NICKEL IN OIL DEPOSITS OF THE DNIPRO-DONETSK DEPRESSION (UKRAINE)

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The article contains the results of long-term research of geochemical features of nickel in oils from 36 deposits of the main oil and gas region of Ukraine - the Dnipro-Donetsk basin. These are such deposits: Bakhmachske, Prylukske, Krasnozayarske, Kachalivske, Kremenivske, Karaykozovske, Korobochkynske, Kulychykhinske, Lipovodolynske, Monastyryshchenske, Matlakhivske, Malosorochynske, Novo-Mykolayivske, Perekopivske, Prokopenkivske, Radchenkovske, Raspashnovske, Sofiivske, Sukhodolivske, Solontsivske, Solokhivske, Talalaivske, Trostyanets'ke, Turutynske, Zakhidno-Kharkivtsivske, Shchurynske, Yuryivske, Yaroshivske, Khukhryanske, Sagaidatske №1, Sagaidatsk №13, Kybytsivske №5, Kybytsivske №51, Kybytsivske №52, Kybytsivske №56, Kybytsivske №1.

The results of correlation and regression analyzes revealed the character and forms of the relationship between the nickel content in oils and vanadium; zinc; chromium; the total content of V, Zn, Cr, Mn, Co, Fe, Hg, Al; average thickness of the productive horizon; oil density values; oil viscosity values; resin content; formation water density from the productive horizon; sulfur content in oil; manganese; cobalt; metal; mercury; aluminum; the current depth of the productive horizon; modern temperature of the productive horizon; modern pressure in the productive horizon; oil initial boiling point temperature; the content of paraffins; salinity values of formation water from the productive horizon; content of asphaltenes. The calculated correlation coefficients, linear pair regression equations and their graphs between these parameters are given. Based on the results of cluster analysis, a dendrogram of the results of clustering by the weighted centroid method of deposits on the nickel content in the oils of the considered deposits was constructed.

Considering the statistically significant character of nickel connections, it is proposed to divide all geochemical and geological-technological parameters into a group of genetically and / or paragenetically related to the accumulation of nickel in oil and a group of negatively associated with increasing nickel in oil. Based on the results of clustering by the weighted centroid method, the first natural classification of deposits by nickel content in oils was developed. It has been proved that asphaltenes are the main nickel concentrators in the oil of the studied deposits. It is shown that according to the results of cluster analysis, the sample averages of nickel concentrations that differ significantly between individual deposits or groups of deposits in the established series can be interpreted in the terminology of qualitative assessment as: abnormally low; low; below average; medium; above average; high; abnormally high. The implementation of this approach makes it possible to visually compare and interpret in geological terms experimentally obtained all different-scale and diverse indicators of oil deposits.

Attention to the problems of accumulation and migration of microelements, in particular nickel 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, above all, gasoline and diesel fuel. It is known, that metals in small quantities are part of the oils of different regions of the world. The 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 deposition of compounds of this metal on the active surface, blocking the pore space and destroying the catalyst structure. In addition, inorganic metal compounds formed during oil refining contribute to high-temperature corrosion of equipment surfaces, reduce the service life of turbojet, diesel and boiler plants, gas corrosion of active elements of gas turbine engines and increase environmentally harmful emissions. However, metals, including rare and rare earth, are valuable by-products, the content of which in oils and residues of their processing may even exceed their content in ore sources [1]. However, in Ukraine, the industrial production of metals (in particular, nickel) from crude oil is still not mastered, although in the world practice of oil refining there are technologies that allow for the simultaneous production of concentrates with a high content of various metals. In particular, about 8% of the world's vanadium production is obtained from crude oil abroad, and in some countries this percentage 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 especially priority in industrial and environmental importance - vanadium, mercury, cobalt, nickel, iron, manganese, aluminum, titanium, chromium and zinc. This work is devoted to the results of research of the geochemical characteristics of nickel in the oils of the main existing oil deposits of the main oil and gas region of Ukraine - the Dnipro-Donetsk basin.

