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Effect of oxidation processing on the surface properties and floatability of Meizhiyou long-flame coal

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ABSTRACT

The surface properties of coal play a crucial role in its flotation, therefore it is of great significance to investigate the changes in both chemical structure and surface morphology in oxidation process of low rank coal. In this paper, the mechanism of difficult floatation of oxidized coal was highlighted. The surface hydrophobicity and floatability of Meizhiyou long-flame coal before and after oxidation processing with H_2O_2 solution at different concentration were evaluated by induction time and contact angle analyses as well as flotation tests, while the changes in its surface properties in the oxidation process were analyzed by XPS, FTIR, BET and SEM measurements. The maximum increase extent of induction time between bubbles and oxidized coal particles reached to 13217% while the maximum reduction extent of combustible matter recovery reached to 95.28%, which indicated the floatability of oxidized coal particles almost decreased exponentially along with the increase of concentration of H_2O_2 solution. Additionally, the results suggested the active chemical functional groups of $> CH_2$ peak at 1437 cm^{-1}, $-CH_3$ peak at 1373 cm^{-1} and C—O—C peak at 1215 cm^{-1} were susceptible to oxidation. After oxidation processing, on the one hand, the content of hydrophobic groups on coal surface showed an obvious decrease while that of hydrophilic groups showed a significant increase. What's more, the content of carbonyl group had a close correlation with the extent of oxidation of the coal sample. On the other hand, it was found that the surface morphology of coals was significantly changed after oxidation process, and there were more pores and cracks on the coal surface. As a result, the contact angle of coals showed a significant decline after oxidation processing and it declined more quickly with the increase of contact time. Consequently, the poor flotation performance of oxidized coals may be attributed to the dramatic changes in both surface chemical structure and surface morphology in oxidation process.

1. Introduction

Coal is an important fossil energy source for economic development in the world, particularly in China, and it is taken as the dominant primary energy source. Coal was of vital importance to China's economic development over the past decades, and it was predicted that coal's share of China's primary energy consumption would still be 47% in 2035. Whereas, with the depletion of high-quality coal resources, low rank coals (i.e., lignite, long-flame coal, Non-caking coal and slightly-caking coal) accounting for 45.68% of proven coal reserves provide an important guarantee for China's economy and society developments as well as security of energy supply. As a result, much attention has been paid to obtain available clean fuels by upgrading low rank coals as well as coals difficult to float.

Froth flotation is widely taken as the most efficient separation method for the cleaning of fine coals, which is based on the differences of the physical and chemical properties of mineral surface [1,2]. In flotation, the coal particles with natural hydrophobicity adhere themselves onto air bubbles thus are transferred to froth products, while gangue minerals with good hydrophilicity fail to accomplish the attachment and mineralization processes thus are discharged as tailings. Consequently, the surface properties of coal play a crucial role in its flotation process [3,4]. However, low rank coals are difficult to float using conventional collectors, diesel oil and kerosene, because of strong surface hydrophilicity caused by the presence of abundant oxygenated functional groups [5–9]. What's more, due to a lot of active chemical groups on the surface resulting from low degree of coalification, the oxidation of low rank coal is very easy to occur even the presence of small amounts of oxygen [10–13]. As a consequence of oxidation, both surface chemical structure and surface morphology of the coal surface

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are changed [10,13–15], among which the most notable change is the increase of surface oxygen content [16]. Meanwhile, the influence of changes in surface topography, such as pore structure, pore volume, pore diameter and surface area, on floatability can not be ignored. Both them further increased the surface hydrophilicity of low rank coals [12,17,18].

It is very widespread that oxidation reaction of coals and oxygen at atmospheric conditions, ranging from low rank sub-bituminous to high rank anthracite [11]. Coal oxidation at low temperatures is a complicated process, which focuses on the oxidation of coal in oxygen or air below 200 °C [12]. It was reported that the oxidation process mainly included the following steps. Firstly, adsorption of oxygen molecules on surface of coal particles and transport within coal pores took place. Subsequently, the physical adsorption and chemical reactions between coal and molecules of O_2 occurred at both surfaces of coal particles and coal pores, which gave rise to the generation of oxygenated functional groups and gaseous products. Meanwhile, in the latter process, a large quantity of heat was released [10,19,20]. Furthermore, changes in chemical groups during oxidation have been investigated by many researchers. It was concluded that, initially, peroxygen (−OO−) was formed [19], hydroperoxides (−O−OH) were formed later as an intermediate [10,21,22]. It was also reported that the decomposition of hydroxyl groups (−OH) resulted in the generation of carbonyl groups (−C═O) and subsequently brought about the formation of carboxyl groups (−COOH) [19,21]. What's more, Calemma et al. [23] investigated the chemical changes during dry phase oxidation of a sub-bituminous coal within the 200 to 275 °C temperature range through FTIR analysis, and it was found that the content of oxygenated functional groups increased with the increase of temperature. Additionally, the oxidation reactivity of aliphatic structure was stronger than that of aromatic structure. Similar research indicated the α-CH2 groups to polyaromatics were found to be most susceptible to oxidation [24,25]. Xia et al. [26] also found the content of hydrophilic functional groups of anthracite coal after high temperature heating process showed a significant increase, while the content of hydrophobic functional groups decreased, making the hydrophobicity of anthracite coal decreased. Furthermore, Xia and Yang [27] studied the changes in surface properties of anthracite coal before and after inside/outside weathering processes by XPS and SEM analyses, and the similar results were obtained. In addition, it was found that the surface roughness of anthracite coal was increased after the weathering processes based on the SEM results, and the contact angle was correspondingly reduced.

