the pores mainly are open large pores, Ink bottle-shaped pores.

(3) The two peaks are at  $6\mu m$  and  $2nm$  in pore size. The pore volume ranges from  $0.0234ml/g$  to  $0.0527ml/g$ , and the average is  $0.0414ml/g$ . The macropores and mesopores volume account for 85% and they provide most gas accumulation space. The specific surface ranges from  $6.37m^2/g$  to  $12.55m^2/g$ , and the average is  $9.56m^2/g$ . The micropores and mesopores specific surface account for 97.86% and they enhance the adsorption capacity of shale.

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