THE QUESTION OF ENVIRONMENTAL CONSEQUENCES AT HORIZONTAL DRILLING OF SHALE FORMATIONS IN CONNECTION WITH THEIR ENRICHMENT WITH MICROELEMENTS

S.A. Punanova[1], D. Nukenov[2]*
[1]*Oil and Gas Research Institute of the Russian Academy of Sciences, Moscow, Russia*
[2]*TOO «Kaz-Waterhunters», Aktay, Kazakhstan*

Abstract. Priority directions of horizontal drilling in shale formations in the USA (Bakken, Barnett, Monterey, etc.) are considered. Growth and further development of this type of drilling in the territory of shale plays of the USA and other countries, as well as productive horizons of the Western Siberia, was noted. With a fairly detailed coverage in the domestic and foreign literature of all the pros and cons of shale horizontal drilling projects, and in particular the negative environmental consequences of hydraulic fracturing, the problem associated with the high content of metals and nonmetals in shales and oils is practically not considered. A significant number of them belong to the category of potentially toxic microelements, dangerous for the habitat. The article presents the average trace elements content in the combustible and black shale from various basins of the world, the concentrations of a number of elements markedly exceeding in shale the clark content of clay rocks. High concentrations of a number of elements in the Kenderlik shale of the Republic of Kazakhstan, domanic deposits of the Volga-Ural oil and gas basin are shown, as well as some features of the distribution of radioactive elements and mercury in oils and shales. The release of toxic elements significantly increases with the thermal impact on the formation and some processes of hydrocarbon processing. In the case of hydraulic fracturing, it is possible that toxic elements from both shales and from the naphthides contained in them could be discharged to the environment. In the course of horizontal drilling, as with any other processes of impact on the reservoir, additional studies should be conducted to assess the microelements composition of the shale formations and the hydrocarbons contained therein for monitoring environmental processes.

Keywords: horizontal drilling, ecology, shale formations, microelements, potentially toxic elements, radioactive elements, mercury

DOI: https://doi.org/10.18599/grs.19.3.15

For citation: Punanova S.A., Nukenov D. The Question of Environmental Consequences at Horizontal Drilling of Shale Formations in Connection with their Enrichment with Microelements. *Georesursy = Georesources.* 2017. V. 19. No. 3. Part 1. Pp. 239-248. DOI: https://doi.org/10.18599/grs.19.3.15

Introduction

With the conquest of the market by shale oil and shale gas, the method of horizontal drilling is widely used in oil and gas basins around the world. Importance and high economic effect, all the pros and cons of this type of drilling are reflected in the extensive domestic and foreign literature (Dmitrievsky, Vysotsky, 2010; Ivanov, 2014; Yarakhanova, 2014; Averyanova, 2015; Yurova, 2016; Johnson et al., 2016; Nemec, 2016 and others).

Opening the scientific and practical conference in 2015 “Black Shale” in Yakutsk in the Institute of Oil and Gas Problems of the Siberian Branch of the Russian Academy of Sciences, corresponding member of the RAS A.F. Safronov noted that in Russia, as conventional oil reserves are being depleted, it will be necessary to involve shale oil extraction of more actively even in the medium term.

Moreover, the oil recovery from clay plays can be more profitable than, for example, the production of hydrocarbons on the shelf of the Arctic seas. A.F. Safronov drew attention to the fact that in the early 70s of the last century Academician Nikolai Chersky, who headed the Yakutsk Scientific Center for more than 20 years, proposed using hydraulic fracturing to extract natural gas from the low permeable rocks of the Permian age of the Khapchagai megaswell.

The EAGE conference “Horizontal Wells 2017. Problems and Prospects”, held in Kazan on May 15-19, 2017, highlighted the large role played by horizontal wells in improving the efficiency of oil and gas fields development in Russia and abroad. The chairman of the organizing committee, Vladimir Vorobyov, the head of the geology and development department of Gazpromneft-Angara LLC, repeatedly emphasized that in modern market conditions, when the cost of oil has significantly decreased, horizontal drilling allows minimizing the risks of lack of inflow, increasing the level of reservoir opening and well flow rates, improve the profitability of projects. It was also noted that

*Corresponding author: Svetlana A. Punanova
E-mail: punanova@mail.ru*

Tatarstan and Bashkiria show a rational approach to the development of hydrocarbon fields, while projects with horizontal wells are widely implemented, the share of which in the Volga-Ural oil and gas basin is very high.

The 14th International Exhibition of Oil and Gas Equipment and Technologies "OIL&GAS"/MIOGE 2017 was held in the central exhibition complex "Expocenter" in Moscow on June 27-30, 2017. The exhibition advertised equipment for horizontal drilling. Unfortunately, foreign companies in this exhibition were few. We can note the American company Scientific Drilling International from Texas (Houston), Cognitive Technologies (UK) Limited (London), APA-KANDT GmbH Germany, Hamburg and some others, offering a wide range of technical tools for horizontal drilling.

Horizontal drilling of shale formations in the USA and productive deposits of Western Siberia

The development of oil shale deposits, primarily in the United States, has completely refocused the international oil market in recent years. Having made the shale revolution in the beginning of 2010, American producers have become one of the key suppliers of raw materials in the world, having increased production by 10% to 9.3 million barrels per day since mid-2016, which is close to the levels of Saudi Arabia and Russia (http://rusjev.net/2017/05/30/sanktsii-zadushili-slantsevuyu-neft-v-rf/). Great success was achieved with the use of horizontal and/ or cluster drilling.

The beginning of industrial gas production from oil shale dates back to the 80s of the last century. Shallow vertical wells (150-750 m) were drilled in the northeast of Texas and, using hydraulic stimulation, they began to extract gas from the Barnett Formation shale plays. The well production rates were about 3 thousand m3 per day, and the reserves for the well were estimated at an average of 7 million m^3. Gradually, the extraction technology was improved, and by the year 2000 it had already reached 13 billion m^3. In 2002, a new technological stage began – drilling horizontal wells with multistage hydraulic fracturing and proppant injection. Production began to grow, and in 2005 amounted to 23 billion m^3 (Dmitrievsky, Vysotsky, 2010). Shale formations are located mainly in the sedimentary basins as a platform (Perm, Michigan, Illinois, etc.), and intra-fold (Green River, Winta, Paradox, etc.) types.

Below are a few examples and statements of the leaders of major US corporations (Johnson, 2016; Nemec, 2016, etc.).

WPX Energy from Oklahoma is drilling in various American basins: the Bakken (North Dakota) and the Barnett (clayey coal shales) Formations of the Perm Basin (western Texas and eastern New Mexico). The head of the company Rick Moncrief, who is the pioneer of horizontal drilling in Bakken (it was on his initiative in 1987 that the first horizontal well was laid here), compares the two shale formations. He believes that there are high prospects both in Bakken and in the Perm basin, despite the fact that in 2016 Bakken's production rate fell.

