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FEATURES OF VANADIUM GEOCHEMISTRY IN OILS FROM THE OIL AND GAS FIELDS OF EASTERN REGION OF UKRAINE

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Abstract. The results of long-term studies of the geochemical features of vanadium in the oil from 36 deposits of the Eastern oil and gas region of Ukraine. Based on the results of correlation and regression analyses, the nature and forms of the relationship between the vanadium content in oil and nickel, zinc, chromium, manganese, cobalt, iron, mercury, aluminum and the total content of these metals were determined; average capacity of the productive horizon; oil density value; oil viscosity value; resin content; the density of formation water from the productive horizon; sulfur content in oil; actual depth of the productive horizon; actual temperature of the productive horizon; actual pressure of the productive horizon; oil boiling point; paraffin content; the value of mineralization for formation water from the productive horizon; content of asphaltenes. Correlation coefficients, pairwise linear regression equations as well as curves that illustrate relationships between these parameters are obtained. Based on the results of the cluster analysis, a dendrogram of the results for clustering by means of the weighted centroid method of the considered fields by the content of vanadium in the oils was elaborated. Based on the results of clustering by means of the weighted centroid method, the first natural classification of oil and gas fields of eastern region of Ukraine according to the content of vanadium in oils was developed. It has been proven that heteroatomic low-molecular sulfur-containing components of the petroleum system are the main concentrators of vanadium in the oil for the studied deposits. It has been shown that, based on the results of the cluster analysis, sample average values of vanadium concentrations that vary significantly between individual deposits or groups of deposits for established ranges could be interpreted in terms of qualitative assessment as follows: abnormally low; low; below average; average; above average; high; abnormally high. The implementation of this kind of approach makes it possible to visually compare and interpret in terms of geology various scale and various indicators of oil deposits obtained by means of experimental study.

Key words: vanadium, oil deposits, cluster analysis, linear regression equations, geochemical oil parameters, correlation coefficient.

1. Introduction

Problems of accumulation and migration of microelements, in particular nickel content in oil is related to actual scientific and technical issues of hydrocarbon genesis, with possibility of their industrial extraction in oil refining for further sale, as related raw materials, as well as the ability to determine the environmental risks of using these oils as raw materials for the production of petroleum products and, foremost, gasoline and diesel fuel are of particular interest. It is known, that all the types of crude oil contain metals in small quantities. High content of metals, in particular nickel, is also a serious problem in the processing of crude oil as it leads to irreversible deactivation of catalysts as a result of compounds deposition for this metal on the active surface as well as pore space and the catalyst structure get blocked and destroyed respectively. In addition, inorganic metal compounds formed during oil refining contribute to high-temperature corrosion of equipment surfaces, reduce the service life of turbojets, diesel engines and power plants, gas corrosion of active elements for gas turbine engines as well as increase of harmful environmental impact of emissions. However, metals, including rare earth ones, are valuable by-products, which content in oils and residues of their processing may even exceed their content in raw ore [1]. However, in Ukraine, the industrial production of metals (in particular, nickel) from crude oil has not sufficiently developed so far, although in the world practice of oil refining some technologies that allow simultaneous production of concentrates with a high content of various metals has been developed. In particular, about 8% of the world's vanadium production is obtained from crude oil abroad, and in some countries this share reaches 20% (USA) [2]. Besides, the presence and content of metals in oils from different deposits allows to establish patterns of their migration and concentration in hydrocarbon systems. Among them, in particular, should be mentioned metals of special industrial and environmental significance, specifically vanadium, mercury, cobalt, nickel, iron, manganese, aluminum, titanium, chromium and zinc.

This study is devoted to the results of research for the features of the geochemistry of vanadium in the oils for the major deposits from the oil and gas fields of Eastern region of Ukraine, which is the largest one in terms of proven reserves, forecast resources and production. In tectonic terms, this region is located within the Dnipro-Donetsk depression, which is a complex intra-platform rift structure, and the latter, in turn, at a different scale level, is a link of the heterogeneous transcontinental Sarmatian-Turanian lineament, spatially traced from the western borders of Belarus to the off spurs of Tien Shan.

Recent achievements. One of the first classifications of oils according to their general properties of metal content was made up by Barwise in 1990. He considered the chemical composition, physical properties and content of metals in oil samples [3]. Later in 2007, Shniukov published a very interesting review article about content of vanadium and nickel in the world's natural oils [4]. It discusses in detail the concentrations of heavy metals in oils in relation to their genesis. A year later in 2008, Sukhanov considered the current state of oil reserves assessment and, therefore, related oil components (including heavy metals) as sources of high quality metal raw materials [5]. In 2010, Yakutseni published the results of a study of the relationship between the deep zoning of hydrocarbons and the enrichment of oils with heavy impurities [6]. The paper indicates the presence of a correlation between the content of heavy metals in oils with the depth of oil deposits. Back in 2014, Akpoveta analyzed the content of heavy metals in petroleum products of the Nigerian deposits (Agbor) [7]. The authors note that the high content of heavy metals in oils could pose a serious environmental threat. It should be noted that not all heavy metal impurities in oils are of a natural genesis. In Ukraine, such studies were conducted in 2013 on high-sulfur oil of the Carpathian Depression [8]. This paper not only investigated the fractional composition and physical-chemical properties of light fractions selected from oil of the Orkhovytskyi oil field, but also studied the potential content of fractions for which density, refractive index, molecular weight, sulfur content were determined. Later, Wilberforce conducted studies of heavy metals in crude oil used in medicine [9]. In this work, the levels of Cd, Ni, V and Pb were investigated by means of atomic absorption spectrophotometry. As a result of the study, the average concentration of metals was determined, indicating their impact on the human body. Previously, some geochemical features of metals in oils from deposits of the Dnipro-

Donetsk depression were considered and the creation of a natural classification of these oil deposits by metal content using clustering methods was substantiated [10-22]. At the same time, there are no studies aimed at studying the geochemical features of vanadium in the oil deposits of the Dnipro-Donetsk Basin.

Thus, the study of metals, including nickel in oils from different deposits of Ukraine, which provides an opportunity to determine their genetic parameters and environmental consequences of use is an urgent problem, the solution of which will help develop a set of predictive criteria for hydrocarbon accumulation and scientifically prove geological, economic and environmental assessment of their use.

The research aims. Establishment of geochemical features for nickel in oils of deposits of the Dnipro-Donetsk depression which are in operation as well as creation of their classification according to the content of this metal has been elaborated.

