Physicochem. Probl. Miner. Process. 53(1), 2017, 227−239

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

Physicochemical Problems
of Mineral Processing

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

Received March 1, 2016; Reviewed April 11, 2016; Accepted June 14, 2016

RESEARCH ON QUANTIFYING THE HYDROPHILICITY OF LEACHED COALS BY FTIR SPECTROSCOPY

Jie WANG[*], Yaqun HE[*, **], Yong YANG[*], Weining XIE[*], Xiangyang LING[*]

[*] School of Chemical Engineering and Technology, China University of Mining & Technology, Xuzhou, Jiangsu 221116, China

[**] Advanced Analysis and Computation Center, China University of Mining and Technology, Xuzhou, Jiangsu, 221116, China, yqhe_cumt@126.com

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Abstract: Surface properties play important roles in characterization of structural parameters and the hydrophilicity index. Accurate analysis of the macerals rather than the average properties of the macerals and minerals are crucial for these parameters and indexes. In order to improve the accuracy of analyzing coal surface property, HF/HCl acid leaching was applied to eliminate the interference of minerals. FTIR was used to characterize the differences in surface chemical composition between raw and processed coal. Moreover, each functional group was analyzed quantitatively. Based on these quantitative data, the structural parameters and hydrophilicity indexes were calculated. From the results of FTIR, the peaks of mineral cover up the types of the organic peaks, such as -COOH and aromatic CH stretching. In addition, they decrease the intensity of the peak such as C=C and aromatics CHx out-of-plane deformation in the spectra of raw coals. However, it provided the accurate types and contents of organic functional groups of the macerals after acid leaching. The structural parameter results indicate that the values cannot reflect the coal ranks through the surface properties of raw coals while they show a good relationship with the degree of coalification in the analysis of processed coals. Besides, the hydrophilicity indexes are verified by the natural floatability of coal macerals of the processed coals. It is also found that the processed lignite coal cannot be floated despite elimination of the hydrophilic minerals. The main reason of hard-to-float property of lignite coal lies in a strong hydrophilicity of macerals.

Keywords: *chemical-structural properties, macerals, hydrophilicity, functional group*

Introduction

Coal, a heterogeneous organic sedimentary rock, contains organic matter as macerals and inorganic matter mostly in the form of minerals. For beneficiation of fine coals, flotation is a typical way of separating the coal macerals composition and minerals, such as calcite, dolomite, quartz and clay minerals from the fine coals.

http://dx.doi.org/10.5277/ppmp170119

In the flotation process, to enhance the difference of hydrophobicity of two kinds of materials, some hydrocarbon oils, such as dodecane, kerosene and diesel oil, are applied as the collector to adsorb on the hydrophobic surface of macerals for increasing their hydrophobicity in froth flotation process (Harris et al., 1995; Vasumathi et al., 2015). A low consumption of oily collectors can achieve a positive effect for the medium/higher rank of coals. However, oily collectors are hard to spread on the surface of low rank coals, which leads to poor performance of flotation process. Even though consuming more oily collectors, the recovery of low rank coal is still moderate (Gutierrez-Rodriguez and Aplan, 1984). As the flotation method depends on the differences in surface properties of macerals and minerals such as floatability, wettability and hydrophobicity, experts have conducted many investigations and found that coal floatability is determined by its hydrophobicity (Chau et al., 2009; Ulusoy et al., 2003). Furthermore the hydrophobicity of coals is related to the surface functional groups (Fuerstenau et al., 1987; Fuerstenau and Diao, 1990; Xia et al., 2012). Thus, it is often necessary to deduce the degree of hydrophobicity from knowledge of the surface chemistry property to evaluate the floatability of a coal sample. Fourier transform infrared spectroscopy (FTIR) is one of the most versatile analytical techniques for obtaining information on coal structure (Painter et al., 1985; Liang et al., 2015). Originated in FTIR spectra, many structural parameters have been used to evaluate the maturation level of raw coals (Mastalerz and Bustin, 1995). Nevertheless, coal is an extremely complex system, including organic macerals and various kinds and contents of inorganic minerals. It is not clear whether the existence of minerals affects the accuracy of parameters. Based on the FTIR results, the hydrophilicity of coals has also been calculated to estimate the floatability in flotation process (Ye et al., 1988; Jena et al., 2008; Çinar, 2009). While the majority of investigations have traditionally established only based on average properties. Basing on them conclusion were made that the hydrophilicity decreases with the increase of coal rank. This conclusion may not completely explain the hard-to-float property of lignite coal. Furthermore, the influence of the inorganic chemical composition on the hydrophilicity of lignite macerals is not clear. Studying data on structure and properties of pure coal samples could be an important contribution. To obtain pure macerals, chemical methods are used having high efficiency of removing minerals (John et al. 1989). Research of Strydom et al. showed that the chemical method of HF and HCl acid leaching can effectively dissolve most minerals including clays, quartz and carbonate minerals without affecting the chemical properties of organic macerals (Strydom et al. 2011).

