Atlantis Highlights in Material Sciences and Technology (AHMST), volume 1
International Symposium "Engineering and Earth Sciences: Applied and Fundamental Research" (ISEES 2019)

The Ecological Assessment of Petroleum Industry Wastes

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***Abstract* – The ecological assessment of waste is an important indicator of industrial enterprise operations. The article discusses the results of research (type of environment, salt content, heavy metal and petroleum product content), encompassing ten types of different petroleum industry waste. During the research the radioactivity levels of samples were determined, and the biotesting was carried out. The main focus was on the influence of the water extract from waste on living organisms. The biotesting was carried out on water fleas, ciliates, aquarium fish and high flora seeds. Besides, the ecological characteristics of waste were studied with help of microorganisms. Based on the complex analysis of samples it was determined that the studied waste types belong to either the IV or V hazard classes (low hazard) according to national norms. As a result of the research possible methods of waste recycling were offered.**

Keywords – waste; ecological assessment; petroleum industry; biotesting; hazard class; recycling; environment.

I. Introduction

The generation of wastes that contain a wide range of pollutants is one of the main ecological problems in petroleum industry. The comprehensive assessment of wastes is a necessary condition to determine their impact on the environment, possible methods of waste recycling in different sectors of economy and the eligibility of currently non-recyclable waste for biological recultivation.

One of the main problem in petroleum industry waste recycling is the development of a normative framework that includes standards, eligibility requirements and technical specifications for their use. The comprehensive assessment and recycling is a key factor in applying low-waste technologies, while using waste in other sectors of economy allows to reduce areas of land for storing this waste and cut prices for renting this land.

The advantages of the comprehensive waste assessment is obvious for many operated oil fields, as non-waste oil production almost doesn't exist and it is not always technologically possible and cost effective to solve the problem of complete waste use.

Oil production enterprises generate significant quantities of different wastes.

Traditionally, chemical analysis methods are used for environmental monitoring of waste. They help to determine the levels of pollutants that are compared to approved norms: maximum acceptable concentration and approximate permissible concentration (MAC and APC), approved by the Ministry of Health of Russia. However, it is not possible to assess the danger of waste accurately based on the chemical analysis only. This is due to the limited number of current national norms as well as complexity of wastes and the content of toxic, unknown pollutants in them [1, 2]. Moreover, the use of alternative methods for the environmental assessment of waste may be the result of considerable effort in terms of time and resources. Thus, the modern assessment of different wastes should use not only the chemical analysis, but toxicology data obtained using biological methods [3–5].

These methods include biotesting, using living test organisms in a lab environment. They show a combined impact of pollutants on test organisms and the presence or absence of toxicity in an analyzed sample [6, 7]. In the previous research we analyzed drilling mud, formed during well-drilling, that constitutes the main bulk of petroleum industry waste [8].

The current research aims at assessing different types of petroleum industry waste and possible ways for their recycling.

II. Methods and Materials

The wastes of an oil production enterprise, located in Western Siberia, were the subject of this study.

The analytical and experimental studies to determine the hazard class of wastes were carried out on ten composite samples of different wastes represented in tables for chapter III. Results and numbered as follows: 1 – oil contaminated quartz sand ceramic proppants; 2 – drilling mud resulting from major well workover in crude oil, natural gas and natural gas liquids production; 3 – solid residue from oily wastes burning; 4 – stabilized silt of domestic and combined wastewater from biological treatment plants; 5 – asphalt and asphalt-concrete waste; 6 – concrete products waste in chunks; 7 – soil resulting from excavation works, not contaminated by hazardous substances; 8 – the waste of construction aggregate, not contaminated; 9 – reinforced concrete waste in chunks; 10 – brick waste.

