

## Utilization of Oil Wastes for Production of Road-building Materials

Z.A. Mansurov\*, E.K. Ongarbaev, B.K. Tuleutaev

Department of Chemical Physics, Al-Farabi Kazakh State National University,  
95 Karasai Batyr Str., Almaty 480012, Kazakhstan

### Abstract

The pollution of environment by oil spills in the process of extraction, refining and transporting of oil is an important ecological problem of oil industry. Composition and properties of the oil sludge and oil contaminated soil taken from the area of Zhetybai – Uzen – Atyrau pipeline failure have been investigated aiming at development of oil waste utilization methods. The offered thermal method of organic fraction extraction allows to decrease the organic fraction content by 15–20 %. It is shown that the recovered oil may be used for the bitumen production, and the solid residue – as a component of cold asphalt concrete.

### Introduction

The intensive development of oil-gas industry is resulting in very grave ecological consequences. At present all processes, involving oil processing are impending danger for the ecology. The oil industry encounters the paramount problem of oil waste utilization accumulated and stored by refineries. The considerable pollution of ground and water by drilling sludge, containing the hydrocarbons, heavy metals and polymers, is resulting of the drilling rigs. The oil spills during its mining cause numerous negative phenomena resulting in soil corrosion. The pipeline failures causes the enormous oil losses and oil contamination of areas [1,2].

The oil sludge resulted of oil waste processing, stable nondistrict emulsions production, reservoirs scarfing, agents discharges and other oil mining and processing operations should be unloaded into the special waste storage precipitators. Besides that, the oil recovered from the sewer systems, oil pumps (with soil) pipeline failures is discharged into these storage precipitators.

The getting of oil and its components in the environment, i.e. into the air, water and soils alters their physical, chemical, biological properties and characteristics, disturb natural bio-chemical processes. In process of oil hydrocarbons transforming they are enable to form toxic compounds, having dangerous for the human's health properties and are characterized by stable to the microbiologic destruction.

Usually, the oil waste represent heavy oil residues, containing in average (mass %): petroleum products – 10-70, water – 10-40, solid impurities – 5-80 [3]. Till now the problems of oil waste processing and utilization aren't overcome due to oil waste stability, inherent properties and characteristics, altered being exposed to atmosphere effects when they are stored in open collector-ponds. With time, the waste "aging" is due to evaporating of light fractions, oxidation and oil gumming, addition of non-organic impurities. The difficulty of the problem consists both in its scale and in loughening of control requirements and needing elaboration of advanced methods enabling to overcome this difficulty and the problems of ecological pollution.

In general, among the methods currently used and the most promising ones of oil waste utilization there may be mentioned [1,4]: thermal processing (burning, cracking or pyrolysis, water steam treatment), physical methods of processing (magnetic or acoustic fields, divers types of irradiation), treatment by adsorbents, separation methods (membranes, filters etc), biological methods of treatment. Furthermore, there are some recommendations on using of oil sludge without separation stages, e.g. by burning, in the road building [5-7] or in building materials productions.

Conway [5] considers the technology of ground stabilization by bitumen emulsion for oil contaminated soil fixation. The contaminated soils are used as source row materials to produce stable material with bitumen emulsion. Then such materials are used as a foundation of road coatings. The recycle process includes

\*corresponding author. E-mail: mansurov@lorton.com

the mixing of bitumen emulsion with oil contaminated soil.

The method of cold asphalt bitumen production and oil contaminated soil fixing is well known [6]. The pieces of asphalt coating are mixed with hydrocarbon bearing oil contaminated soil and mineral compound. Then the obtained mixture is filled with bitumen emulsion to produce cold asphalt concrete.

It is necessary to study the properties and compositions both of organic and mineral fractions of oil waste aiming at development of technology of its utilization. The study of oil waste composition and properties allows developing efficient methods of processing and further utilization of such waste depending on its characteristics.

In this connection, the work is aimed to study compositions and properties of oil waste and to work out ways of processing and further utilization.

