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COMPARISON OF FLOAT-SINK AND PROGRESSIVE RELEASE FLOTATION OF GROUND PRODUCTS OF COAL MIDDLINGS

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Abstract: An additional recovery of cooking coal middlings can be utilized for increasing of yield of concentrate cooking coal. A combined flow sheet of comminution and flotation can realize this target. To investigate the effect of grinding process on further flotation of ground products, the progressive release flotation tests were used to compare with the float-sink tests, which were regarded as a criterion. Coal middlings were ground by wet-milling with iron balls to <0.5 mm. Curves of ash vs. cumulative yields of sized products indicated that the concentrate yield of coal separated by progressive release flotation was lower than that of coal benefited by the float-sink test, with the same ash for four size fractions (0.5-0.25 mm, 0.25-0.125 mm, 0.125-0.074 mm and <0.074 mm). Distributions of elements conducted by energy disperse spectroscopy (EDX) showed that associated kaolinite was liberated and exposed on the surface. It led to the shift of local surface property from hydrophobicity to hydrophilicity. Meanwhile, analyses of chemical property performed by an X-Ray photoelectron spectrometer (XPS) depicted that the hydrophilic mineral FeOOH, which generated in the grinding process, was adsorbed on the coal surface. Floatability of ground products were worsened due to the increase of hydrophilicity of the coal surface.

Keywords: *coal, middlings, floatation, progressive release flotation, XPS, EDX*

Introduction

Nowadays, a grinding process has become an important method in utilization of coal by areas of gasification, liquification and combustion (Zuo et al., 2013; Elham et al., 2013; Shi and Zuo, 2014). For coal beneficiation, comminution was proposed especially for the recovery of coal middlings, which are associated with mineral (Lytle et al., 1983; Bokanyi and Csoke, 2003; Cui et al., 2007). The liberated ground

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products can be re-separated by either gravity concentration or flotation, according to differences in either density or surface wettability of coals.

Comminution of coal cannot only realize size reduction and mineral liberation, but also exposes the inner interface (Xia et al., 2013). In this case, Xie et al. (2013) studied the liberation characteristics of coal middlings comminuted by a jaw crusher and ball mill, respectively. Based on liberation of minerals during grinding, ultra clean coal was produced by flotation (Bokanyi and Csoke, 2003; Fu and Shan, 2006). Despite these, changes in surface properties also occur because of the exposure of inner surface. Recently, Sokolovic et al. (2012) introduced the methods of attrition to improve floatability of oxidized anthracite waste coal (Sokolovic). Xia et al. (2013) found the changes of amounts functional groups of Taixi coal ground by a dry rod mill, and the flotation behavior of coals treated by this method was improved. The objects of these studies are coals with the size below 0.5 mm, which are suitable to be separated by flotation. The purpose is to liberate macerals from minerals. A number of studies of combined flow sheet of comminution and flotation for lump coal is relatively low. Nevertheless, this technique is utilized for beneficiation of metallic ores (Moslemi et al., 2011; Miettunen et al., 2012). Bruckard and Sparrow (2011) found that abrasion of media in the grinding process can influence the selective attachment of reagent to the mineral surface. Goncalves et al. (2011) evaluated the effect of availability of iron oxide and newly generated hydroxide compounds on flotation of sulphide copper ore ground by wet-milling with different media. A method of X-ray photoelectron spectrometer (XPS) analysis was also utilized by mineral processing researchers to evaluate the effect of grinding on further flotation (Liu et al., 2011). In this regard, in our studies the sampled coking coal middlings were firstly ground by wet-milling of ball mill with iron balls. Progressive release flotation tests of sized products (0.5-0.25, 0.25-0.125, 0.125-0.074 and <0.074 mm) were performed in comparison to the float-sink tests. Simultaneously, distributions of elements and chemical composition of ground products were analyzed by energy disperse spectroscopy (EDX) and XPS, respectively. Meanwhile, the maceral composition of sized ground products was also determined. Combination of various analyses of properties of ground products were used to explain the difference of cumulative yields of clean coal with the same ash between these two methods. The reason of changes in the surface properties of coal was also discussed in this paper.

Materials and methods

The coking coal middlings, which were sampled from a coal preparation plant, were chosen as the experimental materials. The content of ash and sulfur was 29.84 and 1.5%, respectively. Before the wet-milling process, the investigated samples were firstly crushed to size of 3-0.5 mm by a jaw crusher. The wet-milling process was conducted to reduce the size to <0.5 mm. Then, the slimes were filtrated and dried at the room temperature. The ground products were sieved into four size fractions, with a series of stainless steel sieves with sizes of 0.25, 0.125 and 0.074 mm.