While economically the Perm basin now looks more attractive, Rick Moncrief evaluates the positive outlook of his company in both basins, where the average cost per well has been reduced to $ 5-5.5 million in mid-2016. "I would like to have more plots in Bakken," said Rick Moncrief. He breaks the Permian basin from east to west into three plots: Midland, East Central and Delaware. Today WPX Energy is the 'new player' of the Perm basin due to the acquisition in 2015 of license areas (94,000 acres) in the area of Delawar. WPX Energy also has plots in the Williston Basin (North Dakota) and the San Juan Basin (New Mexico). In the first quarter of 2016, WPX Energy set a new peak in oil production with an average of 41,500 barrels per day and plans to invest 350-450 million dollars in 2016, more than half of these funds are destined for the Perm section of Delaware. Many executives of large corporations note that technology improvements of horizontal drilling leads to a reduction in costs, pushing the slogan – "less money, but more oil."

Improving hydraulic fracturing technology with multiple inlets (perforations) reduces costs and increases productivity, says Jim Volker, executive director of Whiting Petroleum Corporation, based in Denver. The 10,000-foot (3048 meters) lateral branches, 6 million pounds (2,700 tons) of sand, 200,000 barrels of water allow Whiting Petroleum to reach a capacity of 900,000 barrels per well. According to Gerbert Schoonman, vice president of Hess Corporation, his company managed to reduce the time of drilling the well from 45 to 16 days, thereby reducing costs for each from 34 million to 5.1 million dollars.

Don Hrap, president of Conoco Phillips (the part that operates in 48 continental US states), emphasizes that, because of the new technology, US oil reserves have increased by 90% over the past 6 years, and natural gas reserves by 125% over the past 20 years. "At the moment, North America has enough natural gas for the next 100 years," said Don Hrap.

The use of the latest technologies is of great importance: fiber optics and fiber coils are used to diagnose the performance of each perforation. Temperature, acoustics and some other parameters are evaluated for their reuse. A new fiber-optic monitoring system, jointly developed by Shell and Baker Hughes global oil exploration and production department, allows monitoring the distribution of stresses and strains in wells using anti-sand filters. This system can record even minor changes in casing and well bracing in real time (http://worldcrisis.ru/crisis/1518031; http://neftianka.ru/zima-trevogi-nashej/).

The new multi-trunk well construction technology was successfully used in 2017 at the Novoportovsky oil and gas condensate field, one of the largest hydrocarbon fields in the Yamal-Nenets Autonomous District. This allowed Gazpromneft-Yamal to increase the oil recovery of the reservoir and significantly improve the development efficiency of the field. The multi-trunk well has a vertical trunk, called the main one, from which a number of sidetracks are drilled. The intersection of the main trunk with a branch must be above the productive layer. Thanks to this technology, it is possible to open new productive horizons, continuing drilling of existing wells. The used drilling technology involves securing in each horizontal wellbore a metal pipe, the so-called shank, to prevent the rock from shedding and the loss of the drilled stem during its operation. The length of each trunk of the first 2-well borehole constructed at the Novoportovsky field is 1000 m. The initial production rate of the well is recorded at a level of more than 400 tons/day of oil.

Currently, five such wells have been constructed and are functioning at the Novoportovsky field, and each new well is drilled much faster than the previous one, which significantly reduces its cost. As a result, the specialists managed to reach a record speed of drilling multi-trunk wells for the company – 5.87 days/1000 m, which is comparable to the best results for drilling single-trunk horizontal wells. The recoverable reserves amount to more than 250 million tons of oil and gas condensate, more than 320 billion cubic meters of gas. Operational drilling began at the end of June 2014. The new grade of oil, known as Novy Port, is classified as average density by its properties. It should be noted that Gazprom Neft is actively developing modern technologies that are being introduced into exploration, production and processing (http://neftegaz.ru/news/view/158224-Proryv.-Gazpromneft-Yamal-postroila-na-Novoportovskom-mestorozhdenii-2-stvolnye-gorizontalnye-skvazhiny).

Ecological problems

The negative impact of this technology is well known and many times noted by many practitioners and scientists, which causes enormous harm to the environment. So T.I. Dvenadtsatova (2015) states that in recent times the controversy over the environmental consequences of the shale gas recovery and its role in the future of world energy has not only not abated, but inflames with renewed vigor (Fig. 1). The author cites the following risks that arise when drilling horizontal wells and using hydraulic fracturing:

1) Growth of seismic activity due to changes in the structure of subsoil;

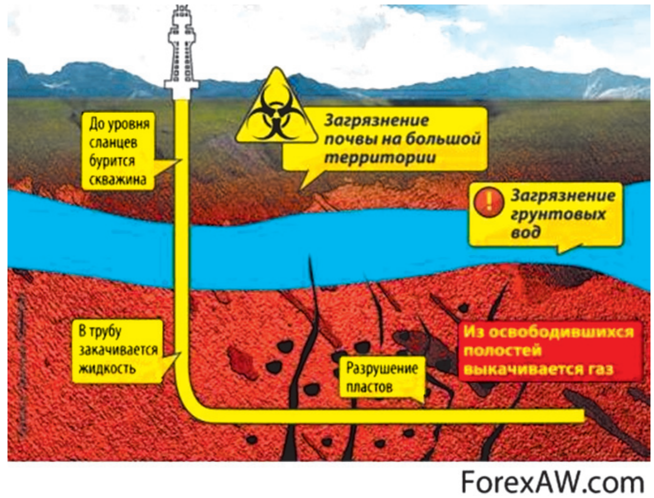

*Fig. 1. Scheme of horizontal drilling and deplorable consequences of the shale revolution (*http://economic-definition.com/Energy/Slancevaya_neft__Shale_oil__eto.html*).*

2) Pollution of groundwater, which is directly related to the subsequent contamination of drinking water in areas close to production («The Process of Shale Gas Development», http://shalegas-europe.eu/shale-gas-explained/the-process-of-shale-gas-development/, https://www.worldwatch.org/files/pdf/Hydraulic%20Fracturing%20Paper.pdf);

3) Contamination of surface water and soil (http://www.eriras.ru/files/Sorokin_Goryachev_OEPEE_slanec.pdf);

4) Methane emission («Texas Republicans work to squash local fracking ban», Laura Clawson, Daily Kos, 2014, https://www.dailykos.com/stories/2014/11/17/1345523/-Texas-Republicans-work-to-squash-local-fracking-ban#).

