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# STUDY OF RADIATION-CHEMICAL TRANSFORMATIONS AND COMPOSITION OF DEPOSIT IN OIL PIPELINE

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***Abstract:*** The composition and radiation-chemical transformations of oil deposit (OD) have been studied. The studies have been carried out within the ranges of absorption dose D=0-326 kGy at dose rate P=0,19 Gy/sec of gamma-radiation. It has been determined the radiation-chemical gas yields obtained within radiolysis of oil deposit, activation energy processes, PAH content in the composition of deposit, influence of radiolysis on cleavage of carcinogenic polycyclic aromatic hydrocarbons.

Research results will allow evaluating the environmental aspects of possibility of using the radiation-chemical technology in cleaning oil pipelines from sediments.

***Keywords:*** radiation, oil, oil deposit, toxicity, polycyclic aromatic hydrocarbons

## 1. Introduction

Currently, pipeline transport is the main means of transportation of oil and oil products.

Within the transportation of oil through pipes due to the fluctuations in ambient temperature and other factors, the oil deposit (OD) ooze out from oil and are deposited on the inner wall of pipeline. It decreases boom drift diameter of pipe, but in the case of formation of significant deposits they eventually may limit the extraction of oil which will require stopping the transportation.

OD consists mainly of paraffins, asphaltenes, resins and mineral impurities. Moreover, they usually contain sulfur, metals, as well as a small amount of water, containing dissolved chloride salts, and sodium, calcium and magnesium hydrocarbonates, sulfates and carbonates /1/.

There are two ways of solving the problem of oil deposit in oil extraction: prevention of deposit and elimination of already formed deposits. Practice has shown that the prevention of deposit of oil compounds is less expensive method than their permanent elimination.

In this regard, the study of the composition of oil deposit is of practical importance for determining optimal methods of controlling them. In addition, oil deposit contains many valuable components which can be used as an additive to fuel oil, in construction while manufacturing lubricant compositions.

In order to select the most effective way to eliminate oil deposit from chemical point of view, it is necessary to get an idea about the composition, properties and structure of these deposits /2/.

In the work it has been studied the radiation-chemical transformations of oil deposit formed on the surface of pipeline within the transportation of oil, in which composition there are carcinogenic polycyclic aromatic hydrocarbons (PAH) /3/.

## 2. Experimental method

Gamma-radiation isotope source $Co^{60}$ – "MPX – γ -30" has been used as a source of ionizing radiation. The studies have been carried out within the ranges of absorption dose D=0-

326 kGy at dose rate P=0,19 Gy/sec of gamma-radiation. Gas and liquid products have been analyzed with the chromatography method using devices «Цвет-102» and chromatography-spectrometry apparatus GC/MS Trace DSQ (Thermo Electron Finngan USA 2005).

Molecular-mass distribution of paraffin hydrocarbons contained in OD samples has been determined. Paraffin hydrocarbons are represented by the homological series of n-alkanes from $C_{10}$ to $C_{35}$ with the maximum, attributable to $C_{15}$. As it is seen, alkanes $C_{14}$ - $C_{19}$ compile the main part in the composition of OD.