2. Methods

Actual basis of the research is the results of analysis for the metal content in oils from 36 fields: Bakhmachske, Prylukske, Krasnozayarske, Kachalivske, Kremenivske, Karaikozovske, Korobochkynske, Kulychykhinske, Lipovodolynske, Monastyryshchenske, Matlakhivske, Malosorochynske, Novo-Mykolaivske, Perekopivske, Prokopenkivske, Radchenkovske, Raspashnovske, Sofiivske, Sukhodolivske, Solontsivske, Solokhivske, Talalaivske, Trostianetske, Turutynske, Zakhidno-Kharkivtsivske, Shchurynske, Yuriivske, Yaroshivske, Khukhrianske, Sahaidatske #1, Sahaidatsk #13, Kybytsivske #5, Kybytsivske #51, Kybytsivske #52, Kybytsivske #56, Kybytsivske #1. Investigations of oil samples from these deposits over nickel content were performed using X-ray fluorescence analysis by means of the energy-dispersive spectrometer "Octopus" SEF 01. Spectrum accumulation time is 600 s. Samples preparation as well as their analysis were carried out according to the standard ASTM D 4927 “Determination of the elemental composition for the components of lubricants by means of X-ray fluorescence spectroscopy with a dispersion of wavelength”. The following samples served as standard ones for metal impurities: PM 23 (DSZU 022.122-00) MSO 0243: 2001 with certified values of Cd, Mn, Pb, Zn; PM 24 (DSZU 022.123-00) MSO 0244: 2001 with certified values of Fe, Co, Cu, Ni; RM 26 (DSZU 022.125-00) MSO 0246: 2001 with certified values of V, Mo, Ti, Cr. Thus, 30 oil samples overall were analyzed from each of the 36 fields. Then the values of nickel and other indicators were normalized by the expression as follows:

$$X_{i\ norm.} = (X_i - X_{i\ min}) / (X_{i\ max} - X_{i\ min}),$$

where $X_{i\ norm.}$ – normalized unit value of oil sample from a specific deposit; X_i – unit value of oil sample from a specific deposit; $X_{i\ min}$ – minimum value of oil sample from a specific deposit; $X_{i\ max}$ – maximum value of oil sample from a specific deposit.

Thus, normalized values of oil samples from each deposit were processed using the statistics tool kit, which performed the calculation of descriptive statistics, correlation, regression, cluster analysis as well as graphical visualization of the study results.

3. Results and discussions

The average content of vanadium in the oil of the considered deposits is 5.65ppm±1.47 with a confidence interval of 0.95, the sample variance is 77.93, the standard deviation is 8.83, the median value is 1.01ppm, the kurtosis is equal to 1.44, the asymmetry is 1,58. According to the results of the Kolmogorov-Smirnov and Shapiro-Wilk tests, the distribution of the values for the average vanadium content in the oil sample for all considered fields complies with the log-normal distribution. At the same time, a more complicated distribution is observed for samples from individual deposits. It turned out that for the majority of deposits (64% of cases for the considered samples), the density distribution of the vanadium content complies with the log-normal distribution, while for other samples the density distribution complies with the normal distribution. Establishing the distribution law is of great genetic importance, since the conditions for the normal and log-normal distribution laws occurrence are determined by the implementation of various mechanisms of formation. The log-normal distribution is formed as a result of the action of a single or a very limited number of factors that differ significantly in their influence on the final result. The normal distribution according to the central limit theorem describes geochemical processes that occur under the influence of many independent factors that are similar in their contribution to the final result.

The minimum average content of vanadium is equal to 0.02ppm for the oils of the Karaikozovske, Korobochkynske, and Zakhidno-Kharkivtsivske Kachanivske deposits. Maximum average value for this indicator reaches out 31ppm and describes the oil of the Kybytsivske #51 deposit.

According to the results of the correlation and regression analysis and taking into account the Chaddock scale in the oil samples from the considered deposits, it was established the presence of a very weak correlation between the content of vanadium and nickel (correlation coefficient is 0.08), asphaltenes (correlation coefficient is 0.02), paraffins (correlation coefficient is 0.09), resin (correlation coefficient is 0.24), oil viscosity values (correlation coefficient is 0.15); very weak inverse correlation between the content of vanadium and iron (correlation coefficient is -0.13), the average thickness of the productive horizon (correlation coefficient is -0.13); weak direct correlation between the content of vanadium and the temperature of the oil boiling (correlation coefficient is 0.3), the total content of metals Ni, V, Zn, Cr, Mn, Co, Fe, Hg, Al (correlation coefficient is 0.45); average direct correlation of vanadium and zinc content (correlation coefficient is 0.59), manganese (correlation coefficient is 0.61), oil density values (correlation coefficient is 0.52), average inverse correlation of vanadium content and current temperature of productive horizon (correlation coefficient is -0.53), current depth of the productive horizon (correlation coefficient is -0.67); strong direct correlation of the vanadium content and sulfur in oil (correlation coefficient is 0.77), mercury (correlation coefficient is 0.85), aluminum (correlation coefficient is 0.86), chromium (correlation coefficient is

0.88) strong reverse correlation between vanadium content and values of current pressure within productive horizons (correlation coefficient is -0.7), formation water mineralization from productive horizons (correlation coefficient is -0.72), density of formation water from productive horizons (correlation coefficient is -0.87); very strong direct correlation between the vanadium content and cobalt in oil (correlation coefficient is 0.91).

The calculated linear regression equations (Table 1) are indicated below and their curves are shown in Fig. 1 – 22 respectively.

Table 1 – Linear regression equations between nickel content as well as geochemical and geological-technological parameters of oil

$V = 0.1664 + 0.0886 \times Ni$	between vanadium and nickel content
$V = 0.0391 + 0.6799 \times A$	between vanadium and asphaltenes content
$V = 0.1436 + 0{,}1351 \times C$	between vanadium and paraffin content
$V = 0.1119 + 0.3433 \times Re_{oil}$	between vanadium and resin content
$V = 0.1276 + 0.1764 \times \eta_{oil}$	between vanadium and oil viscosity
$V = 0.1976 - 0.2099 \times Fe$	between vanadium and iron content
$V = 0.2024 - 0.2183 \times m$	between vanadium and deposit thickness
$V = 0.0559 + 0.4366 \times T_{init.\ boil.\ point}$	between vanadium and oil boiling temperature
$V = 0.048 + 0.6462 \times Me_{total}$	between vanadium and total metal content
$V = 0.0025 + 0.6243 \times Zn$	between vanadium and zinc content
$V = -0.0052 + 0.8485 \times Mn$	between vanadium and manganese content
$V = -0.0858 + 0.6185 \times \rho_{oil}$	between vanadium and oil density
$V = 0.4491 - 0.496 \times T$	between vanadium and the current temperature of the deposits
$V = 0.4956 - 0.6276 \times h$	between vanadium and depth of productive horizon
$V = -0.0197 + 0.798 \times S$	between vanadium and sulfur content
$V = 0.0494 + 1.0316 \times Hg$	between vanadium and mercury content
$V = 0.0321 + 0.9097 \times Al$	between vanadium and aluminum content
$V = 0.0417 + 0.9041 \times Cr$	between vanadium and chromium content
$V = 0.5339 - 0.691 \times P$	between vanadium and current pressure
$V = 0.5449 - 0.7806 \times M_{layered\ water}$	between vanadium and mineralization of formation water
$V = 0.5449 - 0.7806 \times \rho_{layered\ water}$	between vanadium and density of formation water from the productive horizon
$V = 0.0537 + 0.9385 \times Co$	between vanadium and cobalt content

