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# Analysis of technological processes by processing of oil sludges with application of highly technological equipment for receiving high quality products

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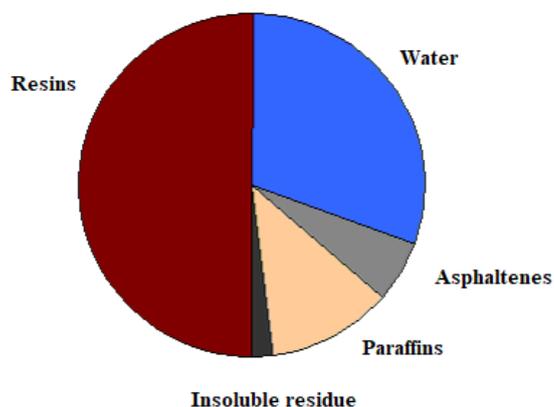
**Abstract.** Any economic activity executed according to modern requirements of nature management should not lead to irreversible violations of the natural environment; it is very seldom achieved in practice. Mining, transportation, storage and usage of oil products are the most aggressive sectors by the amount of technogenic factors that negatively influence the natural environment. At the modern stage of development of technologies, applied in the oil industry, and because of various accidents, more than 3 million tons of oil waste is generated only in Russia annually, the predominant amount of the waste is accumulated in sludge pits [1]. About 100 million tons of the oil waste has been accumulated in total. The waste of the oil industry is a source of environmental pollution and represents danger, because an effective technology of waste disposal is missing [2]. Analysis of technological solutions for the oil products waste processing with the production of materials applied in construction and other sectors during processing will not only reduce ecological damage from accumulation and storage of waste, but also provide quality products.

## 1. Introduction

The management of an enterprise or organisation whose fault causes pollution is responsible for environmental damage and for elimination of the damage consequences. But carrying out competent measures for the processing and disposal of the oil sludges (oily liquid waste) provides direct benefits, related to the absence of additional expenses, decrease of production costs, expansion of sales market production, economy of fixed capital, increasing the potential for investment.

Oil sludges are complex physical and chemical mixtures, which consist of oil products, mechanical impurities (clay, metal oxides, sand) and water. The proportion of components of oil sludges elements can vary greatly (Figure 1).





**Figure 1.** The composition of oil sludge in sludge pits.

Depending on the way of formation and, correspondingly, physical and chemical composition of the oil sludges, they are divided into several types:

- near-bottom, they are produced at the bottom of different reservoirs after the oil spill;
- oil-containing drilling fluids used in the production of drilling works;
- formed in the process of extraction, preparation and processing of oil;
- tank (the oil sludges from settling tanks), the waste that is generated in various tanks by storage and transporting of the oil;
- ground, they are the product of the compound of soil and the oil spilled on it (the reason may be both a technological process and an accident);

Oily waste can be divided conditionally into recyclable, that after regeneration can be used in production, and unrecyclable, that are subject to neutralization because of their physical and mechanical features [3].

The problem solution of the oil and petrochemical waste disposal on the territory of the Russian Federation is currently under control of the President of the country, who, at a survey of the sludge tank in the city of Dzerzhinsk, set the task to bring in bills on ecology to the State Duma as soon as possible. European technological manuals, characterized by strict requirements to oil and petrochemical companies, will be taken as a base for elaboration of the new norms [4].

The decisive factor defining the polluting features of sludges, the directions of their processing and neutralization of harmful influence on natural environment objects is the composition and physical and chemical features.

Contemporary methods of processing of oil sludges, their advantages and disadvantages are represented in table 1.

**Table 1.** The main methods of processing of the oil sludges

Method	Kind of influence on oil sludge	Main advantages	Restrictions of use
<b>Physical</b>	Gravity settling	Does not require large capital and operational expenditures	Low separation efficiency
	Separation in centrifugal field	The possibility of intensification of the process. The possibility of release of pure oil products	Necessity for special expensive equipment. Incompleteness of separation of the oil products from formed sediments and water fraction
	Filtering separation	Relatively low expenditures.	The necessity of replacement

