

## **EFFECT OF OXIDATION ON FLOTATION AND ELECTROKINETIC PROPERTIES OF COAL**

**Jovica SOKOLOVIĆ<sup>#</sup>, Rodoljub STANOJLOVIĆ,  
Zoran S. MARKOVIĆ**

*\* University of Belgrade, Technical faculty at Bor,  
VJ 12, 19210 Bor, Serbia*

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### **Abstract**

*In processes such as coal flotation, the surface properties of coal-pyrite and other types of gangue presents in coal plays a major role in determining its separation from coal. Oxidation also leads to the formation of various oxygen functional groups and soluble inorganic that can adsorb on the coal surface and modify its wettability and floatability. These groups have remarkable impacts on surface charge, which controls film-thinning process and thus flotation kinetics [1].*

*In the previous studies, it was found that the results of coal flotation are lower than the results that are expected in consideration on the natural floatability of coal from anthracite mine "Vrška Čuka". The slight decreased in the coal recovery and increased concentrate ash content may be explained by oxidation of coal [6].*

*Oxidation kinetics and effect of oxidation on hydrophobicity of fresh surfaces of coal, coal-pyrite and alumo-silicate minerals has been investigated through electrokinetic's, microflotation and standard flotation studies in systems open to the atmosphere. A good correlation was obtained between the zeta potential and floatability. Results from all electrochemical tests confirme negatively effect of oxidation on the coal recovery and also the final effect of coal flotation process.*

**Key words:** *coal, flotation, surface, oxidation.*

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*<sup>#</sup> Corresponding author: jsokolovic@tf.bor.ac.yu*

## 1. Introduction

The flotation of coal, which depends on the surface properties of coal particles, can be drastically affected by oxidation and by the presence of various inorganics [3].

Oxidation of coal is a very complex process that involves physical and chemical adsorption of oxygen on the surface of coal and the formation of various acidic groups, peroxides and phenols [1]. The oxidation of coal starts with the physical adsorption of oxygen on the surface to form a complex, and then chemical adsorption to form peroxides. As oxidation proceeds, these organic materials lead to the formation of various humic acids and degradation of the humic acids into soluble acids [2].

The mineral matter in raw coal is comprised of hydrophilic minerals, mainly clays such as kaolinite and montmorillonite, quartz, carbonate minerals such as calcite and dolomite, gypsum and pyrite. Pyrite is the most widespread and abundant of naturally occurring metal sulfides. It is commonly present in base metal sulfides and frequently appears in coal as a major source of sulfur in coal. Oxidation of pyrite also leads to the generation of various soluble inorganics that can adsorb on the coal surface and modify its wettability and floatability

## 2. Experimental

The samples used in this study were from anthracite coal mine Vrška Čuka, Serbia and Montenegro. The samples were hand ground, crushed and sieved in order to obtain (-1+0.5), (-0.5+0.1), (-0.1+0.038) and (-0.038+0) mm size fractions.

The (-38+0)  $\mu\text{m}$  fraction was used for micro flotation tests and electrokinetic's studies, respectively. A technical analysis of the coal and a chemical analysis of coal-pyrite and alumo-silicate samples are given in Table 1 and 2.

**Table 1.** Technical analysis of the coal sample used in the tests

| Sample | Fixed carbon | Volatile matter | Calorific value | Ash  | S    |
|--------|--------------|-----------------|-----------------|------|------|
| Coal   | 83.26        | 9.21            | 33586           | 7.53 | 1.40 |

**Table 2.** Chemical analysis of the coal-pyrite and alumo-silicate samples used in the tests

| Sample         | Element (wt. %) |       |                                |      |       |                  |       |
|----------------|-----------------|-------|--------------------------------|------|-------|------------------|-------|
|                | Fe              | S     | Al <sub>2</sub> O <sub>3</sub> | CaO  | MgO   | SiO <sub>2</sub> | Ash   |
| Coal-pyrite    | 29.10           | 33.75 | 0.72                           | 0.11 | 0.027 | 3.54             | 75.15 |
| Alumo-silicate | 4.77            | 0.57  | 25.98                          | 6.20 | 0.86  | 40.98            | 84.00 |

Electrokinetic, microflotation and standard flotation studies are considered to be an efficient method to determine the surface properties of coal and gangue minerals.

Micro flotation tests were carried out using a modified Hallimond flotation tube. One gram of sample was conditioned in 100 ml solution at the different pH for 3 min. Following the conditioning step, the pulp was transferred to the Hallimond tube for flotation, which was carried out for 1 min using air at a flow rate of 0.1 l/min.