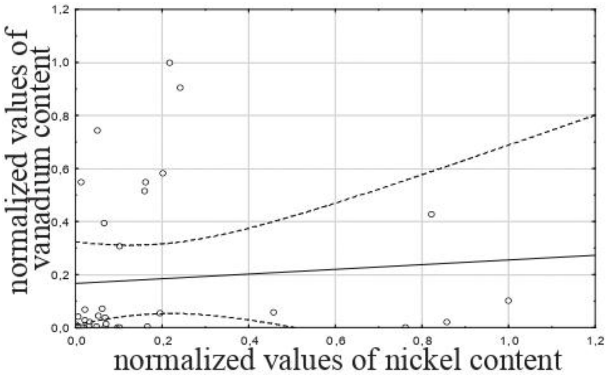


Figure 1 – Curves of the linear regression equation between the content of nickel and vanadium

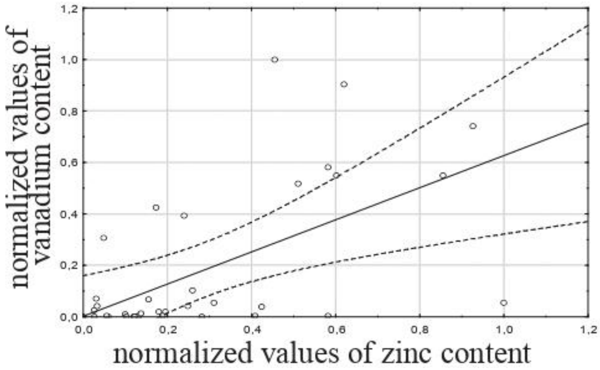


Figure 2 – Curves of the linear regression equation between nickel and zinc content

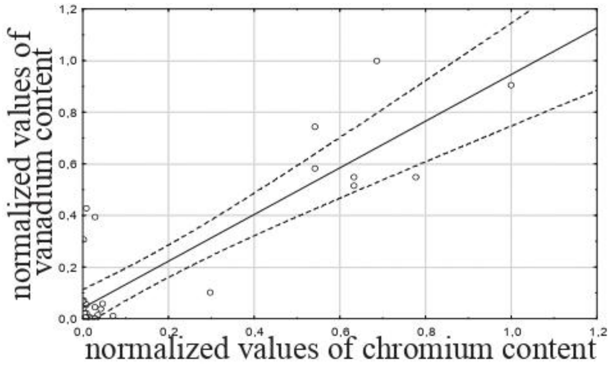


Figure 3 – Curves of the linear regression equation between nickel and chromium content

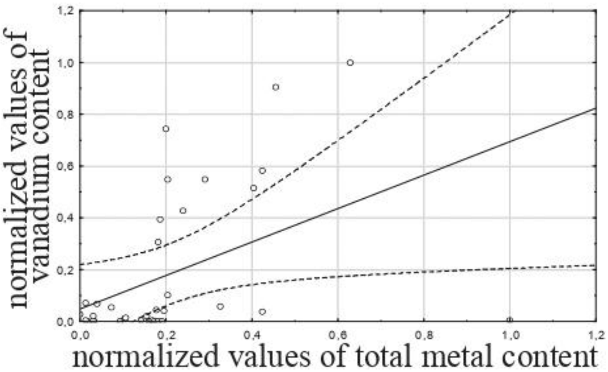


Figure 4 – Curves of the linear regression equation between nickel and total metal content

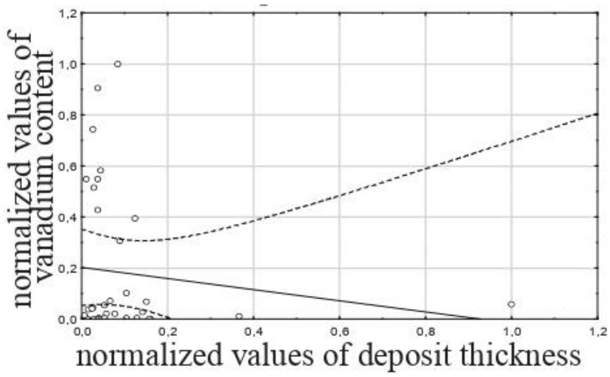


Figure 5 – Curves of the linear regression equation between nickel and deposits thickness

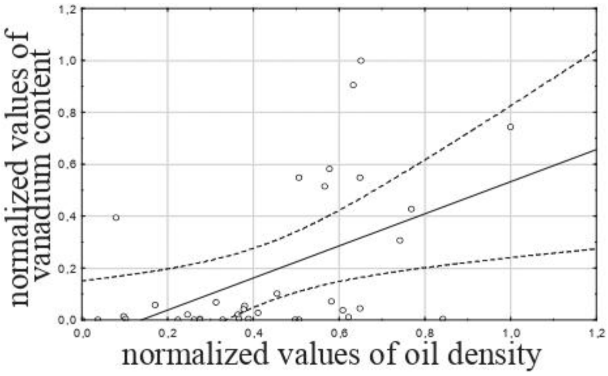


Figure 6 – Curves of the linear regression equation between nickel and oil density

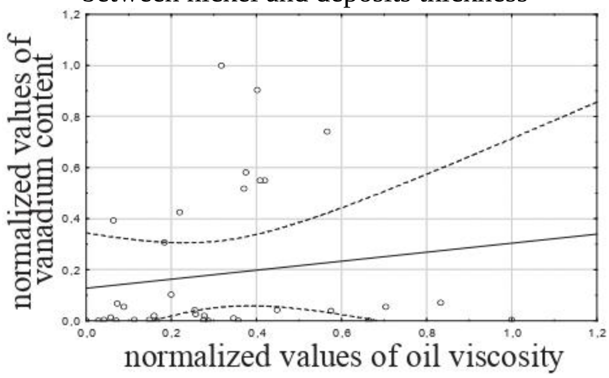


Figure 7 – Curves of the linear regression equation between nickel and oil viscosity

