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SCHOLARENA

Journal of Environmental Pollution and Management

SHORT COMMUNICATION

ISSN: 2639-7269

The Research and Radiolysis of the Composition of Oil Deposits

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Citation: Guliyeva NK, Mustafaev II, Chichek F, Mamedova SM (2023) The research and radiolysis of the composition of oil deposits. J Environ Pollut and Manage 5: 103

Abstract

Oil deposits (OD) formed in the processes of oil production, transportation and storage are a serious problem for oil producing and oil refining plants from both technical-economic and environmental points of view. The solution to the problem of preventing the formation of deposits in downhole equipment and combating the formation of OD is very urgent. To solve this problem and to develop technologies with strong resistance to accumulation, it is necessary to thoroughly study their composition, properties and structure before using any method to tackle it. The need to resist these adverse events increases the cost of production, reduces the efficiency of oil pipelines, and leads to large energy overruns for pumping and, inevitably, equipment clean-up costs. All these complicate the oil technology and increase the cost of oil, and the sludge accumulated in the storage facilities during stripping of pipes and equipment is a potential source of environmental pollution and creates serious environmental problems [1-3].

The resulting oil deposits are not an inevitable waste of oil supply in terms of their value, on the contrary, their preservation in marketable oil composition can expand the range of petroleum products derived from it. In addition, it should be noted that OD formed in technological equipment at the stages of transportation contain many valuable components that can be successfully used as additives to fuel oil, used in the construction industry, in the preparation of lubricant compositions, etc.

Controlling the process of selecting effective solvents for the removal of asphalt, resin and paraffin residues in oilfield and refinery equipment and investigating their qualified use requires a good knowledge of their physical and chemical properties. To date, there are many methods for combating OD, which are used quite effectively, mostly based on thermochemical methods, the use of which is associated with high costs and a decrease in the level of safety of the work performed [4].

Interest in the possibility of using physical processing methods, especially ultrasonic technologies and radiation-chemical technology in general, are proposed to be used for cleaning oil equipment from oil deposits and has increased significantly [5].

Keywords: oil deposits; radiation-chemical technology; radionuclides; environment

Introduction

Oil deposits mainly consist of paraffins, asphaltenes, resins and mineral impurities. In addition, they contain sulfur, metals, as well as a small amount of water in which salts are dissolved - these are chlorides and bicarbonates of sodium, calcium and magnesium, sulfates and carbonates [6-8]. To date, the industry uses various methods to combat oil deposits.

Basically, these methods differ in preventive (prevention of deposits) and direct control of deposits that have already accumulated. Cleaning permanent oil storage tanks from petroleum product residues is one of the most pressing and important problems in the operation of tanks. Petroleum products stored in tanks are subjected to various processes (oxidation, decomposition and temperature stratification, oil saturation, chemical and biological degradation) that affect the release and accumulation of oil deposits on the inner surfaces of the tanks. Practice has shown that it is less costly to prevent the accumulation of oil compounds than to permanently eliminate them.

In this regard, the study of the composition of oil deposits is of practical importance for determining the most appropriate methods of dealing with them. To choose the most chemically effective ways of extracting oil deposits, it is necessary to understand the composition, properties and the structure of these deposits.

Methodical Part

In order to evaluate the role of radiation in the processes of spilling oil deposits into the environment and to develop a radiation-chemical technology to prevent the formation of OD, the composition and physical and chemical properties of oil deposits formed during oil transportation in the pipeline were investigated. Previously, the composition and physical and chemical properties of the oil deposits formed in the pipeline during the transportation of oil from the Azerbaijani fields were studied [9]. In this study, we also examined the radiation-chemical transformations of polycyclic aromatic hydrocarbons (PAHs) in OD, the compositions of radionuclides and metals in OD, and determined the radiation-chemical yields of gaseous products during OD radiolysis.

Isotope gamma radiation source Co^{60} – «MPX-γ-30» was used as an ionizing radiation source. Studies were conducted in the range of absorbed doses of gamma radiation D=3.4-326.4 kGy at a dose rate of P=0.19 gR/sec. Gas products were analyzed on an Agilent GC 7890A chromatograph, liquid products on a GCFID (GS-450, Varian-2010 USA) and 16EPA polycyclic aromatic hydrocarbons on a mass spectrometer (GMS Trace DSQ-Thermo Electron, Finngan, 205).).

