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CHANGES IN THE FLOTATION KINETICS OF BITUMINOUS COAL BEFORE AND AFTER NATURAL WEATHERING PROCESSES

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Abstract: Natural weathering processes can make coal surface more hydrophilic due to the increase of content of hydrophilic functional groups (C-O, C=O, and COOH) and the decrease of content of hydrophobic functional groups (C-C and C-H) on coal surface, and hence the flotation recovery of fine coal is reduced. In this paper, a series of flotation tests were conducted in order to investigate the changes in the flotation kinetic of bituminous coal before and after natural weathering processes. Additionally, XPS was used to indicate the changes in surface properties of bituminous coal. In the investigations the flotation kinetic was changing. The classical first-order rate constant (k) of bituminous coal flotation was reduced after the natural weathering processes. A relationship between the classical first-order rate constant (k) and the hydrophilicity ability (HA) was given.

Keywords: *flotation kinetic, classical first-order rate constant, natural weathering processes, XPS, contact angle*

Introduction

The surface properties of coal can be changed by the weathering/oxidation processes. The obvious changes are due to the increase of oxygen containing functional groups on coal surface which are hydrophilic groups (Pietrzak and Wachowska, 2003; Pilawa et al., 2002; Kozłowski et al., 2002; Grzybek et al., 2002, 2006). Natural weathering processes usually make coal surface more hydrophilic, and hence the flotation recovery of fine coal is reduced. In most cases, it is difficult to float the oxidized coal

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using the common oily collectors such as kerosene and diesel oil (Xia and Yang, 2013; Wang et al., 2013; Xia et al. 2013, 2014a).

It is necessary to seek the useful ways for improving the flotation recovery of oxidized coal. In the literature, the ultrasound treatment, premixing treatment, grinding treatment, and surface attrition treatment have been considered and they can remove the oxidized layer from oxidized coal surface (Ozkan, 2012; Feng and Aldrich, 2005; Piskin and Akgun, 1997; Sokolovic et al., 2012a, 2012b; Xia et al., 2012). Microwave pretreatment could improve the floatability of oxidized coal through reducing the moisture content of coal samples (Xia et al., 2013). Besides these treatments before the flotation processes, the efficient collectors and promoters were also found to enhance the flotation of oxidized coal. Oxidized coal could be well floated by the new collectors or surfactants. For example, blending of hydrocarbons and non-hydrocarbon collectors such as copolymers, long chain amines, and fatty acid amides could improve the floatability of oxidized coal (Polat et al., 2003; Ahmed and Drzymala, 2012).

Although the flotation recovery of oxidized coal could be enhanced or improved by pretreatments, new collectors and surfactants, the flotation kinetic of coal before and after natural weathering processes have been little investigated. In this paper, bituminous coal was used as coal samples and XPS was used to indicate the changes in surface properties of bituminous coal before and after natural weathering processes. A series of flotation tests were conducted in order to investigate the changes in the flotation kinetic of bituminous coal before and after natural weathering processes. The classical first-order rate constant (k) of flotation of bituminous coal before and after natural weathering processes was investigated.

Experimental method and procedure

Materials and experiment design

Bituminous coal sample was obtained from Shanxi Province of China. The coal sample was dry-ground in a laboratory mill to pass a 0.5 mm sieve. Natural weathering processes of bituminous coal were conducted on the roof. The weathering times were three and six months. Bituminous coal underwent the breakdowns from the sun, wind, and water. The oxidation processes occurred under natural environment.

The coal samples used in this study were three types: $Coal_1$ (fresh coal), $Coal_2$ (coal was oxidized for 3 months), and $Coal_3$ (coal was oxidized for 6 months). The proximate analyses of three coal samples are presented in Table 1, where M_{ad} is the moisture content, V_{ad} the volatile matter content, FC_{ad} the fixed carbon content, and A_{ad} is the ash content on an air dry basis.

Table 1 shows that the moisture content and ash content of the coal samples increased after the weathering processes while the volatile matter content and fixed carbon content reduced. This clearly indicates that natural weathering processes should change both the chemical and physical properties of bituminous coal.

Table 1. Proximate analysis of fresh and oxidized coals (air dried, wt. %)

Coal types	M_{ad}	V_{ad}	FC_{ad}	A_{ad}
$Coal_1$	2.91	16.54	58.32	22.23
$Coal_2$	3.60	16.27	56.55	23.58
$Coal_3$	5.14	15.79	52.03	27.04

XPS and contact angle measurements

Before the XPS experiments, coal samples were pressed into plates. Three plates were obtained from three types of coal samples. Then, these plates were moved to the test room. 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^{-9} mbar. 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 while 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 Peak fit 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.