As mentioned above, the present investigations on coal surface properties focus on the average property of inorganic minerals and organic macerals. Few researches mentioned the influence of minerals on the analysis of coal structure and hydrophobicity/hydrophilicity. The influence of minerals definitely cannot be ignored because the minerals are hydrophilic which would decrease the hydrophobicity of coal macerals, particularly for hard-to-float lignite coal. This paper aims to improve the accuracy of characterizing the coal surface properties through eliminating the interference of minerals. Acid leaching was applied to pretreat the coal samples of lignite, gas coal and anthracite coal samples. FTIR was used to characterize the surface properties of the coal particles before and after the process. Functional groups were calculated by the Gaussian peak fitting method quantitatively. Based on the quantitative data, the structural parameters and hydrophilic indexes of different coals were calculated and compared. Effects of the minerals on the accuracy of structural parameters and hydrophilicity index were also discussed. In addition, the relationship between hydrophilicity and the chemical composition was tested by the natural floatability tests. This research would be helpful to detect the fundamental cause of hydrophilicity in lignite coal.

Experiments

Experiment materials

Three Chinese coals ranging in rank (lignite, gas coal and anthracite coal) were studied to determine their surface chemistry-structural properties after acid leaching process. Coal samples were ground in a universal crusher and sieved to the particle size ranging from -0.25 +0.1 mm. Coals were then stored in sealed containers to reduce the possibility of surface oxidation. The mineral matter contents of the three coals were measured as 38.70%, 41.97% and 15.32% for lignite, gas coal and anthracite coals, respectively.

HF and HCl bought from the Shanghai Su Yi Chemical Reagent Company were both of analytical grade with mass fraction of 40% and 36-38%. Deionized water was purchased from a local producer.

Experiment process

The coal samples were treated with combination of HF and HCl acid. The process of acid leaching could be divided into four steps, which is shown in Table 1. The first step was to leach the coal samples three times with HCl. According to the liquid-to-solid ratio of 5:1, 50 cm^3 HCl and 10 g coal were added to a 250 cm^3 plastic beaker, then the plastic beaker was put in a 70 ℃ water bath. Discarding the supernatant liquor, the residual coals were next leached twice with HCl. The second step was HF leaching. The residual coal particles from the first step were treated with 50 cm^3 HF. After a certain time the supernatant liquor was removed. The third step covered leaching with a binary mixture of HCl and HF acids, with the volume ratio of HCl and HF as 2:1. Finally, in order to remove the absorbed HCl and HF from the residual coal surface, plenty of boiled deionized water was used in a rinsing step until the pH of filtrate was 7.0. Finally, the residual coal samples were dried in a vacuum oven at 105 ^oC (John et al. 1989, Strydom et al. 2011).