Electrokinetic's studies were carried out with 10 g sample and 1000 ml solution of a known pH value. The zeta potential was determined using a Riddick Zeta Meter and 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 measurements using the Smoluchowski equation. The experiments were carried out at room temperature and atmospheric pressure with mixing.

Coal flotation test were conducted with a 1 l single-chamber laboratory flotation machine type 136FL using 100 g mixture of coal, coal-pyrite and alumo-silicate minerals in ratio 63:15:22 at a pulp density of 10 % solids at the  $pH_{iep}$  of coal. In each flotation test, the pulp was first agitated in the flotation cell at 1900 rpm and room temperature for 3 min. Then, the following reagents were added: kerosene (1kg/t), tannic acid (200 g/t), water glass (200 g/t) and pine oil (45 g/t). The pulp was conditioned for an additional minute. After collecting, the flotation products for 3.5 min, the concentrate and tailing were filtered, dried and weighed. The ash content of the samples was analyzed, the results of which were used to calculate combustible recovery.

All the experiments were conducted using distilled water. 0.1 M HClO<sub>4</sub> acid and 0.1 M NaOH base solutions were used as pH modifiers.

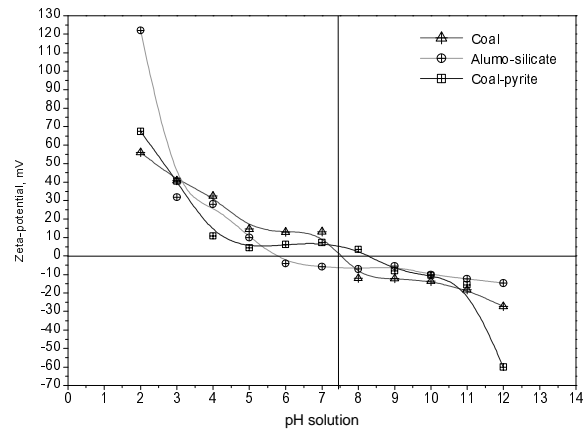
### 3. Results and discussion

Coal is a complex heterogeneous material composed of a variety of organic and inorganic constituents in different forms. In processes such as coal flotation, the surface properties of coal-pyrite and other types of gangue presents in coal plays a major role in determining its separation from coal. There are many chemical and physical processes operative in the coal flotation which may alter the mineral surface. Coal and mineral oxidation is one such process.

Oxidation is a complex phenomenon and can only be understood if all the species involved in this oxidation process are taken into account.

A number of studies have been performed on the electrokinetic's behavior of coal and coal-pyrite in the past. It has been reported that the pH during flotation process provides a good deal of information an the state of oxidation of coal and In this paper, the effects of oxidation, pretreatment and dissolved species on coal flotation are discussed.

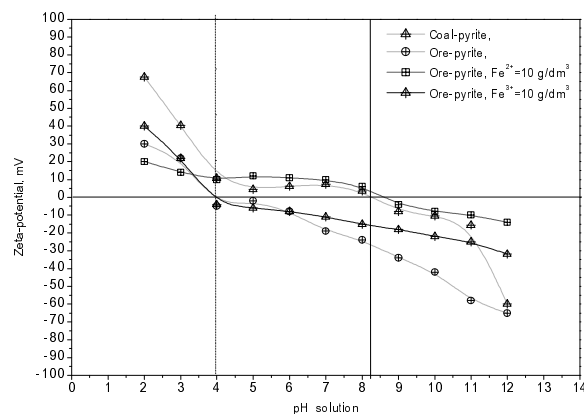
Figure 1 shows the zeta potentials of coal, coal-pyrite and alumo-silicate minerals as a function of pH.



**Fig. 1.** Zeta potential of coal, alumo-silicate and coal-pyrite as a function of solution pH

The IEP of coal is about pH 7.5 and that of the alumo-silicate minerals is about pH 5.7. Figure 1 shows that coal-pyrite's isoelectric point (IEP) is at about pH of 8.2. Since the  $pH_{IEP}$  of non-oxidized pyrite has been reported to be about 2 (Fuerstenau et al., 1968; Fornasiero et al., 1992; Bebie et al., 1998) and that of ferric oxides to range between 5.2 and 8.6 (Parks, 1965), this  $pH_{IEP}$  at 8.2 is an indicative that the surface of coal-pyrite, when exposed to oxidation, is of heterogeneous nature with patches of ferric-oxyhydroxide and  $FeS_2$ . The high IEP value obtained for coal-pyrite (about pH of 8.2) may be due to the presence of a high concentration of ferrous ions which results from the high solubility of coal-pyrite (figure 2.).

