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INFLUENCE OF DEGRADATION RATE OF OIL ON ITS RADIATION STABILITY

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Abstract: Regularities of radiation-chemical transformations of heavy fractions of Surakhani oil fields of Azerbaijan taken from the surface of the basin were studied. Studies were conducted at the range of absorbed doses of γ-radiation 3,8 – 109,5 kGy at dose rate of P=0,21 Gy/s. It was established radiation-chemical yields of gases obtained within the radiolysis of oil fractions and determined structural-group composition of the components. The research results will allow evaluating the possibility of applying radiation-chemical technology in purification of water from degraded oil products.

***Keywords*:** oil, degradation, water, γ-radiation, environment

1. Introduction

In terms of negative impact on the environment, the oil industry is in one of the first places among the leading sectors of the economy. The problem of water pollution with oil and oil products are becoming more urgent each year. The last accidents (in the Gulf of Mexico, on Amur, in Azerbaijan) clearly show the need for application of new methods of water purification from oil /1/.

Oil and oil products fall into the body of water in different ways: with storm water, within pipeline accidents, dumping of industrial sewage, etc. According to experts, each year about 10 million tons of oil and oil products get in the world ocean /2/. Only Azerbaijan dumps more than 500 mln m^3 of normative-treated water in the Caspian Sea every year, as a result of which the sea gets more than 3 thousand tons of oil products, 25 tons of phenols, 28 thousand tons of suspended materials, 520 thousand tons of synthetic surfactant /3/. Within the ingress of oil on the surface of water objects the greatest danger is its spread to large areas, leading to disruption of ecological balance in the environment.

Oil consisting of mainly hydrocarbon molecules, insoluble in water, spreads on the surface of the water during a disaster. Under the action of waves and current, the oil patch divided into many parts. Volatile fractions evaporate in the first hours of the accident; further processes occurring within the contact of oil with water depend on oil composition and environmental changes. Protection of water resources from pollution by oil and oil products is one of the main tasks of modern time. There are many methods of water purification from oil and oil products /4/. In this regard, the application of advanced technologies of water purification from oil is very important.

In order to evaluate the role of radiation in the process of finding oil on basin surfaces and to reveal the usage opportunities of radiation-chemical technology in water purification from oil contamination, as well as to compare the samples taken from the well, some patterns of radiation-chemical transformations of oil samples after long stay on water surface were studied.

2. Experimental technique

The research results of the changes in physical-chemical properties of oil in Surakhani, Azerbaijan, taken from water surface under the influence of the environmental factors and ionizing radiation have been presented in the article.

Contents of the main components – hydrocarbons, tar and asphaltenes were determined in the isolated oil samples in accordance with GOST 1158-66.

In order to determine the structural-group composition of these components it was used the methods of absorption spectroscopy (IR-spectra) – on spetrophotometer "Varian 640-IR" in the wavelength range of 600-4000 cm^{-1}. Assignment of bands of the obtained spectra was carried out according to /5/. Gamma-radiation isotopic source ^{60}Co –MPX-γ-30 with dose rate P=0,21Gy/s was used as a source of ionizing radiation. The absorbed doses were changed D=3,8 –109,5 kGy. Gas products were analyzed by gas chromatography method on the devices "Tsvet -102" and "Gazokhrom-3101".

3. Experimental results and discussion

The studied oil samples were isolated from water by extraction. As an extractant it was used benzene. The oil samples taken directly from the nearby well were used for comparison.

In table 1 it is given the contents of the main components of oil taken from well and surface of water body of Surakhani, Azerbaijan – hydrocarbons, tars and asphaltenes (%).

Table 1. Fractional composition of oil samples, taken from well and water surface

Sample	Hydrocarbons	Tars	Asphaltenes
From well	92,5	7,45	0,05
From water surface	82,8	16,8	0,4

The above-drawn table shows that after a long stay of oil on water surface under the influence of natural factors its material composition changes – hydrocarbon content decreases, tars and asphaltenes increase. It is explained by the influence of solar radiation, atmospheric oxygen and radiation of different origin on destructive transformation of heavy oil components /6/.

The results obtained by IR-spectroscopy indicate the formation of more condensed aromatic collars in the oil structure after a long stay in water and under irradiation influence.

Figures 1-2 show the IR-spectra of original samples of resinous oil fractions from well and water surface.