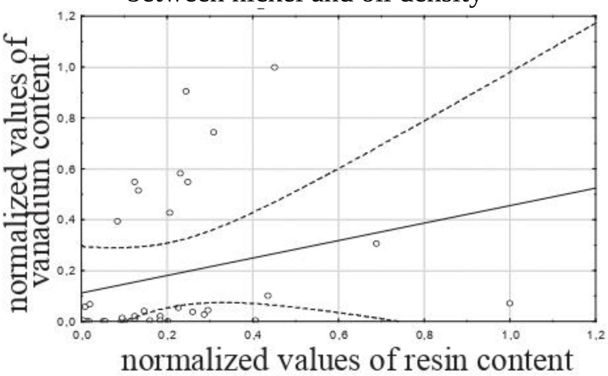


Figure 8 – Curves of the linear regression equation between nickel and resin content

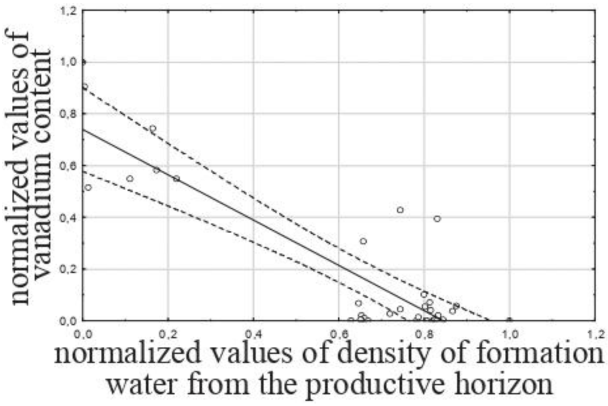


Figure 9 – Curves of the linear regression equation between nickel and density of formation water from the productive horizon

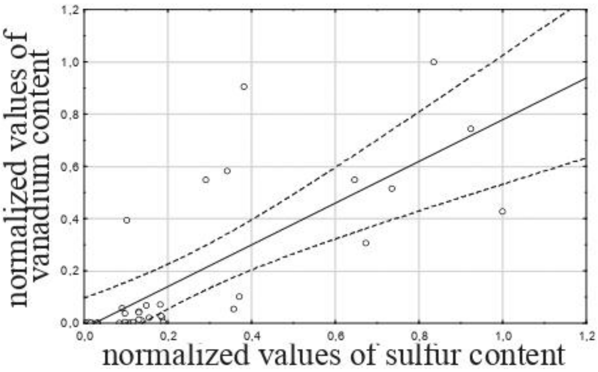


Figure 10 – Curves of the linear regression equation between nickel and sulfur content

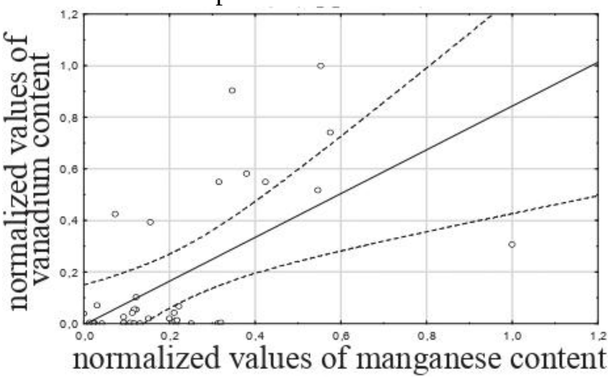


Figure 11 – Curves of the linear regression equation between nickel and manganese content

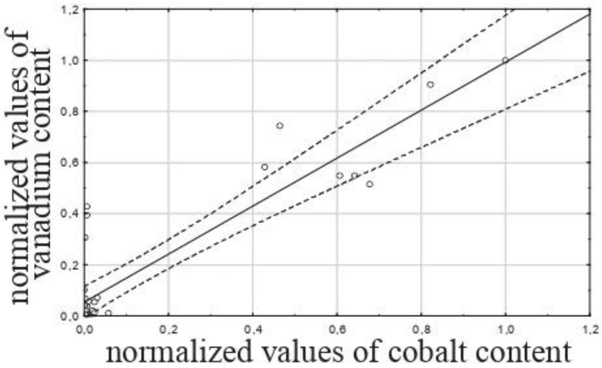


Figure 12 – Curves of the linear regression equation between nickel and cobalt content

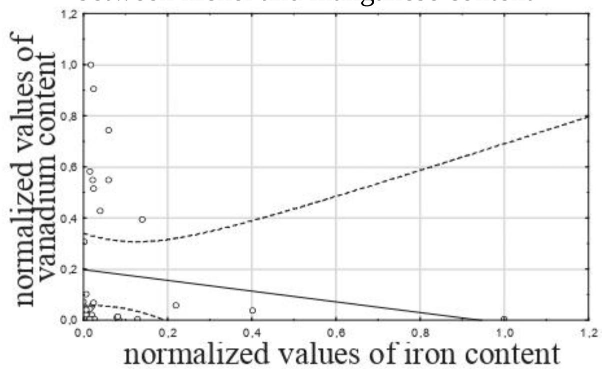


Figure 13 – Curves of the linear regression equation between nickel and iron content

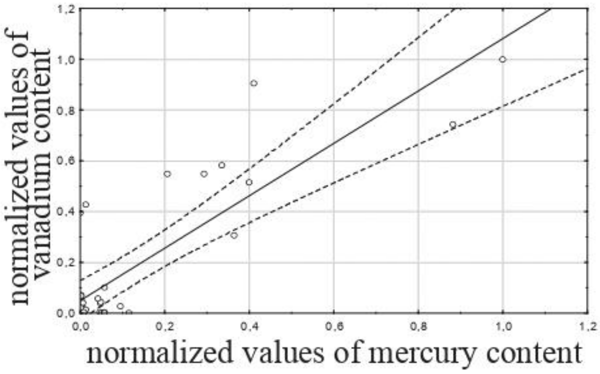


Figure 14 - Curves of the linear regression equation between nickel and mercury content

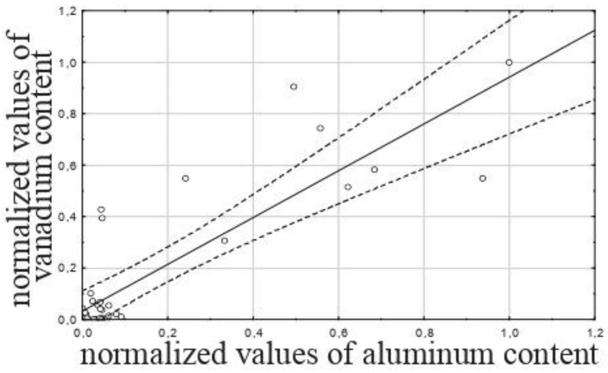


Figure 15 - Curves of the linear regression equation between nickel and aluminum content

