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Changes in sulfur form during coal desulfurization with microwave: Effect on coal properties

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ABSTRACT

The changes in sulfur form in coal were analyzed by sulfur K-XANES (K-edge X-ray absorption near edge structures) spectra before and after the coal microwave desulfurization in a NaOH solution. After the desulfurization, the pyritic sulfur content of coal decreased significantly from 53.6% to 39.2%, while the sulfate sulfur content increased from 17.3% to 34.6%. Only a small amount of thiophene sulfur (20.1–16.1%) was removed. Some sulfur-containing components were oxidized to sulfate sulfur. Under the optimum conditions, the ash content decreased, while the volatile content increased. The calorific value of coal slightly decreased with a slight variation in the amplitudes. The overall structure of coal did not change significantly based on Fourier transform infrared (FTIR) spectral analyses. Thus, the desulfurization of coal with microwave irradiation in a NaOH solution did not significantly change the properties of coal.

1. Introduction

With the increasing emphasis on environmental issues, the clean utilization of high sulfur coal has attracted much attention. At present, many methods have been used for coal desulfurization before combustion by physical, chemical and biological ways [1,2]. Coal desulfurization by microwave irradiation is a new sulfur removal method adopted in recent years. As a high-energy source, microwave heating is faster, uniform, and localized (selective) than conventional heating. Microwave has been widely used in different fields such as in mineral leaching, wastewater treatment, environmental engineering, and crude oil and petroleum upgrading [3–8]. With increasing emphasis on environmental issues, the application of microwave technology in clean coal technology has attracted much attention [9–16].

Coal is an inhomogeneous compound, and the sulfur-containing components are better absorber of microwave energy than coal matrix, which leads to selectively heating and chemical changes to the sulfur-containing components accordingly. And when the sulfur-containing components are heated and activated quickly, the temperature of coal matrix still remains low. In such a case, the sulfur in coal may be removed without damage to the coal properties. There is lack of enough understanding of sulfur-containing functional groups, especially organic sulfur functional groups in coal due to the complexity of coal macromolecular structure and limitation of the existing testing equipment and means. As a result, the change rule of sulfur chemical forms during microwave desulfurization remains unclear, thus influencing the further development of this technology.

In this study, Chongqing Songzao high-sulfur bituminous coal (raw coal) was used as the study material. A desulfurization test was conducted by the microwave method in a NaOH solution to analyze the changes in the chemical forms of sulfur before and after the desulfurization and its effects on the properties of coal. The mechanism of coal desulfurization with microwave irradiation was also evaluated.

2. Experimental

2.1. Coal sample

The coal sample from Chongqing Songzao is high-sulfur bituminous coal. The results of the proximate analysis and elemental analysis on the raw coal are shown in Tables 1 and 2.

Determination and calculation results of total sulfur and various forms of sulfur in raw coal are shown in Table 3.

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Table 1
Proximate analysis of raw coal.

Item	M_{ad} (%)	A_d (%)	V_{daf} (%)	FC_{daf} (%)
Content	1.75	36.28	14.50	85.50

Table 2
Ultimate analysis of raw coal.

Item	C_{daf} (%)	H_{daf} (%)	N_{daf} (%)	S_{daf} (%)	O_{daf} (%)
Content	81.86	2.56	1.92	6.50	7.41

Table 3
Determination of total sulfur and sulfur forms in raw coal.

Item	$S_{t,d}$ (%)	$S_{s,d}$ (%)	$S_{p,d}$ (%)	$S_{o,d}$ (%)
Content	4.14	0.16	3.37	0.61

2.2. Methods

The microwave reaction equipment Model No. MAS-II is manufactured by Sineo Microwave Chemistry Technology (Shanghai) Co., Ltd. The microwave frequency is 2.45 GHz. The schematic diagram is shown in Fig. 1.

Mixed with NaOH solution 10 g coal samples was reacting at the set irradiation time and power in the microwave reaction equipment; after reaction, coal samples were washed several times with hot ionized water and dried to the air dried state.

