ACTIVATION OF OXIDIZED SURFACE OF ANTHRACITE WASTE COAL BY ATTRITION

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Abstract. In this paper the activation of oxidized surface of anthracite waste coal was investigated. Coal weathering leads to physical and chemical changes on the coal surfaces and a reduction of its hydrophobicity and floatability. The changes and the presence of oxygen functional groups in the structure and surfaces coal was confirmed by the FTIR study on the raw and waste coal. The groups have remarkable impacts on surface charge and thus flotation kinetics. The floatability of oxidized coal may be improved by the creation of fresh, unoxidized surfaces on coal by attrition at high solid concentration prior to introducing coal to the froth flotation process. This paper presents the results of the effects of attrition on the floatability of the oxidized surface of waste coal, coal pyrite and alumino-silicate minerals through electrokinetics and microflotation experiments. The results show that the attrition, in the viscous pulp with the solid content of 50%, lead to the mechanical cleaning of oxidized surface and activation of the surface of coal particles, which agrees with the change of zeta potential and increasing floatability of coal by 10%. Obviously that the mechanical scrubbing may be able to restore the natural floatability of superficially oxidized coal by removing the thin oxidation layer from the coal surface. The results show that attrition time is an important parameter from the point of view of activating the oxidized coal surface, and positive changes in zeta potential and floatability. The change of zeta potential, as a measure surface charge state of coal particles, from -15 mV to about 0 mV, after attrition for 30 minutes, confirms positive application of attrition. Zeta potential approaching 0 mV resulted in increasing floatability down to the real possibilities of the attrition process prior the coal flotation.

keywords: waste coal, oxidation, FTIR, attrition, zeta potential, floatability

1. Introduction

A large amount of waste coal is created annually in the anthracite Vrska Cuka coal mine, Avramica, Serbia. It is becoming necessary to beneficiate the large quantity of discarded coal fines. Apart from adding value to a waste product, there is also an environmental issue (the fines are generally dumped into large ponds). Such waste

coal shows reduced natural floatability and it is not suitable for the application in a flotation process.

It is known that coal weathering, which occurs when coal is exposed to the atmosphere in natural conditions, is a very complex physico-chemical process (Iglesias et al., 1998). The atmospheric oxidation of coal by weathering or by storage starts with the physical adsorption of oxygen on the surface to form various oxygen functional groups such as hydroxyl (phenolic –OH), carbonyl (C=O) and carboxyl (–COOH) groups and soluble inorganic species on the coal surface (Somasundaran et al., 2000; Jia et al., 2000). The presence of these functional groups in coal structure strongly affects coal surface properties and reduces the hydrophobicity of the coal surface, as a results, its floatability (Sun, 1954; Swann et al., 1972; Wen and Sun, 1981; Fuerstenau et al., 1983, 1992; Philips et al., 1987; Laskowski, 1995), because the surface functional groups are hydrophilic (Beafore et al., 1984). According to Fuerstenau et al. (1983), coal surface properties are determined by the surface functional groups (especially the phenolic and carboxylic oxygen groups) more than by total oxygen content. Other studies have shown that coal oxidation increased oxygen functional groups such as carboxyl (COOH), carbonyl (C=O), and phenol, altering the surface hydrophobicity through the hydrophobic and hydrophilic balance (Fuerstenau et al., 1983; Miller et al., 1983).

Recently, many researchers determined these functional groups on the coal surface by various analytical techniques. FTIR methods can be a powerful tool for studying the surface components of coal and their changes during oxidation (Calemma et al., 1988: Kister et al., 1988; Xiao et al., 1990; Iglesias et al., 1998; Pietrzak and Wachowska, 2003; Saikia et al., 2007). Also, a number of indirect techniques are used to measure the degree of oxidation of coal surface by determining the wettability and floatability of the coal. The zeta potential measurement of coal can provide useful mechanism information of the surface changes. The zeta potential of oxidized coal is generally found to be lower than that of un-oxidized coal (Fuerstenau et al., 1987; Sadowski et al., 1988) and the isoelectric point usually shift toward the acid pH range (Sokolovic et al., 2006). Obviously, the zeta potential of coal is a function of active oxygen groups. An increase in the hydroxyl and carboxylic functional groups on the coal surface increases the negative zeta potential (Woodburn et al., 1983).

