ГЕОЭКОЛОГИЯ, РАЦИОНАЛЬНОЕ ПРИРОДОПОЛЬЗОВАНИЕ

DOI: 10.21440/0536-1028-2021-4-57-63

Environmental impact assessment of preventive emulsion based on heavy oil residue on organic pollution of water

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Abstract
***Introduction**. Dusty surfaces insulation with preventive emulsions based on heavy oil residue (HOR) is a promising environmental technology in open-pit mining. To assess the environmental safety of these emulsions, it is required to assess the possible scale of organic pollutants emission into the technogenic leakage fluxes occurring due to the interaction of HOR insulation with precipitation.*
***Research aim** is to assess the scale of organic pollutants leaching occurring due to the interaction of HOR insulation with precipitation.*
***Research methods.** Laboratory modeling of HOR samples and water interaction and assessment of the scale of organic compounds (bitumen and oil products) discharge into the water environment.*
***Results.** Studies have shown that the addition of an insulating emulsion based on heavy oil residue leads to the creation of an organo-mineral mixture with hydrophobic properties, determining low solubility of hydrocarbons in water and posing no threat of excess organic pollution to the hydrosphere.*

Keywords: *open-pit mining; means of dust suppression; insulating mixtures; heavy oil residue; emulsions; leaching; organic pollutants.*

Acknowledgements. *Analytical studies have been carried out in the Laboratory of the mining regions geoecology, Mining Institute UB RAS (Certificate of Accreditation no ROSS RU.0001.517043).*

Introduction. Considerable dusting of open-pit surface and automobile roads require special measures to be implemented to reduce dust emission [1]. In this sphere, the technology of fixing dusting surfaces with preventive emulsions containing surface-active agents (surfactants), latex, and water-based particulate has wide practical applications [2]. The drawbacks of the technology that reduce its economic efficiency are as follows: limited operation time due to its water solubility [3] and the need for expensive dissolving agents or addition agents [4].

Recently, the proposal has been made to apply preventive emulsions based on oil products residue due to their cheapness and ability to improve the water resistance of the forming insulation [5]. The products of straight run tar processing are ascribed to heavy oil residue (HOR): road, construction, and roofing bitumen, etc. [6] (table 1).

Moreover, the use of petroleum residue requires assessing the scale of possible emission of organic pollutants occurring due to the insulating surfaces interaction with precipitation. Methods of laboratory testing are usually used for this purpose [7–9], modeling the interaction between the residue and water and providing insight about the scale of the examined components leaching [10].

Research methods. The study objects are the bricks of silt burden that were shaped using petroleum residue from LLC LUKOIL-Nizhegorodnefteorgsintez as a preventive binding agent.

The base of the bricks is the sinter iron ore concentrate (STO standard 00186826-026-2015) of the Novolipetsk Steel (NLMK) used at production site as a road surface. The concentrate represents black dry powder with the bulk density of 2.75 kg/dm^3. Material specification is presented in table 2.

Table 1. Specification of heavy oil residue
Таблица 1. Технические характеристики тяжелых нефтяных остатков

HOR	Softening point by the ring and ball method, °C	Density ρ^{20}, g/m^3	Viscosity η under 120 °C, mPa · s
Tar (ZapSib)	35	995	358.0
Propane deasphaltization asphalt*	38	1010	367.5
Cracking residue of tar visbreaking	47	1019	320.5
Bitumen BN 70/30	70	1012	910.0

* Propane deasphaltization asphalt of tar PD 36 is used as raw material to produce preventive binder PS-1.

The applied preventive binding agent PS-1 was obtained from propane-deasphalted asphalt (STO standard 05747181-016-2012) (*Preventive binding agent PS-1. Asphalt. Specification. STO standard 47678749-001-2015. Ekaterinburg: Asphaltite Research and Development Center; 2015*). Specification of PS-1 is presented in table 1. According to GOST 12.1067-76 "Occupational safety standards system. Noxious substances. Classification and general safety requirements", propane-deasphalted asphalt (PDA) of tar refers to low toxicity substances of hazard class 4.

