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The New Classification of Reserves and Resources of Oil and Combustible Gas – Movement Onward or Backward?

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Abstract. The new classification of reserves and resources of oil and combustible gas is officially introduced since 2016. The paper evaluates the advantages and disadvantages of the new classification and compares it with previous existing classifications of reserves in the Russian Federation, as well as with the similar major classifications of the Western countries. The author evaluate the usefulness and relevance of the new classification in the approval process and the use of oil reserves. The conclusion is made that the new classification and accompanied documents will not improve but worsen the situation in the Russian subsoil use, methods of calculation and accounting of reserves, and reliability of field development parameters. A more rigid approach of the Soviet era is replaced by a formal liberal one; the degree of reserves reliability is substantially lower, economic calculations are complicated and highly bureaucratized with no apparent need; labour content and complexity of procedures increases considerably. The classification essentially withholds the fundamental problems (the concepts of absolute and effective pore space, geological and balance reserves, the ideology of building geological and hydrodynamic models). The new classification does not solve urgent issue of placing reserves into different categories according to their possible cost-effective and efficient development, namely placing hydrocarbon reserves in hard-to-recover and (or) unconventional, the development of which requires the use of new, more expensive technologies and fold increase in capital and operating production costs.

Keywords: categories of reserves and resources, new classification of reserves, geological, balance, recoverable oil reserves, reserves difficult to recover, unconventional oil deposits, geological, geological and hydrodynamic models, the state commission on reserves, oil companies.

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There are 150 classifications in the world of resources of energy commodities, built on different parameters and different interpretations of the same terms. Naturally, this causes confusion and discourages potential investors to participate in projects of development of deposits.

To solve this problem, the Economic Commission for Europe about 10 years ago proposed the development of an international United Nations Framework Classification for the fields of solid fuels, uranium and hydrocarbon crude, which was implemented. The UN countries currently use the Framework Classification for Fossil Energy and Mineral Reserves and Resources of 2009 (UNFC-2009). It is a universal system in which quantities are classified on the basis of three fundamental criteria: economic and social viability of the project (E), status and validity of the field development project (F), and geological knowledge (G), using a numerical code system. Combinations of these criteria provide three-dimensional system.

In the US, at the same time there are several reserves classifications: Classification of the Securities and Exchange Commission (SEC), Classification of the Society of Petroleum Engineers (SPE), classification of the American Association of Petroleum Geologists (AAPG), and others.

In Russia, the main issues of functioning of the oil and gas industry are solved by a single reserves classification. Prior to 2016, "Temporary Classification of field reserves, perspective and inferred resources of oil and combustible gases" of 2001 was valid. It established uniform principles for the Russian Federation of calculation and state accounting of field reserves and prospective resources of oil and combustible gases in the subsoil according to their degree of knowledge and economic significance, conditions that determine the readiness of the explored fields for industrial development, as well as the basic principles of assessment of inferred oil and gas resources.

Prior to that, classification of the Soviet period successfully worked, which was approved in 1983. It provided common principles of accounting oil and gas reserves in the subsoil by categories based on the degree of knowledge of these reserves and their readiness for commercial development. It has stood the test of time and was a document that optimized accounting and reporting for the Russian Federation reserves. But then, in order to bring the Russian classification of reserves to the western standards new classification has been developed and adopted, "Classification of reserves, perspective and inferred resources of oil and combustible gases", which supposedly maintains continuity with the current classification for the allocation of categories of resources and reserves a t the level of geological knowledge and confidence. In it, oil and gas reserves are classified by the degree of geological exploration, industrial development and economic efficiency of development.

The new classification of reserves had to be implemented in 2009. But for transition it was necessary to conduct an audit of the reserves balance in all oil and gas fields of the country with hydrodynamic and economic calculations on the accepted categories. This great work was physically impossible to carry out in due time. But there was nothing wrong with that. The transition to the international classification is needed mainly to attract foreign investment. But even in the absence of Western sanctions against Russia, investments attracted a limited number of oil companies, which held annually inaudit of reserves by well-known western consulting companies, by the results of which Western banks were granting a credit.

Our classification of the Soviet era provided the necessary accuracy for oil companies and the government of reserves and resources of oil and gas. In this respect it is more progressive and would continue to function. There was no need to change anything. Those oil companies who want to attract foreign investment, may do so by conducting audit of reserves by Western companies. Nevertheless, it had to be done regardless of transition of Russia to the new classification. But due to the introduction of Western sanctions against the Russian Federation currently the matter was dropped.

Therefore, there was no rush in the introduction of new reserves classification. However, the higher authorities thought otherwise and without sufficient study, expertise and extensive discussion adopted the new reserves classification and introduced it into effect from 2016. They did not even have time to prepare the necessary documents on the project of the State Commission on reserves for the implementation of the new reserves classification.

In Soviet times, there was the notion of balance reserves, which stood out from the geological reserves, using the so-called conditional values of reservoir rocks. Conditional values are limit values of properties for hydrocarbon-saturated rocks, dividing them into reservoirs and non-reservoirs, as well as reservoirs with different field characteristics. These limit values are also called lower limits of productive reservoir properties (by porosity, permeability and oil saturation). Objects that have parameters below conditional are not included, and we simply do not take them into account.

In the classification of 2001 the concept of balance reserves was automatically replaced by geological reserves, which was a gross mistake of the authors (Zakirov and others, 2006; Muslimov, 2003).

At present, the State Commission on reserves is not ready for drastic changes in matters of reserve calculation. But at the design of development, we still need to proceed from the fundamental principles of geology.

In 1933, on the basis of studying the characteristics of productive strata regimes of Novogroznensky region, V.M. Nikolaev made an important conclusion that every oil reservoir should be regarded as dual physical field that combines several physical fields, and particular importance should be given to the study of pressure, temperature fields and hydraulic regime of the strata : "... the study should not be limited only to the oil-bearing area, it is necessary to study the entire hydraulic system, which must have a beginning and an end." Thus, one of the main points underlying in the "new approach" to the geological and reservoir simulation, was stated more than 70 years ago, and, as noted by V.N. Shchelkachev, this idea of V.M. Nikolaev, while being advanced, still lies in the foundation of the modern petroleum science.

American geologists on the results of geological and hydrodynamic analysis of oil production facilities in the 1960-1962 showed that liquid system in the sedimentary complex is a continuous medium. The flow of liquid through the sedimentary section should be evaluated for all kinds of rocks, regardless of their capacity, that is, from highly permeable to the least permeable clays. Therefore, there is no need to draw the boundary between the permeable and impermeable rocks. Indeed, with new technologies, modern techniques of well completion, hydraulic fracturing etc. it became possible to produce hydrocarbons in the industrial scale from rocks that were previously considered impenetrable. This was brilliantly confirmed by oil and gas revolution in the United States.

VNIIneft conducted in 1980 on the Uzen field studies of cumulative distribution curves of permeability for receiving and non-receiving reservoirs and separately for productive horizons and jointly for all of these horizons. They have convincingly shown that virtually all rocks are linked with mutual transitions, and that there is no sharp boundary between reservoir and non-reservoir.

In view of the above, there is a need to reassess the geological oil resources as balance and recoverable reserves in the old sense leave behind unconditional reserves, and they, according to preliminary estimates, could amount to 15-20% of the approved reserves. Thus, the geological reserves should mean all the amount of oil that is in the depths, regardless of whether it is possible today to remove from the interior or not (Fig. 1). As can be seen from Fig. 1 such an approach total resources will increase and value of oil recovery factor will decrease.

It seems appropriate to develop a methodology for calculation of geological reserves in view of the huge progress in the West of geological exploration and extraction of hydrocarbons experience from dense rocks (or even shale); in order to avoid registration of unconditional by today's standards reserves, we should recall that earlier oil and gas fields on the economic significance were divided into two groups, subject to a separate accounting: balance reserves, involvement in the development of which is now economically feasible, and off-balance reserves, the involvement of which currently economically impractical or impossible technically and technologically, but which further with the development of technologies can be transferred to the balance reserves.

Currently, this term, unfortunately, is not used. In this case, we will not put on record inflated reserves. But in the total

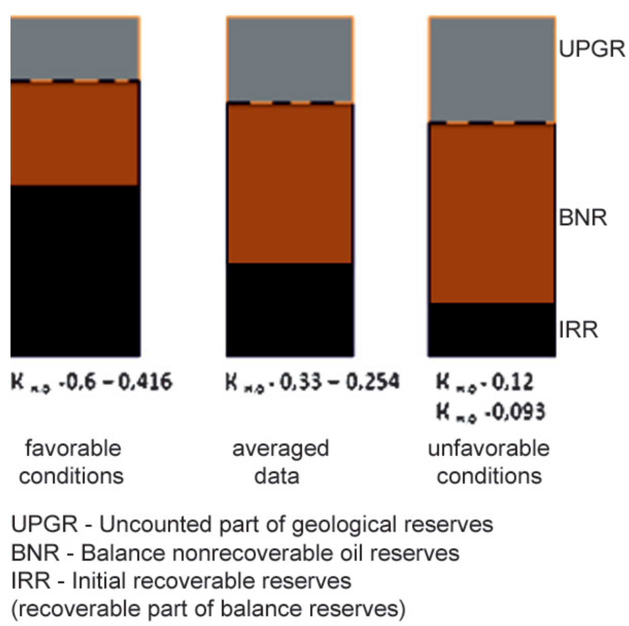


Fig. 1. Schematic representation of geological balance and recoverable oil reserves.

balance unconditional reserves will be as object of activity of oil company to conduct R&D and pilot development and find ways to extract them (the so-called off-balance reserves). With the new technology created we could translate them into the category of balance reserves, and then extract. This approach will help to improve the efficiency of drawing up development projects.

Advances in the development of oil fields will be more significant if we radically change the ideology of geological and then geological and hydrodynamic models. Models practiced today do not take into account geological features of the accumulation and transformation of sediments and the formation of oil deposits.

S.N. Zakirov (Zakirov et al., 2006) rightly considers wrong the ideology of building models. In his opinion, guidance documents require to not include "non-reservoirs" into 3D geological models. That is, all (almost all) created 3D geological models in the country are defective. Since they distort geology of fields manually. This was have repeatedly written (Muslimov, 2003; 2012; 2014).

Fig. 2 shows the new models of the horizon D1 of Romashkino field: with justified in a number of papers (Khusainov, 2011; Afanasiev et al, 2011) conditional values of reservoir rocks (permeability> 1 mDa, porosity <11, content of pelitic fraction> 0.20), we obtain a model (Figure 2b), and taking into account all the so-called dense partitions – completely different model (Figure 2c).

The construction of such models is of particular importance for carbonate rocks. Currently used methods of building models for reservoir intervals from the roof to the oil-water contact account only part of the so-called effective oil-saturated thickness of reservoir rocks. This part in different conditions ranges from 20 to 75-80 % of the total oil saturation thickness. Oil is in almost entire thickness of the rocks. But most importantly – researches conducted in Tatarstan have proven active participation of so-called dense partitions in filtration processes (Khusainov 2011; Muslimov 2014).

In modern conditions it is time to move on to the next level of calculating indicators of development.

To this day, due to the concept of absolute pore space, initial petrophysical results are based on mass definition of non-informative values of the absolute permeability coefficient of gas and open porosity (by dry cores!).

According to the concept of effective pore space (EPS) (Zakirov et al., 2006), it is necessary to built petrophysical relationships on the results of determining the actual coefficient of effective permeability and effective porosity, because the reliability of petrophysical relationships within the EPS concept is significantly higher than in the concept of absolute pore space (APS). Then it is obvious that the accuracy of logging data to build 3D models will be much higher.

In our opinion, we need to change the ideology of building models, taking into account the allocation of geological, balance, off-balance, and recoverable reserves. But to build such models it is not sufficient to use current methods for the preparation of information. First of all, we need to diversify and deepen the laboratory research of rocks and fluids saturating them, as well as improving logging techniques.

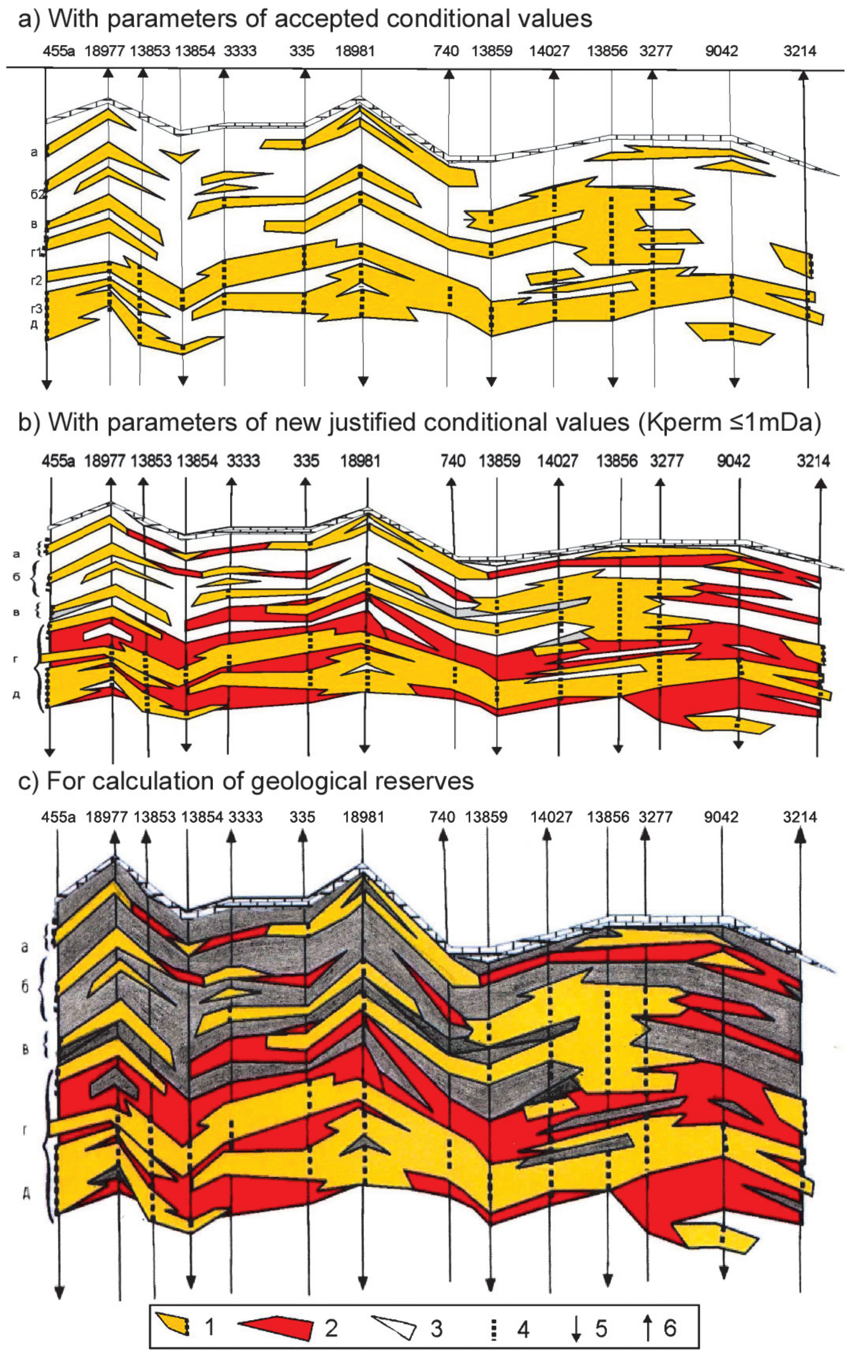


Fig. 2. Geological profile through line of wells No. 455a-3214 of Abdrahmanovsky area of Romashkino field. 1 - Reserves with parameters of officially accepted conditional values (Kperm ≤30mDa); 2 - Reserves with parameters of new justified conditional values (Kperm ≤1mDa); 3 – Not accounted oil-saturated rocks; 4 -Injection well; 5 - Production well.

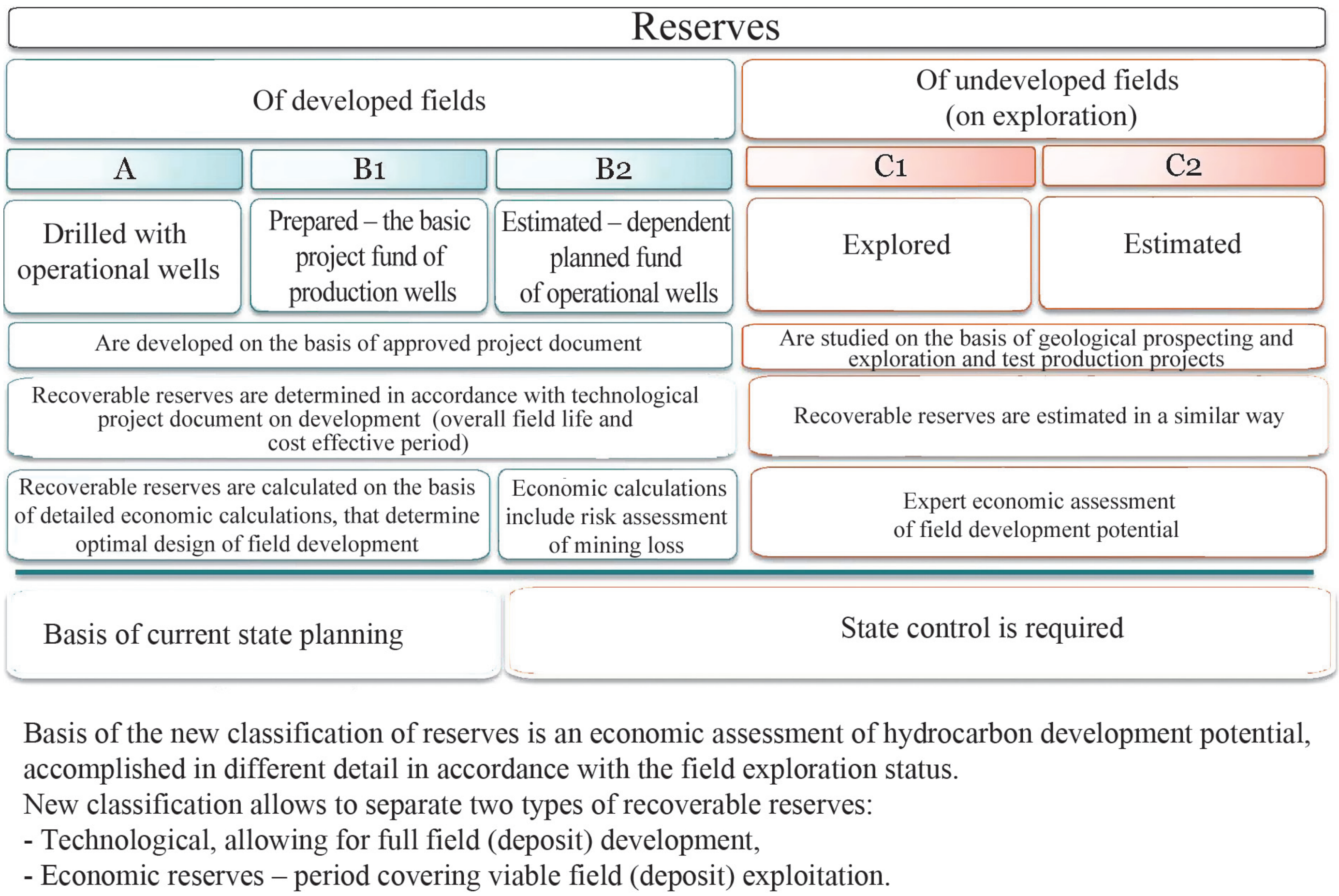


Fig. 3. Basic principles of the new reserves classification of hydrocarbons (by I.V.Shpurov).

The above relates to the fundamental provisions. Probably, we will not immediately solve them and move to the new models. But it is time to set out the problem and work on it. Compared to the Soviet period in the practice of oil reserves approval, there has been a trend of weakening attention to authenticity of oil reserves taken into balance. This results in a lighter attitude toward C_2 category. In the design of development and reports on growth of oil reserves, as a rule, all reserves of categories A + B + C_1 + C_2 are accounted. But the category C_2 is considered as pre-estimated. In practice, the conversion factors in the C_2 category reserves are higher (verifiability rates) up to the different conditions from 0.4 to 0.7-0.8, and sometimes higher. Earlier the category C_2 was treated more gently – it

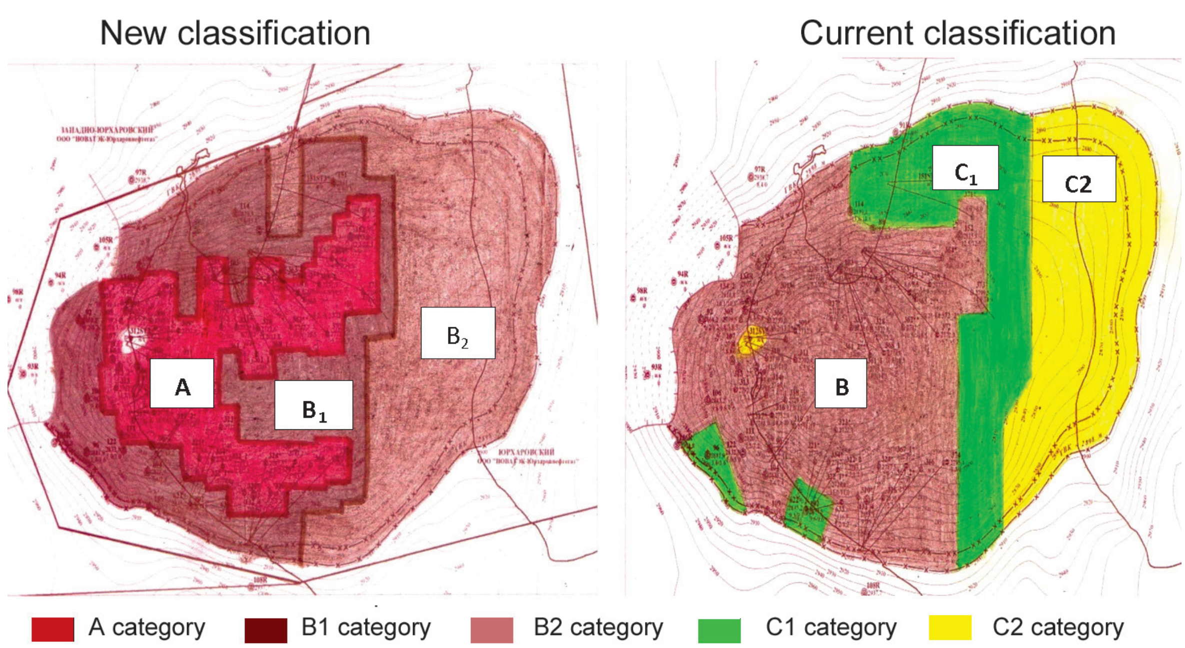


Fig. 4. Comparison of the reserves allocation by categories according to the current and new classifications of reserves.

	Russian Federation	Current classification of reserves – Russian Federation		New classification of reserves – Russian Federation		Western classification of reserves
Reserves	Explored	A	Drilled with operational wells, developed	A	Drilled with operational wells	Drilled, developed
		B	Drilled with operational wells	B_1	Prepared – the basic project fund of production wells	Undeveloped
				B_2	Estimated – dependent planned fund of operational wells	
		C_1	Exploration wells are drilled	C_1	Explored	Marked
	Preliminarily estimated	C_2	In contour deposits, adjoined to areas of higher categories	C_2	Estimated	Probable (calculated)
Resources	Prospective	D_0 (C_3)		D_0		Possible
	Expected localized	$D_{1Л}$		$D_{1Л}$		Hypothetical
	Expected	D_1		D_1		
		D_2		D_2		Theoretical

Table 1. Comparison of old and new Russian classification of reserves and their comparison with Western analogues.

was allowed to design reserves, when the proportion of C_2 did not exceed 20% of the total reserves received for the design. The State Commission on reserves was tougher on accepting reserves of C_2 category. This provided higher reliability of the resource base for the planning; especially design of the development of specific fields.

However, the assessment of the reserves reliability in the new reserves classification is even more reduced. Fig. 3 shows the basic principles of the new reserves classification (According to I.V. Shpurov). There reserves of category A are in the areas drilled with operational wells. It seems that the same requirement remained in the new reserves classification. But in the old sense, and in the western classifications the concept of developed areas was added to drilled areas. Practice and experience of development shows that not all reserves drilled by project wells are produced. Depending on the complexity of geological structure of drilled area at full introduction of the waterflooding system, 50-80 %, rarely more percent of reserves are involved into the development. It takes decades of additional various geological and technical measures to engage in the development of major (95-100 %) reserves of operational object (Romashkino field experience).

Earlier Category B had always been considered in the areas actually drilled by project well grid. In the new reserves classification we have more than a vague concept: B1 – prepared – the basic fund of production wells and re-allocated category B2 – estimated – dependent fund of operational wells (while it is not quite clear what dependent fund is). Therefore to category B we can include areas where design well point are marked on the map, and not actually drilled. Based on the development experience, confirmation of design reserves with actual drilling out is 70-80 %, less – up to 90-100 % (depending on the geological complexity of the area). Categories C_1 and C_2 are even more uncertain. In fact, reserves of categories B_2, C_1, C_2 according to the new reserves classification can be attributed as B1, without conducting any work on the field, but simply placing the project wells on paper (Fig. 4). The Western countries more accurately refer to the categories C_1 and C_2, as well as perspective and inferred resources (Table 1).

Even greater difficulties arise with the economic assessment of reserves. The economic assessment of recoverable reserves of categories A, B1, B2 is required as part of the coordination of each development option of the operational facility. According to the analysis of JSC Neftekonsortsium, the appendices contain 37 tables on economic evaluation, in three options (37*3) = 111 tables on a single object. And if they are 5, then there will be 555 tables only by industrial categories. If we take Romashkinsko field with 15 productive horizons and with development period up to 2150, it turns to be 1665 tables (about 70,000 pages). For typical for Tatarstan small deposit (5 million tons of the initial recoverable reserves) there should be 555 tables. Preparing data for 37 economic tables and carrying out economic calculations will require a long-term operation of the subsoil user and designers, multiple appreciation of the work.

Instead of reducing administrative barriers and reducing the time of work on the documents we obtain an increase in terms and a multiple increase in the cost of works.

Table 2 shows our assessment of the usefulness and relevance of the new classification on reserves for the approval and use of oil reserves. Based on the above it can be said that the introduction of the new classification and related documents will not improve, but worsen the situation in the domestic subsoil use, in the methodology of calculation and accounting of reserves and the reliability of calculating development parameters.