Yarar and Leja (1981) established a correlation between the zeta potential of weathered coal and its flotation response. It was found that naturally weathered coal flotation follows a pattern parallel to zeta potential. These studies were directed towards establishing the relationships between the degree of oxidation and surface oxidations of coal as well as its flotation response.

The floatability of minerals can be directly correlated to their zeta potentials changes. A correlation between concentration of phenolic and carboxylic groups and the flotation behavior of several different coals has been discussed by Fuerstenau et al. (1983; 1987; 1994). The ionizable phenolic and carboxylic groups have a great effect on froth flotation since these groups affect the zeta potential of coal and modify its

wettability and floatability (Sarikaya, 1995). It was shown, using film flotation and zeta potential measurements that the maximum flotation response for coal occurs close to its isoelectric point (IEP) (Fuerstenau et al., 1983; Diao and Fuerstenau, 1991; Laskowski, 2001).

It is known that floatability oxidized coals can be improved in various ways, by adding certain agents (Horsley, 1951-1952; Gayle et al., 1965; Karsilayan et al., 1992; Bolat et al., 1998; Jia et al., 2000) or application of various physical and mechanical processes (Buttermore and Slomka, 1991; Piskin and Akguen, 1997; Ozkan and Kuyumcu, 2006).

In this study we investigated the activation of oxidized surface of anthracite waste coal using attrition. The floatability of oxidized waste coal can be improved by the creation of fresh, unoxidized surface of the coal by attrition. Mechanical scrubbing may be able to restore the natural floatability of superficially oxidized coal by removing the thin oxidation layer from the coal surface (Tao et al., 2002). Various techniques, including FTIR, electrokinetic and microflotation tests have been employed in our research works. The results of investigations of the effects of attrition on the floatability of the oxidized surface of waste coal, coal pyrite and alumino-silicate minerals are presented in the paper. The results are compared with floatability and zeta potential of raw coal.

2. Material and methods

2.1. Materials

Samples were taken from anthracite coal mine Vrska Cuka in Serbia. The first pure representative samples were collected manually from raw coal (marked as coal (C)) and second, from the waste ponds (marked as waste coal (WC), alumino-silicates (AS) and coal pyrite (CP). The collected pure sample of about 250 kg was subsampled by coning and quartering to obtain a representative sample. All samples, from 50 to 100 mm size range, were crushed and screened to obtain different size fractions. The (-38+0) μm fraction was used for proximate, ultimate analyses, micro flotation tests and electrokinetic's measurements, respectively. The characterization of coal samples provides a fundamental understanding of its oxidation state. The data that is obtained usually indicates whether or not coal is easily floated. Proximate analysis includes the analytical determination of the combustion matter content, volatile matter and ash content in the coal sample. The fixed carbon content was calculated by subtracting the ash and volatile matter content from 100%. Ultimate analysis consists of measuring of carbon, hydrogen, sulphur and, nitrogen. The oxygen content of the coal is calculated by subtracting the sum of the carbon content, hydrogen content, sulphur content and nitrogen content from 100%. The results of proximate and ultimate analyses of the raw and waste samples are given in Tables 1 to 3.

The average content of ash in raw coal is about 7.5%, calorific value in comparison with other kinds of coal is higher, allways over 33.5 MJ/kg. According to data from

Table 1, a significant increased in ash content was found in the waste coal (WC) sample as a result of the coal weathering and storage. The average ash content in waste coal sample increased and was about 17.3 %.

Table 1. Proximate analysis of coal (C) and waste coal (WC) sample

Sample	Combustion matter (%)	Volatile matter (%)	Coke (%)	Fixed carbon (%)	Calorific value (kJ/kg)	Ash (%)	Total sulphur (%)
Coal (C)	92.47	9.21	90.79	83.26	33586	7.53	1.40
Waste coal (WC)	82.70	6.43	93.57	76.27	29754	17.30	1.61

Table 2. Proximate analysis of associated mineral matters samples

Sample	Combustion matter (%)	Calorific value (kJ/kg)	Ash (%)
Alumino-silicates (AS)	14.05	-	85.95
Coal pyrite (CP)	24.85	5927	75.15