Table 1. Details of leaching process

Step	Temperature (℃)	Liquid	Vol (cm^3)	Time (min)
1*	70	HCl**	50	30
2	70	HF**	50	60
3	70	HF + HCl	60	30
4	100	deionized water	abundant	abundant

* HCl leaching process was conducted three times
**acid leaching was conducted with concentrated acids

The ratio of demineralization, E_d (Eq. (1), was introduced to quantify the extent of removal of minerals. It was described as the ratio of the mineral matter removed or 'demineralized' to the original ash yield of the sample on the air dry basis, expressed in per cent

$$E_d = \left(\frac{A_r - A_p}{A_r} \right) \times 100\% \tag{1}$$

where A_r is the ash yield of raw coal sample (wt. %) and A_p is the ash yield of the processed coal sample.

FTIR of surface functional groups

Characteristics of the coal surface functional groups were recorded with Bruker Vertex 80v providing wave number from 4000 cm^{-1} to 400 cm^{-1} with resolution of $4cm^{-1}$. Pure KBr was used to obtain a reference spectrum. The coal sample was dried in a far infrared oven for 2 hours. Approximately 100 mg potassium bromide (KBr) powder and a small amount of dried coal sample, with the mass ratio of coal to KBr as about 1:100, were placed in an agate mortar to be thoroughly mixed and then put in a diffuse reflectance test apparatus. Each spectrum was compiled from 32 scans.

Flotation process

Flotation tests were conducted on demineralized lignite, gas coal and anthracite coal in a miniature flotation cell. The experiments were performed in distilled water using 50 cm^3/min of air flow rate and 400 rpm rotating speed. No flotation reagent was used for the flotation test. The experiments were designed as a slow flotation by using a low air flow rate and long flotation times to avoid the transport of coal particles by turbulent bubble motion. In this case, the true floatability of the coal particles was measured.

Results and discussion

Quantitative ratios of functional groups

Ash content of coal samples in rank from lignite, gas coal to anthracite coal before and after the acid leaching process is presented in Table 2. It indicates that the ash contents of the processed coals decrease to a very low level and the removal ratios tend to be 100%. The inorganic minerals can be removed predominantly through the HF/HCl acid leaching process. With the ash content lower than 4%, the processed coal samples can be considered as consisting of pure macerals in the analysis with FTIR.

Table 2. Analysis of ash content for coal samples

Coal sample	Ash content (%)		Removal ratio (%)
	raw coal	processed coal	
Lignite coal	38.70	1.47	99.96
Gas coal	41.97	3.69	99.91
Anthracite coal	15.32	0.30	99.98

The standard FTIR spectra of coal samples from raw to processed lignite, gas coal and anthracite coal are presented in Figures 1 to 3. The FTIR signals deriving from the chemical functional groups are listed in Table 3 (Painter et al., 1981, 1985; Wang and Griffith, 1985). Quantitative ratios of these organic peaks are calculated by the method of Gaussian peak fitting.

Table 3. Band assignments for the FTIR spectra of coals

Wavenumber (cm^{-1})	Functional groups
3400-3700	-OH(minerals)
3100-3400	-OH
3000-3100	Aromatic CHx stretching
2800-3000	Aliphatic CH_x stretching
1650-1800	-COOH
1550-1650	Aromatic C=C ring stretching
1300-1550	Aliphatic CH_x bending
1100-1300	C-O-C stretching
900-1100	Si-O stretching
650-900	Aromatics CHx Out-of-plane deformation
-650	Al-O formation, Si-O

Figures 1a and b show that the surface characteristics based on FTIR spectra of lignite coal before and after the acid leaching process. In Figure 1a, the peaks of the minerals involved –OH, Si-O-Si, Si-O, and Al-O dominate in the FTIR spectrum of raw lignite coal, and the intensity of organic peaks are comparatively inferior. After the demineralization, nearly all the mineral absorbance peaks disappeared in processed lignite coal (Figure 1b). Compared with the characteristics of raw lignite coal, the organic peak of –COOH at 1700 cm^{-1} is present in the processed lignite coal and the intensity of other organic peaks increased for aromatic C=C at 1607 cm^{-1} and aliphatic CHx at 2920cm^{-1}, 2851 cm^{-1} and 1507 cm^{-1} groups. The peaks in the region from 2000 cm^{-1} to 1000 cm^{-1} in Figure 1a and b, indicate strong mineral peaks of Si-O-Si and Si-O resulting from the decrease of the organic peaks. The relative contents of each functional group are illustrated through the quantitative calculation of each functional group. It is peculiar that the content of aliphatic CHx is nearly equal to that of aliphatic CHx in raw lignite coal. However, the quantitative analysis of processed lignite presents higher content of aliphatic CHx than the aromatic CHx groups, which is expected for the low rank coal. In terms of oxygen functional groups, three kinds of groups including (C-O-C, –COOH and –OH) are found in processed coal. Especially a high content of–OH plays the major role in the hydrophilicity of lignite coal.