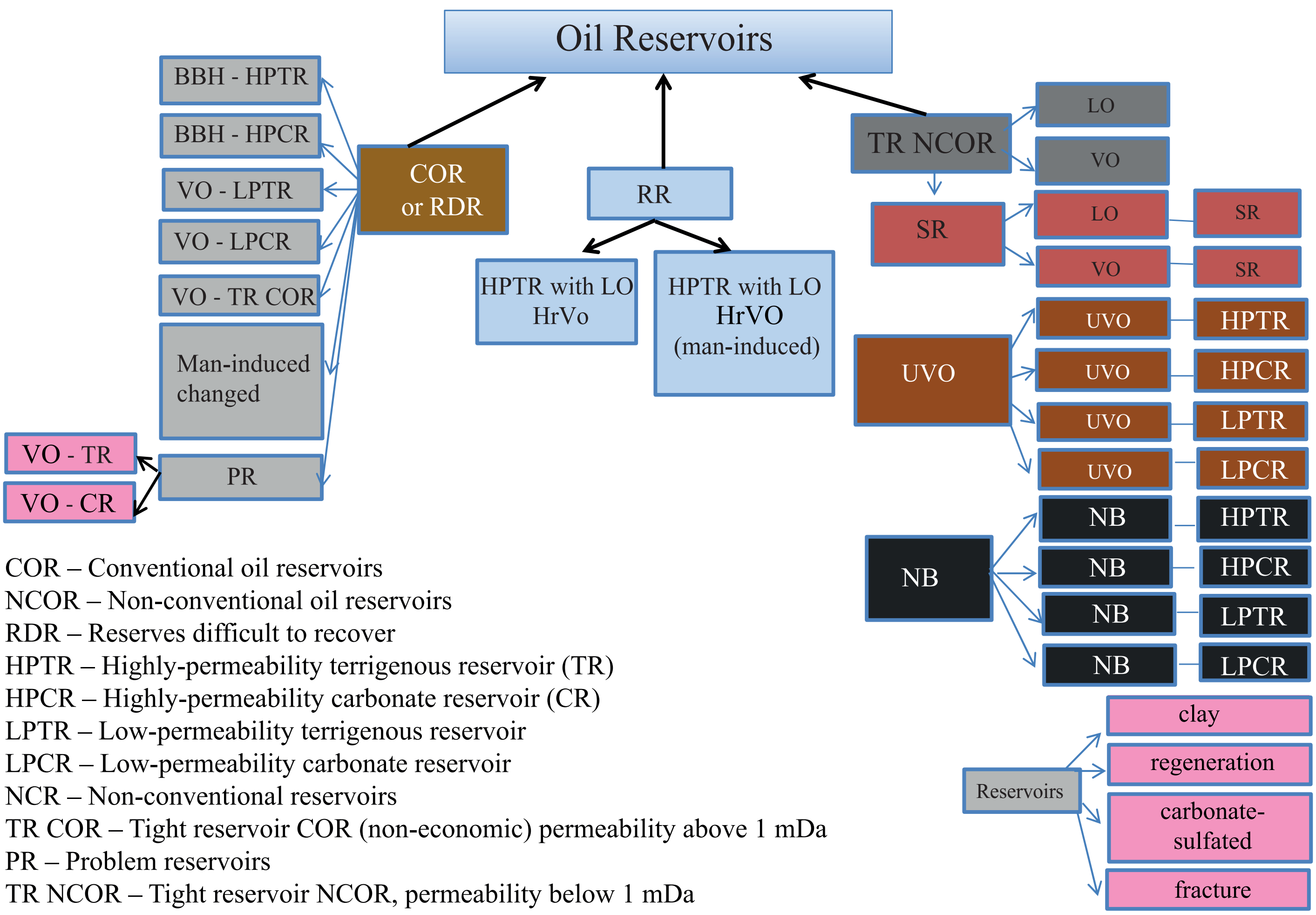
The new reserves classification does not solve topical issues of development of the oil industry, namely, placing reserves into different categories according to their possibilities of cost-effective and efficient development. Here we are referring to the assignment of hydrocarbon reserves to difficult to recover and (or) unconventional, the development of which requires the use of new, more expensive technologies and multiple increase of capital and current production costs.

On the basis of the new classification on reserves it is required to develop a classifier, which would give a clear definition of the various concepts (reserves difficult to recover, unconventional reserves, ets.). The revised terms would form the basis for the creation of new techniques and technologies.

The classification issue is not only of a scientific and technical nature. Without its solution it is impossible to build strategic plans for development of the industry, as well as the development of oil companies themselves. But other than that, the classification is necessary for government agencies to establish tax regimes that provide input to the development of deposits with reserves difficult to recover, unprofitable under the current taxation. At the end of the last century the Russian geologists have undertaken a number of efforts to develop a classification for the tax authorities.

According to the classification developed 20 years ago in 1994 year by N. Lisovskoy and E. Khalimov, four criteria were allocated for classifying reserves as difficult to recover. They are: viscosity (30 cps at reservoir conditions), the presence of low permeability reservoirs (below 0.03 darcy), depletion (over 70%) and regional coefficient (in the range 1, 2) (TrIZ: turn the brain on?.., 2014) . This classification caused great objections of experts and therefore was not accepted.

Today, the Tax Code contains very different values, allowing to rank deposits to reserves difficult to recover: viscosity – 200 cps, permeability – 2 mDa, depletion – 80%. Regional coefficient is replaced by a list of specific areas in which reserves can be considered hard-to-recover. Today it is possible to recognize that such criteria are not scientifically justified.



COR – Conventional oil reservoirs
NCOR – Non-conventional oil reservoirs
RDR – Reserves difficult to recover
HPTR – Highly-permeability terrigenous reservoir (TR)
HPCR – Highly-permeability carbonate reservoir (CR)
LPTR – Low-permeability terrigenous reservoir
LPCR – Low-permeability carbonate reservoir
NCR – Non-conventional reservoirs
TR COR – Tight reservoir COR (non-economic) permeability above 1 mDa
PR – Problem reservoirs
TR NCOR – Tight reservoir NCOR, permeability below 1 mDa
SR – Shale reservoirs
LO – Light oil (viscosity below 10 centipoise)
HrVO – Higher viscosity oil (viscosity 10-200 centipoise)
HVO – High-viscosity oil (viscosity 200-1000 centipoise)
UVO – Ultra viscous oil (viscosity 1000-10000 centipoise)
NB – Natural bitumen (viscosity >10000 centipoise)
VO – More than 20 centipoise viscosity oil

Fig. 5. Classification of oil fields with reserves difficult to recover, conventional and non-conventional oil (by R.Kh. Muslimov).

The benefits of the new scheme of reserves approval according to the New Classification of Reserves (by Shpurov I.V.)	**The actual impact of the New Classification of Reserves on the approval process and reserves use (by Muslimov R.Kh.)**
It provides the basis for the current and medium-term state planning of the raw material production levels	Tough approach to the reserves approval of the Soviet era is replaced by a less strict (volatile) in the new classification (categorization is unreasonably overstated – drilling with production wells does not guarantee involvement in the development of drilled reserves; projected coverage of reserves by project wells grid does not guarantee confirmation of reserves based on actual results, and designation of current reserves C_1 and C_2 as the B_2 is generally incorrect. The basis for the development design does not guarantee the necessary level of production planning.
It creates a basis for scientifically justified mechanism for promoting the development of reserves difficult to recover.	It is not clear - at the expense of what? To address this issue, special geological and commercial classifications are required, depending on the geological conditions of the regions and (or) regulations.
Reduction of administrative barriers - implementation of a single-window principle.	Due to what? The volume of materials has increased multiple times.
Reliable geological model is the basis of design solutions.	Reliable geological model can be obtained only on the results of drilling by the project wells grid, development of waterflooding system, analysis of the development of reserves. Practical volume of recoverable reserves often does not correspond to the project one.
The volume of recoverable reserves corresponds to the actual volume according to the Project technical documents for the development of fields.	**Long overdue positive decision.**
The concepts are applied - technologically recoverable reserves and recoverable reserves for the cost-effective development period.	These concepts are present in the projects for a long time. But in today's volatile conditions (especially in Russia) for determining parameters (price on the world and domestic markets, permanently changing legislation on subsoil use, taxes, inflation, expenses, etc.) it does not make sense.
Time for the documents preparation is significantly (by 40%) reduced.	**It has increased substantially**
Recoverable reserves are harmonized with international classifications and can be used as a basis for decision-making on investment in the development of fields	Harmonization with international classifications is not visible; it is not possible to use it for justifying investments.
Conclusion: A more rigid approach of the Soviet era is replaced by a formal liberal one; the degree of reserves reliability is substantially lower, economic calculations are highly bureaucratized and complicated with no apparent need, the cost and the complexity of procedures increases considerably. Classification is essentially silent about the fundamental problems (absolute pore space, effective pore space, geological and commercial reserves, construction ideology of geological and hydrodynamic models)	

Table 2. The so-called benefits of the new scheme on reserves approval.

In order to solve practical problems of development of the industry we need to have workers of classification, allowing purposefully carry out work on the development of new technologies of reservoir development and application of methods for enhanced oil recovery.

These classifications have been developed in Tatarstan for the past 30 years.

The latest classification is developed by R.Kh. Muslimov (Fig. 5). Such classifications should be developed for the major oil regions, as they may reflect the specifics of the geological structure of deposits in different regions, since it is different. However, for the public use and issues of referring hydrocarbons to reserves difficult to recover and unconventional reserves, for the purpose of tax incentives we need to develop criteria for placing reserves into different categories. This will help to create for them different taxation systems and solve the problem of supplying Russia with oil and gas.

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Comprehensive Analysis of Geological-geophysical Data and Development Parameters to Justify System of Bedded Deposits in Allochthon and Autochthon of Vuktyl Oil and Gas Condensate Field

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Abstract. Comprehensive analysis of injected 'dry' gas distribution and well production, composed correlation schemes of productive Artinian-Lower Carboniferous sediments, reservoir pressure distribution over sediments of various age revealed that the well-known massive deposit of Vuktyl field is characterized as a system of bedded deposits, apparently, with its own gas-water contact. This model allows the most efficient control and management of processes in the productive section when using the injection of 'dry' gas in allochthonous part of the field.

According to drilling and 2D, 3D seismic survey in the north of Vuktyl field an autochthonous fold with amplitude of up to 125 m is established in carbonate deposits of Lower Permian-Lower Carboniferous, to which bedded deposits may be confined, as evidenced by the abundant oil flow and oil and gas shows in drilled wells. Total resources of the autochthonous bedded deposits could reach tens of billions of cubic meters.

Keywords: Vuktyl field, section, allochthon, autochthon, well, gas condensate deposit, injection of 'dry' gas, seismic survey, productive deposits.

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The study and specification of the geological structure of Vuktyl oil and gas condensate field was carried out since it was discovered in 1964 in the exploration, development and commercial operation of the current development. Vuktyl structure is structurally complex swell-like high-amplitude asymmetric fold with submeridional two structural levels: the upper overthrust-allochthonous and lower low dislocation-autochthonous. The field with productivity level up to 1500 m and large size has unique in its reserves Lower Permian coal-gas condensate deposit, confined to allochthonous part. The deposit is considered to be a massive tectonically shielded with a common gas-water contact (Fig. 1).

In component composition Vuktyl formation gas belongs to a group with a high content of condensate, the value of which for the initial pressure and temperature conditions (reservoir pressure of 36.3 MPa) was 360 g/m^3. Development of the deposit up to 1993 was carried out in the depletion mode of natural energy of the reservoir. Extraction from formation was accompanied with reservoir pressure loss, resulting in a significant loss of liquid hydrocarbons in the formation. By this time, reservoir pressure passed the threshold of maximum condensation and decreased to 3.78 MPa.

To increase the condensate since 1993 the technology of active influence on the exhausted gas condensate deposit was being implemented on the field. The effectiveness of the technology used is determined by the achievement of maximum coverage of productive intervals by 'dry' gas and, as a result, production of hydrocarbons fell in the formation.

At present, the influence of 'dry' gas covered a large area of the field: injection is performed at the gas treatment plant-1, 2, 4, 8.

The control of injection and extraction processes realized on the basis of standard geophysical, gas condensate and gas-dynamic research complexes is conducted on two groups of wells: injection and production.

Analysis of geophysical researches of wells, which resulted in more detail studied geological sections of exposed deposits, allows determining the depth of productive horizons, their reservoir properties, including porosity, permeability, fluid saturation, and track gas yielding and absorbing intervals of production and injection wells, respectively.

According to the results of gas condensate research, as well as operational control over the component composition of gas by production wells, the ways of 'dry' gas productive deposits from injection wells to production were traced.

Based on the results of pilot projects two options were identified for promoting injected 'dry' gas into production wells. The first option – injection and extraction occur on deposits, confined to a single stratigraphic horizon; the second option – injection is carried out in the sediments of the same age, and production – in multi-aged deposits. This is facilitated by conducting tectonic violations established by drilling and seismic data (Pankratova, 2013). As an example, Fig. 2 shows geological profiles through wells in sites UKPG-1 and UKPG-2 (gas treatment plants), which displays options for promoting injected 'dry' gas.

On the basis of investigations balance calculations of hydrocarbons are carried out on the productive deposits, confined to different stratigraphic horizons. On the example UKPG-1, where Tyumen gas sweeps the entire productive interval, the distribution of Tyumen gas production and retrograde condensate for each well is shown.

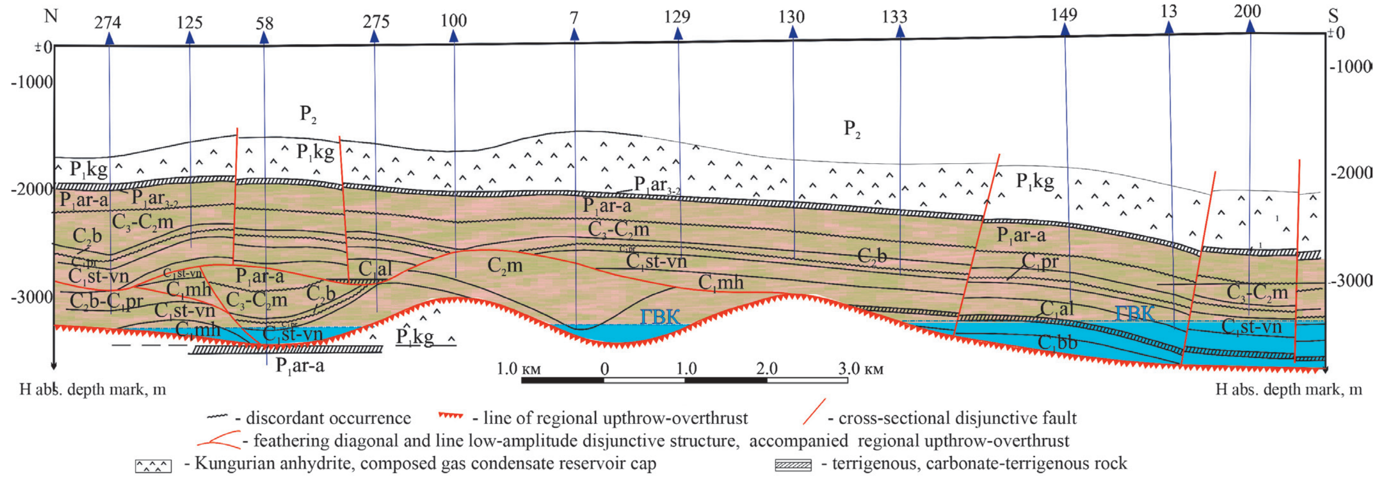

Fig. 1. Longitudinal profile of site of Vuktyl field.

Theoretically, it is assumed that in massive deposit precipitated condensate takes hypsometrically low depth. However, the authors of this article conducted analysis of retrograde condensate production from the beginning of injection. It showed that the deposited condensate is present in all productive deposits, regardless of the depth of their occurrence (P_1art-C_1) (Fig. 3).

In this regard, there was an assumption that the well-known massive deposit may have a different geological structure. On this basis, a more detailed analysis of the geological section of productive deposits is performed; the correlation scheme is made up for the Lower Permian, Upper Carboniferous, Moscovian, Bashkirian, Serpukhovian tiers (Fig. 4). Moscovian stage consists of three parts: the upper and lower characterized by the clays and clay varieties of carbonate rocks, the middle part with highly porous dolomites and limestones. A detailed comparison of sediments showed that the three packs of rocks are traced in all wells. According to the geophysical and petrophysical studies of core samples gas-saturated reservoirs were allocated with good reservoir properties, which are confirmed by test results. The top and base of the Bashkirian deposits also contain clay carbonates with thickness up to 15-30 m, between which limestones and dolomites lie (Pankratova, 2014).

According to the correlation of sections, the analysis of injecting ‘dry’ gas and product extraction it be assumed that the reservoirs of Moscovian, Bashkirian, Serpukhovian tiers are separated by confining beds, which are referred to clay

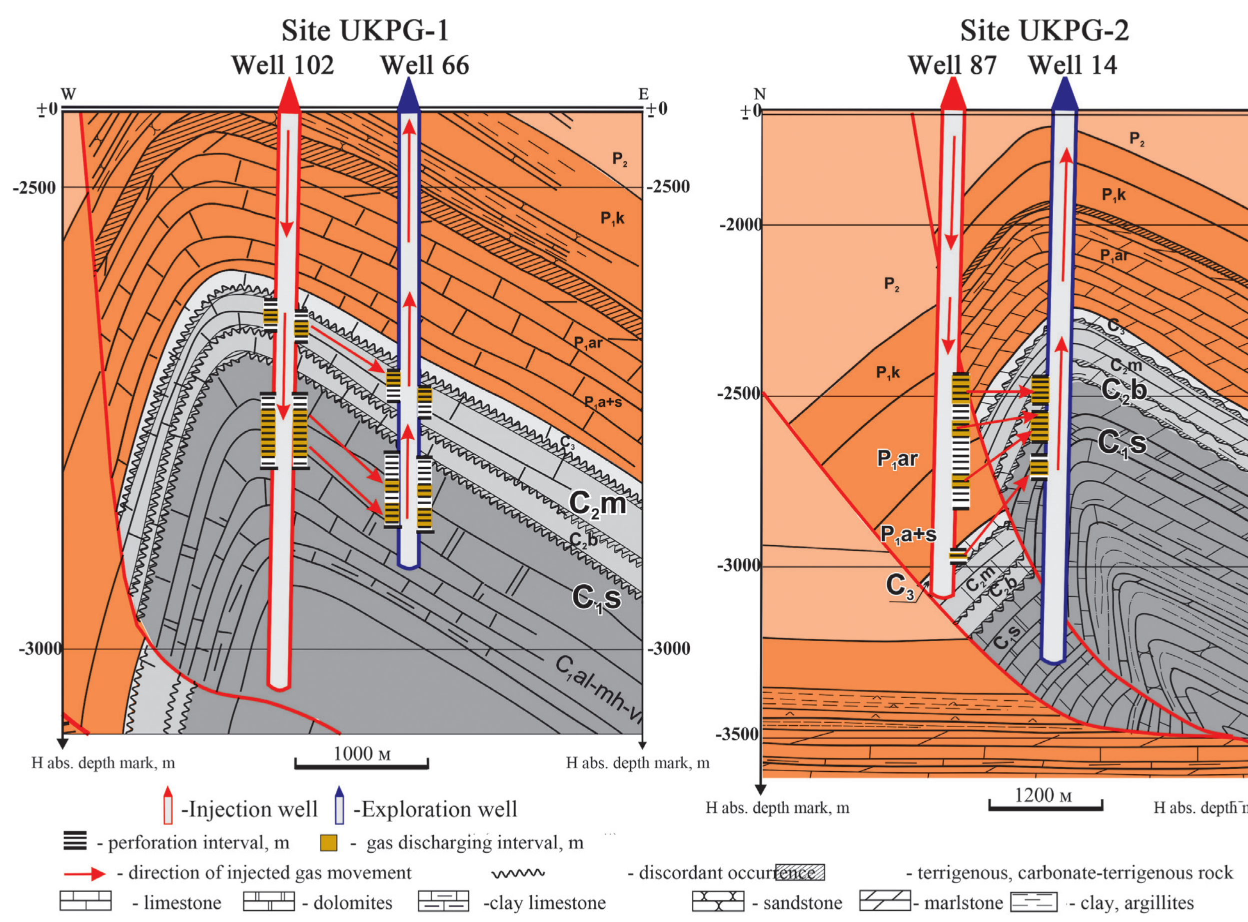

Fig. 2. Geological profiles through wells of sites UKPG-1 and UKPG-2.

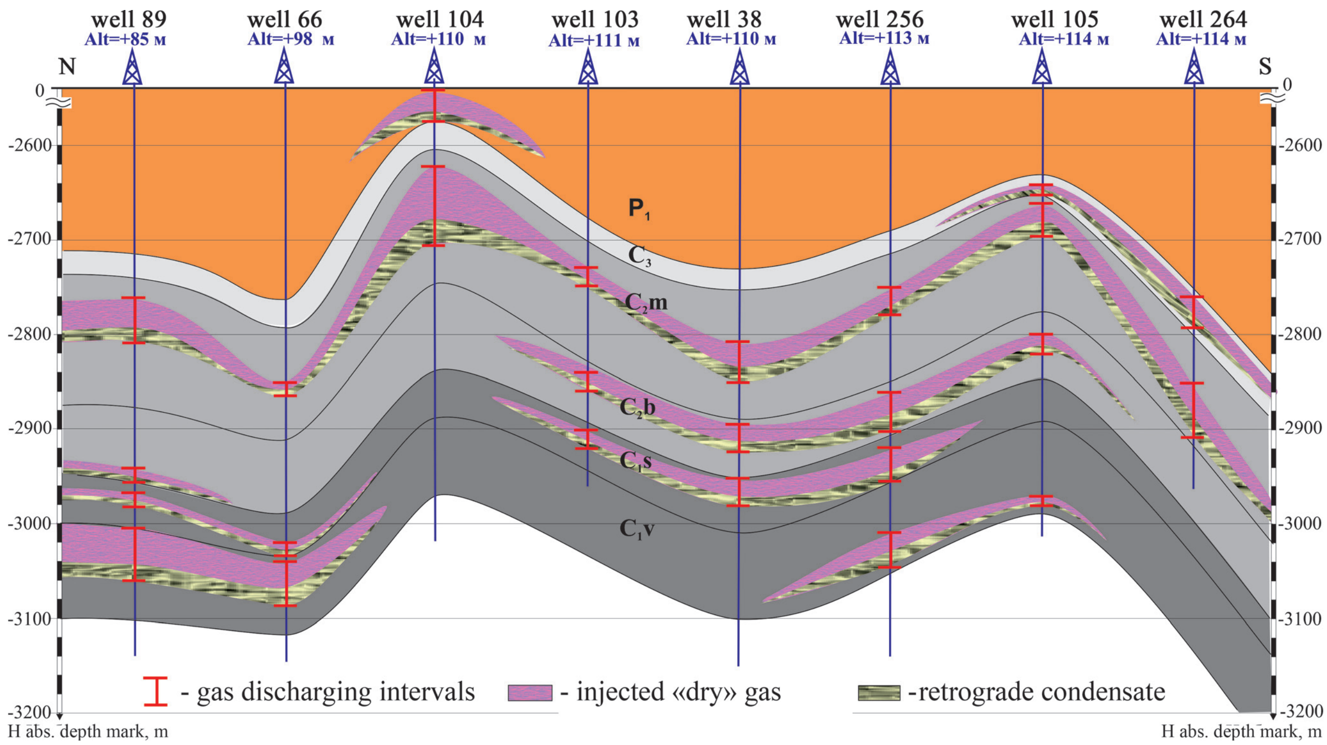

Fig. 3. Profile of the well through the area of Vuktyl field.

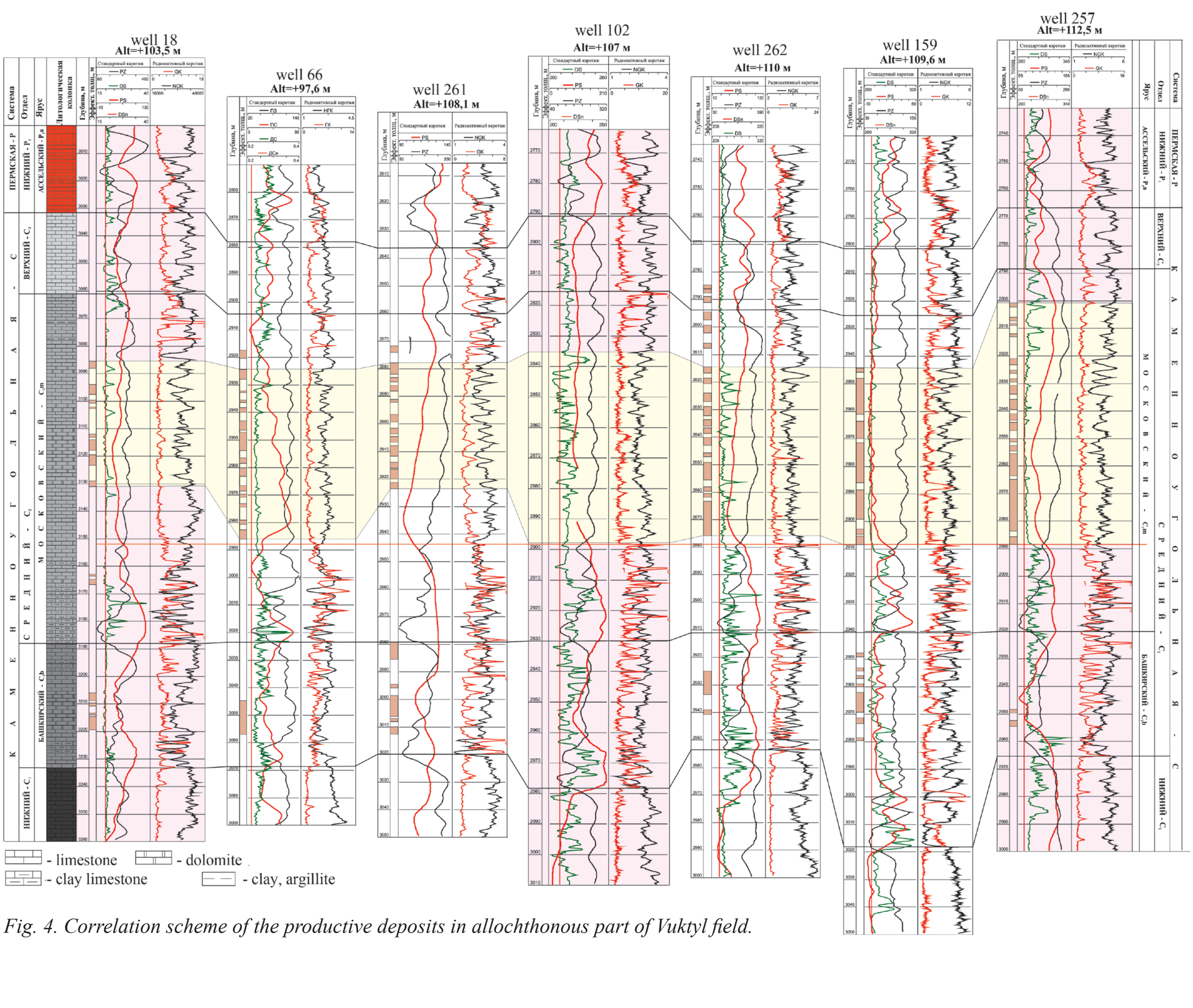

Fig. 4. Correlation scheme of the productive deposits in allochthonous part of Vuktyl field.

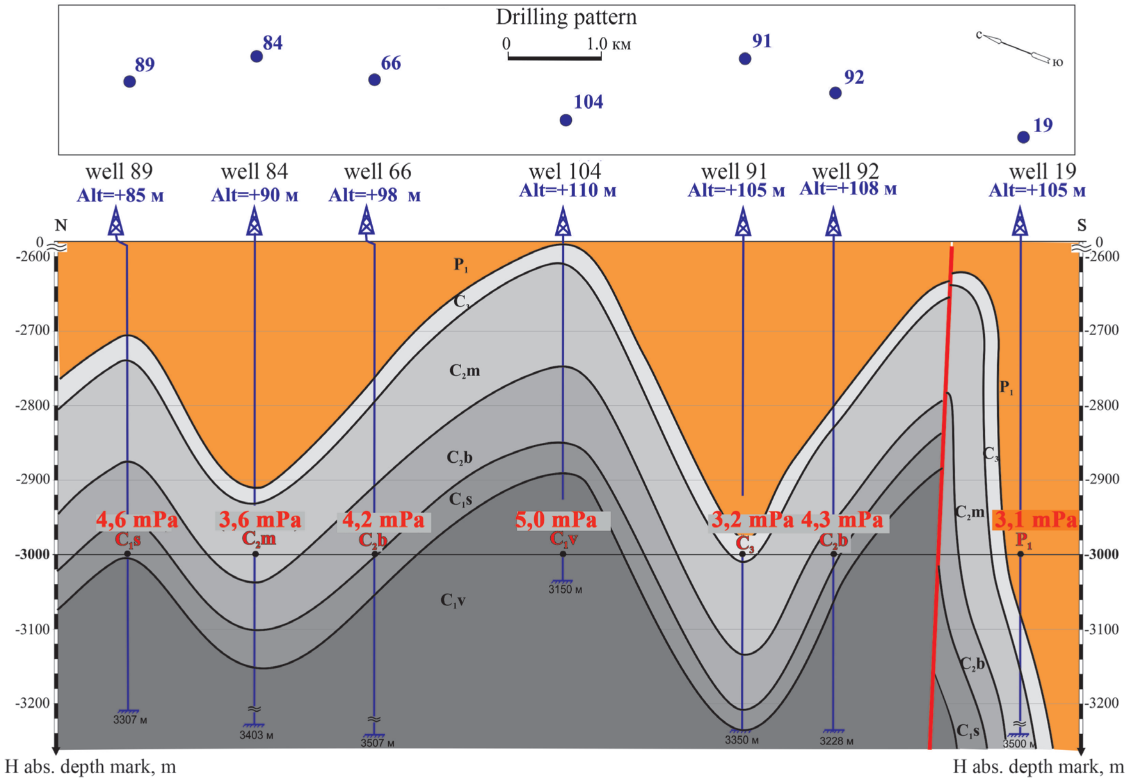

Fig. 5. The reservoir pressure distribution of productive deposits, reduced to an absolute marks of 3000 m.