Table 3. Ultimate analysis of coal and waste coal and associated mineral matters samples

Sample	Element (wt. %)			
	C	N	H	S
Coal (C)	73.15	3.15	2.07	0.72
Waste coal (WC)	56.83	2.84	1.33	0.50
Alumino-silicates (AS)	9.25	1.27	-	-
Coal pyrite (CP)	8.06	0.70	-	31.27

Table 4. Chemical analysis of ash of coal and waste coal and associated mineral matters samples

Sample	Element (wt. %)					
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3
Coal (C)	11.56	10.30	31.00	3.82	6.29	28.50
Waste coal (WC)	39.68	18.90	12.72	1.79	4.59	11.95
Alumino-silicates (AS)	60.16	17.95	2.54	0.91	9.21	2.55
Coal pyrite (CP)	0.80	1.01	11.45	3.44	47.64	19.65

A comparison in the elemental composition of both coal samples is given in Table 3. The results of qualitative composition of elements in the raw and waste coal show increase of O (calculated by difference to 100 %) and reduction of C/H ratio (obtained from ultimate analysis) in the waste coal, indicating the sensitivity of the coal surface to oxidation (weathering). Chemical analysis of all analyzed samples confirms a presence of associated mineral matters such as coal pyrite and alumino-silicates.

2.2. Methods

2.2.1. FTIR spectroscopy

Infrared spectroscopy is an important and widely used analytical tool for determining the structure of coal material. FTIR spectra were recorded on a Nicolet Nexus IR 6700 with KBr pellet in the range of wave numbers 4000-400 cm^{-1}. Scans were collected at a resolution of 2 cm^{-1}. The coal/KBr disks were prepared at ratio 150 mg KBr and 1 mg sample.

2.2.2. Zeta potential measurements

Electrokinetic studies were carried on a defined size fraction of -38 μm, with 10 grams of the sample and 1 dm^3 solution of different pH values. The zeta potential was determined using a Riddick Zeta Meter and an electrophoretic cell. After conditioning, the pulp was transferred to the electrophoretic cell and the mobility of at least 10 particles was measured. The zeta potential was calculated from the electrophoretic mobility. In determining the zeta potential value adjustments were made for temperature which varied in the range of 20 to 25°C.

2.2.3. Microflotation experiments

Micro-flotation tests were carried out using a modified Hallimond flotation glass tube. Sample was conditioned in 100 cm^3 solution at the different pH values. Conditioning time was 3 minutes. Following the conditioning step, the pulp was transferred to the Hallimond tube for flotation, which was carried out for 1 minute using air at a flow rate of 0.1 dm^3/min. All experiments were conducted using distilled water. The 0.1 M HClO$_4$ acid and 0.1 M NaOH base solutions were used as pH modifiers.

3. Results and discussion

Current knowledge on the flotation of oxidized coals shows that the investigation of physical-chemical properties and phenomena at interfaces, as well as the identification of compounds on the surfaces of coal, can establish a correlation between the functional groups as well as zeta potential and floatability.

3.1. Identification of functional groups on the surface of coal by FTIR analysis

Concentration, type and distribution of functional groups on the surface of coal can vary widely depending on the type and degree of coal oxidation. Figures 1a and 1b present the spectra of the raw and waste coal samples.

The FTIR spectra of both studied coal samples show a certain number of common absorption bands, different shapes and intensities, with characteristic peaks, which can be divided into the following functional groups:

- bands in the range from 3600 to 3700 cm^{-1} assigned to vibrations of hydrogen strongly bonded of OH groups. These bands indicate the presence of small concentrations of alcohol and phenol

- in the wavelength range of 2850 to 2950 cm^{-1}, and 3000 to 3100 cm^{-1}, fresh raw coal shows weak bands with characteristic peaks at 2910 and 3031 cm^{-1}. Both bands assigned to asymmetric stretching vibration of CH$_2$ groups, or asymmetric and symmetric vibration of aromatic =C-H compounds, respectively. The absence of these groups on the spectra of waste coal shows that the intensity of this bands decreases as a result of surface oxidation and the aromatic structures in coal subject to oxidation

