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Exploring effect of water immersion on the structure and low-temperature oxidation of coal: A case study of Shendong long flame coal, China

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ABSTRACT

To investigate the effect of water immersion on the structure and low-temperature oxidation of coal, the untreated coal and soaked coal for 90 days and 180 days were prepared and compared. The surface morphology, pore structure, physical oxygen absorption and free radical parameters were characterized by scanning electron microscope (SEM), N_2 adsorption, chromatography oxygen absorption and electron spin resonance spectrometer (ESR). The crossing point temperature (CPT) and oxidation products of coal samples were investigated using oxidation kinetics experiment. Compared with the untreated coal, larger average pore diameter, more free radical species and concentration were found in the soaked coal. Moreover, more pores with diameter > 10 nm were formed due to soaking process, which would improve the transport capacity of O_2 in pores to react with active sites on pore surfaces in the soaked coal. At the same time, the soaking process increased the physical oxygen absorption of coal by opening up more obturator channels. Moreover, the longer the soaking time, the more obvious the effect of the soaking process on the long flame coal. In addition, immersion process increased the indicator gas production rate of the soaked coal, and decreased its crossing point temperature, increased the risk of spontaneous combustion of Shendong long flame coal in general.

1. Introduction

The spontaneous combustion of coal (mainly the low temperature oxidation) is one of the most important disasters in the process of coal exploitation. There are many factors affecting the spontaneous combustion of coal and the casualty accident, waste of resources, and environmental pollution attributed to the spontaneous combustion were very serious [1–5]. Since the large demand for coal, the mining depth continuously increases due to the exhaustion of shallow coal reserves, and the lower coal seams began to be exploited such as the coal mine in the west of China – Shendong Bulianta mine. According to the field situation, although the geological conditions and metamorphic degrees are similar, coal spontaneous combustion accidents occurred more frequent in the upper coal goaf then the lower goaf, and the time interval of ignition is shorter. This was because the surface water and ground water leaked to the upper gob along the mining fissures, which put the residual coal in the state of water immersion for a long time. When the lower coal seam is mined, it is necessary to probe and release water for safety, which would cause the “water-gas replacement”. In addition, the exploitation of the lower coal seam caused the redevelopment of the upper cracks and resulted in severe air leakage, creating an appropriate oxygen environment for the oxidation of the remaining coal and greatly increasing the risk of spontaneous combustion of the remaining coal.

The coal in goaf would be swollen by water immersion for a long time. The soluble organic and inorganic matter in the coal would be dissolved in water, and there will be a certain physical and chemical change [6–8]. Therefore, it is urgent to study the low temperature oxidation characteristics of the coal that had been prolonged immersion. Many papers have reported the effect of soaking process on coal structure and properties. Norinaga [9] found when partially or completely dried brown coals or lignites exposed to water, they swell, often do not regain their original volumes. This is due to the swellable colloidal nature of coal. The increase in the free volume of coal macromolecules gives the coal a larger surface area. And the lower rank coals are swollen by water to a greater extent because of their greater hydrophilicity. The swelling effect of water on 15 coal samples at normal temperature and atmospheric pressure was studied by Fry [10], the results showed that the volumetric swelling induced by moisture sorption ranged from about 0.5% to 5%, immersion of the coal in water

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served to completely fill these pores. Volumetric moisture sorption and swelling were found to be closely related according to a single linear relationship and there was no further swelling of the coal under fully saturated conditions. Jones [11] studied the swelling behavior of lignite in two component mixtures of acetone-water and methanol-water, and found that coal had a certain swelling due principally to imbibition of solvent. Liu [12] demonstrated that the volumetric swelling strains attained high volatile bituminous coal at equilibrium showed a near-linear relation with relative humidity, reaching a value of 1.37–1.43% at around 95% relative humidity. In addition, many studies have been made on the effect of water on spontaneous combustion of coal at home and abroad. Wang [13–14] believed the physical combination of water in coal can prevent oxygen molecules from moving in the pores of the coal, and the oxygen consumption rate decreases when the coal samples increase in water content. While the loss of chemically bound water means the change of hydrophilic structure of coal, which can slow down the rate of peroxide production during coal chemical adsorption of oxygen. Xu [15] used TA-DSC showed that moisture content has different effects on the spontaneous combustion tendency of different kinds of coal, and the most vulnerable spontaneous combustion critical water content is obtained. Zhang [16] claimed that water molecules can destroy the hydrogen bonds between molecules, which will result in the increase of cavity volume and interconnectivity, and this change is conducive to the diffusion of O_2 molecules. The above studies mainly unilaterally aimed at the effect of the structural change of the coal after immersion or the influence of natural water or artificially added water in coal on the spontaneous combustion characteristics, little attention has been devoted to investigate the effective combination of the two to analyze the structural changes and oxidation spontaneous combustion characteristics of coal after immersion in water. In view of this situation, we started from pore change, and deeply analyzed the low temperature oxidation characteristics of the long-term soaked coal in terms of free radical characteristics, CPT and indicator gas.