The float-sink tests were conducted according to the criterion of GB/T 478-2008. Densities used in the float-sink tests were 1.3, 1.4, 1.5, 1.6, 1.8 and 2.0 kg/dm^3. For the tests of coal middlings, heavy media of different densities were prepared by putting different amount of $ZnCl_2$ into water. As the $ZnCl_2$ was not easy to dissolve, hot water was firstly used and float-sink tests were conducted after the temperature of a medium decreased to the room temperature. For the tests of ground products, the heavy media of different densities were obtained by adjusting the proportions of benzene (0.88 kg/dm^3), CCl_4 (1.55 kg/dm^3) and $CHBr_3$ (2.89 kg/dm^3).

In the progressive release flotation tests, n-dodecane and 2-octanol were used as the collector and frother, respectively. As the flotation selectivity of ground coal was poor, flotation tailings were separated with relatively low ash and high yield. In this case, a flotation flow sheet was optimized to improve the quality of flotation tailings. The optimized timed-release flotation flow sheet is shown as Fig. 1. Herein, dosages of n-dodecane and 2-octanol were 1.0 and 0.1 kg/Mg at the stage of roughing flotation, respectively. For the scavenging flotation, dosages of n-dodecane and 2-octanol decreased to 0.35 and 0.04 kg/Mg.

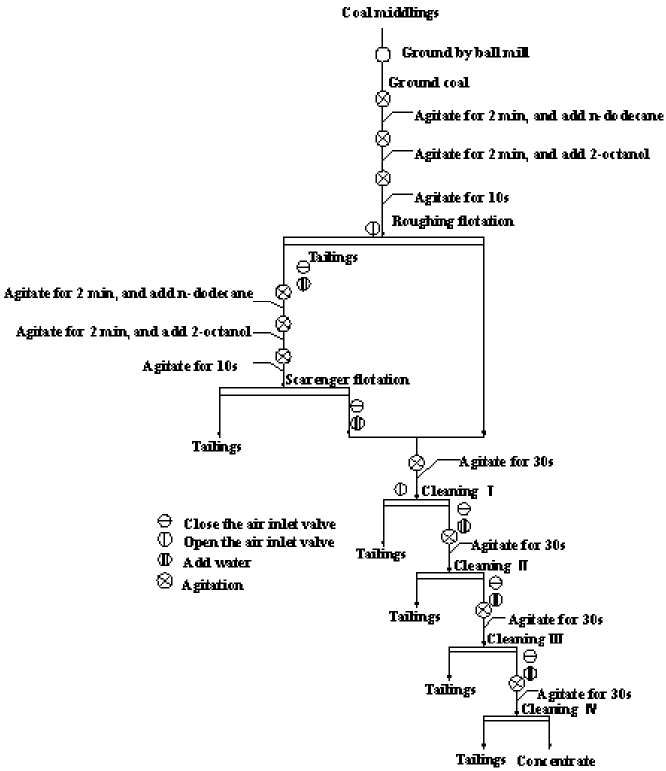


Fig. 1. Flow sheet of optimized progressive release flotation

A mineral composition of the original coal was investigated by a D8 Advance X-ray Diffractometer (XRD) made by BRUKER AXS. Cu-Kα radiation was generated at a tube voltage of 40 kV and a tube current of 30 mA. The incident beam was focused onto a beam spot of 250 um in a diameter by a collimeter. A scanning velocity was 0.1 sec/step and a sampling interval was 0.01945^0.

A distribution of elements on the surface of ground products was conducted by EDX. As the first procedure, the unsized ground products were solidified in the mixture of epothin epoxy resin (20-8140-128) and epothin epoxy hardener (20-8142-064) with the proportion of 5 to 2 for more than 48 h (Xie et al., 2013). An EDX instrument, namely Bruker Quantax400-10, was utilized. Operating parameters for elemental analysis were as follows: Target: Rh anode, operating voltage: 25 kV, X-ray path: vacuum, ketector: Si (Li), measurement time: 300 s.

After the investigation of distribution of elements, maceral compositions of the sized ground products were analyzed by the polarizing microscope. Over 500 points were observed for each sample. A content of each maceral was determined.