Research Results and Discussion

The formation of oil deposits with increased natural radionuclide content on technological equipment poses a potential environmental pollution threat [10]. Sources of radioactive contamination are natural radionuclides of the U-238 and Th-232 series, as well as K-40 found in the earth's crust and brought to the surface by oil production. The level of radioactive pollution of oil pipelines is determined, first of all, by the isotopes Ra-226 and Ra-228, which are found in the corresponding formation waters of oil fields. Radioactive substances accumulate in the form of salt deposits on the inner surfaces of the oil pipeline.

In this context, the content of radionuclides in the composition of oil deposits was investigated using a combination of ICP/MS and gamma spectrometry methods (see Table 1).

Radionuclides	Units of measurement	Content
U238 (ICP/MS)	mg/kg	0.523
Th232 (ICP/MS)	mg/kg	<0.04
Ra226	mBq/g	<1.4
Ra228(Th232)	mBq/g	2.8
K40	mBq/g	8.7
Co60	mBq/g	<0.4
Cs134	mBq/g	<0.6
C137	mBq/g	<0.6
Tl 208	mBq/g	0.95
Pb212	mBq/g	2.3
Bi214	mBq/g	3.1
Pb214	mBq/g	4.2
Ra226	mBq/g	<1.4

Table 1: The content of radionuclides in oil deposits

The table shows that the studied oil deposits do not pose a radiation hazard.

The characteristics of the impact of oil pipeline transport on the environment is that during pipeline accidents and oil spills, water, air, vegetation and animal life are exposed to the harmful effects of many components contained in crude oil. Among petroleum hydrocarbons that cause serious pollution, PAHs and their degradation products are the most toxic [11-12].

Table 2 lists the toxicity indexes of priority PAHs contained in oil deposits, the so-called 16 EPA (16 PAH pollutants recommended by the U.S. Environmental Protection Agency (EPA).

Note that this group of PAHs is of prime importance in ecology.

PAH	Toxicity index	C, mg/kg	%
Naphthalene	0.001	44.485	51.527
Acenaphthylene	0.001	1.573	2.489
Acenaphnaften	0.001	1.074	1.499
Fluorene	0.001	7.743	10.391
Phenantrene	0.001	18.697	23.171
Anthracene	0.01	1.777	2.329
Fluoranthene	0.001	0.339	0.342
Pyrene	0.001	1.083	1.355
Benzo(a)anthracene	0.1	0.600	0.824
Chrysen	0.01	2.204	3.806
Benzo(c)fluoranthene	0.1	0.326	0.475
Benzo(c)fluoranthene	0.1	0.076	0.105
Benzo(a)pyrene	1.0	0.546	0.689

Indeno(1,2,3-c,d)pyrene	0.1	0.064	0.075
Benzo(g, h, i) perylene	0.01	0.588	0.626
Dibenzo(a,h)anthracene	5	0.25	0.287
Σ EPA 16		**81.42**	**100**

Table 2: Concentrations and toxicities of 16 EPA PAHs in oil deposits

It can be seen that the total content of the 16 EPA in the composition of OD is 81.42 mg/kg, of which 90% are PAHs with a smaller number of benzene rings and low toxicity. The high toxicity of components of OD significantly increases the consequences of oil pollution. Taking into account the environmental aspects of the above-mentioned PAH toxicity indicators, that is, the toxicity of individual PAHs increases 1000 and 5000 times, it is interesting to study the change of their concentrations under the influence of radiation in oil deposits.

Radiation-chemical transformations of 16 EPA polycyclic aromatic hydrocarbons were studied. Figure 1 shows dose dependences of changes in concentrations of polycyclic aromatic hydrocarbons (C,mg/kg) during OD radiolysis. The figure shows that significant changes in concentrations were observed for PAHs with the increased benzene ring content in their composition. The concentration of benzoanthracene decreased by 15%, benzapyrene by 25%, and dibenzoanthracene by 75% in the investigated intervals of radiation exposure.

