ORE CONCENTRATIONS OF METALS IN NAPHTHIDES OF HYPERGENESIS ZONE: ASSESSMENT AND ENVIRONMENTAL ASPECT

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ABSTRACT

The study examines the formation of secondary-altered crude oils associated with the processes of modern or ancient hypergenesis. As a result of geological processes during intense upward movement of the earth's crust, oil undergoes physical weathering, inorganic oxidation, washing out with water, biodegradation and sulfurization, and turn into heavy oils and hard bitumen. In zones of hypergenesis, the loss of light fractions occurs and the absolute concentration of trace elements (TE) associated with resinous-asphaltene components, such as V, Ni, Co, Mo, Cr, Cu, etc. sharply increases. In addition, oils absorb elements of variable valence (V, Fe, U) from low-salinity stratal waters. As a result of experimental studies on the interaction of oils with low mineralization waters, which are characteristic of hypergenesis zones, leaching of some elements (e.g., Zn) from oils and absorption of others from contacting waters (for example, concentrations of newly-formed organometallic compounds V and Fe increased by 1.3-12 times) were found.

The author utilized the method of neutron-activation analysis to study the content of TE in oils and natural bitumens of the Volga-Ural, Timan-Pechora, Kazakhstan, Tajikistan, and etc. Ore-level concentration values were found, for example: 180-1162 ppm for V and up to 100 ppm for Ni in the oils of the Melekess depression in Tatarstan, and 940 ppm for V and 130 ppm for Ni in the oils of Kazakhstan deposits.

Classification of oils by the content of “biogenic” elements V, Ni, Fe and by physical and chemical properties revealed significant differences of hypergene-altered oils in the general cycle of genesis of naphthides. Deposits of secondarily-altered oils are found in a wide stratigraphic range in oil and gas basins of various geostructural types in traps of the combined morphology – lithologically and tectonically shielded.

During the development of oil deposits that contain high concentrations of TE, it is necessary to take into account ecological aspects. The environmental aspect is due to the fact that many metals contained in oils – V, Ni, Cd, As, Hg, U, etc. belong to highly toxic compound chemicals.

Keywords: *naphthides, environment, ecological aspects, zones of hypergenesis, trace elements*

INTRODUCTION

The formation of secondarily altered oils is due to the processes of modern or ancient retrograde diagenesis (hypergenesis). As a result of intensive upward movement, the oils get into areas of biochemical and/or chemical oxidation processes either on migration routes or in the reservoirs and are subjected to physical weathering, inorganic oxidation, leaching with waters (washout), biodegradation, and sulfurization. The accumulation zones of hypergenetic oils are confined mainly to large positive structures (arches, megaswells, swells) that have experienced intense upward movement in the final stages of their development. The most altered oils occur in zones of active water exchange at water-oil contact (WOC) and at relatively shallow depths.

In the hypergenesis zones, the processes listed above result in changes in the concentration of TE and their ratio [4], [11]. Due to the loss of light fractions, the absolute concentration of the elements V, Ni, Co, Mo, Cr, Cu, etc. associated with the resinous-asphaltenic components significantly increases in the oils. In addition, resin-asphaltene heteroatomic components of oils that contact with slightly mineralized formation waters in the hypergenesis zone are capable of absorbing variable valence elements V, Fe, and U from water.

As a result of secondary transformations of oils in the hypergenesis zone, large and giant heavy oil and natural bitumen fields have been formed in Western Canada, Eastern and Western Venezuela, the United States, Russia, and other regions [1], [2], [3], [4], [5], [6], [12], [13]. When assessing resources, these accumulations are unconventional and recognized as commercially viable with ore concentrations of metals in naphthides in many regions, and therefore, they are considered a complex raw material for the recovery of hydrocarbons and associated metals (Table 1).