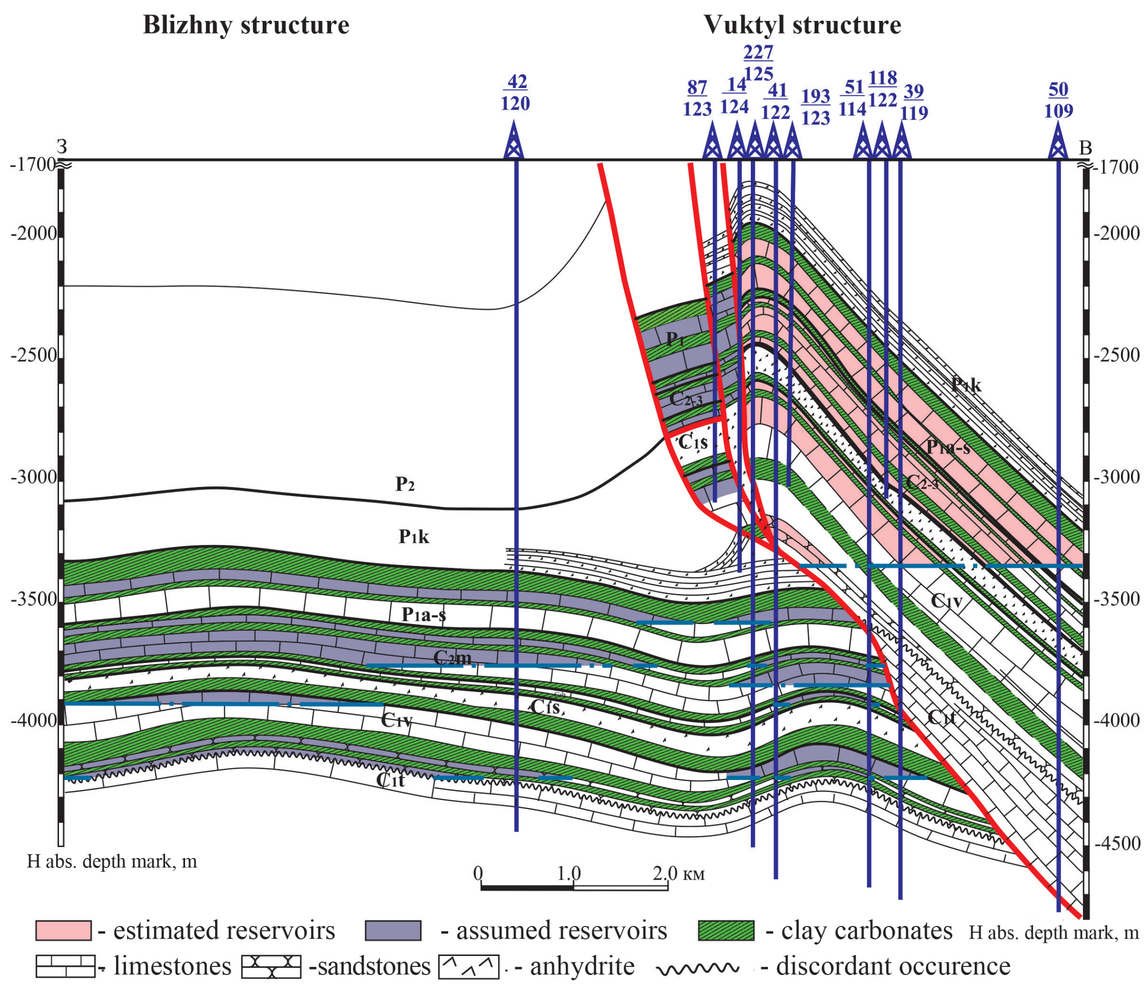

Fig. 6. Geological section with the system of reservoirs in allochthon and autochthone of Vuktyl field.

packs and argillaceous carbonates. And this, in turn, points to the fact that the Lower Permian – Serpukhovian reservoirs of Vuktyl field contain separated formations in the reservoirs of the Lower Permian, Moscovian, Bashkirian and Serpukhovian tiers.

Analysis, in which on the basis of measured wellhead static pressure and taking into account reservoir gas composition, pressure given on a single depth (for illustrative purpose) has been made for clarification of distribution pattern of reservoir pressure across a productive section from the Lower Permian to the Lower Carboniferous.

It should be noted that for the calculation data were taken for each well over the whole period of operation on the natural depletion mode. After analyzing the materials, it can be noted that each uneven pack of the same depth is characterized by its pressures.

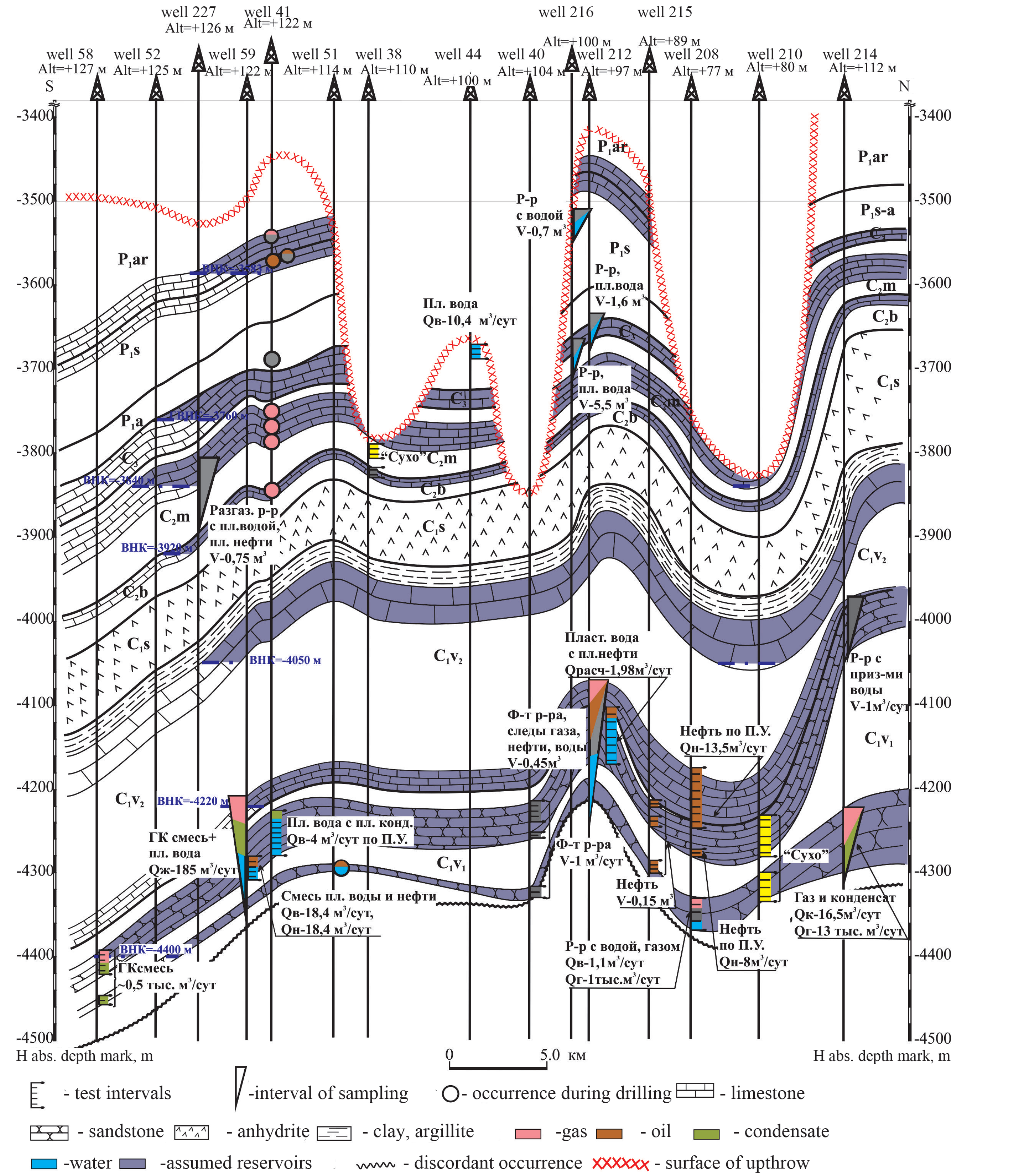

Fig. 7. Structure of hydrocarbon deposits in the autochthon of Vuktyl field.

The values of reservoir pressure are correlated with the reservoir properties of different horizons. For illustrative purpose the profile is drawn up by the line of wells for northern dome of Vuktyl structure that penetrated the entire productive interval (P_1art-C_1), which shows that reservoir pressure in the sediments of different ages have their own values (Fig. 5).

Thus, a comprehensive analysis of geological and geophysical data and parameters of Vuktyl field development allows us to offer its another geological structure and to prove that the deposit of allochthone considered to be massive deposit with a single hydrodynamic system, is characterized by formation of deposits, possibly with their gas-water contacts.

The analysis was a prerequisite to support oil and gas potential in Lower Permian – Visean sediments in the autochthonous part of the field.

For the geological analysis of autochthonous part of Vuktyl field, a correlation scheme has been drawn up of Carboniferous-Permian sediments, which indicated the presence of the reservoirs, separated by argillaceous carbonates and clays as confining beds, as has been shown by us for allochthone.

It should be noted that the productivity of Ordovician-Lower Permian sediments of autochthonous in Vuktyl fold was set a long time ago: T.G. Grinko in the manufacturing report notes that "in the autochthon of Vuktylsky area during drilling and testing of wells, almost throughout the section of Artinskian-Ordovician formations oil and gas occurrences were observed of different nature and intensity: from the degassing of the mud and increased gas values at gas logging to gas fountain. For example, in the Late Visean-Early Permian carbonates when drilling well No. 41 at a depth of 3690 m (Asselian) oil appeared; in 1.5 h 15 m^3 of oil came out with density of 0.95 g/cm^3. Oil films were observed in the solution during penetration of Asselian and Moscovian formations in well 42, Protvino-Bashkirian – in well 39, Early Artinskian and Sakmarian – in well 59.

Also oil shows are marked in two lithological packs of Yasnopolyansky clastic strata in underthrust of Vuktyl area – layers IIa and IIb. Deposits in these sediments are associated with both lithological and structural factors. They are isolated from each other and are associated with lenticular sandstones, replaced by dense clay rocks up to the rise in the monocline. Deposits of oil in the reservoir IIa are detected by well 225: when testing in the interval 4514-4487 m, a gushing flow (density 0.790 g/cm^3) is received with 40.1 m/day of light oil and 122 thousand m3/day of gas. The layer has also been penetrated by wells 224, 39, 42, 58, 59. In the preliminary assessment of oil reserves made in the software "Severgasprom" in 1987, the following parameters are taken for the calculation by category at the position of oil-water contact, on absolute elevation -4364 m, reservoir area of 2.9997 km2, height 76 m, average effective thickness -4 m, open porosity of 10%, oil saturation factor of 0.65.

Oil deposits in the formation IIb were penetrated in the well 51, where from the interval 4362-4375 m oil was produced with a low content of formation water (up to 25%), liquid flow rate of 22 m^3/day. Also they were penetrated by well 59, in which from a depth of 4428-4409 meters mixture of formation water and oil was extracted with total flow rate of 36.8 m^3/day (50% water, 50% oil). These oil fields are isolated from each other in the area between wells 51 and 41, where the layer II_b is almost completely replaced by dense siltstones and sandstones. According to preliminary estimates the area of deposits in the well 51 is 9.361 km^2, well 59 – 27.485 km^2, the other parameters of calculation are the same as for the formation II_a.

Perhaps the main points for new oil and gas potential of Vuktyl field are research results presented below. As a result of generalization of CDP-3D, 2D seismic survey, held in the northern part of Vuktyl structure, along the lines of seismic and geological profiles in the the autochthonous part of Permian-Carboniferous sediments we mapped anticline folds with amplitude up to 50-125 m at the size of 22 x1 m, petroleum prospects of which were not evaluated.

Based on the massive structure of the Permian-Visean deposits of Vuktyl field, the massive deposit in the autochthon will have a height up to 50-125 meters, and is unlikely to sustain geological-economic assessment for the development (Pankratova, Bogdanov 2014). However, based on the model with system of formation deposits (Fig. 6), we obtain a completely different geological and economic evaluation. With certain assumptions we can transform structural construction of OG IIv report on the interpretation of 3D-2D data into schematic structural maps of seven reservoirs, the size of each can make 22x1-3 km at amplitude of up to 125 m (Pankratova, Bogdanov, 2015).

Analysis of drilling wells that penetrated the autochthon of Vuktyl fold including oil and gas shows when conducting, and testing examined sediments, allowed us to make an overall model of Vuktyl oil and gas condensate field consisting of hydrocarbon reservoir systems in Artinskian-Sakmarian, Upper Carboniferous, Moscovian, Bashkirian, Serpukhovian and Visean autochthonous and allochthonous sediments (Fig. 6 and 7).

For each of the potential reservoir, resources were evaluated. The total resource estimate for the reservoirs of autochthon in the north of Vuktyl structure in Lower Artinskian, Asselian-Sakmarian, Upper Carboniferous, Moscovian, Bashkirian, Serpukhovian, Visean carbonate sediments can reach many tens of billions of cubic meters of gas, and tens of millions of tons of condensate.

Thus, the totality of the research led to the following conclusions.

1. Comprehensive analysis of the distribution of injected 'dry' gas and product extraction from wells, created correlation schemes of productive Artinskian – Lower Carboniferous sediment, distribution pattern of formation pressures at various aged sediments revealed that the well-known massive deposit of Vuktyl field has a different geological structure and is characterized as a system of formation deposits, apparently, with its own gas-water contacts.

2. This position of deposit type changing in Vuktyl requires additional confirmation in further work in the field, but we can already say that this model allows us to more effectively monitor and control processes in the productive section using injection technology of 'dry' gas in allochthonous part of the field. The results of complex analysis were taken into account when changing the system 'injection – production', as well as the justification of a dual injection for productive deposits. The Program of pilot projects to increase hydrocarbon recovery on Vuktyl oil and gas condensate field is approved in PJSC Gazprom.

3. According to drilling and 2D, 3D seismic survey in the north of Vuktyl field in carbonate deposits of Lower Permian-Lower Carboniferous an autochthonous fold is established with sizes up to 22x 1 to 3 km, at an amplitude of up to 125 m, to which seven of reservoirs can be confined with total resources tens of billions of cubic meters. Based on paleo-facies conditions the best reservoir properties are projected in autochtone.

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Influence of Erosion-karst Processes on Lithological Features of Productive Strata in Bobrikovian-Tournasian Oil Reservoir

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Abstract. Erosion-karst processes on the surface of Tournaisian land, formed as a result of regression of Devonian-Tournasian Sea, led to both significant morphological transformation of Tournasian paleorelief and formation in the Late Radaevskian-Bobrikovian transgression of sand lenses with secondary clay-carbonate cement with a predominance of carbonate component. On the example of two adjacent wells it is shown that sandstones with abundant clay-carbonate cement during logging interpretation may be taken for carbonate reservoir rocks, if factors are not taken into account such as increased calcium in seawater of Radaevskian-Bobrikovian basin and carbon dioxide in the atmosphere of Lower Carboniferous. They led to the development of carbonate cement in Visean sandstone and secondary calcitization in Tournaisian rocks.

Keywords: erosion-karst processes, incision, reservoir, oil saturation, correlation of sections, clay-carbonate cement, carbonate and clastic rocks.

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Karst processes are now widely distributed in that part of the earth's surface, which is composed of karst rocks - limestone, dolomite, gypsum (Gvozdetsky, 1954). Very peculiar landforms are the results of these processes. They can be observed in different geographical and climatic zones (Spain, Austria, the Crimea, China, Australia and others).

These corrosion processes had no less widespread occurrence in the past geological epochs. Underestimation of their role in creating sculptural forms of paleorelief and voids of karst rocks may lead to erroneous practical consequences.

An example of this is the comparison of the Lower Carboniferous sections from two wells (No. 2345 and 2507) on Zyuzeevsky field. The wells are located 300 meters from each other in the central part of brachyanticline uplift of the III order on the roof of Tulskian horizon, which controls oil deposits in Tournaisian carbonate reservoirs and Visean clastic rocks (sandstones, siltstones), and the Middle Carboniferous intervals – Bashkirian and Vereiskian sediments.

Modern forms of Tournaisian surface in Zyuzeevsky uplift, in our opinion, have been created as a result of erosion and karst processes on Tournaisian land in Elkhovskian- Early Radayevskian time. Denudation and corrosion processes have also had a significant, albeit indirect impact on Radayevskian-Bobrikovian clastic rocks, filled post-Tournaisian 'incisions' on the uplift, and Tulskian rocks overlapping Radayevskian-Bobrikovian strata. Excluding this factor, the interpretation of sections of neighboring wells by logging can be very different both on stratigraphic and lithological content as well as the nature of reservoirs saturation.

As concluded by logging, in the wells 2345 and 2507 the roof of the Tulskian horizon is close to absolute elevations – -1150.5 and -1156.2 m, respectively (Fig. 1). Well No. 2345 penetrated Visean incision: Radayevskian-Bobrikovian clastic rocks in its section lie on the eroded surface of Zavolzhskian horizon of the Upper Devonian Famennian tier, i.e. Tournaisian deposits are denuded entirety in the area of wells. Thickness of Visean complex is 78.6 m. The following oil-saturated reservoirs are marked in the well: Tulskian Stl-4 in the top of the horizon, Sbr-3, Sbr-2, which merges with the formation Sbr-1, and in incision – lenses of sandstones united in the Sbr-1 formation. Reservoirs are underlain and overlain by mudstone packs with thickness 2.5-15 m.

In well 2507 the roof of Tournaisian deposits is conducted by logging at a depth of 1331.2 m (absolute mark – 1199 m) on the 'traditional' sign: decrease of gamma-ray values and increase of neutron gamma-ray values at the border 'clay-limestone' and indications of caliper log on this level. However, clay packs can be traced below the section in the intervals 1350.4-1354.4 m, 1362.6-1365.2 m, and 1367.4-1371.2 m, i.e. in Tournaisian deposits. Marked between them carbonate interlayers have porosity of 23-23.8 %, 16.7-20 %, in the interval 1365.2-1367.4 m – 8.1%; The formation resistivity for these intervals is 8-16.8 ohmmeter. In terms of porosity they are highly porous reservoir rocks, in terms of resistivity – water-saturated rocks.

From the logging interpretation of two neighboring wells it follows that in the well 2345 the bottom of general oil-saturated interval is at an altitude -1224.4 m, while the roof of water-saturated interval in the well 2507 is at an altitude -1199 m, i.e. 25 m above.

Comparison of well logs suggests that their sections are correlated with each other quite well. In the well 2507 all reservoirs between clay packs are not the carbonate but sandstones on clay-calcareous cement, with a predominance of carbonate component over clay. The well 2507 penetrated the same Visean 'incision' which was penetrated by the well 2345. The thickness of Visean deposits is 84.2 m. Radaevskian-Bobrikovian clastic strata in the incision lies on the eroded surface of compacted limestone of Zavolzhsky horizon of the Upper Devonian Famennian tier. As in well No. 2345, Tournaisian deposits in the well 2507 are completely eroded (Fig. 2).

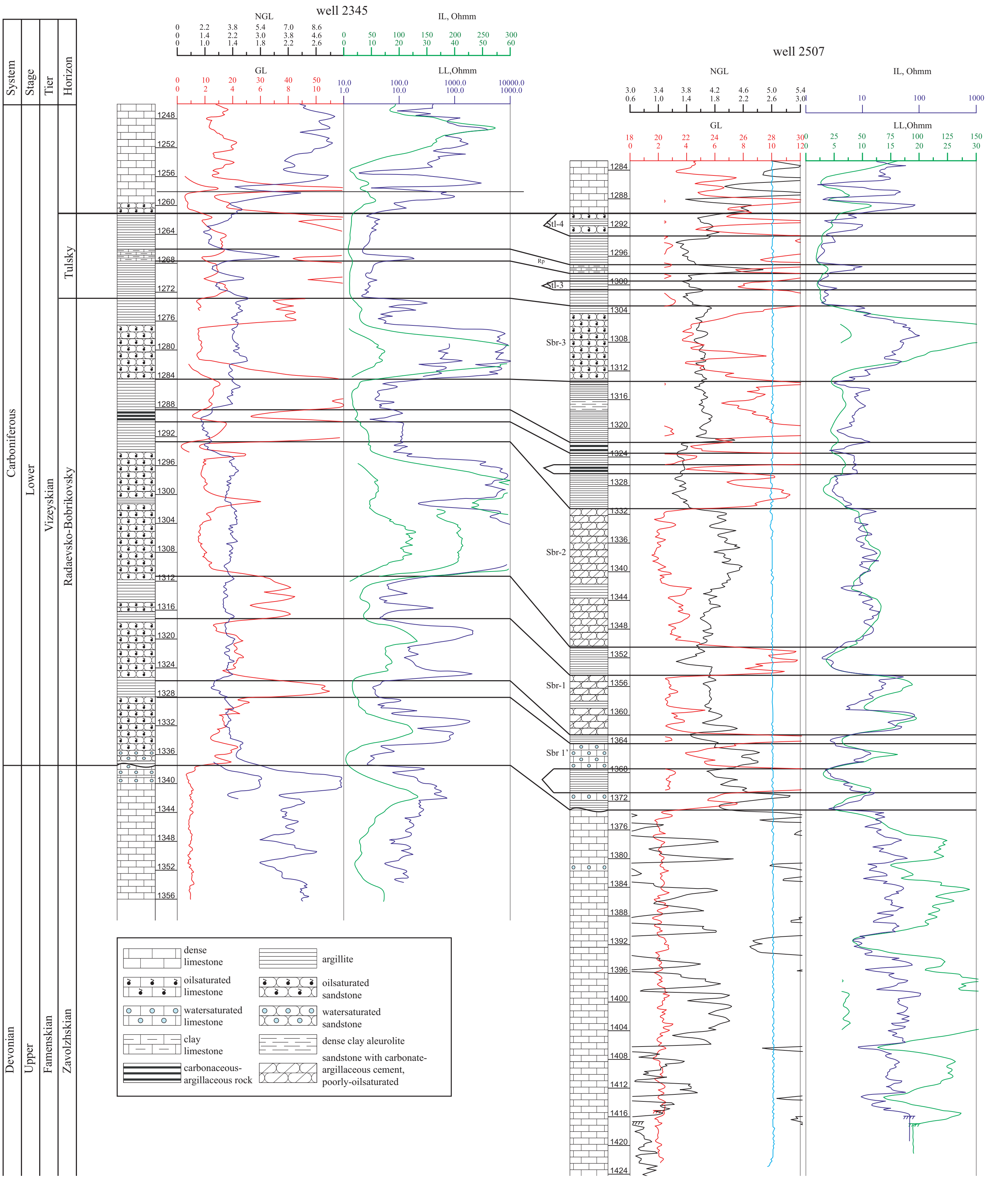

Fig. 1. Schematic comparison of the Lower Carboniferous deposits for wells No. 2345, 2507. Vertical scale 1:500.

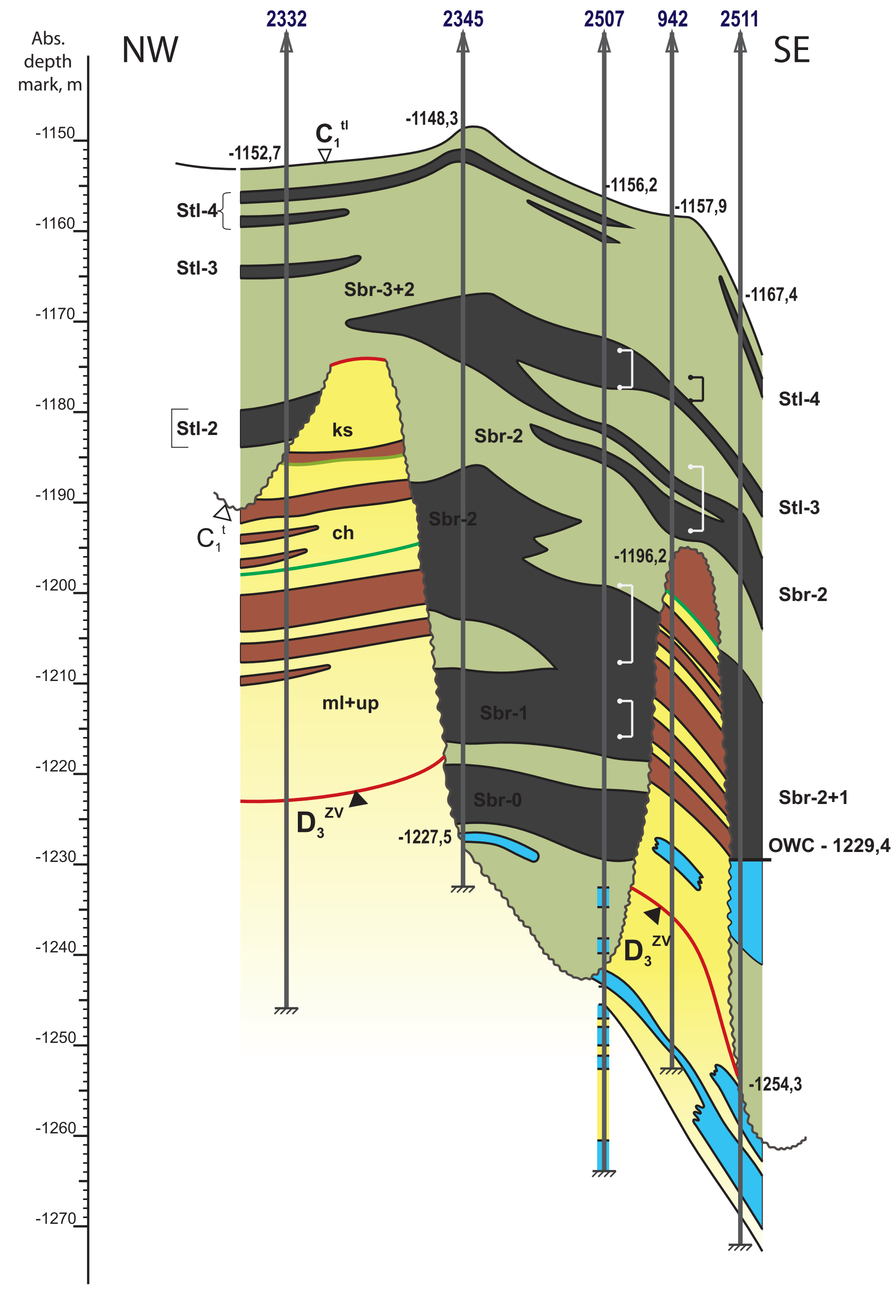

Fig. 2. Fragment of the schematic geological profile of the Lower Carboniferous productive deposits. Horizontal scale 1: 10,000, vertical scale 1:500.

Values of formation resistivity (8-12 ohmmeter) in general interval 1199-1229 m for carbonate reservoirs mean that they are water-saturated, values of 12-15 ohmmeter indicate their residual or weak oil saturation, whereas for sandstone this measure of oil saturation ceteris paribus.

Thus, in the section of well 2507 in the Visean clastic rocks there are reservoirs Stl-4, Sbr-3, Sbr-2, series of layers Sbr-1 that are oil-saturated as in neighboring wells on the profile (Fig. 2).

The relatively low value of permeability coefficient by logging – 5.7-91.9 mm2 indirectly indicate on clay-calcareous nature of the cement sandstone in the well 2507. The carbonate component of sandstone cement is secondary in relation to the previously formed sand lenses.

Reservoirs Sbr-1, partly Sbr-2, with interbedded mudstones and filling 'incisions' were deposited in relatively shallow marine conditions established in the lower areas of the continent as a result of the first cycle of sea transgression in Late Radayevskian-Bobrikovian. The waters of this sea contained a significant amount of dissolved calcium compounds transferred there with eroded and karst Tournaisian land, as well as water of Bobrikovian-Tuslkian basin, overlapped the entire surface of the east of the Russian Platform in the next cycle of marine transgression.