These wastes were analyzed using different norms and methods. Physico-chemical and physical methods included the determination of pH value in the water extract by a potentiometric method (GOST 26423-85); the study of elemental composition of waste with OPTIMA-2100 DV inductively coupled plasma emission spectrometer; the testing for the presence of mercury with RA-915 analyzer; the determination of oil content by infrared spectrometry with AN-2 analyzer according to PNDF 16.1:2.2.22-98 (FR.1.31.2015.20500) environmental regulations "Measurement techniques to determine the content of oil in mineral, organic and mineral-organic soils and sediments using infrared spectroscopy". The level of specific radioactivity of radionuclide was determined with gamma-spectrometer on the basis of scintillation. The following regulatory documentation was used during measurements: 1) Radiation safety standards (NRB–99/2009), SanPiN 2.6.1.2523-09; 2) Basic sanitary regulations for ensuring radiation safety (OSPORB-99/2010), SP 2.6.1.2612-10; 3) Hygienic requirements for limiting the exposure of population to radiation through natural sources of ionizing radiation. SanPiN 2.6.1.2800-10.

As no biological species can be a separate universal indicator [9, 10], the biotesting was carried out using test organisms from different systematic groups: hydrobionts (*Daphnia magna Straus* crustaceans, *Paramecium caudatum* ciliates, *Brachidanio rerio* aquarium fish), higher plants (*Avena sativa* oat) and the natural set of microorganisms. The toxicity of a sample was determined by the most sensitive variant.

The analysis of toxicity by the elution methods (using water extract) was carried out on samples with sample-water ratio 1:10. The samples were analyzed without dilution and with 10 or 100-fold dilution (based on the toxicity of a sample).

The toxicity of wastes was determined by the method of substrate biotesting, included in the FR.1.39.2004.01061 registry. A natural set of microorganisms, contained in the analyzed substrate, was used as a testing environment. The level of toxicity was determined by the changes in microbiological activity of analyzed samples in comparison with controls. The hazard class was determined by the statistically significant decrease in the maximum daily level of CO_2 emission by the microflora of tested samples in comparison with the control substrate after adding glucose.

The assessment of samples' high toxicity using *Daphnia magna* was carried out in accordance with approved techniques [11]. The death of 50% or more of species in tested samples was an indicator of high toxicity.

The analysis of samples' toxicity using *Paramecium caudatum* was carried out in accordance with current national technique [12]. The method is based on the ability of ciliates react on substances in water, that are harmful for their living and move along the density gradient of these substances, avoiding their harmful effect. Samples were classified into three categories according to the level of toxicity. I – permissible level of toxicity ($0{,}00<T\leq 0{,}40$); II – moderate level ($0{,}00<T\leq 0{,}70$); III – high level ($T>0{,}70$).

Plant testing is an inseparable part of a general biotesting when analyzing the toxicity of wastes. Phytotoxicity was analyzed using *Avena sativa* oat seeds. According to the national technique [13] the eluate (extract) is toxic if the length of germ roots in a sample is more than 20% lower than the length of control roots.

The testing of samples on *Brachidanio rerio* according to national techniques [14-16] was carried out using the roe and prolarva of these fish. Embryonic development, prolarva hatching and survival were observed in water extracts.

The assessment of the hazard class was carried out based on the combined approach, described in the following regulatory documents: SP 2.1.7-1386-03 "Sanitary rules for determining the hazard class of production and consumption toxic wastes" and "The criteria for classifying wastes into I-V hazard classes according to the level of their negative influence on the environment" (approved by the order of the Ministry of Natural Resources and Ecology of the Russian Federation on 4.12.2014, №536). According to these documents, the hazard class of wastes is defined based on the chemico-analytical characteristics combined with biotesting on living organisms of different levels: microorganisms, hydrobionts, plants and homoiothermic animals. The leading role in determining the hazard class belongs to experimental biological methods.

These biotesting methods involve 10 to 100-fold or more dilution of water extracts in the event of death of living organisms in the original sample. However, the hazard class doesn't change at all or increase by a unit depending on the level of dilution.

We should note some differences in approaches to the determination of wastes' hazard classes: the Ministry of Natural Resources and Ecology of the RF divide all wastes into 5 classes, while the Ministry of Health of the RF divide them into 4 classes.