In the present work, the ultra-low-ash coal collected by float-and-sink experiment was taken as the materials, and H_2O_2 solutions with different concentration were used to simulate the different degrees of oxidation of the coal sample. The study focused on the mechanism of difficult floatation of oxidized coal. The changes in surface properties of coals in oxidation process were investigated by XPS, FTIR, BET and SEM analyses, while the changes in surface hydrophobicity and floatability were evaluated by induction time and contact angle analyses as well as flotation tests.

2. Materials and methods

2.1. Materials

Long-flame coal samples less than 0.5 mm were collected from Meizhiyou Coal Preparation Plant, Shendong Mine Area in Shanxi Province in China, and its ash content is 16.45%. In this investigation, to explore the effect of oxidation on the properties of the coal more precisely, the ultra-low-ash coal (pure coal) less than 1.30 g/cm^3 were obtained with the float-and-sink experiment using a mixed organic heavy liquid of benzene and carbon tetrachloride (CCl_4), which ash content is 1.91%. In order to simulate the different degrees of oxidation of low rank coal in the natural environment, the 15 wt%, 30 wt%, 40 wt %, and 50 wt% H_2O_2 solutions were employed. About 8.0 g pure fine coal particles were immersed in 80 ml H_2O_2 aqueous solution in a 250 ml conical flask for 24 h at room temperature. The pure coals before and after oxidation by different peroxide solutions were recorded as M0, M15, M30, M40 and M50, respectively. The coal samples were filtered, vacuum dried and stored in a dry dish for SEM and BET measurements.

2.2. XPS measurements

In order to investigate the surface elements and functional groups of pure raw/oxidized coals with XPS analysis more precisely, the pure coal was first ground to −0.074 mm then the oxidation processing was taken. The XPS analysis was performed with X-ray photoelectron spectroscopy (ESCALAB 250Xi) equipped with Al Kα (1486.6 eV) source. The analyses were carried out in an ultra high vacuum environment at a constant temperature of 25 °C. The wide scanning test for the elements of carbon, oxygen, nitrogen, silicon and aluminum and the narrow scanning of carbon were performed with step energies of 1 eV and 0.05 eV respectively. After smoothing the spectra and subtracting the Shirley background, binding energy calibration was performed by setting the C1s peak at 284.8 eV. The XPSpeak4.1 software was employed for the further data analysis, i.e., peak fitting.

2.3. FTIR measurements

Like sample preparation for XPS measurements, coal particles were first ground then oxidized with H_2O_2 solutions. The fine coal powder was filtered, vacuum dried then with potassium bromide (KBr, about 200 mg) pressed into pellets for the measurements with Fourier Transform Infrared Spectroscopy (Vertex 80v, Bruker). The detailed operating parameters for FTIR measurements were as follows: scanning frequency was 32 and the spectra resolution power was 4 cm^{-1}; scanning range was between 4000 and 400 cm^{-1}; wave number accuracy was less than 0.1 cm^{-1}. The data processing of smoothing and subtracting background for spectra was conducted with Peakfit v4.12 software.

2.4. Contact angle measurements

Coal samples prepared with the above grinding and oxidation processing were pressed into thin circular plates with about 15 MPa pressure then used to take the contact angle measurements with a contact angle measurement apparatus. Angle measurement way was used in the measurement. Three trials were conducted for the reproducible result in each measurement. The variation of contact angle along with contact time was recorded.

2.5. BET measurements

The pore structure of long-flame coal, including pore volume, specific surface area, pore size distribution and average pore diameter, is critical to its hydrophobicity as well as its flotation. Pores in coal are filled with water in flotation pulp, leading to a decrease in hydrophobicity. In this work, specific surface area measurements were performed with Automatic Specific Surface Area/Pore Analyzer (BEL Company, Japan). For a typical measurement, about 0.6 g coal particles was held in the sample tube and sample degassing processing was taken for 12 hours under vacuum condition at 105 °C. Afterwards, liquid nitrogen adsorption and desorption at 77 K were carried out and the adsorption/desorption isotherms were obtained. Based on the isotherms, the total pore volume, specific surface area and average pore diameter were analyzed by means of the Brunauer–Emmett–Teller (BET) method.