The K edge X-ray absorption near edge structure (XANES) spectroscopy was applied to analyze the changes in chemical forms of the sulfur element before and after desulfurization. The Fourier transform infrared spectroscopy (FTIR) was used to compare variations in functional groups in coal before and after desulfurization and analyze the effect of desulfurization with microwave on radicals containing sulfur in coal.

3. Results and discussion

3.1. Sulfur K-edge X-ray absorption near-edge structure (K-XANES) spectroscopic analysis

The optimum technological parameters were obtained by a single-factor test and an orthogonal test in the preliminary study. The optimum parameters are as follows: particle size, 0.125–0.074 mm; microwave power, 1000 W; treatment time, 5 min; solid-to-liquid ratio, 1:4; and NaOH liquor concentration, 300 g/L.

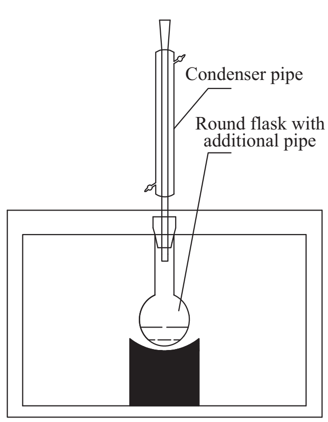

Fig. 1. Microwave oven used for experiments.

Under these conditions, the content of total sulfur decreased from 4.09% in raw coal to 1.79% in clean coal; the contents of sulfate sulfur, pyritic sulfur, and organic sulfur changed from 0.17%, 3.27%, and 0.65% to 0.35%, 1.06%, and 0.38% respectively, with a desulfurization rate of 58.94%. The raw coal and desulfurized clean coal obtained under the optimum conditions were analyzed by sulfur K-XANES spectroscopy.

For the sulfur K-XANES spectroscopic analyses, the model compounds were mercaptan, pyrite, elemental sulfur, sulfate, thiophene, and sulfoxide. A fitting analysis was conducted for XANES by the least square method. The K-XANES spectra for the model sulfur compounds are shown in Fig. 2.

The K-XANES fitting spectra of raw coal are shown in Fig. 3. In the K-XANES spectra, the peak areas of the absorption peaks were used to calculate the sulfur content in the coal and expressed in percentage. The percentage contents of various sulfur-containing components in the coal sample before and after the desulfurization are listed in Table 4.

Table 4 shows that the primary sulfur form in the raw coal is pyritic sulfur, and the content is less than that previously measured by a chemical method. This is because XANES is more sensitive to the sulfur form present in the oxidation state (e.g., sulfate sulfur) than in the reduction state (pyritic sulfur). Therefore, the measured amount of the sulfur-containing components in the oxidation state may be higher. Based on the results, the organic sulfur in raw coal primarily exists in the form of thiophene with better thermostability.

After the desulfurization with microwave irradiation in a NaOH solution, the content of pyritic sulfur in the sample decreased significantly. The sulfur-containing components in coal were oxidized to the sulfur form in the oxidation state, and the final product was the positive hexavalent sulfur. The organic sulfur removal in the coal is not significant because it primarily exists in the form of thiophene.

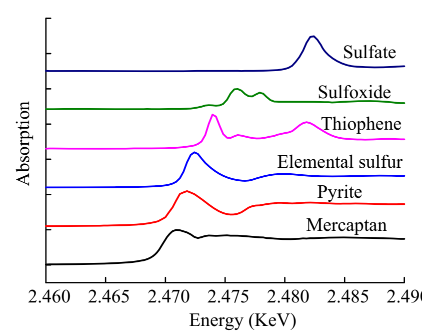

Fig. 2. Sulfur K-edge XANES spectra of model compounds.

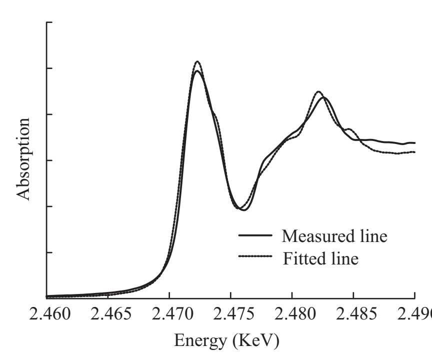

Fig. 3. Sulfur K-edge XANES fitting spectra of raw coal.