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FLOTATION OF LIGNITE PRETREATED BY SORBITAN MONOOLEATE

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Abstract: In this study, sorbitan monooleate was used to pretreat lignite prior to flotation tests. First, the lignite sample and water were mixed with 0%, 0.5%, 1%, 1.5% and 2% (on the basis of the weight of the coal) of sorbitan monooleate to produce five types of flotation slurries. FTIR, XPS and SEM were used to analyze the surface properties of the lignite sample. The flotation tests were used to indicate the improvements in flotation of lignite after the sorbitan monooleate pre-treatment. FTIR and XPS results showed that there are many oxygenated functional groups in lignite such as carboxyl group and hydroxyl groups. Furthermore, SEM results showed that there are many holes on the lignite surface. These holes will be filled with water in the flotation pulp. The flotation results indicated that sorbitan monooleate can improve the lignite flotation at low concentrations of sorbitan monooleate. However, the flotation behavior of lignite deteriorated at higher concentrations of sorbitan monooleate.

***Keywords:** sorbitan monooleate, flotation, lignite, FTIR, XPS, SEM*

Introduction

Flotation is a common and useful method to upgrade fine coals (<0.5 mm). Flotation usually uses the difference in hydrophobicity between coals and minerals to obtain froth product. However, it is recognized that lignite is difficult to float using oily collectors. Atesok and Celik (2000) achieved a remarkable increase in combustible matter recovery and a decrease in ash content using an addition of pitch in dry grinding process of low rank coal. Celik and Seyhan (1995) investigated the effect of heat treatment on the improvement in hydrophobicity of lignite. Lignite hydrophobicity would have a remarkable increase after heat treatment at 105 °C for 4 hr (Cinar, 2009). Ozbayoglu et al. (2009) found that microwave radiation could improve the flotation of lignite since the moisture content in pore or on the surface of lignite could be reduced. Lignite became easy to float as the hydrophobicity of lignite could be raised using microwave treatment. At the same time, Taixi oxidized coal in China is also difficult to float as

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oxidized coal surface has some similar properties to lignite surface, and oxidized coal flotation can be improved by pretreatments (Xia et al. 2012, 2013).

In addition, surfactants have been widely applied in improving low rank coal flotation (Yu et al. 1990; Burkin and Bramley 1963; Aston et al. 1981; Chander et al. 1987; Moxton et al. 1987; Jia et al. 2000). Surfactants were added at low concentrations may make coal hydrophobic, whereas, at high concentration, they may make it hydrophilic. The conditions for flotation of lignite of Tuncbilek were investigated to achieve the best flotation performance since flotation conditions always had a significant effect on coal flotation (Sahbaz 2013; Li et al. 2013).

In this study, sorbitan monooleate was used to improve the flotation of Neimeng lignite from China. The effect of different sorbitan monooleate concentrations on flotation performance of lignite was investigated. Fourier Transform Infrared (FTIR), X-ray Photoelectron Spectroscopic (XPS), and Scanning Electron Microscopy (SEM) were used to analyze the surface properties of the lignite. The flotation tests were performed to indicate the improvements in the flotation of the lignite after sorbitan monooleate pretreatment, and FTIR, XPS, and SEM results were used to understand the flotation behavior of the lignite.

Materials and methods

Materials

The coal samples were obtained from Neimeng Province of China. The samples were dry-ground in a laboratory mill to pass 0.074 mm sieve. The proximate analysis of lignite samples can be shown as follows, M_{ad}=8.12%, V_{ad}=20.49%, FC_{ad}=41.31%, A_{ad}=30.08%, S_t=1.67%, where M_{ad} is the moisture content, V_{ad} the volatile content, FC_{ad} the fixed carbon content, A_{ad} the ash content, and S_t is the total sulfur content on a dry basis. Sorbitan monooleate used in this study was supplied by Shanghai in China.

Methods

FTIR, XPS and SEM measurements

A Perkin Elmer Spectrum 2000 model spectrometer was used for the FTIR analyses, and the spectrum was obtained at 2 cm^{-1} resolution, between 4000 and 400 cm^{-1}. FTIR spectrum of lignite was obtained with KBr pellets, prepared with <0.074 mm coal samples and analytical grade KBr. The ratio of the coal to KBr was 1 to 100.