One of the first systematization of oils according to their general characteristics of metal content was carried out by Barwise A. J. G. in 1990. He considered the chemical composition, physical properties and content of metals in oil samples [3]. Later in 2007, Shniukov Ye.F. 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 A.A. considered the current state of assessment of reserves of related oil components (including heavy metals) as sources of high quality liquid metal raw materials [5]. In 2010, Yakutseni S.P. published the results of a study of the relationship between the deep zonation 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. Already in 2014, Akpoveta O. V. analyzed the content of heavy metals in petroleum products from the deposits of Nigeria (Agbor) [7]. The authors note that the high content of heavy metals in oils can pose a serious environmental threat. It should be noted that not all heavy metal impurities in oils have 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 physicochemical 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. A little later, Wilberforce J.O. 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 atomic absorption spectrophotometry. As a result of the study, the average concentration of metals was determined, indicating their impact on the human body. Earlier [10-35], the authors have already considered some geochemical features of vanadium in oils from the deposits of the Dnipro-Donetsk basin and substantiated the creation using clustering methods of natural classification of oil deposits by metal content on the example of vanadium and spatial distribution of impurity elements in coal seams of Donbas. At the same time, research aimed at studying the geochemical characteristics of nickel in the oils of the Dnipro-Donetsk basin is absent.

Thus, the study of metals, including nickel in oils from different deposits of Ukraine, which provides an opportunity to determine their genetic characteristics 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 sound geological, economic and environmental assessment of their use.

Establishment of geochemical features of nickel in oils of existing deposits of the Dnipro-Donetsk basin and creation of their classification according to the content of this metal. The factual basis of the work were the results of analyzes of metal content in oils from 36 deposits: Bakhmachske, Prylukske, Krasnozayarske, Kachalivske, Kremenivske, Karaykozovske, Korobochkynske, Kulychykhinske, Lipovodolynske, Monastyryshchenske, Matlakhivske, Malosorochynske, Novo-Mykolayivske, Perekopivske, Prokopenkivske, Radchenkovske, Raspashnovske, Sofiivske, Sukhodolivske, Solontsivske, Solokhivske, Talalaivske, Trostyanets'ke, Turutynske, Zakhidno-Kharkivtsivske, Shchurynske, Yuryivske, Yaroshivske, Khukhryanske, Sagaidatske №1, Sagaidatsk №13, Kybytsivske №5, Kybytsivske №51, Kybytsivske №52, Kybytsivske №56, Kybytsivske №1. Investigations of oil samples from these deposits for nickel content were performed using X-ray fluorescence analysis on the energy-dispersion spectrometer "Octopus" SEF 01. Spectrum accumulation time 600 sec. Analyst - Yerofieiev A.M. Preparation and analysis was carried out according to the standard ASTM D 4927 - Determination of the elemental composition of the components of lubricants by X-ray fluorescence spectroscopy with a dispersion of wavelength. The following samples served as standard samples of 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 were analyzed from each of the 36 deposits. Then the values of nickel and all other indicators were normalized by the formula:

$Xi_{norm.} = (Xi - Xi_{min})/(Xi_{max} - Xi_{min})$,

where $Xi_{norm.}$ – normalized unit value of oil sample from a specific deposit, Xi - unit value of oil sample from a specific deposit, Xi_{min} – minimum value of oil sample from a specific deposit, Xi_{max} – maximum value of oil sample from a specific deposit.

Thus, the normalized values of oil samples from each deposit were processed using the program STATISTICA 11.6, which performed the calculation of descriptive statistics, correlation, regression, cluster analysis and graphical visualization of the results of all studies.

The average Ni content in the oil of the deposits under consideration is 6.88ppm ± 1.67 with a confidence interval of 0.95, sample variance 99.88, standard deviation 9.99, median value is 2.91ppm, kurtosis is 3.63, asymmetry is 2.15. The minimum average Ni content is 0.35ppm for oil from the Kachanovske deposit, and the maximum average value of this indicator of 38.1ppm characterizes the oil from the Khukhryanske deposit.