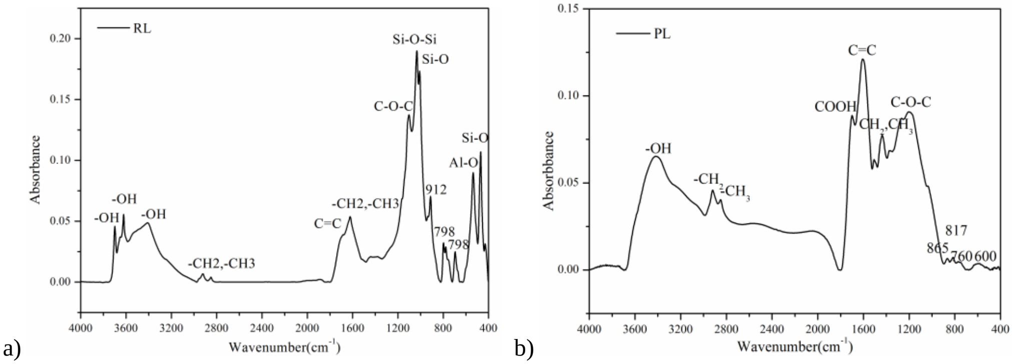


Fig. 1. FTIR spectra of lignite coal (a) raw coal, (b) processed coal

Figure 2 presents the surface functional groups in the gas coal sample. In raw gas coal, the mineral peaks mainly appear in the region from 1200 cm^{-1} to 400 cm^{-1}, e.g. the strong peaks of Si-O-Si at 1093 cm^{-1}and Si-O at 486 cm^{-1}. After demineralization, nearly all the mineral absorbance peaks vanish in processed gas coal (Figure 2b). Besides the disappearance of the peaks of minerals, several new organic peaks are appear for processed coal including peaks of aromatic CHx stretching and -COOH groups at 3047 cm^{-1} and 1904 cm^{-1}, respectively. In addition, the intensity of peaks of aliphatic CHx, aromatic C=C and C-O-C groups are strengthened (Fig. 2b). The organic functional groups interfered by the minerals result in an inaccuracy in calculating their contents quantitatively. It is presented that the content of aliphatic CHx groups is still higher than these of aromatic CHx groups in the quantitative analysis of processed gas coal. However, in comparison with processed lignite coal, this content decreases apparently by about 10%, which agrees with the increase of coal rank. Despite of the high content 36.86% of C-O-C groups, -OH still occupies 10.57% in processed gas coal. It is not difficult to find that the amount of C-O-C groups increases by about 14% but –OH decreases by nearly 15%, when compared with the processed lignite coal.