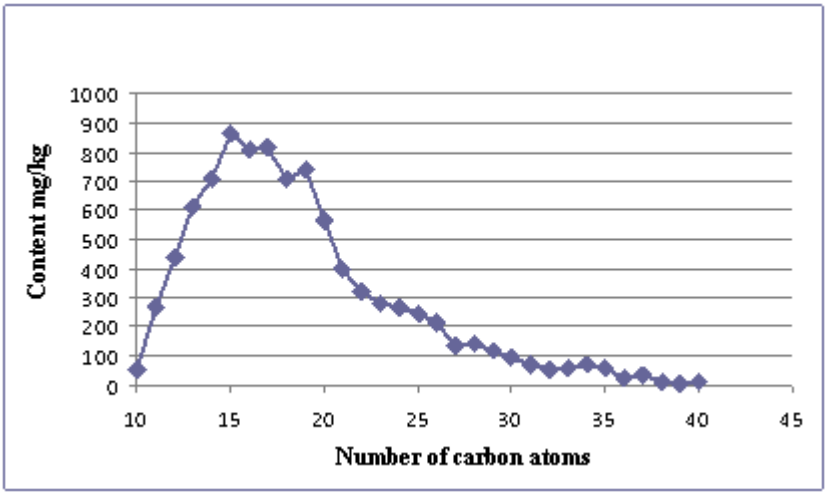


*Fig. 1 Molecular-mass distribution of n-alkanes*

Some patterns of radiation-chemical transformations of oil deposit samples have been studied in order to evaluate the role of radiation in the process of purification of oil pipelines from sediments and to determine the radiation resistance of OD. The kinetics of accumulation of gases at the radiation-chemical transformations of OD is shown in Fig. 2-3.

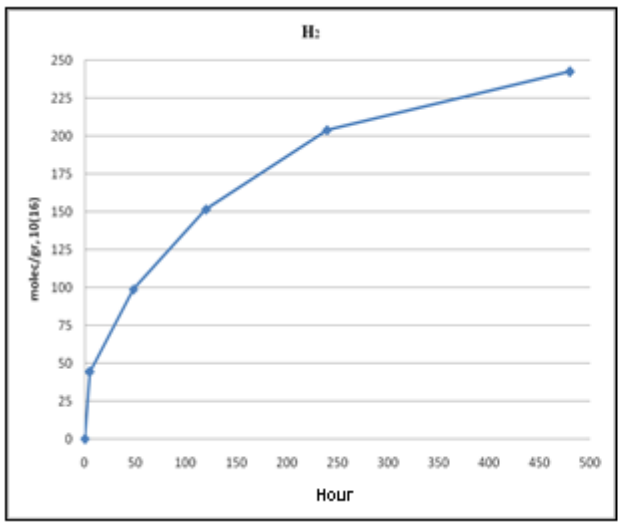


*Fig. 2 Kinetics of hydrogen formation in the radiolysis of OD*

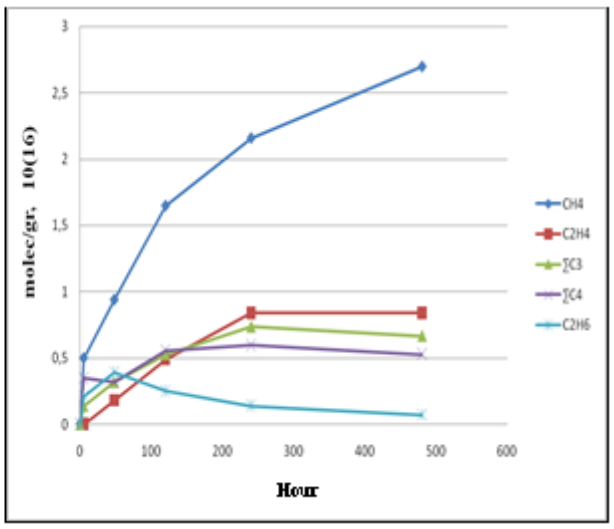


*Fig. 3 Kinetics of formation of $C_1$-$C_6$ gases in the radiolysis of OD*

Formation process of oil deposit in the pipeline is determined by many factors, including

changes in temperature, oil flow, so it is important to the study the influence of temperature on change of radiation-chemical yield of gases.

Table 1 shows the temperature dependence of the radiation-chemical yields of gases in the radiolysis of OD.