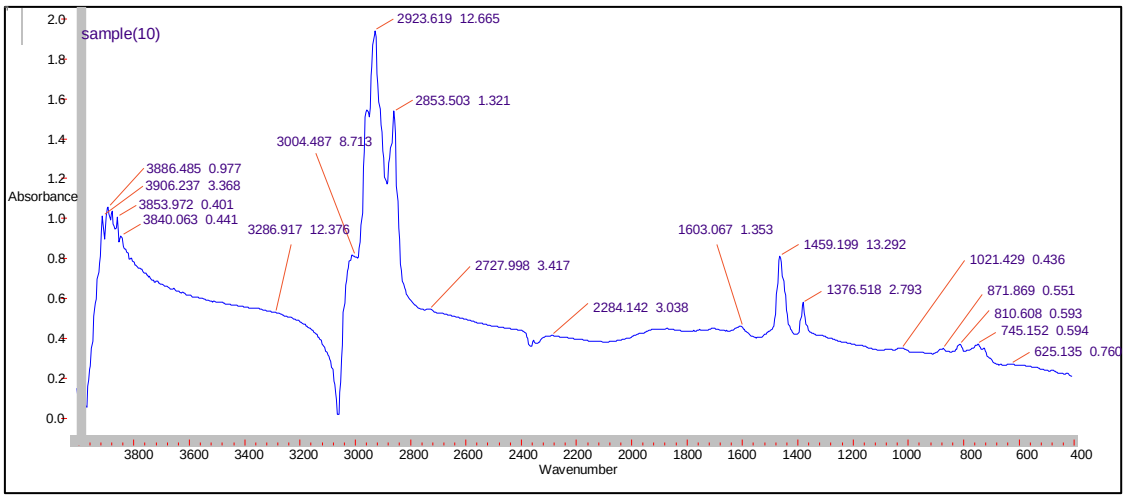

Fig.1. IR-spectrum of resinous oil fraction from well (D=0)

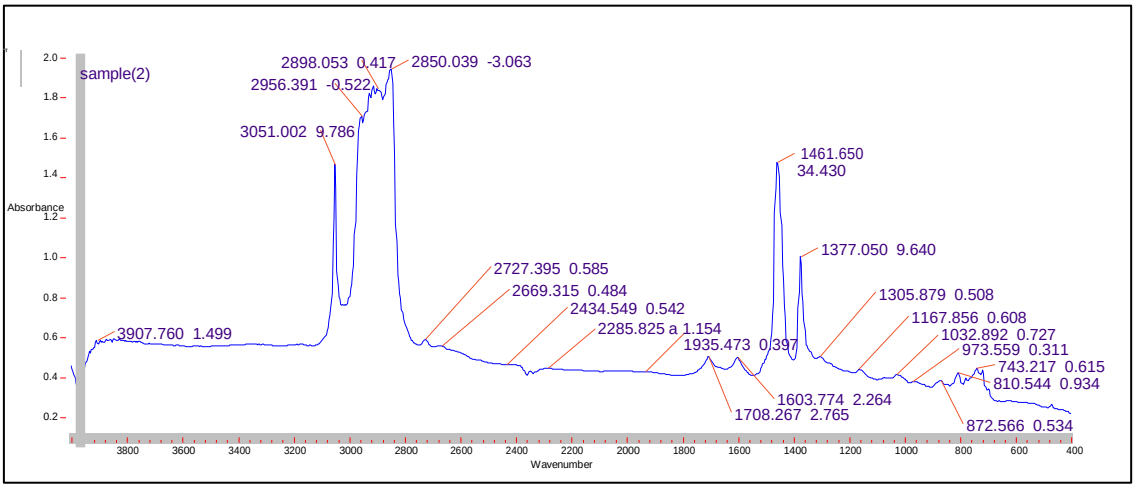

Fig.2. IR-spectrum of resinous oil fraction from water surface (D=0)

IR-spectra analysis of the original samples of resinous oil fractions showed that oxidation process of tars occurs after a long stay of oil on water surface as a result of degradation, of which the appearance of the bands at 1708 cm^{-1}, concerning to C=O groups, is indicative. This absorption band is an objective criterion for accumulation of oxygen-containing products. Intense absorption bands are also observed at 3051 and 1603 cm^{-1}, characteristic for valence oscillations of C=C bond of cyclic or benzene (aromatic) ring, bands of 1030 cm^{-1} corresponding to binuclear aromatic structure appear. There is a stronger accumulation of aromatic rings – by 3-4 times in comparison with the samples from well – increase in condensed aromatic rings. Also, absorption bands are strongly appear within the wavelengths of 600 – 1000 cm^{-1}, corresponding to deformation vibrations of - CH_2 - and CH_3 group in the range of 1461 cm^{-1} and 1377 cm^{-1} – intense increase in the above-shown groups.