The XPS experiments were carried out at room temperature in an ultra high vacuum (UHV) system with the surface analysis system (ESCALAB 250Xi, America). The base pressure of the analysis chamber during the measurements was lower than 1.0×10^{-7} Pa. Al Ka radiation (hv=1486.6 eV) from a monochromatized X-ray source was used for XPS. For all analyses, the take-off angle of the photoelectrons was 90° and the spot size was 900 μm. The spectra of survey scan were recorded with the pass energy of 100 eV; the energy step size was 1.00 eV. High resolution spectra were recorded with the pass energy of 20 eV, and the energy step size was 0.05 eV. The data processing (peak fitting) was performed with XPS Peakfit software using a Smart type background subtraction and Gaussian/Lorentzian peak shapes. The binding energies were corrected by setting the C1s hydrocarbon (-CH_2-CH_2-bonds) peak at 284.6 eV.

The FEI Quanta 250 SEM was used to analyze the surface morphology of lignite. The magnification times were fixed at 1000, 2000, 4000 and 10000. The coal samples were prepared by surface cleaning using absolute ethyl alcohol. After the surface cleaning, the coal samples were dried in air. Before the SEM, the coal samples were sputter-coated with a layer of gold. The details operating parameters of the SEM were as follows: HV was 30.00 kV; WD was 20.2 mm; Pressure was $1.21.10^{-4}$ Pa; Spot was 2.5.

Flotation tests

Diesel and 2-octanol was used as collector and frother, respectively. The flotation tests were conducted in a 1.5 dm^3 XFD flotation cell using 100 g of coal for each flotation test. The impeller speed of flotation machine was kept as 1910 rpm, and airflow rate was 1.2 dm^3/min. Collector dosage was 10 kg/Mg coal, and frother dosage was 1 kg/Mg. Sorbitan monooleate concentration were as 0%, 0.5%, 1%, 1.5% and 2% (on the basis of the weight of the lignite).

For each test, the pulp was first agitated in the flotation cell for 1 min, and second sorbitan monooleate was added, and agitated for an additional 3 min. After this, diesel was added to the pulp, and agitated for another 3 min. Then, the frother was, and the pulp was conditioned for an additional minute. At last, the air inlet was opened and the froth product was collected.

The flotation concentrate was analyzed by three indexes: Combustible matter recovery, Flotation efficiency index, and Ash content. Eq. (1) and (2) were used to calculate the combustible matter recovery and flotation efficiency index for the flotation experiments:

$$\textit{Combustible Matter Recovery}\ (\%)= \frac{M_C(100-A_C)}{M_F(100-A_F)}\cdot 100 \tag{1}$$

$$\textit{Flotation Efficiency Index}\ (\%) = \frac{M_C(A_F-A_C)}{M_F A_F(100-A_F)}\cdot 100 \tag{2}$$

where M_C is weight of the concentrate (%), M_F weight of the feed (%), A_C the ash content of the concentrate (%), and A_F is the ash content of the feed (%).

Results and Discussion

FTIR, XPS and SEM analysis

As shown in Fig. 1, FTIR spectrum of lignite shows that C-C, CH_3 and CH_2 stretching vibration region are characterized by peaks at 2920 cm^{-1} and 2850 cm^{-1}. The peak at

1384 cm^{-1} may be -CH_3 stretching vibration. The peaks around 1100 cm^{-1}, 1190 cm^{-1} and 1035 cm^{-1} may be attributable to C-O-C vibration (Sun et al. 2010). The peaks at 3420 cm^{-1} is for OH, at 1620 cm^{-1} is for C=O or COOH. The peaks around 697 cm^{-1} and 915 cm^{-1} indicate the presence of benzene rings. However, the major hydrophobic functional groups at 1430 cm^{-1} for R-H and at 3030 cm^{-1} for aromatic hydrogen groups cannot be found in this spectrum (Yuh and Wolt 1983; Jena et al. 2008). The peaks around 3600 cm^{-1} may be attributed to the moisture content in lignite. It indicates that lignite has few hydrophobic functional groups but many oxygen containing functional groups on its surface. Therefore, lignite is difficult to float with common oily collectors.