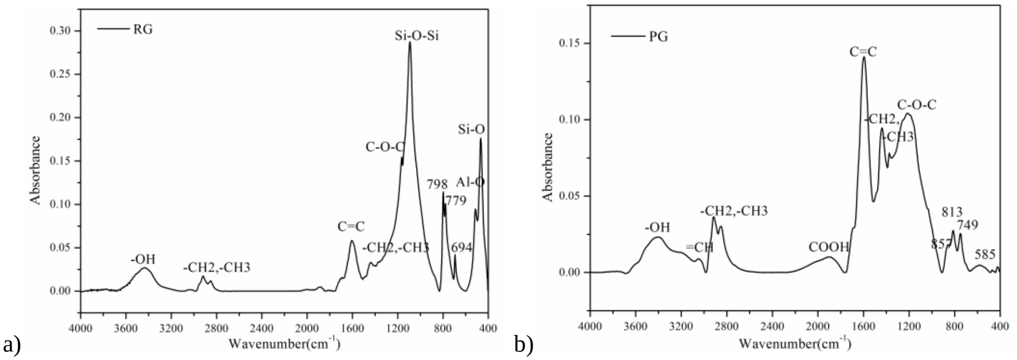
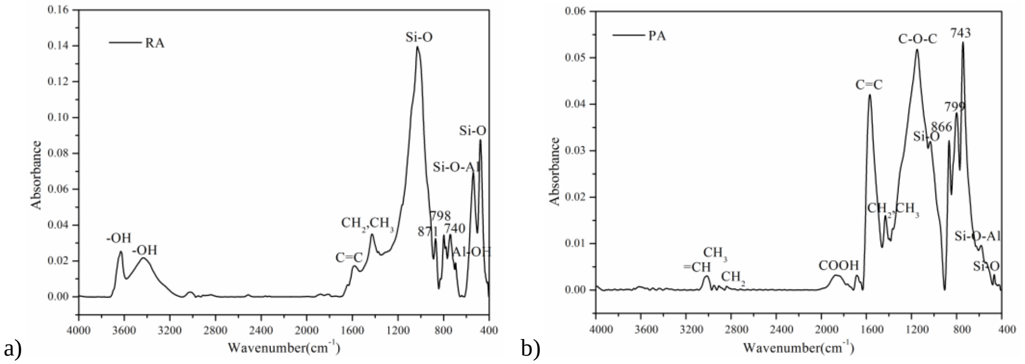


Fig. 2. FTIR spectra of gas coal (a) raw coal, (b) processed coal

Figure 3a and b show the FTIR spectra of raw and processed anthracite coal, respectively. For raw anthracite coal, peaks of minerals, including –OH, Si-O and Si-O-Al., predominate in the spectrum, and the intensities of organic absorbance peaks are much weaker. However, in the case of processed anthracite coal, the types and intensity of organic peaks apparently exceed that of minerals. Comparison between Figure 3a and b shows obvious changes on anthracite coal surface after leaching. Particularly, the organic absorbance peaks at 1650-3700 cm^{-1} and 1000-1300 cm^{-1} appear in the FTIR spectra of processed anthracite coal. Moreover, the absorbance intensity of C=C and aromatic CHx groups characterized by the out-of-plane deformations at 1550-1650 cm^{-1} and 650-900 cm^{-1} increase remarkably (Figure 3b) after demineralization process. As mentioned above, most vibration signals of minerals have disappeared in processed anthracite coal. Quantitative analysis of the organic functional groups in raw anthracite just shows three kinds of organic peaks including aromatic C=C, aromatic CHx and aliphatic CHx. From the perspective of the position at which organic peak is present, it can be deduced that -COOH is affected by strong mineral peaks and the position of the C-O-C group is occupied by the adjacent strong mineral peak of Si-O-Si. The quantitative analysis of organic functional groups indicates that the aromatic functional groups, including aromatic C=C and CHx, hold the dominant content, reflecting the relative high coal rank. The C-O-C groups play an important role among the oxygen functional groups, indicating its stability during the coalification process.



a) b)

Fig. 3. FTIR spectra of anthracite coal (a) raw coal, (b) processed coal

In conclusion, the peak of -COOH group is absent in all the three raw coals, though its real content is low in processed coals. Thus, it can be demonstrated that the improved approach can really produce more accurate information about the coal macerals. The absorbance of –OH and aliphatic CHx groups stretching decrease obviously with the increase of coal rank as can be seen from the quantitative analysis. However, the ratios of C-O-C and aromatic CHx groups increase prominently with the increase of the coal rank. However, the proportion of -COOH to aromatic C=C groups does not change significantly in the three processed coal samples. From the analysis of processed coals, the peaks of –OH, aliphatic CHx, C-O-C and aromatic CHx groups could be representative in terms of the coal rank, but this conclusion cannot be obtained for the raw coals.