The observed data indicate the significant changes in oil composition, relating to the influence of environmental factors.

The influence of gamma-radiation on the structural-group composition of oil fractions from well and water surface was studied.

The results of IR-spectroscopy of the samples indicate the changes of structural-group composition of resinous oil fraction under irradiation influence.

IR-spectra of the irradiated samples of resinous oil fraction, taken from water surface are presented in figures 3-4.

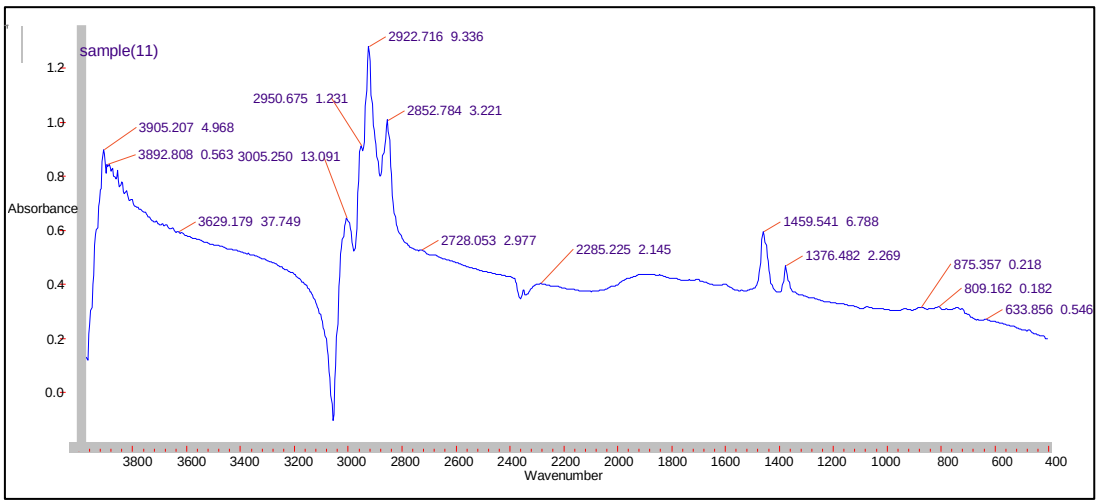

Fig. 3. IR-spectrum of the sample of resinous oil fraction from water surface (D=54,7kGy)

As it is seen from figure 3, within 72 hours (54,7kGy) irradiation of the samples with water surface on IR-spectra it is observed the highest intensity of absorption bands at 3005 cm^{-1}, corresponding to polycondensation processes. After 144 hours irradiation (109,5 kGy) the samples of the bands disappear, which indicates the destructive processes. The changes in absorption bands are also observed within 2920 and 2860 cm^{-1}, corresponding to valence vibrations of $-CH_3$, $-CH_2$ – groups, which is associated with the dissipation of radiation energy I functional groups (fig.4). At the same time the absorption bands 1708 and 1603cm^{-1}, corresponding to C=C bonds of aromatic ring and C=O carbonyl bonds disappear in IR-spectra after irradiation, which is apparently related with the condensation of aromatic rings after irradiation.