- peak at 1587 cm^{-1} in the wavelength range 1500 to 1600 cm^{-1} in the FTIR spectra of raw coal, assigned to the symmetrical vibrations of C-C=C bond of aromatic rings. These absorption bands confirms the change in surface coal

- the observed peaks of different intensities, with maximum at 1424 cm^{-1} in the spectra of raw coal (RC) and the 1434 cm^{-1} in the spectra of waste coal (WC) corresponding to the deformation of bending vibrations of methyl -CH$_3$ and methylene -CH$_2$ groups. The intensity of these vibrations are also reduced as a result of surface oxidation of coal

- the intensity of the absorption bands with maximum at 1030 cm^{-1} in the spectrum of waste coal is a consequence of the symmetrical vibration of aliphatic ether group, C-O-C and possibly due to vibrations of S = O groups, because the stretching vibrations of these groups occurs in the range of 1030 to 1070 cm^{-1} (Pietrzak and Wachowska, 2003). The absence of S = O groups on the surfaces of raw coal, as well as the formation of sulfoxides on the surfaces of waste coal indicates the effects of surface oxidation of coal

- absorption bands with peaks at 1006, and 1004 cm^{-1} in the spectra of raw and waste coal, respectively, originate from the deformation vibration of C-H group of alkenes. Lower intensity of these vibrations in the spectrum of waste coal confirms changes during coal oxidation by weathering

- formation of carboxyl group (acid) during oxidation can be explained by changes observed in the spectrum of waste coal. In the wavelength range from 880 to 960 cm^{-1} and with a characteristic peak at 910 cm^{-1}, it can be assigned to deformation vibration of OH-O group

- reduction of aromatic hydrogen was observed in the spectrum of waste coal, in the wavelength range from 650 to 900 cm^{-1}, characterized by varying intensity, can be assigned to vibrations of C-H groups of aromatic rings.

Comparing the FTIR spectra of raw and waste coal provide the following conclusions: on the surfaces of waste coal, as a result of oxidation, there is a formation of different oxygen functional groups (COOH, S=O, C-O-C) and absence of C-C=C of the aromatic compounds and reduction of aromatic and aliphatic C-H groups. All previous conclusions confirm the changes on the surfaces, which are the result of surface oxidation, occurred during weathering or storage.
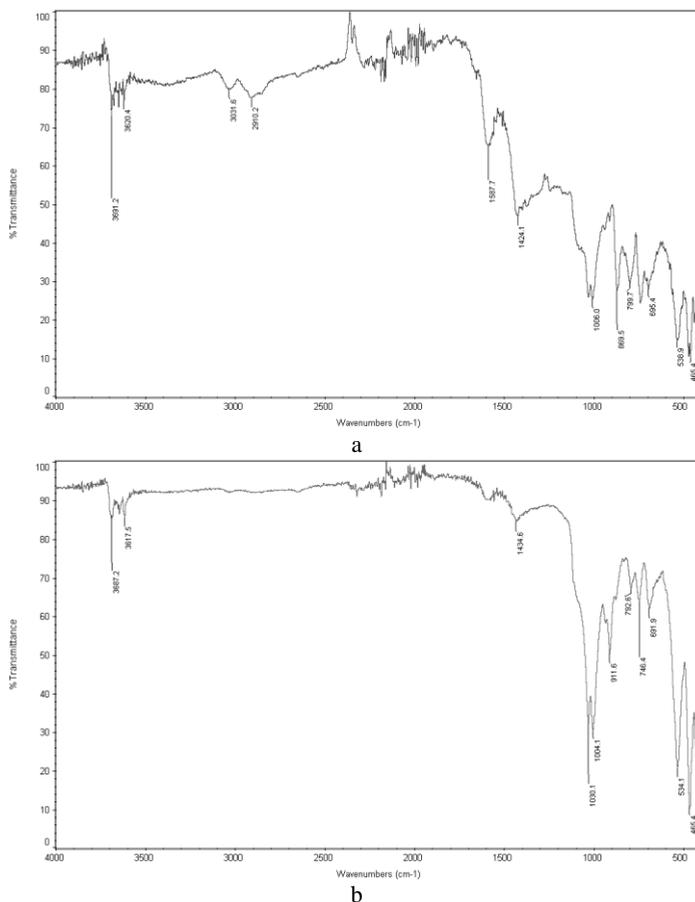
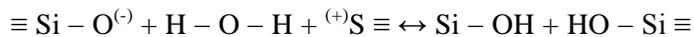Fig. 1. FTIR spectra of a) coal (C) and b) waste coal (WC) samples

