

*Original Research*

# Oil Sludge and Methods of Its Disposal

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## Abstract

One of the most promising ways to utilize wastes from the oil extracting and oil refining industries, in particular oil sludge, is their processing into valuable construction and road materials. Solving this issue can help reduce the negative impact on the environment, rational use of natural resources and improve the state's economy. In this regard, it is important to conduct research on the physical and chemical properties and thermal characteristics of oil sludge samples taken at oil refineries of the Republic of Kazakhstan, as well as the possibility of using them as an additive for bitumen grade BND 70/100.

**Keywords:** oil sludge, modifier, bituminous binders, dissolving compositions, asphalt concrete

## Introduction

In the process of extraction, storage and processing of oil and oil products, a significant amount of waste is generated which includes drilling fluid, petroleum wastewater, bottom tank sludge, etc [1]. Oil sludge, which causes colossal damage to the state of soil, atmosphere, water resources and pollution of the ecosystem, is among the largest-tonnage waste of oil-extracting and oil-refining industries. A large number of scientific studies and works are focused on developing methods for the disposal and recycling of this waste.

Usually, oil sludge is proposed to be disposed of by oxidation, microbiological degradation, stabilization/solidification [2].

Stabilization/solidification is one of the effective recycling processes [3] which consists in decontaminating harmful substances into a less soluble (stable) form and stabilizing hazardous substances in a matrix form by encapsulation (solidification) [2].

The biological treatment of oil sludge uses microorganisms to decompose the sludge into its components through microbial growth and degradation. The main advantage of this method is the ability to convert petroleum hydrocarbons into harmless soil components through a natural process, which is achieved at lower operating costs [4]. However [5], these methods have limited capabilities and can also generate secondary pollutants.

The pyrolysis method is widely used, because of its high recovery of energy potential and a relatively small amount of pollutant discharge [6]. This method consists in the thermal decomposition of organic materials in the composition of oil sludge at elevated temperatures (up to 1000°C), the final products are usually gases, a liquid

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phase, and coal, depending on the reaction conditions [7]. However, the use of the pyrolysis process is limited due to the high temperatures used, the heating rate, as well as the characteristics of the sludge and chemical additives, which makes the process unprofitable, and the products contain an increased content of polyaromatic hydrocarbons [1].

On the other hand, oil sludge is usually a complex emulsified mixture of oil, water, drilling fluid, heavy metals, solid particles, and various surfactants [8] with a content of up to 10-60 wt.% oil. This fact allows us to consider them as a potential resource of crude oil. In this regard, recycling and recovery seems to be preferable due to the environmental impact and the huge volume of production.

The methods of froth flotation, ultrasonic radiation, centrifugation, extraction with solvents, etc. have found application to remove the oil part in oil sludge [9]. The process of froth flotation is quite effective, however, the properties of oil sludge, such as viscosity, solids content, density, and duration of treatment, can be influenced [1].

Ultrasonic treatment is an efficient and fast method of oil sludge treatment, which uses ultrasonic irradiation to separate the solid phase from the liquid even in highly concentrated oil sludge suspensions by reducing the stability of the mixture [10]. The application of this method is limited by several factors, such as treatment time, frequency, water content in the mixture, temperature, particle size hardness, ultrasound power and density, salinity, and the presence of surfactants [11].

The method of oil sludge disposal by extraction consists in the different solubility of oil in two immiscible solvents, which are subsequently separated by distillation to extract petroleum hydrocarbons [8]. However, the use of this disposal method is limited by the physical and chemical characteristics and composition of oil sludge.

But, despite a significant amount of research, the possibility of using oil sludge taken from various sampling sites of oil refineries of the Republic of Kazakhstan has not yet been determined. In this connection, the main purpose of this study was to study oil sludge formed in the conditions of an oil refinery in the Republic of Kazakhstan in order to study the possibility of its transformation into a valuable product.

