Physicochem. Probl. Miner. Process. 51(2), 2015, 675−684

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received February 4, 2014; reviewed; accepted September 11, 2014

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

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Abstract: An additional recovery of coking coal middlings can be utilized for increasing of the concentrate yield of coking 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, 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. Flotation of the ground products were worsened due to the increase of hydrophilicity of the coal surface.

Keywords: *coal middlings, float-sink, 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 ash minerals (Lytle et al., 1983; Bokanyi and Csoke, 2003; Cui et al., 2007). The liberated ground products can be

http://dx.doi.org/10.5277/ppmp150225

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

Comminution of coal can not 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. 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 in a 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 GB/T 478-2008 standard. 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 using different amount of $ZnCl_2$ in water. As the $ZnCl_2$ was not easy to dissolve, hot water was firstly used and the float-sink tests were conducted after the temperature of a medium decreased to the room temperature. For the tests of the 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 stage, respectively. For the scavenging, the dosages of n-dodecane and 2-octanol decreased to 0.35 and 0.04 kg/Mg.

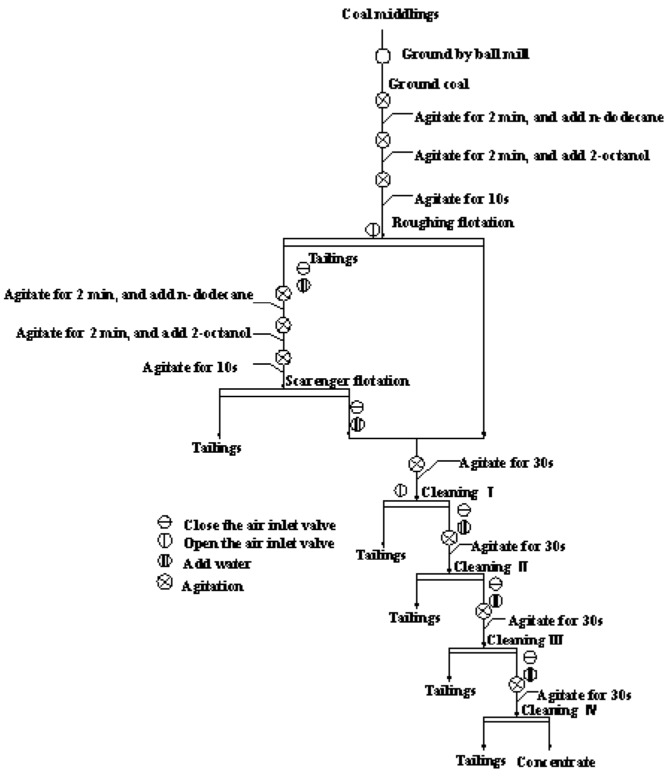


Fig. 1. Flow sheet of optimized progressive release flotation

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 analysis of elements on the surface of ground products was conducted by EDX. In 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 with a 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 the sample. A relative content of kaolinite is the

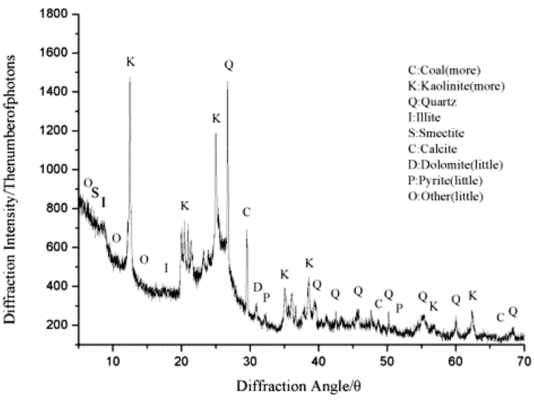


Fig. 2. Phase composition of coal middlings investigated by XRD

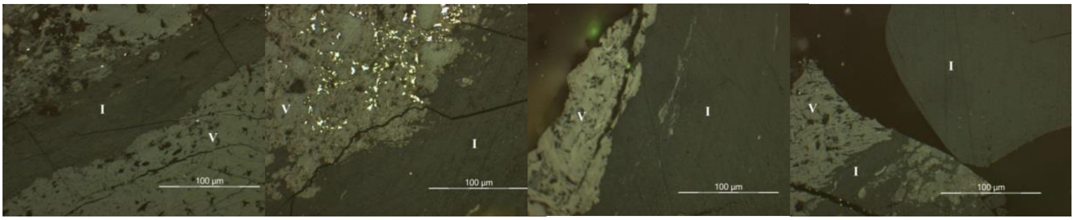
highest in all minerals. As kaolinite is hydrophilic, the flotation behavior of the ground products may be worsened if kaolinite is present on the surface. The contents of quartz, illite, smectite, dolomite and pyrite are relatively low.