Table 1. Main areas of hypergenetically altered naphthides secondarily enriched in TE

Oil and gas basin (OGB), oil and gas region, structural elements	Main deposits, age of oil and gas play	TE content in hypergenetically altered naphthides, ppm	
		V	Ni
Western Canadian OGB	Peace River, Wabasca, Athabasca; K1	168 *290	80 *120
Uintah-Paysens, Utah, Rocky Mountains OGB	Asphalt Ridge, WhiteRocks; P-T, J2, K1-Upper Paleogene	110	30
Eastern Venezuela (Orinoco) OGB	Oficina, Temblador, Cerro Negro; K, Oligocene-Pliocene	182 *470	72 *90
Western Venezuela (Maracaibo) OGB	West Mara, Mara, Bochakero; K, Paleogene-Neogene	216-1000 *935-1250	96 *110-150
Lena-Tunguska OGB, Lena-Aldan,Olenek arch	Olenek; PR2, J3	124 *3640	53.6 *640
South Mangyshlak OGB, Buzachinskii arch	Northern Buzachi, Karajanbas; J2, K1	70-384	50-164
Surkhan-Vakhsh OGB, Afghan-Tajik depression	Uchkizyl, Haudag, Koshkar; Paleocene, Bukhara formation	570	170

Timan-Pechora OGB, Ukh-ta-Izhma swell, Varandei-Adzvinskaya structure	Ust'-Voiskoe, Izhma, Usa, Yarega; D, C-P	253	100
Volga-Urals OGB, South Tatar arch, Melekes depress	Nurlatskoe, Ashalchinskoe, Sugushlinskoe; C1, P1, P2	900 *1200	100 *340

** V and Ni content in natural bitumens.*

RESULTS AND DISCUSSION

Our generalization is based on the author's data on TE composition of naphthides from the Volga-Ural and Timan-Pechora OGB as well as the Buzachi arch (Kazakhstan) and Afghan-Tajik depression (Tajikistan). In addition, we processed a great body of factual material on oils and solid bitumens from petroleum basins of Russia, the United States, Canada, Brazil, and Venezuela. The productive sediments from the upper sedimentary sequences of the Tatarstan and Ul'yanov district often contain heavy (0.902-0.984 g/cm^3), high in sulfur (3.5-4.6%), viscous oils with high contents of resinous-asphaltic components. The contents of TE reach high values (in ppm): V (180-1162), Fe (131), Ni (up to 124), Cu (38), Mn (12), Pb (8.0), Zn (6.0), Ti (4.0), Cr (0.7), and Ge (0.7). Average TE data on oils of Tatarstan [8] are shown in Table 2.

Table 2. Average characteristics of TE composition of oils of the Volga-Ural OGB [8]

Region	Tectonic element	Age	Content in oil			V/Ni	Influence of Hypergenesis
			V, pmm	Ni, ppm	S, %		
Tatar-stan	Melekes Basin	C_{1-2}	500.2	82	3.8	6.1	++
		D_3	147	34	2.6	4.3	-
	South Tatar arch	C_{1-2}	250	57	4.7	4.4	+
		D_3	70	34	1.6	2.1	-

** Hypergenesis processes: the dash denotes that the processes were not manifested; plus, manifested; two pluses, strongly manifested*

The oils from Devonian, Carboniferous, and Permian sediments of the South Tatar and Bashkir arches and Bira saddle presumably belong to the vanadium type initially enriched in TE and likely unaffected by hypergenesis. The oils in Carboniferous sediments of the Tatar arch bear clear evidence of hypergene transformations, which manifested themselves in the Melekes depression [8]. The highest V and Ni contents, correlated with elevated sulfur content, were found in oils from Lower Carboniferous reservoirs in the eastern flank of the Melekes basin, for instance, at the Stepnoozerskoe (870 and 74 ppm, respectively) and Nurlatskoe (658 and 93 ppm) fields. The bituminous sequences of Tarastan are most studied on the western slope of the South Tatar arch and the eastern flank of the Melekes depression. Accumulations of bitumens are mainly situated at depths up to 400 m in the Permian sediments. Maximal average concentrations of V and Ni were found in bitumens from lower Permian deposits (V = 910 ppm, Ni = 177 ppm) [7].