## Material and Methods

Samples of oil sludge formed at POCR LLP were selected as the objects of research (OS 1 - oil sludge taken after the screw conveyor for unloading the solid phase; OS 2 - oil sludge from the R-21/2 storage tank; OS 3 - oil sludge from the drying area).

The component composition of oil sludge was studied according to ASTM D 6560-17. Fractional composition of oil sludge was determined using an

automatic analyzer PAC OptiDist™. The study of functional groups in the composition of the oil residue by IR spectroscopy was carried out at a temperature of 20°C on an ALPHA FT-IR spectrometer (Bruker). The determination of the content of metals in the oil sludge samples was carried out by X-ray fluorescence analysis on an X-Ray Innov-X Systems device. Thermogravimetric analysis of oil sludge samples was carried out in the temperature range 25-600°C on a Netzsch STA 449 F3 device with a linear heating rate of 5°C/min.

To study the possibility of modifying road bases, road bitumen of the BND 70/100 brand was used, the characteristics of which are given in Table 1.

Modification of bitumen with oil sludge was carried out by mixing bitumen binder and oil sludge in the amount of 1.0; 2.0; 5.0; 7.0 and 10.0% at a temperature of 160°C for 90 minutes.

For the original and modified bitumen, we determined the melting point according to ring-and-ball method (ASTM D36), penetration at 25 and 0°C (ASTM D 5), ductility (ASTM D113) and brittle point (GOST 11507-78).

## Results and Discussion

The results of studying the physical and chemical properties of oil sludge samples are presented in Table 2.

It is known that the stabilizers of emulsions and oil sludge are mechanical impurities. In the samples under study, a high content of mechanical impurities was found: for samples taken from the drying area and after the screw conveyor, it reaches 48%.

The studied samples of oil sludge have a high density, which is due to the high content of aromatic and high-boiling components, such as resins and asphaltenes, which in turn are natural emulsifiers, contributing to the high stability of oil sludge. For further studies, samples of oil sludge were preliminarily dehydrated by settling.

As a result of the fractional composition of oil sludge, the content of light fractions has been established, so about 51- 53% of the mass of samples OS 3 and OS 1, respectively, boils up to a temperature of 350°C, and for OS 2 this indicator is 68%, which is

Table 1. Physical and chemical properties of bitumen grade BND 70/100.

| Parameter                   | Value |
|-----------------------------|-------|
| Penetration, 0,1 mm at 25°C | 71    |
| Ductility, mm               | 70    |
| Melting point, °C           | 52    |
| Brittle point, °C           | -15   |

Table 2. Physical and chemical properties of oil sludge.

| Properties                 | OS 1  | OS 2  | OS 3  |
|----------------------------|-------|-------|-------|
| Density, kg/m <sup>3</sup> | 977.4 | 933.1 | 987.3 |
| Content, %                 |       |       |       |
| Mechanical impurities      | 48.2  | 3.6   | 48.0  |
| Water                      | 30.8  | 74.9  | 19.5  |
| Paraffin                   | 2.219 | 0.346 | 2.440 |
| Resins                     | 8,34  | 1.384 | 4.04  |
| Asphaltenes                | 4.94  | 1.34  | 9.895 |
| Fractional composition:    |       |       |       |
| IBP, °C                    | 104.7 | 95.6  | 106.4 |
| Boiling up at T, wt %      |       |       |       |
| 150-250                    | 14.2  | 21.0  | 13.0  |
| 250-350                    | 39.0  | 47.0  | 38.6  |
| 350-400                    | 16.6  | 8.1   | 15.8  |
| Residue                    | 30.2  | 23.9  | 32.6  |

consistent with the data on the component composition of waste. Based on the data obtained on the physical and chemical composition of oil sludge, it can be concluded that their use as a resource for the extraction of primary motor fractions is unprofitable.

To establish the structural and group features of the oil sludge, studies were carried out using the method of IR spectroscopy (Fig. 1).

