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RADIOLYSIS OF OIL DEGRADED IN SOIL

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Abstract: The patterns of structural changes in oil when it is in the soil, as well as during the radiation-chemical decomposition of degraded and freshly extracted oil, have been studied. The kinetics of the formation of gas products during radiolysis of oil and resin fractions of oil is presented and it is established that the radiation resistance of oil relative to gas formation during degradation increases significantly. From the given IR spectra of the original and irradiated samples of oil and resin fractions, the polycondensation processes that occur during oil degradation have been established. The study of changes in oil degraded in the soil under the influence of natural factors, as well as knowledge of changes in the composition of oil pollution under the influence of radiation, are one of the conditions for choosing methods for cleaning soil from oil degraded in the environment.

Keywords: oil degradation, oil pollution, radiation-chemical transformations.

1. Introduction

Oil and oil products, entering the soil cause significant negative changes in agrochemical properties. Soils are most susceptible to contamination by organic compounds, of which petroleum hydrocarbons are the most widespread. When oil remains in the environment for a long time, the soil becomes impregnated with it, and an oil layer forms on the surface of water bodies. In these environments, the crude oil undergoes changes due to natural factors, the lighter part of the oil evaporates, the middle fraction penetrates deep into the ground, and the heavier part undergoes destructive and polycondensation transformations under the influence of solar radiation, air oxygen, micro-organisms and catalysts, which are components of the near-surface soil layer [1].

Over the last 35-40 years, serious research has been carried out on the clean-up of lands from oil contamination. However, the issues of oil degradation in soil are insufficiently studied. At the same time, the degree of oil degradation considerably influences the efficiency of treatment processes of oil-contaminated soils [2]. In addition, radionuclides of natural origin in the formation of water are released into the environment during oil extraction. The influence of radiation from these radionuclides on oil over a long period of time leads to the formation of gases and changes in the structure and composition of oil. The study of radiation-chemical transformations of oil is essential both to assess the role of radiation in degradation processes in the environment and to develop the radiation-chemical technology for the processing of degraded oils. This issue is also of interest for the collection of oil products from the environment [3].

2. Research methods

The studied samples were isolated from the soil by extraction. Benzene was used as an extractant (the ratio of benzene to the sample was 3:1 by volume). In the separated samples of oil products, the content of the main components - hydrocarbons, resins, and asphaltenes was determined according to GOST 11858-66.

Methods of absorption spectroscopy and chromatography were used to determine the structural-group composition of these components.

Results of a study of regularities of structural changes of oil at its presence in the soil as well as at radiation-chemical decomposition of degraded and freshly produced oil from the Surakhani field of Azerbaijan are given in the work. As a source of ionizing radiation, an isotopic source of gamma radiation ^{60}Co – "MPX-γ-30" was used. Studies were carried out in a range of absorbed doses of gamma-radiation D=0-110 kGy at a dose rate of P=0.21 Gy/sec.

3. Results and discussion

Since oil is a very complex mixture consisting of aliphatic and naphthenic hydrocarbons, aromatic compounds, and asphalt-resinous substances, the changes under the influence of various environmental factors can be different, to understand the mechanism of the ongoing processes, oil samples after cleaning from impurities were divided into three fractions - oil, resin and asphaltene, and changes in the composition of oil after being in the soil and radiation-chemical transformations of degraded oil were studied using these fractions as an example.

The conducted experiments showed that the content of the components differs in the composition of the samples taken from oil-impregnated soil and directly from the well (Table 1).

Table 1

Fractional composition (mass %) of oil samples taken from the well and soil

Sample	Oil	Resin	Asphaltene
Oil from well	90.9	9.0	0.1
Oil from soil	71.1	22.4	6.5

After a long-term presence of oil on the soil surface, the physical composition of oil changes under the influence of natural factors - the content of hydrocarbons decreases by 10%, and the content of resins and asphaltenes increases tenfold. This is due to the influence of solar radiation, the presence of humic acids in the soil, atmospheric oxygen, and radiation of various origins on the destructive transformations of heavy oil components [4].

To determine the radiation resistance of degraded oils, the radiolysis of oil fractions and the effect of the absorbed dose of gamma radiation on the yield of gaseous products (H_2, CH_4, C_1-C_5 hydrocarbons) were studied during the radiation-chemical transformations of oil and resin fractions of freshly produced and degraded oil degraded in the soil of the Surakhani oil field in the soil.

As an example, Figures 1-2 show the kinetics of the formation of hydrogen during the radiation-chemical decomposition of oil and resin fractions of fresh and degraded oil in the soil.