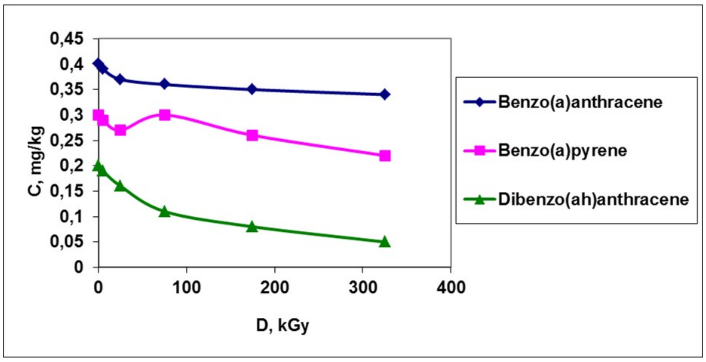

Figure 1: Dependence of the concentrations of individual PAHs on the radiation dose

The environmental impact of PAHs is much higher than that of other hydrocarbon groups due to the possibility of their accumulation in oil-contaminated soils and bottom sediments of water bodies, as well as the toxicity of their effects on living organisms.

The impact of PAHs on the environment significantly exceeds the impact of other hydrocarbon groups due to the possibility of accumulation in oil-contaminated soils and bottom sediments of water bodies, as well as the toxicity of their effects on living organisms.

The toxicity of individual PAHs can differ thousands of times from each other, for example, PAHs with a high content of benzene rings are much more toxic. For example, the ratio of toxicity in PAHs - anthracene:benzoanthracene:dibenzoanthracene is 1:10:50, which indicates a high environmental impact of benzo groups.

To evaluate the role of radiation in the processes of cleaning oil pipelines from deposits and to determine the radiation resistance of OD, some models of radiation-chemical transformations of oil deposit samples were studied. The kinetics of gas accumulation during radiation-chemical transformations of OD is shown in Figure 2-3.

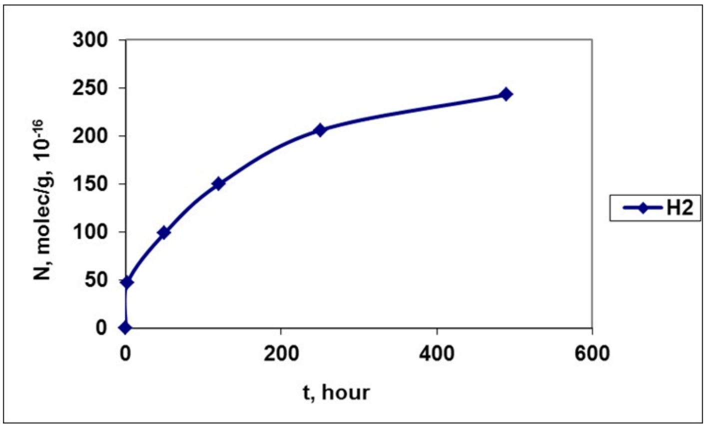

Figure 2: Kinetics of hydrogen formation during OD radiolysis

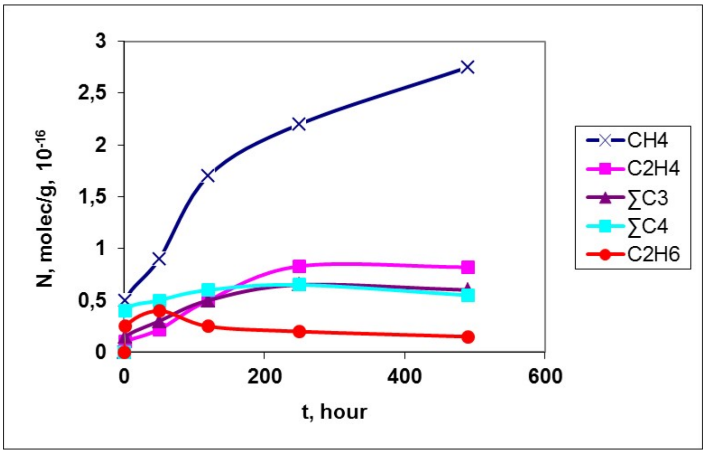

Figure 3: Kinetics of formation of C_1-C_6 gases during OD radiolysis

From the graph of the temperature dependence of the ratios in Arrhenius coordinates, the values of the activation energy of the radiation-thermal processes of gas formation during OD radiolysis were calculated (Table 3).

