Ozonized petrochemical products used to intensify coal flotation

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Abstract. The ozonization method was used to improve the efficiency of oil-based flotation agents for coal dressing. Ozonation of petroleum products contributes to transformation of their hydrocarbon composition with the formation of oxygen-containing compounds of different functionality. The resulting reagents acquire the properties of complex reagents such as collector + foaming agent. The use of ozonized petroleum products leads to an increase in the efficiency of flotation of coking coals: a decrease in reagent consumption, an increase in the yield of concentrate and ash content of waste. Analytical processing of petroleum products is more effective for crude light oils, medium-temperature oil fractions and mixtures of low-boiling and high-boiling fractions.

1. Introduction

Flotation process is intensified by special reagent modes enabling production of low-ash coal concentrates at high recovery ratio. The efficient flotation reagents improve selectivity of the process, lower reagent consumption rates and residual reagent concentration in a liquid phase, viz., they enable to diminish costs of reagents and industrial water treatment. In view of the above the search for novel efficient components and ways to modify routine reagents in order to improve their specific flotation properties acquires specific significance.

The products and wastes of oil refining and petrochemistry are widely used in coal flotation. Apolar reagents: kerosene, thermogasol, diesel fuel [1, 2] and heavy oil fractures in combination with light ones [3] are selected as collectors. Frothers are reagents with polar functional groups and hydrocarbon radicals, for example, residual oil in butyl production (RBA agent) or polypropylene glycol (PROH agent) [1–3].

Flotation modes can be modified by applying a combination of apolar and heteropolar reagents: petrohydrocarbons (gasol) and technical mixtures of alcohols and esters (RBA, PROH, etc) [3–5] olefin oxides [6]. Compounds with functional O-groups, contained in them are capable to participate in both donor and acceptor interaction with active centers of coal particles and to promote higher flotation efficiency [6, 7].

Apart from surfactant additions the coal flotation performance can be improved by oxidative modifications of apolar oil fractions [8]. Thereto, catalytic oxidation of kerosene fractions leads to their higher flotation activity, 3–4-fold less reagent consumption rate as compared to the conventional reagent mixtures [9]. Of interest is also electrochemical oxidation of apolar collectors where hydrocarbons can be oxidized to respective acids [6].
The other promising, in authors’ opinion, method of oxidative modification is ozonization. The objective of the present research is investigation into ozonization effect on variations in chemical composition of apolar petrochemicals in order to improve their flotation properties in coal processing.

2. Results of the laboratory experiments
The study objects are marketable specimens of West-Siberian low-viscosity oil, kerosene TS (TU 10227-86), Thermogasol (TU-38.301-18-31-19) and mazut M-100 (GOST 10585-99). Specifications of hydrocarbon reagents are reported in Table 1.

Table 1. Specifications of flotoreagents used.

| Reagent     | Specimen | Density, kg/m³ | Kinematic viscosity, mm²/s | Amount of adsorbed ozone, g/kg | Acid number AN, mg/100 g | K₀  |
|-------------|----------|----------------|---------------------------|-------------------------------|--------------------------|-----|
| Kerosene    | Initial  | 820            | 1.25                      | —                             | 0.5                      | 0.12|
|             | Ozonized | —*             | —                         | 14.3                          | 4.7                      | 0.47|
| Oil         | Initial  | 860            | 8.0                       | —                             | 1.0                      | 0.23|
|             | Ozonized | —              | —                         | 36.7                          | 19.2                     | 1.32|
| Thermogasol | Initial  | 910            | 15.0                      | —                             | 0.5                      | 0.04|
|             | Ozonized | —              | —                         | 34.5                          | 19.2                     | 0.77|
| Mazut       | Initial  | 990            | 115.0                     | —                             | 5.0                      | 0.24|
|             | Ozonized | —              | —                         | 25.6                          | 9.3                      | 0.32|

*These parameters were not determined for ozonized specimens

Ozonation of petroleum oil was performed at room temperature and atmospheric pressure in a jet-type reactor in a stream of ozone-oxygen mixture (ozone concentration of about 100 mg/l). Ozone concentration was determined by UV-gas analyzer (adsorption by ozone in ultra-violent spectrum brand at wave length of approximately 250 nm).