In addition, atmospheric water transferred to the sea basin contained a significant amount of carbon dioxide; frequent and heavy rains washed away destruction products from the Tournaisian surface, before it was overlapped by Bobrikovian-Tulskian transgression. These destruction products were kind of weathering crust in the karst valleys and depressions. All this gave a peculiar litho-facies appearance to Visean clastic strata, especially in 'incisions'.

The weathering crust consists of insoluble residue, fragments of native limestone rock ('trash'), cemented with clay-silt precipitated mass. It is marked on the Tournaisian surface in a number of wells (No. 942, 2363, 2344 etc). In the well 2507, landslip limestone debris with porosity values of (8.1-8.3%) lie in a number of intervals 1365.4-1367.4 m and 1370.4-1372 m. The debris is underlain and overlain by mudstone packs. Similar intervals are found in other sections of wells (No. 2511).

Geological model construction of deposits at Zyuzeevsky uplift, which is complicated with 'incisions' of different directions and depths, lenses of sandstones in the Visean strata, should be based on the correlation of adjacent well sections. In turn, it must take into account the effect of erosion and karst processes on the reservoir properties of Visean sandstone and preserved by denudation Tournaisian rocks. It also should be based on the well testing data.

Thus, the formation of modern Tournasian relief occurred in the regression of Tournasian marine basin and subsequent Kosvinskian – Early Radayevskian break in sedimentation, established on the Russian Platform (Igolkina et al., 1977). This relief was created by the action of erosion and karst processes. Late Radayevskian – Bobrikovian and Tulskian cycles of marine transgression led to the restoration of the marine environment and deposition of clastic rocks – Visean mudstones and sandstones. Features of physical and chemical composition of seawater, determined by lithology of destroyed surface, caused secondary calcitization and claying of both Visean sandstone and Tournasian carbonate rocks.

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Calculation of Ball Jet Drilling Processes in the Optimal Mode of Rock Destruction

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Abstract. This article is devoted to the study of ball jet drilling method, which in the future may increase the mechanical speed and driving of the bit during drilling of solid rocks for various purposes. Ball jet method of drilling wells is to destroy rocks by strikes of metal balls continuously circulating in the near wellbore area by means of a jet system, laid to the basis of ball jet – ejector drilling unit. The main advantages of ball jet drilling include simplicity of drill construction, absence of necessity in the bit rotation and creation of axial load on it. Destruction of rocks by ball strikes can occur in a variety of modes, the most effective of which is the optimal (volumetric), accompanied by the formation of a large chipping funnel. The aim of this work is to develop methods for calculating ball jet drilling processes in the optimal mode of rock destruction.

Method of calculation is based on the results obtained by the authors of theoretical and experimental studies, as well as some provisions of the predecessors. It allows us to determine the optimal geometric parameters of the drilling units, rational technological parameters of drilling mode, and also to make the choice of pumping equipment for specific geological and technical conditions. In the proposed calculation method the values of the washing liquid flow are limited in the presence of intervals intent to erosion of the borehole walls, the ejection rate of the jet device and the pressure drop on the nozzle to prevent its intense wear at the expiration of the drilling fluid.

Keywords: destruction of rocks, rock destruction tool, ball jet drilling, ball jet - ejector drilling unit, jet device, solid rocks.

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Introduction

Analysis of technical and economic indicators of drilling exploration, water intake, explosive and technical wells in solid rocks indicate on insufficiently high rate of penetration and headway per bit. Increasing the efficiency of the mechanical drilling in solid rocks can be implemented in two ways: creation of new materials and new structures of rock cutting tools.

Despite the constant improvement of rock cutting tool, drilling by mechanical means in the solid rock is not sufficiently effective. Therefore, it is important to develop alternative methods of rock destruction. According to some researchers (Davidenko, Ignatov, 2013; Kovalev et al., 2015; Kozhevnikov, Davidenko, 1987) one of the most promising methods is the hydrodynamic method implemented by a high-speed jet. By this way it is possible to pass a significant hydraulic power on the bottomhole, while the speed of drilling and headway of the bit can increase multiple times.

However, the method in its conventional form is not promising for drilling in solid rocks. Ball jet method of drilling is of great interest, the essence of which consists in the destruction of rocks at the bottomhole as a result of the impact of steel or carbide balls moving at high speed and continuously circulating in the well bottom zone due to the jet device. This method allows us to solve a number of technical and technological problems in the implementation of the hydrodynamic method of rocks destruction.

Fig. 1 shows a schematic all jet-ejector drilling unit, developed at the Department of drilling wells of the National Research Tomsk Polytechnic University (Kovalyov et al., 2015). Its working principle is as follows: the working fluid supplied through the supply chamber 1 is accelerated in the nozzle 2 and flows therefrom into the mixing chamber 5. In the space surrounding the nozzle exit 2 from the outside, discharge zone is formed. The unit body has inlet ports 4, through which due to discharge, working fluid is sucked with suspended balls from the annulus. Next, the two-phase mixture passes through the mixing chamber 5 and the diffuser 6, followed by hitting the rock, causing its destruction. Delay device 3 is intended to guide the ascending annular cutters balls into the inlet window and to center the drill in the borehole.

The main advantages of ball jet drilling by units of described design are:

- Design simplicity of ball jet-ejector drilling unit;
- There is no need in the rotation of the bit and creating axial load.

Analysis of papers devoted to destruction of solid rock using ball jet-ejector drilling unit indicates that this method may be more effective than the conventional ones. Results of trial application of the drilling method (Uvakov, 1969; Strasser, 1966; Zaurbekov, 1995) show that when drilling rocks of VIII drillability category and above, the value of penetration rates increases compared to using a conventional cutter tool. Industrial trials performed by Zaurbekov S.A. have shown excess mechanical speed of oil well drilling with diameter of 215.9 mm by 20%, headway per bit by 43% in comparison with the rock bits (Zaurbekov, 1995).

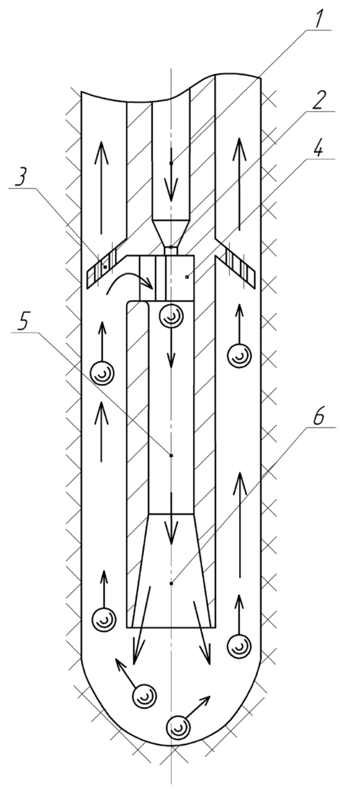

Fig. 1. Structural scheme of ball jet-ejector drilling unit: 1 – chamber supplying a working fluid; 2 – nozzle; 3 – delay device; 4 – inlet windows; 5 – mixing chamber; 6 – diffuser.

Modes of rock destruction

According to the results of theoretical and experimental studies (Uvakov, 1969; Shtrasser, 1966) the destruction of rocks by the impact of steel or carbide balls may occur in different conditions. Rock destruction mode is determined by the contact pressure at the ball interaction with the breed, which depends on the speed of collision.

Fig. 2 shows the modes of rock destruction by hitting balls. Area 1 characterizes rock surface abrasion mode. The relationship between the rate of drilling and magnitude of contact pressure is linear. When the contact pressure exceeds the limit of rock fatigue, destruction process is fatigue. At the same time the growth rate of the drilling speed is higher than

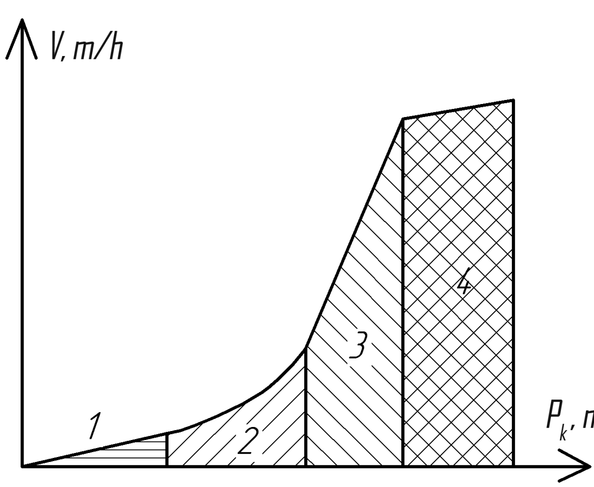

Fig. 2. Modes of rock destruction by hitting balls: 1 – mode of surface abrasion; 2 – fatigue mode of destruction; 3 – initial stage of optimal destruction; 4 – optimal destruction.

the growth rate of contact pressure (area 2). Upon reaching the contact stresses of rock hardness values, effective destruction begins. The dependence of the penetration rate of the contact pressure again becomes linear (area 3), rock destruction mode is close to the optimum – the ball hitting process culminates in the formation of large cleavage along the contour. At the optimum destruction mode (area 4) contact pressures are as sufficient to implement the first jump in the destruction with the formation of a large funnel of chipping. A further increase in contact pressure does not significantly increase rate of penetration (Uvakov, 1969).

Development of the calculation method of technological processes in an optimum mode of rocks destruction

The purpose of this paper is to provide a method for calculating ball jet drilling processes in the optimal mode of rocks destruction at the bottomhole.

Presented below calculation method for ball jet drilling process in the optimal mode of rocks destruction determines the optimal geometric parameters of the drilling units, rational technological parameters of drilling mode, and also allows making a choice of pumping equipment for specific geotechnical drilling conditions.

The proposed method of calculation is based on the results obtained by the authors from theoretical and experimental studies (Isaev et al., 2014; Kovalev et al., 2015; Konstantinov

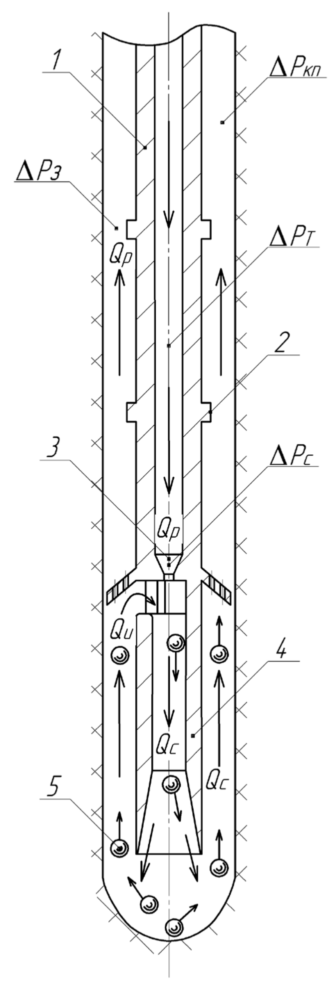

Fig. 3. Schematic diagram of the ball jet drilling: 1 – drill string; 2 – interlocks of drill pipes; 3 – nozzle; 4 – drilling unit; 5 – balls.

et al., 2015), as well as certain provisions of the A.B. Uvakov, V.V. Strasser, L.V. Ledgerwood, etc. (Ledgerwood, 1961; Uvakov, 1969; Strasser, 1966).

The concept of ball jet drilling method is shown in Fig. 3.

Initial data for calculation are as follows: rock properties (dynamic hardness P_c, modulus of elasticity E_1, Poisson's ratio μ_1); well parameters (diameter $D_{скв}$, maximum drilling depth $L_{скв max}$); drilling fluid properties (density $\rho_{бр}$, dynamic shear stress τ_0, dynamic viscosity η), geometric parameters of the drill pipe column (outer $d_н$ and inner $d_в$ diameter of drill pipe, outer diameter of interlock $d_з$, average length of drill pipe l_{1T}); 5. Properties of rock destructing balls (density $\rho_ш$, modulus of elasticity E_2, Poisson's ratio μ_2).

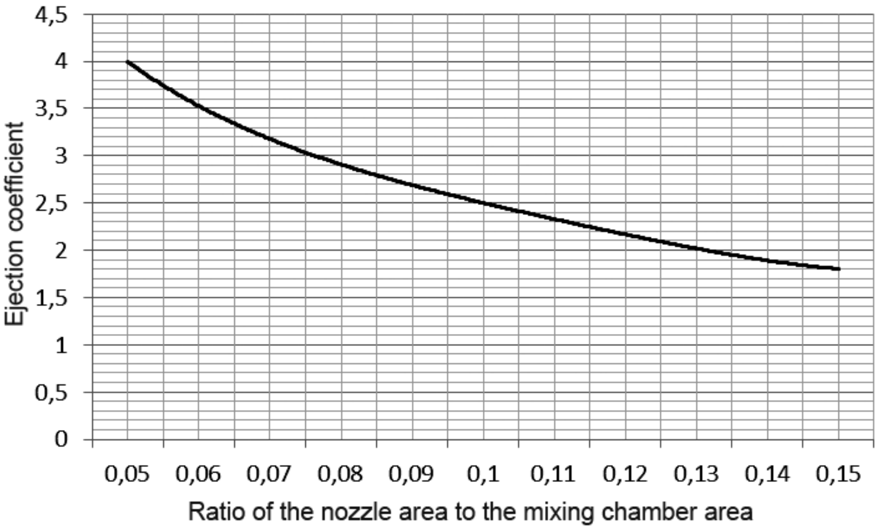

Fig. 4. Dependence of the ejection coefficient and the ratio of the nozzle area to the mixing chamber area (Eckel et al., 1956).

The sequence of engineering calculation of ball jet drilling in the optimal mode of rocks destruction is as follows.

1. Determine the rational diameter of the balls

$$d_ш = \frac{D_{скв}}{6,6}. \quad (1)$$

2. Calculate the diameter and area of the mixing chamber section

$$d_{кс} = 2,2 d_ш, \quad (2)$$

$$S_{КС} = \frac{\pi d_{кс}^2}{4}. \quad (3)$$

3. Calculate the outer diameter of the drilling unit

$$d_{бсн} = D_{скв} - 2,2 d_ш. \quad (4)$$

4. Determine the length of the mixing chamber

$$l_{кс} = 8 d_{кс}. \quad (5)$$

5. Calculate the height of technological windows

$$h_{то} = 1,25 d_ш. \quad (6)$$

6. Calculate the optimum mass portions of balls

$$m_ш = m_{1ш} \cdot N_ш = \frac{\rho_ш \pi d_ш^3 N_ш}{6}, \quad (7)$$

where $N_ш$ – number of rising balls in the annulus, calculated according to the formula:

$$N_ш = \frac{l_{бс}}{d_ш C_1} \cdot \frac{\pi (d_{бс} + D_{скв})}{2 d_ш C_2}, \quad (8)$$

where C_1 – coefficient taking into account the gap between the rows of balls C_1 = 1.5; C – coefficient taking into account the gap between the rows of balls C_2 = 1.5.

Equations (1) – (8) were obtained based on the results of studies conducted by the authors.

7. Determine the velocity of the balls necessary for breaking rock in the optimal mode (Uvakov, 1969; Strasser, 1966):

$$v_{опт} = 2,15 \cdot \left(\frac{4(1-\mu_1^2)}{E_1} + \frac{4(1-\mu_2^2)}{E_2}\right)^2 \cdot \sqrt{\frac{g P_c^5}{\rho_ш d_ш^3 \left(\frac{4}{d_ш} - \frac{4}{0,78 D_{скв}}\right)^2}} \quad (9)$$

8. When penetrating wells at intervals tend to erosion, calculate the maximum possible flow of drilling Q_{pmax}:

$$Q_{p\max} = S_{сквбт} v_{кп\max}, \quad (10)$$

where $S_{сквбт}$ – sectional area of the annulus between the drill pipes and well walls; $V_{кпmax}$ – maximum allowable speed of fluid flow in the annulus, which is equal to 1.5 m/s.

9. According to the technical characteristics of the mud pump, flow rate Q_p is selected, the value of which must be less than the maximum possible flow rate Q_{pmax}.

10. The magnitude of the required average velocity of washing liquid in the drilling unit is defined by the formula:

$$V_{бс} = V_{опт} / \varepsilon, \quad (11)$$

where ε – the ratio of ball speed to the fluid velocity in the drilling unit, taken as equal to 0.7 (Eckel et al., 1956).

11. Determine the desired ejection rate:

$$n = \frac{S_{кс} v_{бс}}{Q_p} - 1. \quad (12)$$

12. Verify that the balls rise in the gap between the bit and the well wall, i.e. compare the velocity of the fluid in its flow between the drilling unit and the well wall with balls falling at a rate of transitional and turbulent flow regimes of balls, calculated according to the formula of Rittinger:

$$v_{кп} = \frac{Q_c}{S_{кскбс}} = \frac{4(1+n)Q_p}{\pi (D_{скв}^2 - d_{бс}^2)} \geq 5,11 \sqrt{\frac{d_ш(\rho_ш - \rho_{бр})}{\rho_{бр}}}. \quad (13)$$

13. According to the dependence scheme of ejection coefficient and the ratio of ejection nozzle area to the area of mixing chamber (Fig. 4) with a constant diameter of the mixing chamber, the desired ratio of $\alpha = S_c/S_{кс}$ is determined.

It is found that the values of the ejection rate in the range from 2 to 4 are the most suitable. In case of its excess, sludge removal is deteriorating, thereby reducing the efficiency of the jet device, and additional energy is expended on its grinding.

14. Determine the diameter and cross-sectional area of the nozzle outlet (

$$S_c = \alpha \cdot S_{кс}, \quad (14)$$

$$d_c = \sqrt{\frac{4 \cdot S_{кс} \cdot \alpha}{\pi}}. \quad (15)$$

15. The pressure drop in the nozzle is calculated by the formula (Popov et al., 2003)

$$\Delta P_c = \frac{Q_p^2 \cdot \rho_{бр}}{\gamma^2 \cdot 2 \cdot S_c^2}, \quad (16)$$

where γ – nozzle discharge coefficient, for conoidal nozzles equal to 0.985.

According to (Kirsanov et al., 1981; Popov et al., 2003) calculated pressure drop in the nozzle should not exceed 13 MPa for preventing intensive nozzle wear for flow of drilling mud.

16. According to well-known techniques, pressure loss is calculated in the circulation system $\Sigma(\Delta P_i)$

$$\sum(\Delta P_i) = \Delta P_T + \Delta P_{КП} + \Delta P_З, \quad (17)$$

where ΔP_T – pressure losses in the drill column, $\Delta P_{КП}$ – pressure losses in the annulus, $\Delta P_З$– pressure drop in the gap between the interlock and the well wall.

Due to the low values do not take into account the loss of pressure in the circulation system of the following elements: the riser, the drilling arm, swivel, lead pipe and drill delay device.

17. Based on the values of Q_p, ΔP_c, $\Sigma(\Delta P_i)$ the parameters of the mud pump are selected. It should be guided by the following conditions:

$$Q_H \geq Q, \quad (18)$$

$$kP_H > \sum(\Delta P_i) + \Delta P_C, \quad (19)$$

where $Q_н$ and $P_н$ – flow and pressure developed of one or more drill pumps; k – coefficient taking into account the fact that operating pressure of the mud pump discharge should be, according to the rules of drilling operations, fewer the rated pressure by 20-30 %, k = 0.7-0.8 (Popov et al., 2003).

Conclusions

The following conclusions can be drawn on the results of the work conducted.

1. The calculation method of ball jet drilling at an optimum mode of rocks destruction at the bottom is calculated, which allows us to determine the optimal geometric parameters of the drilling units, rational technological parameters of drilling mode, and also to make the choice of pumping equipment for specific geological and technical conditions.

2. In the proposed calculation method of ball jet drilling following restrictions must be considered:

- In the penetration of wells at intervals tend to erosion it is necessary to limit the upward flow rate through the introduction of the limit values of the washing liquid flow;
- To improve cuttings transport conditions, drilling units should be designed with the ejection ratio of not more than 4;
- Calculated pressure drop in the nozzle should not be more than 13 MPa for preventing intensive nozzle wear for flow of drilling mud.

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The Efficiency of Drilling Wells in the Korobkovsky Area of Bavlinsky Field

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Abstract. Kizelian horizon of Tournasian in the Bavlinsky field is composed of limestone, the development of which was started in 1976. The block No.6 is the most drilled both by vertical and horizontal wells on the Kizelian area, which accounts for 53% of horizontal wells drilled in the field. In 2002, the Institute TatNIPIneft in close collaboration with the geological survey of oil-and-gas production department Bavlyneft proposed a new complex technology for the development of carbonate reservoirs. The technology includes a nine-point areal location of wells with horizontal and vertical trunks and injection well in the center of the element. Drilling of the field is recommended in a certain order – primarily to drill wells for the inter-well pumping of water, and then, after studying the geological features of drillable element, to drill injection wells. According to the drilling results geological structure is studied, structure maps, general and oil-saturated strata maps are constructed. Reservoir capacity, reservoir pressure parameters are measured. Drilling of wells for inter-well pumping of water and injection wells from a single group can reduce the cost of high-pressure water pipelines and pumping of water without cooling it, i.e., to take advantage of the isothermal flooding. Annual growth of oil production in the Kizelian horizon of Korobkovsky area of Bavlinsky oil field has become the result of the technology application.

Keywords: oil production, experiment, well, Kizelian horizon.
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Kizelian horizon of Bavlinsky field in the Republic of Tatarstan is oil-bearing in the carbonate deposits of Tournasian tier. The roof of the productive horizon is characterized by the best reservoir properties, as compared with the middle and bottom part of Kizelian horizon, composed of solid, weakly oil-saturated rocks. Oil deposit is of massive type. Kizelian horizon of Tournasian tier consists of limestone. Development of this site in Bavlinsky field was started in 1976.

The total thickness of Kizelian horizon averages of 21.4 m, the effective average net pay thickness – 5.8 m, stratification factor –1.4 unit fraction, gross sand reservoir share – 0.69 unit fraction. Oil is characterized by medium viscosity of 20.8 mPa*s, density – 872.5 kg/m^3 at reservoir conditions, saturation pressure – 3.3 MPa. According to the content of sulfur oil is sour.

Block number 6 is the most drilled both by vertical and horizontal wells on Kizelian object, which accounts for 53% of horizontal wells drilled at the field (Khisamov et al., 2015).

Fig. 1 shows the development system of Kizelian horizon in Korobkovsky site of Bavlinsky field.

In 2002, the Institute TatNIPIneft in close collaboration with the Geological Survey of oil-and-gas department "Bavlyneft" proposed a new complex technology of carbonate reservoirs development.

The technology includes a nine-point areal location system of wells with horizontal and vertical shafts and injection wells in the center of the element. The distance from the injection to the horizontal production well is 450 m, to a vertical corner

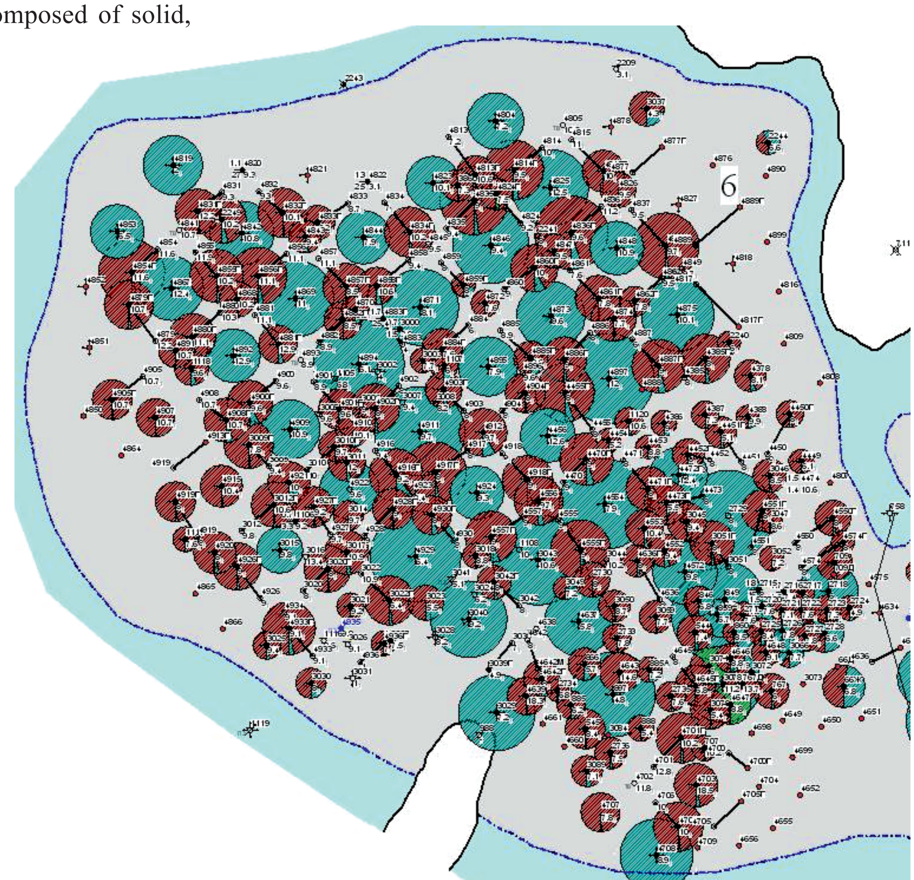

Fig. 1. The development of block 6 of Kizelian horizon in Korobkovsky area of Bavlinsky field.

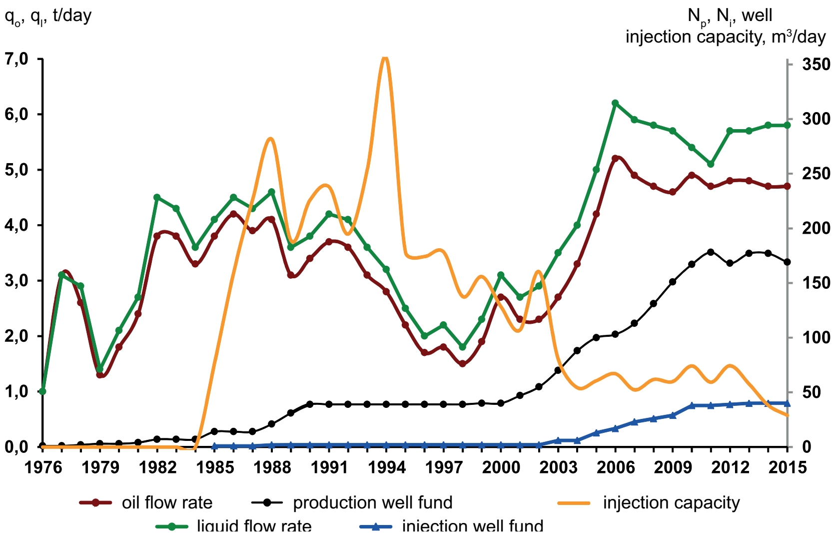

Fig. 2. Dynamics of the major development parameters of block 6 of Kizelian horizon in Korobkovsky area.

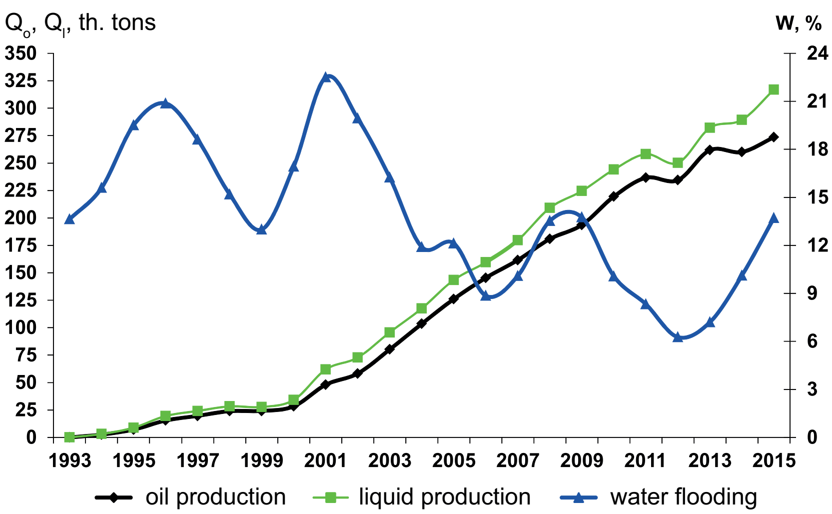

Fig. 3. Dynamics of horizontal well operation in Kizelian horizon of Korobkovsky area.

production well is 635 m. Drilling of deposit is recommended in a certain order: first the drilling of wells is performed for inter-well pumping of water and then, after studying the geological features of drillable element, to drill injection wells. According to the results of drilling, geological structure is studied, structural maps, general and oil-saturated strata maps are built. Measurements are made of reservoir capacity and reservoir pressure (Khisamov et al., 2001).

