A New Method of Determining the Lower Limit of Pore in Saturated Kerosene

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Abstract. To determine the lower limit of the pore size of saturated kerosene indirectly for testing porosity, the combined total porosity was first calculated using carbon dioxide adsorption, nitrogen adsorption, and mercury intrusion tests. Then the combined porosity is gradually accumulated from large pores to tiny pores. When the accumulation is equal to the total kerosene porosity, the corresponding pore diameter is a minor pore diameter measured by kerosene porosity. A total of 5 samples were collected this time. The lower limit of kerosene porosity was determined as 3.1nm, which shows that the kerosene saturation method can describe most of the shale's mesopores and macropores. This method can also be extended to determine the lower limit of the pore size by the porosity method, such as helium.

1. Introduction

The pore diameters of conventional oil and gas reservoirs generally range from millimeters to micrometers, and the pore diameters of shale reservoirs are mainly nanometers. According to the classification standards of the International Union of Theoretical and Applied Chemistry (IUPAC) \cite{1}, shale pores are divided into the following three categories according to the pore size: $\textcircled{1}$<2nm, belong to micropores; $\textcircled{2}$2-50nm, belong to mesopores or mesopores; $\textcircled{3}$>50nm, belong to macropores.

The pore size difference between the two is several orders of magnitude, making it challenging to evaluate conventional oil and gas reservoirs' pore size to describe the shale pore size distribution \cite{2} fully. At present, there are mainly quantitative methods and qualitative methods for determining unconventional reservoirs. Method \cite{3}. Currently, there are two methods for quantitative research: small-angle neutron dispersion single method (pore diameter resolution 1-100nm\cite{4}) and carbon dioxide adsorption (pore diameter resolution 0.3053-2nm), nitrogen adsorption (pore diameter resolution 1nm-300nm) \cite{5}) Mercury intrusion (hole diameter resolution 3.6-100000nm \cite{5}) three combined methods, due to the pore diameters' coincidence, so the cut-off method is currently used. The cut-off way is used currently. Carbon dioxide adsorption is especially suitable for mesopore 2-50nm characterization. Nitrogen adsorption is mainly suitable for 0.4-2nm evaluation \cite{5,6,7}. The mercury injection method is primarily suited for the description of pore diameters more significant than 50nm. This method is widely used in the complete aperture evaluation of shale gas reservoirs, and
some conclusive results have been obtained [8, 9,10,11].

2. Application of different porosity test-methods

2.1. The method, principle, and application of the triple method

The pore diameter of shale gas reservoirs is generally from 10-10m to 10-5m. The span is generally five orders of magnitude, which requires a combination of multiple measurement methods to be identified. At present, the description of nano-scale full pore diameters is primarily used in the triple method by domestic scholars: the combined description method of mercury intrusion analysis and testing, low-temperature nitrogen adsorption, and low-temperature carbon dioxide adsorption.

The mercury intrusion method's principle to determine the pore size is that according to the Laplace equation, under the action of external pressure, it overcomes the resistance brought by the surface tension of the mercury. Pores with different pore diameters have different resistance to mercury. The greater the additional external pressure, the smaller the pore diameter in the rock that mercury can occupy. The pore volume and pore radius in the stone can be obtained concerning the relevant parameters.

Low-temperature nitrogen adsorption uses the principle of physical adsorption of nitrogen on the solid surface and capillary condensation under the saturated temperature condition for testing and its measurable range for hole diameter.

Low-temperature carbon dioxide adsorption uses the principle of physical adsorption and capillary condensation of carbon dioxide gas on a solid surface under saturated temperature conditions for testing.

2.2. Principle and measurement method of saturated kerosene porosity

The conventional porosity determination is based on the Archimedes principle. The rock sample dried to constant weight after pumping oil is called its mass m1 and then pumped out to use it. The mass m2 of the rock sample saturated with kerosene in the kerosene and the mass m3 of the rock sample saturated with kerosene is calculated by the formula as follows:

\[
\text{Porosity}(\Phi) = \frac{(m3-m1)}{(m3-m2)} \times 100\%
\]

The saturated kerosene method calculates the effective porosity. According to the Chinese petroleum industry-standard, effective porosity is defined as the percentage of the pore volume in which fluid can flow freely to the rock's total volume.

3. Determining the lower limit of saturated kerosene porosity pore size using the triple method

The development of micro-porosity characterization technology has extensively promoted the study of rock properties of unconventional reservoirs. Porosity is a simple concept, but it is affected by the extremely low permeability of shale and complex mineral composition, coupled with different experimental methods and the different resolutions of other test methods, resulting in significantly different test results.

