



## OIL SLUDGE OF THE LANDFILL OF JSC “OZENMUNAYGAS,” MANGYSTAU REGION

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<https://doi.org/10.26782/jmcmms.spl.10/2020.06.00038>

### Abstract

*Over the past decades, environmental protection and the rational use of natural resources in the conditions of development and rapid growth of industrial production, especially in the oil and gas industry, have become the most pressing problems. In this regard, the issues of sparing of oil and gas resources and recycling of waste into target products, the introduction of non-waste technology in the Mangystau region of the Republic of Kazakhstan, are considered to be of paramount importance. The present study on the production monitoring of oil-saturated waste soil cover in the Mangystau oil field and the subdivisions of OzenMunayGazJSC of the Mangystau region of the Republic of Kazakhstan was carried out on the basis of “Methodological recommendations for conducting comprehensive research and assessing environmental pollution in areas that are likely to be affected by intense anthropogenic impact.” The use of oil resources, transportation of oil and oil products is accompanied by the emergence and wide spread of various environmental problems causing technological, biological and other negative effects to the environment. In the fields of oil and gas production, tens of thousands of tons of oil sludge are formed annually, a certain part of this amount being stored in sludge collectors or in special areas designated for this purpose. Oil sludge is waste generated during the extraction, transportation and refining of oil from which it is possible to produce target products. The chemical composition and physical-mechanical properties of various groups of oil sludge are very diverse. The organic part of oil sludge contains 80% of hydrocarbons and their derivatives, of which paraffin-naphthenic hydrocarbons make up 74-75%, resins - 21-22% and asphaltenes - 3-4%. The organic fraction of oil sludge contains phenols in the amount*

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Mels T. Oshakbaev et al*

*A Special Issue on “Quantative Methods in Modern Science” organized by Academic Paper Ltd, Russia.*

of 0.075-0.0144 mg/dm<sup>3</sup>. In bituminous soils, on the contrary, 75% is the inorganic part of the soil cover. The organic part contains organometallic compounds, where vanadium and titanium have the highest content (1,990-2,000 mg/kg and 970-1,000 mg/kg, respectively). In this regard, there is a need to monitor the area and to implement a set of effective measures to protect it against the adverse effects on public health and the environment. This article presents the main components of the organic and inorganic parts of oil sludge and bituminous soils of the landfills of JSC "OzenMunayGas." The organic part of sludge contains paraffin hydrocarbons, resinous compounds and organometallic complexes. The analysis of oil sludge shows the potential of its use for the production of paraffins, bitumen and the extraction of metals.

**Keywords:** Oil sludge; bituminous soil; fractional distillation; gas chromatography; infrared spectrometry; atomic absorption spectroscopy.

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## **I. Introduction**

It is well known that the fuel and energy complex based on oil and gas, which are the driving force of the economy, creates many problems associated with the non-compliance with production safety rules and unforeseen circumstances. Tens of thousands of tons of oil sludge are annually formed on each of the oil and gas fields: groundwater, reservoir, biologically active sludge wastes, wastes of structures for mechanical and chemical wastewater treatment [III, VI, XVI]. A certain part of sludge is stored in sludge collectors or in special areas designed for this purpose and cause environmental problems [II, XXVIII, IV]. Oil sludge is also the wastes that are formed during the extraction, transportation and processing of oil which can be used to produce the target products [IX, XXIX, XXIV, XXV, XXVI]. The chemical composition and the physical-mechanical properties of various groups of oil sludge are very diverse. The content of hydrocarbons and their derivatives in oil wastes, the release of toxic gases and air pollution depend on the composition of the original oil, the level of processing of raw materials and the degree of introduction of waste-free technology. In addition, the service life of equipment and many other factors ultimately require a rational method of disposal and processing them into target products. In connection with the aggravating problem of environmental protection and the shortage of energy-intensive raw materials, the most promising direction of processing and disposal of oil sludge is to extract oil, oil products and solid residues from it and then use them for their intended purpose. Improving the environmental situation and rational economic use of natural resources is becoming the most important national task of the region. In this regard, the following measures are urgent: the timely assessment of the ecological state of the territory polluted with oil products and oil wastes, chemical and biological soil studies, the study of anthropogenic impact on the soil, the analysis of the content of heavy metals and hydrocarbons in soils, as well as the development of practical recommendations for reducing anthropogenic pollution of the territory, the methods of disposal of industrial wastes by oil and gas companies [VIII, VII, XXXI, XIX, XVIII, XXI].