Hypergenesis leads to a sharp increase of TE in vein asphaltites relative to asphalts and solid bitumens, i.e., in the series of their genetic transformations from oils to solid bitumens (Table 3). As noted by Yakutseni [13], naphthides also differ in Au and Re contents. Asphaltites are considerably enriched in these metals.

Table 3. Variations of trace elements (ppm) in heavy oils and natural bitumens of the Ural-Volga area [13]

Element	Heavy oils	Maltha, asphaltenes	Asphaltites, veined
V	200-1400	230-2000	2350-4800
Ni	100-195	100-190	520-708
Mo	2.2-15	-	22
U	-	5.9	-

Oils of the Buzachi Arch (Kazakhstan) are ascribed to the hypergene-altered type, based on all of their features. Regardless of their localization, they are heavy (0.920-0.940 g/cm^3), highly resinous (18-30%), sulfurous (up to 2%), highly viscous (up to 500 mPa/s), highly cyclic oils with low solidification temperature (20-27°C), and are undersaturated with gas under stratal conditions. These parameters increase from the arch part to the outlines. The oils are enriched in TE. The studied oil composition, namely of Fe, V, Ni, Cr, Cu, Mn elements, of the Northern Buzachi and Karazhanbas fields is shown in Table 4 [11].

Table 4. Trace element composition of oils from the Buzachi petroleum area [11]

Deposit	Age	Depth, m	Density, g/cm^3	Content of trace elements, ppm						V/Ni
				Fe	V	Ni	Cr	Cu	Mn	
Northern Buzachi	J_2	470	0.940	660	240	29	3.8	2.2	1.3	8.3
Karazhanbas	K_1	267	0.930	1300	190	50	8.5	0.3	0.5	3.8
Karazhanbas	J_2	370	0.920	450	70	45	2.4	0.8	0.1	1.5

Oils of Paleogene sequences of the Afghan-Tajik depression are genetically related to the carbonate sequence of the Paleocene Bukhara Beds of the Surkhandar'ya and Vakhsh synclinorium zones and the southern part of the Kafirnigan anticlinal zone. They are characterized as heavy (density of 0.970 g/cm^3), viscous, resinous-asphaltene (sum of resins and asphaltenes is 43.2%), and sulfuric (S = 5.2%) oils subjected to intense and long-term impact of hypergenesis factors [11]. These oils have elevated concentrations of V, Ni, Cu, Fe, Co, and other elements. Intense manifestation of hypergenesis processes leads to their sequential transformation into maltha and asphaltenes (Surkhandar'ya zone).

Figure 1 demonstrates distribution of ten metals in hypergenesis altered oils and their ash from the Afghan-Tajik depression as compared to the TE distribution in clay rocks, and in unaltered oils from the same region.

TE are arranged in order of increasing content in clays. Oils and especially oil ashes of the Afghan-Tajik depression are enriched in V (1000 times), Ni and Cu (100 times), Co (10 times), and Cr (5 times) with respect to the average contents.

The approved criteria of oil hypergenesis include not only increase in the concentrations of TE in naphthides, but also changes in their ratios, for instance, Zn/Co and V/Ni. The comparison of oils from the Devonian terrigenous sequence of the Timan and Izhma-Pechora depression from the deepest strata position (Dzh'er deposit) toward their exposure on the surface (Yarega field) revealed systematic decrease of Zn/Co ratio from 15.5 to 1.2 with intensification of hypergenesis. Lowered Zn/Co ratios occur because Zn gets flushed into the water. Similarly, Zn/Co ratio in Brazil oils changes from 8.2 to 0.8 during supergenesis [2].