T°	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	ΣC_4	ΣC_5	ΣC_6	ΣC_7
E(20-200°C)	2.15	2.68	3.45	3.15	3.06	1.75	5.65	7.88	7.13
E(200-400°C)	41.63	44.88	100.87	33.25	96.93	41.55	88.53	89.78	70.47

Table 3: Activation energies (kcal/mol) in different temperature ranges

Values of activation energy at high temperatures significantly exceed the corresponding values at low temperatures. This is due to the fact that the activation energy values of dissociation reactions significantly exceed the activation energy of diffusion processes, which limit radiation-chemical processes to a temperature of 200° C. The organic part of sediments during oil transport has high radiation resistance up to 200°C. At high temperatures, there is an increase in radiation-thermal destruction processes with the formation of hydrogen and C1-C7 hydrocarbons.

It has been established that more than 60 elements are found in oils of various origins, and about 30 of them belong to metals. Soil pollution with petroleum-based heavy metals, which are very dangerous substances for humans, is an important environmental problem, especially in regions related to the production, transportation and processing of petroleum. An unfavorable situation develops in case of accidental oil spills, which can occur as a result of mechanical damage to oil pipelines [13].

The atomic absorption method determined the concentrations of metals in the oil deposits of the oil pipeline, and the results are shown in Table 4. For comparison, available literature data on the content of some of these metals in the resinous fraction of oil are also given here.

Metals	Concentration in OD, mg/kg	Resinous fraction of oil, mg/kg
Antimony (Sb)	2.55	0.02
Arsenic (As)	15.2	12.9
Barium (Ba)	512	0.5
Cadmium(Cd)	0.021	1.05
Chromium(Cr)	532	20
Cobalt(Co)	16.9	0.2
Copper(Cu)	174	31
Lead (Pb)	123	30
Mercury (Hg)	3.31	0.14
Nickel(Ni)	150	8
Selenium(Se)	1.06	0.075
Tin (Sn)	4.28	0.08
Vanadium(V)	247	3.5
Zinc (Zn)	18.1	8
U238 (İCP/MS)	0.497	-
Th232 (İCP/MS)	<0.05	-
Total	**1682.9**	

Table 4: Concentrations of metals in oil deposits and resinous fraction of oil

As can be seen from the table, the concentrations of many metals found in OD- barium, chromium, copper, lead, vanadium - are above 100 mg/kg, and the most toxic metals, mercury and lead, have concentrations of 3.31 and 123 mg/kg, respectively. Concentrations of other metals are tens of times higher than the concentrations of oil fractions.

This shows that during the transportation of oil, metals are mainly collected in oil sediments, and determining the sources of accumulation of these metals in oil residues is of great importance from the point of view of the environmental safety of the oil industry. This provides grounds for inclusion of oil deposits in the hazardous waste category and requires consideration in their management.

Results

Oil deposits that accumulate on the internal surfaces of pipelines during oil transportation have a complex composition, and the results of studying their physical and chemical characteristics are of practical importance for developing optimal methods for their prevention and removal, as well as for the management and disposal of these wastes. If the composition of waste or what is dangerous in it is known, its use becomes rational. Decomposition or polycondensation processes of benzo compounds lead to reduced toxicity of OD. Based on the concentrations of radioactive substances and polycyclic aromatic hydrocarbons present in the studied samples of oil deposits, it can be concluded that in this case, according to these parameters, they do not pose an environmental hazard and facilitate the possibility of environmental management of oil deposits.

The possibilities of radiation impact on the decomposition of carcinogenic polycyclic hydrocarbons in the composition of oil deposits are revealed, which is of practical interest in order to clean oil transportation waste from them. The solution to the problem of prevention of sediments and the combat against the formation of oil deposits in a well and pipeline is very urgent. To solve this problem and to develop technologies with strong resistance to accumulation of OD, it is necessary to thoroughly study the composition, properties and structure of OD before using any method to combat it.

The results of the research will allow to assess the environmental aspects of the possibilities of using radiation-chemical technologies for cleaning oil pipelines from deposits.

Conclusion

Oil deposits that accumulate on the internal surfaces of pipelines during oil transportation have a complex composition, and the results of studying their physical and chemical characteristics are of practical importance for developing optimal methods for their prevention and removal, as well as for the management and disposal of these wastes. If the composition of waste or what is dangerous in it is known, its use becomes rational. Decomposition or polycondensation processes of benzo compounds lead to reduced toxicity of OD. Based on the concentrations of radioactive substances and polycyclic aromatic hydrocarbons present in the studied samples of oil deposits, it can be concluded that in this case, according to these parameters, they do not pose an environmental hazard and facilitate the possibility of environmental management of oil deposits.

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