

Multi-scale Characterization of Pore Structure of Shale: a Case Study of the First Member of Qingshankou Formation in the Songliao Basin

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Abstract—The Songliao Basin, located in northeastern China, is rich in organic matter and develops organic shales deposited in continental environments. However, previous studies have mainly focused on marine shales, and there has been little research on terrestrial shales. The complex pore structure characteristics of shale reservoirs in the 1st member of Qingshankou in the Cologne Sag, Songliao Basin were studied by means of high-pressure mercury intrusion analysis and low-pressure nitrogen adsorption experiments. The results show that the transition pore is the most obvious in continental shale, followed by micro-pore, meso-pore and macro-pore. Transition pores contribute most to the volume and specific surface area of the pores. In addition, plate-shaped and flaky pores dominate, and connectivity is poor. This study is of great significance in understanding the pore structure of continental shale and the permeability mechanism of shale gas. The research results provide reference for the development, utilization and protection of the reservoir.

Keywords—pore types; reservoir space; cologne sag; mud shale

I. INTRODUCTION

There is a growing shortage of resources in the world today. As an unconventional oil and gas resource, shale gas has become more and more profound in its research. The development of advanced technologies such as horizontal drilling and multistage hydraulic fracturing has greatly promoted the commercialization of shale gas in North America. Shale gas accounts for 17 percent of total domestic natural gas production. At present, the global shale gas reserves are about $456.24 \times 10^{12} \text{ m}^3$ ^[1]. Under the impetus of the shale gas revolution in North America, many countries including China, Canada, and India have successively conducted research on shale gas.

The data show that the micro-structure of shale reservoir has been observed and analyzed at home and abroad, through high resolution scanning electron microscope, supplemented by nano-CT scanning, argon ion polishing technology, etc. These techniques intuitively describe the pore density and connectivity of shale reservoir. Although this method is

intuitionistic, it can not describe the pore structure characteristics of shale reservoir completely.

Therefore, this paper uses the method of high pressure mercury injection experiment and N₂ adsorption experiment to describe the pore structure of shale reservoir and finally combine it with each other^[2]. The pore structure characteristics of Qing 1 member in northern Songliao Basin are described and analyzed.

II. GEOLOGICAL SETTING

Songliao basin lies in the north of the tectonic region of the Pacific Rim between Siberia and the sino-korean platform, which is one of the most important petroliferous basins in the middle part of Heilongjiang province. Songliao Basin is a sedimentary basin which mainly deposited Jurassic and Cretaceous strata with an area of about 260,000 square kilometers and is a continental sedimentary basin^[3]. The Cretaceous strata are mainly deposited in Songliao basin. It is widely distributed in Songliao Basin with large sedimentary thickness, which is the main source reservoir rock of the basin^[4].

The object of the study is the shale of upper cretaceous Qingshankou formation. In Songliao Basin, a continental basin ranging from the edge of the basin to the center of the basin, the delta phase gradually change to the deep lake phase transition^[5]. The hydrodynamic and sedimentary environment gradually changed, and the Delta facies, the lakeside facies sand mudstone interbedded layer, the shallow lacustrine sand mudstone interbedded layer, the semi deep lake-deep lacustrine facies black mudstone and the shale stratum were developed sequentially^[6].

The sedimentary environment and the sedimentary cycle environment in which the reservoir is developed affect the abundance, thickness and mode of the sediment, and the lithologic characteristics of the reservoir, thus affecting the characteristics of the reservoir lithofacies^[7]. The horizon in the study area belongs to the continental sedimentary environment^[8]. According to its lithology and sedimentary characteristics, it can be judged that the horizon as a whole

presents a half-cycle model of medium-term decline^[9]. The TOC content in these shale samples was between 1-2% or > 2.0%. This indicates that the sample has higher abundance of organic matter and better types of source rock.^[10] Most of the organic matter belongs to type I and type II, which indicates that the organic matter of shale in this formation is of good type, and the organic matter is in the immature or low-mature stage, which indicates that the layer is relatively shallow buried, the burial time is shorter, and it has better hydrocarbon generation potential.

