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Pore Structure of Coal Samples from Chengzhuang No. 3 Coal Seam by High-pressure Mercury Testing

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Abstract: Matrix pores in coal reservoirs are important storage sites for adsorbed and free state CBM, and their adsorption amount is closely related to the development of pores and pore structure characteristics in coal. In this paper, the pore structure characteristics of coal and its influence on adsorption performance were studied by using the high-pressure mercuric pressure method with coal samples from No. 3 coal seam of Chengzhuang Mine as the research object. The results show that: the degree of openness of the pores of the coal samples in the study area is small, most of the pores in the coal are semi-closed pores, and the pore connectivity is poor; in the coal samples in the study area, the mesopores and macropores with a diameter larger than 100 nm are less developed, and the micropores and micropores with a diameter of less than 100 nm are developed; the pore volume of the coal samples of the No. 3 coal seam in the study area ranges from 0.0127 to 0.0168 cm3/g, with an average volume of 0.0144 cm3/g, and the pore volume content of each pore size of the samples was microporous>small pore>massive pore>medium pore; the specific surface area of the coal samples from the No. 3 coal seam in the study area ranged from 5.2259 to 6.4032 m2/g, with an average of 5.8816 m2/g, and the micropores and small pores provided a large amount of specific surface area for pores, which provided large space for the reservoir of CBM, and was favorable for the adsorption of methane gas by the pores of the coal. The above research results are intended to provide a theoretical basis for the exploitation and production of CBM in the study area.

Keywords: Anthracite; Pore Structure; Mercuric Pressure; Adsorption.

1. Introduction

Matrix pores in coal reservoirs are important storage sites for adsorbed and free state CBM, and their adsorption amount is closely related to the development of pores and pore structure characteristics in coal[1-4]. Coal matrix nanopores are smaller in size and larger in number, with high contribution to the specific surface area, which creates favorable conditions for the storage of CBM. The existence form of CBM in coal beds is mainly in adsorption state, which accounts for about 80%~90%[5,6]. The current research on pore structure has achieved some results, mainly in the study of pore structure of different coal steps[7,8], the types of causes of pore structure[9], and the study of various test methods[10,11]. Previous research results show that the characteristics of the pore structure in coal determine the size of its adsorption capacity. Therefore, it is of great practical significance to study the pore structure of coal matrix. The author chose the high-pressure mercury test method to study the pore structure of coal samples from No. 3 coal seam in the study area, and the results of the study are intended to provide theoretical basis for the exploitation and production of coalbed methane in the study area.

2. Geological Background of the Study Area

The Chengzhuang well field is located in the southern section of the north-northeast fold belt of the eastern sub-tectonic unit of the Qinshui block depression of the Lvliang-Taibang fault block in the North China fault block, namely, the Zhanshang-Wuxiang-Yangcheng north-north-east fold belt (Figure 1). The depression was formed in the Mesozoic, is a rectangular fault block surrounded by fractures, is formed by horizontal extrusion of the depression, the overall north-north-east spreading, the main part of the Permian and Triassic exposed, peripheral uplift, the lower Paleozoic exposed. Compared with the surrounding tectonic units, the Qinshui depression is more stable, and the deformation intensity decreases from the edge to the interior. The exposed strata in the well field are mainly the Upper Stone Box Formation and the Shiqianfeng Formation, while the Lower Stone Box Formation and the Shanxi Formation are sporadically exposed in the southeastern part of the well field, and the Quaternary System is scattered on the sides of the mountain beams, ridges and valleys. The coal-bearing strata in the wellfield are mainly the upper Carboniferous Taiyuan Formation (C_3t) and the lower Permian Shanxi Formation (P_1s). The object of this study is the No.3 coal seam of Shanxi Formation, which is located in the lower part of Shanxi Formation with stable deposition, 27.60-46.75m from K_8 sandstone on the upper side, averaging 34.91m, and 0-6.50m from the top surface of K_7 sandstone on the lower side, averaging 2.11m.

3. Experimental Apparatus and Methods

3.1. Experimental Apparatus and Parameters

The model of the pressurized instrument used in this study is US-McMurray Tick-AutoporeV 9620, as shown in Fig. 2. This instrument is a high-performance fully automated mercuric pressurization instrument used for the determination of the physical properties of powder and solid materials, including porosity, pore size distribution, total pore volume, total pore area, median pore size, and the density of the sample, etc. It can measure pore size ranging from 3.5 nm to 800 um, and test pressure ranging from 0.2 psi to 60,000 psi.