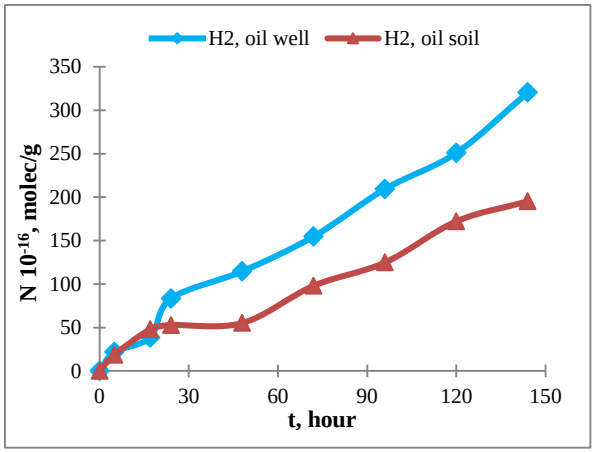

Fig. 1. Kinetics of hydrogen formation during radiolysis of the oil fraction of petroleum.

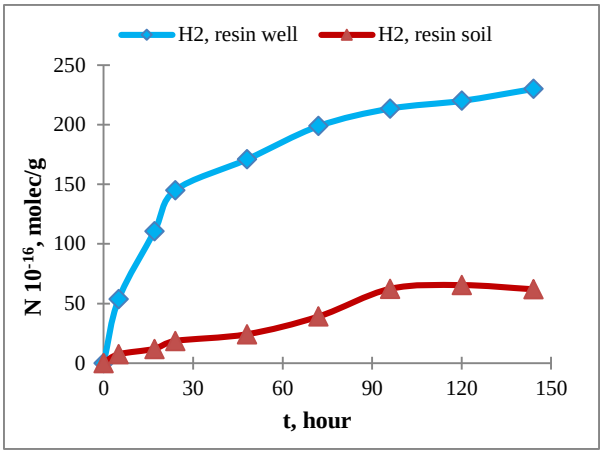

Fig. 2. Kinetics of hydrogen formation during radiolysis of the resin fraction of petroleum.

The average values (at different irradiation times) of radiation-chemical yields were calculated from the kinetics of gas formation (Table 2).

Table 2

Average values of radiation-chemical yields of gases (molec/100eV)

	H_2	**CH_4**	**C_2H_6**	**C_2H_4**	**$\sum C_3$**	**$\sum C_4$**	**$\sum C_5$**
Oil fraction from the well	0.57	0.06	0.10	0.08	0.05	0.02	0.016
Oil fraction from the soil	0.41	0.043	0.073	0.018	0.031	0.012	0.005
Resin fraction from the well	0.94	0.06	0.08	0.05	0.04	0.022	0.022
Resin fraction from the soil	0.15	0.02	0.03	0.011	0.014	0.013	0.2

From the obtained results, it is visible that during the radiolysis of oil samples in the range of absorbed dose up to 110 kGy, the highest hydrogen yield is observed in oil samples from the well. Oil samples taken from the soil are characterized by low hydrogen yields, that is, they have the highest radiation resistance. This regularity is explained by structural changes of oil while in the soil, namely, by an increase in resins and asphaltenes resistant to radiation in their composition [5].

As follows from Figures 1-2 and Table 2, the radiation resistance of oil relative to gas formation during degradation increases significantly. This seems to be due to the decomposition of lightly bonded functional groups during degradation. These groups are the source of gas products in the oil composition. On the kinetic curves of the formation of C_2-C_5 gases at doses higher than 40 kGy, saturation is observed. The saturation state can be due to two reasons: the occurrence of reverse radiation-chemical reactions of consumption of gas products and the limited resources of these gases in the initial component. Studies show that in the reaction zone at doses of 40-60 kGy, the concentration of these gases does not exceed 10^{17} molec/ml, so the occurrence of reverse radiation-chemical reactions is unlikely. The saturation state on kinetic curves of the formation of relatively heavy gases is probably due to limited resources of -CH_3, -C_2H_5, and other radicals. Therefore, as the molecular weight of gases increases, their radiation-

chemical yields decrease. For this reason, gas yields in crude oil are higher than in degraded oil, and gas yields in the oil fraction are higher than in the resin fraction. Naturally, the role of radiation-stimulated polycondensation in increasing the radiation resistance of crude and degraded oil cannot be neglected here. During irradiation, the release of functional groups and the formation of a network structure in the organic mass leads to an increase in radiation resistance, and the rate of gas formation decreases.

Oil degradation in the environment was studied by absorption spectroscopy and mass spectroscopy. Studies of the regularity of degradation processes were carried out on the example of oil and resin fractions isolated from fresh and degraded petroleum. Studies were carried out using IR spectra and chromatograms of samples of oil and resin fractions of petroleum.