The ground products with the size below 74 μm were sieved and pressed into a pellet for XPS analysis. High resolution spectra were obtained by XPS at the room temperature in an ultra-high vacuum, with the surface analysis system (THERMO ESCALAB 250Xi, America). Passing energy was 20 eV and step size of energy was 0.05 eV. Scan numbers of high resolution spectra for different elements were ranged from 5 to 20. Binding energies were corrected by setting the C 1s hydrocarbon ($–CH_2–CH_2–$bonds) peak at 284.8 eV (Becker and Cherkashinin, 2013).

Results

Analyses of mineral and maceral compositions

The mineral composition of coal middlings is shown in Fig. 2. About 8 kinds of associated minerals were found in this sample. A relative content of kaolinite is the

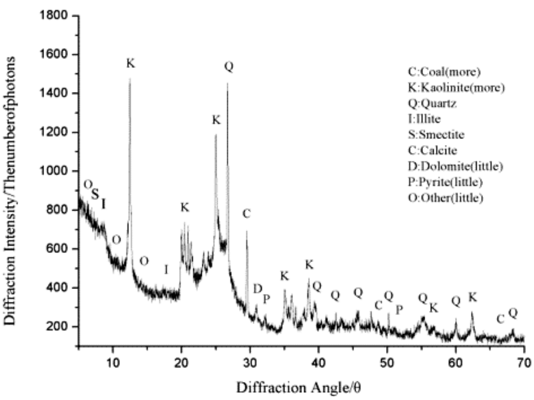


Fig. 2. Phase composition of coal middlings investigated by XRD

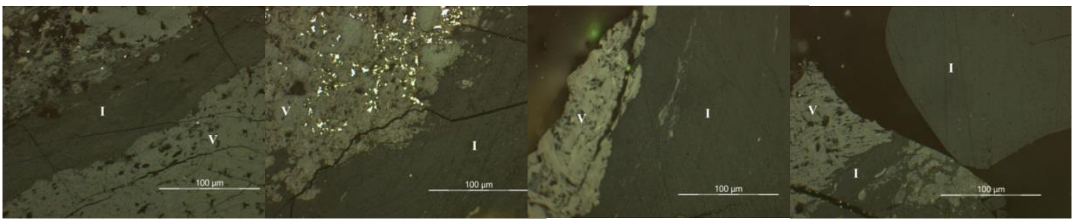
highest one among all minerals. As kaolinite shows a property of hydrophilicity, the flotation behavior of the ground products may be worsened if kaolinite is exposed on the surface. The contents of quartz, illite, smectite, dolomite and pyrite is relatively low.

The maceral composition of the sized ground products are shown in Table 1. The contents of exinite in these four sized products is less than 4%. It indicates that this maceral nearly has no effect on the total flotation behavior of coal. For another two macerals, the content of vitrinite increases with the particle size but the inertinite shows the contrary relationship. Some images which were observed by a polarizing microscope, are shown in Fig. 3. Figure 3 shows that liberation of different macerals was not successful. Vitrinite is liberated with inertinite but still they are associated with each other. These two main macerals are easy to float and flotability of vitrinite is a little bit better than that of inertinite (Zhao., 2010; Guo et al., 2013). Although, Bokanyi and Csoke (2003) disclosed for Mecsek coal that floatability of vitrinite is usual higher than that of exiuite, and floatability of inertinite is poor. In this case, the difference of flotability of the sized ground products might be relatively small from this viewpoint.

Table 1. Maceral composition of sized ground products

Size fraction, mm	Vitrinite	Inertinite	Exinite
0.5-0.25	58.47	39.35	2.18
0.25-0.125	54.19	42.17	3.64
0.125-0.074	48.55	48.66	2.79
<0.074	46.08	52.31	1.61

The difference in the sized ground products and original coal is relatively small, which is less than 3%. Float-sink curves of these four progenies are nearly the same. Simultaneously, associated minerals found in the original coal were investigated in the ground products. These results indicate that no selective grinding happened during comminution of coal middlings in the ball mill.



(a) (b) (c) (d)

Fig. 3. Imagines of macerals of ground products

Liberation of coal middlings by grinding

Usually, the wet-milling process can not only reduce the size to a small level, but also promote liberation of associated minerals to coal substance. Herein, float-sink tests of ground products can illustrate the liberation clearly. Figure 4 shows the density vs. cumulative yield of coking coal middlings and ground products, respectively. Cumulative yields of ground products with lower density are obviously higher than those of coal middlings. At the density of 1.5 kg/dm^3, the difference of cumulative yield is nearly 20%. In comparison to the original coal, the grinding process of coal middlings could increase the yield of coal with small or large density at the same time. Thus, the potential of beneficiation is improved. Meanwhile, the difference in the surface wettabilities between liberated coals and minerals is relatively high, the ground products can be efficiently separated by flotation.