Table 2. Specification of sinter iron ore concentrate (STO standard norm)
Таблица 2. Технические характеристики железорудного концентрата агломерационного (норма по СТО)

Iron content, %	66.3
Iron content tolerance, %	–0.3
Moisture content, %	10.0
Moisture content tolerance, %	+0.5
Silicon dioxide content, %	6.9
Silicon dioxide content tolerance, %	±0.5

Burden was combined with the binding agent in a 9:1 ratio and pressed into cylinders under a pressure of 400 kgf/cm^2 (GOST 12801-98, testing mineral filler with bitumen). The obtained monoliths (cylinder bricks) were used to analyze 4 samples:

I – monolith no. 1 with a mass of 259.32 g and 102.05 cm^2 surface area;

I′ – monolith no. 1 with a mass of 259.32 g, ground to 3 × 3 mm particles;

II – combined monoliths no. 2 and 3 with the overall mass of 541.77 g and 541.77 cm^2 surface area;

III – monolith no. 4 with a mass of 538.1 g and 164.85 cm^2 surface area.

Such grouping of samples makes it possible to achieve wide dispersion of the surface area, i.e. helps to assess the range of organic compounds solubility under various water contact areas. Besides, it is possible to assess the possible solubility of organic compounds in case of insulation disintegration due to one of the samples grinding to 3 × 3 mm particles resulting in maximum interaction of sample particles with water.

When analyzing an organic constituent (OC), chloroform bitumen A (hereinafter CBA, a combination of organic compounds extracted from samples by chloroform) together with its hydrocarbon fraction (oil products) were the main objects of research, being the most capable of migration among all OC fraction [11]. The oil products (OP) parameter reflects the total content of hydrocarbons in samples (GOST 17.1.4.01-80). It was determined through the method of IR photometry (*Guideline document RD 52.24.476-2007. Mass concentration of oil products in water. The procedure of measuring by the method of IR photometry. Rostov-on-Don; 2007*) using the concentration meter IKN-025 (0.02 mg/dm^3 lower limit of detection).

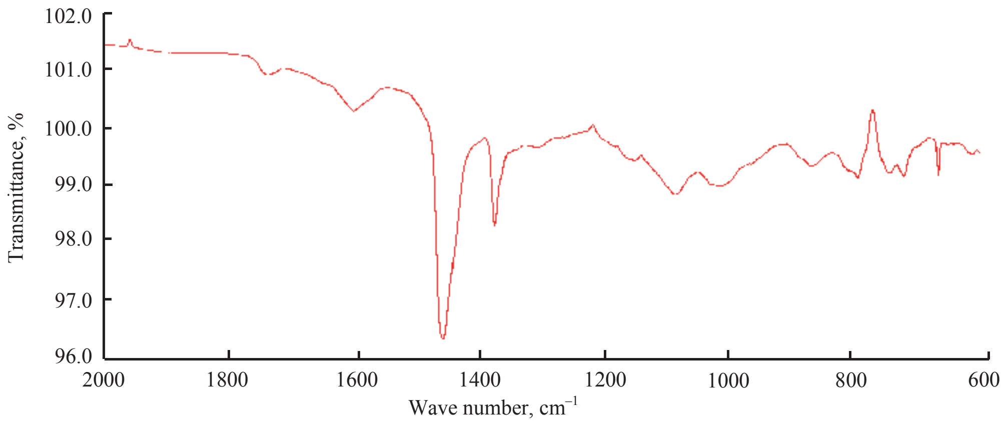

Fig. 1. IR spectrum of CBA sample I′
Рис. 1. ИК-спектр ХБА пробы I′

Structural and group analysis of bitumen was made by the method of IR spectroscopy (IRS) using the PerkinElmer Inc. Frontier IR-Fourier spectrometer [12]. Organic compounds were identified by both particular regions of spectrum and by absorption characteristic bands common for all the samples, using the organic compounds spectral library [13].

