Utilization of used motor oils as non-ionogenic collectors in the flotation process

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Abstract. This paper deals with the possibility of the utilization of used motor oils as non-ionic collectors in the flotation separation. Flotation tests were performed on a sample of coal from Poland. The criterion was to achieve the yield of concentrate over 70% and ash content below 10%. The results of laboratory investigations have shown that the application of used motor oils as flotation agents is possible.

1. Introduction

Flotation is an efficient technological process used for the treatment of mineral and secondary raw materials in many areas of industry that can ensure a rational and complex use of the resources. It allows us to obtain fine water-dispersed useful components. Flotation agents represent a very important part of the flotation process, and they should be economically affordable and environmentally friendly at the same time.

Bituminous coal flotation is dependent on the natural properties characterizing this coal, but also on the variable factors that can be adjusted so as to achieve the optimal course and results of the flotation. The natural properties of coal include mainly the degree of coalification, the size of the floated particles and the oxidation of the particle surface. The variable parameters include the suspension condensation, the quality and dosage of the flotation agents, the pH value, the suspension aeration, the degree of dispersion, or the flotation time. Other important factors may include, for example, the technological parameters of the flotation machines [1-7].

Various lubricating oils, fuel oil, kerosene, fractional oil distillation products, transformer oil, and others are usually used as the non-polar collectors. Their consumption in the flotation process ranges from 300 to 2000 g·t⁻¹ of the raw material. A high consumption of these hydrocarbons is caused by the formation of a coarse oil layer on the surface of air bubbles as well. Oil is also insoluble in an aqueous environment and forms an emulsion [8].

Motor lubricating oil consists of two basic parts, namely the base oil and the performance additive mixtures. Mechanical impurities, present in oil as a result of its gradual wear, become an unavoidable component of oil [8]. The type of base oil determines the kind of oil (mineral, synthetic or semi-synthetic). The base oil is a mixture of chemical substances that form an oil carrier representing up to 90% of the oil volume. The additives that improve the properties of oil are viscosity-increasing substances, in particular in relation to temperature, antioxidants, detergents, inhibitors, dispersants, and substances reducing corrosion and oil foaming [9].
2. Chemical characteristics of the samples of used motor oils
The oil samples intended for the flotation tests were characterized by means of infrared spectroscopy with Fourier transform using Nicolet 380 FT-IR instrument and ATR crystal from ZnSe material. The spectra were measured within the range of 4000 to 650 cm$^{-1}$.

2.1. Used mineral motor oil (SAE 15W-40)
The SAE 15W-40 sample spectrum has shown a clear low absorption band in the area of 1710 cm$^{-1}$ related to the vibrations of C = O bond in the carboxyl groups. Compared to the previous samples, there were no clear absorptions belonging to the vibrations of N-H and S = O bonds of nitration and sulphation products visible in the spectrum. In the 980 cm$^{-1}$ area, there was a distinctive absorption band typical for zinc dithiophosphate anti-wear and antioxidant additive.

2.2. Used synthetic motor oil (SAE 5W-30)
The SAE 5W-30 sample contained oxidation products that were clearly visible in the spectrum in the range of 1710 cm$^{-1}$. A slight absorption in the range of 1630 cm$^{-1}$ showed an increased content of nitration products and an absorption band of 1150 cm$^{-1}$ an increased content of sulphation products. In the range of 1050-950 cm$^{-1}$, there was only a slight absorption, indicating the exhaustion of the zinc dithiophosphate additive (ZDDP).

2.3. Used semi-synthetic motor oil (SAE 10W-40)
The SAE 10W-40 sample contained a small amount of water, which was evident from a very mild absorption in the range of 3400 cm$^{-1}$ and a more significant one in the range of 1600 cm$^{-1}$. The sample also showed a significant absorption in the range of 1740 cm$^{-1}$. This band belongs to a viscosity additive based on polymethacrylates. In addition, the band was boosted by a high content of ester oxidation products. The oxidation of oil was further demonstrated by a band in the range of 1710 cm$^{-1}$ typical for the vibrations of C = O bond of carboxyl groups. A mild absorption band in the range of 1630 cm$^{-1}$ belonged to the nitration degradation products, namely the vibrations of N-H bond of amines and amides. In the wave number of 1150 cm$^{-1}$ range, there was a clear band characteristic for the vibrations of S = O group of sulphation products. From a mild absorption in the range of 1040 cm$^{-1}$ and 1080 cm$^{-1}$ belonging to the vibrations of C-O, we can deduce a small amount of ethylene glycol in the oil. In the area of about 800 cm$^{-1}$, there were absorption bands typical for diesel content. This is the area in which the vibrations in the molecule of naphthalene are absorbed.