It is recommended to perform offset vertical profiling in injection wells for fracture studies. Pressure of cracks closure is determined. The required volume of water injection is estimated from the conservation of the initial reservoir pressure after the liquid withdrawal from the reservoir. The bottom part of the formation is perforated in injection wells. Anticipatory cyclic water injection is conducted, thus preparing the formation for oil extraction. Injection of reservoir water as a displacing agent must be alternating (Bakirov et al., 2013).

Drilling of wells for inter-well water pumping and injection wells from one cluster can reduce the cost of the water main pipes of high pressure and pump water without cooling it, i.e. take advantage of the isothermal flooding.

After specification of the geological structure of the drillable element, deviated and horizontal wells are drilled equidistant from injection wells. The horizontal shaft, as well as perforations in the deviated production wells must be carried out in the top part of the reservoir. This ensures a uniform coverage with filtration flow from the bottom up. Withdrawal of well production, as water injection is performed in a cyclic mode.

Development parameters	After the introduction of technology													
	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Production well fund, well	58	70	89	97	102	111	132	150	158	170	168	177	177	172
including horizontal (put in over year)	3 (2)	8 (5)	14 (6)	23 (9)	27 (4)	37 (10)	46 (9)	57 (11)	65 (8)	71 (6)	71(0)	71(0)	71(0)	71(0)
Injection well fund, well	2	6	6	14	21	24	25	29	38	38	39	40	40	40
including horizontal				1	2	2	2	2	2	2	1	1	1	1
Oil production over year, th. tons	37,4	53,8	83,2	127,8	157,5	174,4	204,0	223,2	249,3	277,2	278,9	285,5	287,5	293,6
including by horizontal	2,7	11,1	26,5	48,1	66,4	80,6	104,7	121,8	146,0	165,3	169,4	178,4	175,6	181,2
Liquid production over year, th. tons	45,8	63,9	94,6	140,3	169,9	189,0	225,6	251,5	278,9	306,9	305,5	315,8	326,5	343,6
including by horizontal	2,9	12,0	28,0	51,5	69,3	84,4	112,2	131,8	155,7	173,7	175,7	189,7	189,4	201,0
Water flooding over year, %	18,3	15,8	12,1	8,9	7,3	7,7	9,6	11,3	10,6	9,7	8,7	9,6	12	14,6
Cumulative oil production, th. tons	578,9	632,8	716,2	844,1	1002,1	1175,7	1379,6	1602,8	1852,1	2129,3	2408,2	2693,7	2981,2	3274,8
including by horizontal	2,7	13,8	40,3	88,4	154,8	235,4	340,1	461,9	607,9	773,2	942,6	1121,0	1296,6	1477,8
Average flow rate, th. tons:														
- in whole	2,3	2,7	3,3	4,2	5,2	4,9	4,7	4,6	4,9	4,7	4,8	4,8	4,7	5,1
- by vertical	2,1	2,2	3,2	3,1	3,4	4	3,1	3,2	3,8	3,2	3,3	3,7	3,6	3,7
- by horizontal	3,8	5,9	6,8	8,3	8,4	8,1	7,7	7,3	7,0	6,8	6,8	8,4	7	7,5
Water injection over year, th. m^3	39,8	31,3	48,1	104,2	147,4	175,5	271,4	279,0	338,3	270,2	348,2	276,5	183,1	72,0
- sewage	39,8	29,2	37,8	40,8	53,6	58,3	68,3	55,4	72,1	48,4	47,7	50,9	52,5	32,3
- formation		2,1	10,3	63,4	93,9	117,2	203,1	223,6	266,3	221,8	300,5	225,6	130,6	39,7

Table 1. Development parameters of Kizelian horizon of Korobkovsky area after the introduction of technology.

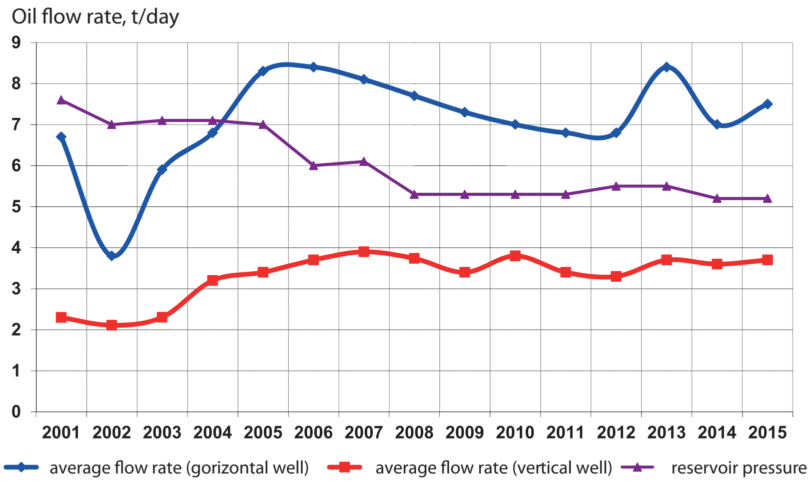

Fig. 4. Dynamics of production rates for vertical and horizontal well in Kizelian horizon of Korobkovsky area.

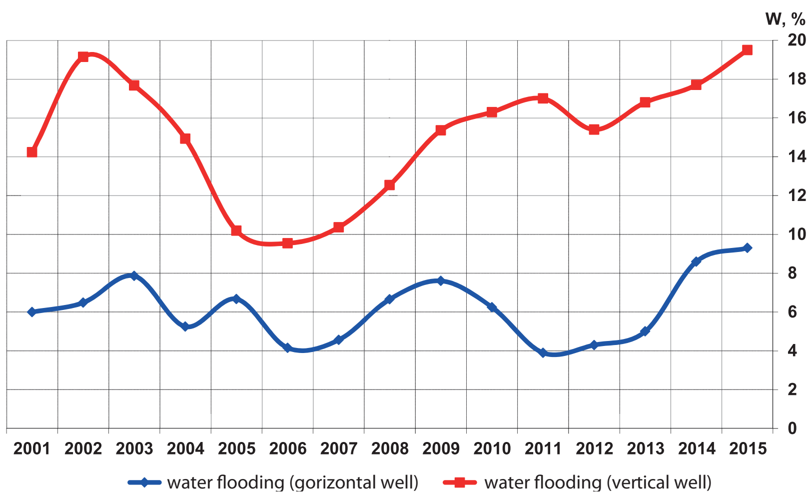

Fig. 5. Dynamics of water cut for vertical and horizontal well in Kizelian horizon of Korobkovsky area.

To increase the rate of oil recovery and enhanced oil recovery, application of subsequent hydrochloric acid treatment is provided with decreasing productivity of wells by diverter technologies. Since 2002, the drilling and operation of Korobkovsky site is made by adopted technology.

The dynamics of main indicators of Kizelian horizon development in Korobkovsky site of Bavlinsky field is shown in Fig. 2-3 since the beginning of commercial operation of an industrial facility.

During the analyzed period (1976-2015), the annual daily average oil production rate and fluid had wave pattern, and since the use of new technology, there has been a tendency to increase. Since the average flow rate increased from 2.3 tons/day in 2002 to 5.1 tons/day in 2015 due to the introduction of new and optimization of existing wells (Fig. 2).

Basic technological parameters of development based on works on the experimental plot since 2002 are given in Table 1.

To date (01.01.2016) there are 172 production wells (71 – horizontal wells) and 40 injection wells (1 – horizontal well), of which 8 are in the permanent operation from the group pumping station (KNS-12), the remaining injection wells are operated from wells that provide technical water in a cyclic mode.

In 2015, the oil production of the object in question amounted to 293.6 thousand tons, the recovery rate of the initial recoverable reserves – 6.9%, 343.6 thousand tons of was produced with water cut of 14.6%. In order to maintain reservoir pressure 72 thousand m^3 of water was pumped.

Figures 4-5 show the dynamics of horizontal and vertical wells after the introduction of technology. Oil flow rates for horizontal wells since 2002 (3.8 tons/day) increased to 7.5 tons/day in 2015. However, it should be noted that the average maximum flow rate (8.4 tons/ day) was achieved in 2006 and 2013.

It is not correct to compare the current average production rate of horizontal wells with flow rate of 2001. Thus, well stock in 2001 was only 3 wells, including 2 horizontal wells drilled in 2001, and in 2015 there are 71 horizontal wells in operation.

The average annual production rate of oil by vertical wells increased slightly from 2.2 tons/day in 2002 to 3.7 tons/day in 2015. Maximum annual average production rate was achieved in 2007; it amounted to 4 tons/day.

Water cut in both vertical and horizontal wells did not significantly increase as compared to 2002. In 2015, the water cut of vertical wells was less than 20%, and for horizontal wells it was less than 10%.

The result of the experiment was the annual growth in oil production for Kizelian horizon in Korobkovsky area. 7 horizontal wells are remained to be drilled and put into operation.

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Geochemistry of Organic Matter in Permian Deposits in the Northeast of Korotaihinsky Depression

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Abstract. The article presents results of geochemical studies of Permian deposits in the northeastern part of Korotaihinsky depression. We show the distribution of organic carbon and bitumen in various lithological varieties of rocks. The smallest (0.04-0.7 %) concentrations of organic carbon are confined to the limestone and sandy-silty varieties; the maximum ones are set in the mudstone, carbonaceous mudstones (1.0-1.7 %) and coal (26 %). Deposits of Late Permian age are characterized by a high content of bitumen (0,018-0,293 %). The distribution of n-alkanes and isoprenoids in the hydrocarbon fraction of bitumen shows a significant proportion of sapropel organic matter with a small contribution of humic compounds. Permian bitumen is mixed – autochthonous with a dash of allochthonous hydrocarbons. Results of pyrolytic studies show low residual generating potential of rocks (HI < 65 mgHC/g Corg), due to the composition of organic matter and its catagenetic transformation.

Keywords: Permian sediments, organic matter, bitumen, n-alkanes
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Introduction

Korotaihinsky depression is one of the least studied structures in the geochemical aspect in the northeast of the Timan-Pechora Basin. Geochemical characteristics of organic matter (OM), its oil and gas generating potential in sedimentary complexes of the depression are provided in the few works on the basis of individual wells and natural exposures (Anischenko et al., 2004, Bazhenova et al., 2010, 2008; Kotik 2015; 2016). Therefore, conducting geochemical studies and obtaining new data will allow us to complement the information on the properties of oil and gas source rocks in the sedimentary cover of Korotaihinsky depression.

Area and object of the research

The area under study is located in the northeast of Korotaihinsky depression within the most dislocated part – Sabriyaginsky and Pestanshorsky fold-thrust zones. The main objects of our studies were the Permian clastic sediments that are exposed fragmentally in natural outcrops in the mean flow of the river Silovayaha (Fig. 1). Comprehensive geochemical study of rocks was conducted in three outcrops, which opened different stratigraphic intervals of the Permian: sezymskian (P_1Sz) and goosinian (P_1gs) formations (outcrop 16), lekvorkutskian (P_1lv) formation (outcrop 15), sylovskian (P_{2-3}sl) formation (outcrop 13).

Complex of geochemical studies, including definition of the organic carbon content in the rock (TOC, %), extraction of chloroform bitumen A (CBA%), determination of the aliphatic hydrocarbons composition by gas chromatography (GC) was performed on the basis of Common Use Center "Geoscience" in the Institute of Geology of Komi of the R&D center of the Ural Branch of the Russian Academy of Sciences (Syktyvkar). Pyrolysis studies by Rock-Eval method were conducted in VNIGNI (Moscow).

The Permian section begins with limestone of Sezymskian formation of Asselian-Sakmarian age that with a stratigraphic unconformity lie in the Middle Carboniferous deposits (Fig. 2). They are overlapped with clastic sediments of Artinskian ties (P_1gs-tl), represented by sandstones, siltstones and mudstones, in the upper part with predominance of sandstone and siltstone. Overlying sediments of Vorkutinskian series (P1lv-in) of Kungurian-Ufimian are composed of cyclic alternation of sandstone, siltstone, mudstone, carbonaceous mudstone and coal. At the top of the series (Intinskian formation, P1in) the content of coarse clastic rocks (sandstone grits, conglomerates) is increased up to 50% (Puhonto, 1998). Section of Pechora series (P_{1-3}pc) in the lower part (seidinskian formation, P_{1-2}sd) is composed mainly of argillites and siltstones interbedded with sandstones. The most significant upper part of the section (Seidinskian and Silovskian formations) composed of conglomerates, which are subject to silt-clay rocks containing coal seams (Puhonto, 1998). Permian sediments are overlapped with Triassic deposits, which are separated from them with basalts (Fig. 1).

Results and discussion

The concentration of organic carbon in rocks ranges from 0.2 to 1.78%, reaching 26% in coal (Fig. 2). The lowest values of TOC (0.04-0.09 %) are set in the limestone of Sizimskian formation. In clastic rocks the increase of TOC occurs naturally in the sequence of: sandstone (0.23-0.26 %) – siltstone (0.47-0.72 %) – mudstone (1.01-1.78). Yield of chloroform bitumen from Lower Permian clay rocks is 0.006-0.012 %. Rocks of the Upper Permian interval contains the greatest concentration of chloroform bitumen (CB) 0.018-0.039 % – for clay varieties, and with a maximum of 0.293 % – for coal. Values of bitumoid rate (β_{CB}) are changed with the same tendency. In the Lower

Permian rocks β_{CB} is 0.3-1.6 %, rising to 2.4-2.6 % in the Upper Permian. These low values of the indicators вCB characterize bitumens as the autochthonous, including residuals that gave its migration part.

Catagenetic transformation of OM in Permian complex in the area under study varies from the middle of mesocatagenesis to the beginning of apokatagenesis (Anischenko et al., 2004). Catagenesis of OM in Kazanian-Tatarian deposits are located on gradations MK_3-MK_5. In the mean flow of the river Silovayaha coal deposit of the same name is explored, where in Pechora series coals are of brand K (coking) and OS (lean caking) that matches the gradations MK_4-MK_5 (Coal Base of Russia, 2000). Catagenesis of OM of underlying Artinskian-Kungurian deposits reaches gradation MK_5-AK.

High maturity of OM is also confirmed by pyrolysis Rock-Eval.

In samples from Kungurian and Artinskian sediments, values of S1 (content of free hydrocarbons) and S_2 (content of fixed hydrocarbons) are, respectively, 0.01 and 0.06-0.15 mgHC/g of rock. At such low values, indicators of T_{max} (maximum yield temperature of fixed hydrocarbons in the thermal degradation of kerogen) and HI (hydrogen index) are not defined. In samples of the Upper Permian interval higher values are recorded: S_1 – 0.03-0.73; S_2 – 0.45-18.64; HI – 27.65 mgHC/g of TOC. The residual hydrocarbon potential of OM from the Upper Permian rocks is characterized by very low values, due to the specific composition and the maturity degree of OM.

The proportion of saturated hydrocarbons in bitumen is not significant, on its concentration it is accounted from 3 to 34.78% of the total weight of CBA. Almost on the whole section Permian bitumen (except for samples of 15-04, 15-05 and 16-06) is characterized by a similar molecular weight distribution of low molecular normal alkanes of the composition C_{13}-C_{18}, the concentration of which varies from 67.33 to 76.17% (Table). Distribution histograms of alkane hydrocarbons have a unimodal distribution with a maximum at n-C_{16} or n-C_{17} except for sample 13-06 (coal), in which the distribution maximum is shifted to n-C_{14} (Fig. 3a, b).

The concentration of alkanes C_{19}-C_{24} varies from 11.51 to 18.06%. The samples are characterized by low background of macromolecular compounds in the n-C_{25}-C_{35}, their concentration is extremely low and the average is 1-3 %.

Among the examined samples coal (sample 13-06) has the highest content of high molecular weight alkanes normal structure – 8.93% and the lowest values of the ratio n-C_{17}/nC_{25} – 5.34 and $K_{odd}C_{17}$ – 0.96.

Ratio of n-alkane sum in series C_{14}-C_{20} to C_{21}-C_{30} varies in a wide range from 5.37 to 11.58.

Odd ratio $K_{odd}C_{17}$ varies between 0.96-1.24.

The predominance of medium molecular odd n-alkanes ($K_{odd}C_{17} > 1$) reflects the part of algal OM in the composition of the initial biomass (Hunt 1982; Tissot, Welte, 1984).

Value of even ratio $K_{even}C_{16}$ of 1.12-1.53 indicates on microbial material in the composition of source OM. In some samples there is a slight predominance of even compounds $K_{odd}C_{15}$-C_{21} – 0.94-0.97 (Table). According to some researchers, the predominance of even compounds among C_{14}-C_{22} is inherited from the fat of marine organisms (Tissot, Welte, 1984).

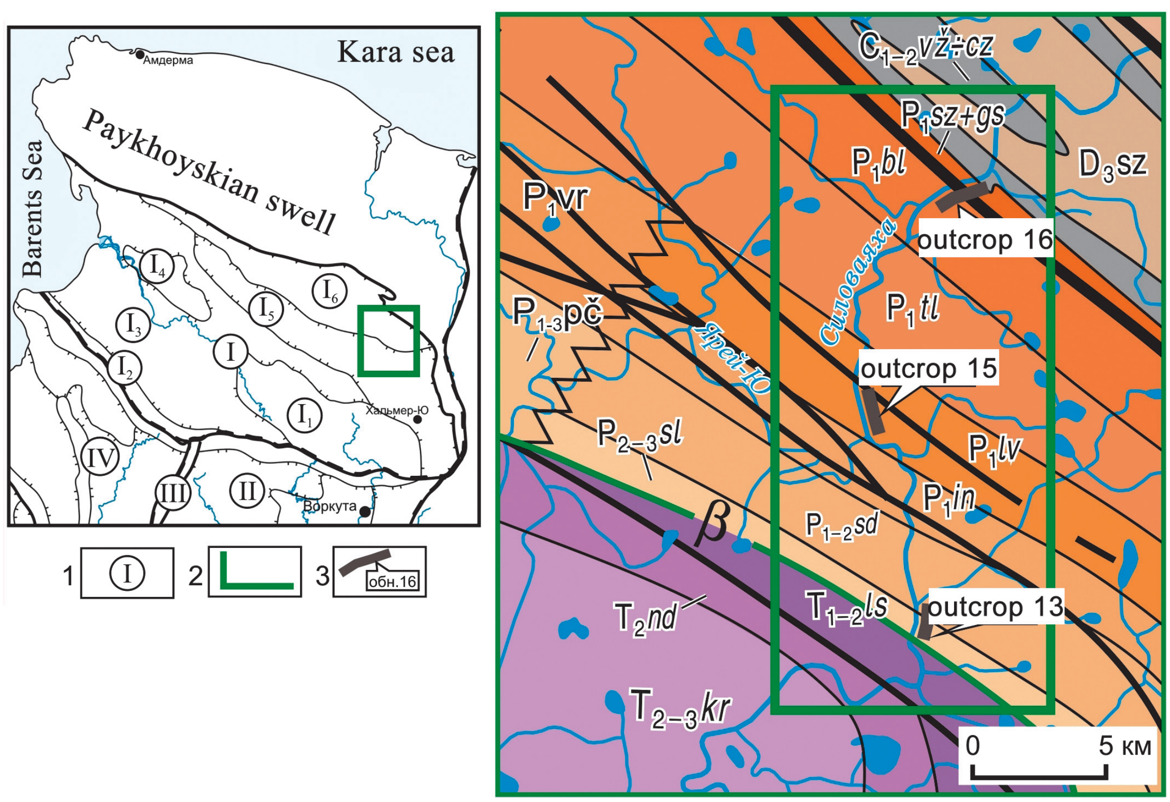

Fig. 1. Geological map of the area under study (Shishkin et al., 2012). 1 – numbers of tectonic elements, 2 – boundary of investigations region, 3 – studied outcrops and their numbers. Tectonic elements: I – Korotaihinsky depression, I1 – Verhnevorkutinsky dislocation zone, I_2 – Vashutkino-Talotinsky thrust, I_3 – Labogeysky ledge, I_4 – Odindoksky anticlinal zone, I_5-I_6 – fold-thrust zones (I_5 – Pestanshorsky, I6 – Sabriyaginsky); II – Vorkutinsky cross uplift; III – Chernyshev ridge; IV – Varandey-Adzvinsky structural zone.

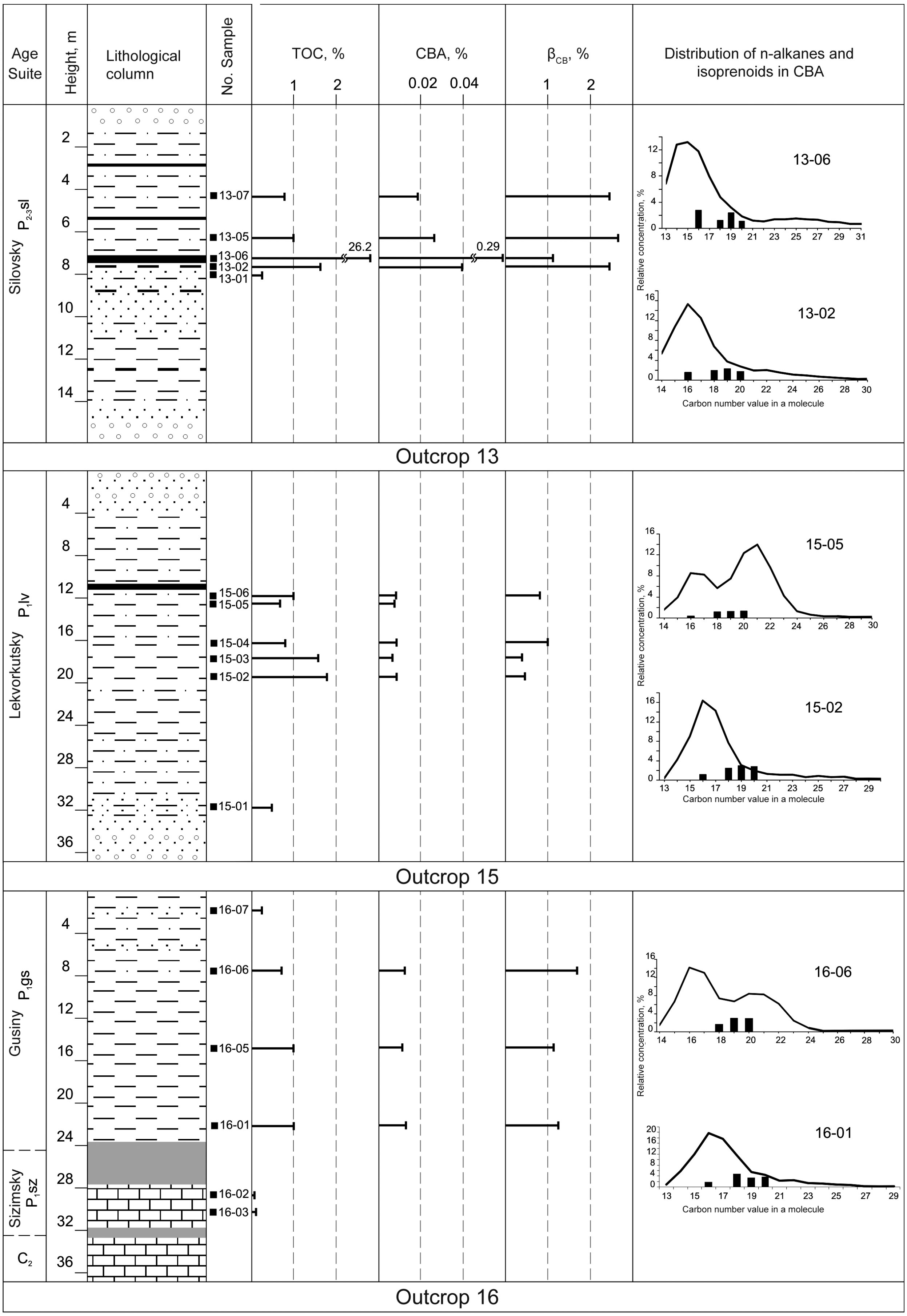

Fig. 2. Lithological-geochemical section of the Permian sediments along the river Silovayaha. 1 – conglomerate, gravelite; 2 – sandstone; 3 – siltstone; 4 – mudstone, 5 – carbonaceous mudstone; 6 – coal; 7 – limestone; 8 – interval without outcrops.

Age	$P_{2\text{-}3}sl$				P_1lv					P_1gs		
Sample	*13-02*	*13-05*	*13-06*	*13-07*	15-02	15-03	15-04	15-05	15-06	*16-01*	*16-05*	*16-06*
Catagenesis gradation	$МК_3$–$МК_5$				$МК_5$					АК		
C_{13}-C_{18}	68,85	76,17	69,91	67,80	71,46	73,96	57,28	33,93	71,85	67,33	70,06	51,38
C_{19}-C_{24}	17,56	14,79	12,04	18,06	12,67	11,51	29,27	59,44	15,17	17,46	16,15	39,48
$>C_{25}$	3,28	0,94	8,93	2,53	2,88	0,99	4,82	1,52	0,87	1,55	0,00	0,00
∑i-alcanes	10,31	8,10	9,11	11,61	12,99	13,54	8,62	5,11	12,11	13,65	13,79	9,14
$\sum н(C_{14}$-$C_{20})/\sum н(C_{21}$-$C_{30})$	6,44	11,58	5,37	8,94	9,04	11,84	2,85	1,58	10,15	8,41	10,82	3,26
$К_{нч}C_{15}$-C_{21}	1,02	1,03	1,06	1,06	0,97	0,95	0,94	1,06	0,95	0,94	1,00	1,03
$*К_чC_{16}$	1,32	1,32	1,12	1,20	1,40	1,53	1,46	1,40	1,53	1,34	1,42	1,44
$**К_{нч}C_{17}$	1,13	1,24	0,96	1,24	1,19	1,16	1,24	1,17	1,15	1,12	1,09	1,21
$н$-$C_{17}/н$-C_{25}	14,01	22,20	5,34	18,42	17,52	20,82	6,25	13,80	23,18	20,59	–	–
Pr/Ph	1,36	1,03	2,15	0,94	1,06	1,12	1,04	0,94	1,09	0,89	1,09	1,02
Pr/$н$-C_{17}	0,19	0,14	0,30	0,18	0,21	0,21	0,17	0,15	0,19	0,19	0,25	0,23
Ph/$н$-C_{18}	0,25	0,26	0,23	0,31	0,37	0,39	0,31	0,24	0,35	0,33	0,42	0,40
Pr+Ph/ $нC_{17}+нC_{18}$	0,21	0,18	0,28	0,23	0,26	0,27	0,22	0,19	0,24	0,24	0,31	0,29

Table. Geochemical parameters of saturated hydrocarbons in Permian deposits in the northeast of Korotaihinsky depression (river Silovayaha). $*$ – $2 * C_{16} / (C_{15} + C_{17})$ $**$ – $2 * C_{17} / (C_{16} + C_{18})$.

The distribution of n-alkanes reflects the predominance of sapropel base in the OM, but with a small admixture of humus component, more manifested in coal. Despite the formation of the considered coal in marsh environments, a large proportion of light hydrocarbons characterize allochthonous bitumen, which once again confirms the increased sorption capacity of carbonaceous rocks.