Its measurable pore size range is from 3.5nm to 800um, the test pressure range is from 0.2psi to 60,000psi, and the accuracy of the inlet and outlet mercury volume is better than 0.1 μL.

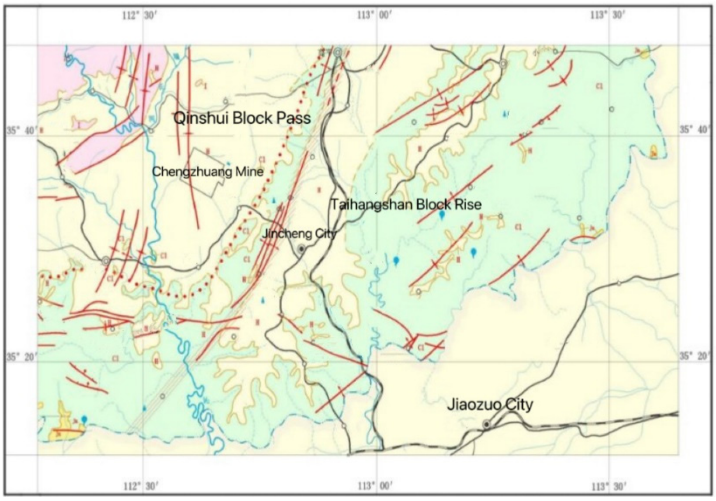


Figure 1. Regional tectonic map

Figure 2. Fully automated pressure pumping pore size analyzer AutoPore V 9620

3.2. Experimental Principle

Mercury-in-pressure (MIP) is the most common method to measure the pore volume and pore size distribution of mesopores and macropores, and the basic principle of its test is that mercury can not wet the surface of the solid material, and only by means of pressurization, so that it is subjected to a greater force can enter the pores of the porous medium to be measured, and when the greater the force exerted, the mercury will be able to flow into the finer pore space. We regard the coal as composed of many capillary tubes, based on the principle of liquid lift in the capillary tube, the mercury injection process of pressure P and capillary radius r relationship by the WASHBURN[12] equation can be obtained, as in equation 1:

$$P = \frac{2\sigma\cos\theta}{r} \tag{1}$$

Where: p is the pressure exerted during indentation of mercury; θ is the wetting contact angle between coal and mercury; σ is the surface tension of mercury; and r is the radius of the capillary.

3.3. Sample Preparation

The accurate preparation of samples has a greater impact on the accuracy of the experimental results, take fresh samples from the No. 3 coal seam in the study area, wrapped in plastic to prevent oxidation. The coal samples were crushed to make them as small as possible into $1cm^3$ pieces, and then the prepared samples were placed in a constant temperature drying oven at 80 °C for 12 h. Finally, the dried and processed coal samples were placed in an expansion meter to be tested under vacuum conditions, and the specific operation of the testing process was based on the national standard (GB/T 21650.1-2008/ISO 15901-1:2005). Determination of Pore Size Distribution and Porosity of Solid Materials by Mercury Piezometry and Gas Adsorption-Part 1: Mercury Piezometry" for the mercury piezometric testing of coal samples from No.3 coal seam in the study area.

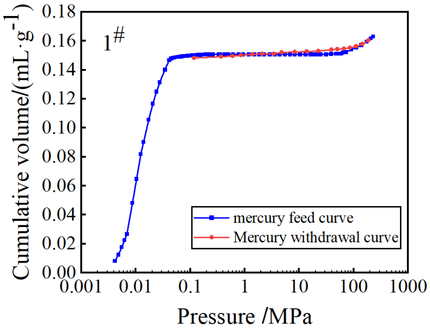
4. Experimental Results and Analysis

4.1. Pressed Mercury Curve and Pore Morphology

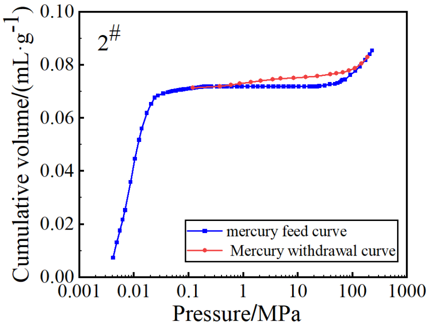
Coal is a typical porous adsorption material, and its internal structure consists of a large number of pores and clefts, which play an important role in the adsorption, desorption and other physicochemical processes of coal. Therefore, an in-depth study of the pore structure of coal is of great significance in understanding the adsorption properties of coal and the permeability of coal seams. A large number of scholars have proved that the adsorption and desorption in coal has a "hysteresis" effect, and the hysteresis loop types are different in different pores due to the different pore morphologies and connectivity, so the morphology of the pores in coal can be analyzed by the hysteresis loop types.