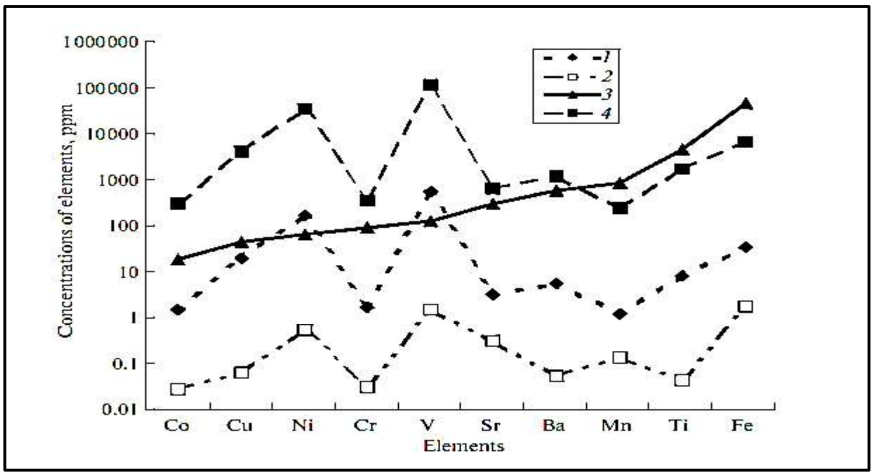

Fig. 1. Content of TE in oils from fields of the Afghan-Tajik basin, which were subjected (1) or not (2) to the hypergenesis, as well as in clays (3) and ash of hypergenesis transformed oils (4)

The study of TE composition of oils in the WOC zone, in particular, variations of Zn/Co and V/Ni ratios in oils depending on sapling position relative to the WOC zone, was carried out at the multibed Western Tebuk field of the Timan-Pechora OGB. Oils taken from the WOC zone have lowered Zn/Co ratios (5.6), while samples from boreholes located at a significant distance from it (>300 m) and at the top of the reservoir have the higher ratios (up to 23.7). Oils in the WOC zone are also distinguished by a high Fe content and increased V/Ni ratios (up to 14.5) (Table 5). Similar conclusions were obtained when studying the oil of the Piltun-Astokhskoye and Odoptu-Sea deposits of Northern Sakhalin [9].

Table 5. Change in hydrocarbon and ME indicators in the oils of the Western Tebuk field depending on the position of the oil extraction point relative to the WOC [11]

Oil sampling interval position regarding WOC	Zn/Co	V/Ni	$\frac{iC_{19}+iC_{20}}{nC_{17}+nC_{18}}$	$\frac{iC_{19}+iC_{20}}{\Sigma\,(iC_{14}\text{–}iC_{18})}$
Top of the reservoir	23.7	3.0	0.8	1.5
Located far from WOC (> 300 m)	20.7	2.7	0.8	1.1
Located close to the zone WOC (< 300 m)	10.0	4.4	2.2	2.1
From zone of WOC	5.6	14.5	3.9	3.3

Analytical data on hydrocarbon composition of oils from the Western Tebuk field confirm biodegradation in the WOC zone [11]. Experimental studies of oil interaction with low salinity waters as exemplifying the bottom waters of the oil field showed that concentrations of most elements remain unchanged in oils. It was established that Zn is rinsed from oils at the WOC, which results in the decrease of Zn/Co ratio. In addition, it was experimentally proved that when oils are in contact with water, the water becomes enriched in resine and asphaltenes. In the WOC zone, the latter are potentially sorption components and capable of sorbing V, and partly Fe from water. This also explains an increase of these elements in oils and the considerable growth of V/Ni ratio in the WOC zone.

Ascending movements in regional and local petroleum basins and lateral migration of oils in reservoirs, open to the hydrogeological discharge zone, facilitate entrance of oil into hypergenesis zones, thus triggering mechanisms of TE accumulation in them [4-6]. The main driving force of these phenomena is geodynamic activity of the OGB. Table 6 shows the amplitudes of the uplifting of sedimentary cover of the OGB in the Cenozoic [11].