Drilling of vertical oil and gas wells with various directions, including controlled directional and horizontal, is carried out by Batys-Munai in the city of Aktobe, Republic of Kazakhstan. Studies of scientists of Kazakhstan (Ozdoev, Tsireltson, 2014, etc.) noted large environmental risks associated with the implementation of hydraulic fracturing, which resulted in the following problems:

1) The technology requires huge water reserves; from 5,000 to 20,000 tons of water, sand and chemicals for one fracturing, and such fracturing is performed in dozens in one year on a single well;

2) Large amounts of spent chemical contaminated water accumulate near the deposits, which inevitably falls into the soil, destroying its fertility and polluting groundwater;

3) The extraction of shale gas leads to a significant contamination of groundwater with toluene, benzene, dimethylbenzene, ethylbenzene, arsenic and other dangerous substances (in particular, in September 2014 unsafe amount of arsenic was discovered in the water well of Barnett shale, one of the largest gas storage facilities in Texas, (http://www.publicintegrity.org/2014/12/11/16477/sick-barnett-shale);

4) 80-300 tons of chemicals for up to 500 items are used for one operation;

5) The probability of contamination with radioactive substances that will be released to the surface as a result of shale gas recovery (http://neft-gas.kz/d/877050/d/slantsevyygaz-plyusyiminusy.pdf).

Microelement composition of shale formations

With a fairly detailed coverage of all the advantages and disadvantages of horizontal drilling of shale plays, and in particular the negative environmental consequences of hydraulic fracturing, the problem of the microelement composition of both shales and shale oil is practically not addressed. However, when developing and extracting oil and gas resources of shale formations, it is necessary to take into account the large contents of metals and nonmetals concentrating in them. Investigations of the environmental consequences of oil fields development of with an increased content of toxic elements were carried out by Yakutseni (2005). His review monograph "The prevalence of hydrocarbons enriched with heavy element-impurities. Assessment of environmental risks" is devoted to the geological and geochemical regularities of formation and distribution in the subsoil of hydrocarbon raw materials enriched with heavy impurity elements and its biological (toxic) activity.

The book contains a database on the content of microelements in oil of the oil and gas basins of the world and Russia. The great importance of the monograph lies in the fact that it "puts on the shield" environmental problems, environmental risks, urging humanity to take a more serious and scientific approach to these issues. It details the impact on humans of those harmful compounds that are formed during the disposal of oil production waste. The author analyzes toxic risks and suggests the basics of a strategy for preventive protection of the environment from negative effects when developing hydrocarbons enriched with potentially toxic elements. In the subsequent work (Yakutseni, 2010), deep zonation in the accumulation of microelements in oils was analyzed and attention was drawn to sufficiently high concentrations of toxic and volatile elements Cd, Hg, As , Tn, Se, Mo, etc. in oils from deep horizons (more than 4.5 km) with a low content of asphalt-tar components. Oil of this composition can also occur at shallow depths and, as a rule, are associated with rifts and young deflections. It is likely that they can also enrich the extracted shale hydrocarbons.

The estimation of associated heavy oil components in Russia, as well as the current problem of highly vanadium-rich oils are presented in the works (Sukhanov et al., 2012). The estimation of the vanadium resource base in the largest accumulations of metalliferous oils and natural bitumen abroad and in Russia is given, as well as the volume of losses *V* in the development of metalliferous oil raw materials. The existing foreign and domestic technologies for extraction of *V* and other valuable metals from oils, natural bitumen and products of their processing are analyzed. The authors urge manufacturers to think about those irrecoverable losses of valuable metals, which are due to the lack of cost-effective technology for their production.

In general, as S.P. Yakutseni (2005) believes, a paradoxical situation has developed. Against the background of relatively high study of the properties and consequences of hydrocarbon impact on the environment, many toxo-dangerous microelements present in the hydrocarbon raw materials remained practically without research. But about 15-20% of raw materials produced by HC already contain in their composition toxic microelements in quantities exceeding their safe level, and the volumes of its production increase with the years. Hg, Cd, As, etc. are the most migratory-mobile and volatile of them. Among the strongly chemically bound in complex organometallic compounds in hydrocarbons are V, Ni, Co, Cr, Cu, Zn and other biologically inert in natural oil and bitumens, but actively dangerous in the microdispersed state after anthropogenic impact on raw materials, especially at high-temperature (>450^{o}C). Actinides, regardless of the bond strength with the molecular structures of hydrocarbons, enter the class of actively dangerous in any state. Therefore, the content of such highly toxic and volatile elements as Cd, Hg, As, Se, Mo, etc. should be assessed at the preliminary stages of the development of any hydrocarbon deposits, including shale deposits.

Thermal effect on the reservoir, increase in pressure, injection of chemical reagents during hydraulic fracturing with a large number of perforations over a long horizontal section can lead to the release of organoelement compounds, possibly volatile metals and their release into the environment. Thus, it is known that thermochemical methods, for example, in-situ combustion in the development of reserves of vanadienous naphthides are not acceptable in view of the significant losses of metals in the reservoir, and also because of the possible entry of V and Ni into the overlying aquifers used for water supply of the population. Similar is already recorded on the section of in-situ combustion of the Karazhanbas field: according to T.V. Khismetova (1992), analysis of reservoir water samples from the wells of this section showed the presence in them of vanadium and other microelements.

Let us consider and estimate in greater detail the content of microelements in black and combustible shales.

Shales are rocks of mixed lithologic composition, consist of aleuritic and pelitic fractions, have schistose content and high content of OM. The permeability of shales, as a rule, is below 1 mD, the minimum is 0.01-0.001 mD.

Combustible shale is a sedimentary rock, clayey, calcareous, siliceous, thin-layered, with weathering leafy or massive; color is brownish-gray, brownish-yellow. Organic matter is aquatic, the stage of transformation does not exceed the initial mesokatagenetic, it is not soluble in low-boiling organic solvents, but generates a significant amount of liquid organic products during thermal destruction. Combustible shales are known in the Phanerozoic rocks of many countries of the world. Black shales are fine-grained sedimentary rocks of black or brown color, sapropel type of a higher transformation stage. The content of OM in them is lower than in oil shales and is from 8 to 20%. The amount of clay fraction, as a rule, does not exceed 30% of the volume fraction (Claire et al., 1988; Level, Sumberg, 1992; Spirt, Punanova, 2009).

When the OM content is below 8%, the black shales are converted to ordinary clay or clay-carbonate rocks. The black shales are also called domanicites, which, according to the ideas of geochemists, are typical oil source beds. The oil-producing transformation occurs at higher reservoir temperatures, which ensure the generation of sufficiently large quantities of gaseous and liquid hydrocarbons. These deposits are the main oil generators in many oil and gas basins of the world (West Siberian, Mexican, Timan-Pechora, etc.). Combustible shales at the present stage of their development are poorly transformed analogues of future oil deposits. Thus, shales are interesting as possible source oil beds, and additional information related to the great interest of the modern world in the study of shale gas and shale oil for further development is important in scientific and practical terms (Shpirt, Punanova, 2017).