3.2. Effect of pH on the zeta potential and floatability

Correlation between zeta potentials of waste (oxidized) coal, coal-pyrite and alumino-silicates minerals from old tailings ponds and flotation responses is a useful indicator of degree of oxidation and floatability of coal. The value of the zeta potential of coal is a key tool of theoretical analyses concerning the behavior of coal in the process of coal flotation. Figure 2 shows the correlation between zeta potential and floatability of waste (oxidized) coal, coal-pyrite and alumino-silicates minerals as a function of pH.

Comparing measured zeta potential and floatability curves, different trends of curves depending on pH can be observed, both from the view point of obtaining isoelectric points of zeta potential as well as optimal flotation response that are important both at the theory and practical use of coal flotation.

The results confirm that H^+ ions are potential determining species. Therefore, different concentrations of hydronium and hydroxyl ions not only change the magnitude of the zeta potential but also its sign. The zeta potential curves show that the isoelectric point (IEP) of waste coal is about pH 6.5. Compared with IEP of raw (unoxidized) coal, which is achieved at pH 7.5 (Sokolovic et al., 2006), results show that the surface of coal particles becomes negatively charged due to oxidation. Obviously, the zeta potential of coal is a function of active oxygen groups and IEP of waste coal lies on the lower pH, as a consequence of oxidation by weathering.

The zeta potentials of alumino-silicates as a function of solution pH are given in Fig. 2b, which shows IEP of alumino-silicates and coal-pyrite at pH 5.7. The position of isoelectric point depends not only on the concentration of H^+ ions, but also the concentration of silanol groups (HO−Si≡) that are formed on the surfaces as a result of oxidation. The reaction is:

$$\equiv Si - O^{(-)} + H - O - H + {}^{(+)}S \equiv \, \leftrightarrow Si - OH + HO - Si \equiv$$
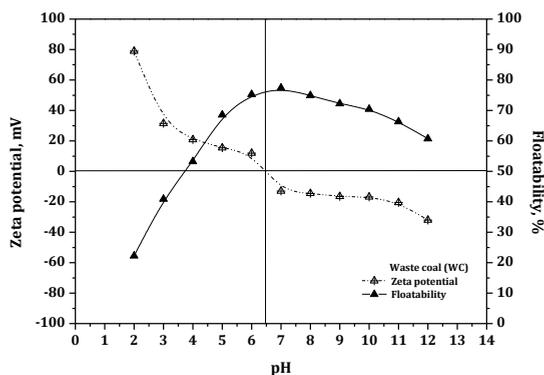
It is believed that these groups show negative charge and the potential determining ions for all SiO_2 modifications are hydroxyl ions. Figure 2b shows that coal-pyrite's isoelectric point (IEP) is at about pH of 8.4. The high IEP value obtained for coal-pyrite may be due to the presence of a high concentration of ferrous ions which results from the high solubility of coal-pyrite. Previous studies of Sokolovic et al. (2006) have shown that addition of ferrous ions shifts the IEP of ore-pyrite from pH 4.0 to 8, and the magnitude of the zeta potential of ore-pyrite is lowered. Comparing zeta potential curves, it is clear that the zeta potential behavior of coal-pyrite is analogous to that of ore-pyrite in the presence of ferrous ions with the same IEP at pH 8. Such results are consistent with the results of Jiang et al. (1998).