Based on the high-pressure autoclave test, it was found that the inward and outward mercury curves of the No. 3 coal seam in Chengzhuang Mine did not completely coincide with each other, and there existed a hysteresis loop, as shown in Fig. 3, and the inward and outward curves of the coal samples could be clearly divided into three stages. In the first stage, when the pressure is less than 0.03 MPa, the mercury can enter the pores with a pore diameter greater than 40,000 nm. In this stage, the mercury inlet curve shows a steep slope growth and the amount of mercury inlet increases rapidly, which indicates that larger pores and fissures are developed in the coal in this pressure range. In the second stage, when the pressure is between 0.03 MPa and 12.4 MPa, the mercury enters into the pore size range of 100~40,000 nm, the growth of the mercury feed curve in this stage is relatively small, and the increase of the mercury feed is slow, which indicates that the number of pores in the coal in this pressure range is relatively small. In the third stage, when the pressure is greater than 12.4 MPa, the mercury is able to enter the pores with a pore size of less than 100 nm. At this time, the mercury inlet curve rises rapidly again, and the amount of mercury inlet shows a rising trend, which indicates that small pores and micropores are more developed in the coal in this pressure range.

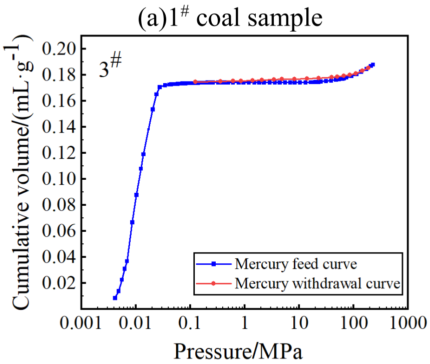
The shape of the inlet and outlet curves can reflect the degree of development and openness of the pores. In the coal samples from No.3 coal seam of Chengzhuang Mine, the difference between the Hg in curve and Hg out curve is not big and the "hysteresis loop" is not obvious, which indicates that the degree of openness of the pores in the coal samples in the study area is small, and most of the pores in the coals are semi-closed pores, and the connectivity of the pores is poor.



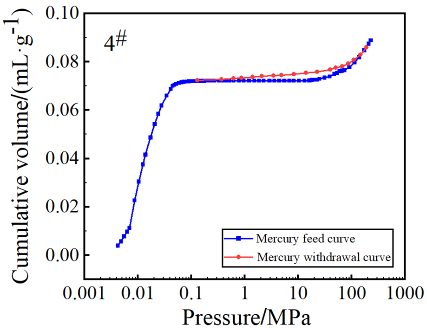
(a)1# coal sample



(b)2# coal sample



(c)3# coal sample



(d)4# coal sample

Figure 3. Coal Sample Mercury Input and Output Curves

4.2. Pore Volume

Pore volume in coal is an important parameter of the pore structure characteristics of coal, which has an important influence on the adsorption performance and permeability of coal. Pore volume in coal is the total volume of pores in coal per unit mass, usually expressed in ml/g or cm^3/g. Based on the experimental test results, the pore volume and its percentage of the pore structure of the coal samples in the study area were analyzed according to B.B. Hodot's decimal four classification standard[13]. The results of high-pressure mercury pressure testing of coal samples from No. 3 coal seam in Chengzhuang showed that the pore volume of coal samples from No. 3 coal seam in the study area ranged from 0.0127 to 0.0168 cm^3/g, with an average pore volume of 0.0144 cm^3/g. The proportion of micropores in the total pore volume varied from 52.54% to 58.79%, with an average of 55.19%, the proportion of small pores varied from 35.69% to 44.14%, with an average of 41.05%, and the proportion of medium pores varied from 35.69% to 44.14%, with an average of 41.05%. 41.05%; the proportion of medium pores varied from 0.26% to 1.3%, with an average of 0.92%; the proportion of large pores varied from 1.02% to 4.22%, with an average of 2.84%. The pore volume content of each pore size of the samples showed that microporous > small pore > large pore > mesopore, as shown in Table 1.