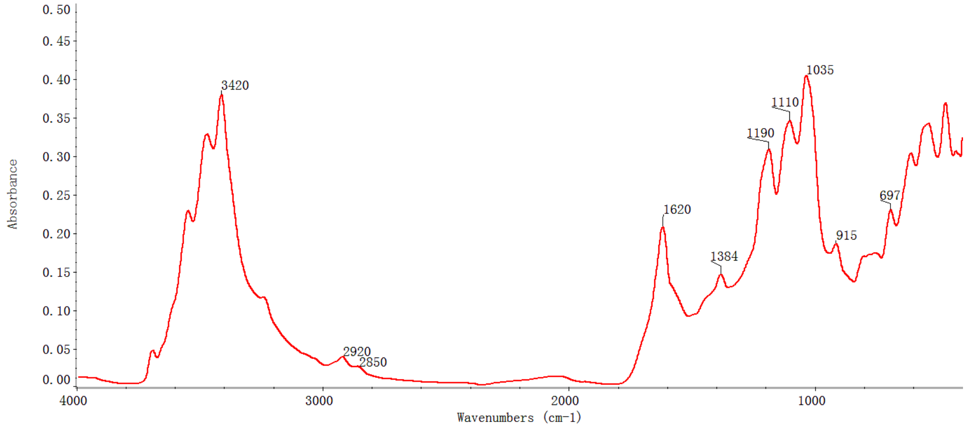

Fig. 1. FTIR spectrum of lignite

The binding energies corresponding to appropriate peaks in coals are as follows. C1s peaks at binding energies of 284.6 eV, 286.1 eV, 287.6 eV and 289.1 eV are corresponding to the following groups: C-C or C-H, C-O (alcohol, phenol or ether), C=O (carbonyl or chinone) or O-C-O (in low rank coals) and COO$^-$ (carboxyl) (Desimoni et al. 1990, 1992; Fiedler and Bendler 1992; Xia and Yang, 2013a, 2013b).

The C1s peaks are fitted as shown in Fig. 2. The relative contents of carbon forms on the surface of lignite are calculated. The content of C-C and C-H groups is 5.64%. The content of C-O group is 60.75%. The content of C=O group is 25.65% and the content of COOH group is 7.96%. Hydrophilic functional groups are C=O, C-O and COOH. Hydrophobic functional groups are C-H and C-C. The content of hydrophobic functional groups is very small while that of hydrophilic functional groups is very high. Hydrophilic functional groups will be bonded with water by hydrogen bond, and lignite coal surface will be covered by a thick hydration shell in flotation pulp. Therefore, lignite is difficult to float.

As shown in Fig. 3, surface morphology of lignite is rough with lots of holes. Lignite surface is like a honeycomb. These holes will be filled with water in flotation pulp. Lignite surface will be covered by a thick hydration shell in flotation pulp and become hydrophilic. Therefore, lignite is difficult to float.