III. Results

The results showed that the analyzed wastes have a neutral or alkaline reaction. The degree of pH in the water extract vary from 6,5 (sample 7) to 11,8-11,9 (samples 6, 8, 9). The analysis of solid from water extracts of samples showed that sample 3 is highly saline (the content of salt is 4.74%), sample 4 is medium saline and samples number 2, 6, 9 are low saline. The rest of the samples (1, 5, 7, 8, 10) are nonsaline.

In comparison with APC, the sample 3 had exceeding levels of copper, nickel, lead and zinc. A little excessive amount of zinc was found in samples 4, 6, 9.

The oil content was above level in samples 4 and 5. During the extraction of oil products from asphalt waste the hydrocarbons of bitumens and asphaltenes also transfer to the extract. The content of oil in waste is not rated.

The high content of organic substances in stabilized silt (sample 4) and its high sorption capacity lead to the high content of oil products. The planned use of silt as fertilizer for land reclamation should be careful and well-grounded. It is more viable to use that silt during land reclamation on industrial waste landfills.

The effective specific activity of natural radioactive nuclides in the samples of production wastes averaged 50-175 Bq/kg and didn't surpass 215 Bq/kg with error taken in account. The wastes with the effective specific activity less than 370 Bq/kg can be used for any kinds of construction without limitations on the level of radiation. The low levels of the effective specific activity of natural radioactive nuclides are typical to the analyzed wastes and drilling mud from the oil fields of Western Siberia.

The results of biotesting on different test objects are given in table I.

TABLE I. THE TOXICITY OF SAMPLES BASED ON THE BIOTESTING RESULTS

№ of waste	The level of toxicity							
	Daphnia magna Straus		*Paramecium caudatum*		*Avena sativa*		*Brachidanio rerio*	
	The survival rate of water fleas, %, without dilution	Nontoxic dilution factor	The toxicity index T, units, without dilution	Nontoxic dilution factor	Toxicity E, %, without dilution	Nontoxic dilution factor	The survival rate of larvae, %, without dilution	Nontoxic dilution factor
1	90.0	n/t	0.17	n/t	+24.1	n/t	100	n/t
2	100	n/t	0.06	n/t	-4.8	n/t	100	n/t
3	0	1:100	0.18	n/t	-57.9	1:10	0	1:100
4	100	n/t	0.09	n/t	+23.4	n/t	0	1:100
5	93.0	n/t	0.11	n/t	+18.6	n/t	100	n/t
6	0	1:10	0.27	n/t	+36.6	n/t	0	1:100
7	100	n/t	0.06	n/t	+29.0	n/t	100	n/t
8	0	1:10	0.19	n/t	+24.8	n/t	100	n/t
9	0	1:10	0.01	n/t	+21.4	n/t	0	1:100
10	90.0	n/t	0.21	n/t	+30.3	n/t	6.7	1:100

[a] Note: n/t means nontoxic water extract.

The biotesting on *Daphnia magna* that most water extracts of wastes (samples 1, 2, 4, 5, 7, 10) didn't cause toxic effects on water fleas: the death rate of crustaceans didn't exceed the level of 10% in comparison with the test sample. These wastes belong to the V hazard class (nontoxic). The water extracts from samples 3, 6, 8, 9 were highly toxic for water fleas and lead to the 100% death rate of crustaceans. The 10-fold dilution of extracts from samples 6, 8, 9 by aquarium water fully removed toxicity leading to the 100% survival rate of water fleas. To eliminate the toxicity of sample 3 it was diluted 100-fold. This resulted in the increase of the survival rate of water fleas up to 90%. Thus the wastes in samples 3, 6, 8, 9 belong to the IV hazard class.

During testing on *Paramecium caudatum* the toxicity index changed from 0.01 to 0.27. Thus we can conclude that all wastes are nontoxic for this test organism.

Plant testing using *Avena sativa* showed that only sample 3 was toxic, which was eliminated by the 10-fold dilution of the extract. Based on the results of plant testing we can say that all substances belong to the V hazard class according to the criteria of the Ministry of Natural Resources and Ecology of RF and the IV class according to SP 2.1.71386-03.

The biotesting of samples on *Brachidanio rerio* showed that wastes in samples 1, 2, 5, 7, 8 are not toxic for fish. The toxicity in the rest of extracts (samples 3, 4, 6, 9, 10) disappeared after the 1:100 dilution.

