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The evolution and formation mechanisms of closed pores in coal

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HIGHLIGHTS

- The closed pore volume represents a low-high-low evolution trend during coalification.
- Tectonic action increases the closed pore volume and specific surface area.
- Heterogeneous matrix shrinkage and tectonic stress are the main causes of closed pore formation.
- The closed pore formation models are proposed.

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ABSTRACT

Closed pores, which have been confirmed to exist in coal, have a dual significance in illustrating the tremendous gas outburst content in coal mining and ascertaining the exact methane content in coal, although it is unknown if this methane can be exploited and utilized. In this paper, the principal objective is to explore the evolution and formation mechanisms of closed pores, regarding which there is a lack of knowledge and understanding. We investigated the varieties of closed pore contents in coalification, combining the small angle X-ray scattering (SAXS) and liquid nitrogen adsorption methods (LNA), and simultaneously analyzed the surface topography of closed pores by scanning electron microscopy (SEM). The closed pore volume represents a low-high-low evolution trend during coalification owing to the appearance of gas pores in the pyrogenic hydrocarbon generation stage. However, the specific surface area increases uniformly due to the increase in the number of micro-pores. The tectonic deformation effect impels the increase of closed pores, which reflected in the larger pore volume and specific surface area in strong deformation coal than that in weak deformation coal. The genesis of closed pores can be summarized as a result of heterogeneous matrix shrinkage, the tectonic compressive stress and the tectonic shear stress. Finally, this work provides a novel method to investigate the mechanism of geological CO_2 sequestration.

1. Introduction

As energy becomes increasingly scarce, more attention has been given to the exploitation of unconventional petroleum, which mainly includes tight oil, tight gas, shale oil, shale gas, heavy oil, tar sand, and coalbed methane (CBM) [1]. Among all of the unconventional gas reservoirs, CBM is a significant resource with a relatively low risk of development, and its utilization has increased rapidly in the last few decades. Coal permeability and gas content are the two most important parameters in the successful recovery of CBM, and both are closely related to the micro-structure of coal [2,3]. The structure and quantity of pores in coal restrict the gas content level.

The strong heterogeneity of coal has been observed in previous studies [4–6], supporting the inference that pores that have formed in coal possess different morphologies. Nie et al. [7] divided the pores in coal into passing, interconnected, dead-end and closed pores according to the coal pore connectivity, the former three types being termed open pores because their better connectivity has a strong influence on the gas adsorption, desorption and diffusion in coal. Closed pores are important because they influence the overall extraction efficiency of methane from coal, and Diamond et al. confirmed that powdering the coal may therefore result in an overestimation of the amount of gas that can be extracted from coal seams [8]. In addition, the existence of closed pores can

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explain the tremendous gas outburst content experienced in mining exploitation. However, the research in this area is limited.

Alexeev et al. [9] found that the contribution of closed pores to total porosity exceeds 60% in most cases, and the tendency of closed pore volumes to increase in outburst-prone coals was also identified. Cai et al. [10] concluded that the closed pore porosity is generally no less than 40% of the bulk porosity for the high-rank coal, and no less than 30% for middle- and low-rank coals. He et al. [11], using deuterated methane injection and SANS methodology, determined that 12–36% of all pores might not be accessible in low-rank coal. Although scholars have performed some investigation into this issue, much controversy still exists surrounding the content of closed pores. Accordingly, the explanation of how coal can form closed pores during its evolution remains an unresolved issue.

Closed pores cannot be easily and directly detected because they are not generally found in contact with the sample exterior. Various methods have been used to study the microstructure of coal, which is quantified by the pore size distribution, specific surface area and pore volume. The most common methodologies are mercury injection porosimetry, and nitrogen, carbon dioxide and methane adsorption [12–14], which all rely on the injection of various fluid probes to reflect the microscopic characteristics of the coal. Other techniques that are also used to characterize porosity, pore size distribution and microcosmic topography mainly include scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), micro-computed tomography (CT), small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) [15–19]. The use of a single experimental method would provide an insufficient investigation because each experimental method has its own advantages and disadvantages, as shown in Table 1. Therefore, our investigation combines different methods that complement one another.

