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Coal pore size distributions controlled by the coalification process: An experimental study of coals from the Junggar, Ordos and Qinshui basins in China

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HIGHLIGHTS

- Pore size distributions of different rank coals were systematically studied.
- Key variation points of coal pores evolution were recognized.
- Explanation of the factors controlling pores characteristic was presented.
- The physical parameters of coals from three typical CBM basins in China were studied.

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ABSTRACT

Various sizes of pores in coal, which are generally formed by organic matter during the coalification process, have a direct influence on coalbed methane extraction. However, few studies have investigated the pore size distributions across the thermal evolution of coal from peat to anthracite. In this project, three series of coal samples collected from three key CBM development basins with graded vitrinite reflectance values (R_o), the eastern Junggar basin (R_o of approximately 0.5%), eastern Ordos basin (R_o of approximately 2.2%) and southern Qinshui basin (R_o of approximately 3.0%), were systematically characterized by optical observations, low-temperature nitrogen adsorption/desorption, and nuclear magnetic resonance (NMR) methods. The average pore radius calculated by the Brunauer-Emmett-Teller (BET) method shows that the low-rank (*L*) series (averaging 14.17 nm) has values higher than either the middle-rank (*M*, 12.70 nm) or high-rank (*H*, 12.66 nm) samples. Bright and semi-bright coals (determined by the overall relative lustre and percentage of bright components) are generally distributed with relatively higher pore radii (averaging 16.86 nm for all 3 series) than the semi-dull and dull coals (9.50 nm). The range of pore sizes decreases as the coal rank increases, and the NMR transverse relaxation (T_2) spectrum decreases from bi-modal and tri-modal (*M* and *L* series) to unimodal curves (*H* series). However, the pore surfaces and complexity inside the coal increase with the coal rank, with the fractal results showing a three-stage fitting slope of the *H* series compared with the *M* (two-stage) and *L* (one-stage) coals. The observations are generally caused by the *L* coals, which mainly include plant tissue pores, while the *M* series coals are characterized by circle-shaped tissue pores and gas pores. The *H* series of flattened tissue pores and more diverse gas pores are identified in the higher-rank coals. Combined with the thermogenic gas generation process of coal, three key transition points were recognized: (1) R_o of approximately 0.5%, transition of dehydration to bituminization with coals being much more compacted, shown as the >100 nm range pores decreasing sharply; (2) R_o of approximately 1.2%, the beginning of the debituminization stage with the intensive generation of thermogenic gas, with pores ranging between 10 and 50 nm increasing quickly; and (3) R_o of approximately 1.9%, coal being transformed into anthracite, becoming much more compacted with the induction of cleats/fractures, shown as another decrease in >100 nm range pores but an increase in 50–100 nm range pores. These observations could deepen the

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understanding of the complex pore size distribution differences between different coal ranks and the impact of the thermal evolution on the coal heterogeneity and its reservoir characteristics.

1. Introduction

Similar to other unconventional natural gas reservoirs, e.g., shale gas and tight sand gas reservoirs, coal has been comprehensively studied as a porous medium by constantly updated methods in recent years, including (1) microscope methods with 2D images of scanning electron microscope (SEM) and transmission electron microscopy (TEM) methods; (2) fluid intrusion methods of high-pressure mercury intrusion porosimetry (MIP), low-temperature nitrogen and carbon dioxide adsorption/desorption, and nuclear magnetic resonance (NMR); and (3) three-dimensional (3D) structure construction by X-ray computed topography (CT), focused ion beam scanning electron microscopy (FIB-SEM), and atomic force microscopy (AFM) [1–8]. Different methods generally have different detectable scales, and a combination of different experimental technologies is necessary for a systematic illustration of the different pore distributions and pore structure variations. It was reported by Levine that the macropores (>50 nm) decreased and the micropores (<2 nm) increased with the rank, but other studies showed some discrepancy and did not necessarily support the variation trend [9–11]. Thus, to understand the nature of the pores in coal and reveal the critical variation point of the pore distribution during the coalification process, systematic work is still needed.

The pores of coal can be classified into micro (0–10 nm), transition (10–100 nm), meso (100–1000 nm) and macro (>1000 nm) pores, as stated by Hodot in 1966, and another widely accepted classification of <2 nm, 2–50 nm, and >50 nm was provided by the International Union of Pure and Applied Chemistry (IUPAC) [12,13]. The limits of the accuracy and detection range of different experiment machines determine their applications, e.g., the MIP easily reflects large pores (>18 nm with a maximum intrusion pressure of 35 MPa), while the CO_2 adsorption/desorption can only detect microspores ranging <2 nm [8,14]. The connectively can generally be reflected by the intrusion–extrusion curves of the MIP and nitrogen adsorption–desorption curves, following the classification methods provided by Sing et al. [15]. Recently, the NMR, high-accuracy CT, and FIB-SEM have become more and more widely used for classifying the pore structure and connectivity, even though most of the works are focused on specific basins with specific thermal evolution coals [8,16–19].