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. In the case of other two macerals, the content of vitrinite increases with the particle size, while inertinite shows an opposite trend. Images, which were observed with a polarizing microscope, are shown in Fig. 3. Figure 3 shows that liberation of different macerals was not significant. Vitrinite was liberated from inertinite but still they were associated with each other. These two main macerals are easy-to-float and flotation of vitrinite is a little better than that of inertinite (Zhao., 2010; Guo et al., 2013). Although, Bokanyi and Csoke (2003) showed for Mecsek coal that flotation of vitrinite is usual better than that of exiuite, and flotation of inertinite is poor. From this view of point the difference of flotation of the sized ground products might be relatively small.

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 between the sized ground products and original coal is relatively small and is less than 3%. The float-sink curves of the four samples are nearly the same. Simultaneously, associated minerals found in original coal were also investigated in the ground products. The results of investigations indicate that no selective grinding occurs 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 cannot only reduce the size, but also promote liberation of associated minerals from coal particles. The float-sink tests of the ground products can illustrate the results of liberation. Figure 4 shows the density vs. cumulative yield of coking coal middlings and ground products, respectively. The cumulative yields of the 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 increases 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. Thus, the ground products can be efficiently processed by flotation.

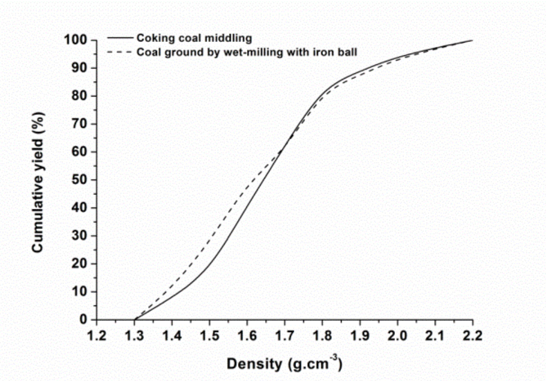


Fig. 4. Cumulative yield vs. density of coking coal middlings and ground products

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

Figure 5 presents the cumulative yield vs. ash of the sized ground coals separated by float-sink and progressive release flotation tests. The results of the float-sink tests indicate that the difference in the cumulative yield of these four sized products is not significant, except for the 0.5-0.25 mm size fraction of coals. If comparing the cumulative yield of clean coal with ash of 10%, the results for the 0.5-0.25 mm size fraction of coal are better. The flotation results for the 0.125-0.074 mm and <0.074 mm coals are better than those for the other two fractions. In comparison to the results of the float-sink tests of the sized coals, the yield of flotation concentrate with a low ash content for each sized ground products are worse, since flotation of liberated coal and gangue is different. Especially for coals of 0.5-0.25 mm and 0.25-0.125 mm in size, the difference increases 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.

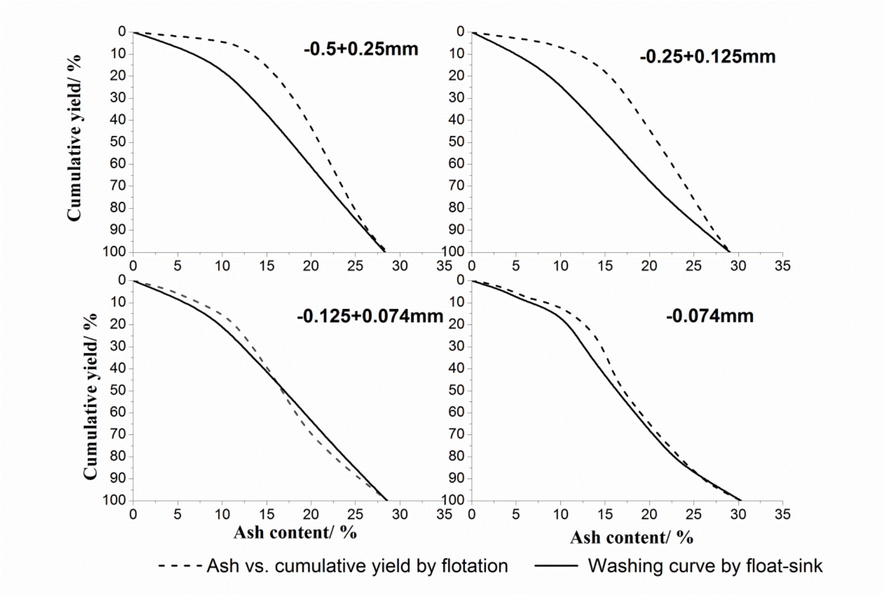


Fig. 5. Cumulative yield vs. ash of ground products separated by float-sink and progressive release flotation