Structural parameters of coal

The structural parameters derived from the FTIR characteristics of the coal surface are listed in Table 4. Differences are shown in this table between structural parameters of raw and processed coals.

Table 4. Quantitative ratios derived from FTIR spectra

Quantitative index	Index calculation	Index value					
		RL	RG	RA	PL	PG	PA
Aromaticity 1 (A1)	CHar stretching/ (CHal stretching + Aliphatic CHx bending)	0	0	0	0	0.04	0.2
Aromaticity 2 (A2)	CHar out-of-plane deformation/ (CHal stretching+ Aliphatic CHx bending)	0.82	2.52	0.99	0.02	0.21	7.35
Degree of condensation 1 (D1)	CHar stretching / C=C stretching	0	0	0	0	0.045	0.05
Degree of condensation 2 (D2)	CHar out-of-plane deformation / C=C stretching	3.49	0.97	2.76	0.06	0.22	1.85

Aromaticity index indicates the ratio of aromatic H for different vibrations of stretching (A1) and out-of-plane deformation (A2) versus aliphatic H (Painter et al., 1981). There are quite few CHar stretching peaks in the coal samples (Ye et al., 1988) and this peak is absent in raw coals having minerals, whereas it appears in the processed coals after demineralization (Figure 1-3b). Thus, values A1, indicating CHar stretching for the three raw coals are zero. The observed slow and continuous increase of A1 in processed coals demonstrates a gradually growing coalification level. In the case of A2, the aromatic CHx out-of-plane deformation increases remarkably from lignite coal to anthracite coal after eliminating the influence of minerals. However, A2 varies randomly with the coal rank in raw coals and cannot represent the coalification level. The degree of condensation suggests the ratio of aromatic H various vibrations versus aromatic C=C stretching (Painter et al., 1981). In terms of the raw coal samples, A1 and A2, D1 of the three raw coals are equal to zero and D2 changes irregularly with the increase of coal rank. While D1 increased slowly for a negligible value for processed lignite coal to anthracite coal, D2 displayed a more apparent tendency with the steep gap between gas coal and anthracite coal. Thus, the FTIR analysis of raw coal could bring inaccuracy and misunderstanding in evaluating the coal ranks through FTIR without eliminating the interference of inorganic minerals. If the structural parameters for evaluating the coalification levels are obtained through the analysis of the surface chemical composition, the minerals should be removed for eliminating the interference.

Hydrophilicity index

Based on the surface hydrophilic (hydroxyl and carboxyl) and hydrophobic groups (aliphatic and aromatic CHx), the hydrophilicity index could be characterized by the chemical composition of the coal surface. The index has been formulated (Yuh and Wolt, 1983; Paiter et al., 1983) as:

$$\text{Hydrophilicity index} = \frac{K_i\left(HL\right)_i}{K_j\left(HO\right)_j} \tag{2}$$

where $(HL)_i$ is a measure of abundance of the hydrophilic functional group i and $(HO)_j$ is a measure of abundance of the hydrophobic functional group j at the coal surface, respectively. K_i and K_j are corresponding coefficients and may be determined either theoretically or experimentally. If the aliphatic and aromatic CHx groups are the only hydrophobic functional groups and the hydroxyl and carboxyl groups are the only hydrophilic groups, then the hydrophilicity index given above can be simplified to (Ye et al., 1988, Celik, 1995, Çinar, 2009; Biswal, 2001; Biswal et al., 2003):

$$\text{Hydrophilicity index} = \frac{\lambda\left(-\mathrm{COOH}\right)+2\lambda\left(-\mathrm{OH}\right)}{\lambda\left(R-\mathrm{H}\right)+\lambda(\mathrm{Ar}-\mathrm{H})} \tag{3}$$