The different flotation and surface properties of ore- and coal-pyrite may result from differences in their chemical composition and oxidation behavior. This was confirmed by measuring zeta potential of ore-pyrite as a function of solution pH in the absence and presence of  $Fe^{3+}$  and  $Fe^{2+}$  (figure 2). For this investigation we used a pure sample of mineral pyrite with next assay: 33,86 % Fe, 31,45 % S, 1,34 %  $SiO_2$ , 0,72 %  $Al_2O_3$ , 8,72 % CaO and 2,28 % MgO.

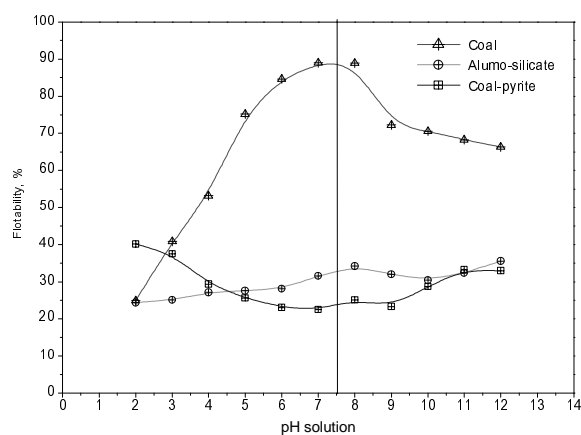


**Fig. 2.** The zeta potentials of coal- and ore-pyrite as a function of solution pH

The zeta potentials of ore- and coal-pyrite as a function of solution pH are given in figure 2, which shows IEP of ore- and coal-pyrite at pH 4.0 and 8.2, respectively.

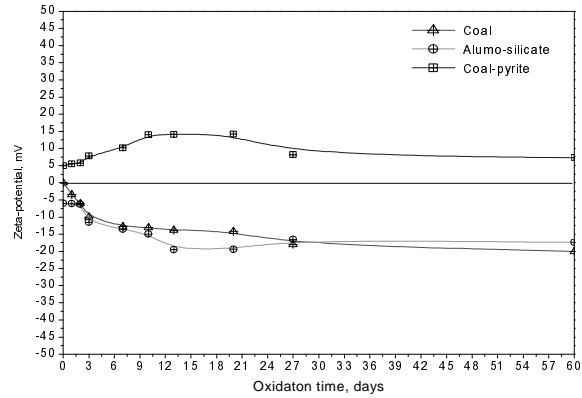
The effect of ferric and ferrous ion on the zeta potential of ore-pyrite is shown also in figure 2. In the presence of 10 g/dm<sup>3</sup> ferric ions, the IEP of the ore-pyrite nearly remains the same at around pH 4.0, except that the surface becomes more positively charged below pH 6.0.

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. Figure 3 compares the floatabilities of coal, coal-pyrite and alumo-silicate minerals as a function of a solution pH.

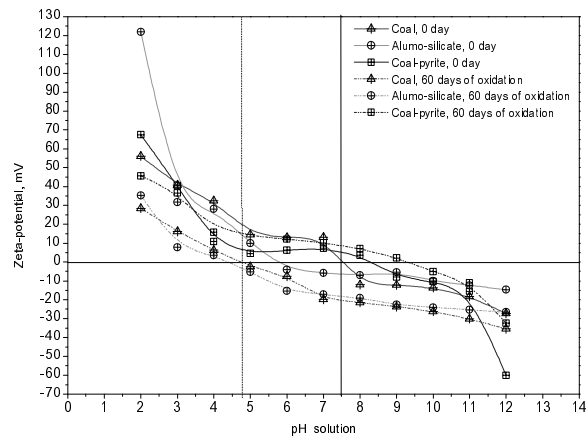


**Fig. 3.** Floatability of coal, alumo-silicate and coal-pyrite as a function of solution pH

The flotation behavior of all samples were found to be dependent on solution pH. It can be seen from figure 3 that coal and alumo-silicate minerals are highly floatable at a pH between 7 and 8. It was stated that coal-pyrite is not readily floatable at neutral pH, although it becomes highly floatable at acidic pH. However, at around neutral pH region, the recoveries of coal-pyrite decrease drastically. Beside this, the coal-pyrite studied show that a minimum oxidation rate was observed around neutral to slightly alkaline pH.