The present article analyses the physical and chemical characteristics of the oil sludge of JSC “OzenMunayGas” in order to find the possibilities of processing them into target products.

## **II. Materials and Methods**

The analysis and methodology of experimental work was carried out in accordance with standards and GOSTs: GOST 17.4.3.01 –83 Nature Conservation. Soils.General requirements for sampling. GOST 17.4.3.03 - 85 Nature Conservation. Soils.General requirements for methods for the determination of pollutants.GOST 2177 - 99 Oil products.Methods for determining the fractional composition.GOST 2517 - 12 Oil and oil products.Sampling methods. The fractional distillation of oil and oil sludge was carried out according to GOST 11011–85 using APH-3 (ARN-3) unit for oil products distillation. To isolate mechanical impurities from oil sludge (bituminous soil), hot water was used (80-900°C). Isolation of paraffin-naphthenic and resinous hydrocarbons from asphaltenes was carried out using n-heptane solvent.

The analysis of hydrocarbons released at the temperature of up to 3000 ° C was carried out on a gas chromatograph DANI Master GC (Variancapillary Column CP-PoraPlotQ; 27.5m, 0.32mm, 10µm). The evaporator temperature is 350°C, and the column temperature is 200 ° C. Detection - flame ionization detector (FID). Fractions at 160–320°C of oil sludge were also analyzed by chromatography-mass spectrometry.

IR spectra were taken on an ИКC-29 (IKS-29) spectrometer (4,000-400 cm<sup>-1</sup>) in potassium bromide tablets and liquid paraffin.

The accuracy of the measurement results was evaluated according to the standard deviation by a statistical method. The reagents used were benzene, toluene, styrene, o- and p-xylene, and reagent-grade n-heptane. Field surveys of industrial sites and ГY-27 НГДY-4 ЦДНГ-4 landfill of “OzenMunayGas” JSC were carried out.

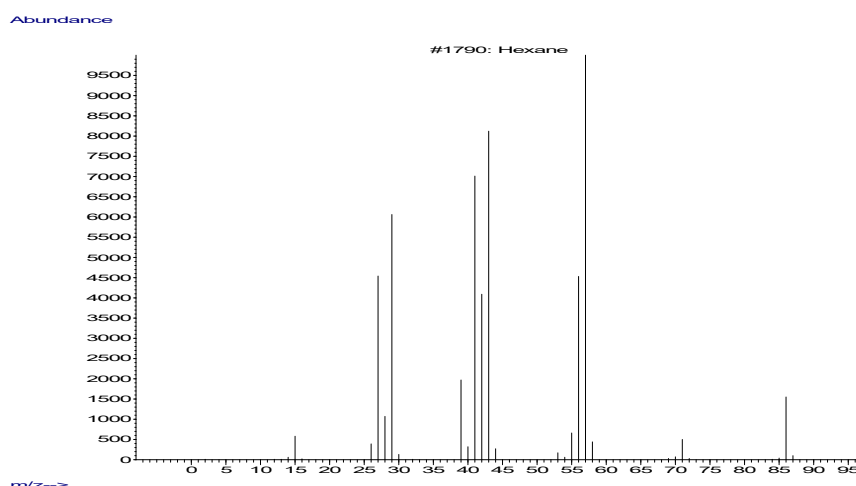
## **III. Results and Discussion**

The total content of hydrocarbons and constituent groups of the organic part of the bituminous soil and sludge from the ГY-27 НГДY-4 ЦДНГ-4 landfill of “OzenMunayGas” JSC is presented in Table 1. From the table data, it follows that by the content of hydrocarbons and their derivatives, oil sludge differs from bituminous soils. The total hydrocarbon content in the sludge is 79% compared with samples of bituminous soil No. 1 and No. 3, where these values are 13% and 15%, respectively. Despite the different content of hydrocarbons, their organic part mainly consists of paraffinic, naphthenic hydrocarbons and resinous compounds, whose content is consistent with the data of Stogova, Lysenko, Faizov, et al. [XXVII, X-XIV, V, XXX]. The content of asphaltenes does not exceed 5-6% of the total amount of hydrocarbons in the sludge and bituminous soils.