*Table 1*

Temperature dependence of radiation-chemical yield of gases (mol/100eV)

| TC | G($H_2$) | G ($CH_4$) | G ($C_2H_4$) | G ($C_2H_6$) | G($C_3$) | G ($C_4$) | G($C_5$) | G($C_6$) |
|---|---|---|---|---|---|---|---|---|
| 20 | 0,8 | 0,032 | 0,009 | 0,003 | 0,003 | 0,016 | 0,001 | 0,001 |
| 100 | 1,10 | 0,040 | 0,012 | 0,005 | 0,008 | 0,022 | 0,001 | 0,003 |
| 200 | 2,790 | 0,07 | 0,018 | 0,007 | 0,010 | 0,031 | 0,002 | 0,007 |
| 300 | 30,297 | 0,364 | 0,032 | 0,222 | 0,028 | 0,074 | 0,007 | 0,014 |
| 400 | 783,051 | 29,838 | 9,075 | 4,506 | 6,317 | 7,348 | 0,011 | 2,193 |

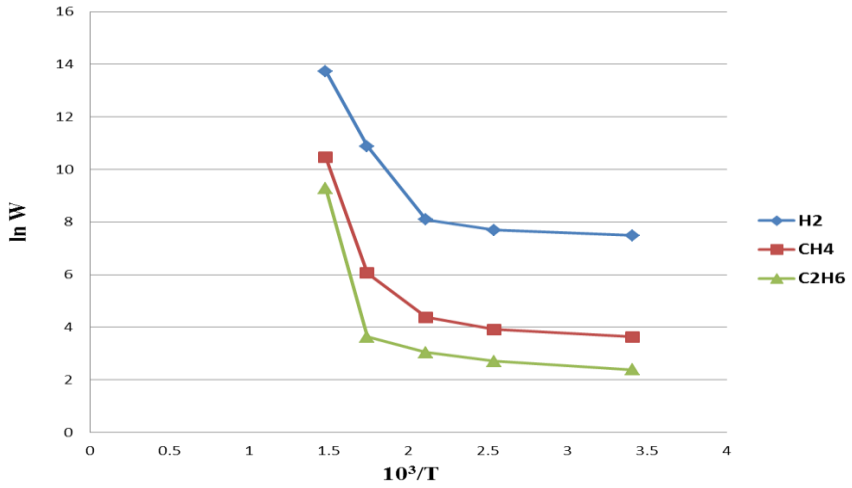


*Fig. 4 Temperature dependence of formation rate of gases in the radiolysis of OD*

It is calculated the values of activation energy of radiation-thermal processes of gas formation in the radiolysis of OD from the graph of temperature dependence of rates in the Arrhenius coordinates (Table 2).

*Table 2*

Values of activation energy at different temperature ranges (kcal / mol)

| | $H_2$ | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_3H_8$ | $\Sigma C_4$ | $\Sigma C_5$ | $\Sigma C_6$ | $\Sigma C_7$ |
|---|---|---|---|---|---|---|---|---|---|
| E(20-200C) | 2,15 | 2,68 | 3,45 | 3,15 | 3,06 | 1,75 | 5,65 | 7,88 | 7,13 |
| E(200-400C) | 41,63 | 44,88 | 100,87 | 33,25 | 96,93 | 41,55 | 88,53 | 89,78 | 70,47 |

Values of activation energy at higher temperatures significantly exceed the corresponding values at lower temperatures. This is due to the fact that the activation energy of abstraction reaction significantly exceeds the activation energy of diffusion processes, limiting the radiation-chemical processes up to the $200^0$C temperature.

The most toxic from petroleum hydrocarbons, causing serious pollution, are polycyclic aromatic hydrocarbons and their decay products / 4 /. Table 3 shows the indices of PAH toxicity – the group of 16 EPA (16 priority pollutants of PAH proposed by US Environmental Protection Agency (EPA)).