Table 6. The scale of sediment uplifts in the OGB at the inverse stage of their development in the Cenozoic

Oil and gas basin	Maximum amplitude of uplift, in m
Western Canadian	2000
Eastern Venezuelan	1800
Uinta Piceance, United States (Rocky Mountains)	1500
Tungusska, Eastern Siberia	1000
Volga-Ural (Tatar arch)	300-400
Timan-Pechora	200-300

CONCLUSION

Typification of oils by content of the “biogenic” elements V, Ni, Fe and physicochemical properties revealed significant differences of supergene altered oils in a general cycle of naphthidogenesis. They were distinguished by us as an independent group and ascribed to naphthides secondarily enriched in TE, thus sharply differing from primarily enriched oils [10]. These are vanadium (V > Ni > Fe) or ferroan (Fe > V > Ni) types of oils with the genetic criterion V/Ni > 1 (Fig. 2). The foundation of the classification was based on the analysis of the scientific literature and studies covering the wide range of deposits around the world. Deposits of secondarily altered oils are found in a wide stratigraphic range (Upper Proterozoic-Neogene) in oil and gas basins of various geostructural types in traps of the combined type – lithologically and tectonically shielded.

The contents of V and Ni in oils of many deposits exceed, respectively, more than 100 and 50 ppm. They also have elevated concentrations of Mo, Cu, Zn, Re, and other elements (from 0.1 to 4 ppm). The oils are biodegraded, heavy (average density 0.954 g/cm^3), resinous (sum of resins and asphaltenes average 29%), sulfurous (average 4.2%), and highly viscous. The reservoirs of this type are frequently situated at shallow depths (< 2.0 km) in platform areas, but also occur in the mobile zones, rift, aulacogens, marginal troughs, and intermountain depressions.

Of great importance is the connection of the oil composition with the predicted trap. It can be argued that it is precisely the oils of the hypergenesis zone that are often confined to traps of complex combined structure – lithologically and stratigraphically limited, to traps of erosive incisions, and to traps with tectonic restriction. With geological inversions and the restructuring of structural plans in the hypergenesis zone along tectonic faults that limit the trap along the channels that arise during this, potentially toxic elements of heavy oils and solid bitumen can penetrate into the environment. This process causes tremendous damage to our nature.

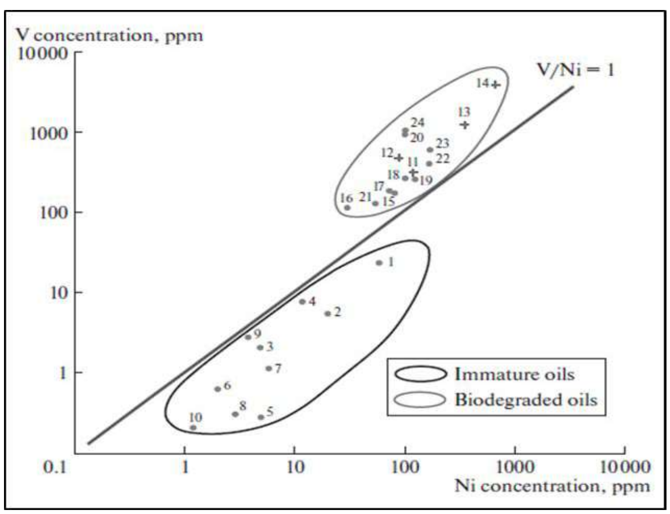

__Fig. 2.__ Concentrations and V/Ni ratios in immature and hypergene oils and natural bitumens in various regions

Legend

Zone of immature oils:

1 – California; 2 – Belarus; 3 – Sakhalin; 4 – Japan; 5 – Azerbaijan; 6 – Georgia; 7 – Ciscaucasia; 8 – China; 9 – Western Siberia (Cenoman); 10 – New Zealand.