A number of bitumen samples are characterized by a different distribution of saturated hydrocarbons (Fig. 2). In samples of 15-04, 15-05 and 16-06, where the proportion of low molecular weight alkanes of n-C_{13}-C_{18} falls from 33.93 to 57.28%, and content of medium n-alkanes increased to 29.27-59.44 % (Table), the chromatograms clearly show bimodal distribution with n-alkane peaks at n-C_{16}, n-C17 and n-C_{21} (Fig. 3 c,d). These samples have the lowest ratios $\Sigma n(C_{14}$-$C_{20})/\Sigma n(C_{21}$-$C_{30})$ – 1.58-2.36. This character of the

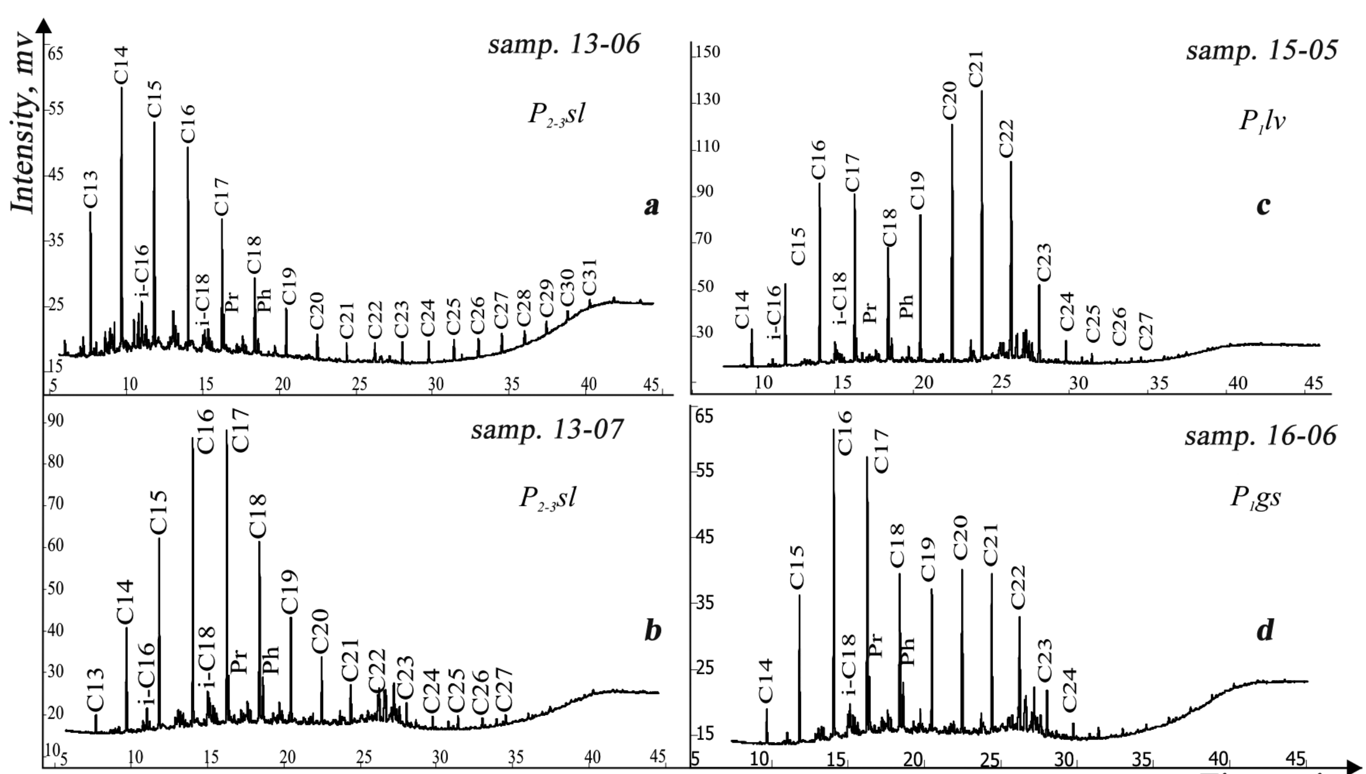

Fig. 3. Chromatograms of the molecular weight distribution of normal and isoprenoid alkanes in bitumens.

molecular weight distribution in bitumen indicates of different initial composition of OM.

All isoprenoid samples studied (where we could identify i-C_{16}-C_{20}) are characterized by low concentrations. They accounted from 5.11 to 13.79%. It is believed that the ratio of pristane (i-C_{19}) to phytane (i-C_{20}) (Pr/Ph) is indicative of redox conditions in diagenesis for the initial OM (Hunt 1982; Tissot, Welte, 1984; Peters, Moldowan, 1993). In most of the samples there is slight predominance of pristane-phytane ratio. The ratio of Pr/Ph ranges from 0.94 to 1.36, and only for one sample it is increased to 2.15 (Table). This may indicate that the accumulation of the initial OM proceeded in sub-oxidizing environment.

Results of katagenesis modeling (Koopmans et al., 1998; Bushnev et al., 2004) suggest a possible increase in the value of this ratio in the range 0.6-1.5 only due to the growth of the thermal transformation of OM. In general, considered bitumens differ in the composition of the original OM, its accumulation conditions and maturity. OM is very mature, as evidenced by geochemical parameters, namely the maturity coefficient K_i=(Pr+Ph)/(C_{17} + C_{18})<0,3 (it is known that increasing catagenesis of OM leads to a decrease in this ratio (Connan, Cassow, 1980)), as well as the ratio of pristane to heptadecane (Pr/n-C_{17}) and phytane to n-oktadecane (Ph/n-C_{18}), the values of which are generally less 0.4.

The above patterns of molecular weight distribution of iso- and n-alkanes indicate the presence of similar biological markers in bitumens formed in different depositional conditions. The main source of HC generation was sapropel OM, but there was a mixed substance with various impurities of humus component. Bitumens of considered deposits are also mixed (residual autochthonous and allochthonous), in which there are one or other allochthonous fractions of hydrocarbons. Similar features in the composition of bitumen are also noted in the surrounding areas of Korotaihinsky and Kosyu-Rogovsky depressions, where Permian deposits contain genetically heterogeneous mixed bitumens (Anischenko et al., 2004; Bazhenova et al., 2008; Kotik, 2015; 2016).

Conclusion

The content of organic carbon in the Permian sediments increases regularly in clay-carbonaceous rocks at higher bitumen content in the Upper Permian part of the section. The distribution of n-alkanes and isoprenoids in bitumens indicates a mixed nature with their significant contribution to the sapropel component of OM and the presence of migration of light hydrocarbons.

The values of geochemical and pyrolytic data characterize the Permian deposits as primarily gas-source with low and middle generating potential. The high maturity degree of OM and implementation of its hydrocarbon potential is confirmed by pyrolytic, coal-petrographic and bitumen research methods.

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The Formation of the Upper Vendian – Middle Cambrian Clay Strata of Subclint Area

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Abstract. Silt-clay strata of Upper Vendian (Kotlinskian horizon) and Lower Cambrian age can be traced along the denudation ledge of Ladoga-Baltic clint. The study area is located in subclint area where sediments were studied in scattered shallow outcrops and wells from the estuary of the river Voronka in the west to the river Tosno in the south-eastern part of the clint ledge. Deposits are related to Vasileostrovskian (r. Chernaya) and Voronkovskian (r. Voronka) suites of Upper Vendian, Lomonosovskian (r. Kovash) and Siverskian (r. Tosno) suites of Lower Cambrian. Sedimentation occurred most likely in the lagoon environment periodically alternating with coastal shallow environment. Accumulation of thick bottom sediments is possibly due to the active areal physical weathering on the adjacent land.

For a number of lithological and petrographic features, close chemical composition, X-ray modeling of clay minerals, as well as findings of similar prokaryote residues may be assumed that the accumulation of boundary clay strata at the boundary of the Vendian and Cambrian subclint area occurred without a long break in the studied area.

Key words: clay strata, subclint area, sedimentation, Upper Vendian, Lower Cambrian, lithological and petrographic features, chemical composition.

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Clay deposits of Upper Vendian-Lower Cambrian are traced in a narrow strip along the ledge of the Baltic-Ladoga limestone cliff, which stretches along the southern coast of the Gulf of Finland. Despite the long study history starting from works of A.A. Inostrantsev and F.B. Shmidt, B.S. Sokolov and K. Mene to N.A. Volkova and V.N. Podkovyrov et al., the matter of age and origin of boundary clay strata in Vendian-Cambrian deposits in the northwest of Russian platform remains unsolved.

Vendian-Cambrian deposits are represented by silty-clay strata, studied by the author in disparate thin sections (natural outcrops are very rare) and penetrated by wells (materials of A.S. Yanovsky from St. Petersburg exploration company). We also used materials of A.M. Nikulenkov (Faculty of Geography and Geoecology of St. Petersburg State University) and core from wells drilled on the territory of St. Petersburg atomic power station. We studied the Lower Cambrian deposits attributable to the Lomonosovskian formation in small outcrops on the river Kovash and deposits of Siverskian formation ('blue clay') in the clint ledge in the stratigraphic sections of the Cambrian-Ordovician on the river Tosno.

Schematic sections (Fig. 1) were compared by lithologic features using materials of hydrogeological survey of A. Yanovsky and legend of Ilmenskian series of sheets (Yanovsky, 1999). Materials require further micropaleontological research and age correlation.

In the analysis of some sections we used descriptions of thin sections composed by V.V. Kostyleva. The definitions of cyanobacteria are made by V.N. Sergeyev (previously not carried out on test sections); V.V Krupskaya participated in modeling clay mineral radiographs (Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences). The materials used in the study are not always clear: the core description of most wells is taken from production reports, and stratigraphic units allocated by different authors are not always comparable, for example, in the columns of wells on the territory of St. Petersburg atomic power station voronkovskian formation is not allocated.

Vasileostrovskian Laminaria clay observed in the core of well drilled in the yard of the former Geolkom (current All-Russian Geological Research Institute) (Yanishevsky, 1939) and exposed at the museum of A.P. Karpinsky Russian Geological Research Institute, outwardly indistinguishable from the Lower Cambrian clays of Lomonosovskian formation and 'blue' clay of Lower Cambrian Siverskian formation. The outward similarity of the above clays is confirmed by the same particle size distribution and physical-mechanical properties, studied in research to create underground burial of radioactive wastes in them (Anderson et al., 2006).

Stratigraphic referencing of the studied section

Vendian. Upper Section.

Kotlinskian Horizon. Vasileoostrovskian Formation

One of the key objects for understanding the structure is a natural outcrop in the river Chernaya near the village B. Izhora (section 'I'; Fig. 2).

In the nip of the left bank of the river Chernaya in the outcrop with height of about 10 m and length of about 20 m Upper Vendian (Upper Kotlinskian) clay is observed of blue and greenish-gray color, ocherous silty with horizontal and wavy bedding, underlined by layers of silt material, pinky gray color with laminaria films on the bedding surfaces associated with transformation of organic matter.

Laminaria clay is thin, less massive microstructure, tape thin-layered texture, due to the alternation of dark gray clay and light-gray siltstone and coarse pelitic stratums (0.1-3 mm). The silt layers have flat lenticular siderite nodules.

There are interlayers with ferruginized clayey siltstone and unevenly positioned silt material. Probably interlayers are cracking crust formed after the break and consolidation of the underlying sediments.

Lens silt material is visible in kaolin clay substrate. The clay-silty substrate has ferruginated remains of fossil prokaryotic cells, forming a chain by determination of V.N. Sergeev Bavlinella taveolata Schepeleva (1962?), Ostiana cf. microcystis Hermann (1976).

Currently, the age of the observable Vendian part of the section is confirmed by definitions of Vendotaenia antiqna Gnilovskaya.

Vasileostrovskian clays, penetrated by well C-5, have remains of prokaryotes in thin sections, determined by

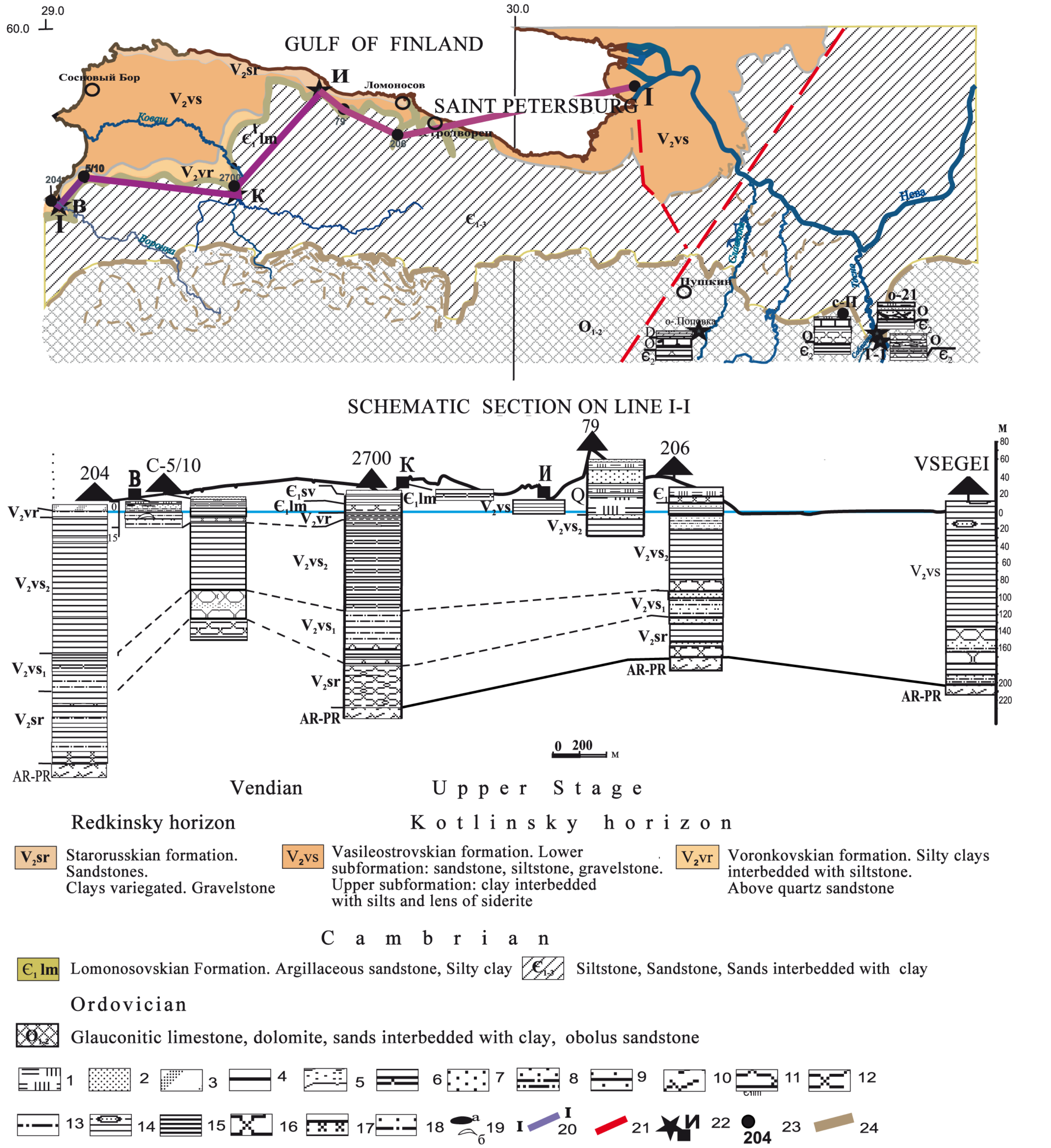


Fig. 1. Geological map of the studied area (using materials of A.S. Yanovsky). 1 – Clay remolded ('blue') with boulders, 2 – Sands uneven-grained, 3 – Sandy soil, 4 – Dictyonema shale, 5 – Sands interbedded with sandstones, 6 – Clay interbedded with sandstones, 7 – Sands with lenses of ferruginous sandstone, 8 – Sands and silts with interbedded sandstones, 9 – Silt clay, 10 – Gneiss, granodiorite, 11 – Sandstones uneven-grained, interbedded with clay, 12 – Sandstones uneven-grained, 13 – Alternating argillites, mica-kaolinite with argillaceous siltstone, 14 – Clay lenses of quartz sand, 15 – Clay thin-bedded, 16 – Sandstones interbedded with siltstone, 17 – Clay with silty and siderite layers, 18 – Siltstone interbedded with silts, 19 – Lenses a- siderite, b – lepidocrocite, 20 – the section line, 21 – faults, 22 – outcrops, 23 – wells, 24 – boundary of the Ladoga-Baltic clint.

V.N. Sergeyev as pterospermopsimorphic, spheromorphic, colonial coccoid forms. In this section remains of algae were found in clays.

Found remains of prokaryotes indicate the presence of free oxygen in the bottom muds, possibly due to activation of weathering processes on the adjacent land.

The overlying silt-clay strata of Upper Vendian attributable to the Voronkovskian formation (Yanovsky, 1999) and extending in a westerly direction to the northern Estonia, is exposed near the mouth of the river Voronka (section 'B-1'; Fig. 2).

In the fine-grained bluish-gray sandstones, strong (below the water line), there are compacted greenish and bluish-gray clay with laminaria ferruginated films. This part of the section may be referred to Vasileostrovskian formation at finding of M. Leonov (Paleontological Institute of the Russian Academy of Sciences) Vendotaenia antiqua. The overlying sediments are likely to be voronkovskian.

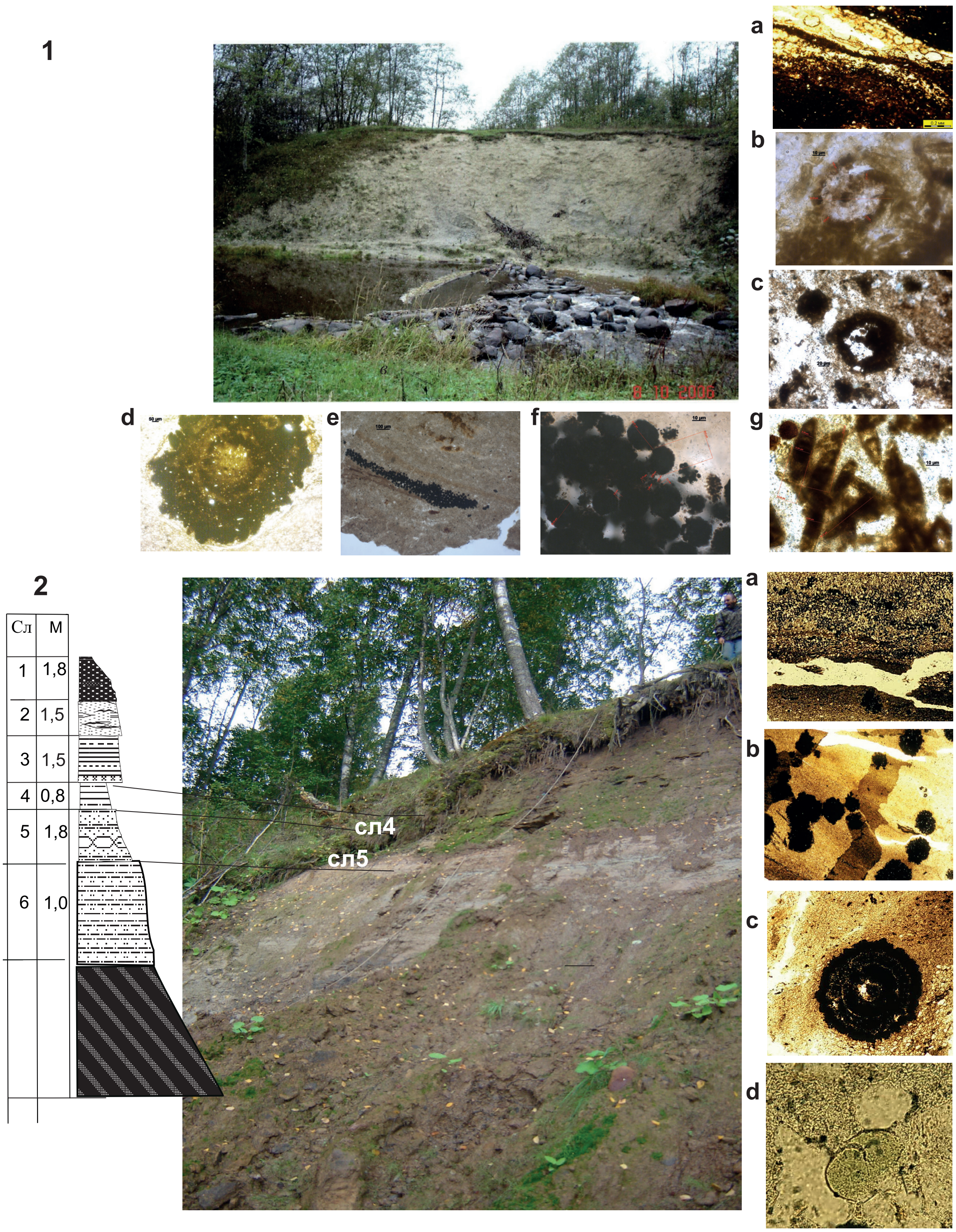


Fig. 2. Section of Kotlinskian deposits: 1 – Vasileostrovskian formation on the river Chernaya (I), a-microbial mat; b – Siphorophycus Kestron Schopf, 1968, c-Paleo Palaeolyngbya cf.P.Basghoorniana, d, e, f – pyrite along colonies of cyanobacteria, g – Oscillatoriopsis aff.O.meding. 2 – Voronkovskian formation on the river Voronka (B-1): a – siltstone layers alternating with layers of siltstone clay; b – Silty clay with mud-eaters traces and glandular inclusions; c – ferrigenous inclusions; g – globules of glauconite in sandstone.

Voronkovskian Formation

Pack of centimeter-decimeter interbedded silty mudstone, mica-kaolinite clay, micaceous siltstone with occasional fine sand.

Sands are weakly ochreous with interbedded sandstones ferruginized to 15 cm thick and lenticular bluish streaks of pink silty clay with horizontal wavy discontinuous layering of 1-3 cm thick. In silt layers there are flattened lenticular and large up to 15 cm siderite nodules destroyed with black glandular rim.

Up the section silt thickness increases.

In the upper part of the section there is a pack of (thickness 0.8 m) clays of blue, purple and yellow shades with lenticular sand layers (less than a centimeter). Pack is crowned with interbedded argillaceous rocks of bright yellow color, and is clearly seen on the outcrop.

The presence of lepidocrocite, whose formation (Chukhrov et al., 1973) involves the dissolution of siderite, when iron goes into solution in the form of $Fe(HCO_3)_2$, ochreous rocks on silt layers, and ochreous and black halos of iron hydroxides on the periphery of siderite nodules indicate the possible formation of rocks pack in subaerial conditions and may be indicative of the existence of the weathering crust, described in Vendian sections of Baltic (Bessonova et al, 1980;. Mene, Pirrus, 1969) and observed in wells 204 and 2700.

Above there is a pack of whitish quartz, fine sand and silt clay with thin centimeter lenticular streaks of rust (ferruginized) sandstones. The pack is covered by Quaternary boulder loams.

According to M. Leonov (Paleontological Institute of the Russian Academy of Sciences), in clays at the water's edge the remains are found of Vendotaenia antiqua Gnilovskaya (1974) typical for sediment of Vendian Kotlinskian horizon (Ediacaria) in the East European platform (other finds of fossil remains are not found in these outcrops). In other sections of border deposits Planolites and N.A. Volkova acritarchs were recently discovered and described.

Quaternary sediments close the overlying part of section in the studied area. Natural outcrops with contact of Vasileostrovskian and Lomonosovskian deposits are not there, it was opened by wells, but the core has not been preserved and it is not available (wells on the territory of Leningrad atomic power station).

Cambrian. Lower Section
Lomonosovskian Formation

According to drilling within the city of Lomonosov (well 206), this part of the section, above the gray clay, is represented by sands, poorly cemented by sandstones and clays of Lomonosovskian Formation of the Lower Cambrian. Sandstone of Lomonosovskian Formation, observed in wells 206 and P-5 and exposures "K-1" and "K-2" (Fig. 1), may be attributed to Voronkovskian.

In the middle stream of the river Kovash in scattered small outcrops (up to 2 m thick) silty clay is exposed that looks very similar to voronkovskian.

Clay lies monoclinally with a gentle fall in the southeast dipping towards the northwest wing of the Moscow syncline at angles of 9-12°.

Blue plastic and dense clay has unclear bedding, and shelly conchoidal fracture. The surfaces of the bedding are 'sprinkled' with leaves of mica (mm). Closer to the water's edge blue color becomes more intense.

In some interlayers greenish tint appear due to glauconite observed in thin sections, and confined to the silt interlayers in clay. On the surfaces of the bedding ferruginized film (mm), possibly laminaria remains and ocher spots are observed. Surface of bedding is smooth. At 1 m from the base interlayer (3-5 cm) is traced of blue-gray fine-grained sandstones with thin horizontal stratification (mm), accentuated by dark gray layers every 3-5 mm. Bedding surfaces of sandstone are covered with ferruginous films, in some portions ripple marks are observed with shallow ridges with a height of up to 2 mm.

By particle size distribution clay can be attributed to silt. In clays of section 'K-1' A.Yu. Ivantsov found Sabellidites cambriensis Janischevskii.

Siverskian Formation

In the sections of river Tosno and near the mouth of the river Sablinka clay underlying sands of Sablinskian suite was studied (section "T-1" and repeatedly described section "Outcrop 21", Fig. 1). Clay is blue, when wet green, homogeneous plastic, contains rare quartz grains up to 1 mm. In thin sections lenses are observed of silt material and occasionally filamentous remains of prokaryotes, filled with pyrite, emphasizing fuzzy bedding. On clays sandstones overlie sands of Sablinskian suite.

Material composition of clays

Clay minerals have been studied in thin sections by X-ray diffraction using Rietveld method for processing results of quantitative analysis (Fig. 3). Silicate analysis and electron microscopy carried out to determine the chemical composition of clay minerals (Fig. 4).

Vasileostrovskian Formation

Laminaria clays (section "I") are fine dispersed, weakly silted, chlorite-kaolinite-mica with a heterogeneous structure, pelitic and aleuropelitic. Microtexture in some portions is massive or micro-lenticular-wavy. In lenses and micro-layers fine quartz-silt material is accumulated. There is micro-cloggy separateness. The majority is of light olive color. Under crossed Nicols kaolinite is observed in the majority having a low birefringence and interference of gray color. Spheroidal separation of kaolinite occurs (Fig. 4). Among the kaolinite mass a significant amount of mica and illite-smectite is observed. Sometimes mica forms oriented in one direction or lenticular accumulations or microlayers that determine the effect of wavy extinction. In some portions rock is of green color, which is probably due to the admixture of chlorite, possibly associated with the finely divided fragments of chloride biotite.

By particle size distribution silt varieties contain 10-20% of fraction 0.01-0.1 mm. The mineralogical composition of silt and pelitic fractions us polymictic. Among the clastic minerals dimensions of 60-90% are for muscovite, biotite, brown and green, 10% are for quartz and feldspars. The rock consists of siderite, pyrite, magnetite, ilmenite – up to 1%, there are individual grains of tourmaline, zircon. The clay fraction contains up to 15-20% of kaolinite.

Voronkovskian Formation

Silty mudstones are mica-kaolinite (packs of mudstone and siltstone alternation in the bottom part of the section “B-1”), have silty-pelitic and silt structure and horizontal obscure, in some portions disturbed texture (interlayers of silt material about 1-1.5 mm). The argillic interlayers have quartz impurity of 15-25%, a lot of fine micaceous detritus. The composition of silt and sand-silt interlayers: siltstone, quartz, feldspar (no more than 1-3%.). Roundness of clastic material is bad; sorting is bad and average. Large round siderite is characteristic (7-8 in the section), probably by algae (up to 0.7 mm). There is a lot of fine dispersed organic matter in the rock.

In silty clays of the upper part of the section “B-1” (multicolored rocks) coarse siltstone with mica flakes are observed, alternating with layers of fine-grained siltstone and silty clay with ferruginous cement, distributed in layers. Glandular rounded inclusions occur in fine-grained siltstone, possibly formed by organic residues.

Quartz prevails among the debris (25%), modified, layered, green, probably chloride-biotite (up 5%); there are single grains of microcline. Grains of quartz are of average roundness; on the individual grains regeneration rims are observed. Cement is glandular, silty. In some parts it is carbonate. The cement has pretty much elongated crystals of illite-smectite composition, often emphasizing layering. Structure is subidioblastic, granoblastic. Grains are elongated. Texture is layered.

According to the results of X-ray diffraction in multi-colored clays lepidocrocite is found in addition to kaolinite and mica.