Many researchers note that black shale formations are characterized by extremely low rates of sedimentation (i.e., conditions of severe undercompensation) and fossilization of OM by organomontmorillonite compounds in relatively deep seas or inland basins. In the section they form low-thickness (the first tens of m) and homogeneous packs, distributed in large areas with OM up to 20%. The most favorable conditions for the formation of shale deposits are associated (Safronov, 2015) with zones of transition from continent to ocean. Within this zone, during its evolution, the rift regime changed by the regime of the continental margin. Here the accumulation of huge masses of phyto- and zooplankton with elements of benthos occurred. The upwelling zones (the rise of deep cold waters to the surface) are the most productive; there is a unique enrichment of OM sediments (300 g C_{org}/m^2 per year), for example, over the continental shelf of the western coast of the American and African continents. This process involved the introduction of nutrient-rich solutions into the sedimentation basin, which resulted in an outbreak of plankton and other bios development. Goldberg et al. (1990) believe that the sharp enrichment of domanicites is due to a prolonged contact of sediments with seawater – sources of these elements, intensive diagenesis, including sulphide formation, high sorption and preserving ability of organomontmorillonite compounds. In diagenesis in humic acids in addition to organic compounds, heavy metals U, V, Cu, Ni, etc. were apparently concentrated (Tissot, Welte, 1981).

The possibility of mass transfer of ore and organic material by pore waters, pressed from clay rocks with a high OM content under conditions of geodynamic loads, is confirmed by experimental studies on the compaction of oil shales (kukersites) and the separation of pore waters significantly enriched by microelements (Abramova, Abukova, 2015) (Fig. 2).

The calculated concentration coefficients (for the whole mass of Qi and for the mineral matter, the ash Q_i^A), representing the ratio of the element content in shales to its clark (K) in clays (Vinogradov, 1956), allow us to evaluate the processes of their concentration in shales. Table 1 shows typomorphic elements (according to Ketris, Yudovich, 2009, these are the elements for which Qi > K) in the shales of different regions (according to analytical data (Kler et al, 1988, etc.).

The highest levels of microelements are established for oil shales in the Central Asia. In the Baysunsky field (Paleogene), the contents of a large number of elements: Yb, Co, Be, Ni, V, Ag, Mo, Re (calculated on dry matter of shale) exceed their clarks, with Qi values reaching very high values: for Re – 500, For Mo – 692, for Ag – 143. The total amount of microelements reaches 5-7 kg/t. For Suzak shale (Tajikistan, Ordovician) Qi values are a bit lower, but also very high. In these shales, the contents of Zn, V, Ni, Ag and Mo are also significantly higher than clarks. The maximum values of Qi are characteristic for Ag – 71 and Mo – 461. The shales in Ukraine and Belarus

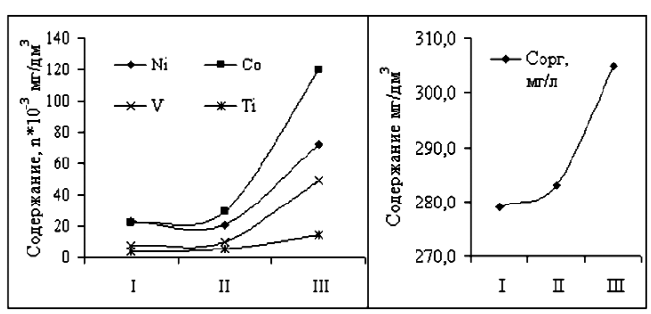

Fig. 2. The content of ore elements and organic substances in pore waters separated from oil shale (Abramova, Abukova, 2015). I – smooth increase in pressure from 0 to 20 MPa at a temperature of 25 °C; II – increase of pressure up to 40 MPa and temperature up to 40 °C with alternating loads; III – increase of pressure up to 60 MPa and temperature up to 80 °C with the influence of vibroacoustic oscillations from 5 to 60 kHz.

Field, region, age	Typomorphic ME	
	on a dry basis $Q_i > 1,4$	on a mineral substance $Q_i^A > 2,0$
The Baltic basin (kukersite), Ordovician	Sc, Ag, Mo, Hg, Re	*Sc*, **Ag, Mo**, Hg, Re
Volga-Pechora Province, Jura	Zn, Pb, Hg, Mo, Ag, Sc, Re	Mn, Ge, Zn, *Pb*, Hg, **Mo, Ag**, *Sc*, Re
Minelite shales of the Carpathians, Paleogene	V, Zn, Pb, Cu, Mo, Ag	Zn, *Pb*, Cu, **Mo, Ag**
Boltysh deposit (Ukraine), Paleogene	Zr, Sn, Pb, Sc	Ge, Zr, Sn, *Pb*, *Sc*
Novodmitrovskoe deposit (Ukraine), Paleogene	–	–
Turovskoye deposit (Byelorussia), Devonian	Ag, Mo, Pb, W	**Ag, Mo,** *Pb*, W
Baysun deposit (Uzbekistan), Paleogene	Pb, Ga, Ge, Cr, Yb, Co, Be, Ni, V, Ag, Re, Mo	*Pb*, Ga, Ge, Cr, Yb, Co, Be, Ni, V, **Ag,** Re, **Mo**
The Suzak horizon (Tajikistan), the Paleogene	Cr, Co, Ga, Pb, Cu, Ge, Zn, V, Ni, Ag, Mo	Cr, Co, Ga, *Pb*, Cu, Ge, Zn, V, Ni, **Ag, Mo**
Kenderlik field (Kazakhstan), carboniferous	Mn, Mo, Hg, Ag, Sc	Sn, Mn, **Mo,** Hg, **Ag,** *Sc*

Table 1. Classification of typomorphic microelements in shales of different regions (Shpirt, Punanova, 2012). In bold type, typomorphic elements are identified in terms of the mineral substance of the shales for practically all basins: Mo, Ag; in italics – many: Sc, Pb. The microelements are shown in ascending order of Qi and Q_i^A.

contain fewer typomorphic elements per dry matter, and shales of the Novodmitrovsky field generally do not have such elements. When recalculating to ash (mineral matter), a greater amount of microelements falls into the rank of typomorphic ones, since the Q_i^A values become significantly higher. For example, the Q_i^A for Mo in the Boysun field is 1225, for Ag – 253, for Re – 885; and in the shale from the Suzakskian horizon, the Q_i^A values for Mo are equal 816, and for Ag 126. The Re contents are also very high (in ash and dry weight) in the kukersite of the Baltic and the combustible Jurassic shales of the Volga-Pechora province, reaching values of 885 and 500 (Q_i^A) respectively (Shpirt, Punanova, 2012).