The scale of organic compounds discharge into the water environment was assessed by analyzing the composition of the waters that contact the studied samples for 24 hours (water extracts). Such modeling was carried out under static conditions (1:5 *sample–distilled water ratio*) with recurring agitation, natural pH medium, and the temperature of 25 °C; pH (using the millivoltmeter pH-150MI) and total dissolved solids (using the Zepter TDS meter) were determined in water samples together with CBA and OP. After the water extracts data analysis, the samples were filled up with the distillate again in the same ratios and left for 7 days. After 7 days the composition of the water extracts was analyzed again.

Results and discussion. The analysis of the I′ ground sample has shown that the content of CBA is 97.532 g/kg and the content of OP is 17.429 g/kg, which means that adding extra emulsion based on PS-1 heavy oil residue results in a high level of organic pollution of the forming monoliths. By comparison, soil samples are considered uncontaminated at CBA content less than 10 g/kg and OP content less than 1 g/kg. According to the IR spectrum data (IRS, fig. 1), the chloroform bitumen is represented by mainly aliphatic and aromatic hydrocarbons with the subsidiary content of various oxygen-containing compounds.

The presence of intensive absorption band under 1458 cm^{-1}, conditioned by the deformation vibrations of CH_2 methylene groups, indicate the prevalence of compounds with polymethylene chains. Besides, the presence of aliphatic hydrocarbons in samples explains the presence of a weak absorption band under 720 cm^{-1} (CH_2).

Table 3. Results of analytical studies of water extracts
Таблица 3. Результаты аналитических исследований водных вытяжек

Sample	pH	Mineralization, mg/dm^3	CBA, mg/dm^3	OP, mg/dm^3
24-hour contact rock-water				
I (monolith no. 1)	6.32	4	0.89	< 0.02
I′ (ground sample no. 1)	6.70	28	0.89	< 0.02
II (monoliths no. 2 and 3)	6.29	4	0.80	0.02
III (monolith no. 4)	6.30	4	0.93	< 0.02
7 day contact rock-water				
I′ (ground sample no. 1)	6.81	25	0.54	< 0.02
II (monoliths no. 2 and 3)	6.97	4	0.61	–
III (monolith no. 4)	6.95	3	0.61	–

The second most intensive absorption band under 1376 cm^{-1} corresponds to the deformation vibrations of terminal CH_3 methyl groups. Wide absorption band in the range of 1200–1000 cm^{-1} with two peaks under 1087 cm^{-1} and 1013 cm^{-1} is typical for C–O–C bonds asymmetric stretch in simple ethers and acetals, and O–H bonds stretch in alcohols and phenols. In the same area, there are weak absorption bands, carbonyl compounds (ketones, aldehydes, carboxylic acids, and esters), the presence of which is attested by the absorption band under1736 cm^{-1}.

Wide weak absorption band under 1600 cm^{-1} is connected with the stretch of the aromatic ring with the skeletal vibration of the aliphatic compounds with long double bond conjugation systems. Plane deformation vibrations of these structures are recorded under 870 cm^{-1}. Heteroaromatic structures have an absorption band under 800 cm^{-1}.

The intensity of C=O (1720 cm^{-1}) carbonyl group absorption band manifestation is minor and lower than that of the methyl and methylene groups, which reflects a low degree of bitumen oxidation: oxidation factor $K_2 = I_{1723}/I_{1460} = 0.1$.

Laboratory modeling results show that the solubility of organic compounds is minor (table 3).