Lomonosovskian Formation

Silty clay (sections “K-1” and “K-2”) has kaolinite, chlorite and illite-smectite composition, pelitic structure, layered, oriented parallel to the bedding texture due to interbedded with thin layers of sand and silt material. The silty-sand impurity has quartz, plagioclase grains. Grains are sharp-edged, less half-rounded. Organic matter is fine scattered, oriented parallel to bedding. There are single grains of fine chlorite. The major minerals are dominated by quartz – up to 40%; illite-smectite – up to 25%, green biotite – up to 15%, feldspars -up to 5%. Clay layers consist of illite-smectite 80%, kaolinite – about 10%. In the heavy fraction titaniferous minerals, epidote and zircon are found. The fine portion is

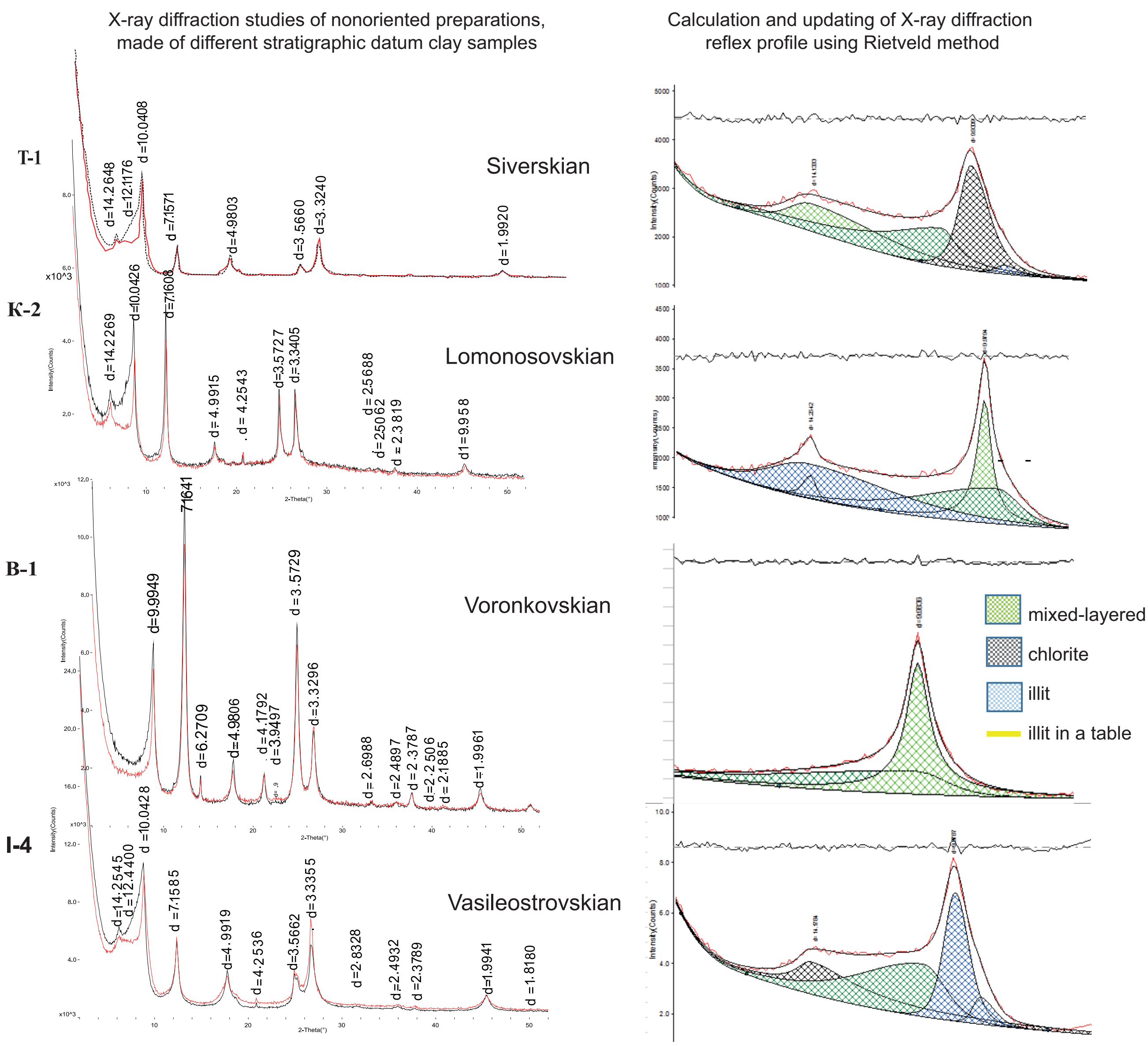
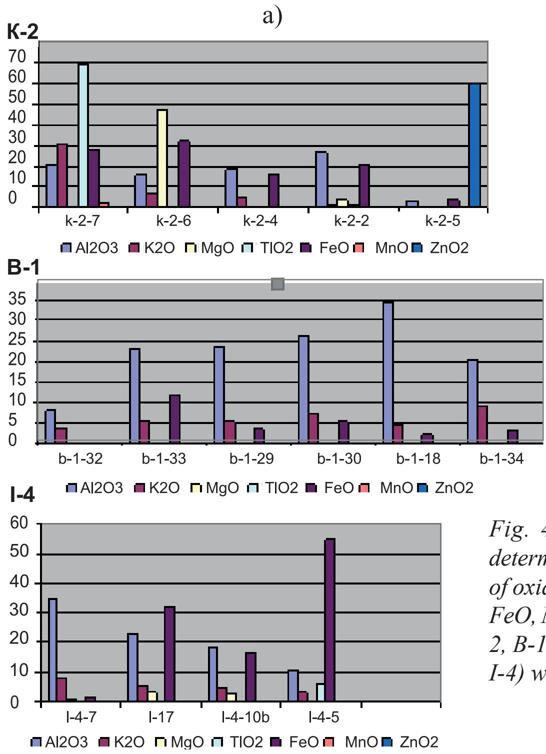


Fig. 3. The mineral composition of clay fraction.

a)



b)

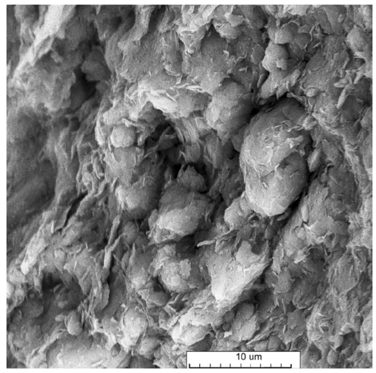


Fig. 4. The chemical composition of clay, determined by electron microscopy: a) diagram of oxides distribution (Al_2O_3, K_2O, MgO, TiO_2, FeO, MnO, ZnO) of examined clay samples (K-2, B-1, I-4); b) microstructure of clay (sample I-4) with spheroidal kaolinite.

represented with hydromicas, glauconite, and, rarely, chlorite, montmorillonite. Sporadically in fine-grained clay mass there are large grains of quartz, glauconite, feldspar, pyrite.

Siverskian Formation

In clays over 80% of particles are attributed to fraction of less than 0.01 mm. More than 50% are mixed-layered formations and chlorite. The fine clays have lenses of silt material with grains of quartz. Kaolinite was identified when conducting diffractometric studies.

As a result of silicate analysis of samples taken from clays and siltstones in Vasileostrovskian, Voronkovskian and Lomonosovskian formations, the chemical composition of deposits is stable.

Diffraction patterns of clay from Vasileostrovskian, Voronkovskian and Lomonosovskian formations have a similar appearance (Fig. 3).

Crystallite thickness decreases down the section (to Vasileostrovskian part of the section). The presence of illite-smectite components and the amount of illite in sediments of Lomonosovskian and Sablinskian formations (sections "K-1", "K-2" and "T-1") are comparable with the composition of Vasileostrovskian deposits (section "I"). In the rocks of the section "K-1" illite is probably redeposited.

The presence of chlorite in the rocks indicates on the difference in sedimentation conditions in Voronkovskian and Vasileostrovskian time. In deposits of the section 'B-1' chlorite is not revealed, and in the section "I" chlorite is more ferruginous (14 and 3,54A°), perhaps indicating the humid conditions of sedimentation. In the sections "K-1" and "T-1" the amount of chlorite increases, which suggests the formation of sediments near the shore in cold climates.

The presence of layers of glauconite and sandstones suggests the formation of silt-clay formation in the conditions of the coastal shallows. According to the potassium-argon method for glauconite (Anderson et al., 2006), the absolute age of Cambrian clay was determined as the 530-590 million years.

These data indicate on the isolation of K-Ar system in a relatively easy metamorphosed mineral, and therefore, long-term stability of the entire clay formation for half a billion years.

The rocks of voronkovskian suite (section "B-1") include illite material, catagenetic kaolinite; there is no smectite, which is typical for sea level fluctuations. In Kotlinskian time the basin was deeper and warmer, possibly with alternating wet and dry periods. The material accumulated at large distances from the source of ablation – in the rocks of the section "I" there is a significant amount of smectite.

Slightly higher clarke contents of Fe – up to 5.56% in clays of voronkovskian suite is probably due to supergene processes.

To restore the paleoclimatic conditions of accumulation of fine-grained sediments, relationships of petrochemical modules were used (Akulynina, 1985).

In relation $A1_2O_3/TiO_2$ in the fine fraction of clay – from 19.76 to 20.11 (<20 unit) and in terms of the index of chemical weathering $CIA = [Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)] \times 100$ from 75.95 to 79.62 (> 70 units) we may assume humid conditions of sediments accumulation under intense chemical weathering on adjacent land in the Vendian and Cambrian time.

Low titanium content and high aluminum content probably characterize open sea conditions. Stable values of Ni/Co ratio (from 0.88 to 3.66) and V/Cr (<2) indicate that the formation of the Vendian and Cambrian clays occurred under oxidizing conditions with good aeration of bottom waters.

At the Cambrian time sedimentary conditions have changed a bit – the basin became open shallow water, as evidenced by the appearance of sand layers with glauconite. Compared with silty rocks, the content of V (115-126) and Cr (80-104) increased slightly in clay.

Conclusions

1. From the combination of lithological features and higher content of iron, formation of Upper Vendian and Lower Cambrian silt-clay deposits occur in the lagoon environment, periodically changing with coastal shallow environment. Kaolinite-smectite -illite clay composition and the presence of fossil prokaryotes in debris, probably indicate on a moderately humid climate and areal active physical weathering on the adjacent land.

2. At the same mineral composition and grain size as well as its physical and mechanical properties the strata do not differ from each other.

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Features of the Structure and Origin of Oil and Gas Generating Shale Strata in the Permian Deposits of the Urals

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Abstract. The composition and structure of oil and gas generating shale strata in the Permian deposits of the Urals are considered by the example of the geology of Mount Yangantau, which consists mainly of yangantauskian suite of bituminous minerals, containing components peculiar to domanicites (carbonates, clay material, sufficient amount of silica, organic matter content from 3 to 12 %). The geological structure of the object is caused by a combination of several natural factors: geomorphological, material-stratigraphic, hydrogeological and structural-tectonic. The latter is characterized by high values of tangential tectonic stress that results from the presence of olistostromes, which according to modern concepts is an indicator of such regime. The interaction of these factors provides a natural mechanism for the extraction of hydrocarbons from shale strata comparable with the known technological methods.

Keywords: oil and gas generating shale strata, Permian deposits, the Urals.
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The stated problem in the title of the article is considered on the example of mountain Yangantau, which is in the border zone of Karatau structure and Yuryuzano-Sylvinsky depression of the Ural foredeep (Fig. 1).

Yangantau Mountain is the container of healing hot vapor and gas used by the well-known mountain resort of the same name. They are confined mainly to yangantauskian suite, provided with bituminous minerals, containing components inherent to domanicites, and also have shale structure. The geological structure of the Yangantau object is determined by special natural factors: geomorphology, material, stratigraphic, hydrogeological and structural-tectonic. Their interaction creates the uniqueness of this natural phenomenon.

I. Geomorphological factor. Yangantau Mountain is a hill, extending from southwest to northeast along the right bank of the river Yuryuzan between villages Chulpan and Iltaevo of Salavat region in the Republic of Bashkortostan. Ravine system dismembered it into separate flat tops. The altitude of the top – 416 m, the bottom – 252 m above sea level. Side of the mountain that faces the river Yuryuzan – is steep, with scarp areas, down to the riverbed. The rocks are strongly fractured, because the slope is well purged.

II. Material-stratigraphic factor. Yangantau Mountain and its surroundings are composed primarily of Permian Artinskian deposits. On the surface, they are well studied by researchers from the Urals region: V.D. Nalivkin, N.M. Strakhov, G.A. Dmitriev, A.I. Osipov, N.G. Chochia, S.M. Domcharev, S.V. Maximova, K.A. and LA Milovidovy, G.V. Vakhrushev and many others. Within Yuryuzano-Sylvinsky depression, these deposits are subject to significant facial changes: more clayey and calcareous, common in the southwestern part of the region, replaced to the east and northeast by sandstones and conglomerates. The deposits are represented by two substages: the lower, the fauna of fusulinid relevant to Burtsevskian and Irginskian horizons, and the upper, which includes Sarginskian and Saraninskian horizons.

Deposits of Burtsevskian and Irginskian horizons N.G. Chochia and S.M. Domrachev identified in balzyakskian formation of sandstones and conglomerates (Nalivkin, 1950). It is exposed at the foot of the mountain Yangantau, tracing along the band from the mouth of river Urdali in the northeast. In the southern part of the Mesyagutovsky anticline its structure is dominated by medium-grained sandstones with lenses of conglomerates that reach considerable thickness north of the village Chulpon. Among their clastic material quite large, deformed lumps of limestone occur, the dimensions of which reach 10 meters. When conducting combined with V.D. Nalivkin inspection we attributed them to olistoliths composed of chulpanskian olistrostrome (Fig. 2.3).

The total thickness of the horizon ranges from 100 to 200 m. In the area of the mouth of the river Urdali Balzyakskian formation is represented by shales with interbedded sandstone

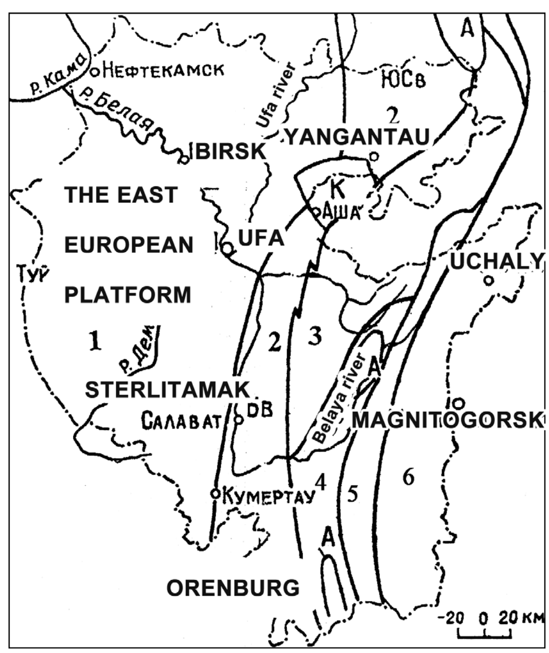

Fig. 1. Tectonic zoning of Bashkortostan. 1 – East European platform, 2 – Pre-Urals fore deep, 3 – Bashkir Anticlinorium, 4 – Zilair Synclinorium, 5 – Uraltau zone, 6 – Magnitogorsk Synclinorium; Bv – Belsky depression, YuSv – Yuryuzano-Sylvinsky depression, A – large allochthons in the western slope of the South Urals, K-Karatau allochthon.

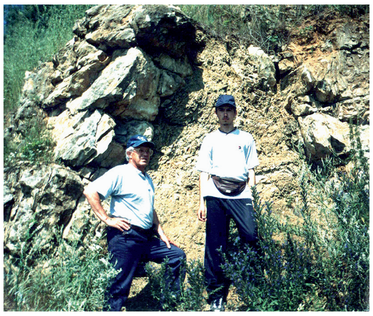

Fig. 2. Deformed olistoliths of limestone in Balzyakskian formation. The right bank of the river Yuryuzan, below the village Chulpan.

Fig. 3. Deformed olistoliths of limestone in Balzyakskian formation. The right bank of the river Yuryuzan, below the village Chulpan.

Fig. 4. The lens of flint among shale of Yangantauskian formation on the eastern slope of Yangantau Mountain.

and marl. To the east of the river Yuryuzan as part of the formation, the role of conglomerates increases, the thickest layer of which appears in the formation base on the meridian of Turnali village. The upper part of Balzyakskian formation consists mainly of mudstone interbedded with marl and sandstone. Thickness along the river Yuryuzan is 100-180 m.

Strata of bituminous marl lying over Balzyakskian formation contains organic material in an amount of 3-5 %, in some areas up to 12%. N.G. Chochia and V.D. Nalivkin named it Yangantauskian formation. In addition to marl, it contains shales, limestones, dolomites, clastic rocks, and appreciable amount of silica. The most complete characterization of the formation composition is contained in the paper (Strakhov, Osipov, 1935), according to which the homogeneous marl stratum towards the east takes the shape of a typical flysch. This suite can be traced as a strip along the northern slope of the Karatau ridge, on the wings of Mesyagutovsky and Yukalikulevsky anticlines. Its best outcrops are known on the river Saldash, on mountains Kutkantau, Yangantau, Kantuntau, along the rivers Yuryuzan and Ai.

The rocks of Yangantauskian formation are characterized by foliation. One characteristic feature of Yangantauskian formation is a kind of layering, called ‘lense-layering’. Its essence is that the rock consists of alternating stripes of different colors represented by the lenses of 1-2 mm in thickness and from 1-2 cm to several tens cm in length. Another variety of marl is characterized by thin bedding. The rock consists of close, extremely thin (share of millimeter), straight, black colored microlayers, which are located between the lighter layers. According to G.V. Vakhrushev in the western part of Yangantau Mountain outcrops also consist of two basic varieties of bituminous marl: thin-layered, foliated (layer with thickness from 1 mm to 1 cm) and massive (thickness of lens 10 cm to 5-10 m). Massive marl in some places are silicified and pyritized. Color for both thin and thick-bedded marl in most cases is dark gray.

Textural features of Yangantauskian formation are displayed on a photograph taken by us when performing material-structural studies of the late twentieth – early twenty-first century (Fig. 4), as well as sketches of the author (Fig. 5). In addition to the usual foliation, lenticular and wavy foliation is observed (Fig. 6).

On the mountains Saldash and Kutkantau only the upper part of the formation is exposed. Here layers of shale and sandstones are absent, but there are rare interlayers of marl and limestone with fauna. To the east, on the Yangantau Mountain, there are several thin layers of shale, and even further to the east, on the Kantuntau Mountain these shales compose a large part of the section. Probably these are the rocks that are currently under consideration as a source of shale gas -domanicites or oil-gas generation formations with hydrocarbon reserves difficult to recover (Kazantseva, 2013, 2014; Ismagilov, 2013).

On the Yangantau Mountain there are areas with rocks colored in red, which many researchers regard as a ‘roasting’ of bituminous marl and surrounding rocks. However, the red color of the rocks is well explained by the transition of limonite to hematite associated with zones of tectonic disturbances.

Formation thickness in the southern part of the Mesyagutovsky anticline reaches 200 m, on the Yangantau

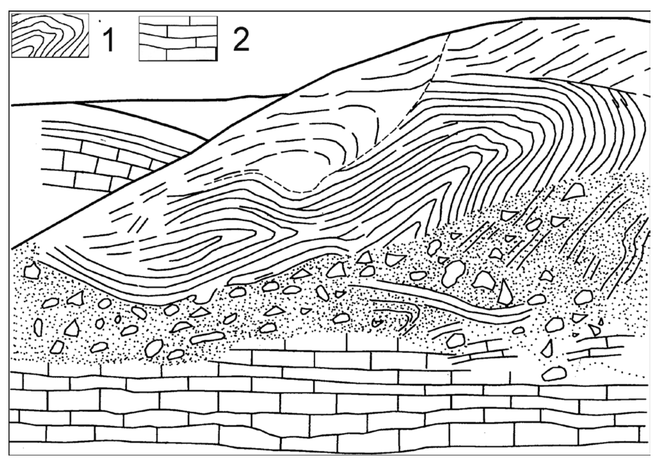

Fig. 5. The dislocation nature of shale layers in Yangantauskian formation. Sketch of exposure against the village Iltayevo. 1 – the dislocation nature of clay shale in Yangantauskian formation; 2 – limestone.

Fig. 6. Lens-layering nature of Yangantauskian formation northeast of Yangantau Mountain.

Mountain – 260 m, and on the Kantuntau Mountain (below the mouth of the river Urdali) – 340 m.

According to (Strakhov, Osipov, 1935) bituminous marl of mountains Kutkantau, Saldash, Yangantau represents a huge lens that tapers in both directions on the east and west. To the west it becomes organogenic-clastic limestone (partly bituminous), to the east – clastic rocks (sandstones and mudstones) of flysch type. Stretching of the actual marl part of the lens is measured about 40 km. Actually, the most important feature of the fore deeps is observed in this region, which consists in the regular sequence of formations laterally from the platform to the folded area: reef, carbonate, depression (shale), flysch (Kazantsev, 1984; Kamaletdinov et al., 1981).

Above bituminous marl of Yangantauskian formation I.G. Chochia and V.D. Nalivkin identified Tandakskian formation of sandstone and siliceous limestone. The formation can be traced from the village of Malaya Biyanki, along the northern slope of the Karatau ridge, on both wings of Mesyagutovsky anticline until Tandak River, northeast of Mesyagutovo and the northwest wing of Yukalikulevsky anticline.

A distinctive feature is the presence of packs and lenses of siliceous limestone among sand-shale deposits. Boundary of the formation is carried along the lower stratum of limestone. Directly on the Yangantau Mountain on the formation of bituminous marl, interbedded sandstones, siliceous and clay shale, marls occur. They are assigned to the bottom of the Tandakskian formation. In the border area there are lenses of siliceous limestone. They also contain an organic matter, but in an amount less than in Yangantauskian formation. Thickness of sandstone layers is from 20 to 50 cm, shale – 2-3 m. In many places a small folding is marked with discontinuity layers of sedimentation nature.

So, carbonates, clays dominate as part of the Yangantauskian formation (calcite and dolomite), in clastic material there are a lot of silica and organic matter, mostly 3-6 %, sometimes as much as 10% or more. Shale structure is characteristic. These features of the composition and structure of Yangantauskian formation allows classifying them as ‘domanicites’. The origin of hydrocarbons in them should be seen as a result of special occurrences of geodynamic regime associated with the tectonic forces. Earlier continuous shale texture was accepted as a result of dynamic metamorphism in the traditional sense of the process from the fixation perspective.

The alternation of shale and non-shale structures in a single section, observed autonomic active dislocations of the first among the second, inconsistency of the bedding foliation elements and layering can be explained only by the regime of tectonic tangential compression, propagating from the active zone of fold region. Consequently, the observation of the foliation nature and its scale suggests the direction and type of tectonic stress, as well as fixation of the periodization. By changing the composition and structural-textural features of coeval formations across the strike of the whole folded area we can judge of the character of geodynamic regime in time and throughout the space.

But subhorizontal tectonic compression is responsible not only for the foliation of strata, but also for mechanical activation of rocks, most fully realized in the areas of thrusts, where crushing, mylonitization and foliation occur very active. This is confirmed by experimental studies of N.V. Chersky and others, who came to the conclusion that: “Mechanical fixed and variable loads accelerate the transformation processes of fossil organic matter ten times, even at low temperatures (20-40 °C), and go with high intensity»(Chersky et al., 1982, p. 21). In this regard, earlier data of N.B. Vassoevich, Yu.I. Korchagin, N.V. Lopatin and V.V. Chernyshev are indicative (Vassoevich et al., 1969).

Even in 1969 they gave an example of experimentation with mudstone that did not dive below a depth of 700 m. Under the pressure of 150 kg/cm^2 bitumen was extracted from it 2 times more than under the pressure of 5 kg/cm^2. At that, the composition of the chloroform bitumen significantly changed. If before applying pressure of 150 kg/cm^2 asphaltenes predominated over hydrocarbons in chloroform bitumen, after – hydrocarbon content increased by 3.5 times and their quantity became 5 times greater than asphaltenes. This is consistent with the concept of oil and gas generation in argillaceous rocks, however, as many of ore minerals, resulting from directional tectonic pressure.

III. Hydrogeological factor. At the level of river Yuryuzan in the bottom part of the Yangantau Mountain, a single water-bearing zone is located with an active circulation in the upper parts. This zone is divided into separate aquifer intervals. There are numerous outputs of groundwater at the river Yuryuzan at the bottom of Yangantau Mountain, between the village Chulpan and a sharp bend of the river upstream of its flow. They represent the major reservoir bodies, or individual sources. It is believed that water outputs do not rise above 1-2 m from the low-water level of the river and flooded during spring floods. Water is mineralized, hydro-sulphate-calcium and magnesium-calcium, sometimes weakly radioactive, with a value of radiation up to 17 units of Mach.

Mineralization of water increases with the depth. Intake areas of the described aquifer are outputs of Yangantauskian formation to the north of the mountain. Here, at high elevations completely waterless areas are located with numerous and deep ravines. The water absorbed by these highly fractured array, moving eastwards and filling in Yuryuzano-Aiskian basin, are discharged in excess part on the bank of Yuryuzan River, under the mountain Yangantau. Well 3-K, laid on top of the mountain, at the level of 414.66 m, entered the water-bearing zone at a depth of 156.5 m and deepened in it by 24.5 m, at the absolute elevation of 258.16 m. Well 2-K lies at the level of 332.8 m in the eastern ravine bordering the mountain. The total depth is 127.5 m. At a depth of 73.23 meters it went into the water-bearing zone and revealed it at 53.27 m. Consequently, approximately 20 m in depth refers to the aquifer horizon. The chemical composition of the water, with the deepening in the water-bearing zone has changed in the direction of increasing salinity. At a depth of 124.5 m, this well went into slow circulation area.

Thus, in the bottom part of Yangantau Mountain there is a single water-bearing zone with an active circulation in the upper parts.

According to sources No. 3, 8 and wells 2-K and 3-K V.V. Shtilmark composed hydrogeological scheme of the aquifer, where hydroisohypses are displayed with the condensed nature of the distribution in the upper part. It follows that the movement of an underground stream is carried out towards the river Yuryuzan. Unloading here is significant, which is consistent with the features of contour thickening (Fig. 7).

Fresh sources are usually located approximately at the level of the spring waters of Yuryuzan River. As a consequence, during the spring flood water-bearing zone may be partially fed by its waters. During this period, the dip of hydroisohypses should be the opposite, i.e., inside the mountain. This stream can be diluted with groundwater, lowering mineralization and simultaneously cooling them. Sulfur sources are frequently encountered, which are usually placed at low-water level of standing water in the river. Among these sources sulphide water is marked, concentrated near the mouth of the eastern mountain ravine and upstream the river Yuryuzan. They have a low flow rate (less than 0.1 l/s), fluctuating temperature and hydrogen sulfide content of not more than 3-4 mg/l. G.V. Vahrushev indicates that some sources of Yangantau, except hydrogen sulphide, have also smell of oil. It is known that fresh water springs flowing from the mountain Yangantau contains radium emanation 0.37, and the water from the river Yuryuzan – 0.08 units of Mach.

Besides warm radioactive source Kurgazak, near Yangantau and 20 km downstream the river Yuryuzan, at the foot of the mountain Kutkan and at the lower end of the village Kuselyarovo there is a number of hydrogen sulphide springs with water temperature of 16°-19° Celsius. Some of these sources have very high capacity – about 20-30 l/s each. According to observations of G.V. Vakhrushev, under the mountain Yangantau sulfur springs are warmed up to 19°. Fresh water flowing 0.5-1 m hypsometrically above, are

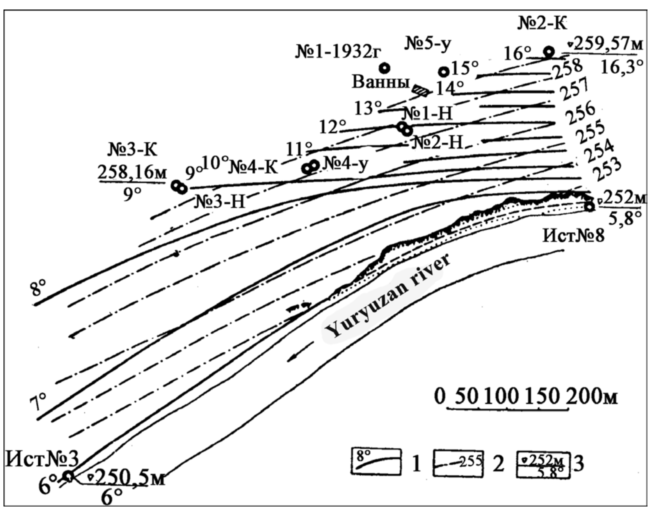

Fig. 7. Scheme of hydroisohypses and geoisotherms in the aquifer zone of Yangantau Mountain (by Shtilmark, 1960). 1 – geoisotherms; 2 – hydroisohypses; 3 – absolute elevation of water level and water temperature.

warmed up only to 6°-7°. Similar sulfur springs are found on the left bank of Yuryuzan River, under the mountain Kutkantau. Judging by the white fly of amorphous sulfur on the rocks, there are the outputs of sulfur sources at the bottom of river Yuryuzan.