Based on the results of correlation and regression analysis and taking into account the Chadok scale, the presence of a very weak direct correlation between the contents of nickel and vanadium (correlation coefficient 0.08), zinc (correlation coefficient 0.08), chromium (correlation coefficient 0.05), the total content of V, Zn, Cr, Mn, Co, Fe, Hg, Al (correlation coefficient 0.01), the average thickness of the productive horizon (correlation coefficient 0.2), oil density values (correlation coefficient 0.15), values of oil viscosity (correlation coefficient 0.08), resin content (correlation coefficient 0.12), density of formation water from the productive horizon (correlation coefficient 0.03), sulfur content in oil (correlation coefficient 0.29), very weak inverse correlation between the contents of nickel and manganese (correlation coefficient -0.09), cobalt (correlation coefficient -0.02), iron (correlation coefficient -0.01), mercury (correlation coefficient -0.06), aluminum (correlation coefficient -0.02), modern depth of the productive horizon (correlation coefficient -0.08), modern temperature of the productive horizon (correlation coefficient -0.17), modern pressure in the productive horizon (correlation coefficient -0.04), initial temperature boiling point of oil (correlation coefficient -0.07); the content of paraffins (correlation coefficient -0.05); salinity values of formation water from the productive horizon (correlation coefficient -0.03); high direct correlation between the contents of nickel and asphaltenes (correlation coefficient 0.72).

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

Ni = 0,1592 + 0,0765 x V	between nickel and vanadium content
Ni = 0,1501 + 0,0799 x Zn	between nickel and zinc content
Ni = 0,1655 + 0,0489 x Cr	between nickel and chromium content
Ni = 0,1445 + 0,1379 x Me_{total}	between nickel and total metal content
Ni = 0,1444 + 0,3032 x m	between nickel and thickness of the deposits
Ni = 0,1006 + 0,1675 x ρ_{oil}	between nickel and oil density
Ni = 0,1439 + 0,0949 x η_{oil}	between nickel and oil viscosity
Ni = 0,1441 + 0,1427 x Re_{oil}	between nickel and resin content in the oil
Ni = 0,1588 + 0,0225 x $\rho_{layered\ water}$	between nickel and density of layered water from the horizons
Ni = 0,1051 + 0,2694 x S	between nickel and sulfur content
Ni = 0,1994 - 0,1197 x Mn	between nickel and manganese content
Ni = 0,1756 - 0,0185 x Co	between nickel and cobalt content
Ni = 0,1846 - 0,1534 x Fe	between nickel and iron content
Ni = 0,1796 - 0,0509 x Hg	between nickel and mercury content
Ni = 0,1791 - 0,0364 x Al	between nickel and aluminum content
Ni = 0,2063 - 0,0665 x h	between nickel and depth of development
Ni = 0,2503 - 0,1433 x T	between nickel and the current temperature of the deposits
Ni = 0,1938 - 0,4068 x P	between nickel and current pressure
Ni = 0,1993 - 0,0911 x $T_{boil.\ point}$	between nickel and boiling point of oil
Ni = 0,1910 - 0,0637 x C	between nickel and paraffin content in the oil
Ni = 0,1875 - 0,0311 x $M_{layered\ water}$	between nickel and mineralization of layered water
Ni = 0,0391 + 0,6799 x A	between nickel and asphaltene content in oils

