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Desulfurization of coal by an electrochemical-reduction flotation technique

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Abstract: The optimum conditions for sulfur removal from coal by electrochemical reduction flotation in an aqueous NaCl solution were determined from orthogonal experiments. The effect of electrolytic conditions on the desulfurization ratio was also studied. The electrochemical-reduction processed coal was examined by X-ray diffraction, Fourier transform infrared spectroscopy and wet chemical analysis. The results show that electrochemical reduction converts hydrophobic pyrite in Nantong coal into hydrophilic FeS and S^{2-} and leads to an increase in the concentration of hydroxyl groups and aliphatic moieties and a corresponding decrease in carboxyl and carbonyl groups, which enhances the flotation desulfurization of the coal.

Key words: desulfurization; coal; electrolytic reduction; flotation

1 Introduction

Coal combustion produces sulfur oxides, which contribute to air pollution, acid rain and other ecological problems. Therefore, desulphurization of coal has attracted the attention of scientists around the world.

The methods of desulfurizing coal include physical, chemical, biological, ultrasonic and microbial methods. Physical methods are economical. However, they only remove inorganic sulfur. Biological and chemical methods can remove both inorganic and organic sulfur but they are very expensive and there has been some discrepancy noted between theory and practice. The search for efficient, economical and clean methods of desulphurization has drawn wide attention[1–6].

Therefore, clean and mild electrochemical approaches to desulphurization such as the electrochemical desulfurization (ED) technique are being given more and more importance[7–9]. Oxidation at the anode is the key step for ED of coal. During the process the coal structure is usually destroyed to an appreciable, or significant, extent[10–12]. Although electrolytic reduction (ER) destroys the coal structure to a very small extent desulfurization is not effective. However, during the process of ER coal and pyrite in the coal are reduced at the cathode, which may lead to remarkable differences in hydrophilicity between the organic matter and the pyrite in the coal. Sulfur in the coal can be then be removed effectively by subsequent flotation. We investigated the combined effect of ED and ER on desulfurization, and report here on our research studying the electrochemical reduction of coal. Our analytical methods included X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and wet chemical analysis.

2 Experimental

2.1 Materials and instruments

Coal was collected from the Nantong coal mine, Chonqing, China. Table 1 shows the proximate analysis and sulfur content of the coal. Sodium chloride (analytical reagent grade purchased from Shanghai Chemical Reagent Plant) was used as a supporting electrolyte.

Table 1 Proximate analysis and sulfur content of Nantong coal (%, ad)

Proximate analysis			Sulfur content			
Moisture	Ash	Volatile matter	Total	Pyritic	Sulfate	Organic
1.7	35.9	28.3	4.3	2.3	0.1	1.9

The instruments used in the experiments included a potentiostat, a magnetic agitator, a Pyrex electrolytic trough, a ZCL sulfur analyzer, a D/Max-3B X-ray diffraction instrument and a Magna-IR 560 Fourier transform infrared spectrometer.

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2.2 Experimental procedure

Stainless steel mesh, Pt and NaCl were used as the cathode, the anode and the supporting electrolyte, respectively. A prescribed amount of coal sample and electrolyte were put into an electrolytic trough under a nitrogen atmosphere. The electrolytic trough was heated to an indicated temperature. After being electrolyzed, a part of the resulting slurry was immediately put into a flotation column. The floating coal was washed, dried in vacuum at 80 °C for 4 h and then subjected to sulfur, caloric value, ash content, XRD and FTIR analysis. The total sulfur removed, R (%, daf), from the coal was calculated as:

$$R = (100S_r - Y_s * S_s) * 100\%/S_r$$

where S_r and S_s are the total sulfur content of the raw coal and the treated coal on a daf basis, respectively, and; Y_s is the yield of separated coal on the same basis.

2.3 Conditions of XRD analysis

A D/Max-3B X-ray diffraction instrument made by Rigaku Co. of Japan was used for collecting the XRD spectra. The voltage on the Cu target, the current and the scanning velocity were 35 kV, 30 mA and 3°/min, respectively.

3 Results and discussion

3.1 Effect of electrolysis conditions on the desulfurization ratio

3.1.1 Electrolysis temperature

Fig. 1 shows that the desulfurization ratio first increases as the electrolysis temperature increases. Maximum desulfurization occurs at 55 °C. The ratio then decreases as the temperature increases. The reason for this is that the temperature not only affects the reaction rate and the mass transfer rate but also affects the property of the electric double-layers and the dielectric constant of the electrolyte. Because the electrochemical reaction releases heat, a rise in temperature is not favorable for the reaction. On one hand, when the temperature is too low the solution viscosity is high and the diffusion coefficient is small. Then the velocity of mass transfer is very low. On the other hand, when the temperature is too high the reaction rate is restrained. At the same time, high temperatures also enhance the interaction between coal particles and water molecules and increase the hydration of the coal particle surfaces. This decreases the float-ability of the coal, which is not favorable for flotation desulfurization of the coal. Therefore temperatures should be controlled at an optimal point.

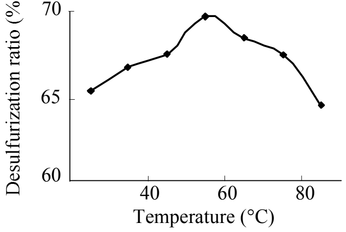

Fig. 1 Effect of electrolysis temperature on desulfurization

3.1.2 Electrolysis time

From Fig. 2, we can see that the ratio of desulfurization increases at first and then decreases as time passes. When the electrolysis time is less than 20 min, both the hydrophobicity of the coal particle surface and the hydrophilicity of the pyrite keep increasing with reaction time, which is favorable for flotation desulfurization. But when the electrolysis time is too short the reduction of coal, and pyrite within the coal, is not complete. So the desulfuri- zation ratio increases with time during the first 20 min. But as the reaction time continues to increase the Cl_2 produced by the anode and the O_2 in the air can oxidize the surface of the coal and the pyrite resulting in a decreased hydrophobicity of the coal, which is not favorable for the flotation desulfurization of the coal. So the desulfurization ratio decreases when electrolysis time exceeds 20 min.

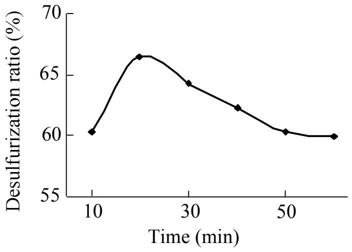

Fig. 2 Effect of electrolysis time on desulfurization

3.1.3 Electrolysis voltage

Fig. 3 indicates that the ratio of desulfurization first increases but then decreases with an increase in the voltage: the turning point is 10 V. The cause may be that the reaction conditions at the electrode surface are severe under the conditions of high voltage making the anode form Cl_2 in large quantities, which may affect the surface property of the pyrite and the coal particles. In addition, it is possible that some side reactions take place.

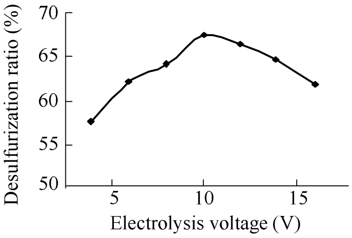

Fig. 3 Effect of electrolysis voltage on desulfurization

3.1.4 Coal slurry concentration

As shown in Fig. 4, the rate of desulfurization first increases and then decreases, reaching a maximum when the coal slurry concentration is 60 g/L. Because