The obtained IR spectra of oil sludge are characterized by stretching vibrations of methyl groups (CH<sub>3</sub>), which are observed in the form of two absorption bands at 2950 and 2850 cm<sup>-1</sup>. Authors [12] consider stretching vibrations of methylene groups (CH<sub>2</sub>) are also observed in the form of two absorption bands (2920 and 2850 cm<sup>-1</sup>), caused by antisymmetric (vasCH<sub>2</sub>) and symmetric (vsCH<sub>2</sub>) stretching vibrations. The content of absorption bands at 720, 1380, and 1454-1465 cm<sup>-1</sup> also indicates the presence of methyl and methylene groups in paraffinic hydrocarbons. The IR spectra revealed that the studied samples are characterized by a high content of paraffin structures of both normal and branched isostructures.

The IR spectra of oil sludge samples OS 1 and OS 3 show the presence of absorption bands in the region of 3400-3200 cm<sup>-1</sup>, which can be attributed to asphaltogenic acids.

Boiko et al. [13] consider that absorption bands at 1600 cm<sup>-1</sup> are most informative for studying aromatic structures. The spectra of all samples are characterized by the presence of absorption bands in the range of 1665-1600 cm<sup>-1</sup>: the high intensity of these peaks for the oil sludge samples taken after the screw conveyor and from the drying area, which indicates a high content of aromatic hydrocarbons in it. The presence of an intense

absorption band at 1025-1040 cm<sup>-1</sup>, characteristic of the SO<sub>2</sub> group, is also noted for this oil sludge.

The results of determining the content of metals in oil sludge samples are presented in Table 3.

As a result of the studies carried out in the oil sludge from the drying area and after the screw conveyor, the following were found: Ti, Mn, Cr, Cu, Zn, Ni, Cd, Ag, Sn, Sb, Mo, Pd of approximately the same content. For oil sludge from the R-21/2 storage tank, the metal content is noticeably reduced.

The integral thermos-gravimetric curve (TG) and differential scanning calorimetry (DSC) analysis of the studied oil sludge samples are shown in Fig. 2.

On the thermograms of oil sludge samples (Fig. 2), a number of thermal effects are observed, accompanied by a loss of sample mass.

The endothermic effect of low intensity at a temperature of 110°C can be attributed to the loss of residual adsorbed water (moisture); the weight loss in this interval was 5,4-7,2%.

The DSC curves show the presence of exothermic peaks for all samples of oil sludge at temperatures of 318°C and 393-395°C, at this stage the weight loss of the samples occurs due to the evaporation of light organic fractions, the content of which reaches 45-48%.

The exothermic peak in the range of 508-511°C is due to the destruction of the main structural fragments of asphalt-resinous substances with the formation of mainly low-molecular volatile products and high-molecular coke precursors. According to the TGA curve, weight loss ranges from 9.6; 12.8 and 12.1% for samples OS 1, OS 2 and OS 3, respectively.

From the analysis of the weight loss curves, it is obvious that the maximum rate of weight loss for the samples starts within the range of 128-140°C. According to Liu et al. (2020) exothermic peaks at 150-600°C are characteristic of organic substances: for samples OS 1 and OS 2, a weight loss of about 68.3% is observed, and for OS 3-63.5%, which is consistent with the data of component composition of oil sludge samples and indicates a high content of hydrocarbon fractions in them. The residual mass of oil sludge samples when heated to 600°C was 31.7-36.5%, presumably by the decomposition of coke and inorganic substances in the composition of mechanical impurities.

Therefore, in this work, a detailed analysis of the main physical and chemical properties and thermal characteristics of oil sludge samples is presented and an increased content of high-boiling fractions is established, which indicates the unsuitability of the use of oil sludge for the production of straight-run gasoline and diesel distillates.

However, the presence of an impressive amount of asphalt-resinous components suggests its use as binders in road building materials.