where $\lambda(-\mathrm{COOH})$, $\lambda(-\mathrm{OH})$, $\lambda(R-\mathrm{H})$ and $\lambda(\mathrm{Ar}-\mathrm{H})$ are the measures of abundance for carboxyl, hydroxyl, aliphatic CH and aromatic CH groups, which are shown in Figure 1 to 3 for different coals. As analyzed in section 3.1, -COOH groups are absent in all the three raw coals, so hydroxyl, in which cannot be distinguished between in organic and inorganic materials, becomes the only hydrophilic functional group in the Hydrophilicity Index. In addition, the contents of aliphatic CH and aromatic CH groups affected by the mineral peaks. Based on the quantitative calculation data of Figure 1 to 3, the average Hydrophilicity Index, calculated from Eq. (3), is 2.73, 1.33 and 1.61, for raw lignite to anthracite coal, respectively. Since the FTIR spectra of processed coals are obtained without the interference of minerals, the more accurate hydrophilicity indexes could be calculated according to Eq. (3). The Hydrophilicity Indexes are calculated as 1.60, 0.92 and 0.07 for processed lignite, gas coal and anthracite coal, respectively. The hydrophilicity index decreases with the increase of the rank of coal gradually. This index reflects the hydrophilicity of coal macerals without the interference of inorganic minerals, while the Hydrophilicity Index of raw coal involves coal macerals and minerals.

Experimental results of the micro-flotation tests are given in Table 5. After thirty minutes of flotation with no reagent added, processed lignite coal particles nearly could not be recovered, whereas yields of 66.4% and 89.86% were achieved in processed gas coal and anthracite coal flotation, respectively. It indicates that the hydrophilicity decreases with the increase of coal rank levels. Comparing the index of processed coal with the flotation yield, it is demonstrated that the hydrophobicity of the coal surface decreases with the increase of the Hydrophilicity Index. Thus, this index can be used to forecast the coal flotation yield. Furthermore, the improved approach helps to make it clear that the hydrophilic property of lignite coal is still strong even without the influence of minerals.

Table 5. Flotation yield of lignite, gas coal and anthracite coal by using miniature flotation cell

Coal samples	Flotation time /min	Yield /%
Lignite coal	30	1.54
Gas coal	30	66.43
Anthracite coal	30	89.86

Conclusions

In order to improve the accuracy of analysis of coal surface property, HF/HCl acid leaching was applied to eliminate the interference of minerals. The FTIR results indicated the differences in accuracy of surface properties determination between the raw and processed coal. The studies showed the following.

The organic peaks of aromatic CHx stretching and –COOH groups are covered up and intensity of C=C and aromatics CHx out-of-plane deformation are decreased to some extent with the existence of minerals. Demineralization provides the FTIR spectra of organic peaks with almost no peaks due to minerals. These FTIR spectra are more representative for chemistry composition of macerals surface, while the existence of mineral peaks affects the types and contents of the organic peaks through the analysis of raw coal. Furthermore, the structure parameters of Aromaticity 1 and Degree of Condensation 1 are calculated to be zero for all the three raw coal samples and the values of Aromaticity 2 and Degree of Condensation 2 change randomly through the analysis of raw coal surface. Thus, the FTIR analysis of raw coal is inaccurate and misleading in evaluating the coal ranks. However, the values of these parameters increase with increase of the coal rank for processed coals. On the other hand, the hydrophilicity indexes are calculated to be 2.73, 1.33, and 1.61 for raw coal samples in the order of low to high rank, larger than those of 1.60, 0.92 and 0.07, respectively because the former values represent the average hydrophilicity of macerals and minerals. Furthermore, the flotation yields of processed lignite, gas coal and anthracite coal are 1.54%, 66.43% and 89.86% respectively. It increases with the decrease of hydrophilicity index of processed coal. It is found that the lignite coal cannot be floated in spite of eliminating the hydrophilic minerals. The inner reason in hard-to-float property lies in the strong hydrophilicity of macerals. However, in order to separate the hydrophilic lignite coal macerals and minerals in flotation process, the difference in hydrophilicity between them should be confirmed in a further research.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No.51274196). We also want to thank the support of Science Innovation Research of College Graduate in Jiangsu Province of China (No. KYLX15_1415). We would like to thank Advanced Analysis and Computation Center of China University of Mining and Technology for their technical support.

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