Before the contact angle measurement, the coal samples were also pressed into plates. Three plates were also obtained from three types of coal samples. The plates of coal samples were subjected contact angle measurements in a JC2000D analyser putting a water droplet on the surface of coal plates in air.

Flotation tests

In these tests, the coal samples were pre-wetted in a flotation cell for 3 min at the impeller speed of 1910 rpm. After the pre-wetting process, the collector was added into the flotation pulp, and the pulp was conditioned for 3 min. At last, 2-octanol frother was added, and the pulp was conditioned for another 1 min.

The collector and frother dosages were chosen 800 g/Mg and 300 g/Mg, respectively. The flotation tests were conducted in a 1.5 dm^3 XFG flotation cell using 100 g of coal. The flotation rate tests were conducted, i.e., the whole flotation processes were divided into five stages from the beginning to the end, and the time lengths of five stages were 0.5, 0.5, 1.0, 1.0, and 2.0 min, respectively. The flotation concentrate was analyzed for combustible matter recovery and concentrate ash content. Equation (1) was used to calculate the combustible matter recovery:

$$\text{Combustible matter recovery (\%)} = [M_C(100-A_C)/M_F(100-A_F)]\times 100 \tag{1}$$

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

XPS and contact angle analysis

Figure 1 shows the C1s peaks for bituminous coal surface before and after natural weathering processes. Peaks at binding energies of 284.6 eV, 285.6 eV, 286.6 eV, and 289.1 eV correspond to the following groups: C-C or C-H, C-O, C=O, and O=C-O (Xia and Yang 2013; Wang et al. 2013). The contents of these groups can be calculated (Table 2). The content of C-C and C-H groups decreased from 55.31% to 8.79% while the content of O=C-O group increased from zero to 8.77% after natural weathering processes (from $Coal_1$ to $Coal_3$). Meanwhile, the content of C-O increased from 38.74% to 50.99% and the content of C=O increased from 5.95% to 31.45% after natural weathering processes (from $Coal_1$ to $Coal_3$). The C-C and C-H groups can be oxidized to C-O groups. Then, C-O group can be oxidized to C=O group, and C=O group can be oxidized to COOH group. At last, COOH group can be further oxidized, and release some gas components (CO_2, CO) and water. The functional groups are changing by the process of the natural weathering (Xie et al., 2014; Nie et al., 2013; Wang et al., 2014).

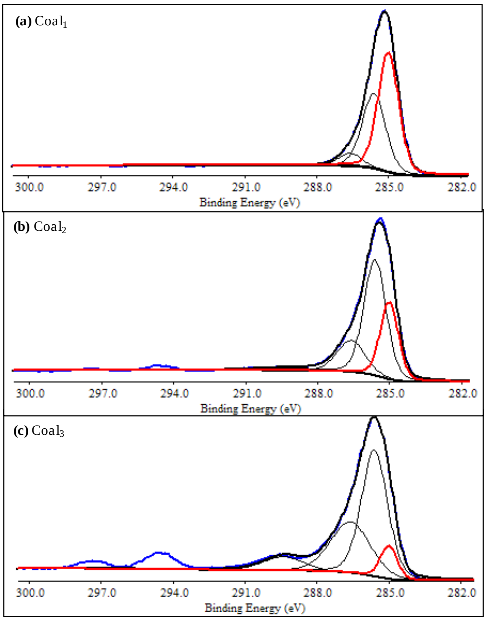


Fig. 1. C1s peaks for bituminous coal surface before and after natural weathering processes

Table 2. Fraction of C on bituminous coal surface before and after natural weathering processes (relative % of C1s)

Coal types	C-C, C-H (%)	C-O (%)	C=O (%)	O=C-O (%)
$Coal_1$	55.31	38.74	5.95	0.00
$Coal_2$	27.80	50.94	18.83	2.42
$Coal_3$	8.79	50.99	31.45	8.77