The pores of the five layers in this study were tested both by the conventional porosity measured by the saturated kerosene and the triple method's full-pore porosity. And to study the relationship between the porosity by the triple process and the saturated kerosene ways, the statistical analysis systematically analyzes the relationship between the two porosities. The lower limit of the conventional porosity was determined when the volume is equal.

The kerosene porosity of the Long-113 layer in Well Z-206 is 3.76%, the porosity of triple method is 7.19%, the porosity of kerosene accounts for 52.3% of the porosity of the triple method, and the absolute difference of the porosity is 3.43%; The kerosene porosity is 3.99% of the Longyi 11 layer in Well Z-206, the triple method porosity is 7.61%, the kerosene porosity accounts for 52.4% of the triple method porosity, and the absolute difference in porosity is 3.62% respectively.

The kerosene porosity of Wufeng Formation in Well Zu-206 is 2.96%, the porosity of triple method is 4.66%, the porosity of kerosene accounts for 63.5% of the triple, and the absolute difference of porosity is 1.7%; the porosity of Long-13 small layer of kerosene in Well Z-205 is 4.08%, the porosity
of the triple method is 7.16% respectively, the porosity of kerosene accounts for 57% of the porosity of the triple method, and the absolute difference of the porosity is 3.08%; the kerosene porosity of the Longyi 13 small bed in Well Z-205 is 3.98%, and the porosity of the triple method is 3.98% respectively, and the triple is 5.68%, the kerosene porosity accounts for 70.1% of the triple porosity, and the absolute difference of the porosity is 1.7% (Table 1, Figure 1).

The lower limit of the porosity pore size measured by the triple method is smaller than that of the kerosene porosity. The triple porosity is cumulatively added from the large pore to the small pore until it is precisely equal to the kerosene porosity. When the porosity is equal, the pore diameter by the triple can be considered the lower limit of the pore diameter of the porosity measured by kerosene. The absolute difference between the kerosene porosity and the triple porosity is 1.7%-3.62%, with an average of 2.7% (Figure 1 and Figure 2); the average diameter is 3.1nm.

Table 1. Comparison of kerosene porosity and triple porosity in the different testing method

| Well   | Layer | kerosene porosity (%) | triple porosity (%) | Porosity ratio (%) | Absolute Porosity Difference (%) |
|--------|-------|------------------------|---------------------|--------------------|----------------------------------|
| Z206   | Longyi 13 | 3.76                   | 7.19               | 52.3               | 3.43                             |
| Z206   | Longyi 11 | 3.99                   | 7.61               | 52.4               | 3.62                             |
| Z206   | Wufeng   | 2.96                   | 4.66               | 63.5               | 1.7                              |
| Z205   | Longyi 13 | 4.08                   | 7.16               | 57.0               | 3.08                             |
| Z203   | Longyi 13 | 3.98                   | 5.68               | 70.1               | 1.7                              |

Figure 1. Comparison of porosity between kerosene method and triple method
4. Discussion
Compared with the mercury injection method and the gas adsorption method, the kerosene method has less interference from external conditions, namely a mass proportion method that uses buoyancy law under natural conditions, so it is relatively more accurate, and the test result is the effective pores. Using the triple method to measure the total porosity, combined the kerosene method to measure the effective porosity, when the cumulative addition method of pores from large to minor until the cumulative porosity is equal to the effective porosity of saturated kerosene, the corresponding diameter is the lower limit of diameter by kerosene measurement, and its lower limit is 3.1nm. From this, it can be concluded that the liquid with a pore diameter larger than 3.1nm can flow; and for gas (the main component of standard shale gas, methane has a molecular diameter of 0.38nm and water has a diameter of 0.4nm), it must also be effective porosity to flow. This quantitative method plays a significant role in measuring shale reservoir porosity and the determination of the measurement range.

5. Conclusion
To determine the lower limit of the porosity, the measures for porosity testing were investigated and discussed. Conclusions and suggestions are as follows:
(1) The lower limit of the conventional kerosene method's effective porosity is 3.1 nanometers; the kerosene porosity accounts for more than 50% of the total porosity.
(2) To use the triple method to accumulate the porosity from the large pore size to the small pore size until it is just equal to the kerosene porosity, the corresponding pore by the triple method is the lower limit of the porosity, which equals to one by the conventional kerosene method.
(3) If the porosity is measured by the helium method, the minimum pore size can be determined when the gas flows freely.

Acknowledgments
Chongqing Science and Technology Commission Project financially supported this research, "Key Technologies and Research Application of Middle-Deep Shale Gas Exploration and Development in Chongqing Area" (Grant No. cstc2017zdcy-zdyfX0040)

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