It is known that the important operational properties of the road base depend on the content of oil products in the sludge; therefore, to study the possibility of using as a component of road surfaces, oil sludge taken from

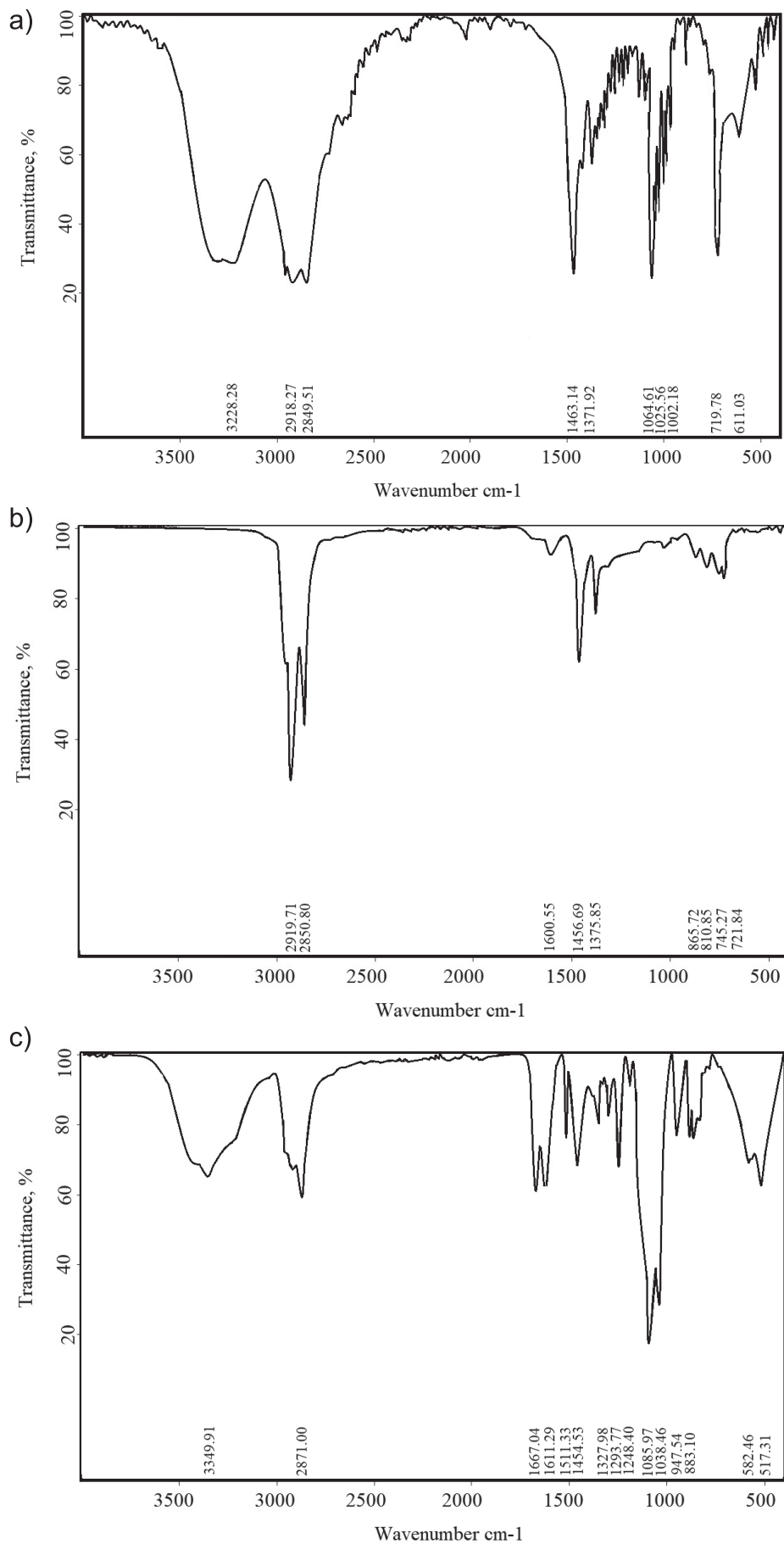


Fig. 1 a) IR spectrum of the OS 1, b) IR spectrum of the OS 2, c) IR spectrum of the OS 3.