## Experimental

The extraction of organic fraction from oil waste was carried out by extraction and thermal methods. The method of hot extraction was used for oil separation from oil waste in Soxhlet's apparatus by spirit-benzene mixture.

Besides, the extraction of organic fractions from oil waste was carried out on the stationary laboratory unit of thermal processing. The raw material is supplied via the hopper in the tubular reactor with the screw conveyor mounted inside of the tube. The heat of gas burner is used as a heat carrier. Oil containing waste was processed in the heating zone, where the temperature from 200 to 250°C is maintained by propane-butane mixture flame, till to obtain liquid-flow state of organic fraction with further separation of liquid oil from solid remainder. The slope angle and rotation velocity of the screw depend on the composition of initial waste. The propane and butane mixture consumption is 130 cm<sup>3</sup>/min, air consumption is 5000 cm<sup>3</sup>/min. The temperature of the burner flame in the glowing zone reaches up to 800-900°C. The temperature of oil flow is 150-200°C, the temperature of soil residue is 180°C.

The oil sludge was processed in the mixture with sand (20 mass %) because of low content of mechanical fillers. After oil separation obtained, the solid residues were processed by hot extraction with spirit-benzene mixture to determine residual quantity of organic fraction.

The component group composition of extracted oil

was determined by the adsorptive chromatography method. The extracted oil was deasphaltized by petroleum ether with the boiling point to 45°C, taking in 40 – times volume. Adsorptive – chromatographic separation was carried out in the two-stage column with descending flow of solvent, using activated silica gel as a sorbent. The obtained deasphaltizers were separated into oils and three groups of tars, eluted by benzene, petroleum-benzene and spirit-benzene mixtures. The oils contents of paraffin-naphthene hydrocarbons and aromatic hydrocarbons were determined.

The fractional composition of oil extracted from oil sludge was determined by distillation under vacuum at 4 mm Hg in the apparatus ARN-2.

The method of IR spectroscopy and X-ray phase analysis were used to determine the structure-group composition of hydrocarbons and mineral components in oil waste. The IR spectra within 400-4000 cm<sup>-1</sup> range were obtained by the device UR-20 in thin layer of substance on the KBr plate. The spectra of X-ray diffraction were registered with diffractometer DRON-3M at copper filtered radiation.

In addition, the oxidation of organic fraction of oil sludge was carried out. The main element of the oxidation installation is the stainless steel reactor with a bubbler, heating system and thermoregulation system. The volume of air, fed by compressor was measured by rotameter. The oxidation by hot air was carried out providing 5 hours exposure in periodic duty at 250°C and air consumption up to 2 l/min per 1 kg of raw material.

The performance parameters of obtained bitumen and asphalt concrete were determined by the standard methods.

## Results and discussion

The objects of study were oil sludges constituted of oil reservoir scarfings and oil contaminated soils from the oil storages with oil spills recovered on the failures of the main oil pipeline Zhetybai – Uzen – Atyrau. The physical and chemical characteristics and component compositions of these sludges are presented in Table 1.

As is evident from the Table 1, 81,8 mass % of organic substance are extracted from oil sludge and 23,6 mass % - from the oil contaminated soil by extraction method.

The oil sludge content of water is 10,2 mass % while the contaminated soil contains only 1,2 mass % of water. The main fraction of contaminated soil is

**Table 1**

Physical and chemical characteristics and component compositions of oil waste.

Characteristics	Oil wastes	
	oil sludge	oil contaminated soil
Density (kg/m <sup>3</sup> )	1260	1665
Component composition (mass %):		
Organic fraction	81.8	23.6
Water	10.2	1.2
Mineral fraction	8.0	75.2
pH	4.8	–
Congelation temperature, °C	+ 40	+ 36

constituted by mechanical impurities (75,2 mass %), while their content in oil sludge is negligible.