It can be seen from the presented data that under the insignificant discharge of water-soluble salts (total dissolved solids less than 25–28 mg/dm^3), the content of CBA in water extracts after 24-hour contact ranges between 0.80 and 0.93 mg/dm^3. These concentrations do not depend on the weight and surface area of the analyzed samples. The content of oil products in water extracts is even lower, being not more than 0.02 mg/dm^3, which is lower than the accepted fishery TLV (0.05 mg/dm^3). The time of *water-rock* contact increased up to 7 days hasn't resulted in the increase of organic compounds discharge into the water phase: CBA content has reduced to 0.54–0.61 mg/dm^3 and the content of oil products is less than 0.02 mg/dm^3.

According to IRS data of the 24-hours and 7 day water extracts CBA, the quality content of aqua bitumen has not changed in this period (fig. 2).

IR spectra are characterized by a significant content of oxygen-containing compounds; intensive absorption band under 1740 cm^{-1} indicates the presence of carbonyl structures. Within the interval of 1300–1000 cm^{-1} ("ether band"), a vast "crest" with peaks under

1024 cm^{-1}, 1098 cm^{-1}, 1168 cm^{-1}, and 1260 cm^{-1} has appeared, which indicates the presence of simple ethers, acetals, alcohols, and phenols with different hydrocarbon skeletal structures (aliphatic and cyclic structures, including aromatic and heterocyclic) in aqua bitumen.

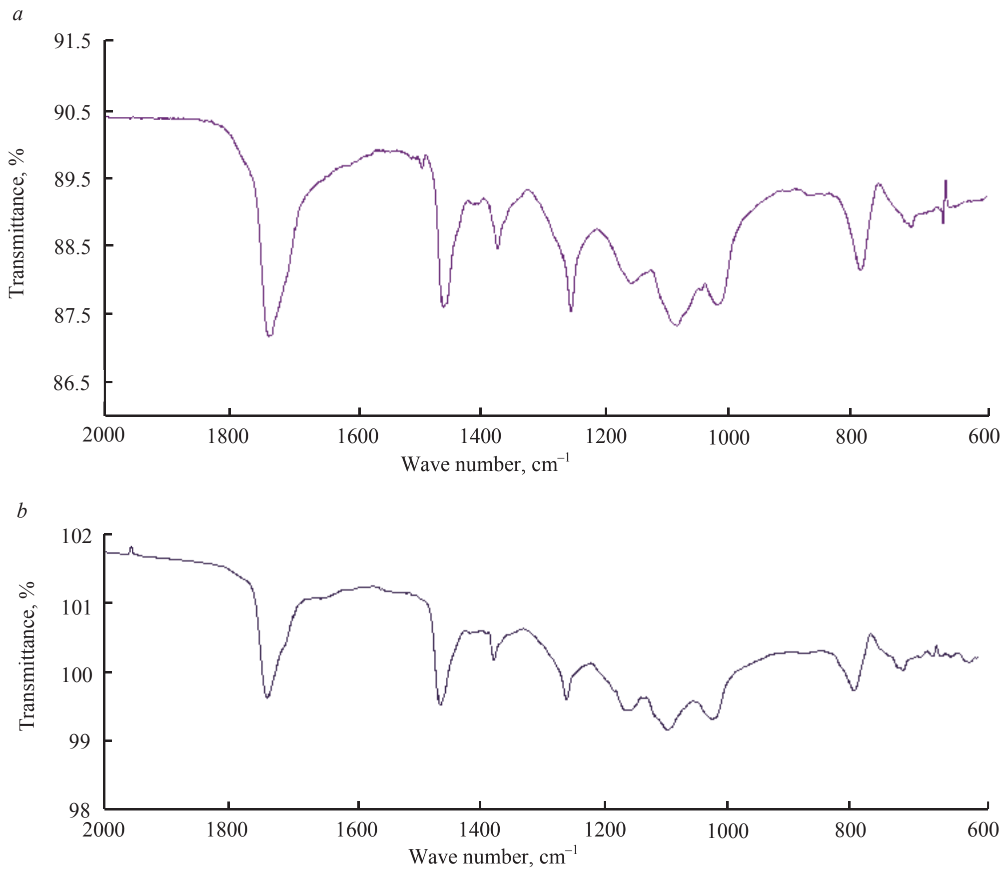

Fig. 2. IR spectra of water extracts CBA:
a – 24-hour contact; *b* – 7 day contact
Рис. 2. ИК-спектры ХБА водных вытяжек:
а – контакт 1 сутки; *b* – контакт 7 суток