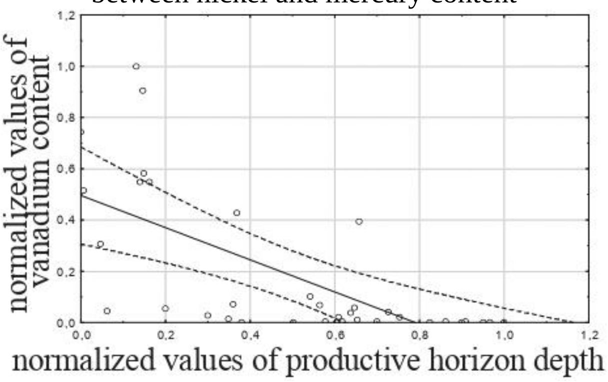


Figure 16 – Curves of the linear regression equation between nickel and productive horizon depth

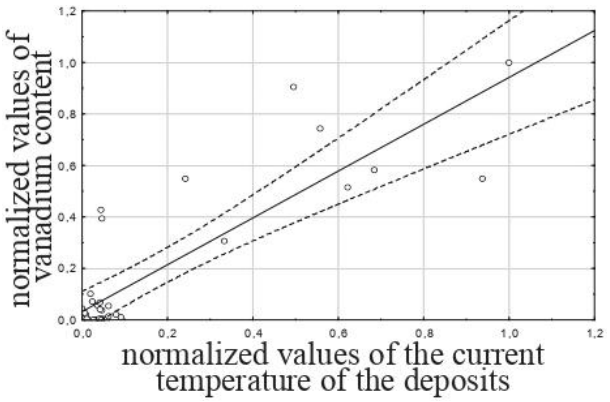


Figure 17 – Curves of the linear regression equation between nickel and the current temperature of the deposits

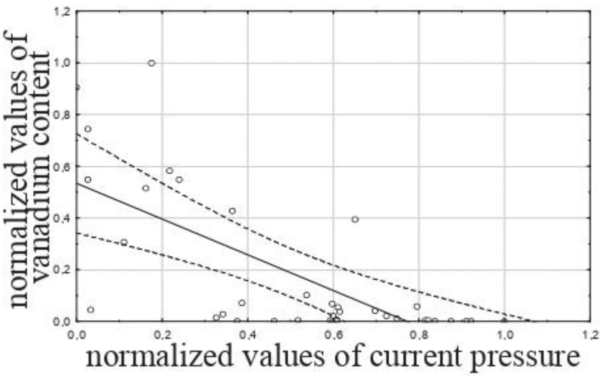


Figure 18 - Curves of the linear regression equation between nickel and current pressure

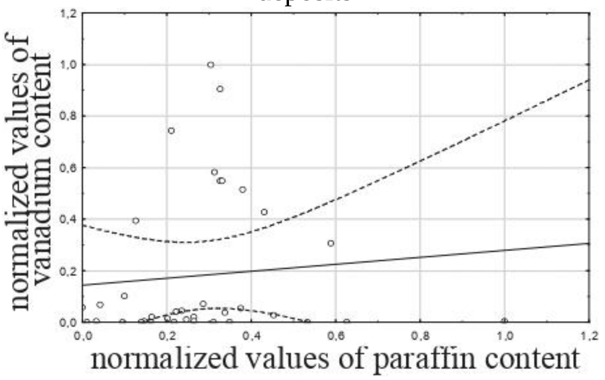


Figure 19 - Curves of the linear regression equation between nickel and oil boiling temperature

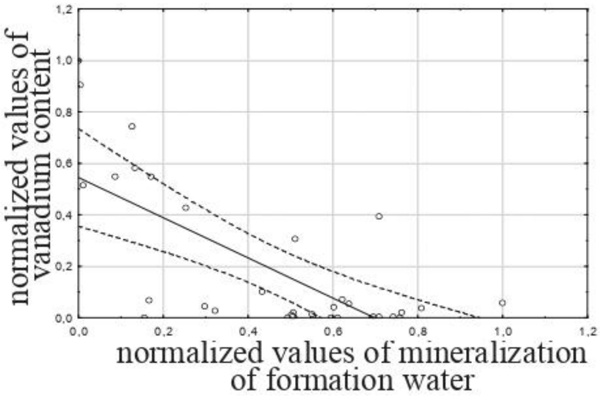


Figure 21 - Curves of the linear regression equation between nickel and mineralization of formation water

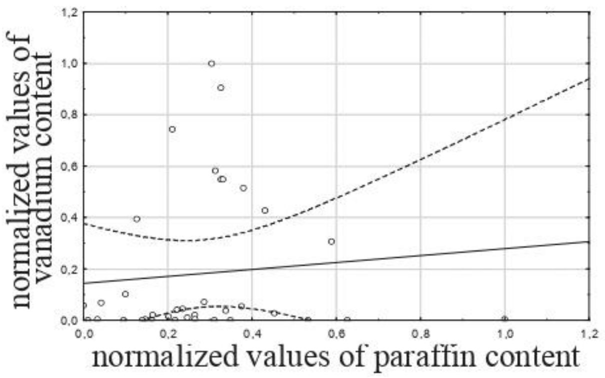


Figure 20 - Curves of the linear regression equation between nickel and paraffin content