**Fig. 4.** Zeta potential of coal, alumo-silicate and coal-pyrite as a function of oxidation time



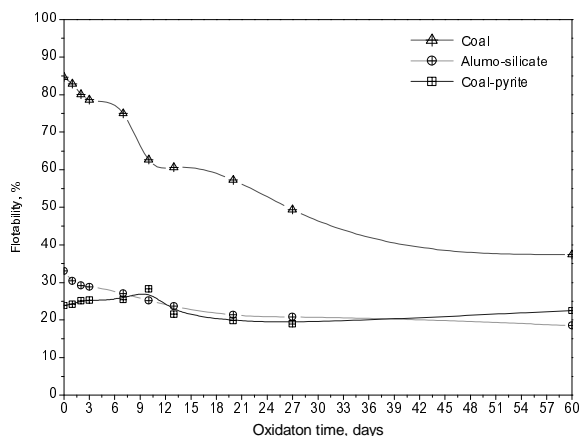
**Fig. 5.** Zeta potential of coal, alumo-silicate and coal-pyrite after 60 days of oxidation

From the results given in figure 4, it can be seen that the surface of coal becomes more negatively charged with increasing oxidation time. It was found that zeta potential of coal changed between 0 and -20 mV at

about pH 7.5. Also, oxidation decrease zeta potential of alumo-silicate and increase zeta potential of coal-pyrite minerals. The zeta potential of coal-pyrite during lab-oxidizing conditions increased from approximately 5 mV at the beginning of the tests to 15 mV after 15 days.

The changes in the zeta potential versus pH curves during 60 days of mineral oxidation are shown in figure 5.

The zeta potential of coal and alumo-silicate mineral become negatively charged in the whole pH region. Obviously, the zeta potential of coal is a function of active oxygen groups. These functional groups were found to not only control the wettability through the hydrophobic/hydrophilic balance, but also control flotation kinetics by their influence on the surface charge of coal particles [1]. Similar changes are given in the measurements of the zeta potential of alumo-silicate mineral. Oxidation results in the formation of silanal groups ( $\text{HO-Si} \equiv$ ) on the surface of quartz that reduce surface charge and hydrophobicity. The IEP of coal-pyrite mineral shifts to higher pH values, an observation which is consistent with the adsorption and/or surface precipitation of positively charged hydroxide species.

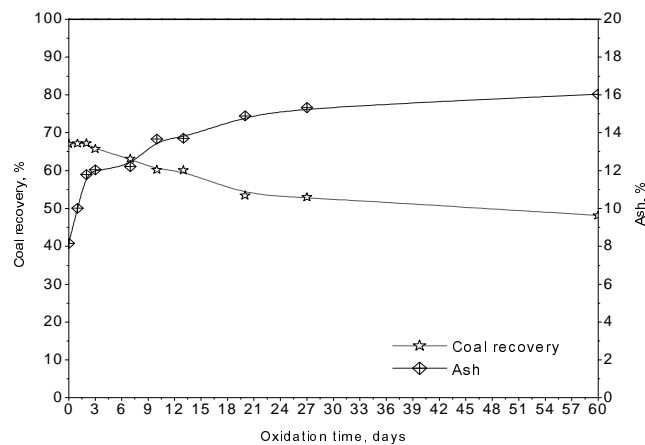


**Fig. 6.** Floatability of coal, alumo-silicate and coal-pyrite as a function of oxidation time



Since the zeta potential decreases with time, it indicates that coal surface become more hydrophilic after oxidation. Results from figure 6, show that, under similar lab-oxidizing conditions, oxidation significant decrease coal and slightly decrease alumo-silicate mineral floatability at a neutral pH. These results confirm that oxidation is a very complex process which, in turn, results in the increased formation of oxygenated functional groups on the coal surface, resulting in more hydrophilic surfaces and continuously decreases the hydrophobicity of coal. Also, oxidation for a short period of time increase coal-pyrite floatability. It confirms that a sulfur rich surface is produced in the first step of coal-pyrite mineral oxidation.. After 10 days of oxidation they found that the change of floatability of coal-pyrite is a good correlation with formation of positively charged hydroxide layer who's covering the sulfur-rich coal-pyrite surface. The metal hydroxide precipitation produces a hydrophilic surface [7].

The kinetics and mechanism of the oxidation of raw coal, together with the flotation behavior in the presence of collectors (kerosene, pine oil, tannic acid and water glass) is a subject of next phase of investigation. How these phenomenon affect coal flotation can be seen from the plots given in figure 7.