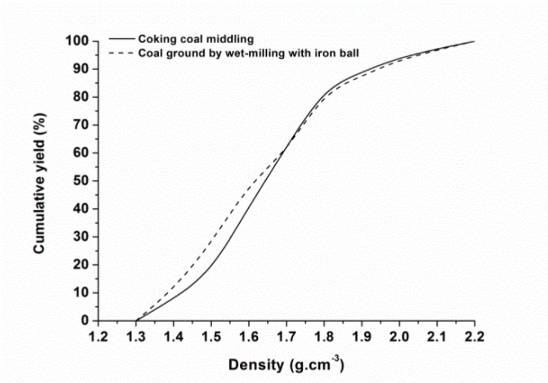


Fig. 4. Cumulative yield vs. density of coking coal middlings and ground products

Comparison between float-sink and progressive release flotation of the sized coal

Figure 5 depicts the cumulative yield vs. ash of the sized ground coals separated by float-sink and progressive release flotation tests, respectively. The results of the float-sink tests of progenies elucidate that the difference in the cumulative yield of these four sized products is not remarkable for the same ash, except for coals of 0.5-0.25 mm. For example, if comparing the cumulative yield of clean coal with ash of 10%, results of coals of 0.5-0.25 mm are the best. The flotation results of coals with size of 0.125-0.074 mm and <0.074 mm are better than those of another two fractions. In comparison to the results of float-sink tests of sized coals, the yield of flotation concentrate with low ash of each sized ground products is less, since floatability between liberated coal and gangue is different. Especially for coals of 0.5-0.25 mm and 0.25-0.125 mm, the difference is expanded to nearly 15%, if the ash is 10%. The changes in the surface properties of ground products during the wet-milling process may be the reason of the difference between the results obtained by these two methods.

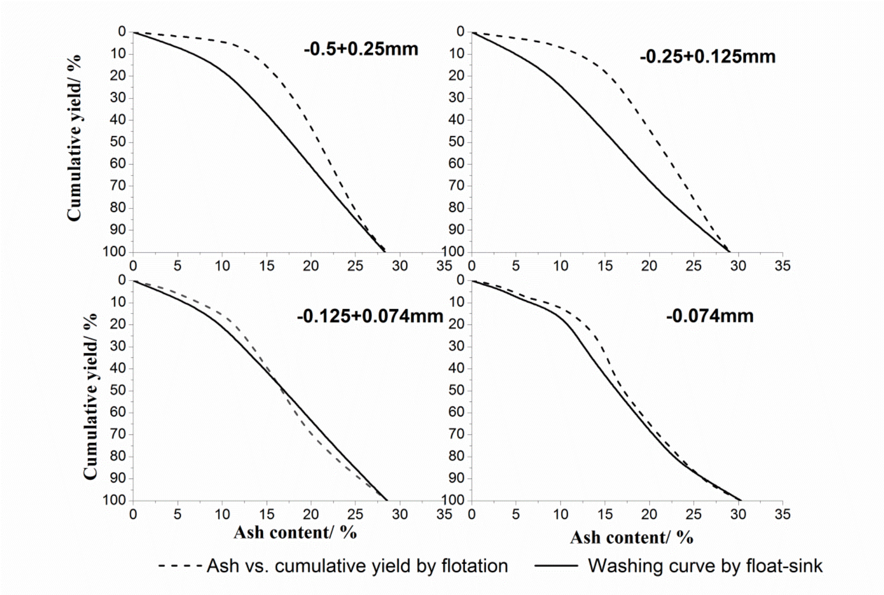


Fig. 5. Cumulative yield vs. ash of ground products separated by float-sink and progressive release flotation

Discussion

Distributions of elements on the newly generated surface

Just as mentioned above, kaolinite was the main associated mineral. This mineral shows a property of hydrophilicity and had a negative influence on the flotation behavior of ground products. In this case, the microscopic image and distribution relationship of elements on the new surface were conducted by SEM and EDX, respectively. The results are shown in Fig. 6. Figure 6 shows that in the selected area, the distribution character of Al and Si is the same. This phenomenon indicates that kaolinite is exposed on the surface. Meanwhile, Fig. 6 also indicates that the particles,