As a result of previous studies [21], we substantiated the method of weighted centroid cluster analysis, as the most optimal for the development of a classification of oil deposits in the Dnipro-Donetsk depression by metal content as free as possible from the subjective approach of researchers. In the process of its realization, a dendrogram was built in Fig. 1, reflecting the mutual natural hierarchy of the deposits under consideration in terms of nickel content. Seven main clusters are identified on the clustering dendrogram. Cluster 1.1.1.1.1 combines Kachalivske, Kulychykhinske, Perekopivske, Shchurynske, Yaroshivske, Korobochkynske, Sagaidatske No. 1 and Zakhidno-Kharkivtsivske oil deposits with a Ni content of 0.35 ppm to 1.57 ppm. In general, the average content of Ni in the cluster is 0.89 ppm, which corresponds to abnormally low values. Cluster 1.1.1.1.2 is formed by Krasnozayarske, Sagaidatske №13, Radchenkovske, Malosorochynske, Talalaivske and Novo-Mykolayivske deposits with Ni content in oils from 2.17 ppm to 3.06 ppm. The average content of Ni in the oils of the deposits of this cluster is 2.67 ppm, which corresponds to the low values of this indicator. Cluster 1.1.1.2 is composed of Karaykozovske, Yuryivske and Lipovodolynske deposits with values of Ni content below average: 4.07 ppm - 4.25 ppm. The average value of Ni content in cluster deposits corresponds to 4.18 ppm. Cluster 1.1.2.1 combines the deposits Kybytsivske №5, Kybytsivske №52 and Monastyryshchenske with Ni contents from 6.4ppm to 6.61ppm. The average content in the cluster is 6.51 ppm, which is not statistically significantly different from the average for all deposits. Cluster 1.1.2.2 is formed by Prylukske, Kybytsivske №56, Kybytsivske №51 and Kybytsivske №1 deposits with Ni content in the range from 7.77 ppm to 9.5 ppm. The average value in the cluster with Ni content is above average and corresponds to 8.47 ppm. Cluster 1.2 is represented by only one field - Raspashnovske with high average concentrations of Ni - 17.6 ppm. Abnormally high Ni content is observed in the oils of the Sukhodolivske, Prokopenkivske, Bakhmachske and Khukhryanske deposits, which form cluster 2, with fluctuations from 29.1 ppm to 38.1 ppm. The values of the average concentration of this metal in the cluster reach 32.83 ppm.