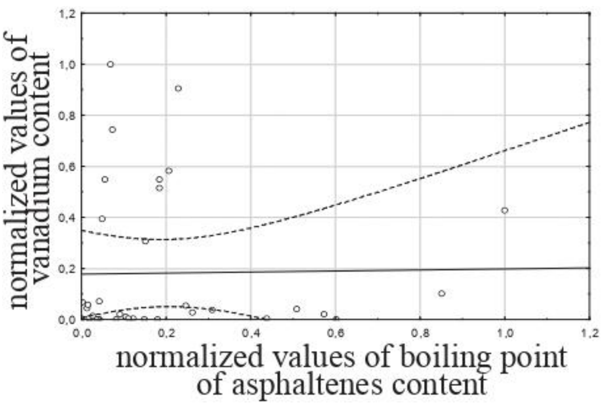


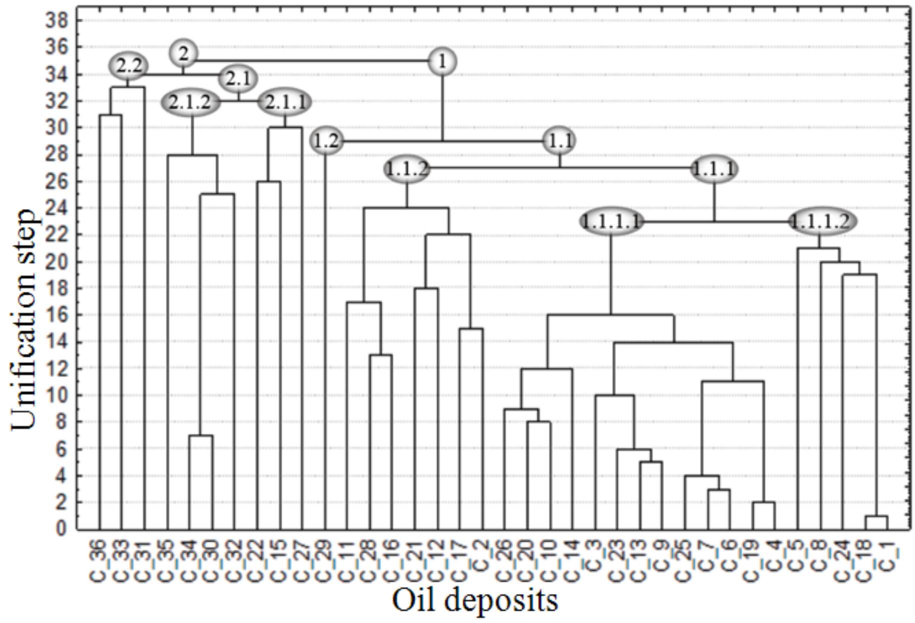
Figure 22 - Curves of the linear regression equation between nickel and asphaltenes content

As a result of previous studies [23], the method of weighted centroid cluster analysis has been proven as the most suitable for the classification elaboration of oil deposits of the Dnipro-Donetsk depression according to the content of metals taking into account various approaches of previous studies. In the process of its implementation, a dendrogram is made up (Fig. 23), which reflects the mutual natural hierarchy of the analyzed deposits by vanadium concentration.

On the dendrogram of clustering for coal seams by vanadium content (Fig. 23), seven stable clusters were identified: 1.1.1.1, 1.1.1.2, 1.1.2, 1.2, 2.1.1, 2.1.2 і 2.2.

Cluster 1.1.1.1 is formed by the deposits as follows: Karaikozovske, Korobochkynske, Zakhidno-Kharkivtsivske, Kachalivske, Sukhodolivske, Lipovodolynske, Novo-Mykolaivske, Trostianetske, Krasnozaiarske, Perekopivske, Shchurynske, Solontsivske, and Monastyryshchenske with an abnormally low vanadium content of 0.02 ppm (Karaikozovske, Korobochkynske and Zakhidno-Kharkivtsivske) up to 0.17 ppm (Monastyryshchenske deposit), while the average value of this indicator is 0.08 ppm.

Cluster 1.1.1.2 comprises deposits as follows: Kulychykhinske, Turutynske, Bakhmachske, Sofiivske and Kremenivske with a low content of 0.32 ppm (Kulychikhinske deposit) - 0.82 ppm (Kremenivske deposit), with an average value of 0.56 ppm.



1, 2, 1.1, 1.2, 2.1, 2.2, 2.3 – clusters; Oil deposits: 1 – Bakhmachske, 2 – Prylukske, 3 – Krasnozaiarske, 4 – Kachalivske, 5 – Kremenivske, 6 – Karaikozovske, 7 – Korobochkynske, 8 – Kulychykhinske, 9 – Lipovodolynske, 10 – Monastyryshchenske, 11 – Matlakhivske, 12 – Malosorochynske, 13 – Novo-Mykolaivske, 14 – Perekopivske, 15 – Prokopenkivske, 16 – Radchenkovske, 17 – Raspashnovske, 18 – Sofiivske, 19 – Sukhodolivske, 20 – Solontsivske, 21 – Solokhivske, 22 – Talalaivske, 23 – Trostianets'ke, 24 – Turutynske, 25 – Zakhidno-Kharkivtsivske, 26 – Shchurynske, 27 - Yuriivske, 28 – Yaroshivske, 29 – Khukhrianske, 30 – Sahaidatske #1, 31 – Sahaidatske #13, 32 – Kybytsivske #5, 33 – Kybytsivske #51, 34 – Kybytsivske #52, 35 – Kybytsivske #56, 36 – Kybytsivske #1

Figure 23 - Dendrogram of the clustering results performed by means of the weighted centroid method of vanadium content in oil deposits

Cluster 1.1.2 is represented by the following deposits: Matlakhovske, Yaroshivske, Radchenkovske, Prylutske, Raspashnovskyi, Solokhivskyi and Malosorochynskyi with a concentration below the average value of 1.2 ppm (Matlakhovske deposit) - 2.17 ppm (Malosorochynske deposit), the average content for the cluster is 1.64 ppm.

The average content has the Khukhrianske deposit of cluster 1.2 with a value of 3.8 ppm.

Cluster 2.1.1 is formed by the Yuriivske, Talalaivske, and Prokopenkivske deposits with above-average values fall between 9.5 ppm (Yuryivske deposit) and 13.2 ppm (Prokopenkivske deposit), with an average cluster concentration of 11.63 ppm.

The following deposits have a high content value: Kybytsivske #5, Sahaidatske #1, Kybytsivske #52 and Kybytsivske #56 of cluster 2.1.2 with values of 16.0 ppm (Kybytsivske # 5 deposit) – 18.0 ppm (Kybytsivske # 56 deposit), average value for the cluster equals to 17.0 ppm.

Cluster 2.2 is represented by deposits as follows: Sahaidatske #13, Kybytsivske #1 and Kybytsivske #51 with abnormally high vanadium content that falls between 23.0 ppm (Sahaydatske deposit #13) and 31.0 ppm (Kybytsivske deposit #51), with an average value for the cluster of 27.33ppm.

4. Conclusions

The conducted studies allow to form the following conclusions:

- vanadium content in oil samples from 36 deposits of the most significant oil and gas region of Ukraine, i.e. the Eastern oil and gas region, shows significant variations (the difference in significant average concentrations by sampling from the deposits is more than in three orders of magnitude) for an average value of 5.65±1.47 ppm. Considering the vanadium concentration for fundamental scientific advances in the field of oil origin, the obtained results may indirectly indicate the implementation of several genetic models of its formation within this region.