Infrared spectra were recorded at Fourier spectrometer Infralum-FT-801. The oxidation level $K_0$ was calculated relative to ratio of summary intensity (sum of integral optic densities $D$) of brands for adsorption of oxygen-bearing hydroxyl (3400 cm⁻¹) and carboxyl (1730 cm⁻¹) groups to $D_{CH_2}$-aliphatic (1460 cm⁻¹) groups:

$$K_0 = (D_{3400} + D_{1730}) / D_{1460}.$$

Flotation activity of petroleum products was evaluated on processing of slimes of meager-lean coking coal with ash content $A_{ic} = 10–12\%$. The tests were executed at a laboratory flotation machine at reagent consumption of 1.5–5.8 kg/t. Test results were estimated in terms of the yield of concentrate $\gamma_c$ and wastes $\gamma_w$, ash content in concentrate $A_{c}^d$ and wastes $A_{w}^d$, recovery of combustible mass into concentrate $E_c$, solid content in concentrate, height of froth column $h_f$ and selectivity of the process $K_{sel}$:

$$K_{sel} = \frac{A_{w}^d - A_{c}^d}{100 - A_{ic}^d},$$

where $A_{w}^d$, $A_{c}^d$, $A_{ic}^d$ is ash content in wastes, concentrate, initial coal, respectively.

The hydrocarbon reagents (HCR) applied in the present research differ notably in component composition and physical properties (Table 1), this factor explains different solubility of ozone and velocity of its interaction with reactive groups of organic compounds. Components of oil and thermogasol (middle-distillate oil fraction $T_{boil} = 300–350^\circ\text{C}$) exhibit the highest reaction activity; this
effect is demonstrated in relatively large amount of adsorbed ozone per an equal time interval of processing (Table 1). Ozonation of kerosene (low-boiling petroleum fraction, \(T_{\text{boil}} = 200–300^\circ \text{C}\)) and mazut (high-boiling petroleum fraction, \(T_{\text{boil}} > 350^\circ \text{C}\)) results in the yield of products with acid number (AN) and oxidation ratio \(K_0\) of 2–4 times lower as compared to the rest study reagents (HCR). The process is complicated by notable gumming in the case with kerosene and by highered viscosity in the case with mazut.

The interaction of HCR with ozone results in formation of oxygen-bearing groups of different functionality. In IR-spectrum it is notable the increase in intensity of adsorption bands for \(\text{OH}\)-alcohols and carbonic acids (3400 cm\(^{-1}\)), \(\text{C}=\text{O}\) lactones and anhydrides (1780 cm\(^{-1}\)), \(\text{C}=\text{O}\) alifatc (1730 cm\(^{-1}\)) and aromatic (1710 cm\(^{-1}\)) acids, aromatic cetones (1650 cm\(^{-1}\)), \(\text{C}–\text{O}\) cyclic esters, furanes, lactones (1260, 970–1000 cm\(^{-1}\)), \(\text{S}=\text{O}\) sufoxides (1300, 1150, 1050 cm\(^{-1}\)) (Figure 1).

![Figure 1. IR-spectra of thermogasol specimens: 1—initial; 2—ozonated.](image)

Efficiency of flotation with apolar HCR is evaluated in terms of the peculiarities of component composition and rheological properties of petroleum product [3, 4]. Position of the study reagents in the row of growing viscosity (Figure 2) indicated essential aggravation of their flotation properties despite of increased HCR consumption rate (Table 2). Low flotation properties of mazut as a mono-reagent is due to the complexity in formation of high-dispersed water-oil emulsion, attachment and flowing of a mazut drop over surface of a coal particle [3, 4]. The combination of more or less viscous HCR is often used to eliminate these restrictions. As a case in point, the equal-proportion combination of mazut and kerosene soundly boosted the coal flotation performance at much less reagent consumption rate (Table 2).