**Table 1: The total content and group composition of the organic part of bituminous soil and oil sludge**

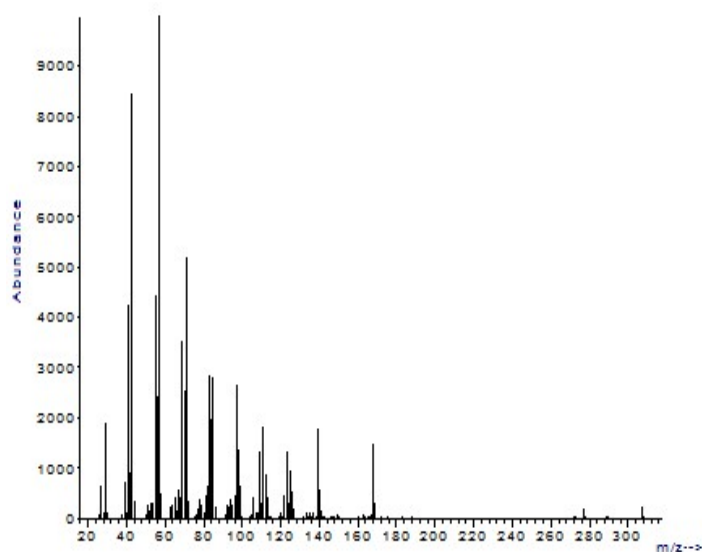
No.	Total hydrocarbon content, g/100g	The content of hydrocarbon groups (% of total content)		
		Paraffinandnaphthenichydrocarbons	Resins	Asphaltenes
Sample1, bituminoussoil	13	68-70	25-28	5-6
Sample2, oil sludge	80	74-75	21-22	3-4
Sample3, bituminoussoil	15	66-68	24-26	4-6

The distillation on the APH-3 (ARN-3) unit of the organic part isolated from oil sludge and bituminous soil indicates the absence of low-boiling gasoline and kerosene fractions. In the beginning, the boiling point is 300°C and 3,100°C at atmospheric pressure for the organic part of the oil sludge and bituminous soil, respectively. The content of hydrocarbons present in the bituminous soil and in the sludge (organic part) was determined by chromatography-mass spectrometry (Fig. 1 and 2; Table 2).



**Fig. 1:** Chromatography-mass spectrometry of the oil sludge organic part

Along with paraffin hydrocarbons, naphthenic hydrocarbons with the content of up to 24% are found in samples of oil sludge, which are absent in samples of bituminous soil. In samples of bituminous soil, there are paraffinic hydrocarbons of normal composition (34%) and isomeric structure (50%).



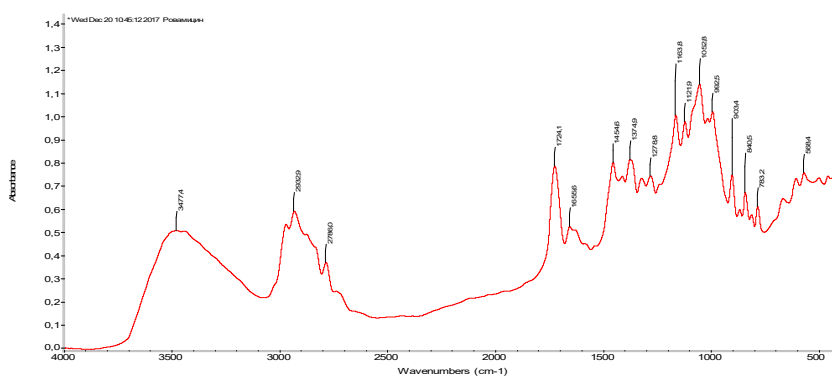
**Fig. 2:** Chromatography-mass spectrometry of oil sludge.

All paraffin hydrocarbons contain 16 or more carbon atoms, while from 12% to 17% of hydrocarbons could not be deciphered. These compounds can refer to hydrocarbon derivatives due to their interaction with ambient components. The content of resinous compounds varies from 16 to 28%, and asphaltenes from 3 to 6%.

To determine other classes of organic compounds in sludge, IR spectra were taken (Fig. 3).