III. SAMPLES AND TEST METHODS

Because the pore distribution range of shale is very wide and the pore structure is very complex, there is no detailed and uniform standard for the classification of shale pore structure in the world at present^[11]. Therefore, based on the research results of pore structure in coal seams, the pore size is divided into four categories: those with pore diameter > 1000 nm are called large pores; those larger than 100 nm than 1000 nm are called mesoporous; those larger than 10 nm but less than 100 nm are called transition pores; and those smaller than 10 nm are called micropores^[12]. The high pressure mercury method is used to describe the large holes and hollow holes, and the micro-pores and the transition pores are described by the nitrogen adsorption method.

A. High Pressure Mercury Injection Method

When the non-wetting phase is injected into the porous medium, the surface tension of the medium will prevent the non-wetting phase from entering the pores. This resistance is the capillary resistance of the pores. In order to inject the non-wet phase into the pores, an additional pressure is applied to overcome the capillary resistance in order to inject the non-wetting phase into the voids. This extra pressure is equal to the pore capillary pressure.

In the determination of capillary pressure by mercury injection method, the samples are first made into core columns, then treated with deoiling, and then dried at 110 °C for 24 hours to remove free water and adsorbed water from the samples, and then vacuum treatment is carried out on the samples. Mercury, as a non-wetting phase liquid, is injected into the pores of rocks, and the amount injected corresponds to the volume of the pores in the rocks. With the increase of pressure, the amount of mercury entering and the saturation of mercury in rock pores increase gradually. As a result, each mercury entry pressure corresponds to a certain capillary resistance, according to the Washburn equation:

$$R = 2\sigma \cos\theta / P_c \quad (1)$$

The PC is the inlet pressure, σ is the interfacial tension (Dane / cm, θ is the contact angle, and R is the pore throat radius^[13].

Therefore, the pore radius corresponding to each mercury injection pressure can be obtained. The corresponding mercury injection amount is the pore volume corresponding to the corresponding pore radius. By gradually increasing the pressure, we can measure the pore volume corresponding to

each pressure, record the pressure corresponding to the shale sample at each pressure point to equilibrium, and the corresponding varying amount of mercury, and map the results of the recorded data^[14]. The capillary pressure curves of each shale sample were obtained. The characteristics of capillary pressure curves of each sample are compared, and the curves with the same characteristics are assembled together to describe the distribution of shale pores.

B. N₂ Adsorption Method

Nitrogen adsorption method is more suitable to study the distribution of nano-scale pores. Therefore, nitrogen adsorption method is mainly used to describe the pore characteristics of pore size in the range of shale transition pores. The pore surface can be physically adsorbed at low temperature. According to BET theory, the experimental samples were first treated in vacuum at 150 °C for 3 h. Nitrogen with purity greater than 99.999% was used as adsorbate in the experiment. Under the condition of -195.8 °C, the specific surface area of shale pore was calculated under the condition of relative pressure (P/P₀ = 0.05) 0.35. According to the principle of capillary condensation, the pore volume of rock pores can be obtained by the content of liquid nitrogen in shale pores. Different relative pressures correspond to different sizes of pore size under capillary condensation. Pore volumes of different pore sizes can be obtained by using liquid nitrogen of different pore sizes.^[15] The adsorption and desorption curves of nitrogen were formed by taking the amount of nitrogen gas adsorbed by the unit mass sample as the vertical coordinate and the relative pressure as the transverse coordinate.

IV. RESULTS

According to the above processing method, the curves with the same characteristics are divided into a class, as shown in the diagram.

As shown in figure 1a) and 1c), the mercury injection curve is in the middle of the image, showing a smooth curve state.