<b>Thermal</b>	Extraction	High degree of reliability of the method. Smaller quality requirements for raw material. Higher quality of desired products Effective removal of unwanted components from the oil products	and regeneration of filter materials, the introduction of special structure-forming fillers. The formation of unrecyclable residues Necessity for special equipment, solvents
	Burning in open pits	Does not require large capital expenditures	Incomplete combustion of the oil products, high danger of air pollution from products of combustion
	Burning in furnaces of different type	Suitable for most types of waste. The amount of formed ash is 10 times smaller than the initial product	Large expenditures for purification and neutralization of flue gases
	Drying in dryers of different structures	The waste volume is 2-3 times lower, the possibility of combination with other nature protection processes	Large consumption of warmth.
	Pyrolysis	High degree of decomposition. The possibility of usage of decomposition products	High material and energy costs
	The combination of thermal separation, pyrolysis and burning	Processing residues are ecologically safe. More economic in comparison to burning	Necessity for expensive equipment
<b>Chemical</b>	Complexation	It is applied to bind heavy metals, radioactive waste, polycyclic and aromatic hydrocarbons, trichloroethylene and the oil products	The instability of binders to atmospheric and ground moisture, quick temperature changes, that leads as a result to destruction of composite material. The volume of the waste decreases by 2 times only
	Sedimentation	High efficiency by neutralization of heavy metals and radionuclides. Reagents can be in liquid and gaseous phases	Increase of the volume of the neutralized mass
	Oxidation-reduction	Possibility to transform compounds of heavy metals and radionuclides to hydroxides difficult to dissolve in water, and destroy cyanides, nitrates, tetrachlorides and other organochlorine compounds	It is necessary to perform additional researches on the environmental impact of the resulting products
	Substitution	High degree of neutralization of different toxic and	The use of special equipment

		dangerous compounds	
<b>Physical and chemical</b>	Ultrasound	A high percentage of release of the oil products. Ecological safety	High material and energy costs
	Electrochemical purification	There is no necessity to organize the reagent facilities. The use of a small production area	High capital and operational expenditures. The formation of explosive mixtures of gases and the appearance of sedimentation on the surfaces of the electrodes.
	Electrokinetic method	High efficiency for purification of clay and loamy soils was shown	Difficulty of realization
<b>Physical and chemical</b>	Flotation	Low capital and operational expenditures	Low efficiency
	Electromagnetic method	High degree of disposal of the oil waste	Application of special equipment, difficult in implementation
	The application of specially chosen surfactants	The possibility of intensification of other methods with relatively small additions of introduced matters	High cost of reagents. The method requires the application of special dosing equipment, mixing devices
<b>Biological</b>	Microbiodegradation of pollutants	High efficiency of processing. Purification of natural objects does not violate the microflora of the environment	Low speed of purification. Dependence on environmental conditions. The necessity of preliminary soil remediation
	Bioabsorption	Minor capital and operational expenditures. Intensification of the process is possible	Significant preparation of land plots is required. Impossible to use year round.
<b>Combined</b>	The redistribution of toxicants	Low expenditures	Special equipment is necessary
	Simultaneous application of several methods	Accomplishment of maximum economic effect. The possibility of receipt of commercial oil	Complicated hardware implementation

The most well-known technologies for the liquidation of sludge pits and the disposal of sludges applied in Russia and abroad include:

- technology of separation of oil sludges into phases with the subsequent burning of sludge by a company KHD Humboldt Wedag AG (Germany);
- the unit for the disposal of oil sludges by FLOTTVEG company (Germany), which allows to get three components of the sludge at the output: solid matter, water and oil;
- the mobile system of the handling and purification of mud and oil and petroleum waste MTU 530 by company ACS 530 (the USA);

- the technology consisting in dissolution, warming and handling with chemical reagents for separation sludge from water and mechanical impurities by ANK “Bashneft” (joint-stock oil company under the laws of the Russian Federation);

- technology for processing of oil-containing sludges by chemical method by LLC “Company “Clean Technologies” (Russia);

- a unit by Tatoi gas company based on emulsion breakdown technology in decanter with preliminary separation of water and mechanical impurities by Meiken company (Germany);

- The technology of burning of oil sludge in the chamber furnace, proposed by BashNII NP (Bashkir Research and Scientific Institute for Oil Processing) and Gorkgiproneftekhim;

- technologies for purification and processing of solid and liquid fractions of the oil sludge used by “ALMAZ-ECO” company and others.