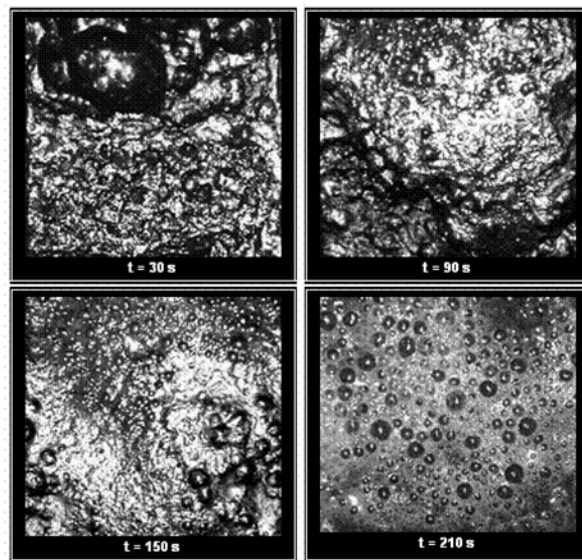


**Fig. 7.** Coal recovery and concentrate ash as a function of oxidation time

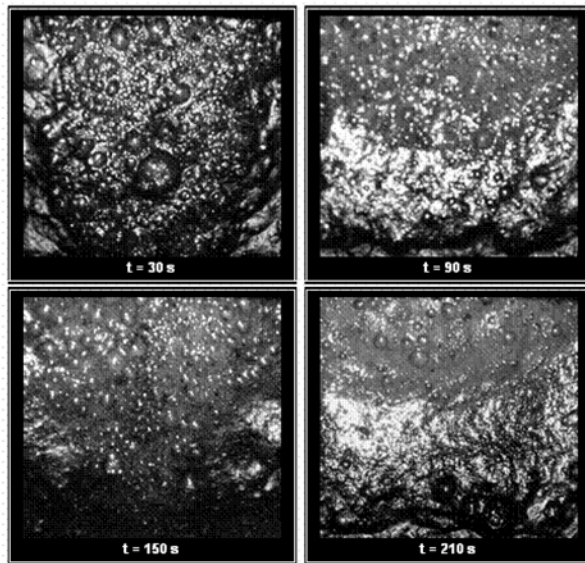
Results from coal flotation test confirm unexpected results that are realized in laboratory flotation test for coal valorization from fine class (-0.5+0) mm of raw coal in anthracite coal mine "Vrska Cuka" Avramica after few weeks. The coal recovery and concentrate quality was decreased at with time of oxidation [5, 6]. The results are in good agreement with electrochemical measurements.

Studies show that the performance of froth flotation is affected by the froth structure, and has a strong relationship with visual information of the froth surface. The determination of the froth structure, therefore, plays a vital role for controlling the process.

Images were recorded by a camera over the flotation cell, where Vrska Cuka coal was used. The cell was located in the base of the frame, directly below the impeller shaft. Photographs of the froth were taken from the top of the froth to determine the changing froth structure during the coal flotation process. Experimental details of the froth flotation tests are summarized in Figure 8 and 9.



**Fig. 8.** The froth structure with flotation time as a function of oxidation (0 day)



**Fig. 9.** The froth structure with flotation time as a function of oxidation (60 days)

It is clearly seen from this figure that there is a strong relationship between the froth depth and the purity of the final product. Also, a good correlation was obtained between the froth structure and oxidation time.

As clearly shown from the images given in Figs. 8 and 9, the mean bubble diameters were smaller at the start of the experiments. As seen in Figs. 8 and 9 the froth depth steadily decreases with time and reaches the highest value towards the beginning of the test.

Results from all off-line image analysis tests confirm the negative effect of oxidation on the coal recovery and also the final effect of the coal flotation process.

#### **4. Conclusion**

The following conclusions can be drawn from the present study:

1. Oxidation of fresh surfaces of coal, coal-pyrite and aluminosilicate minerals and its effect on hydrophobicity can be studied using zeta potential measurements and microflotation and standard flotation tests.

2. The results indicated that the surface of coal becomes more negatively charged with increasing oxidation time. Oxidation decrease zeta potentials alumo-silicate and increase zeta potential of coal-pyrite.
3. These was confirmed by measuring floatability under similar oxidizing conditions, oxidation significant decrease coal and slightly decrease alumo-silicate mineral floatability at a neutral pH.
4. Also, the surface charge property of coal-pyrite is mainly controlled by ferrous ions.
5. The reaction products whose can formed on the surface of coal-pyrite in the presence of oxygen from water make the surface more hydrophobic as indicated by the increasing floatability.
6. The results indicated that the surfaces of the coal oxidized at a faster rate in water system than coal-pyrite.
7. Results from coal flotation test confirme unexpected results that are realized in laboratory flotation test for coal valorization from fine class (-0.5+0) mm of raw coal in anthracite coal mine "Vrška Čuka" Avramica.
8. Oxidation has negatively effect on the coal recovery and also the final effect of coal flotation process.

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