Zone of Hypergenesis (biodegraded) naphthides:

Bitumens: 1 – Western Canada; 12 – Venezuela Orinoco;13 – Volga-Ural; 14 – Lena-Tunguska; **Oils**: 15 – Western Canada; 16 – Rocky Mountain Basin; 17 – Venezuela Orinoco; 18 – Timan-Pechora; 19 – Volga-Ural D-C, 20 – Volga-Ural P; 21– Lena-Tunguska; 22 – Mangyshlak, 23 – Afghan-Tajik Basin; 24 – Venezuela.

During the development of oil deposits that contain high concentrations of TE, it is necessary to take into account the technological (e.g., deterioration of well equipment), industrial (e.g., extraction of valuable metals, such as V, U, Ge, and Mo from raw naphthides), and ecological aspects. The environmental aspect is due to the fact that many metals contained in oils – V, Ni, Cd, As, Hg, U, etc. – belong to highly toxic compounds. Once they enter the atmosphere, hydrosphere, and get on the earth's surface, they have a negative effect on plants and living organisms. In particular, vanadium belongs to the first class of environmentally hazardous chemicals.

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REFERENCES

[1] Akinlua A., Ajayi T.R., Adeleke B.B. Organic and inorganic geochemistry of northwestern Niger delta oils. Geochem. J. Vol. 41, pp. 27-281, 2007.

[2] Duyck C., Miekeley N., Fonseca T., Szatmari P., Neto S. Trace element distributions in biodegraded crude oils and fractions from the Potiguar Basin, Brazil. G. Braz. Chem. Coc. Vol. 19(5), pp. 978-986, 2008.

[3] Escobara M., Márquezc G., Azuajed V., Da Silvad A., Toccoe R. Use of biomarkers, porphyrins, and trace elements to assess the origin, maturity, biodegradation, and migration of Alturitas oils in Venezuela. Fuel. № 7, pp. 186-196, 2012.

[4] Galarraga F., Reategui K., Martïnez A., Martínez M., Llamas J.F., Márquez G. V/Ni ratio as a parameter in palaeoenvironmental characterization of nonmature medium-crude oils from several Latin American basins. Journal of Petroleum Science and Engineering. Vol. 61. № 4, pp. 9-14, 2008.

[5] Goldberg I.S. Naftometallogenetic provinces of the world and the genesis of ore concentrations in heavy oils and bitumen. Geology of oil and gas. No. 3, pp. 2-7, 1990.

[6] Gribkov V.V. One of the possible natural processes of oil enrichment with vanadium. Oil and gas geology. Theory and practice. 2007. Vol. 2. http://www.ngtp.ru/rub/10/010.pdf).

[7] Kayukova G.P., Petrov S.M., Uspenskii B.V. Properties of Permian Heavy Oils and Bitumens of Tatarstan in Natural and Anthropogenic Processes. GEOS, 2015, Moscow, 343 p. [in Russian].

[8] Mukhametshin R.Z., Punanova S.A. Composition of natural bitumens from the Ural-Volga region. Solid Fuel Chemistry, vol. 48, pp. 58-70, 2014.

[9] Popovich T. A. Assessment of Biodegradation of Sakhalin and Shelf Oils: Genesis of Oil and Gas. GEOS, Moscow, 2003, p. 260. [in Russian].

[10] Punanova S. Trace Elements in Naphtides in Oil and Gas Basins. Doklady Earth Sciences. Vol. 488, part 2, pp. 1207-1210. © Pleiades Publishing, Ltd. 2019.

[11] Punanova S.A. Supergene Transformed Naphthides: Peculiarities of Trace Element Composition. Geochemistry International. Vol. 52, No. 1, pp. 57-67. © Pleiades Publishing, 2014.

[12] Sukhanov A.A., Yakutseni V.P., Petrova Yu.E. Assessment of the prospects for the industrial development of the metal-bearing potential of oils and possible ways of its implementation. Oil and Gas Geology. Theory and practice. T. 7. No. 4. 2012. http://www.ngtp.ru.

[13] Yakutseni S.P. Occurrence of Hydrocarbons Enriched in Heavy Trace Elements: Environmental Risk Assessment. Nedra, St. Petersburg, 2005. [in Russian], 372 p.