Different from the successful development of coalbed methane (CBM) first achieved from low-rank coals in the Powder River (subbituminous C-A) and San Juan (subbituminous A to low-volatile bituminous) basins in the USA, China carried out commercial CBM extraction from high-rank coals in the southern Qinshui basin (anthracite) [20,21]. With the growing CBM production in middle-rank coals (high-volatile A bituminous to semi-anthracite) in the east margin of the Ordos basin, more and more works have focused on the low-rank coal reservoirs in the southern and eastern Junggar basin (subbituminous to high-volatile A bituminous) [22–24].

A systematic research into the coal parameters of different rank is fundamental for a clear recognition of the coal pore types evolution, which is also of great significance in understanding the coalification process and its influence on CBM accumulation and migration characteristics. The primary objectives of this study are 3-fold: (1) to determine the pore structure distributions of different coal ranks through comprehensive methods; (2) to document the key variation points of the pore size distributions during the coalification process from lignite to anthracite; and (3) to provide a reliable explanation of the controlling effect on the coal pore size distributions. For a better understanding of the pore systems of the selected coal samples, both N_2 adsorption/desorption and NMR methods focused on revealing the pore structures and the coal basic parameters including maceral compositions and proximate analysis were conducted.

2. Experimental

Fresh coal samples (approximately $15 \times 15 \times 15$ cm^3) were collected from three active coal mine areas in Dacheng (eastern Junggar basin), Hancheng (east margin of Ordos basin) and Jincheng (southern Qinshui basin) (Fig. 1). The samples from the Junggar basin were deposited in a delta-plain environment, as the coal seams are thick in the Badaowan Formation in the Lower Jurassic [24]. The samples from the eastern Ordos basin are generally of middle-rank coals and were sampled from the Shanxi Formation in the Permian, with its sediment environment also delta plain [8]. The southern Qinshui basin is famous for its high-rank coals, and the samples were deposited in a delta environment in the Lower Permian [26] (Fig. 2). All the samples were collected from coal mines, with its burial depth varies between 200–400 m, showing no influence from dykes or faults. The samples were discussed from two perspectives: the variation of the pore structures of same-rank coals of different macrolithotypes and the variation of pore structures of different rank ranges.

A total of 12 samples were prepared, which are separated into 3 series, the high-rank (*H*) series from the Qinshui basin, the middle-rank (*M*) series from the Ordos basin, and the low-rank (*L*) series from the Junggar basin. Each series was tested with four samples of different macrolithotypes (bright, semi-bright, semi-dull and dull coals) [25]. The macrolithotypes were classified by the whole relative lustre and percentage of bright components, with the bright coals having a volume content of vitrain and clarain (*VC*) > 80%, the semi-bright coals having a *VC* content of 50%–80%, the semi-dull coals having a *VC* content of 20%–50%, and the dull coals having a *VC* content < 20% following the Chinese standard of GB/T 18023-2000.

The samples were carefully packed and sent to the laboratory following Chinese Standard Method GB/T 19222-2003. The samples were first cut into columns with a diameter of 2.5 cm for the NMR test, and the residual samples were used for the other tests. The microscopic maceral analysis was prepared on 3×3 cm^2 polished slabs with a total of 500 points (GB/T 6948-1998). The proximate analysis was conducted on all 12 samples following GB/T 212-2001, with the results of the ash, volatiles, moisture and fixed carbon contents of the coals reported on a dry and ash-free basis [8].

The N_2 adsorption–desorption tests were performed at 77 K on an ASAP 2020 specific surface analyser. Both the five-point Brunauer–Emmett–Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volumes were recorded with their variations as with the pore width distributions [27,28]. The NMR measurements have been systematically reported by Yao et al. [3], including the relationship between the T_2 (transverse relaxation time resulting from magnetic-influenced surface interactions) values and pore radius. To obtain the results of the irreducible water saturation of the coals, a centrifuge was used for the middle- and high-rank coal samples. As the structures of the low-rank coals are easily destroyed, only the fully saturated water results of the coals from the eastern Junggar basin were collected.