The study by Yu.N. Zanin et al. (2015) of clay-siliceous differences from the Upper Jurassic-Lower Cretaceous deposits of the Bazhenov Formation of the West Siberian oil and gas basin showed in them increased concentrations (in g/t): Au (0.035-0.02), Pt (0.013-0.005), Ni (336.7, which is 5.3 times higher than the values for ordinary clay rocks), Mo (264.5, 9 times), Co (30.3, 2.6 times), U (66.5), Th (5.0), K (0.81). The investigated deposits of shales are characterized by the highest content of organic carbon and pyrite, as indicators of the reduction regime, with a reduced content of clay material; they are also metalliferous.

At the present time, geochemical studies are conducted on high-carbon rocks of the Kuonamian combustible shale formation of the clay-carbonate and siliceous-carbonate-clayey composition, developed on the Siberian platform in the Cambrian part of the sedimentary cover. It has been established that oil shales are characterized by a high content of microelements: Mo, U, Cu, V, Ni, Co, Cr, Sr, Ba, etc., and can be considered as complex energy and mineral raw materials (Zueva et al., 2015). The authors cite high figures for the content of V. The geochemical background of the rocks of this sequence in V is estimated at 220 g/t. In high-carbon rocks of the Boroulakian horizon, the V content is 2277 g/t. The average concentrations of V, Ni, and Mo reach respectively 1500, 230 and 100 g/t, increasing in the Boraulakian 'metalliferous' horizon by about one and a half times. In the marginal part of the depression (Jelinda River), the mean concentrations of these same metals are equal to 811, 123 and 96 g/t.

We cite the microelement concentrations calculated in the ash of the naphthydes generated by the domanicites and in the shale domanic strata of the East European platform, which are an industrial object of the integrated development of hydrocarbons and metals. The kerogenous fractions of the clayey shale formations of the Ural-Volga region bear a high load in terms of ore content (Fig. 3).

We carried out a comparative analysis of the distribution of average microelement contents in the shales of the Kenderlyksky field from the Republic of Kazakhstan with the composition of microelements in the shale deposits of the former USSR (according to the analytical data of V.R. Kler et al., 1988) and clark contents of elements in clay rocks (Fig. 4).

The analysis showed that the Kenderlik shales contain a large complex of elements in increased concentrations. Compared with the average composition of the oil shale from the former USSR, Kazakhstan's Kenderlik shales are enriched with microelements. Thus, the sum of all identified elements was 2110 g/t, Σ (Mo, Pb, Zn) is equal to 120 g/t, Σ (V, Ni, Cr) reaches 190 g/t. In the shales of the former USSR, these figures are much lower and, accordingly, are (g/t): 1063; 90 and 170. The

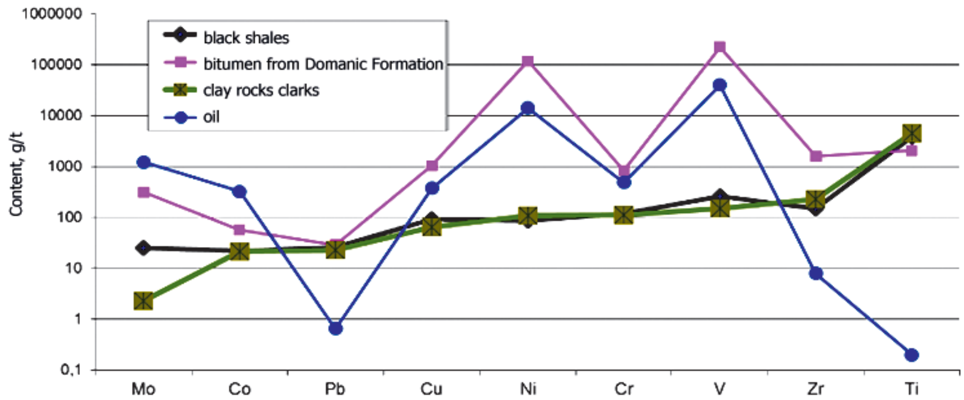

Fig. 3. Comparison of the microelements distribution in ash of bitumen and oil from Domanic Formation of the Volga-Ural (according to the analytical materials (Spravochnik po geokhimii nefti i gaza [Guide on the geochemistry of oil and gas], 1998) with black shales of the world (Shpirt, Punanova, 2012) and clay rocks clarks (Vinogradov, 1956) (ranked by clark content of elements in clay rocks)

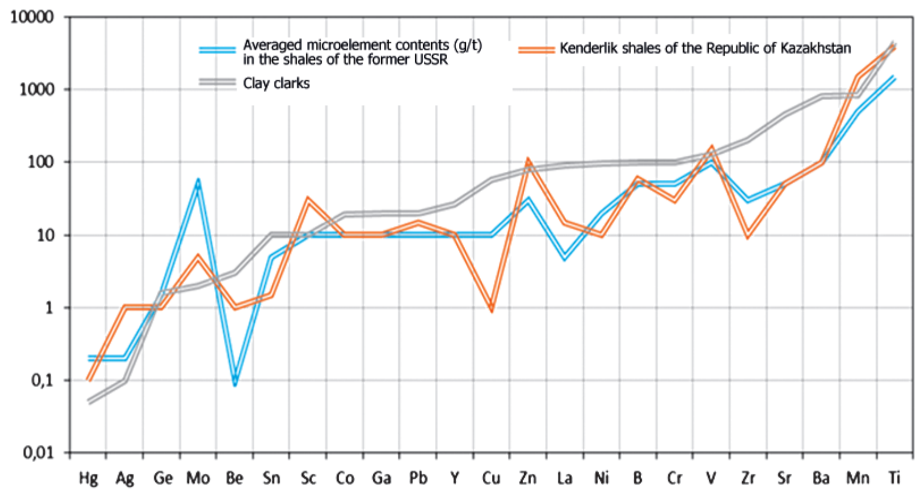

Fig. 4. Comparison of averaged microelement contents (g/t) in the shales of the former USSR, Kenderlik shales of the Republic of Kazakhstan and clay clarks (Vinogradov, 1956), the curves are ranked by clarks

concentrations of Ag, Be, Sc, Pb, Zn, La, Mn and Ti in the Kenderlik shales are much higher than in the shales of the former USSR. In the shales of this field, the content of Ba, Zn and V is ≥ 100 g/t, the concentration of Ti reaches 4000 g/t, and Mn – 4500 g/t. And in comparison with clayey rocks (clark contents), such elements as Ag, Hg, Mo, Sc, Mn, Zn, V, Ti are contained in the Kenderlik shales at higher concentrations. In the oil shale of the Bayhozhinsky field, high contents of Re – rare earth metal, widely used in catalysts and refractory alloys, are also noted.