- Despite the significant variability of the strong correlation for the vanadium content with other geochemical and geological-technological parameters, it is necessary to take into account their statistically significant nature. This, in turn, allows to identify a group genetically and/or paragenetically related to the accumulation of vanadium in oil from all the parameters considered in the study (Co, Al, Hg, Cr, S, Zn, Mn, Ni concentrations; total content of elements V, Zn, Cr, Mn, Co, Fe, Hg, Al, density and viscosity values of oil).

- The established very weak correlation between the vanadium content and asphaltenes, resins, paraffins (high molecular weight compounds) on the one hand, as well as strong correlation with the sulfur content in the oils of the considered deposits on the other hand, indicates the leading role of the main vanadium concentrators for low molecular weight sulfur-containing components of the oil system (thiophyll sulfides, thioethers as well as dithioethers) in deposits of the region.

- According to the results of the cluster analysis, the sample average values of vanadium concentrations that vary significantly between individual deposits or groups of deposits within the established ranges could be interpreted in terms of qualitative assessment as: abnormally low; low; below average; average; above average; high; abnormally high. The implementation of such an approach makes it possible to visually compare and interpret in geological terms all various scales and various indicators of oil deposits obtained in experimental study.

The scientific importance of the study results is the development of a natural classification for oil deposits according to the vanadium content, identification of typomorphic features of the oils from the considered deposits as well as definition that the heteroatomic low-molecular sulfur-containing components of the petroleum system are the main carriers and concentrators of vanadium.

The practical importance of the study results is detemining the average concentration and the possibility of the vanadium content forecasting in oils of the deposits using regression equations obtained in the present paper.

REFERENCES

1. Shpirt, M.Ya., Nukenov, D.N., Punanova, S.A., Visaliev, M.Ya. (2013), Printsipyi polucheniya soedineniy tsennyih metallov iz goryuchih iskopaemyih [Principles of obtaining compounds valuable metals from fossil fuels], Himiya tverdogo topliva, no. 2, pp. 3-8.

2. Raja, B.V.R. (2007), Vanadium market in the world. Steelworld, 2007, V.13, no. 2, pp. 19-22.

3. Barwise, A.J.G. (1990), Role of nickel and vanadium in petroleum classification, Energy Fuels, 1990, no. 4(6), pp. 647-652.

4. Shnyukov, E.F., Gozhik, P.F., Krayushkin, V.A. (2007), Vanadiy i nikel v prirodnyih neftyah Azii, Afriki, Evropyi, Severnoy i Yuzhnoy Ameriki [Vanadium and nickel in natural oils of Asia, Africa, Europe, North and South America], Dopovidi Natsionalnoi akademii nauk Ukrainy 2007, no. 3, pp. 137-141.

5. Suhanov, A.A., Petrova, Yu.E. (2008), Resursnaya baza poputnyih komponentov tyazhelyih neftey Rossii. Neftegazovaya geologiya [Resource base of associated components of heavy oils in Russia], Teoriya i praktika, no.3, pp. 1-11.

6. Yakutseni, S.P. (2010), Glubinnaya zonalnost v obogaschennosti uglevodorodov tyazhelyimi elementami-primesyami. Neftegazovaya geologiya [Deep zoning in the enrichment of hydrocarbons in heavy elements], Teoriya i praktika, no. 5(2). pp. 1-7.

7. Akpoveta, O. V., Osakwe, S. A. (2014), Determination of Heavy Metal Contents in Refined Petroleum, IOSR Journal of Applied Chemistry, 2014, no. 7(6), pp.1-2.

8. Hlibishin, Yu. Ya., Mohamad Shakir Abd Al-Ameri, Grinishin, O. B. (2013), Doslidzhennya distilyatnoyi chastini visokosirkovoyi nafti Orhovitskogo naftovogo rodovischa [Investigation of the distillate part of high-sulfur oil of Orkhovytsia oil field], Visnik Natsionalnogo universitetu "Lvivska politehnika", no.761, pp. 462-465.

9. Wilberforce, J.O. (2016), Profile of Heavy Metals in Crude Oil Commonly Consumed for Medicinal Purposes in Abakaliki, IOSR Journal of Pharmacy and Biological Sciences, no. 11(3). pp. 43-44.

10. Ishkov, V.V., Kozii, Ye.S. (2014), *O klassifikatsii ugolnyih plastov po soderzhaniyu toksichnyih elementov s pomoschyu klasternogo analiza* [About classification of coal seams by the content of toxic elements using cluster analysis], Zbirnyk naukovykh prats Natsionalnoho hirnychoho universytetu, no.45, pp. 209 -221.

11. Koziy, E.S., Ishkov, V.V. (2017), *Klasyfikatsiia vuhillia osnovnykh robochykh plastiv Pavlohradsko-Petropavlivskoho heoloho-promyslovoho raionu po vmistu toksychnykh i potentsiino toksychnykh elementiv* [Coal classification of main working seams of Pavlohrad-Petropavlivka geological and industrial district on content of toxic and potentially toxic elements], Zbirnyk naukovykh prats "Heotekhnichna mekhanika", no. 136, pp. 74-86.

12. Kozar, M.A., Ishkov, V.V., Kozii, Ye.S., Strielnyk, Yu.V. (2021), *Toksychni elementy mineralnoi ta orhanichnoi skladovoi vuhillia nyzhnoho karbonu Zakhidnoho Donbasu* [Toxic elements of mineral and organic composition of lower carbon coal Western Donbas], Proceedings of Conference: Heolohichna nauka v nezalezhnii Ukraini, Kyiv, pp.55-58.

13. Ishkov, V.V., Koziy, E.S. (2021), *Nakoplenie Co i Mn na primere plasta s5 Zapadnogo Donbassa kak rezultat ih migratsii iz kor vyivetrivaniya ukrainskogo kristallicheskogo schita* [Accumulation of Co and Mn using the example of formation c_5 of Western Donbass as a result of their migration from the weathering crust of the Ukrainian crystal shield], Proceedings of the International Conference: Rossyipi i mestorozhdeniya kor vyivetrivaniya XXI veka: zadachi, problemyi, resheniya, pp. 160-162.