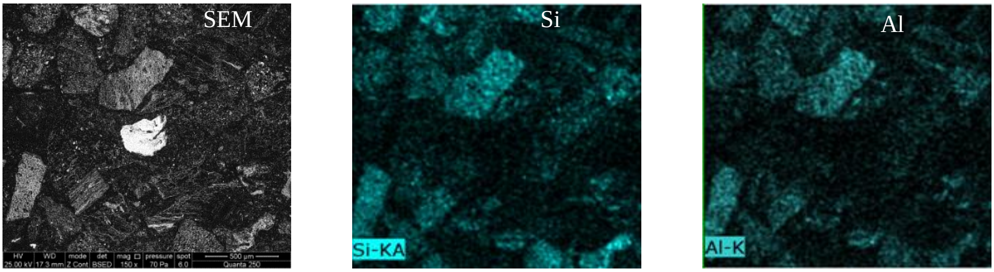


Fig. 6. Distributions of Si and Al on the newly generated surface

which are covered by kaolinite, occupy a relatively high proportion. As kaolinite exhibits the hydrophilic properties, the flotation behavior of ground products is worsened.

XPS analyses of the ground products

Chemical properties were observed by XPS. Firstly, the high resolution spectra of C, O, H, Fe, S, Al, Si and Ca in samples were recorded to investigate the possible changes of chemical valances during grinding. Herein, a new compound was found on the surface. Figures 7 and 8 depict the Fe 2p and O 1s signals of ground products, respectively. Peaks with binding energies of 711.50 eV of Fe and 531.20 eV of O in Figs. 7 and 8 are consistent with FeOOH. Thus, a part of the surface of ground products was covered by FeOOH.

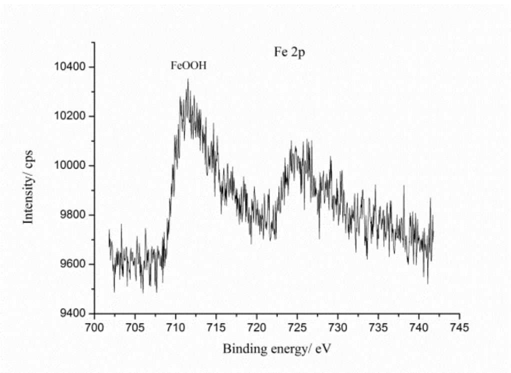


Fig. 7. Fe 2p signal of ground products

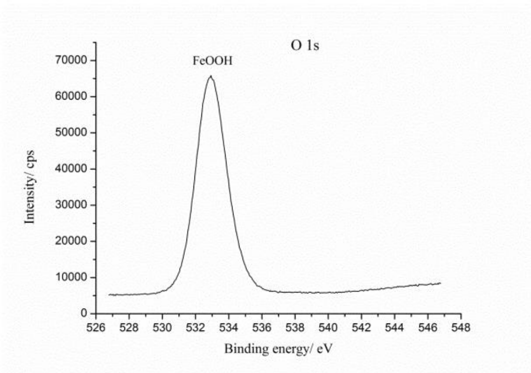


Fig. 8. O 1s signal of ground products

The chemical analysis also shows the presence of pyrite. During the wet-milling process with iron balls, the galvanic coupling phenomenon existed between the grinding medium and the liberated pyrite. Under the effect of galvanic coupling, oxidation reaction happened on the surface of iron ball and reduction reaction occurred on pyrite. The oxidative products of Fe^{3+} would react with the reductive products of OH^{-1} to form a compound of hydroxide of Fe (Gu and Zhong, 2011). The results of XPS indicated that the new compound was FeOOH. FeOOH exhibits the hydrophilic properties and it is adsorbed on the surface of ground products. In this case, the local surface of ground products was shifted from hydrophobic to hydrophilic. The changes in the surface properties worsen the flotation behavior. The cumulative yield of ground coals performed by progressive release flotation dropped when comparing with the results of float-sink tests with the same ash for the sized products.

Conclusions

A grinding process of coal middlings could realize liberation of coal macerals from associated minerals. Float-sink tests of ground products indicated the increase of separation potential in comparison to the original coal. Differences among mineral and macerals compositions of four sized ground products were relatively small. The property of local newly exposed surface was changed during the grinding process. Cumulative yields of sized coals separated by the progressive release flotation were obviously lower than that of coals beneficiated by float-sink, with the same ash. Distributions of elements analyzed by EDX depicted the exposure of hydrophilic kaolinite on the surface of ground products. This led to the change of local surface property from hydrophobicity to hydrophilicity and decrease of floatability of ground products. Meanwhile, the newly generated compound of FeOOH was adsorbed on the local new surface and also might have a weak negative effect on the floatation behavior of coal. It was evident that these changes led to the decrease in cumulative yield.

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