Comparison of the microelement contents in shales of various age shows that a clear connection with the age of the shale bearing formations can not be detected. This is due to the influence of other factors, namely, the facies type of sediments and the geostructural position of the slate-bearing basin. The maximum content of ME in combustible shales is often confined to platform formations (bituminous domanic rocks of the Russian Platform, the Bazhenov Formation of Western Siberia), but some shale formations of geosynclinal regions can also be enriched by microelements (Baysun field of Uzbekistan, Suzak shales of Tajikistan). Such a confinement of increased concentrations of microelements in caustobioliths is due to the fact that in these basins or their parts favorable opportunities were created both for the syngenetic (with the maximum occurence of transport, resource, barrier, environmental and other functions of living and organic matter), and for epigenetic, (temperature, hydrothermal, geodynamic) accumulation of microelements in the studied caustobioliths (Patterson et al, 1987; Mossman et al, 2005; Shpirt, Punanova, 2012).

Enrichment of black and combustible shales by microelements (for some elements the content is higher than 100 g/t) is confirmed by detailed averaged data for 36 microelements (Fig. 5, Table 2).

In recent years, special attention has been paid to assessing the amount of environmentally hazardous pollution of the environment with mercury and its compounds, resulting from the extraction of shales, coals, oils and their processing. Mercury compounds are one the most environmentally hazardous among other potentially toxic microelements, and mercury releases to the environment largely depend on its content in the feedstock. Compared to other caustobioliths, oil ash is

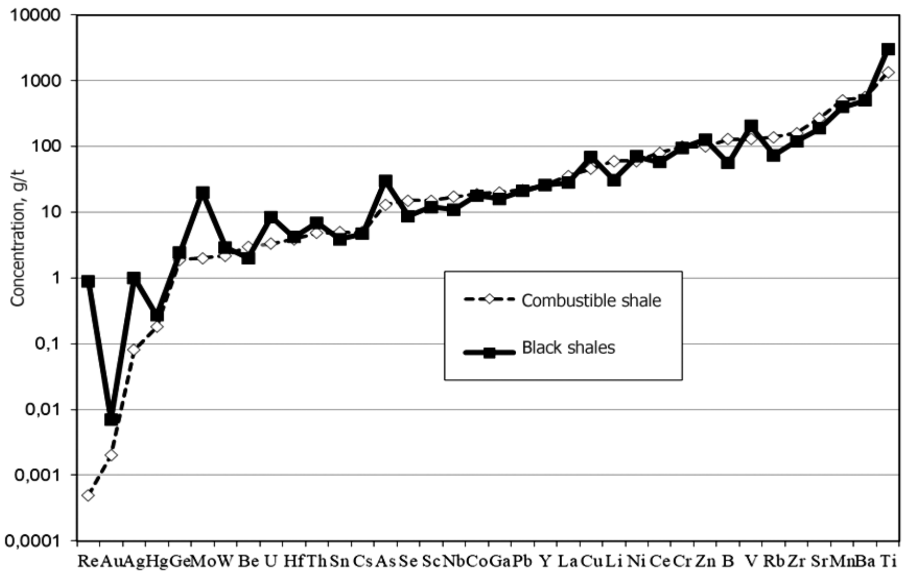

Fig. 5. Comparison of microelements in black and combustible shales (ranked by microelement content in combustible shales)

	Concentration of microelements in shales (by ten days), g/t						
	< 0, 01	0,01–0,1	0,1–1,0	1,0–10	10–100	100–1000	> 1000
Black shale	Au		Hg, Re, Ag	Ge, W, Be, U, Hf, Th, Sn, Cs, Se	Sc, Nb, Co, Ga, Pb, Y, Mo, As, La, Li, Cu, Ce, B, Rb, Ni, Cr	Zr, Sr, Zn, V, Mn, Ba	Ti
Combustible shale	Re, Au	Ag	Hg	Ge, Mo, W, Be, U, Hf, Th, Sn, Cs	As, Se, Sc, Nb, Co, Ga, Pb, Y, La, Cu, Li, Ni, Ce, Cr, Zn	B, V, Rb, Zr, Sr, Mn, Ba	Ti

Table 2. Distribution of averaged data by the microelement content in shales

the richest in microelements (Wilhelmetal, 2007). It is important to emphasize that mercury is practically the only element typomorphic in all types of caustobioliths, that is, the mercury content, both on dry matter and ash of caustobioliths, is much higher than clark. The revealed circumstance shows the wide prevalence of mercury in nature and the importance of estimating its quantities.

The largest number of studies on the assessment of mercury behavior in the combustion of solid and liquid fuels was carried out in the United States under the program for protecting the environment from the hazardous effects of mercury compounds (Kelly et al., 2003), etc. Mercury emissions into the atmosphere during oil combustion can be 1.0 x10^{-3} g/t. The revealed circumstance shows the wide prevalence of mercury in nature and the importance of estimating its quantities. Estimates of the average mercury content (mercury clark) in the oil fields of the Earth, given in the literature, fluctuate over a wide range (from> 0.001 to 2 g/t). Such a large range of calculated average mercury concentrations in oil is due to the different sensitivity and accuracy of the analytical methods used to quantify mercury and other factors (Shpirt, Punanova, 2011). There may have been mistakes in determining the mercury content due to possible losses during transportation through pipelines due to the partial volatilization of metallic mercury or the transition to the walls of pipelines when interacting

	Coal	Black shale *	Combustible shale	Sedimentary rocks	Earth crust**
U	1,9/0,6	9,9/3,1	3,2/1,0	3,0–3,4	2,5–3,0
Th	3,3/0,4	7,8/0,9	12/1,4	7,7–9,9	8–13
Ra	–	–	–	–	10^{-6}

*Table 3. Natural radionuclides content in caustobioliths and sedimentary rocks, g/t. Note. In the numerator – content, g / t, in the denominator – the ratio of the contents in caustobioliths and sedimentary rocks. * Ketris, Yudovich, 2009; ** Vinogradov, 1956*

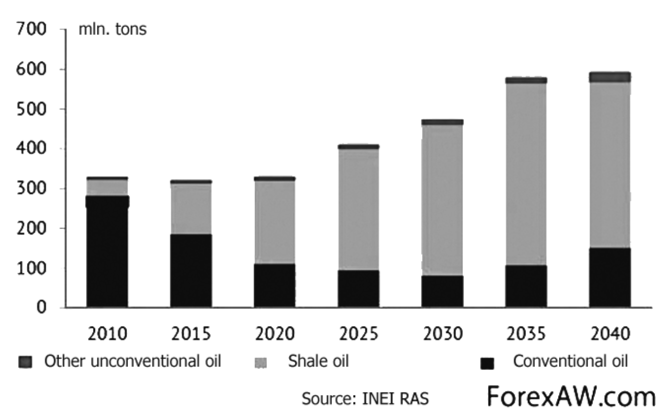

Fig. 6. Forecast of oil production of shale fields according to the Institute for Energy Studies of the Russian Academy of Sciences http://economic-definition.com/Energy/Slancevaya_neft__Shale_oil__eto.html

with metallic iron. The carried out researches allow to draw a conclusion that mercury is present in oils in the form of highly volatile fine droplets of metallic mercury, as the main form of its volatile compounds, mercury dialkyls, as well as nonvolatile sulphides and chemical compounds in asphaltenes, which can be its main component in some oils. Native mercury, its amalgams and the altmarkite mineral (Hg, Pb) (Wilhelm, 2001) are also found in oil. Even according to the lowest estimate of the average mercury content in oil when calculated for a mineral substance, it is many times higher than in sedimentary rocks and the Earth's crust (Shpirt, Punanova, 2015).