Floatability is a critical parameter for control of coal flotation. The flotation behaviors of all samples were found to be dependent on pH. It is shown that the maximum floatability occurs close to the isoelectric points of the coal. The relatively high floatability of waste coal, about 75%, resulted from the sampling method and lower degree of oxidation of crushed and freshly liberated particles of size range - 0.038 mm. It can be seen from Fig. 2b that alumino-silicates minerals are highly floatable (about 35 %) at a pH around 9.
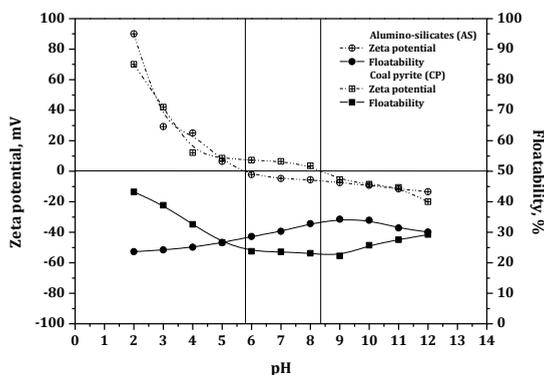
It was found that coal-pyrite is not readily floatable at neutral pH, although it becomes highly floatable at acidic pH. Also, studies have shown that floatability coal pyrite (CP) have maximum (45%) in strong acid solution. However, at around neutral pH region, the recoveries of coal-pyrite decrease drastically. Compared with floatability curves of unoxidized coal-pyrite samples, can be concluded that the waste coal-pyrite, as results of oxidation process, have better floatability properties. There may be several reasons for this behavior. It was known that in neutral and alkaline solutions, the oxidation of coal-pyrite leads to the formation of a hydrated ferric hydroxide and sulphur, which is normally intermediate product of reaction, before

formation of sulphate layers on the mineral surface (Liu et al., 1994). Obviously, the appearance of elemental sulphur, which is believed to be hydrophobic, causes better coal-pyrite floatability.

All measurement of natural floatability confirmed that maximum floatability of waste coal and minimum floatability of coal pyrite is achieved at optimal pH 7.5.
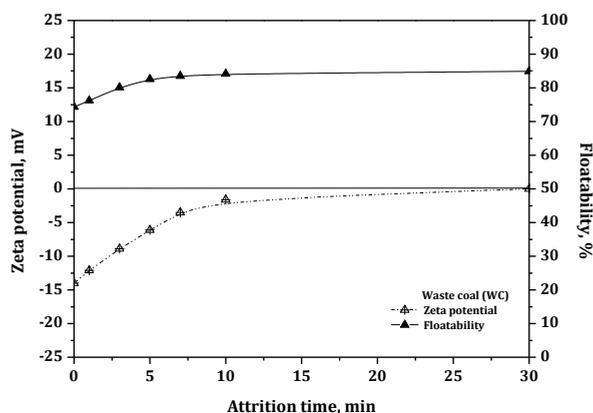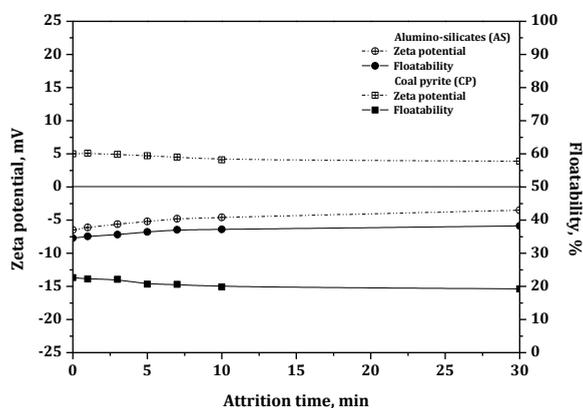

a

b

Fig. 2. Effect of pH on zeta potential and floatability of waste samples
a) coal b) associated mineral matters

3.3. The effect of attrition on the zeta potential and floatability

In order to improve floatability of waste coal, the effect of attrition time on the zeta potential and floatability of waste coal and associated minerals was investigated. All experiments were performed in attrition machine, under optimal test conditions (speed 1600 rpm, the solid content of 50% and the pH value of 7.5). The results are shown in Fig. 3.

Fig. 3. Effect of attrition time on zeta potential and floatability of waste samples
a) coal, b) associated mineral matters

It was found that the surface of coal becomes more positively charged with increasing attrition time from 1 to 30 minutes (Fig. 5a). It was found that the zeta potential changes in the range of -14 mV to 1.6 mV, where, after 20 minutes of attrition, zeta potential is asymptotically approaching 0 mV. Differences in charges suggest changes on the coal surface as a result of the attrition. Obviously the attrition process as well as mechanical scrubbing of negatively charged compounds from the surface of coal leads to the formation of fresh surfaces of coal. Therefore, increasing floatability by about 10% confirms the absence of surface functional groups as phenolic and carboxylic oxygen on the surface of coal. From the standpoint of efficiency of the flotation is a very positive phenomenon.