*Table 3*

Concentration and toxicity contained in OD of PAH - the group of 16 EPA

| **PAH** | Index of toxicity | **C**, mg/kg | % |
|---|---|---|---|
| **Naphthalene** | **0.001** | **44,485** | **51,527** |
| **Acenaphthylene** | **0.001** | **1,573** | **2,489** |
| **Acenaphthene** | **0.001** | **1,074** | **1,499** |
| **Fluorene** | **0.001** | **7,743** | **10,391** |
| **Phenanthrene** | **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** |
| **Chrysene** | **0.01** | **2,204** | **3,806** |
| **Benzo (b) fluoranthene** | **0.1** | **0,326** | **0,475** |
| **Benzo (k) 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** | **0,25** | **0,287** |
| Sum of EPA 16 | | 81,42 | 100 |

Taking into account the environmental aspects of mentioned indicators of PAH toxicity, namely the toxicity of some representatives of PAH increased by 1000 and 5000 times, the study of changes in their concentrations under the influence of radiation on the oil deposit is of interest.

It has been studied radiation-chemical transformations of the following polycyclic aromatic hydrocarbons - 2-6 ring PAH, 16 EPA group, NPD group (naphthalene, phenanthrene, dibenzothiophene).

It has been studied dose dependence of changes in the concentrations of individual groups of polycyclic aromatic hydrocarbons in the radiolysis of OD. Significant changes of concentration are observed for the PAH with an increased content of benzene rings in their structure. Thus, the

decrease in the concentration of benzoanthracene is 15%, benzopyrene - 25%, dibenzo-anthracene - 75 % in the studied ranges of radiation exposure.

### 3. Conclusion

1. Organic part of deposit of oil transportation has high radiation stability up to $200^0$C temperature. At higher temperatures, there is an increase in radiation-thermal processes of degradation with the formation of hydrogen and hydrocarbons $C_1$-$C_6$.
2. It has been revealed the possibility of radiation impact on the splitting of carcinogenic polycyclic hydrocarbons in the composition of oil deposit, which is of practical interest for the purpose of purifying them from transporting oil waste.

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## ИЗУЧЕНИЕ РАДИАЦИОННО-ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ И СОСТАВА ОТЛОЖЕНИЙ В НЕФТЕПРОВОДАХ


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**Резюме:** Изучены состав и закономерности радиационно-химических превращений нефтяных отложений (НО). Исследования проводились в интервалах поглощенных доз гамма-излучения Д=0-326 кГр при мощности дозы Р=0,19 гР/сек. Установлены радиационно-химические выходы газов, полученных при радиолизе нефтяных отложений, энергии активации процессов, содержание в составе отложений ПАУ, воздействие радиолиза на расщепление канцерогенных полициклических ароматических углеводородов.

Результаты исследований позволят оценить экологические аспекты возможности применения радиационно-химической технологии в очистке нефтепроводов от отложений.



**Ключевые слова**: радиация, нефть, нефтяные отложения, токсичность, полициклические ароматические углеводороды.


## NEFT BORULARININ QALIQLARININ RADİASİYA-KİMYƏVİ ÇEVRİLMƏLƏRİNİN VƏ TƏRKİBİNİN TƏDQİQİ


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***Xülasə:*** Qamma-şüalanmanın doza gücünün 0.19 Gy/san, udulan dozanın D=0-326 kGy intervalında neft qalıqlarının radiasiya-kimyəvi çevrilmələri və tərkibi öyrənilmişdir. Radioliz nəticəsində yaranan qazların

radiasiya-kimyəvi çıxımları verilmişdir. Ekoloji baxımdan daha çox maraq kəsb edən politsiklik aromatik karbohidrogenlərin (PAK) radiasiyanın təsirindən çevrilmələrinin tədqiq olunmasıdır.

Tədqiqatların nəticələri neft borularında benzo-birləşmələrin parçalanması, ümumilikdə qalıqların toksiklik dərəcəsinin azalması və bununla da onların ekoloji idarə olunmasını asanlaşdıra bilər.

***Açar sözlər:*** radiasiya, neft, neft qalıqları, toksiklik, politsiklik aromatik karbohidrogenlər.