Hard coal flotation depending on the degree of oxidation of the particle surface

J Kolacek¹ and J Zavada¹

¹Department of Environmental Engineering, VSB-Technical University of Ostrava, 17. listopadu 2172/15, 708 33 Ostrava-Poruba, Czech Republic

Abstract: The paper deals with the problem of floatability of coal with different degree of surface oxidation. It was found that coal floatability decreases with increasing degree of oxidation of its surface. In order to improve the flotation of the oxidized coal sample, mineral motor oil was used as a non-polar collector and oleic acid as a surfactant. Flotation tests showed a significant increase in the floatability of the oxidized coal sample after the addition of oleic acid and the close relationship between the degree of oxidation of the coal surface and the proportion of oleic acid as a collector.

1. Introduction
The foam flotation can be used to recover combustibles from a fine-grained coal material that cannot be easily processed using the gravity method. The coal particles are characterized by their hydrophobic properties and pass into the foam product with the support of non-ionic collectors such as oils [1, 2]. However, after oxidation of the coal surface, the floatability decreases significantly [3]. Oxidation of coal is a common phenomenon that occurs as soon as coal particles come into contact with oxygen in the air. Coal oxidation already takes place during its extraction, storage, transport and treatment. It is a complicated process that involves the mass transfer of oxygen from the environment to the coal surface, where chemical interaction occurs, resulting in the formation of oxidation products, heat emissions, and the release of gaseous products such as carbon dioxide and water. Oxidation is influenced by the diversity of coal types and their different properties. The proportion of oxygen in chemical bonds on the coal surface is then an important factor reducing the floatability of coal [4, 5, 6, 7]. However, when the surfactant is added to the non-ionic collector, the decrease in flotation efficiency is significantly reduced. Polar groups of surfactants combine with oxygenated groups on the surface of oxidized coal, thereby increasing the hydrophobicity of the oxidized coal surface [8, 9, 10]. Therefore, the result should be a collector consisting of a non-polar collector (for example oil or diesel) and a polar collector, in which a satisfactory flotation efficiency of the oxidized coal is achieved in mutual combination.

2. Sample characteristics
A sample of hard coal was obtained from Przedsiębiorstwo Górnice “SILESIA” sp. z o.o. This company operates in southern Poland, and since 2012 has been producing hard coal primarily for the energy sector, as well as specific sorts of hard coal for retail sale. Balance sources exceed about 500 million tonnes of coal [8]. The coal comes from the “Silesia” underground mine, in the towns of Czechowice-Dziedzice, Pszczyna and the villages of Goczałkowice-Zdrój, Bestwina and Miedźna. The grain size of the raw coarse sample ranged from 30 to 60 mm. The reported calorific value was 27.5 MJ/kg, the average ash content was about 7.5%, and the water content was below 8.5%. The sulphur content was 0.7%, and the proportion of volatile matter in the combustible was 40 ± 2%.
3. Characterization of used flotation reagents
Unfused mineral motor oil MOGUL GX 15W40 and oleic acid dissolved in kerosene as a surfactant were selected as a non-ionic flotation collector. The foaming agent was pine oil.

4. Sample preparation for flotation
The coal sample used was ground on a single-support jaw crusher RETSCH and then ground in a vibratory mill. The screening was performed on an analytical screening machine RETSCH to the desired fraction below 0.5 mm. Oversize particles were ground and sieved again. The procedure was repeated until the whole sample fraction was below 0.5 mm.

5. Drying and oxidation of the particle surface
The oxidation of the samples under artificially created conditions was carried out according to the study [3] for 24 and 72 hours in a Memmert UF 110 plus oven at 150 °C. The samples were then homogenized separately with each oxidation step. The average percentages of carbon and oxygen in the sample are given in Table 1.

Table 1. The proportion of carbon and oxygen in the sample [9].

| Oxidation time of the particle surface [hours] | C [%] | O [%] |
|---------------------------------------------|-------|-------|
| 0                                           | 69.5  | 10.5  |
| 24                                          | 67.3  | 15.0  |
| 72                                          | 63.8  | 20.8  |

6. Methodology of flotation
Four emulsions were used for each degree of oxidation of the coal sample, i.e. four flotations were performed for each degree of oxidation (Table 2). The agitation of the pulp with the collector lasted 3 minutes, after which time the foaming agent was added, and the pulp was stirred for an additional minute. The pulp aeration was 300 l·m⁻²·min⁻¹.

Table 2. Composition of flotation collectors [11].

| Collector                              |
|----------------------------------------|
| Flotation 1                           |
| 100 g/t 15W40                         |
| Flotation 2                           |
| 100 g/t 15W40 + 100 g/t oleic acid    |
| Flotation 3                           |
| 100 g/t 15W40 + 300 g/t oleic acid    |
| Flotation 4                           |
| 100 g/t 15W40 + 300 g/t oleic acid    |

7. Analysis of flotation tests
Tables 3, 4 and 5 give an overview of the yields, ash contents and recoveries of the combustible material to the individual flotation products.

Table 3. Flotation product yields overview [11].

| Yields [%] | Concentrate 0h | Waste 0h | Concentrate 24h | Waste 24h | Concentrate 72h | Waste 72h |
|-----------|----------------|----------|-----------------|-----------|-----------------|----------|
| 15W40     | 96.17          | 3.83     | 63.54           | 36.46     | 36.18           | 63.82    |
| 15W40 + 100 g/t | 96.55   | 3.45     | 89.69           | 10.31     | 42.50           | 57.50    |
It is apparent from the results in the tables that with the increase in the coal sample oxidization, the effect of the non-ionic collector on it was decreasing. Ash contents in concentrates with an increasing degree of oxidation increased more than 1.8 times (72 hours). After the addition of oleic acid (500 g/t), this ratio decreased to less than 1.3 times. Conversely, the yields of concentrates and the recoveries of the combustible to the concentrate decreased with the degree of oxidation. Non-oxidized coal with oil had 96.18% recovery due to its hydrophobicity. For the surface oxidized for 24 hours, the recovery was already 33% lower, and for the surface oxidized for 72 hours, it decreased by up to 60% compared to the unoxidized sample. However, with the oleic acid dose, the recovery decreased substantially more slowly. At the highest acid dose (500 g/t), the combustible recovery into the concentrate dropped by only about 2% in the case of a sample oxidized for 24 hours, and by 21% in a sample oxidized for 72 hours. It can be assumed that by further increasing the oleic acid dose, the recovery difference could be further reduced and, moreover, the floatability of the coal would generally be increased since it is already partially oxidized when it comes to the treatment plant. The low increase in the combustible recovery into the concentrate in the case of oxidized coal is due to the presence of hydrophilic oxidized carbon. Therefore, the non-ionic collector, in this case, oil can hardly adsorb on the surface of the oxidized coal. It is clear from the chart in Figure 1 below that as the surfactant dose increases, the combustible recovery into the concentrate in a coal sample with a higher degree of oxidation is also increased.
8. Conclusion
The aim of the experiment was to verify the dependence of the floatability of the given coal sample on the increasing degree of oxidation of the coal surface. At the same time, the aim was to verify whether it is possible to mitigate the decrease in the floatability of oxidized coal with the aid of a surfactant, namely oleic acid, in combination with mineral motor oil MOGUL GX 15W40. The results show that as the degree of oxidation of the coal surface increases, the floatability of hard coal decreases due to the newly formed polar groups on the surface. By adding oleic acid as a surfactant, this decrease in floatability was significantly mitigated. Floatability also increased in the case of artificially non-oxidized coal, since it already comes into contact with oxygen during the extraction and transport to the treatment plant.

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