The characteristics of organic fraction of oil sludge and oil contaminated soil are given in Table 2. The oil extracted from oil sludge contains the paraffin-naphtene (40,84 %), aromatic hydrocarbons (26,08 %). The significant content prevailing of petroleum-benzene tars (11,46 %) over benzene and spirit-benzene tars (4,33 and 4,53 % respectively) is typical for the oils. The asphaltene content is 12,76 %. Thus, the oil, extracted from oil sludge by extraction, differs from the usual oils by high paraffin, asphaltic-tarry substance contents that makes processing of such raw materials quite difficult.

The negligible oil content of paraffin-naphtenes

**Table 2**

Component group composition of oil waste organic fraction, extracted by extraction method

Component group composition (mass %)	Oil waste organic fraction	
	oil sludge	oil contaminated soil
Oils:		
paraffin-naphtene	40.84	6.49
odorous	26.08	28.12
Total of oils	66.92	34.61
Tars:		
petroleum-benzene	11.46	35.80
benzene	4.33	3.09
spirit – benzene	4.53	14.57
Total of tars	20.32	53.46
Asphaltene	12.76	11.91

(6,49 %) and higher aromatics (28,12 %) represents organic fraction of the oil contaminated soil. In comparison with oil from oil sludge, the quantity of tars is very high: petroleum-benzene – 35,80 %, spirit-benzene – 14,57 %, benzene – 3,09 %. The asphaltene content is 11,91 %. So, the hydrocarbon phase of composition of contaminated soil may be classified as high-tarry oil.

The IR-spectroscopy data (Fig. 1) showed that the saturated structures as CH, CH<sub>2</sub>, CH<sub>3</sub> (adsorption band in the region 3000-2800, 1465, 1380 cm<sup>-1</sup>) and CH<sub>2</sub> groups available in long paraffin chains (adsorption band 720 cm<sup>-1</sup> is weakly expressed) are prevailing in chemical structure of the oil. Presence of aromatic structures of divers substitution types (900-750 cm<sup>-1</sup>) (the mono-, bi-, tri-substituted benzene) is notable for all the samples. The adsorption bands within 1700-1740 cm<sup>-1</sup> range attributed to valence fluctuations of oxygen containing compounds are observed in all the spectra.

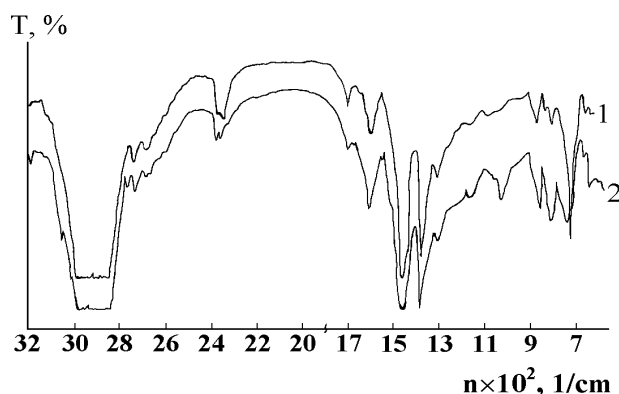


Fig. 1. The IR-spectra of oil wastes' organic fraction: 1–organic fraction of oil sludge, 2–organic fraction of oil contaminated soil.

According to the X-ray phase analysis (Fig. 2) of mineral fractions of oil sludge and oil contaminated soil, the quartz SiO<sub>2</sub> (d<sub>ool</sub> = 3,388 Å), calcite CaCO<sub>3</sub> (d<sub>ool</sub> = 3,025 Å) and feldspars are the rock-forming minerals of oil waste while micas, argillaceous minerals (chlorite and kaolinite Al<sub>4</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>3</sub>) are in subordinated position. As is evident from the rentgenogram of oil sludge its composition is represented by polynaphtene N<sub>ph</sub> (d<sub>ool</sub> = 4,66 Å) and graphitic G<sub>ph</sub> (d<sub>ool</sub> = 3,355 Å) phases. On the oil sludge rentgenogram there are also very intensive peaks, corresponding to hexahydrate of mellitate of aluminium C<sub>6</sub>(COO)<sub>6</sub>Al<sub>2</sub>•6H<sub>2</sub>O (d<sub>ool</sub> = 4,129; 3,704; 2,478; 2,209; 2,087 Å), those presence may be explained by