2. Experimental and methods section

2.1. Coal samples

We selected Shendong long flame coal (SD) for the experimental test, which had the characteristics of shallow buried and immersed frequently, then sealed it and sent it to the laboratory. The coal sample surface was stripped under the vacuum condition by manual crushing, and the sizes of coal particles in the range of 0.18 mm–0.27 mm were sieved. The coal samples were placed in the wide neck flask, then we added distilled water, sealed and soaked coal for 90 days ($-S_{90}$) and 180 days ($-S_{180}$) at room temperature. The ratio of water to coal is 5:1. After soaking the coal, we filtered the wet coal and spread it in the flat bottom evaporating dish and dried it 96 h under indoor air environment. At the same time, we have to control the similarity of the quality and thickness of the padding to ensure the consistency of the moisture content in the air drying. The untreated coal was also placed under the same environmental conditions. Before the experiment, all the coal samples were put into vacuum drying box at 40 °C for 48 h to remove the external moisture of the coal, so as to eliminated the effect of moisture on the experimental results [17]. Proximate and ultimate analysis were summarized in Table 1.

Table 1
Proximate and ultimate analysis of the coal samples.

Coal samples	Proximate analysis (%)				Ultimate analysis (%)				
	M_{ad}	A_d	V_d	FC_d	C_d	H_d	O_d	N_d	$S_{t.d}$
SD	6.34	7.43	31.33	61.24	72.57	3.99	13.52	0.75	1.76
SD-S_{90}	6.63	7.41	31.50	61.09	72.87	3.71	13.44	0.74	1.79
SD-S_{180}	6.53	7.18	31.54	61.28	72.77	3.80	13.47	0.77	1.95

M_{ad} = moisture content (the relative deviation of water content of untreated and soaked coal < 5%); A_d = ash; V_d = volatile matters; FC_d = fixed carbon; ad = air-dry basis; d = dry basis; St.d = total sulfur (dry basis).

2.2. Measurement of micromorphology and pore structure

A scanning electron microscope (SEM, Quanta 250) was employed to observe the change of surface morphology of coal before and after the immersion [18]. The low-temperature N_2 adsorption (BK122W) was employed to determine the microstructure characteristic parameters. After three samples were degassed and weighed, the high purity N_2 was used as the adsorbate to measure the adsorption volume under different pressure at the boiling point temperature of liquid nitrogen (77 K). The BET and BJH model was used to calculate the specific surface area and pore size distribution data of the inner pores [19–20]. These equations were obtained:

$$\text{BET equation:}\quad \frac{P}{V\,(P_0-P)} = \frac{1}{V_m\cdot C} + \frac{C-1}{V_m\cdot C}(P/P_0) \tag{1}$$

where P is the adsorbate partial pressure, P_0 is the saturation vapor pressure, V is the amount absorbed, V_m is the monolayer volume, C is the adsorption energy constant related to the sample,

$$\text{BJH equation:}\quad r_k = -4.14\left(\log\frac{P}{P_0}\right)^{-1} \tag{2}$$

$$t = -4.3\left[\frac{5}{\ln\left(\frac{P}{P_0}\right)}\right]^{-1/3} \tag{3}$$

$$r = r_k + t \tag{4}$$

where r_k is Kelvin radius, t is the thickness of the adsorption layer, r is the radius of pore.

Furthermore, the method of chromatographic oxygen absorption determine the spontaneous combustion tendency of coal by testing the physical oxygen absorption at 30 °C [21–22]. Therefore, this paper used this method to analyze whether the soaking process changes the physical oxygen absorption of the coal to further determine the change of the pore structure.

2.3. Measurement of free radical characteristics

According to the mechanism of free radical chain reaction, it is of great significance for the research of coal spontaneous combustion to study the change regulation of free radical parameters in the process of coal oxygen compound [23–26]. Electron spin resonance spectrometer (ESR, Nissan JES-FA200) was utilized to analyze the free radical characteristics of three kinds of coal samples. We set the center magnetic field intensity is 322.974 mT, the microwave power is 0.998 mW, the scanning width is 5mT, the magnification is 1.6, the center frequency is 9038 MHz, the modulation width is 0.1 MT and the time constant is 0.03 s. The 15 mg samples were weighed and oxidized at the preset temperature (20 °C 50 °C 70 °C 90 °C 120 °C for 3 min, simultaneously, the air with a flow of 30 mL/min was put into it. Then the ESR spectrum was scanned and measured immediately and the scanning time was 1 min. The data was then accurately recorded.

2.4. Measurement of crossing point temperature (CPT) and indicator gas

The crossing point temperature has been used to evaluate the spontaneous combustion characteristics of coal since twentieth Century [27–29]. When the furnace temperature is increased at a certain rate, then the temperature of coal is equal to the furnace temperature due to heat conduction and self heating, the temperature at the cross point of the coal temperature-time curve and the furnace temperature-time curve is the crossing point temperature. The gas products (CO, C_2H_4,