In this paper, the SAXS and LNA are adopted for the closed pore investigation. The SAXS method is able to nondestructively detect all the pore spaces (including open pores and closed pores) in coal, whereas the adsorption method can only provide data on the open pores. The adsorption affinities of CO_2, CH_4 and N_2 in a coal matrix are the highest for CO_2, the lower for CH_4 and the lowest for N_2, suggesting that CO_2 can be adsorbed by the matrix more easily and act to displace the adsorbed methane present on the surface of the coal matrix [20–22]. Therefore, the nitrogen adsorption method may reduce the error caused mostly by the influence of the coal matrix. For this reason, we selected the SAXS and liquid nitrogen adsorption methods (LNA) to quantitatively examine the closed pores in coal. Moreover, AFM and SEM have been applied in previous coal studies, and have been demonstrated to be effective at observing the microcosmic surface morphology [23–27]. The relevant studies to date are as follows: Wu et al. compared the significant contrasts in porosity, shape, size and amount of pores between high-rank anthracite and low-rank bituminous coal by AFM [28], Liu et al. extracted the 3D roughness and fractal characteristics of coal particles using AFM [29], and Pan et al. described the micro-pore shapes and their connectivity using FESEM [30]. Therefore we are able to conclude that AFM and SEM can be used to observe and analyze the microcosmic surface morphology of closed pores in coal.

Therefore, we implemented a combination of different experimental methods (LNA, SAXS, SEM) to quantitatively and qualitatively investigate the changes in closed pores and the microcosmic topography of tectonically deformed coal (TDC). The objective of this study is twofold: (1) to investigate structural characteristics and explore the causes of closed pores in the coal evolution process; (2) to analyze the micro-surface topography and summarize the evolution and formation mechanisms of closed pores in tectonically deformed coal.

Table 1
A comparison of different experimental methods.

Experimental methods	Advantages	Disadvantages
Adsorption methods	They can only be used to quantitatively measure the open pores.	The coal pore microcosmic topography cannot be observed directly.
Optical methods (SEM, AFM, TEM)	They can be used to observe microcosmic topography.	The image is two-dimensional, and three-dimensional quantitative analysis of coal samples is impractical.
Optical methods (micro-CT)	The microcosmic topography can be observed and quantitatively analyzed.	The images and related parameters are given in micron scale instead of nanoscale.
Scattering methods (SAXS, SANS)	The quantitative analysis of total pore space is feasible in nanoscale.	The total pore microcosmic topography is impossible to detect.

2. Experimental

2.1. Samples

To investigate the structural changes in the closed pores of different coal ranks, representative samples were collected for our study. The samples were obtained from coal seams originating in the early Permian (P_1^1) and located in the Pingdingshan colliery of Henan Province, the Hebi colliery of Henan Province, the Zhaozhuang colliery of Shanxi Province, and the Fenghuangshan colliery of Shanxi Province in north China. In accordance with China's coal industry standard MT/T1053-2008, the maximum vitrinite reflectances of the selected samples ($R_{o,max}$ = 1.28–3.80%) were classified as upper intermediate-rank bituminous coal, high-rank bituminous coal, low-rank anthracite coal and middle-rank anthracite coal depending on the degree of metamorphism. Quantitative tests of coal rank and petrographic characteristics were performed on the polished sections of the samples using a standard polarizing microscope and a microdensitometer (MPV-3). The maximum reflectance values of vitrinite, the percentage composition of vitrinite, inertinite, and exinite, and the mineral content were also measured. The general characteristics of the coal samples were shown in Table 2. In addition, the structural descriptions and classifications were presented in Table 3, according to Ju et al. [31]. It should be noted that samples 1, 1-1 and 2, 2-1 are from the same collieries respectively but with different deformation degrees duo to the various distances of sampling location to the folds and faults.

2.2. SAXS measurement

The SAXS data were collected from the SAXSess mc^2 facility produced by Anton Paar GmbH, which emits X-rays (λ = 1.542 Å) using a copper source energized at 45 kV and 50 mA. A three-slit system was used to collimate the incident X-ray beam. The first and the second slits were located downstream from the monochromator with a distance of 0.9 m and 4.8 m, respectively, and they were used to define the beam size and divergence. The third slit was a guard slit, which was placed in the closest possible location to the sample. To protect the detector from the radiation damage of the direct beam, several beam-stops with different sizes and shapes (circular and rectangular) were available [32]. A schematic diagram of the SAXS experimental set-up was shown in Fig. 1. The scattering angle (2θ) ranged from 0.08° to 5°, and SAXSess had an excellent resolution ratio and was able to detect the ~0.2–