The change of zeta potential of coal pyrite and alumino-silicates after attrition is different. Attrition time increases zeta potential of alumino-silicate and decreases zeta

potential of coal-pyrite minerals. The zeta potential of coal pyrite has a positive value and under the lab-attrition conditions zeta potential decreased from approximately 5.1 mV at the beginning of the tests to 3.9 mV after 30 minutes, while the same indicator for the alumino-silicate mineral matter has a negative value and increases from –6.5 to –3.5 mV. These results clearly indicate that there have been no significant changes on the surface of associated mineral matters. It is believed that a partial removing of negative charging of silanal group from the alumino-silicates surfaces by attriton causes a minimal floatability increase to about 3%. Also, attrition of coal pyrite leads to a slight decrease of floatability from 22.64 to 19.24%. This phenomenon can be considered positive.

Based on the results, it can be concluded that attrition time is an important parameter of attrition process from the point of activating the oxidized coal surface, and positive change in zeta potential and floatability. Zeta potential approaching 0 mV can caused displacement of the coal isoelectric point (IEP) to more positive pH values and increase of floatability.

4. Conclusion

The following conclusions can be drawn from this paper.
1. The results of proximate and ultimate analyses of the raw and waste samples show increase of ash and oxygen (calculated by difference in relation to 100 %) and reduction of C/H ratio (obtained from ultimate analysis) in the waste coal, indicating the sensitivity of the coal surface to oxidation (weathering).
2. FTIR analysis of raw and waste coal have shown that on the surface of waste coal, as a result of oxidation by weathering and storing, there is a formation of different oxygen functional groups (COOH, S=O, C-O-C), the absence of C-C=C aromatic compounds and reduction of aromatic and aliphatic C-H groups.
3. Our research confirms that the pH value is one of the most important parameters of the process of flotation.
4. The isoelectric point (IEP) of waste coal is about pH 6.5 and similar to the IEP of raw coal. This value results from a presence of oxygen functional groups on the surfaces of waste coal as a consequence of oxidation by weathering.
5. Maximum floatability of waste coal, from about 75%, is achieved in the pH range in which lies the coal IEP. This high floatability confirms partial oxidation of coal from the dump and the consequence of the lower degree of oxidation of freshly liberated particle of size range -0.038 mm.
6. The zeta potentials of alumino-silicates and coal pyrite show IEP at pH 5.7 and 8.4, respectively. The position of isoelectric point of alumino-silicates depends on the concentration of silanol groups which are formed on the surfaces as a result of oxidation.
7. Also, floatability of coal pyrite have the maximum (45 %) in strongly acidic (pH = 2) and it is, unlike coal, don't occurs close to the isoelectric points

(about 8.4). Such high IEP value can be explained with the presence of ferrous ions produced by dissolution of coal pyrite in the water.

8. It was stated that the maximal floatability of waste coal and minimum floatability of coal pyrite, is achieved at optimal pH 7.5.

9. Results showed that attrition can improve floatability of waste coal.

10. Measurements of zeta potential of waste coal, coal pyrite and alumino-silicate as a function of attrition time, from 1 to 30 minutes, showed that there is a substantial change in the magnitude of the zeta potential from -15 mV to 0 mV for coal, from -6.5 to -3.5 mV for the alumino-silicate minerals, and from 3.9 to 5.1 mV for coal pyrite.

11. Attrition raises the floatability of waste coal and alumino-silicates minerals to 10% and 3%, respectively and reduced the floatability of coal pyrite to 3%. From the view point of flotation of waste coal samples, this phenomenon can be considered positive.

12. Results of all electrochemical and microflotation tests confirm a positive effect of attrition on the waste coal and also the final effect on coal floatation process. The valorization of the waste coal with attrition prior flotation process may cause significant improvement in the economic value of the process of coal preparation as well as the positive contribution on the environment protection.

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