Microbiological testing was carried out using two different types of control. Clean natural clay was used as control 1 and clean natural sand was used as control 2. The results of analysis are shown in table II.

TABLE II. THE MAXIMUM VALUES OF DAILY CO_2 EMISSIONS BY THE SAMPLES OF PRODUCTION WASTE AFTER ADDING GLUCOSE, MG OF CO_2/100 G OF DRY WASTE, DAILY

№ of waste	*CO_2*	*N, %*	*Hazard class*
Control 1 (for waste 2)	20,1±1,1	-	-
Control 2 (for waste 1, 3, 5, 7, 10)	8,7±0,9	-	-
1	9,6±1,0	+10.3	V
2	23,9±0,7	+18.9	V
3	2,2±0	-74.7	III
5	10,5±0.8	+20.7	V
7	15,7±0.2	+80.5	V
10	7,6±0.4	-12.6	V

[b] Note: N is the degree of change in biological activity of wastes in comparison with the control sample.

The waste in samples 1, 2, 5, 7, 10 belonged to the V hazard class according to the developed toxicity coefficient. It means they were almost harmless. Waste 3 belonged to the III hazard class (moderately dangerous).

The addition of glucose to wastes 6, 8, 9 didn't result in carbon dioxide emission. This indicates an insignificant level of biological activity in these materials. It is known that microorganisms in construction materials and petroleum industry wastes can be inactive [17, 18]. Thus, we can say that viable microbial cells were inactive in samples 6, 8 and 9, while wastes themselves weren't toxic for microorganisms. The waste 4 (stabilized silt) wasn't analyzed because of the lack of an adequate control sample.

Based on the research we can conclude that these wastes are suitable for recycling. The classification of wastes into hazard classes and the information about the possible ways of recycling them are shown in table III.

Thus, the results of biotesting on different organisms show all the wastes belong to IV-V hazard classes. The only exception is sample 3 that belong to III-IV classes.

TABLE III. HAZARD CLASSES OF PRODUCTION WASTES AND POSSIBLE WAYS FOR RECYCLING THEM

№ of waste	The name of waste	The hazard class according to approved techniques		The way for recycling
		NR[1]	*HC*[2]	
1	Proppants	IV	IV	As surface material during wellsite construction
2	Drilling mud	V	IV	As surface material during wellsite construction
3	Solid residue from waste burning	III-IV	III-IV	Solid residue can be used on solid communal waste landfills as an insulation layer and on industrial waste landfills.
4	Silts	IV	IV/V	Land reclamation or burning
5	Asphalt waste	IV	IV	Road construction and roadworks
6	Concrete waste	IV	IV	Road construction and road works
7	Soil resulting from excavation works, not contaminated by hazardous substances	IV	IV	Pad and road construction, topographic low filling
8	Construction aggregate waste, not contaminated	IV	IV	Road construction and road works
9	Reinforced concrete waste	IV	IV	Road construction and road works
10	Brick waste	IV	IV	Road construction and road works

c. Note: 1 NR indicates the hazard class according to "The criteria for classifying wastes into I-V hazard classes according to the level of their negative influence on the environment";

d. 2 HC is the hazard class according to SP 2.1.7.1386-03, approved by the Ministry of Health of the Russian Federation.

IV. CONCLUSION

The study of ten types of oil industry waste resulted in their ecological assessment, based on chemical analysis of samples and biotesting methods.

The leading role in determining the hazard class belongs to experimental biological methods. The results of analysis, including chemical composition and the level of radioactivity as well as biotesting on living organisms of different levels show the absence of clearly expressed toxicity in tested samples.

According to the current regulation documents of the Ministry of Health and the Ministry of Natural Resources and Ecology used in Russia, the analyzed wastes can be classified into the IV-V hazard classes (excluding sample 3).

The analyzed wastes can be used for road construction and roadworks as well as wellsite construction. The use of solid residue from oily wastes burning and stabilized silt of domestic and combined wastewater from biological treatment plants should be controlled.

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