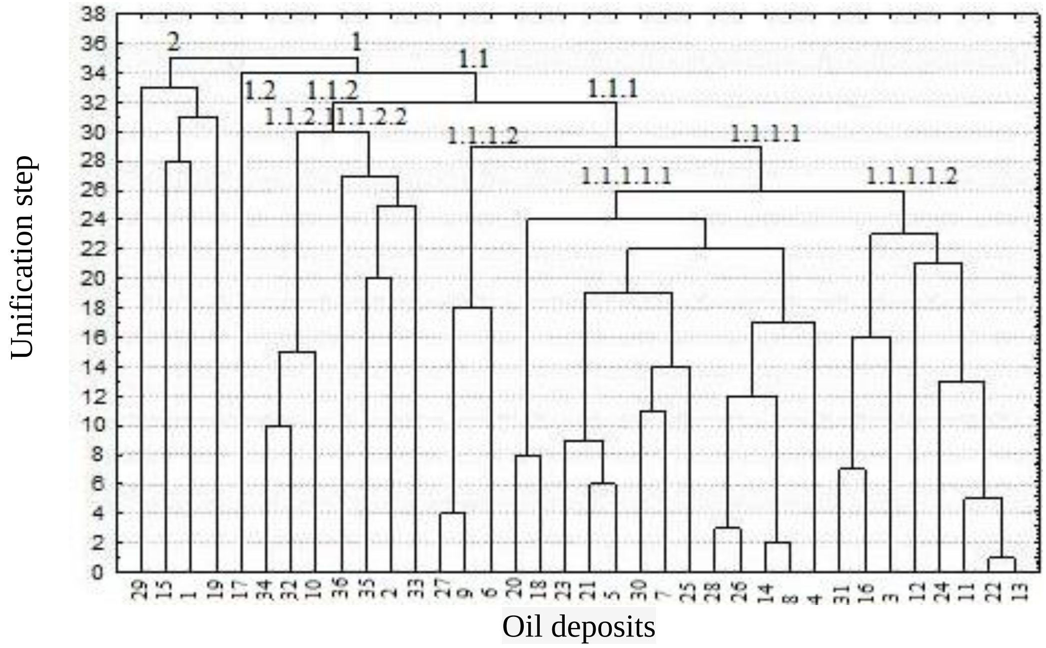

Fig. 1. Dendrogram of the results of clustering by the weighted centroid method of Ni deposits in oil content. Legend: 1, 2, etc. – clusters; Oil deposits: 1 – Bakhmachske, 2 – Prylukske, 3 – Krasnozayarske, 4 – Kachalivske, 5 – Kremenivske, 6 – Karaykozovske, 7 – Korobochkynske, 8 – Kulychykhinske, 9 – Lipovodolynske, 10 – Monastyryshchenske, 11 – Matlakhivske, 12 – Malosorochynske, 13 – Novo-Mykolayivske, 14 – Perekopivske, 15 – Prokopenkivske, 16 – Radchenkovske, 17 – Raspashnovske, 18 – Sofiivske, 19 – Sukhodolivske, 20 – Solontsivske, 21 – Solokhivske, 22 – Talalaivske, 23 – Trostyanets'ke, 24 – Turutynske, 25 – Zakhidno-Kharkivtsivske, 26 – Shchurynske, 27 - Yuryivske, 28 – Yaroshivske, 29 – Khukhryanske, 30 – Sagaidatske №1, 31 – Sagaidatske №13, 32 – Kybytsivske №5, 33 – Kybytsivske №51, 34 – Kybytsivske №52, 35 – Kybytsivske №56, 36 – Kybytsivske №1.

Conclusions. Completed research allow us to formulate the following main conclusions:

1) Nickel contents in oil samples from 36 deposits of the most significant oil and gas province of Ukraine - the Dnipro-Donetsk depression, experience significant variations (the difference in the medium concentration values for a sample of multi-deposits is about two orders of magnitude) with an average value of 6.88ppm ± 1.67. Taking into account the role of nickel concentration for fundamental scientific developments in the field of oil origin, the results obtained indicate heterogeneous mechanisms of its formation in this region.

2) Despite the very weak, in the overwhelming majority of cases, the correlation between the nickel content and other geochemical and geological-technological parameters, it is necessary to take into account their statistically significant character. This in turn allows all parameters to be divided into a group genetically and / or paragenetically related to the accumulation of nickel in oil (vanadium content; zinc; chromium; total content of V, Zn, Cr, Mn, Co, Fe, Hg, Al; average productive capacity horizon; oil density values; oil viscosity values; resin content; formation water density from the productive horizon; sulfur content in oil; asphaltene content in it) and on a group of negatively associated with an increase in nickel content (manganese content; cobalt; iron; mercury; aluminum; current depth of the productive horizon; current temperature of the productive horizon; current pressure in the productive horizon; temperature of the initial boiling point of oil; paraffin content; salinity values of formation water from the productive horizon).

3) The established high direct correlation between the contents of nickel and asphaltenes indicates the role of asphaltenes as the main concentrators of nickel in the oil of the studied fields.

4) Based on the results of cluster analysis, the vibrating mean values of nickel concentrations, which are significantly different from the same deposits and groups of deposits in established ranks, can be interpreted in terms of terminology, such as: abnormally low; low; lower than middle; middle; above average; high; abnormally high. The implementation of this approach makes it possible to visually compare and interpret in geological terms experimentally obtained all different-scale and diverse indicators of oil fields

The scientific importance of the obtained results is in the development of the natural classification of oil deposits by nickel content, the identification of typomorphic features of the oils of the considered deposits and established that exactly asphaltenes from all oil fractions is main carriers and concentrators of nickel.

The practical importance of the results obtained is in establishing the average concentration and the ability to predict the nickel content in the oils of the studied deposits using the calculated regression equations.

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