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Effect of acid treatment on the characteristics and structures of high-sulfur bituminous coal

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HIGHLIGHTS

- A series of modern advanced analysis and measurement technologies have been used to analyze the characteristics of coal samples after the acid treatment.
- The hydrochloric has little influence on the coal characteristics, but the nitric acid takes the oppositie approach.

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ABSTRACT

In this paper, a series of modern advanced analysis and measurement technologies such as X-ray Fluorescence (XRF), X-ray Diffraction (XRD), ^{13}C Nuclear Magnetic Resonance (^{13}C NMR), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) have been used to analyze the sample after acid treatment. The result shows that after hydrochloric acid treatment and combined treatment of hydrochloric acid/nitric acid, the water content of coal sample and fixed carbon increase to some extent while the volatile component and ash content decrease. Acid treatment has reduced the content of carbon, hydrogen and sulfur but increased the oxygen content. In addition, hydrochloric acid treatment has resulted in the increase of chlorine content in coal and nitric acid treatment increase the nitrogen content. Acid treatment will influence the microcrystalline structure of the coal and improve the aromaticity which finally makes the carbon atom arrangement more orderly. After hydrochloric acid treatment, the ratio of methyl carbon, aliphatic carbon attached to oxygen, carboxyl carbon and carbonyl carbon decreases slightly, while that of other carbon functional groups increases correspondingly. The raw coal shows large differences from coal sample after the beneficiation of hydrochloric acid and nitric acid. The content of methyl carbon and the aliphatic carbon attached to oxygen is reduced obviously, while that of methylene and carbonyl carbon is raised dramatically. After acid treatment, the ratio of C—C bond and C—H bond on the coal surface increases gradually, but carbon in oxidation state decreases step by step which means acid treatment will destroy the active functional groups on coal surface and reduce the ratio of oxygen-containing functional groups such as ether bond and hydroxyl group. Meanwhile, acid treatment will influence the organic sulfur such as mercaptan, thioether, sulfoxide, sulfone, and sulfonate, which will change the component of organic sulfur on coal surface and decrease its content. The coal particles have no obvious change after the beneficiation of hydrochloric acid and nitric acid but their surface morphology has changed. The edges of coal particles turn obscure and their surface becomes blurred. The combined treatment of hydrochloric acid/nitric acid has increased the specific surface area of coal sample, leading to more micropores on coal surface, and thus oxygen molecules are more easily absorbed by the coal. In general, hydrochloric acid treatment has little influence on coal characteristics, chemical construction of the organic matter, inorganic minerals, functional groups on coal surface, microstructure, etc., while nitric acid treatment has significant effect on coal quality. Therefore, the influence must be taken into consideration when using the nitric acid to pretreat the coal sample.