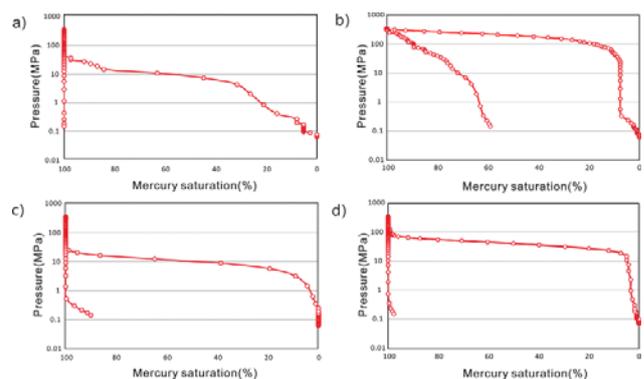


FIGURE I. CAPILLARY PRESSURE CURVE OF SHALE SAMPLES

This indicates that the pore size distribution of this type of shale sample is continuous but uneven. There are relatively many macro holes^[16]. When the pressure is 0.1-0.2 Mpa, the mercury saturation increases to about 10%, from 0.2-10 MPA, the mercury saturation increases rapidly to about 85%, and

then increases slowly with the increase of pressure, when the pressure increases to 50 Mpa, Mercury saturation has reached 100. From the mercury removal curve, it can be seen that when the pressure decreases, almost no regression occurs. The mercury removal efficiency is 0, which indicates that the internal pore throat connectivity of this type of shale sample is poor.

It is the second kind of capillary pressure curve of shale sample (Fig 1b) and 1d). From the mercury injection curve, the whole curve is located at the upper right of the image, and the middle main mercury injection section is flat and long, which indicates that the pore size distribution of shale sample is discontinuous micro-pore and transition pore is more developed^[17]. When the pressure increased to 0.2 MPA, the mercury saturation increased to about 10%, which indicated that the pore size of macro-pore was developed in the shale sample, but less, then with the increase of pressure, the mercury saturation almost did not change, when the pressure reached 15 MPA, The mercury saturation began to increase rapidly, and when the pressure reached 400 MPA, the mercury saturation increased to 100. From the mercury removal curve, we can see that With the decrease of pressure, the mercury saturation decreases gradually, the curve is smooth, and there is no obvious tendency of sudden drop, which indicates that the inner pore throat connectivity of this kind of shale sample is better.

The following drawings are the nitrogen adsorption-desorption curves of four types of shale samples.

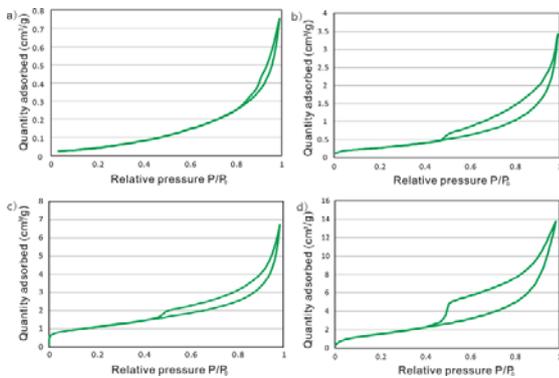


FIGURE II. THE NITROGEN ADSORPTION DESORPTION CURVES OF FOUR TYPES OF SHALE SAMPLES.

As shown in Fig.2a) and c), the adsorption-desorption curves of the first and the third type shale sample are shown. It can be seen from the diagram that when the relative pressure increases, the adsorption capacity of the gas increases gradually, and when the relative pressure is small, the adsorption and desorption branches of the sample show a steady upward trend, but slowly^[18]. When the relative pressure is about 0.85, the slope of the desorption curve is larger than that of the adsorption curve. When the relative pressure approaches 1, the two branches are re-closed. According to the theory of capillary condensation, the retention loop is narrow, which indicates that the pore size in the sample is narrow, and the sample is found by comparison. The curve is closest to H3,

so it can be inferred that the shale sample is an open pore, most of which is a long and narrow fissure pore, which is conducive to the migration and percolation of oil and gas.

The adsorption-desorption curves of the second type shale samples are shown as Fig 2b). It can be seen from the diagram that the pore size range in shale pores is large^[19]. The pores above the large pore pore size are mainly closed at one end of the pore, while the transition pore is the parallel type pore and the open cylindrical pore at both ends. Micropores are mainly sealed at one end of the air-tight hole and fine-necked wide-body ink bottle hole.