3. Characteristics of bituminous coal sample
The results of an analysis of floated coal sample are presented in table 1.

| SN 441377 | ASTM D 7582 | ČSN ISO 1928 | ČSN ISO 1928 | ČSN ISO 19579 | ČSN ISO 19579 | ČSN ISO 562 | ČSN ISO 29541 |
|-----------|-------------|-------------|-------------|---------------|---------------|-------------|---------------|
| $W_t^i$ (%) | All original water | $A^d$ (%) | Anhydrous ash | $Q_i$ (MJ/kg) | Original combustion heat | $Q_i$ (MJ/kg) | Original calorific value | $S_i$ (%) | Original sulphur | $S_m$ (g/MJ) | Specific sulphur content | $V_{daf}$ (%) | Volatile combustible | $C^d$ (%) | Anhydrous carbon |
| 12.40 | 11.14 | 24.82 | 23.61 | 0.46 | 0.19 | 40.6 | 68.884 |

4. Preparation of bituminous coal slurry sample
After transfer to a laboratory, the sample had natural moisture content, which is why it was dried in a dry kiln at 105 °C and subsequently milled in a vibrating mill and sorted to a grain size below 0.5 mm. The flotation tests were performed on the VRF-1 pneumatic-mechanical flotation apparatus.
5. Preparation of a flotation collector
In order to make it possible to efficiently dose the used motor oils into a flotation pulp, an oil / water emulsion had to be created first. The above specified types of oils were dosed into 300 ml of water in a high-speed mixer (according to the flotation test dosing), and they were subsequently mixed for 1 minute. The produced emulsion was prepared for agitation with the sample and for the flotation itself afterwards.

6. Flotation tests
The flotation tests taking advantage of used motor oils took place with the pulp concentration of 100 g/l, collector dose of 500, 1500 and 3000 g/t and foaming agent dose of 500 g/t. The agitation time of the pulp with the collector took 5 minutes and the agitation with the foaming agent 1 minute. The pulp aeration was 300 l/m² min⁻¹. The total flotation time was 12 minutes. The flotation test using Montanol 551 was taking place under the same conditions as in case of previous flotations with oils, only the agent dose was 500 g/t. This dose was chosen on the basis of the results of the authors who were also dealing with this issue and they saw this dose as optimal during bituminous coal slurry flotation. Unlike previous flotations, it was not necessary to use the foaming agent, since it is already contained in Montanol 551. The results of all flotations are shown in the graphs in figures 1–3.
Figure 3. Comparison of the results of sample flotations of the individual oils with a dose of 3000 g/t and Montanol 551.

7. Discussion of the results
The lowest total ash content of all the performed flotations was achieved in case of the dose of 500 g/t of SAE 15W-40 mineral oil, where the determined ash content was 9% with the concentrate yield of 87.06%, which meets the 70% minimum condition. With a dose of 1500 g/t, the ash content was 10.7%, while achieving 75.62% concentrate yield. With a dose of 3000 g/t, the ash content was 9.13%, while achieving 86.78% concentrate yield. After 4 minutes, the foam already showed low mineralization.

The flotation results using SAE 5W-30 synthetic oil show that the lowest dose (500 g/t) achieved the ash content of 11.46% and the yield of 78.25%. With a dose of 1500 g/t, the ash content was 9.99% and the yield was 80.2%. The yield of the concentrate increased by 11.08% in comparison with the previous flotation when the oil dose was 3000 g/t, while the ash content increased (only slightly) by 0.21% to 10.2%. The first minutes resulted in rich and highly mineralized foam. After 3 minutes of flotation, this mineralization began to decrease visibly.

According to the results of the floatation using SAE 10W-40 semi-synthetic oil, it can be stated that the increasing dose of oil was gradually accompanied by the increasing yield of the flotation concentrate. When the doses were 500 g/t and 1500 g/t, similar ash contents of 10.44% and 10.42% were achieved. With a dose of 500 g/t, however, the yield of the concentrate was 74.79%, while a dose of 1500 g/t increased the yield to 87.36%. In case of this collector, the best quality of the flotation concentrate was achieved at 3000 g/t, where 9.64% ash content was achieved with the yield of concentrate of 91.43%. The flotation was similar to that of the previous agents. Compact foam formed first, and it began to disintegrate after 3 minutes and its mineralization was gradually decreasing.

In case of the flotation with commercially used Montanol 551 flotation agent, the yield of concentrate was 68.86% and the ash content was 9.02% with the dose of 500 g/t. When compared with the other collectors, the mineralization of the foam was noticeably reduced over a shorter period of time. After 6 minutes, the foam showed little mineralization.

8. Conclusion
Two types of flotation agents are used nowadays, Belgian Montanol and Czech Flotakol, and their price is high. The aim of the flotation tests was to verify the effectiveness of used motor oils as flotation agents on the basis of a comparison with commercially applied Montanole 551.

The SAE 15W-40 mineral engine oil was the best of the tested samples. With a dose of 500 g/t, the yield of the concentrate was 87.06%. Compared to the other flotations, it has reached the lowest ash content of 9%. It can therefore be said that this flotation test has achieved an excellent result, since the efficiency of this collector was higher than that of Montanol 551.
These tests have shown that used motor oils could be successfully applied as flotation collectors; in some cases they are even more effective than a commercially-used agent. They therefore appear to be an economically viable alternative to conventional collectors, but it is necessary to carry out an economic analysis to determine the actual savings.

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