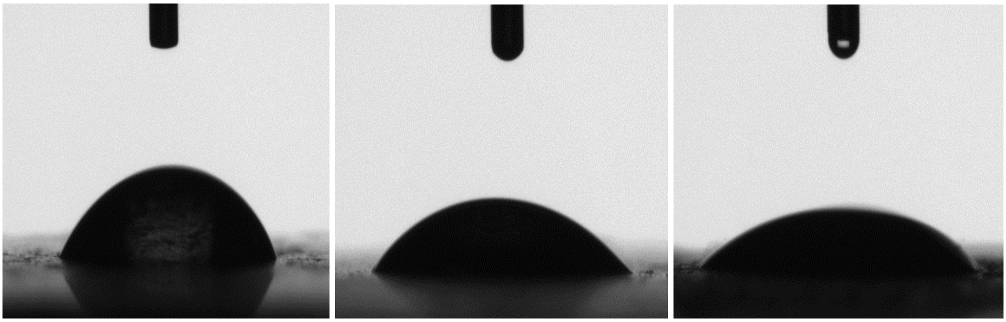
The primary hydrophilic functional groups are C-O, C=O, and O=C-O, and the primary hydrophobic functional groups are C-C and C-H (Xia et al., 2014a; Cinar, 2009). A hydrophilicity index involving the values of absorption intensity for carboxyl, hydroxyl, aliphatic CH, and aromatic CH groups has been developed to determine the hydrophobic/hydrophilic balance at the coal surface (Yuh and Wolt, 1983; Painter et al., 1983; Ye et al., 1988). The value of hydrophilicity index is obtained based on the results of FTIR which is usually a very common testing technology before the 1980s. The XPS technology has been developed in recent years. Considering the testing accuracy of FTIR in the determination of hydrophilicity index is lower than that of XPS. Meanwhile, XPS is used to the surface testing while FTIR focuses on both surface and interface. Therefore, this paper used XPS to determine the hydrophobic/hydrophilic balance at the coal surface by using a new index, such as hydrophilicity ability (HA). The hydrophilicity ability (HA) may be calculated using the ratio of the content of hydrophilic functional groups to the content of hydrophobic functional groups as shown in Eq. (2).

$$\text{Hydrophilicity Ability} = [(C-O)+(C=O)+(O=C-O)]/[(C-H)+(C-H)] \qquad (2)$$

where *C-O*, *C=O*, *O=C-O*, *C-O* and *C-H* are the contents of functional groups shown in Table 2.

The HA value of $Coal_1$ surface is 0.81, HA value of $Coal_2$ surface is 2.60 while HA value of $Coal_3$ surface is 10.38. The HA value of coal surface is increased by the natural weathering processes. It indicates that the hydrophilicity of bituminous coal is increased while the hydrophobicity of bituminous coal is reduced after the natural weathering processes.

The hydrophilic functional groups on coal surface are usually wetted by water easier than the hydrophobic functional groups since the hydrophilic functional groups may be bonded with water by hydrogen bond. After the natural weathering processes, the content of hydrophilic functional groups is increased while the content of hydrophobic functional groups is decreased. Figure 2 is the representative pictures of contact angles of three coal samples. Each contact angle was obtained using the average of three measurements. After the average calculating operation, the contact angle of $Coal_1$ is about 68°, the contact angle of $Coal^2$ is about 47°, while the contact angle of $Coal_3$ is about 35°. It indicates that the contact angle of coal surface is reduced after natural weathering processes. The results of contact angle match well with the results of XPS.



(a) $Coal_1$ (b) $Coal_2$ (c) $Coal_3$

Fig. 2. Contact angles of three coal samples

Flotation results

Figure 3 illustrates the relationship between cumulative combustible matter recovery and flotation time. The combustible matter recovery increases with the increase of floatation time. As shown in Eq. (3), the classical first-order rate constant (*k*) of bituminous coal flotation can be obtained using the curve fitting (Sokolovic et al., 2012b; Wen and Sun, 1981; Fuerstenau et al., 1983).

$$\varepsilon_e = e_w(1-e^{-kt}) \tag{3}$$

where e_w is the maximum combustible matter recovery (%) while k is classical first-order rate constant and t is the flotation time.

As shown in Fig. 3, the classical first-order rate constant (k) is 3.7 for $Coal_1$, 2.5 for $Coal_2$ and 1.2 for $Coal_3$. The k value is reduced by the natural weathering processes. Furthermore, the flotation recovery obviously decreased since the natural weathering processes reduced the hydrophobicity of bituminous coal but increased the hydrophilicity of bituminous coal. After the natural weathering processes, bituminous coal was difficult to float with common oily collectors. Figure 3 also indicates that the flotation behavior of $Coal_3$ is the worst and the flotation behavior of $Coal_1$ is the best. The flotation behavior of $Coal_2$ is between $Coal_1$ and $Coal_2$. The longer the natural weathering process is, the worse the flotation behavior of bituminous coal is.

Figure 4 illustrates the relationship between product ash content and flotation time. The product ash content increases with the increase of floatation time. The product ash content of $Coal_3$ is the highest. The product ash content of $Coal_1$ is similar to that of $Coal_2$. It indicates that mild oxidation processes may have very little effect on the product ash content but the long weathering processes may increase the product ash content obviously.