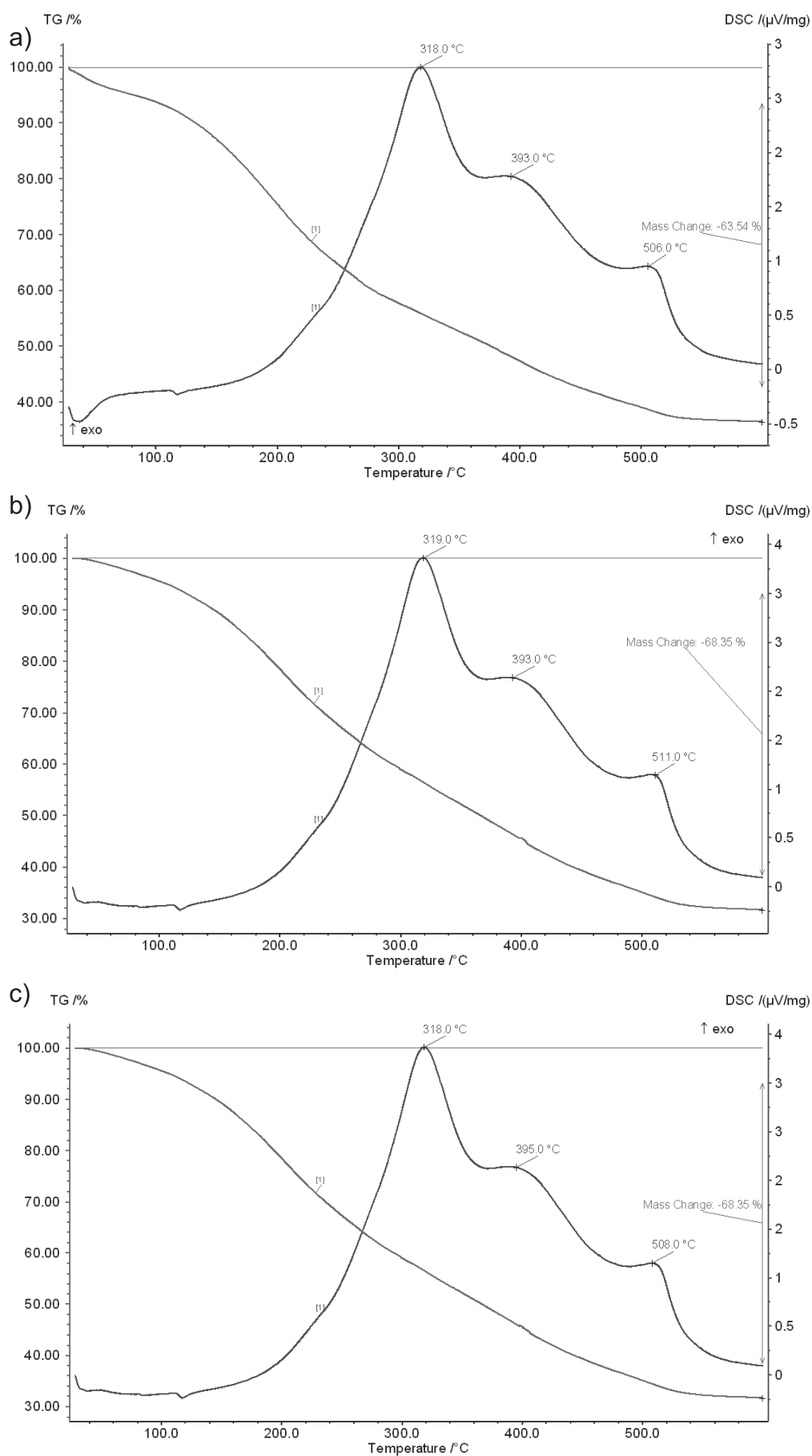


Fig. 2 a) DSC-TG analysis of the OS 1, b) DSC-TG analysis of the OS 2, c) DSC-TG analysis of the OS 3.

the drying site (OS 3) with a content of oil products of 16.375% was used.