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1. Introduction

Coal is a kind of complex mineral which is made up of inorganic minerals and organic matter [1,2]. On the one hand, the content and type of the mineral substances will influence the transportation and storage, the development and usage of the coal in the process of using coal [3–13]. On the other hand, most of pollution problems relating to coal combustion are concerned with the inorganic minerals [14–16]. Generally, all the elements except C, H, O and S are classified into mineral substance and they can be sorted into the following types, namely, clay, sulfide, carbonate, oxide, chloride, silicate, hydroxide and phosphate [17]. The common mineral substances such as quartz, clay, carbonate and pyrite generally account for 90% of the inorganic minerals in coal [18]. People usually separate inorganic minerals from organic minerals because of the complexity of coal structure [19]. The acid leach is a commonly used method to remove minerals in coal. Moreover, from the perspective of clean utilization, acid treatment of deashing plays an important role in the pretreatment of coal, and whether acid treatment will influence the structure and activity of coal has attracted broad attention from scholars [5,13–16,19–24]. Many researches have shown that the acid leach of coal does have impact on its structure and activity, with the impact of hydrochloric acid and hydrofluoric acid on coal structure after demineralization treatment mainly caused by acid-induced chemical processes such as ester hydrolysis reaction and Friedel-Crafts Reaction [25]. Hengel et al. deem that since metallic ions have positive catalytic action on the gasification of lignite, acid treatment has removed most of the metallic ions in coal and reduced the semicoke activity of lignite [26]. Through the comparison of activation energy of 25 lignite samples before and after acid treatment, Hanzade et al. have found that acid treatment will decrease the combustion activity of lignite [27]. Wang et al. have studied the influence of acid treatment on the structure and pyrolysis characteristic of lignite and drawn the conclusion that HNO_3 treatment will obviously change the structure of organic matter in sulfur coal. HF and HNO_3 treatment has positive effect on the pyrolysis reactivity of lignite [28]. Through conducting demineralization treatment on six coal samples with HCl/HF and making extraction and analysis on samples with pyridine solvent, Larsen et al. have drawn the conclusion that acid treatment has little effect on the macromolecular structure of coal and the effect mainly comes from ion exchange and the removal of mineral [25]. Tekely et al. used ^{13}C NMR to test the coal structure before and after acid treatment and the results show that both the aliphatic carbon and alkylated aromatic carbon have changed [29]. Analysis results of Alemany and ^{13}C NMR have demonstrated that there is no enhancement of the signal for coal sample after acid treatment while the reduction of signal may be caused by the change of aliphatic carbon or chemical shift [6]. Wei et al. have adopted ^{13}C NMR to study the change of carbon component of lignite before and after acid treatment. The results have indicated that the combined acid treatment can destroy the polycyclic structure to form a ring structure which decreases the size of aromatic cluster [30]. Murat et al. have found that it is easier for lignite to be oxidized after deashing treatment. It is because the sulfate formed in initial period of oxidation will protect methyl and methylene [31]. Radovic et al. have investigated the gasification characteristics and char reactivity of North Dakota lignite after demineralization treatment by using HCl and HF and have found that demineralization treatment has reduced the reactivity of coal char and increased the amount of pyrolysis tar as well as gaseous hydrocarbons [32]. Rubiera et al. have researched on the combustion characteristics variation of high volatile bituminous coal which is deashed after acid treatment. The results have shown that the combustion characteristics are significantly enhanced and SO_2 release is notably reduced after the treatment [33]. Through conducting deashing and desulfurization treatment on ASSAM coal with alkali and hydrochloric acid, Samit have found that alkali and acid treatment have a good effect on the removal of minerals and sulfur in coal [34]. Although numerous researches have been conducted on the influence of deashing treatment, most of these researches are aimed at lignite, while just few studies focus on the more widely used soft coal. Furthermore, previous studies mainly adopt the combined treatment of hydrochloric acid and hydrofluoric acid, while little attention has been paid to hydrochloric acid and nitric acid treatment. The emission of SO_2 caused by coal combustion has led to serious environmental pollution since S is the primary noxious element in coal. Researches on geochemical property, distribution law, occurrence mode and washing desulfurization of sulfur in coal (organic sulfur and inorganic sulfur) have attracted scholars' attention. From the aspect of clean utilization, the hydrochloric acid can help to remove sulfate from the coal, while the nitric acid can remove iron sulfide. In the existing literature, the nitric acid can be used to remove organic sulfur. In addition, when adopting the modern analysis testing technologies to study organic sulfur, the pretreatment of hydrochloric acid/nitric acid is usually required in order to eliminate the effect of inorganic sulfur [35–39]. Therefore, it is necessary to further study the characteristics and chemical structure of soft coal after hydrochloric acid/nitric acid treatment, so as to provide basis for the hydrochloric acid/nitric acid pretreatment of coal.

2. Experiment

2.1. Coal sample and acid treatment method

The coal sample is medium rank fat coal (TF) which is mined from Taifeng Coal Mine in Weng'an County, Guizhou Province, China. The coal mine belongs to Heguantun village, Bijie city. The proximate analysis, ultimate analysis and analysis of the total sulfur and sulfur form for the raw coal and the coal sample treated by acid is in accordance with the Chinese National Standard GB/T 212-2008, GB/T 476-2001, GB/T 214-2007 and GB/T 215-2003. GB/T15224.2-2004, has classified coal with total sulfur >3.00% as high sulfur coal, so Taifeng coal sample should be classified as high sulfur coal.

Take out 30 g Taifeng raw coal (200–300 μm) and put it into a beaker whose capacity is 500 ml. Pour 250 ml (4.8 N) hydrochloric acid solution into it. Heat it in water bath when the temperature is 70 °C and stir with a glass rod. 30 min later, conduct vacuum filtration for the mixed liquor. Then wash it repeatedly with the distilled water until the PH is neutral. Dry the coal left in the vacuum drying oven of 50 °C for 12 h and then take it out and seal it for standby application. Next, take out the coal sample which has been treated by the hydrochloric acid to conduct the secondary treatment by nitric acid. Put 30 g coal sample which has been treated by the hydrochloric acid into the 500 ml beaker and then pour 250 ml (2 N) nitric acid solution. Heat it in water bath and stir with a glass rod for 30 min. Then conduct the vacuum filtration for the mixed liquor. Wash the liquor repeatedly till the PH is neutral. Dry the coal left in the vacuum drying oven of 50 °C for 12 h and then seal it for standby application [40,41]. The raw coal (TF), coal sample treated by the hydrochloric (TFY) and coal sample jointly treated of hydrochloric acid/nitric acid (TFX) are taken out to conduct the proximate analysis, ultimate analysis, the analysis of sulfur form, XRF analysis, XRD test, ^{13}C NMR test, XPS test and SEM-EDS analysis. As a result, the influence of acid treatment on coal characteristics, the chemical structure of organic matter, inorganic minerals, the functional groups, microstructure on coal surface, etc., which will provide theoretical basis for acid treatment of the