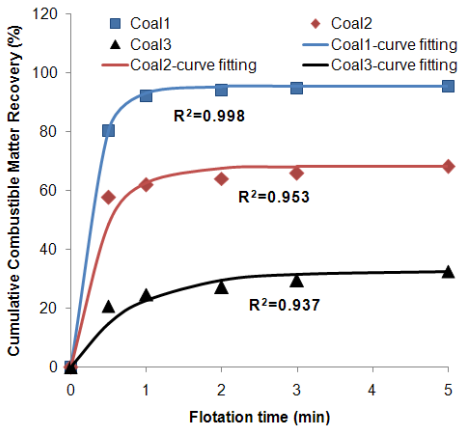


Fig. 3. Cumulative combustible matter recovery changes with flotation time

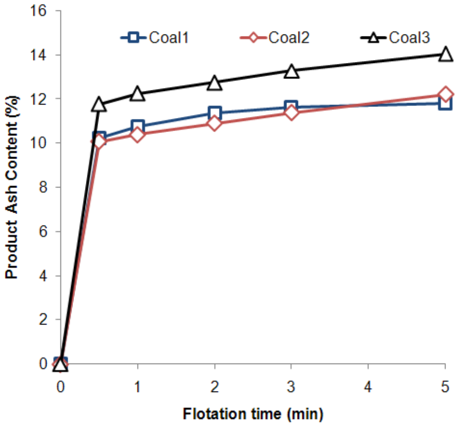


Fig. 4. Product ash content changes with flotation time

Figure 5 illustrates the relationship between the classical first-order rate constant (k) and the hydrophilicity ability (HA). The relationship between the classical first-order rate constant (k) and the hydrophilicity ability (HA) is:

$$k = -0.97\ln(HA) + 3.471. \tag{4}$$

The k value decreases with the increase of HA value. Since the oxidation processes occur on the coal surface during the natural weathering processes, more and more hydrophilic functional groups are produced and the hydrophobicity of coal surface is reduced.

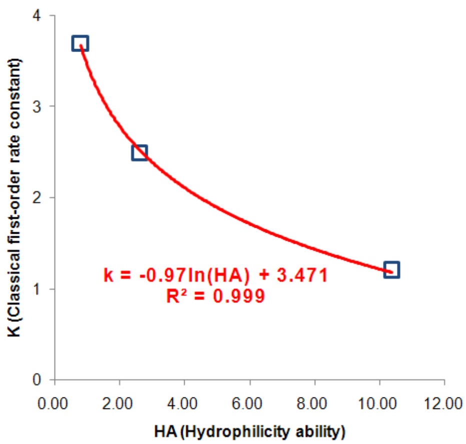


Fig. 5. Relationship between classical first-order rate constant (k) and hydrophilicity ability (HA)

The HA value of coal surface is greatly increased after the natural weathering processes. After the natural weathering processes, the content of the primary hydrophilic functional groups (C-O, C=O and O=C-O) is increased and the content of the primary hydrophobic functional groups (C-C and C-H) is reduced. Therefore, the natural weathering processes make bituminous coal surface more hydrophilic and difficult to float with common oily collectors. The whole combustible matter recovery of $Coal_1$ is much higher than that of $Coal_2$ or $Coal_3$. The natural weathering processes not only reduce the hydrophobicity of coal surface and the combustible matter recovery but also reduce the value of classical first-order rate constant (k). Hence, the classical first-order rate constant (k) is 3.7 for $Coal_1$, 2.5 for $Coal_2$ and 1.2 for $Coal_3$. It indicates that the natural weathering processes make bituminous coal surface less hydrophobic (Xia et al. 2014b, 2014c).

Conclusions

- Natural weathering processes can reduce the content of hydrophobic functional groups (C-H and C-C) but increase the content of hydrophilic functional groups (C-O, C=O and O=C-O) on bituminous coal surface. Therefore, the natural weathering processes make bituminous coal surface more hydrophilic.
- The hydrophilicity ability (*HA*) value of bituminous coal surface is greatly increased by the natural weathering processes. The *HA* value is 0.81 for $Coal_1$ surface, 2.60 for $Coal_2$ surface and 10.38 for $Coal_3$ surface.
- Natural weathering processes not only reduce the whole combustible matter recovery but also reduce the value of classical first-order rate constant (k). The classical first-order rate constant (k) is 3.7 for $Coal_1$, 2.5 for $Coal_2$ and 1.2 for $Coal_3$.
- The relationship between the classical first-order rate constant (k) and the hydrophilicity ability (*HA*) meets the Equation k=-0.97ln (HA) +3.471. The k value decreases with the increase of *HA* value.

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