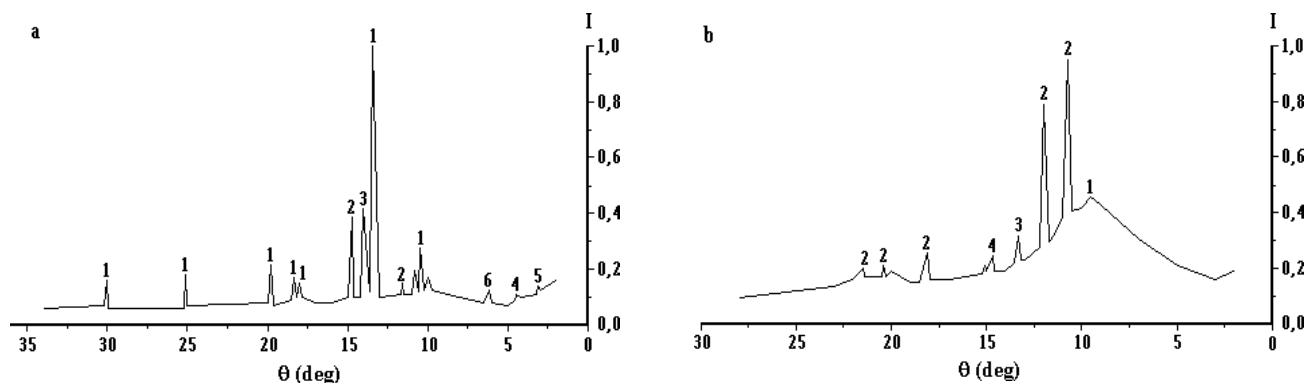


Fig.2. The rentgenograms of oil wastes: a–oil contaminated soil: 1–quartz  $\text{SiO}_2$ , 2–calcite  $\text{CaCO}_3$ , 3–feldspars, 4–micas, 5–chlorite, 6–kaolinite; b–oil sludge: 1–polynaphtene phase, 2–hexahydrate of mellitate of aluminium  $\text{C}_6(\text{COO})_6\text{Al}_2 \cdot 6\text{H}_2\text{O}$ , 3–graphitic phase, 4–calcite  $\text{CaCO}_3$ .

addition of active reagents to oil improving its transportation by pipelines.

In most of the oil separation processes, oil sand deposits are subjected to hot or cold streams of fluids, gases or liquids. Karim et al. [8] examined some aspects of volatilization and combustion of Athabasca tar sand samples when exposed to hot oxidizing low velocity gas streams produced by the burning of very lean mixtures of methane or hydrogen in air at elevated temperatures of up 1200 K at atmospheric pressure. The thermal cracking, providing hydrocarbon separation in presence of mineral fraction of waste, is one of the most promising methods of oil waste processing. The thermal treatment results in decreasing by 15-20 % of organic fraction the waste [9,10]. The component composition of the solid residue of oil sludge and sand after organic fraction separation is 19,1 mass %, mineral fraction is 78,4 mass %. The composition of the solid residue of oil contaminated soil is as follows: organic fraction - 15,8 mass %, mineral fraction - 84,2 mass %.

There is significant difference between the physical and chemical characteristics of the oil obtained by thermal treatment and the oil obtained by extraction. The component group composition of the oil waste organic fraction, extracted by thermal method is shown in Table 3.