Among the innovative technologies can be identified:

- electric fire technology, consisting in a complex approach to the processing and disposal of any oil sludges, and including step by step operations of separation and removal of the upper layer of pure oil products, and the subsequent pure electric fire burning of other heavy fractions of the oil sludges in a strong electric field;

- thermochemical microwave reactor “WUT Termolysis” for waste processing, operation of which is based on the introduction of energy-saving microwave technology in the processes of the processing of hydrocarbon containing components;

- plasma and thermal atomization of wastes introduced at several oil fields of Tomsk region.

The technology of processing of solid fractions of oil sludges, as well as of oil-contaminated soils and grounds into ecologically safe material is performed by the lithification method.

Stages of works execution:

- analysis of the sludge content of pollutants;

- to analyse how much liquid the sludge contains, to define its physical and chemical characteristics;

- preparation of lithification mixtures according to analysis;

- to mix lithification mixture with the oil sludge (the process of mixing can be performed manually or applying a screw mixer with the delivery of reagents to the reaction zone by a carrier);

- the prepared mixture is moved from the reaction area or from the screw mixer to the initial area;

- processed oil sludge (ecologically safe) returns to natural biogeocenosis and is used as a construction material.

Productivity of execution of works on processing of the oil sludge by the lithification method is 50 cubic meters [5].

The advantages of the processing technology are the high purification efficiency and ecologic safety of the units, as well as possibility of processing of overmoistened oil sludges without preliminary dehydration, expensive equipment is the disadvantage.

One of the elements of equipment for the preparation of crude oil, processing of fuel oil and oil waste with a high content of sulfur, salts, paraffins, ash, and different impurities is an oil disperser (the oil and fuel oil and sludge evaporator). It is a device for dispersion of liquid organic media (Figure 2). The improved construction of the disperser was collectively designed and certified by LLC Research and Design Institute for Environmental Problems.

The principle of operation is that raw material passes through a device where, under the influence of physical and chemical and mechanic impact, there are a splitting of molecular chains and a release of weak parts of molecules and fractions (a compound of sulfur, paraffins, chloride salts, water). Thus the application of any catalysts is excluded, special preparation and handling of raw material are not required. The ready oil products are stable and not subject to decomposition.

Production output:

Commercial oil, fuel oil M-40, fuel oil -100, dark furnace fuel (dark domestic furnace fuel).

Technical data of the installation:

- overall dimensions are 22000×13000×3000;

- weight is 47 t;
- power consumption is 30 kilowatt per h;
- power consumption of steam is 1.2 gigacalories;



**Figure 2.** Overall view of the installation for the preparation of crude oil, processing of fuel oil and oil waste with a high content of sulfur, salts, paraffins, ash, and various impurities.

The device has a hull with a vortex chamber, where the initial organic medium undergoes intense turbulence by adding the reagents. As a result, at the output of the device there is the mixture of fractions that are divided by separation.



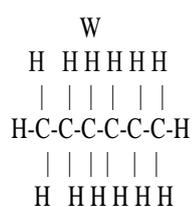
**Figure 3.** The installation for the preparation of crude oil, processing of fuel oil and oil waste with a high content of sulfur, salts, paraffins, ash, and various impurities, view 1.



**Figure 4.** The installation for the preparation of crude oil, processing of fuel oil and oil waste with a high content of sulfur, salts, paraffins, ash, and various impurities, view 2.

The proposed method of cold (at 40-90°C) processing of oil is based on a sharp acceleration of the slow and reversible process of hydrogenation, when the bond between atoms of carbon in a single C-C bond tears, the bond between carbon and hydrogen C-H tears.

This exemplary happens to alkanes, they are saturated hydrocarbons of aliphatic structure (paraffin hydrocarbons, the general formula is  $C_nH_{2n+2}$ ), that are the main components of oil (fuel oil). There are bonds between the C-C and C-H atoms in the molecules of alkanes, for example, in normal hexane C<sub>6</sub>H<sub>14</sub>:



The more susceptible one to external breaking and shifting forces in the hexane molecule is the middle link marked by the “W”. In this place, there is the breaking of the C-C bond, two parts of the hexane molecule are formed, two hydrogen atoms are added to the place of the released valencies of the two carbons. As a result, there are two new molecules of propane C<sub>3</sub>H<sub>8</sub> (Table 2). Unlike normal hexane, propane has much lower melting and boiling temperatures, a lower specific weight, a higher calorific value.