Discussion

Distributions of elements on the newly generated surface

Just as mentioned above, kaolinite was the main associated mineral. This mineral is hydrophilic and it has a negative influence on the flotation of ground products. Therefore, the microscopic image and distribution relationship of elements on the new surface were measured by SEM and EDX. The results are shown in Fig. 6. The figures show that in the selected areas the distribution character of Al and Si are the same. This indicates that kaolinite is present on the surface. Figure 6 also shows that the particles,

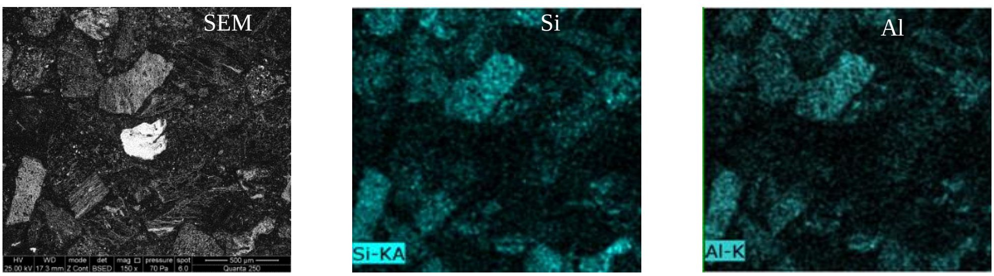


Fig. 6. Distributions of Si and Al on the newly generated surface

which are covered by kaolinite, occupy a relatively high portion of the surface. As kaolinite is hydrophilic, the flotation of the ground products is reduced.

XPS analyses of the ground products

Chemical properties of coals were analyzed by XPS. 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. As a result, 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.

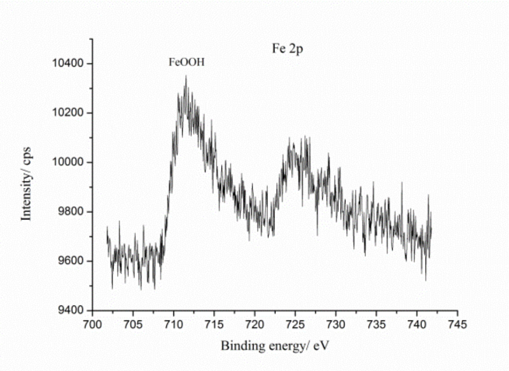


Fig. 7. Fe 2p signal of ground products

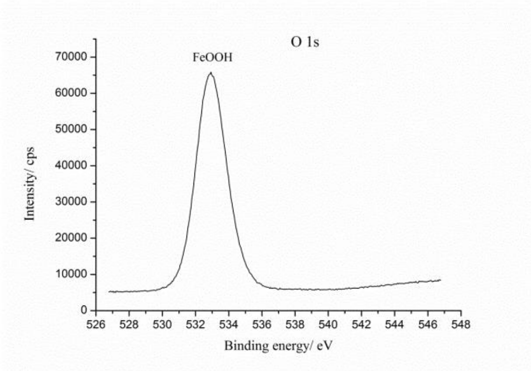


Fig. 8. O 1s signal of ground products

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 liberated pyrite. Due to galvanic coupling, oxidation occurs on the surface of iron ball and reduction reaction occurres on pyrite. The oxidative products of Fe^{3+} react with 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 is hydrophilic. It is adsorbed on the surface of ground products. In this case, the surface of the ground products locally becomes hydrophilic. The changes in the surface properties reduce flotation. The cumulative yield of ground coals performed by progressive release flotation dropped in comparison with the results of the float-sink tests at the same ash for the sized products.

Conclusions

A grinding process of coal middlings leads to liberation of coal macerals from associated minerals. The float-sink tests of ground products indicated the increase of separation potential in comparison to the original coal. The differences between mineral and maceral compositions of the four sized ground products were relatively small. The property of the newly produced surface changed during the grinding process. The cumulative yields of the sized coals separated by using progressive release flotation were obviously lower those of coals beneficiated by float-sink, at the same ash content. The distributions of elements analyzed by EDX indicated the presence of hydrophilic kaolinite on the surface of the ground products. This leads to a change of local surface property from hydrophobic to hydrophilic and a decrease of flotation of the ground products. Meanwhile, the newly generated FeOOH was adsorbed on the local new surface having a weak negative effect on the flotation of coal. It was evident that these changes led to a decrease in the cumulative yield.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No.51274196), Natural Youth Science Foundation of China (No. 51104160, 51404267), High Level Thesis Special Fund of CUMT (2012LWB25), a program sponsored for Science Innovation Research of College Graduate in Jiangsu Province of China (KYLX_1048) and College students' Innovation Entrepreneurship projects of CUMT (201418). We also would like to thank Advanced Analysis and Computation Center of China University of Mining and Technology for their technical support.

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