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Study on the pore structure and oxygen-containing functional groups devoting to the hydrophilic force of dewatered lignite

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ABSTRACT

In order to explore the water-holding capacity of dewatered lignite and the contribution of pore structure and oxygen-containing functional groups to it, a kind of typical Chinese lignite was dried under the atmosphere of nitrogen for different temperatures and times, and then was subjected to a process of moisture re-adsorption at the temperature of 25 °C and relative humidity of 75%. Nitrogen adsorption and chemical titration methods were used to examine the pore structure parameters and amounts of oxygen-containing functional groups, respectively. The results indicate that the porous structure and oxygen-containing functional groups in lignite are two main factors influencing the hydrophilicity of dewatered coal, and their contributions are varied with the change of drying conditions. The change of water-holding capacity of pore structure is primarily attributed to the shrinkage or collapse of macro- and mesoporous and it decreases with the increase of drying temperature. The oxygen-containing functional groups mainly include phenolic hydroxyl, carbonyl, carboxyl and methoxyl groups, and the order of their hydrophilicity is: carboxyl group > phenolic hydroxyl group > carbonyl group > methoxyl group. Moreover, the water-holding capacity for the same kind of oxygen-containing functional groups in dewatered coal obtained at different temperature is not a fixed one, their hydrophilic forces decrease with the increase of drying temperature. For the coal samples dried for 60 min under different temperature, the contribution of pore structure and oxygen-containing functional groups to the equilibrium moisture content (EMC) of dewatered lignite is: pore structure > phenolic hydroxyl group > carboxyl group > carbonyl group > methoxyl group. The contribution of total oxygen-containing functional groups to the EMC at below 280 °C is more obvious, and that of pore structure is the principal factor thereafter.

1. Introduction

Low rank coal is playing an increasingly important role in supplying primary energy based on its rich reserves in the world. But its utilization range is greatly limited due to the feature of high water content, which results in lower calorific value, higher fuel consumption and higher transportation cost [1]. The high moisture content of low rank coal is mainly determined by its porous structure and abundant oxygen-containing functional groups [2,3]. The interaction between pore structure and moisture has been studied widely in literatures. Kelemen et al. [4,5] found that coal samples had gel-like structures which shrank and swelled in response to the loss and uptake of moisture. During the drying process, the pore structure shrank as the moisture was evaporated and the shrinkage was irreversible [6]. The irreversible shrinkage, which altered the initial structure of lignite as a colloidal gel, finally resulted in a relatively less equilibrium moisture content of lignite after re-adsorption. Oxygen-containing functional group acted as the primary adsorption site is also a significant reason for the high water content in lignite [7]. As polar groups, the oxygen-containing functional groups provide with strong hydrophilicity, especially the active oxygen-containing functional groups such as carboxyl group [8,9]. The kinds and amounts of oxygen-containing functional groups decide the water-holding capacity of lignite, to some extent, by hydrogen bonds. It has been suggested that the oxygen-containing groups in lignite mainly existed in the forms of carboxyl group (COOH), phenolic hydroxyl group (Ar—OH), carbonyl group (C=O), methoxyl group (OCH_3) and ether bond (—O—) [10]. Generally, the groups of COOH, Ar—OH, C=O and OCH_3 belong to active oxygen-containing groups and —O— belongs to inactive oxygen-containing groups. The electron cloud density around the active oxygen-containing groups is higher than that of inactive oxygen-containing groups, so moisture molecules are easier to combine

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Table 1
Proximate and ultimate analyses of lignite used in this study.

Proximate analysis/wt%			Ultimate analysis/wt%, daf				
M_t	A_{ad}	V_{daf}	C	H	O[a]	N	S
29.59	11.96	45.15	69.39	4.76	23.57	0.77	1.51

Note: ad is air-dried basis; daf is dry and ash-free basis.
[a] By difference.

with these active oxygen-containing groups by hydrogen bonds. In order to lower the hydrophilicity of coal, several upgraded methods of lignite including heat treatment, vacuum treatment and solvent treatment have been conducted to remove these active oxygen-containing functional groups [11–14].

The active oxygen-containing functional groups and rugged physical structure existed on the surface of lignite lead to its relatively high specific surface energy and strong polarity, which keep the coal samples in non-equilibrium state. According to the lowest energy principle, moisture molecules are easy to attach onto the unstable structure of coal samples to lower the specific surface energy and reach a relatively equalized state. The adsorption capacity of adsorbent on the surface of solid is associated with its physical and chemical properties. [15,16]. The adsorption mechanism of water vapor on the surface of coal has been studied by some researchers and they considered that the interaction bonds between water and coal were mainly free water held by physicochemical forces, adsorbed water determined by hydrogen bonds, and chemically bonded water [17]. With the increase of relative pressure, water molecules firstly combine with the oxygen-containing functional groups on the surface of lignite by hydrogen bonds. Then further adsorption among the water molecules is formed by hydrogen bonds or Van der Waals' force. Finally, the water clusters will condense and fill the structure of micropores and capillary of the coal [18].