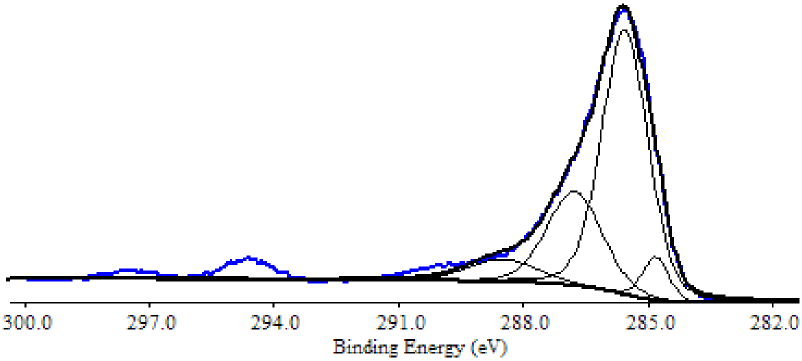

Fig. 2. C1s peaks of lignite

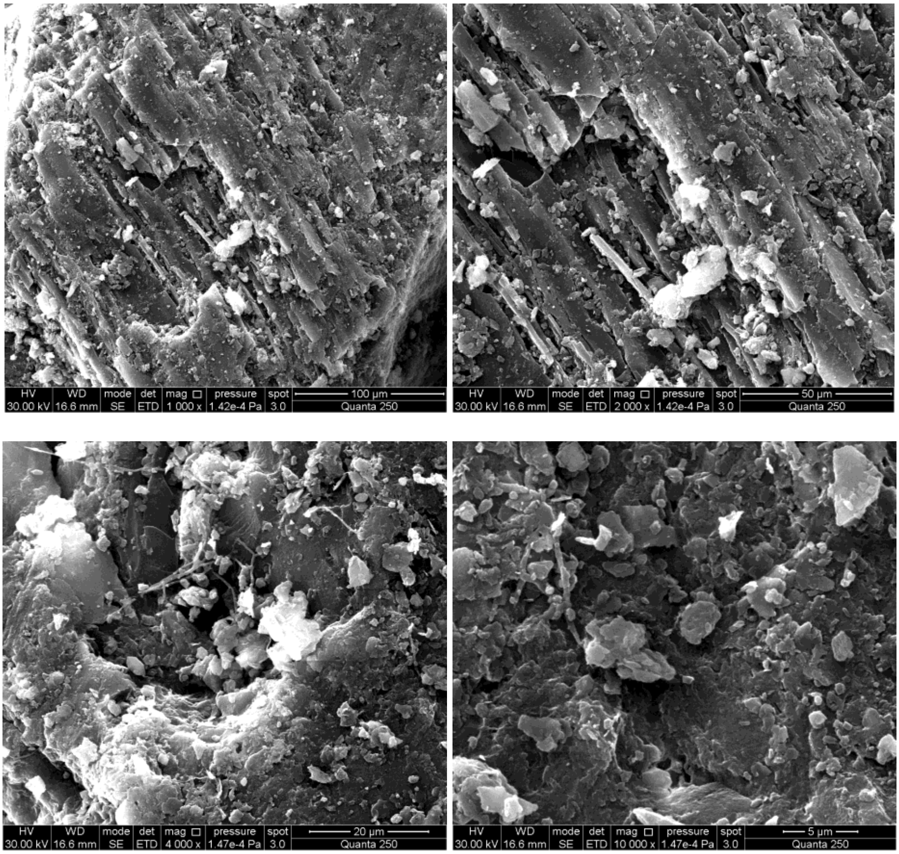

Fig. 3. SEM results of lignite surface

Flotation Experiments

Figure 4 shows that both combustible matter recovery and flotation efficiency index increase with the increase of sorbitan monooleate dosage while sorbitan monooleate dosage is less than 1%. However, both of them decrease with the increase of sorbitan monooleate dosage while it is more than 1%. Sorbitan monooleate can cover lignite surface. It indicates that lignite hydrophobicity may be enhanced by sorbitan monooleate at low concentrations and decreased at high concentrations. In addition, the viscosity of flotation pulp may be increased by a high sorbitan monooleate concentration. A higher viscosity of flotation pulp has a bad effect on flotation recovery. Therefore, lignite particles cannot be easy to float by bubbles in a higher viscosity. Meanwhile, the probable mechanism for decreasing flotation efficiency at higher concentrations of sorbitan monooleate may be a production of bilayer adsorption. Under a higher concentration of sorbitan monooleate, the sorbitan monooleate may cover the coal surface as a bilayer. Therefore, the flotation performance may be damaged by higher concentrations of sorbitan monooleate.

From the ash content in Fig. 4, the ash content has an opposite change compared with the changes of the combustible matter recovery and flotation efficiency index. The lowest ash content is obtained at sorbitan monooleate concentration of 1%.

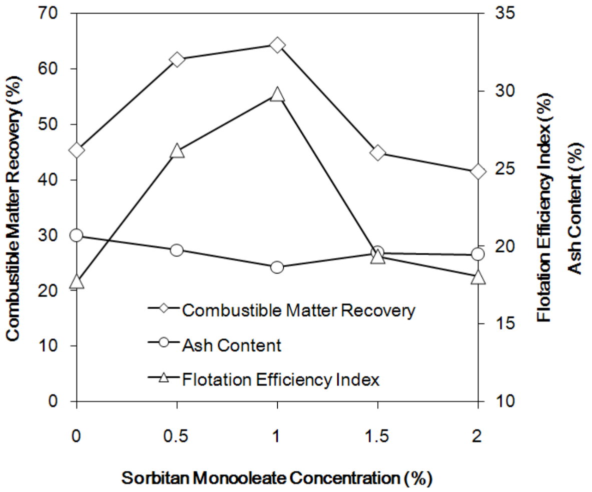

Fig. 4. Flotation results of lignite pre-treated by sorbitan monooleate

Conclusions

FTIR and XPS results show that there are many oxygenated functional groups in lignite such as carboxyl group and hydroxyl groups. SEM result shows that there are many holes on lignite surface. These holes will be filled with water in flotation pulp. Lignite has few hydrophobic functional groups but many oxygen containing functional groups on its surface. It indicates why lignite is difficult to float with common oily collectors. Therefore, sorbitan monooleate was used to enhance the flotation recovery of lignite.

Flotation performance of lignite can be enhanced by sorbitan monooleate. The optimal sorbitan monooleate concentration was 1% in this paper. Higher sorbitan monooleate concentration showed an opposite effect on the flotation performance of lignite. Under a higher concentration of sorbitan monooleate, the sorbitan monooleate may cover the coal surface as a bilayer. In addition, the viscosity of flotation pulp may be increased by a high sorbitan monooleate concentration. A higher viscosity of flotation pulp also showed a bad effect on the flotation recovery.

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