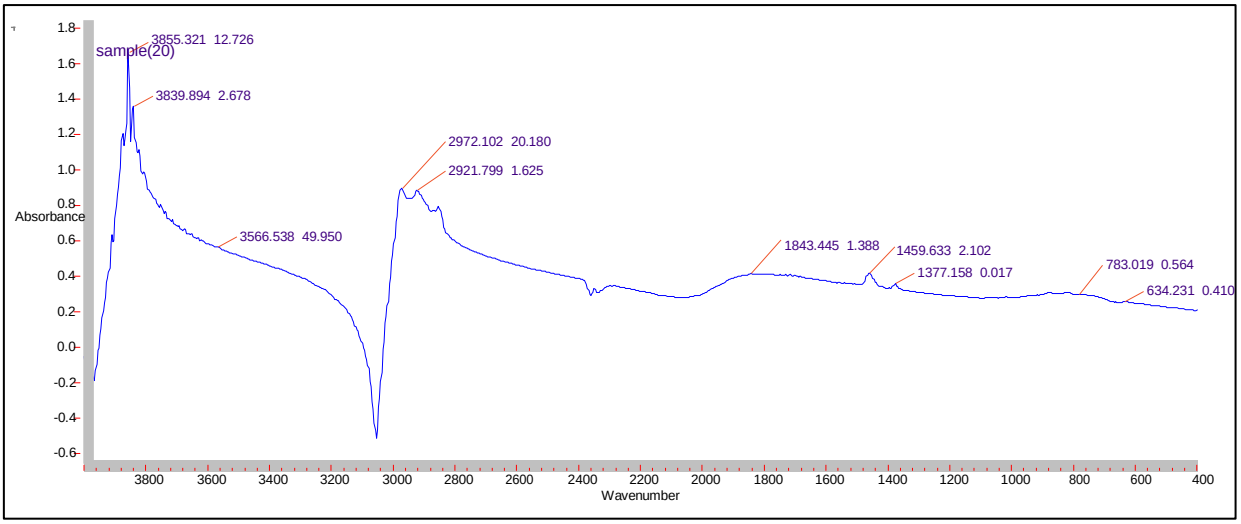

Fig.4. IR-spectrum of resinous oil fraction from water surface D=109,5 kGy

Thus, from IR-spectra of the samples it is seen that within a long stay of oil on water surface, as well as within the influence of radiation its structural-group composition changes. Mainly tar fraction undergoes the changes.

Compared with tar fraction samples, in oil fraction samples it is not observed strong changes in absorption bands, corresponding to aromatic rings. In tars there are hydrocarbons in the form of condensed aromatic cycles with more paraffinic side chains /7/. In IR-spectra of the oil fraction samples after irradiation there is only a redistribution of intensity of $-CH_2-$ and $-CH_3$ group.

Radiolysis of oil fractions and effect of the absorbed dose of γ-radiation on the yield of gas products within the radiation-chemical transformations of oil and tar fractions of degraded oil were studied. Below are the kinetic curves of formation of gas products within the radiolysis of oil and tar fraction of the studied oil samples. The samples of the studied oil were irradiated at various time intervals. Formation rate and radiation-chemical gas yields, formed as a result of gamma-radiolysis of oil and tar fraction, were determined: H_2, CO, CH_4, C_2H_4 ,C_2H_6 ,$\sum C_3 - C_6$. Figures 4-5 show the kinetic curves of hydrogen formation within radiolysis of oil and resinous fraction of oil taken from well and water surface.