The natural radioactivity of caustobioliths is due to the content of so-called natural radionuclides in them: uranium, thorium, ^{40}K isotope and products of radioactive decay of Th, U, primarily radium and gaseous radon. Of all the natural radionuclides in combustible and black shale, the largest information is available for U, which appreciably accumulates in these shales and is undoubtedly a typomorphic (characteristic) element for them (Shpirt, Punanova, 2015).

Its average content in black shale is 8-13 g/t, and anomalously high values are considered to be more than 25 g/t. In this case, the "young" black shale (Phanerozoic) is characterized by a higher concentration of U compared with the Precambrian. In oil shales, the content of Th and U is 12 and 3.2 g/t, respectively (Table 3). The contents of U in oils usually vary for different fields or their sections in the range from $4 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ g/t, and their magnitude is probably influenced by geological processes of their formation, associated with oxidation, loss of light fractions, etc. A distinct tendency is identified of the U content increase with an increase in the density of oil and the amount of tar and asphaltenes in it. Consequently, in terms of the entire mass of caustobiolite, the content of natural radionuclides, in particular uranium is significantly lower in oil than in solid combustible fossils. However, when calculating the mineral matter of oils, which is proportional to their ash content, these figures are slightly different from each other. For example, with an ash content of 0.1%, the maximum uranium concentrations in the ash of oils can reach 5 g/t. When processing cautobioliths, products with increased radioactivity may be obtained in comparison with the initial ones (Ketris, Yudovich, 2009).

Conclusion

Thus, the development of shale formations by the method of horizontal drilling with the use of hydraulic fracturing in order to improve economic indicators remains a priority worldwide. It should be noted that according to the Institute for Energy Studies of the Russian Academy of Sciences, shale oil reserves are 4 times greater than the reserves of oil fields, since shales contain up to 70-80% of organic matter (Fig. 6) (http://economic-definition.com/Energy/Slancevaya_neft__Shale_oil__eto.html).

However, with all the above mentioned advantages, we should not underestimate the negative environmental consequences of hydraulic fracturing in connection with high contents of V, Ni, Mo, Sc, Ti, Zn, Ag, U, Re, Hg, U, As and other microelements in shale and oil. On the one hand, it is worthwhile for industrialists and scientists to think about those irrecoverable losses of valuable industrially significant metals that are due to the lack of cost-effective technologies for their recovery from naphthydes, and on the other hand, potentially toxic elements from shale and hydrocarbons contained in them could enter the downhole equipment and the environment during the hydraulic fracturing. In this regard, in order to take into account the ecological situation in shale plays introduced into the development and to make decisions on an integrated technology for the processing of shale with the recovery of gas, oil and metals, additional studies are needed to assess the microelement composition of both shale deposits and naphthys contained in them.

References

Abramova O.P., Abukova L.A. Clay sediments of sedimentary basins are generators of naphthydo- and ore-forming fluids. *Black shales: geology, lithology, geochemistry, significance for the oil and gas complex, prospects for using as an alternative hydrocarbon raw material: Proc. All-Russian Sci. and Pract. Conf.* Ed. A.F. Safronov. Yakutsk: Akhsaan. 2015. Pp. 9-11. (In Russ.)

Aver'yanova O.Yu. Oil and gas systems of shale maternal formations. *Avtor. diss. kand. geol.-min. nauk* [Abstract Cand. geol. and min. sci. diss.]. St. Petersburg. 2015. 25 p. (In Russ.)

Dvenadtsatova T.I. The ecological back of the shale revolution: risks, bans and prospects. *Neft', Gaz i Pravo*. 2015. No. 6. Pp. 36-46. (In Russ.)

Dmitrievskii A.N., Vysotskii V.I. Shale gas: a new vector in the development of worldwide market of hydrocarbon raw materials]. *Gazovaya promyshlennost' = Gas industry*. 2010. No. 8. Pp. 44-47. (In Russ.)

Gol'dberg I.S., Mitskevich A.A., Lebedeva G.V. Hydrocarbon-metalliferous world regions, its formation and localization. Problems of resource assessment and integrated development of natural bitumen, high-viscosity oils and related metals. Leningrad: VNIGRI. 1990. Pp. 49-60. (In Russ.)

Ivanov N.A. Shale America: US energy policy and the development of non-traditional oil and gas resources. Moscow: Magistr. 2014. 304 p. (In Russ.)

Johnson R.C., Birdwell J.E., Mercier T.J., Brownfield M.E. Geology of Tight Oil and Potential Tight Oil Reservoirs in the Lower Part of the Green River Formation, Uinta, Piceance, and Greater Green River Basins, Utah, Colorado, and Wyoming. Scientific Investigations Report 2016. Geological Survey, Reston, Virginia. U.S. 2016. 75 p.

Kler V.R., Nenakhova F.Ya., Saprykin F.Ya. et al. Metallogeny and geochemistry of coal-bearing and shale-bearing strata of the USSR. Regularities of concentration of elements and methods of their study. Moscow: Nauka Publ. 1988. 256 p. (In Russ.)

Kelly W.R., Long S.E., Mann J.L. Determination of mercury in SRM crude oils and refined products by isotope dilution cold vapor ICP-MS using closed-system combustion. *Anal. Bioanal. Chem*. 2003. No. 376. Pp. 753-758.

Ketris M.P., YudovichYa.E. Estimations of Clarkes for carbonaceous biolithes: World averages for trace element contents in black shales and coals. *Int. J. Coal. Geol.* 2009. V. 78. No. 2. Pp. 135-148.

Mossman D.J., Gauthier-Lafaye F., Jackson S. Black shales, organic matter, ore genesis and hydrocarbon generation in the Paleoproterozoic Franceville Series, Gabon. *Precambrian Research*. 2005. Vol.137. Issues 3-4. Pp. 253-272.

Nemec R. Thriving in a Major U.S. Shale Play the Bakken Unpacked. *Pipeline and Gas Journal*. November, 2016. Pp. 56-60.

Ozdoev S.M., Tsirel'tson B.S. Oil shale of Kazakhstan. *Neft' i gaz = Oil and gas*. 2014. No. 1. Pp. 25. (In Russ.)