The amount of heat produced during the described above splitting reaction is calculated on the known heat of tearing (compound) of the bonds between atoms in the molecule of carbon and hydrogen  $Q_{C-H} = 85,6$  kilocalories per mole:

$$Q \text{ of reaction} = Q_{C-C} - Q_{H-H} + 2Q_{C-H}$$

$$Q \text{ of reaction} = -62.8 - 103.2 + 2 \times 85.6 = 5.2 \text{ kcal/mole}$$

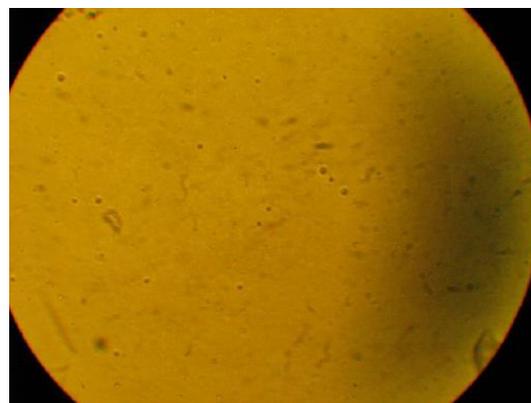
**Table 2.** The division of hexane molecule

Before – hexane	After – propane (2 molecules)	
H H H H H H	H H H	H H H
H-C-C-C-C-C-H	H-C-C-C-H	H-C-C-C-H
H H H H H H	H H H	H H H

Disperser – the evaporator should create alternating tearing and compressive and shifting voltages in the middle part of the oil molecule (the fuel oil) and contribute to the splitting of water into oxygen and hydrogen by thermal energy of the oil molecules separation reaction (our example is  $Q$  of splitting = 5.2 kcal/mole). In figures 5 and 6 the images of fuel oil under a microscope before and after it (6000 times enlarged) are represented.



**Figure 5.** Experimental images of the fuel oil under the microscope (6000 times enlarged) before being treated with a disperser.



**Figure 6.** Experimental images of the fuel oil under the microscope (6000 times enlarged) after being treated with a disperser.

After processing in the disperser, the result is a quality product for various purposes; oil wastes are used as a secondary raw material.

In the common case, the choice of the field of application of the oil sludge is defined on the one hand by the technological, technical and sanitary and hygienic requirements, made for manufactured products, on the other - operational requirements for raw material.

The suitability of oil wastes as a technogenic raw material should be defined during a complex analysis of their origin, composition and features. Directions for recycling in ascending order of the organic part of the oil waste is possible to arrange in hierarchic series: road construction – bitumen production – building materials – waterproof materials – fuel industry.

Physical and chemical features of oil sludges depend on many factors:

- fraction and group composition of the organic component;
- the relation in the waste of organic matter, mechanical impurities, water and other components.

The main disadvantage of the oil wastes as a secondary raw material is the instability of features through time, and the inhomogeneity of the composition, due to the conditions of their formation and storage. The composition and features of the oil wastes are directly dependent on the technological process and applied equipment by the mining, preparation and processing of oil. Conditions and continuation of storage largely influence the structure of the oil sludges.

## Conclusion

By disposal of wastes from the oil sludge pits, it is necessary to separate the mass of wastes into flows with application of different technological methods for every type of waste. All that obstructs the

usage of oil sludge without preliminary preparation as secondary raw material and complicates the technology of its processing.

Thus, separate collection, storing, storage and disposal of qualitatively different flows are necessary to increase the efficiency of the system for handling the oil sludges.

The practical implementation of technical solutions for the usage of the oil sludges will allow to solve two important engineering and environmental problems:

- to reduce the environmental load on the natural environment due to the reduction (or elimination) of the objects of placement of oil-containing sludges;

- to provide a more efficient usage of non-renewable natural resources, using the technologies of substitution of the primary raw material for the secondary one [6-7].

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