The influence of gamma-irradiation on the structural-group composition of fresh and degraded oil was studied by IR spectroscopic analysis [6]. IR spectra of initial and irradiated samples of resin fraction of petroleum taken from soil are shown in Fig. 3-4. Results of infrared spectroscopy of samples indicate the change of structure-group composition of resin fraction of petroleum under the influence of irradiation.

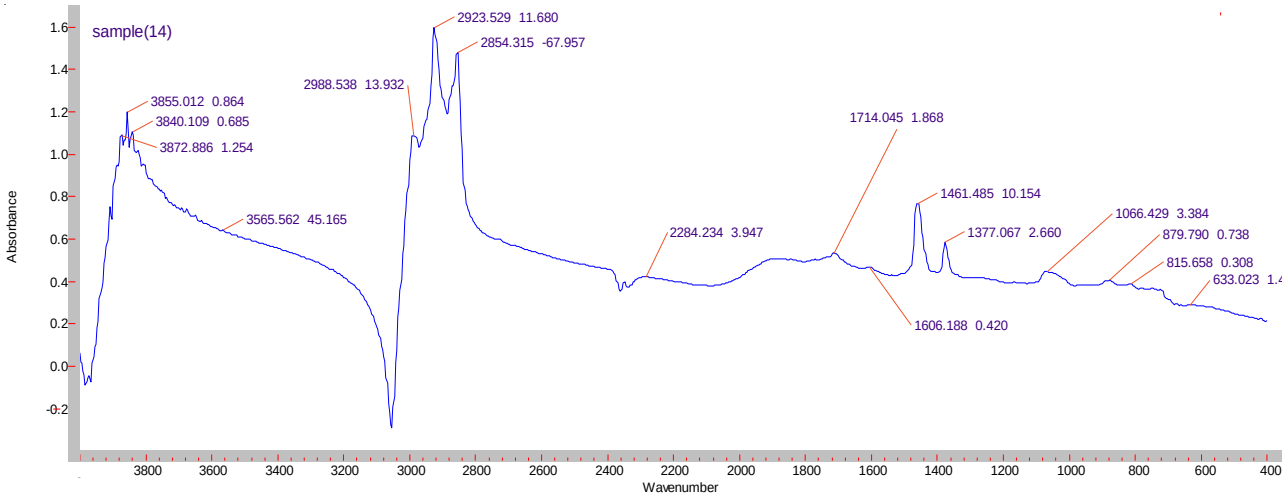

Fig. 3. IR spectrum of the initial samples of the resin fraction of petroleum from the soil surface.

Fig. 4. IR spectrum of irradiated samples of resin fraction of petroleum from the soil surface (D=110 kGy).

Intense absorption bands in the IR spectra of irradiated samples of the resin fraction of petroleum taken from the soil, in comparison with the initial samples, are as follows: 2921, 2852 cm^{-1} – characterize the stretching vibrations of – CH_2– and –CH_3 groups in alkanes, 2975, 2992 cm^{-1} – stretching vibrations of C-H bonds in cyclic alkanes, 1463, 1376 cm^{-1} - bending vibrations of -CH_2- and -CH_3 groups of branched paraffin chains, wavelength range 933-661 cm^{-1} - out-of-plane bending vibrations of the benzene ring of mono- and polynuclear aromatic structures. In the irradiated samples, there is a strong accumulation of condensed aromatic rings in the wavelength range of 600-1000 cm^{-1} - 3-4 times compared with the initial samples from the soil. There is also an increase in the absorption bands corresponding to the bending vibrations of the -CH_2- and -CH_3 groups in the range of 1461 cm^{-1} and 1377 cm^{-1}. The appearance of absorption bands at 1715 cm^{-1} indicates stretching vibrations of C=O groups, and bands at 1300 cm^{-1} indicate bending vibrations of C-H bonds in alkenes HRC=CH_2. The appearance of an intense absorption band at a wavelength of 1885 cm^{-1}, corresponding to the group of aromatic compounds with substitution of the benzene ring, is clearly observed.

The obtained IR spectra of the irradiated samples indicate significant changes in the chemical composition of oil degraded in the soil during its irradiation. An increase in intensity and the appearance of new bands in the region of polycyclic systems (633-933 cm^{-1}) are observed. In addition to the bands from binuclear compounds (naphthalene, acenaphthene), which have strong absorption at 725, 785 cm^{-1}, there are bands that belong to the vibrations of groups with three (879 cm^{-1}), as well as with five and six condensed nuclei at 879-848 cm^{-1}. The intensity of the bands of aliphatic groups -CH_3, -CH_2- (2821, 2852, 1463, 1376 cm^{-1}) increases after irradiation of the samples. This is probably due to the fact that alkyl radicals formed as a result of radiation processes enter into various interactions with the formation of aliphatic products.