As shown in Fig. 2d), the adsorption and desorption curves of the fourth kind of shale samples show a wide range of pore size^[20]. The pores above the large pore pore size are dominated by a closed gas permeability pore at one end, the transition pore is dominated by a long and narrow fissure pore, and the micro-pore pores are mostly fissure.

According to the nitrogen adsorption curves, the shale samples are continuously distributed from micro-pores to macro-pores, and there are many micro-pores and transition pores, which have long and narrow pore structure. In shale pores, the pores above the pore size are mainly confined at one end of the pore, the transition pore is the parallel type of pore, the long and narrow cracks and the open cylindrical pore at both ends are the main ones. Micro-pores are mainly sealed at one end of the air-tight hole and fine-necked wide-body ink bottle hole.

V. DISCUSSION

The adsorption-desorption curves of the samples were calculated by BET equation and BJH method, and the specific surface area and pore size of the samples were obtained. The calculated results show that the pore specific surface area of the sample is 0.0564-28.9602 m/g, the average is 3.8053 m/g, the total pore volume of the sample is from 0.0007 to 0.0278 ml/g, the average is 0.01165 ml/g, and the average pore diameter is from 3.8398-70.8220 nm, with an average of 18.9527 nm. Based on the data obtained from the high pressure mercury injection test and nitrogen adsorption test The results of the joint aperture analysis are as follows:

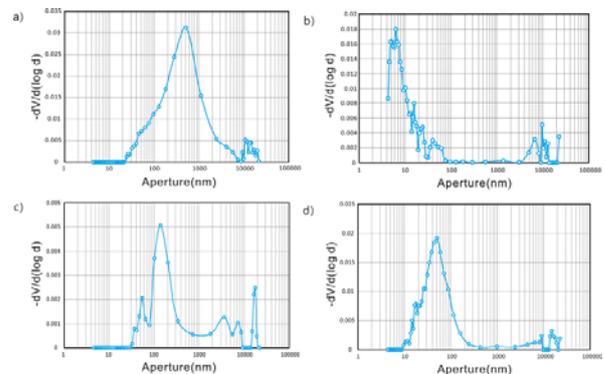


FIGURE III. THE JOINT APERTURE ANALYSIS

Figures 3. correspond to the joint pore size distributions of the first, second, third, and fourth samples, respectively. It can be seen from the diagram that the pore size distribution range of the first kind of sample is wider, the meso-pore and transition pore are the most developed, the micro-pore and the large pore are the second, and the pore distribution of various pore size types is approximately uniform. In the second type, the pore size distribution is concentrated, mainly micro-pore, followed by macro-pore, and transition pore is also developed. The micro-pore and meso-pore are the main samples in the third type, followed by the large pore, the pore size distribution range is very wide, the pore distribution of various pore sizes is more uniform. The fourth kind of sample is similar to the second kind, mainly composed of transition pore and micro-pore, and the macro-pore is also developed.

VI. CONCLUSIONS

1. The pore structure in shale is complex, the pore structure is diverse, and the pore size distribution is wide.

2. In the northern part of Songliao Basin, the internal pores of the first member of the Qingshankou formation are mainly micro-pores and transitional pores, while the meso-pores and macro-pores are less developed, which is beneficial to the adsorption, accumulation and storage of shale gas, but it is not suitable for the migration and seepage of the gas.

3. There are many kinds of pore structures, such as one end closed air permeability pore, open air permeability pore and ink bottle hole, and long and narrow crack type pore and so on. In shale pores, the pores above the pore size are mainly confined at one end of the pore, while the transition pores are composed of parallel type pores and cylindrical pores open at both ends. Micro-pores are mainly sealed at one end of the air-tight hole and fine-necked wide-body ink bottle hole.

4. Due to the shallow buried depth of the first member of the Songliao Basin and the smaller formation pressure, there are large pores in the rock pores. Meanwhile, because of the large amount of clay minerals in the rocks and the smaller granularity, the micro-pores and transition pores are particularly developed in rocks

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