The thermal treatment results in significantly decreasing of paraffin-naphtene and aromatic oils fractions in the oil of oil sludge and contaminated soil compared with the oil, obtained by extraction. The content of high molecular compounds: asphaltenes and tars increases. Thus, the oil, obtained by thermal processing of oil waste, shows increased content of asphaltic-tarry components. Likely it is caused by oxidation of oil waste organic fraction in result of ther-

**Table 3**

Component group composition of oil waste organic fraction, extracted by thermal method

Component group composition (mass %)	Oil waste organic fraction	
	oil sludge	oil contaminated soil
Oils:		
paraffin-naphtene	20.58	4.72
odorous	24.23	11.90
Total of oils	44.81	16.62
Tars:		
petroleum-benzene	11.10	35.21
benzene	5.81	4.28
spirit-benzene	4.88	14.99
Total of tars	21.79	54.48
Asphaltene	28.74	24.31
Carbenes and carboids	4.66	4.59

mal and catalytic processes occurring on the surface of mineral fraction, acting as a catalyst.

The fraction composition data show that in the oil, extracted from oil sludge, there are no light fractions, the mass content of the fractions, boiling at 330°C being only 9,38%: 240-270°C – 3,45 %; 270-300°C – 2,31%; 300-330°C – 3,62 %.

The analysis of background information on the oil waste organic fraction composition shows, that it approaches to the heavy oils of Kazakhstan by its composition and properties. The further work concerning its use in bitumen production is of great interest.

The oxidation of extracted oil was carried out within 5 hours in the laboratory oxidizing column of periodic duty at 250°C and air consumption up to 2 l/min per 1 kg of raw material. The physical and

**Table 4**

Physical and mechanical properties of oil, extracted from oil sludge and bitumen obtained by its further oxidation

Characteristics	Oil sludge organic fraction	Building bitumen, BN 90/10	State standard 6617
Penetration at 25°C (0,1 mm)	167	10.8	5–20
Softening temperature (°C)	98	104.5	Minimum 90–105
Fracture temperature (°C)	–	–25	Maximum – 20
Penetration index	10.4	3.8	

mechanical properties of source oil and obtained bitumen are given in Table 4.

The source oil has high penetration indexes, at 25°C it being up to 167.0,1 mm and softening temperature is 98°C. It is explained by the presence of significant quantity of paraffins. The building bitumen meeting requirements of State standard 6617 there was obtained.

The elaboration and implementation of organic fraction extraction method enabled to find that the thermal treatment of oil waste results in volatilizing of light components of oil. The heavy asphalt-tarry components available in the contaminated soil on the surface of mineral material become sufficiently viscous to provide the required strength and stability of the solid residue. Referred on the oil sludge composition solid residue there may be supposed that one of the most suitable applications is its use in highway engineering as road coatings. Thus, there was found that the investigated solid residues are useful as a component of cold-mix asphalt concrete.

There was prepared asphalt mixture with following component ratio: 40-46 % mass of solid residue with 15-20 mass % of oil product retained in the cold state were mixed with 30 % of mass of natural sand and 20-26 % of mass Cockle-shell dust. The Cockle-shell dust is used as mineral filler of the mixture. Then

**Table 5**

Asphalt mixture composition

Asphalt mixture components	Sample composition (mass %)	
	1	2
Natural sand	30	30
Solid residue of oil sludge and sand	40	-
Solid residue of oil contaminated soil	-	46
Cockle-Shell dust	26	20
Bitumen BND 90/130	4	4

it was stirred within 15 minutes till obtaining of homogeneous viscous mass. The data on asphalt mixture compositions are given in Table 5.