14. Kozar, M.A., Ishkov, V.V., Kozii, Ye.S., Pashchenko P.S. (2020), "New data about the distribution of nickel, lead and chromium in the coal seams of the Donetsk- Makiivka geological and industrial district of the Donbas". Journ. Geol. Geograph. Geoecology, no. 29(4), pp. 722-730. http://doi: 10.15421/112065

15. Koziy, E.S. (2018), *Myshiak, berylii, ftor i rtut u vuhilli plasta s8 v shakhty "Dniprovska" Pavlohradsko-Petropavlivskoho heoloho-promyslovoho raionu* [Arsenic, beryllium, fluorine and mercury in the coal of the layer $c_8^в$ of the "Dniprovska" mine of Pavlogradsko-Petropavlovskiy geological and industrial district], Visnyk Dnipropetrovskoho universytetu. Heolohiia-Heohrafiia, no. 26(1), pp. 113-120. https://doi.org/10.15421/111812

16. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S. (2021), Osoblyvosti vplyvu osnovnykh heoloho-tekhnolohichnykh pokaznykiv naftovykh rodovyshch Ukrainy na vmist vanadiiu [Peculiarities of influence of main geological-technological indicators of oil deposits of Ukraine on vanadium content], Materialy II Mizhnarodnoi naukovoi konferentsii «Suchasni problemy hirnychoi heolohii ta heoekolohii», pp. 115-120.

17. Kozii Ye.S. (2021). Toxic elements in the c1 coal seam of the Blahodatna mine of Pavlohrad-Petropavlivka geological and industrial area of Donbas. Geo-Technical Mechanics, no158. pp.103-116. https://doi.org/10.15407/geotm2021.158.103

18. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S. (2021), Osoblyvosti vplyvu osnovnykh heoloho-tekhnolohichnykh pokaznykiv Kachalivskoho, Kulychykhinskoho, Matlakhovskoho, Malosorochynskoho ta Sofiivskoho rodovyshch na vmist vanadiiu u nafti [Features of the influence of the main geological and technological indicators of Kachalivske, Kulychykhinske, Matlakhovske, Malosorochynske and Sofiyivske deposits on the vanadium content in oil], Materialy XIX Mizhnarodnoi konferentsii molodykh uchenykh «Heotekhnichni problemy rozrobky rodovyshch», pp.84-88.

19. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S. (2021), Rezultaty klasternoho analizu rodovyshch nafty Dniprovsko-Donetskoi zapadyny za vmistom vanadiiu [Results of cluster analysis of oil fields of the Dnipro-Donetsk basin by vanadium content], Materialy IKh Vseukrainskoi naukovo-tekhnichnoi konferentsii «Molod, nauka ta innovatsii», pp. 338-339.

20. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S. (2021), Osoblyvosti vplyvu heoloho-tekhnolohichnykh pokaznykiv deiakykh rodovyshch na vmist vanadiiu u nafti [Features of the influence of geological and technological indicators of some deposits on the content of vanadium in oil], Materialy VIII Vseukrainskoi naukovo-praktychnoi konferentsii studentiv, aspirantiv ta molodykh vchenykh «Perspektyvy rozvytku hirnychoi spravy ta ratsionalnoho vykorystannia pryrodnykh resursiv», pp. 43-46.

21. Yerofieiev A.M., Ishkov V.V., Kozii Ye.S., Bartashevskiy S. Ye. (2021). Geochemical features of nickel in the oils of the Dnipro-Donetsk basin. Geo-Technical Mechanics, no 160. pp.17-30. https://doi.org/10.15407/geotm2021.160.017

22. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S. (2021), Vplyv osnovnykh heoloho-tekhnichnykh pokaznykiv Kachalivskoho, Kulychykhinskoho, Matlakhovskoho, Malosorochynskoho ta Sofiivskoho rodovyshch na vmist vanadiiu u nafti [Influence of main geological and technical indicators of Kachalivskyi, Kulychykhinskyi, Matlakhovskyi, Malosorochynskyi and Sofiivskyi deposits on vanadium content in the oil], Materialy mizhnarodnoi naukovo-tekhnichnoi konferentsii «Ukrainskyi hirnychyi forum», pp. 177-185.

23. Yerofieiev, A.M., Ishkov, V.V., Kozii, Ye.S., Bartashevskiy, S.Ye. (2021), Doslidzhennia metodiv klasterizatsii rodovyshch nafty Dniprovsko-Donetskoi zapadyny z metoiu stvorennia yikh klasyfikatsii za vmistom metaliv (na prykladi V) [Research of clusterization methods of oil deposits in the Dnipro-Donetsk depression with the purpose of creating their classification by metal content (on the vanadium example)], Naukovi pratsi Donetskoho natsionalnoho tekhnichnoho universytetu, Seriia: «Hirnycho-heolohichna», pp. 83-93.

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ОСОБЛИВОСТІ ГЕОХІМІЇ ВАНАДІЮ У НАФТАХ РОДОВИЩ СХІДНОГО НАФТОГАЗОНОСНОГО РЕГІОНУ УКРАЇНИ

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Анотація. Приведені результати багаторічних досліджень геохімічних особливостей ванадію у нафті 36 родовищ Східного нафтогазоносного регіону України. За результатами кореляційного та регресійного аналізів встановлено характер та форми зв’язку між вмістом ванадію у нафті і нікелю, цинку, хрому, марганцю, кобальту, заліза, ртуті, алюмінію та сумарного вмісту цих металів; середньої потужності продуктивного горизонту; значенням густини нафти; величиною в'язкості нафти; вмістом смоли; щільністю пластової води з продуктивного горизонту; вмістом сірки в нафті; сучасної глибини продуктивного горизонту; сучасної температури продуктивного горизонту; сучасного тиску у продуктивному горизонті; температури кипіння нафти; вмісту парафінів; значенню мінералізації пластової води із продуктивного горизонту; вмісту асфальтенів. Наведені розраховані коефіцієнти кореляції, лінійні парні рівняння регресії та їх графіки між цими параметрами. За результатами кластерного аналізу побудовано дендрограму результатів кластеризації зваженим центроїдним методом розглянутих родовищ за вмістом ванадію в нафтах. На підставі результатів кластеризації зваженим центроїдним методом розроблено першу природну класифікацію родовищ східного нафтогазоносного регіону Украйни за вмістом ванадію в нафтах. Доведено, що гетероатомні низькомолекулярні сірковмісні компоненти нафтової системи є основними концентраторами ванадію у нафті досліджуваних родовищ. Показано, що за результатами кластерного аналізу вибіркові середні значення концентрацій ванадію, що значуще відрізняються між окремими родовищами чи групами родовищ у встановлених рядах можна інтерпретувати в термінології якісної оцінки, як: аномально низькі; низькі; нижче за середні; середні; вище за середні; високі; аномально високі. Реалізація такого підходу дає можливість наочно зіставити та інтерпретувати у геологічних поняттях експериментально отримані всі різномасштабні та різноманітні показники нафтових родовищ.

Ключові слова: ванадій, родовища нафти, кластерний аналіз, лінійне рівняння регресії, геохімічні параметри нафти, коефіцієнт кореляції.

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