In this regard, it became necessary to extract oil from oil sludge effectively. Panova [14] conclude that experiments were carried out to select the optimal dissolving mixture for oil sludge and high efficiency of

compositions consisting of gasoline and hexane, hexane and hexene, white spirit and hexene was revealed.

The results of studying the effectiveness of these hydrocarbon compositions as solvents were tested for a sample of oil sludge No. 3, the results are presented in table 4 and it was revealed that the most effective composition for extracting the hydrocarbon portion is a mixture of white spirit and hexene (Table 4).

Further use of oil sludge as a binder is in the joint processing of bitumen and oil sludge. Determination of the effectiveness of bitumen with oil sludge in Table 5.

From the analysis of Table 5, we see that the modification with oil sludge significantly improves the operational properties of bitumen. There is an increase in the values of penetration and extensibility of bitumen samples, as well as an improvement in its low-temperature properties.

The introduction of oil sludge into the composition of bitumen leads to a significant improvement in its frost resistance: the brittleness temperature of the sample decreases from -15 to -19°C for modified bitumen samples with an oil sludge content of 5 wt%. One of the indicators of the quality of bitumen is also the plasticity interval (softening point – brittle point), which increases for the modified samples, especially after the introduction of oil sludge (OS) in an amount of 5 wt. %.

An increase in the concentration of oil sludge in the composition significantly increases ductility and low-temperature properties; however, this dependence is valid only for a concentration of 5-7 mass. %, a further increase in the oil sludge (OS) content leads to a noticeable decrease in plasticity.

Table 3. Metal content in oil sludge.

| Element | Sampling location |      |       |
|---------|-------------------|------|-------|
|         | OS 1              | OS 2 | OS3   |
| Ti      | 0.80              | -    | 0.86  |
| Cr      | 0.26              | 0.08 | 0.37  |
| Mn      | 0.58              | 0.07 | 0.55  |
| Ni      | 0.64              | 0.03 | 2.17  |
| Cu      | 2.08              | 0.09 | 2.03  |
| Zn      | 11.67             | 0.43 | 11.75 |
| Pb      | 0.23              | 0.03 | 0.36  |
| Nb      | 0.31              | 0.10 | 0.29  |
| Mo      | 0.48              | 0.12 | 0.43  |
| Pd      | 1.45              | 0.34 | 1.27  |
| Ag      | 2.40              | 0.57 | 2.23  |
| Cd      | 2.19              | 0.50 | 1.94  |
| Sn      | 2.42              | 0.57 | 2.15  |
| Sb      | 2.33              | 0.50 | 2.10  |
| V       | 0.28              | -    | -     |

Table 4. Results of experiments on the use of dissolving compositions for OS 3 by the extraction-gravimetric method.

| Dissolving composition | Solvent ratio, vol. % | Recovery rate of oil products, % |
|------------------------|-----------------------|----------------------------------|
| White spirit/ hexene   | 95:5                  | 95.94                            |
| Gasoline/ hexene       | 95:5                  | 83.60                            |
| Hexane/ hexene         | 95:5                  | 89.45                            |

Table 5. Changes in the physical and mechanical properties of BND 70/100 bitumen after the introduction of oil sludge into its composition.

| Parameter                   | Value |     |     |     |     |
|-----------------------------|-------|-----|-----|-----|-----|
|                             | 1     | 2   | 5   | 7   | 10  |
| Modifier quantity, %        |       |     |     |     |     |
| Penetration, 0,1 mm at 25°C | 71    | 72  | 75  | 75  | 74  |
| Ductility, mm               | 72    | 74  | 77  | 78  | 76  |
| Softening point, °C         | 52    | 53  | 55  | 55  | 53  |
| Brittle point, °C           | -18   | -18 | -19 | -19 | -17 |

## Conclusions

Therefore, the results obtained indicate good perspectives of using oil sludge as a component of high-quality road bitumen binders that fully meet the requirements of modern standards in the manufacture of asphalt concrete.

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## Conflict of Interest

The authors declare no conflict of interest.

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