**Table 2: Hydrocarbon content in oil sludge (Sample 2) and bituminous soils (Samples 1 and 3).**

Fraction	Hydrocarbon content,%.		
	Sample 1	Sample 2	Sample 3
n-hexadecane			
3-methyl hexadecane			
3.6 dimethyl hexadecane	11	9	11
2,3,5 trimethyl hexadecane	6	5	5
n-heptadecane	7	6	7
2,3,6 trimethylheptadecane	4	5	4
n-octadecane	12	8	13
3 methyl octadecane	8	2	2
3.6 dimethyl octadecane	11	8	12
4.7 dimethyl octadecane	7	3	3
2,3,6 trimethyloctadecane	9	5	8
2,3,8 trimethyloctadecane	2	6	6
2.3-dibutyl5-pentylcyclooctane	3	3	5
2-hexyl 4 methylcyclohexane	4	4	7
2.3dimethyl6cyclohexyldecane	-	6	-
2-methyl 3-cyclohexyltetradecane	-	3	-
2,6,7trimethyl4-cyclopentyldecane	-	5	-
	-	6	-
	-	4	-
Other, undeciphered components	16	12	17



**Fig. 3: Infrared spectrometric analysis of oil sludge.**

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Mels T. Oshakbaev et al*

Figure 3 shows that the IR spectra of oil and sludge have characteristic absorption frequencies of hydrocarbon and functional groups. The frequencies of the absorption bands in the IR spectra with wave numbers of 2,920–2,950  $\text{cm}^{-1}$  and 2,800–2,910  $\text{cm}^{-1}$  belong to the methyl and methylene groups, respectively. Absorption bands of 2,851-2,918  $\text{cm}^{-1}$  are characteristic of naphthenic hydrocarbons, especially of decaline and its derivatives. For the  $S = S_{ar}$  aromatic structures, the absorption bands of 1,635  $\text{cm}^{-1}$  are characteristic, and a set of bands of 722–806  $\text{cm}^{-1}$  is also observed, which belong to the CH aromatic groups. Absorption bands of 1,700-1,760  $\text{cm}^{-1}$  and 1,680-1,700 $\text{cm}^{-1}$  are characteristic of aliphatic and aromatic carboxylic acids. The frequencies of the absorption band of 3,410, 3415  $\text{cm}^{-1}$  are characteristic of OH-groups. The presence in the sludge samples of the absorption band of oxygen-containing groups compared to the original oil, means the interaction of sludge hydrocarbons with oxygen in the air. Absorption bands of 3,380-3,540  $\text{cm}^{-1}$  are characteristic of the associated amino groups with overlapping hydroxyl groups. The absence of amino groups with an absorption frequency of 3,380-3,540  $\text{cm}^{-1}$  in oils and their appearance in oil sludge suggests the likely binding of atmospheric nitrogen to the hydrocarbon part of the oil sludge. Both in oil and in sludge, phenolic hydroxyl is detected at values of 1,140-1,230 $\text{cm}^{-1}$ . The quantitative determination of phenol showed that its content is approximately 6.4 mg/kg. Perhaps some of the waste contains oxidized forms, probably due to exposure to the impact of the ambient components.

In addition, according to literature data, it is well-known that organometallic compounds are present in oils [X-XII]. In the next series of experiments, the presence of metals in the form of compounds was determined by atomic absorption spectroscopic method. The results of atomic absorption spectroscopic analysis of bituminous soil and oil sludge are given in Table 3. The experimental data of the analysis make it possible to conclude that the organic part of sludge contains various compounds of transition metals such as copper, strontium, titanium, nickel, chromium, vanadium, etc. (see Table 3). Vanadium and titanium have the highest content of organometallic compounds (1,990–2,000 mg/kg and 970–1,000 mg/kg, respectively). The content of nickel and copper ranges from 15 to 27mg/kg. Gallium and molybdenum have the lowest content, their concentration not exceeding 0.001 mg/kg.