The physical and mechanical properties of asphalt mixtures are shown in Table 6. From the comparative analysis of the data of Table 6 it is evident, that the physical and mechanical characteristics of asphalt mixtures meet the requirements of State standard 9128-84 [11]. In the beginning the oil residues have diluting effect on the used bitumen and with time in result of oxidation in the open air and bitumen viscosity increasing the strength of asphalt cover increases. The

**Table 6**

Physics-mechanical characteristics asphalt concrete

Physical and mechanical properties	Mixture		State standard 9128-84
	1	2	
Specific weight, g/cm <sup>3</sup>	2.18	2.20	-
Water saturation, vol. %	5.4	5.0	5.0 - 9.0
Swelling, vol. %	0.6	0.4	maximum 2.0
Ultimate strength at compression at 20°C, kgs/cm <sup>2</sup>	12.2	12.4	minimum 12
Water resistance coefficient	0.62	0.63	minimum 0.60

advantage of asphalt mixture is its low cost and homogeneity achieved through natural sand, oil waste and other local materials use to produce cheapest asphalt concrete. There aren't needed scarce rocky materials for asphalt concrete production and the quantity of bitumen additions is substantially reduced.

This investigation confirm that the production about the purposive of bitumen and asphalt concrete from oil waste and other harmful substances, contained in waste, is the most promising and economically efficient way to convert them into valuable and ecologically safe products.

Thus, the oil waste is an available source raw material enabling to create economically efficient manufacture of numerous oil containing materials. The economic benefits of their industrial applications are associated with solution of ecological problems currently encountered by very large oil producing regions.

## Conclusions

The composition and properties of oil sludge and oil contaminated soil from the Zhetybai-Uzen-Atyrau pipeline failures have been studied using the complex of physical and chemical investigation methods. The inherent characteristics of oil waste organic fraction, extracted by extraction method, consist in its increased content of paraffin-naphtene hydrocarbons and tarry-asphalt substances. The advantages of thermal treatment method to organic fraction extract, enabling to decrease organic fraction content by 15-20 %, have been shown. The obtained oil contains more asphalt-tarry compounds and less paraffin oils in comparison with organic fraction of source sample. The technology of bitumen production from oil sludge organic fraction and cold asphalt concrete from solid residue of oil waste has been worked out. The offered way of oil waste utilization enables to solve the important ecological problem and to extend road-building material resources.

## References

1. Parenago O.P. & Davydova S.L. Ecological problems of oil chemistry. *Oil Chemistry*, 39 (1), pp. 3-13, 1999 (In Russian).
2. Kireev M.A. & Nadirov N.K. Ecological problems of oil extraction regions of Kazakhstan and ways of theirs solution. *Oil & Gas of Kazakhstan*, 4, pp. 132-138, 1998 (In Russian).
3. Mazlova E.A. & Mesheriakov S.V. Ecological characteristics of oil sludges. *Chemistry and technology of fuels and oils*, 1, pp. 40-42, 1999 (In Russian).
4. Titus D. Dispose of oily sludge: divide and conquer. *Spec. Suppl. "Envision. Eng."*, p. 27, 1990.
5. Conway M.F. Bench-scale evaluation of asphalt emulsion stabilization of contaminated soils. *Journal of Soil Contamination*, 2 (2), pp. 1-9, 1993.
6. Europe Patent № 448335, 1991.
7. Testa S.M. Chemical aspects of cold-mix asphalt incorporating contaminated soil. *Journal of Soil Contamination*, 4 (2), pp.1-17, 1995.
8. Karim G.A., Ishola G. & Hanafi A. The behaviour of tar sand fragments in steady streams of the products of combustion of lean CH<sub>4</sub>-air or H<sub>2</sub>-air. *ASME Journal of Energy Resources Technology*, 110, pp. 151-156, 1988.
9. Mansurov Z.A., Ongarbaev E.K. & Tuleutaev B.K. Non-waste technology of processing of mazut-polluted grounds. *Abstr. of 2<sup>nd</sup> Int. Seminar "The influence of oil production and main oil pipe-line on the environment"*. Almaty, pp. 44-46, 1998.
10. Mansurov Z.A. Some applied aspects of combustion chemistry. *KSNU Bulletin, physical series*, 5, pp. 19-31, 1997.
11. Mansurov Z.A., Ongarbaev E.K., Tuleutaev B.K. Kazakhstan Patent № 7304, 1999. Method of cold asphalt concrete mixture production.

*Received 15 March 2000.*