![Figure 2. Parameters of coal flotation with petroleum products depending on their viscosity (Table 1): 1—concentrate yield \(\gamma_c\), %; 2—combustible mass yield to concentrate \(E_c\), %; 3—ash content in wastes \(A_w^d\), %; 4—froth height \(h_f\), mm.](image)
Table 2. Flotation of meager-lean coking coal with petroleum hydrocarbon reagents.

| Reagent          | Consumption, kg/t | Concentrate | A_op, % | E_c, % | C_T, g/l | h_f, mm | A_op, % | K_sel |
|------------------|-------------------|-------------|---------|--------|----------|---------|---------|-------|
| Kerosene         | 2.1               | 86.2*       | 8.7     | 94.7   | 160      | 28      | 68.0   | 0.71  |
|                  |                   | 87.7        | 8.6     | 96.4   | 165      | 33      | 75.6   | 0.81  |
| Oil              | 2.4               | 89.0        | 6.4     | 93.4   | 136      | 19      | 46.7   | 0.45  |
|                  |                   | 94.4        | 6.4     | 98.7   | 166      | 40      | 79.6   | 0.82  |
| Thermogasol      | 1.5               | 76.2        | 7.2     | 80.8   | 135      | 12      | 29.7   | 0.26  |
|                  |                   | 91.6        | 6.7     | 97.3   | 187      | 30      | 71.4   | 0.74  |
| Mazut            | 5.8               | 46.9        | 7.2     | 48.9   | 86       | 2       | 14.4   | 0.08  |
|                  |                   | 48.0        | 6.9     | 50.2   | 93       | 4       | 14.7   | 0.09  |
| Mazut 50% + kerosene 50% | 1.8 | 71.1        | 6.5     | 74.6   | 114      | 12      | 21.6   | 0.17  |
|                  |                   | 87.7        | 6.2     | 92.2   | 140      | 30      | 43.2   | 0.41  |

*Top value corresponds to the initial specimen; lower one corresponds to ozonized specimen

Ozonizing modification of apolar HCR contributes differently to higher coal flotation performance: high yield of concentrate, higher solid content, higher recovery of combustable mass into concentrate ash content in wastes (Table 2). Thereto, selectivity ratio \(K_{sel}\) of flotation used to grow 1.1 to 2.8 times for mazut and thermogasol, respectively. High parameters of flotation activity (increase 1.8 times) are exhibited by ozonized light crude oil. Lower ozonation effect on flotation properties of kerosene and mazut is conditioned by initially high adsorption capacity of the first reagent to hydrophobic surface medium-metamorphized coal and a poor dispersability in the pulp of the second reagent. Efficiency of ozonized mazut appreciably grows as HCR in combination with light petroleum fraction (Table 2). The concentrate yield reaches the level of flotation with ozonized kerosene, but ash content in coal descends to the minimum test results (Table 2).

All the ozonized HCR specimens have the increased height of froth column \(h_f\) (Table 2). Arising frothing properties can be explained by additional amount of heteropolar compounds in the composition of petroleum fractions, this is justified by higher values of AN and \(K_0\) (Table 1). As a result, HCR start to exhibit complex properties of a collector and a frother.

3. Conclusions
1. It is established that it is feasible to produce the complex-type reagents with properties of a collector and a frother in one in the coal flotation based on ozonized petroleum products.
2. Ozonation of petroleum products contributes to transformation of their hydrocarbon composition with formation of heteropolar oxygen-containing compounds of different functionality: aldehydes, acids, linear and cyclic esters.
3. Preliminary ozonation of petroleum and its fractions improves coke flotation performance, lowers the reagent consumption rate increases concentrate yield and ash content in wastes.
4. Ozonolytic treatment of petroleum products designed to apply them as flotoreagents is more effective for light crude oils, medium-temperature petroleum fractions and mixtures of low- and high-boiling fractures.

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