To explore exactly the surface stability of dewatered lignite and its influence factors, the pore structure and oxygen-containing functional groups of raw lignite and its dewatered samples from different drying conditions were examined and then associated the relationships between the hydrophilicity of the dewatered lignite and its physical and chemical structures by multiple regression equations.

2. Experimental

2.1. Sample preparation

Lignite from Inner Mongolia in China was used in this study. The raw coal was ground and sieved to the particle sizes of 0.250–0.425 mm under the atmosphere of nitrogen at ambient temperature to avoid the possible effects of oxygen in air. The proximate and ultimate analyses of coal sample are listed in Table 1. M_t refers to the total moisture content which was measured at the temperature of 105 °C for 2 h under nitrogen.

The raw coal was dried in a fixed-bed reactor by being heated in an electric furnace under nitrogen with the flow rate of 400 ml/min to prevent the samples from reacting with oxygen in air. The drying temperature varied from 120 to 360 °C and the drying time ranged among 2.5–60 min. The dewatered coal obtained under drying conditions is marked as $DCT_a t_b$. For example, $DCT_{120}t_{60}$ means the sample of drying lignite 60 min at 120 °C. The drying efficiency (*DE*) of raw lignite sample was calculated according to the following formula (1).

$$DE = \frac{m_R - m_D}{m_t} \times 100\% \quad (1)$$

where, m_R is the initial weight of coal sample, m_D is weight of coal sample after drying, and m_t is total moisture content of coal sample.

2.2. Moisture re-adsorption measurement

A Constant Temperature and Humidity Chamber (HC-II, Shanghai Yiheng of China) was used to examine the moisture re-adsorption behavior of the coal samples. The glass petri dishes contained coal samples were placed in the chamber and maintained at the temperature of 25 °C and with a relative humidity of 75%. The coal samples were weighed every hour until their weight became constant. At this moment, the moisture content of sample is defined as the equilibrium moisture content (EMC) and it is calculated according to Eq. (2).

$$EMC = \frac{m_a - m_b + m_c}{m_d} \quad (2)$$

where, m_a and m_b are the weight of dewatered coal after and before re-adsorption moisture, respectively, m_c is the content of residual moisture in dewatered lignite obtained under drying conditions. And m_d is the weight of absolutely dried coal, which is obtained by subtracting the total moisture content from the raw coal weight.

2.3. Analysis of pore structure

The pore structure of dewatered coal was examined by nitrogen adsorption at 77 K using a nitrogen adsorption analyzer (JW-BK122 W, China). In order to guarantee the experimental accuracy, the coal samples were pretreated at 105 °C for 3 h to remove the moisture or adsorbate attached on their surface. To measure the pore structure of the raw coal, the coal sample was pretreated at 40 °C overnight under vacuum to remove the moisture on its surface but not to destroy its pore structure. The specific surface area was computed according to BET equation, the pore volume and pore size distribution were calculated by BJH model.

2.4. Analysis of oxygen-containing functional groups

The amount of oxygen-containing functional groups in lignite was determined according to the conventional ion exchange and chemical titration methods. The mean value was obtained in bipartite tests after eliminating the accidental error. The margin of error for each titration was kept below ±5% in view of the heterogeneity of coal.

To investigate the amount of carboxyl group, firstly, the raw lignite or its dewatered sample (about 1.0 g) was soaked in the solution of $NaHCO_3$ (0.1 M, 50 ml) at ambient temperature for 24 h and then aqueous HCl solution (0.1 M) was used to determine the amount of $NaHCO_3$ remained in the filtrate. Thus the content of $NaHCO_3$ consumed by carboxyl groups would be obtained. Blank experiment was conducted as a contrast at the same time.

The content of phenolic hydroxyl group was obtained in accordance with the difference value of the amount of total acidic group (summation of phenol and carboxylic acid) and carboxyl group. To determine the amount of the total acidic group, the raw coal or dewatered sample (about 1.0 g) was soaked in $Ba(OH)_2$ (0.05 M, 60 ml) at ambient temperature. After 24 h soaking, the coal sample was filtered and filtrate was neutralized with HCl (0.1 M) to determine the amount of $Ba(OH)_2$ consumed by coal samples. Then the quantities of total acidic group and phenolic hydroxyl group were obtained.

The amount of carbonyl group was examined by converting carbonyl group into phenylhydrazone with phenylhydrazine (20 g/L, 50 mL) at 120 °C for 24 h, and then the excess phenylhydrazine was oxidized by phenanthroline. The amount of phenylhydrazine reacted with carbonyl group could be calculated by the quality of