Patterson J.H., Dale L.S., Fardy I.J. et al. Characterisation of trace elements in Rundle and Condor oil shales. *Fuel*. 1987. No. 3. Pp. 319-322.

Safronov A.F. Upwelling as a one of the factors for the formation of oil shale strata. *Black shales: geology, lithology, geochemistry, significance for the oil and gas complex, prospects for using as an alternative hydrocarbon raw material: Proc. All-Russian Sci. and Pract. Conf*. Ed. A.F. Safronov. Yakutsk: Akhsaan. 2015. Pp. 63-68. (In Russ.)

Spravochnik po geokhimii nefti i gaza [Guide on the geochemistry of oil and gas]. Ed. S.G. Nerucheva. St.Petersburg: Nedra Publ. 1998. 576 p. (In Russ.)

Sukhanov A.A., Yakutseni V.P., Petrova Yu.E. Metalliferous potential of oils – assessment of development prospects and possible ways of implementation. *Neftegazovaya Geologiya. Teoriya I Praktika*. 2012. Vol. 7. No. 4. http://www.ngtp.ru/rub/9/56_2012.pdf (In Russ.)

Shpirt M. Ya., Punanova S.A. Accumulation of Mercury in Petroleum, Coal, and Their Conversion Products. *Solid Fuel Chemistry*. 2011. No. 5. Pp. 330-336.

Shpirt M.Ya., Punanova S.A. Radioactive Elements of Solid Fossil Fuels. Buck of Abstracts. *27-th International Meeting on Organic Geochemistry (IMOG 2015)*. Prague (Praha), Czech Republic. 2015. P. 504.

Shpirt M.Ya., Punanova S.A. Microelements of caustobioliths and shales: problems of their genesis and industrial use. *Geokhimiya = Geochemistry.* 2009. No. 2. Pp. 216-224. (In Russ.)

Shpirt M.Ya., Punanova S.A. Mikroelementy kaustobiolitov. Problemy genezisa i promyshlennogo ispol'zovaniya [Microelements of caustobioliths. Problems of genesis and industrial use]. Saarbrucken. Germany: Lambert Academic Publishing. 2012. 367 p. (In Russ.)

Shpirt M.Ya., Punanova S.A., Mukhametshin R.Z., Nukenov D. Shale strata and oil as a source of hydrocarbons and metals. *Mezhd. nauchno-prakt. konf. «Osobennosti razvedki i razrabotki mestorozhdenii netraditsionnykh uglevodorodov»* [Conf. "Features of exploration and development of deposits of non-traditional hydrocarbons"]. Kazan. 2015. Pp. 80-82. (In Russ.)

Shpirt M.Ya., Punanova S.A. Mercury in caustobioliths: accumulation, burial and geoecology. *Mat. Mezhd. konf. «Resursovosproizvodyashchie, malootkhodnye i prirodookhrannye tekhnologii osvoeniya nedr»* [Proc. Int. Conf. "Resource-reproducing, low-waste and nature protection technologies for subsoil development"]. 2015. Kyrgyzstan, Bishkek. Pp. 158-159. (In Russ.)

Shpirt M.Ya., Punanova S.A. Oils and combustible shales as a raw for potentially trace elements producing. *Neftyanoe khozyaistvo = Oil industry*. 2017. No. 4. Pp. 58-62. (In Russ.)

Tisso B., Vel'te D. Formation and distribution of oil. Moscow: Mir Publ. 1981. 501 p. (In Russ.)

Urov K., Sumberg A. Characteristics of oil shale and shale-like rocks of known deposits and occurrence. Tallinn: Valgus. 1992. 63 p. (In Russ.)

Vinogradov A.P. Regularities of distribution of chemical elements in the Earth's crust. *Geokhimiya = Geochemistry*. 1956. No. 1. Pp. 6-52. (In Russ.)

Wilhelm S.M. Estimate of Mercury Emissions to the Atmosphere from Petroleum. *Environmental Science and Technology*. 2001. 35 (24). Pp. 4704-4710.

Wilhelm S.M., Liang L., Cussen D., Kirchgessner D.A. Mercury in crude oil processed in the United States (2004). *Environmental Science and Technology.* 2007. V. 41. No. 13. Pp. 4509-4514. Yurova M.P. The Prospects and Opportunities to Use Coal Bed Methane as Unconventional Energy Source. *Georesursy = Georesources*. 2016. V. 18. No. 4. Part 2. Pp. 319-324. DOI: 10.18599/grs.18.4.10

Yakutseni S.P. The abundance of hydrocarbons enriched with heavy element-impurities. Assessment of environmental risks. St.Petersburg: Nedra Publ. 2005. 372 p. (In Russ.)

Yakutseni S.P. Deep zoning in concentration of heavy elements-admixtures in hydrocarbons. *Neftegazovaya geologiya. Teoriya i praktika*. 2010. Vol. 5. No. 2. http://www.ngtp.ru/rub/7/30_2010.pdf (In Russ.)

Yarahanova D.G. The use of horizontal wells for extraction of hard-to-recover and non-traditional hydrocarbon reserves. *Proc. Int. Sci. and Prac. Conf. «Hard-to-recover and unconventional hydrocarbon reserves: Experience and prospects»*. Kazan. 2014. Pp. 400-402. (In Russ.)

Zanin Yu.N., Zamirailova A.G., Eder V.G. Regularities in the distribution of some elements in different types of rocks of the Bazhenov suite. *Black shales: geology, lithology, geochemistry, significance for the oil and gas complex, prospects for using as an alternative hydrocarbon raw material: Proc. All-Russian Sci. and Pract. Conf*. Ed. A.F. Safronov. Yakutsk: Akhsaan. 2015. Pp. 128-132. (In Russ.)

Zueva I.N., Chalaya O.N., Kashirtsev V.A., Glyaznetsova Yu.S., Kalinin A.I. Possibilities of using high-carbon rocks of the Cuonam formation as a complex mineral raw material. *Black shales: geology, lithology, geochemistry, significance for the oil and gas complex, prospects for using as an alternative hydrocarbon raw material: Proc. All-Russian Sci. and Pract. Conf*. Ed. A.F. Safronov. Yakutsk: Akhsaan. 2015. Pp. 133-137. (In Russ.)

About the Authors

Svetlana A. Punanova – PhD (Geology and Mineralogy), Lead Researcher, Oil and Gas Research Institute of the Russian Academy of Sciences

Russia, 119333, Moscow, Gubkin str., 3
Tel: +7(499) 135-72-21
R-mail: punanova@mail.ru

Dauit Nukenov – PhD (Engineering), Deputy Director for Research, TOO Kaz-Waterhunters

130000, Kazakhstan, Mangystau region, Aktau, 6 md., 8, off. No. 202

Manuscript received 22 June 2017;
Accepted 27 July 2017;
Published 30 August 2017