Table 1. Distribution of pore volume in each pore size section of high-pressure mercury compression

coal sample	pore volume. cm^3/g					pore volume ratio. %			
	V_1	V_2	V_3	V_4	V_T	V_1/V_T	V_2/V_T	V_3/V_T	V_4/V_T
1#	0.0005	0.0002	0.0045	0.0075	0.0127	4.22	1.300	35.69	58.79
2#	0.0006	0.0001	0.0057	0.0077	0.0141	3.91	0.88	40.37	54.84
3#	0.0003	0.0002	0.0062	0.0074	0.0141	2.21	1.25	44.01	52.54
4#	0.00017	0.0004	0.0074	0.0092	0.0168	1.02	0.26	44.14	54.58

Note: V1 is the pore volume of large pores (d > 1000 nm); V2 is the pore volume of medium pores (100 nm ≤ 1000 nm); V3 is the pore volume of small pores (10 nm < < < 100 nm); V4 is the pore volume of micropores (d ≤ 10 nm); and VT is the total pore volume.

4.3. Specific Surface Area

The specific surface area of coal is the surface area per unit mass of coal, usually expressed in m^2/g. It is an important parameter to measure the complexity of coal pore structure. The size of specific surface area directly affects the adsorption performance of coal, and it is usually believed that the larger the specific surface area, the better the pore adsorption performance of coal[14]. Based on the experimental test results, the specific surface area and its percentage of the pore structure of the coal samples in the study area were analyzed according to B.B. Hodot's decimal four classification standard. The specific surface area of coal samples from No. 3 coal seam in the study area ranged from 5.2259 to 6.4032 m^2/g, with an average of 5.8816 m^2/g. The percentage of micropores in the total specific surface area varied from 75.35% to 77.02%, with an average of 76.13%; the percentage of small pores varied from 22.62 to 24.5%, with an average of 23.69%; and the percentage of medium and large pores was very small, as shown in Table 2. It can be seen that micropores and small pores provide a large amount of specific surface area for pores, which provides a larger space for the reservoir of CBM, and is favorable for the adsorption of methane gas by pores in coal.

Table 2. Specific surface area distribution of each pore size section in high-pressure mercury pressure test

coal sample	specific surface area. m^2/g					specific surface area ratio. %			
	S_1	S_2	S_3	S_4	S_T	S_1/S_T	S_2/S_T	S_3/S_T	S_4/S_T
1#	0.0075	0.0020	1.50	4.89	6.40	0.00005	0.35	22.62	77.02
2#	0.0003	0.0094	1.3233	4.1646	5.4976	0.01	0.17	24.07	75.75
3#	0.0002	0.0082	1.2801	3.9375	5.2259	0.003	0.16	24.50	75.35
4#	0.0001	0.0020	1.5091	4.8911	6.4032	0.00001	0.03	23.57	76.40

Note: S_1 is the specific surface area of large pores (d>1000 nm); S_2 is the specific surface area of medium pores (100 nm≤1000 nm); S_3 is the specific surface area of small pores (10 nm<<100 nm); S_4 is the specific surface area of micropores (d≤10 nm); and ST is the total specific surface area.

5. Conclusion

In this paper, the pore structure of coal samples from No. 3 coal seam of Chengzhuang Mine was tested by high-pressure pressure mercury method, and the pore morphology, pore volume, and specific surface area were analyzed to investigate the characteristics of the pore structure of coal samples in the study area, and the following important conclusions were drawn.

(1) There is a "hysteresis loop" between the Hg in curve and Hg out curve of coal sample from No.3 coal seam of Chengzhuang Mine, the degree of openness of the pores of the coal sample is small, and most of the pores in the coal are semi-closed pores, and the connectivity of the pores is poor.

(2) Micropores and small pores are developed in the coal sample of No.3 coal seam of Chengzhuang Mine, and the pore volume content of each stage of pore size shows micropores>small pores>large pores>medium pores, and micropores and small pores provide a large amount of specific surface area for pores, which provides a large space for the reservoir of coalbed methane gas, and is favorable for the adsorption of methane gas by the pores in the coal.

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