**Table 3: Atomic absorption spectroscopic analysis of bituminous soil and oil sludge**

Elements	Content in SampleNo.: (average),(mg/kg)		
	1	2	3
Copper(Cu)	18	20	15
Strontium (Sr)	<496	<475	<474
Titanium (Ti)	<1,000	<975	<974

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Mels T. Oshakbaev et al*

Molybdenum (Mo)	0.0007	0.00015	0.001
Nickel (Ni)	27	22	24
Chromium (Cr)	0.017	0.05	0.012
Gallium (Ga)	0.001	0.0001	0.0005
Vanadium (V)	<2,000	<1,996	<1,992
Zinc(Zn)	10	8	7
Barium(Ba)	<0.01	<0.02	<0.25
Lead(Pb)	488	490	491

The following elements are detected at the level of the MPC for the soil in the studied bituminous soils (mg/kg): copper (20), nickel (30), zinc (7-10). The remaining elements (molybdenum, gallium, and barium) are contained in a relatively small amount not exceeding the MPC [XXXI, XVII, XXII]. The main part of the bituminous soil and oil sludge is inorganic compounds. The results of the analysis are summarized in Table 4. The results of the analysis of bituminous soil and sludge for the content of chemical elements are given in terms of oxides.

**Table 4: Analysis of the inorganic part of bituminous soil and oil sludge**

The composition of the elements in terms of oxides	Content, %		
	1(bituminous soil)	2(oil sludge)	3(bituminous soil)
SiO <sub>2</sub>	31.61	31.90	28.47
Fe <sub>2</sub> O <sub>3</sub>	7.39	6.44	7.63
Al <sub>2</sub> O <sub>3</sub>	17.85	18.56	18.40
TiO <sub>2</sub>	0.13	< 0.03	0.11
CaO	9.02	11.47	10.36
MgO	11.47	10.50	10.04
Na <sub>2</sub> O	12.53	0.01	10.60
K <sub>2</sub> O	0.90	0.03	0.30
SrO	0.20	traces	0.22
P <sub>2</sub> O <sub>5</sub>	0.11	0.01	0.12



V <sub>2</sub> O <sub>5</sub>	0.01	< 0.01	0.01
MnO	traces	traces	traces
Cr <sub>2</sub> O <sub>3</sub>	0.04	traces	0.03
CuO	0.01	traces	0.02
ZnO	0.04	traces	0.15
PbO	0.02	traces	0.01
CdO	traces	traces	traces
NiO	0.10	traces	0.10
Li <sub>2</sub> O	traces	traces	traces
Ignitionlosses	8.90	19.93	14.4

Analysis of bituminous soil and sludge has shown the content (especially in Sample 1) of a significant amount of oxides of silicon, aluminum, calcium, iron, magnesium, sodium. In general, in the analyzed samples, an increased number of such compounds of microcomponents of chromium, strontium, vanadium, zinc, lead and phosphorus has been detected. Samples of bituminous soil are more saturated with the above microelements. Analysis of the organic fraction of oil sludge has shown the presence in individual samples of a significant content of phenols – 5.7– 6.4 mg/dm<sup>3</sup>, which corresponds to the data in the content of phenolic hydroxyl [XX, I]. The analysis of oil sludge components implies that it is reasonable to process them, which will result in the introduction of waste-free technology as an integral part of oil and gas complexes [XXIII].

#### **IV. Conclusion**

Oil sludge landfills of “OzenMunayGaz” JSC of Mangystau region are a heterogeneous system consisting of organic and inorganic parts. The organic part of sludge contains 80% of hydrocarbons and their derivatives, where paraffin-naphthenic hydrocarbons make up 74-75%, resins – 21-22% and asphaltenes – 3-4%. The organic fraction of sludge contains phenols in the amount of 0.075-0.014mg/dm<sup>3</sup>. In bituminous soils, on the contrary, 75% is the inorganic part of the soil. The organic part contains organometallic compounds, where vanadium and titanium have the highest content of organometallic compounds (1,990–2,000 mg/kg and 970–1,000 mg/kg, respectively). The content of nickel and copper ranges from 15 to 27mg/kg. Gallium and molybdenum have the lowest content, their concentration not exceeding 0.001 mg/kg.

In the soil isolated from the bituminous soil, vanadium, titanium, chromium, and nickel are also present in addition to macro-components, such as silicon, aluminum, and iron.

The following elements are detected at the level of the MPC for the soil in the studied bituminous soils (mg/kg): copper (20), nickel (30), zinc (7-10). The remaining elements (molybdenum, gallium, and barium) are contained in a relatively small amount not exceeding the MPC.

On the basis of the conducted analytical work, it can be concluded that the organic part of the oil sludge, in the long term, in case of developing a rational processing technology, can be used to obtain paraffins and the related target products.

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