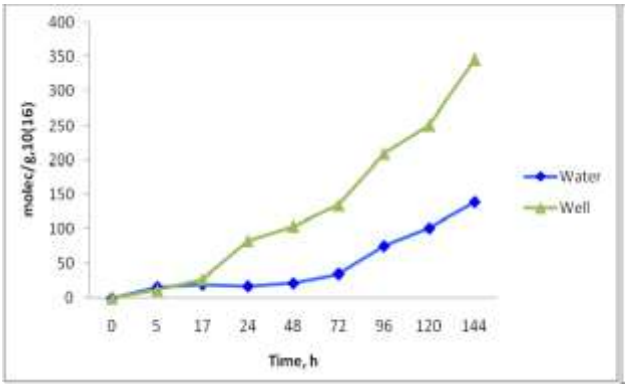

Fig.4. Kinetics of hydrogen formation at the radiolysis of oil fraction

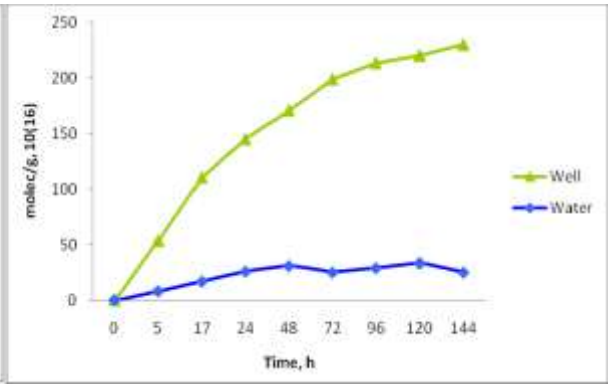

Fig.5. Kinetics of hydrogen formation at the radiolysis of tar fraction

From the kinetics of hydrogen formation within the radiolysis of oil samples in the range of absorbed dose up to 110 kGy it is seen that the highest hydrogen yield is observed in oil samples from well. Oil samples taken from water surface are notable for low hydrogen yields, that is, possess the highest radiation resistance. This pattern is explained by structural changes in oil in the process of finding on water surface, namely by increase of radiation-resistant tars and asphaltenes in their composition. It is particularly observed within the radiolysis of tar fraction which is due to low content of functional groups and higher content of condensed aromatic compounds in the composition of resinous fraction.

4. Results

Due to oil degradation on water surface, there occur polycondensation processes, which lead to structural changes of oil. The nature of changes in properties of oil taken from water surface can be traced by IR-spectra of oil fractions and kinetics of gas formation within radiolysis of oil fractions.

Previously, the authors have developed a patent for water purification from oil impurities (< 1mg/l) by radiation-thermal method /8/. Within conjugate effects of gamma radiation and heat at absorbed doses higher than 3 kGy and temperature of 400^{o}C it is possible to refine about 87% of original oil in water. In optimal mode of radiation-thermal process flow the active radiation-generated radicals initiate chain mode of hydrocarbon decomposition in an aqueous medium.

In this paper, the authors studying the radiation-chemical transformations of oil, taken from water surface, considered the possibility of applying this method for purification of water bodies from degraded oil in the environment.

Study of the changes in oil on water surfaces, as well as under radiation influence and knowledge of the composition of oil contamination on water bodies are necessary conditions for the extraction of additional oil resources from oil-containing sewage. Considering the fact that the greatest hazard to the environment comes from the oil film on the water surface and oil products emulsified in it, the possibility of applying ionizing radiation for removing oil products from sewage is an important consideration in the decision of certain environmental problems.

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ВЛИЯНИЕ СТЕПЕНИ ДЕГРАДАЦИИ НЕФТИ НА ЕЕ РАДИАЦИОННУЮ СТАБИЛЬНОСТЬ

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Резюме: Изучены закономерности радиационно-химических превращений тяжелых нефтяных фракций Сураханского месторождения Азербайджана, взятой с поверхности водоема. Исследования проводились в интервалах поглощенных доз γ-излучения 3,8 – 109,5 кГр при мощности дозы P=0,21 Гр/с. Установлены радиационно-химические выходы газов, полученных при радиолизе нефтяных фракций, определен структурно-групповой состав компонентов. Результаты исследований позволят оценить возможность применения радиационно-химической технологии в очистке воды от деградированных нефтепродуктов.

Ключевые слова: нефть, деградация, вода, γ-излучение, окружающая среда

NEFTİN DEQREDASİYA DƏRƏCƏSİNİN ONUN RADİASİYA STABİLLİYİNƏ TƏSİRİ

S.R. Hacıyeva, N.K. Quliyeva, A.A. Səmədova, S.Z. Məlikova, İ.İ. Mustafayev

Xülasə: Suraxanı neft yataqlarının su hövzələrinin səthindən götürülmüş nümunələrinin ağır fraksiyalarının radiasiya-kimyəvi çevrilməsi qanunauyğunluqları tədqiq edilmişdir. Tədqiqatlar γ-şüalanmanın 3,8 – 109,5 kQr udulma dozalarında P=0,21 Gy/s nisbətində həyata keçirilmişdir. Neft fraksiyalarının radiolizi müddətində alınan qazların radiasiya-kimyəvi çıxımları təyin olunmuş və komponentlərinin struktur-qrup tərkibi müəyyən edilmişdir. Tədqiqatların nəticələri suyun deqredasiyaya uğramış neft məhsullarından təmizlənməsi prosesində radiasiya-kimyəvi texnolagiyaların tətbiqinin mümkünlüyünü qiymətləndirməyə imkan verəcək.

Açar sözlər: neft, deqradasiya, su, γ-şüalanma, ətraf mühit.