It is evident from the obtained results of studies of oil degradation in soil that when oil is on the soil surface for a long time, as well as when it is exposed to radiation, its structural and group composition changes. The use of chromatography and infrared spectroscopy methods makes it possible to analyze the features of changes in the chemical composition of oil-polluting soil under the influence of various components and suggest its transition to a deeper stage of degradation. The obtained data indicate that degradation processes promote aromatization and dewaxing of degraded oil components. Based on the obtained experimental data, it can be assumed that the initial oil passes into a deeper stage of degradation. It is mainly the resin fraction of the petroleum that undergoes changes. Resins are constructed of polycyclic blocks, polynaphthenoaromatic and polycyclic systems. As a result of oil degradation in the soil, polycondensation processes occur in the composition of resin fractions [7]. Oil fractions do not contain a significant number of condensed aromatic rings as are observed in the resin fractions, they are mainly consist of paraffins of a normal structure, and cycloparaffins are mainly monocyclic.

4. Conclusion

It is evident from the results of studies of oil degradation in soil that the structural and group composition of oil changes when it remains on the soil surface for a long time, as well as when it is exposed to radiation. Degraded oil is a complex multiphase heterogeneous medium. The complex compounds contained in oil undergo various processes - oxidation, polycondensation, and destruction. The study of the structural-group composition of oil degraded on the soil, allows the use of rational methods of soil treatment from oil products. Analysis of the transformation of oil contamination when oil enters the soil surface is necessary to optimize the

choice of remediation technologies. Study of changes in oil degraded in soil under the influence of natural factors, as well as knowledge of changes in the composition of oil pollution under the influence of radiation, is one of the conditions for extracting additional oil resources from oil-contaminated soil surfaces and for choosing methods of soil treatment from oil degraded in the environment.

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РАДИОЛИЗ ДЕГРАДИРОВАННОЙ В ПОЧВЕ НЕФТИ

Н.Г. Гулиева, И.И. Мустафаев, С.Ф. Алиева-Чичек

Резюме: Исследованы закономерности структурных изменений нефти при ее нахождении в почве, а также при радиационно-химическом разложении деградированной и свежедобытой нефти. Представлена кинетика образования газовых продуктов при радиолизе масляной и смолистой фракций нефти и установлено, что радиационная стойкость нефти относительно газообразования при деградации значительно возрастает. Из приведенных ИК-спектров исходных и облученных образцов масляной и смолистой фракций установлены процессы поликонденсации, происходящие при деградации нефти. Исследование изменений нефти, деградированной в почве под влиянием природных факторов, а также знание изменения состава нефтяных загрязнений под воздействием излучения являются одним из условий для выбора методов очистки почвы от деградированной в окружающей среде нефти.

Ключевые слова: деградация нефти, нефтяные загрязнения, радиационно-химические превращения.

TORPAQDA DEQRADASİYAYA UĞRAMIŞ NEFTLƏRİN RADİOLİZİ

N.Q. Quliyeva, İ.İ. Mustafayev, S.F. Əliyeva-Çiçek

Xülasə: Torpaqda qalan zaman neftdə baş verən, eləcə də yeni hasil edilmiş və deqradasiyaya uğramış neftlərin radiasiya-kimyəvi parçalanması zamanı meydana gələn struktur dəyişikliklərinin qanunauyğunluqları tədqiq edilmişdir. Neftin yağ və qətran fraksiyalarının radiolizi zamanı qaz məhsullarının yaranma kinetikası göstərilmişdir ki, buradan da neftin deqradasiyası zamanı qaz əmələ gəlməsinə əsasən radiasiyaya davamlılığının əhəmiyyətli dərəcədə artdığını görmək olar. Yağ və qətran fraksiyalarının ilkin və şüalanmış nümunələrinin verilmiş İQ spektrlərindən neftin deqradasiyası zamanı baş verən polikondensasiya prosesləri müəyyən edilmişdir. Təbii amillərin təsiri altında torpaqda deqradasiyaya uğramış neftin dəyişməsinin tədqiqi, o cümlədən şüalanmanın təsiri altında neft çirklənməsinin tərkibində dəyişikliklərin öyrənilməsi torpağın ətraf mühitdə deqradasiyaya uğramış neftdən təmizlənməsi üsullarının seçilməsi üçün əsas şərtlərdən biridir.

Açar sözlər: neftin deqradasiyası, neftlə çirklənmə, radiasiya-kimyəvi çevrilmələr.