The intensity of absorption bands of methylene (1740 cm^{-1} and 720 cm^{-1}) and methyl (1377 cm^{-1}) groups of aliphatic carbon chains is far less than that of the bitumen of rocks; it indicates a minor scale of hydrocarbon compounds discharge into the water phase. They can probably be connected with carbon skeletons of the heterocompounds, including oxygen-containing. The content of oxygen-containing compounds dominates over the hydrocarbon structures: oxidation factor $K_2 = I_{1723}/I_{1460} = 1.1–1.3$.

The presented data show that during rock-water contact, polar oxygen-containing compounds dissolve, while nonpolar hydrocarbons are confined in the mineral matrix.

Summary. The research results show that adding extra emulsion based on heavy oil residue results in the creation of the organo-mineral mixture with hydrophobic properties, determining a low solubility of hydrocarbon compounds in water. Precipitation leaching of surfaces prepared with the use of emulsions based on heavy oil residue poses no threat of excess organic pollution to the hydrosphere.

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Received 17 March 2021

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УДК 622.807:550.84 DOI: 10.21440/0536-1028-2021-4-57-63

Экологическая оценка влияния профилактической эмульсии из тяжелых нефтяных остатков на органическое загрязнение вод

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Реферат

Введение. *К числу перспективных природоохранных технологий при ведении открытых горных работ относится изоляция пылящих поверхностей профилактическими эмульсиями из тяжелых нефтяных остатков (ТНО). Для оценки экологической безопасности использования таких эмульсий требуется оценка возможных масштабов эмиссии органических поллютантов в техногенные потоки рассеяния, формирующиеся при взаимодействии атмосферных осадков с покрытиями на базе ТНО.*
Цель работы. *Оценка масштабов выщелачивания органических поллютантов при взаимодействии атмосферных осадков с покрытиями на базе ТНО.*
Методика. *Лабораторное моделирование взаимодействия образцов на базе ТНО с водой и оценка масштабов перехода органических соединений (битумоидов и нефтепродуктов) в водную среду.*
Результаты. *Проведенные исследования показали, что добавление изолирующей смеси эмульсий из тяжелых нефтяных остатков приводит к формированию органоминеральной смеси, обладающей*

гидрофобными свойствами. Это определяет низкую растворимость углеводородных соединений в воде и не создает угрозы сверхнормативного органического загрязнения гидросферы.

Ключевые слова: *открытые горные работы; средства пылеподавления; изолирующие смеси; тяжелые нефтяные остатки; эмульсии; выщелачивание; органические поллютанты.*

Аналитические исследования выполнены в лаборатории геоэкологии горнодобывающих регионов Горного института УрО РАН (аттестат аккредитации № РОСС RU.0001.517043).

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Поступила в редакцию 17 марта 2021 года

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Для цитирования: Бачурин Б. А., Кошкаров В. Е., Неволин Д. Г. Экологическая оценка влияния профилактической эмульсии из тяжелых нефтяных остатков на органическое загрязнение вод // Известия вузов. Горный журнал. 2021. № 4. С. 57–63 (In Eng.). DOI: 10.21440/0536-1028-2021-4-57-63

For citation: Bachurin B. A., Koshkarov V. E., Nevolin D. G. Environmental impact assessment of preventive emulsion based on heavy oil residue on organic pollution of water. *Izvestiya vysshikh uchebnykh zavedenii. Gornyi zhurnal = News of the Higher Institutions. Mining Journal*. 2021; 4: 57–63. DOI: 10.21440/0536-1028-2021-4-57-63