IV. Structurally-tectonic factor is sufficiently covered in the papers of R.I. Nigmatulin, T.T. Kazantseva, M.A. Kamaletdinov, Yu.V. Kazantsev, A.S. Bobokhov (1998); Kazantseva (2007); S.G. Fattakhutdinov, A.I. Konyukhov, I.A. Khairetdinov (1976), and others. They argued that the structural features and modern geodynamics of Yangantau are determined by its location in the complex node of tectonic interaction of contrasting compositions and structures. On the one hand it is Karatau allochthon, on the other – a set of relatively small-amplitude scales in the southern end of Yuryuzano-Sylvinsky depression of the Ural foredeep. The most characteristic features of these structures were brought. They are as follows. Karatau structure in its present form has the shape of tapered prism with a thickness of 1 to 5 km. It is formed by the surface of the Karatau thrust, Ashinsky and Yuryuzansky strike-slip.

Yuryuzansky strike-slip is reflected by a broad zone of depressions in modern relief that is associated with an extremely high degree of fragmentation and folding of strata, especially at the nodes of its intersection with the front plate parts of Yuryuzano-Sylvinsky depression. One of these areas – Akhunovsky dislocations – is shown in Fig. 8.

The northwest corner of Karatau 'prism' falls on the part of Mesyagutovsky plate, whete Yangantau Mountain is located. Yangantausky dislocations produced Karatau allochthone in the opposite direction to general Urals movements. In the geological past the territory had typical occurrences of high heat values, as coincident with modern thermal anomalies and widespread much wider. Ancient thermal anomalies are consistent with the elements of modern structures (Fig. 9).

All known thermal sources in this area are confined to Yuryuzansky strike-slip influence zone.

Modern geodynamic activity of the mountain is displayed on seismotectonic scheme of Yu. V. Kazantsev, where there is a local section of the annular arrangement of the seismic values from 3 to 8 units. At the same time the highest rates are found in the periphery, dramatically decreasing towards the center (Fig. 10). This researcher has interpreted this feature as discharge of seismic compression in the Yangantau Mountain that is consistent with the geodynamic model of the heat source of this phenomenon. Data of A.S. Bobokhov of connection of modern thermal anomalies and paleotemperatures values with faults (Fig. 9) also confirms their tectonic origin.

Fig. 8. Outcrops of folding zone at the eastern edge of the village Akhunovo.

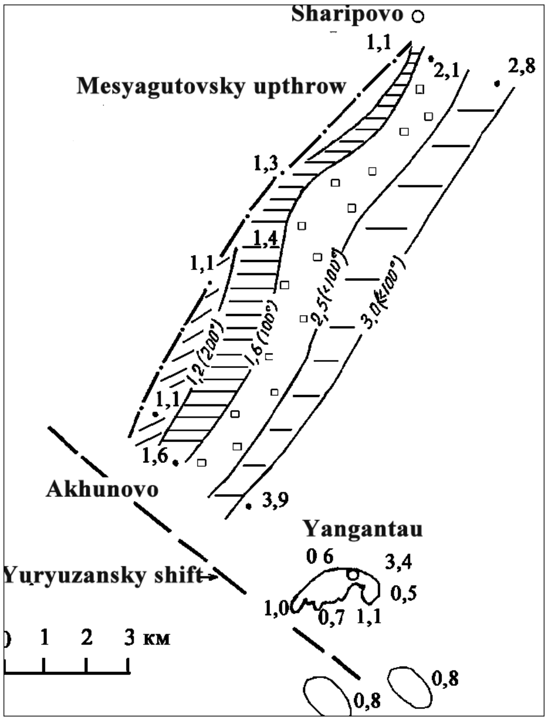

Fig. 9. Paleotemperature regime of the region (by A.S. Bobokhov). Legend: point – sampling; figures from 0,5 to 3,4 – thermal degasifying intensity values; figures in brackets – paleotemperatures in degrees, decreasing from the front of Mesyagutovsky thrust to its rear; thin lines – boundaries of thermal zones.

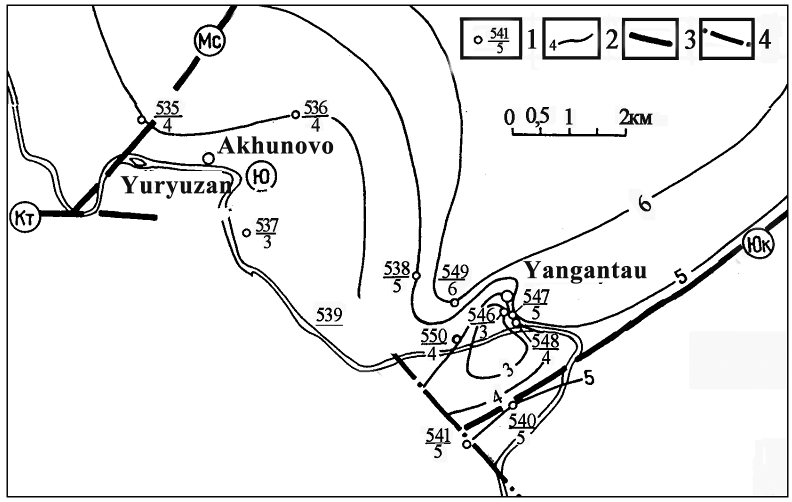

Fig. 10. The isolines nature of seismic noise in the area of Yangantau Mountain. According to Yu.V. Kazantsev. 1 – points of setting seismic devices: number in the numerator, values of seismic noise in the denominator in nanometers, 2 – isolines of seismic noise; 3 – thrusts (Kt – Karatau, Ms – Mesyagutovsky, Yuk – Yukalikulevsky); 4 – strike-slips (Yuryuzansky).

Thus, we identified geological factors involved in “Yangantau phenomenon”: geomorphological, material-stratigraphic, hydrogeological and structural-tectonic. We determined the value of each of them. Auspiciousness of geomorphological factors is in presence of steep eastern slope of the mountain, high fracturing of composing rocks creates an opportunity for good purging by slope winds. Development of bituminous stratum of shale structure in the area – Yangantauskian formation of Permian Artinskian tier – can be considered as oil and gas generating. The presence at the base of the Yangantau Mountain of olistostromes, which according to modern concepts, are indicators of high stress of tangential compression, creating a very active geodynamic regime. Presence of aquifer discharged into the river Yuryuzan provides a fairly powerful stream of water, which is the source of steam. A variety of components that are present in water and rocks (clays, silicates, sulfates, sulfides, radioactive substances, impurities of manganese, vanadium, etc.) supplies water with medicinal properties, and also can serve as catalysts for gas emission. Finding a natural energy source is due to tectonic stresses of horizontal compression of the periodic discharge. We do not accidentally consider shale of Yangantauskian formation as possibly oil and gas generating. There is much talk and write about shale gas, which is produced by using special technology.

It includes: horizontal drilling, hydraulic fracturing using a powerful water flow (under significant pressure and temperature), possibly hydrocracking (with different kinds of catalysts), and the seismic modeling. It is obvious that all of the components of gas production from shale require large energy inputs. This explains the cost of shale gas (technological), which is considerably higher than for the natural gas. It seems to us that in accordance with the above views on geological factors, recorded in the area of this mountain, such conditions can be provided by natural features. In this case, we can assume that the phenomenon of Yangantau Mountain is based on a natural mechanism comparable to technology of producing shale gas.

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Study of Indicator Properties of Chemical Elements, Corresponding to Geochemical Environment of Natural Mineral Water Formation

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Abstract. Studies show that unique hydro-chemical indicators that meet the spatial patterns of geochemical environments characterize each land area. The authors proposed a method to study the regularities in the chemical composition of natural mineral waters and identify the indicator elements that correspond geochemical peculiarities of their formation. The initial material of the study included the results of the water chemical analysis conducted on the mass spectrometer with inductively coupled plasma (ISP-MS) Elan 9000 DRC II (Perkin-Elmer, USA). Mineral waters were characterized by a set of qualitative and quantitative parameters: geochemistry of water migrants, element-by-element comparative analysis of the concentrations, areas of origin and the water extraction conditions. These parameters are linked in the summary table, from which a number of regularities were established. The following indicator elements are identified: Sr, Ba, Mn, Li, Br, B, I, Ge, Rb, corresponding to geochemical parameters of water formation environment.

Keywords: mineral waters, geochemistry of environments, chemical composition, indicators, formation of water.
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Introduction

The chemical composition of groundwater, including mineral water, is a consequence of the interaction of geological rocks with underground hydrosphere, where water as a universal solvent is the main agent of water removal from mineral migrants (Perelman, 1982; Shvartsev, 1998). Specific hydrochemical indicators, acting as regional indicators of groundwater origin, characterize each land area. As our research shows, each of the natural mineral water is characterized by its 'fingerprint' of content and set of chemical elements, which act as 'geographic markers' for origin of water (Amelin et al., 2012). In addition to the practical significance, which is established in the falsification and geographical origin of natural mineral waters, study of chemical composition of water focuses on other tasks, one of which is reduced to the establishment of relationships between the chemical composition of natural mineral waters and geochemistry of their formation.

The purpose of this work is to study regularities in the chemical composition of natural mineral waters, and identify elements-indicators that meet the geochemical features of their formation.

Experimental part

We used a quadrupole mass spectrometer with inductively coupled plasma (ICP-MS) "Elan 9000 DRCII" (Perkin-Elmer, USA). The data were processed by a computer program "Elan ICP-MS Instrument Control ver. 3.4" (Perkin-Elmer, USA).

As standards we used certified 1g/l mono- (K, Mg, Ca, Zn, Fe, Na) (Panreac, Spain) and multi-element solutions for ICP-MS (Perkin-Elmer, USA). The dilutions were carried out in a plastic dish by ultrapure deionized water 15-18 MOhm-cm^2 (TU 2123-002-00213546-2004). For the preparation of samples and blank samples we used concentrated nitric acid "ACS" (GOST 11125-84). The calibration solutions were prepared by diluting the appropriate standards. To review the analysis and identify mineral waters we used semiquantitative "TotalQuant" data collection mode, the advantage of which is in determination of the total isotope elemental composition of the sample in a relatively short measuring time (2-3 min).

Object of research

We investigated the following natural mineral waters: Narzan, Yessentuki number 17, Essentuki number 4, Rychal-Su, Perrier, Vitasnella, Livissima, Serebrany Sokol, Suzdalsky napitki, Lipetsky Byuvet. The initial materials of study were the results of a multi-element analysis and content of the major macro-ingredients (Table 1.2). The analysis was conducted on the data basis of FSBI "Federal Centre for Animal Health" in the framework of the identification of mineral waters, purchased in an open market, by geographical origin. The database was created based on waters of the relevant sources or wells.

Results and discussion

On the basis of a comprehensive approach the authors proposed a method to identify the indicator properties of some chemical elements that emphasize the geochemical characteristics of media formation of natural mineral waters. Mineral waters have been characterized by the following set of parameters: geochemistry of water migrants, element-wise comparative analysis of the concentration, areas of origin and water extraction conditions. The above set of parameters is configured in the summary table.

Geochemical properties of water migrants

The migration properties of most chemical elements are studied fully and are the criteria for geochemical classification,

Detected element (PO*, mcg/L)	Narzan (glass plastic)	Essentuki No. 17 (glass plastic	Essentuki No. 4	Rychal-Su (glass plastic	Serebrany sokol (plastic	Suzdalskiye napitki (plastic	Lipetsky Byuvet (plastic	Vitasnella (plastic)	Livissima (plastic)	Perrier (glass)
Li (0,1)	140 150	1010 990	1100	1600 1500	9,5	3,8	160	1,5	2,0	7,6
Be (0,1)	0,042 0,031	0,021 **-	-	0,37 0,27	-	-	0,011	-	-	-
B (1)	400 420	5900 5800	6600	4400 4500	7,7	3,6	3300	10	36	51
Al (0,1)	1,2 1,7	2,9 3,1	5,2	4,9 3,3	5,6	4,8	3,8	3,0	4,6	7,4
P (10)	21 15	29 30	25	38 64	346	550	0,23	0,14	0,18	10
Sc (1)	4,5 4,7	5,3 5,8	3,9	13 14	5,9	6,4	1,9	2,2	1,4	3,5
Mn (0,1)	120 110	30 20	8,4	15 17	0,26	0,40	59	0,35	0,62	0,18
Co (0,05)	0,22 0,12	0,11 0,092	0,12	0,23 0,20	0,032	0,032	0,18	0,086	0,038	0,15
Ni (0,1)	4,1 3,8	2,5 2,9	3,1	1,8 2,1	3,0	1,3	2,1	1,6	0,77	1,0
Cu (0,05)	3,1 3,5	2,1 1,8	3,7	2,2 1,9	0,71	0,81	9,5	0,52	0,32	3,6
Ge (0,1)	0,18 0,20	6,7 6,1	13	53 56	0,042	0,058	0,051	0,018	0,0006	0,015
Br (10)	1250 1280	13500 14000	13700	3800 3850	35	38	7100	0,012	18	190
Rb (0,05)	9,0 11	16 15	18	20 26	1,8	1,1	2,5	0,02	0,21	1,2
Sr (0,05)	12000 11000	10600 9100	4400	2300 2400	134	85	1700	2000	51	960
Y (0,05)	0,048 0,052	0,081 0,087	0,045	0,097 0,091	0,0004	0,0004	0,0014	0,011	0,023	0,0023
Zr (0,05)	0,20 0,16	2,3 1,7	1,3	1,5 1,3	0,0055	0,0009	0,0007	0,076	0,0095	0,042
Mo (0,1)	4,8 3,8	0,68 0,59	0,084	0,030 0,029	1,5	0,38	0,60	0,95	0,94	2,7
Rh (0,05)	0,68 0,63	0,56 0,32	0,14	0,11 0,10	0,0071	0,0003	0,059	0,16	-	0,027
Ag (0,05)	14 60	0,94 0,13	0,29	0,0007 -	0,0044	120	0,0007	0,0023	0,0031	0,0008
Cd (0,05)	0,0035 0,0043	0,0011 0,0009	0,010	0,0009	0,0071	0,011	0,0008	0,0080	0,0081	0,0009
Sb (0,05)	- 0,36	0,012 0,15	0,012	0,011 0,22	0,33	0,40	0,42	0,61	0,63	0,075
Te (0,05)	0,012 0,013	0,069 0,060	0,069	0,043 -	0,013	-	0,059	0,0050	0,024	-
I (5)	390 480	15000 13000	9900 8900	900 880	37	15	590	110	480	20
Cs (0,05)	2,0 2,4	1,1 1,0	0,97 0,85	0,10 0,081	0,21	0,22	0,087	0,38	0,26	0,0065
Ba (0,05)	11 12	1400 1300	2060	2500 2600	0,17	0,25	6,5	44	5,7	38
La (0,05)	0,0015 0,0011	0,016 0,012	0,024	0,017 0,015	0,0035	0,0031	0,0013	0,0022	0,021	0,0047
Ce (0,05)	0,013 0,0004	0,0052 -	0,0055	0,018 -	0,0065	0,0021	0,0005	0,0039	0,0046	0,024
Eu (0,05)	0,0027 0,0035	0,21 0,18	0,31	0,44 0,45	0,0008	0,0007	0,0003	0,0049	0,0005	0,0099
W (0,05)	0,0169 -	0,36 0,35	0,14	0,14 0,17	0,018	0,047	0,0049	0,02	0,11	0,075
Tl (0,05)	0,84 0,73	0,0020 0,0010	0,0021	- -	0,0005	-	-	-	-	-
Pb (0,05)	0,95 0,93	0,35 0,40	0,045	0,11 0,099	0,18	0,85	0,68	0,049	0,010	0,28
Bi (0,05)	0,46 0,32	0,20 0,15	0,047	0,010 0,0089	0,39	0,077	0,0035	0,0092	0,0051	0,0082
Th (0,05)	0,0022 0,0025	0,021 0,016	0,0076	0,014 0,016	0,0019	0,0019	0,018	0,0007	0,0009	0,0010
U (0,05)	2,4 2,7	0,45 0,43	0,0048	0,020 0,014	1,1	0,32	0,11	6,5	5,0	3,9

*Table 1. The results of the review analysis of natural mineral water (mcg/L, average value of three different batches of water). Note – *PO – the detection limit, **– not detected.*

Mineral water	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}
Suzdalskiye napitki	5-7	8-15	130-160	30-45
Serebrany sokol	<10	<25	200-300	35-70
Lipetsky Byuvet	500-850	1200-1700	200-400	120
Levissima	0,3	13,7	56,8	19,5
Perrier	25	48	445	158
Vitasnella	1,3	80	296	82
Narzan	100-150	300-500	1000-1500	300-400
Rychal-Su	450-550	<25	2500-3000	<25
Essentuki No. 17	1400-2100	<25	5200-6500	<100
Essentuki No. 4	1500-1900	<25	3600-4500	<150

Table 2. The content of basic macro-ingredients of mineral water (mg/L, average value of three different batches of water).

Element	*c*, mcg/L	c_{max}/c_{min}	Element	*c*, mcg/L	c_{max}/c_{min}
Li	1,5-1600	1066	B	3,6-6600	1833
Br	0,012-14000	116666	Sr	51-12000	235
I	15-15000	1000	Ba	0,17-2600	15294
Al	1,2-7,4	6	Ni	0,77-4,1	5,3
Mn	0,18-120	667	Ge	0,0006-56	93333,3
Cu	0,32-3,7	11,56	Mo	0,029-4,8	165,5
Rb	0,02-26	1300	U	0,11-6,5	59
Cs	0,0065-2,4	369			

Table 3. The concentration ranges and value c_{max}/c_{min} for elements in studied mineral waters.

which makes it possible to trace the path of their introduction into the mineral water solutions (Kraynov et al., 2004). At the same time, water migration of such elements as W, Y, Rh, Te, La, Eu, Ce is poorly studied, especially as the concentration of these elements is less than 1mcg /L, along with elements such as Co, Pb, Tl , Th, Zr.

Element-wise comparative analysis of concentrations

In the analysis we used the most informative values: 1) the range of concentrations; 2) ratio of the maximum to the minimum concentrations (c_{max}/c_{min}, Table 3).

The value of cmax/cmin for elements Sr, Ba, Mn, Li, Br, B, I, Ge, Mo, Rb, Cs is measured in hundreds and thousands of times. Concentrations of Mo, Cu, Cs are less 5 mcg/L, which is negligible as compared with other elements. Lets express the value of element concentration in percentage and arrange mineral water in order to increase their concentration (Table 4).

Areas of mineral waters origin

Extraction of water under investigation is carried out both on platform and mountain areas:

1) Water from the platform area of the East European Plain (Serebrany sokol, Suzdalskiye napitki, Lipetsky Byuvet);

2) Water from mountain area of the Alpine region (Levissima, Perrier, Vitasnella) and the Caucasus (Narzan, Rychal-Su, Essentuki number 17, Essentuki number 4).

Water extraction conditions

Information about the method of mineral water extraction and temperature conditions is presented in Table 5.

1	Vitasnella 0,077	Levissima 0,42	Serebrany sokol 0,22	Perrier 0,15	Vitasnella 0,094	Vitasnella 0,000087	Suzdalskiye napitki 0,054	Suzdalskiye napitki 0,1	Levissima 0,0011
2	Levissima 0,81	Suzdalskiye napitki 0,71	Suzdalskiye napitki 0,01	Serebrany sokol 0,22	Levissima 0,125	Levissima 0,13	Serebrany sokol 0,12	Perrier 0,13	Perrier 0,028
3	Suzdalskiye napitki 4,23	Serebrany sokol 1,12	Levissima 0,28	Vitasnella 0,29	Suzdalskiye napitki 0,24	Serebrany sokol 0,25	Vitasnella 0,15	Serebrany sokol 0,12	Vitasnella 0,34
4	Perrier 4,61	Perrier 8	Lipetsky Byuvet 0,26	Suzdalskiye napitki 0,33	Perrier 0,47	Suzdalskiye napitki 0,28	Levissima 0,54	Vitasnella 0,73	Serebrany sokol 0,79
5	Serebrany sokol 6,92	Lipetsky Byuvet 14,17	Narzan 0,44	Levissima 0,51	Serebrany sokol 0,59	Perrier 1,38	Perrier 0,77	Narzan 2,6	Lipetsky Byuvet 0,096
6	Lipetsky Byuvet 9,61	Vitasnella 16,67	Perrier 1,52	Essentuki No. 4 7	Narzan 8,75	Narzan 9,12	Narzan 6,06	Levissima 3,2	Suzdalskiye napitki 0,11
7	Narzan 42,31	Rychal-Su 19,17	Vitasnella 1,76	Rychal-Su 12,5	Lipetsky Byuvet 10	Rychal-Su 27,74	Lipetsky Byuvet 50	Lipetsky Byuvet 3,93	Narzan 0,34
8	Essentuki No. 17 61,54	Essentuki No. 4 36,67	Essentuki No. 17 56	Essentuki No. 17 25	Essentuki No. 17 63,12	Lipetsky Byuvet 51,82	Rychal-Su 66,66	Rychal-Su 6	Essentuki No. 17 12,64
9	Essentuki No. 4 69,23	Essentuki No. 17 88,33	Essentuki No. 4 82,4	Lipetsky Byuvet 49,17	Essentuki No. 4 68,75	Essentuki No. 17 98,54	Essentuki No. 17 89,39	Essentuki No. 4 66	Essentuki No. 4 24,53
10	Rychal-Su 100	Narzan 100	Rychal-Su 100	Narzan 100	Rychal-Su 100	Essentuki No. 4 100	Essentuki No. 4 100	Essentuki No. 17 100	Rychal-Su 100

Table 4. The distribution of mineral water by increase of concentration % in mineral water for Rb, Sr, Ba, Mn, N, Br, B, I, Ge.

The layout of summary table

To identify regularities, the set of parameters is configured in the table 6.

Qualitative parameters:

1) Horizontal line – number of microelements differentiated by properties in aqueous solutions (anions and cations) and by mobility;

2) Vertical line – number of mineral water, grouped on areas of origin – platform (P) or Mountain (G);

3) Method of production – source (Is) or well (Sk, depth);

4) Temperature mode – non-thermal (0), weakly thermal (t), thermal (T).

Quantitative parameters:

5) Values of concentrations of selected items in %, positions in the row;

6) Ranges of element concentrations (mcg/L) and cmax/cmin;

7) Content of macro-ingredients Cl^-, $SO4^{2-}$, $HCO3^-$, Ca^{2+} (mg/L)

Mineral water	**Mineral water extraction**	**Temperature conditions**
Suzdalskiye napitki	source	non-thermal
Serebrany sokol	well, depth 60 m	non-thermal
Lipetsky Byuvet	well, depth 106 m	non-thermal
Levissima	source	non-thermal
Perrier,	source	non-thermal
Vitasnella	source	weakly thermal
Narzan	source	weakly thermal
Rychal-Su	source	weakly thermal
Essentuki No. 17	well, depth 685,8 m	thermal
Essentuki No. 4	well, depth 865 m	thermal

Table 5. The method of extraction and temperature mode of mineral water.

We set the following statements as the result of handling the sum of parameters in the table within the causal chain:

1. High concentrations of bromine, boron and iodine are characteristic of well waters of the Caucasus region, which indicates the presence of boron and iodine-bromine waters, confined to a negative geological structures – troughs of foothill areas. These structures accumulate brine (sodium chloride water) – the most favorable conditions for the accumulation of anions. High concentrations of bromine and boron in Lipetsky Byuvet are due to the inflow of deep brines from the area of stagnant water exchange in the overlying artesian basins.

2. Accumulation of germanium goes in sulfosalts formed under hydrothermal conditions in the surface, shallow, less medium depths that explains waters position relative to each other. First place is given to source of

Mineral water, qualitative parameters			macro-ingredients				microelements								
							anions				cations				
							Br	**I**	**B**	**Ge**	**Rb**	**Li**	**Ba**	**Sr**	**Mn**
							Very Mobile		Mobile	Poorly-Mobile				Mobile	
			Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	**0,012-14000 116666**	**15-15000 1500**	**3,6-6600 1833**	**0,0006-56 93333,3**	**0,02-26 1300**	**1,5-1600 1066**	**0,17-2600 15294**	**51-12000 235**	**0,18-120 667**
Suzdalskiye napitki			5-7	8-15	130-160	30-45	0,28	0,1	0,054	0,109	4,23	0,24	0,01	0,71	0,33
P	Is	0					4	1	1	6	3	3	2	2	4
Serebrany sokol			<10	<25	200-300	35-70	0,25	0,24	0,12	0,079	6,92	0,59	0,0068	1,12	0,22
P	Sk 60	0					3	3	2	4	5	5	1	3	4
Lipetsky Byuvet			500-850	1200-1700	200-400	120	51,82	3,93	50	0,096	9,61	10	0,26	14,17	49,17
P	Sk 106	0					8	7	7	5	6	7	4	5	9
Livissima			0,3	13,7	56,8	19,5	0,13	3,2	0,54	0,00113	0,81	0,125	0,23	0,42	0,51
P	Is	0					2	6	4	1	2	2	3	1	5
Vitasnella			1,3	80	296	82	0,000087	0,73	0,15	0,034	0,077	0,094	1,76	16,67	0,29
G	Is	T					1	4	3	3	1	1	7	6	3
Perrier			25	48	445	158	1,38	0,13	0,77	0,028	4,61	0,47	1,52	8	0,15
G	Is	t					5	2	5	2	4	4	6	4	1
Narzan			100-150	300-500	1000-1500	300-400	9,12	2,6	6,06	0,34	42,31	8,75	0,44	100	100
G	Is	t					6	5	6	7	7	6	5	10	10
Rychal-Su			450-550	<25	2500-3000	<25	27,74	6	66,66	100	100	100	100	19,17	12,5
G	Is	t					7	8	8	10	10	10	10	7	7
Essentuki No. 17			1400-2100	<25	5200-6500	<100	98,54	100	89,39	12,64	61,54	63,12	56	88,33	25
G	Sk 685	T					9	10	9	8	8	8	8	9	8
Essentuki No. 4			1500-1900	<25	3600-4500	<150	100	66	100	24,53	69,23	68,75	82,4	36,67	7
G	Sk 865	T					10	9	10	9	9	9	9	8	6

Table 6. Summary of quantitative and qualitative parameters.

Rychal-Su and the thermal waters of Caucasus, followed by water from the platform region and then alpine water. The last in the chain is non-thermal open source Livissima with a negligible concentration of germanium 0.00113%.

3. Lithium and Rubidium are satellites of active geodynamic processes. Rubidium is found in acid igneous rocks. It personifies the type of igneous rocks – granites and pegmatites, serving as lithological basis of waters extraction point. Comparison of lithium and rubidium concentrations in the waters of the alpine regions and the Caucasus underscores the differences of formation conditions, possibly related to the speed of water exchange. Much of the lithium concentration in the Lipetsky Byuvet confirms fluid connection with the waters of stagnant regime, carried on deep faults.

4. The concentrations of barium and its precipitant SO_4^{2-} are correlated. When contacting the deep non-sulfate waters of chlorite hydrocarbonate composition with infiltration waters, a sulfate barrier arises and barite is precipitated. With increasing depth, miscibility decreases; hence the concentration of barium increases with the depth of water exctraction. Thus, barium can serve as the indicator of the miscibility degree of non-sulfate waters with infiltration waters. Narzan shows a low concentration of barium. Probably, it is connected with enrichment of glacial melt waters. Water Rychal-Su, on the other hand, shows the maximum concentration not only in barium, but also in germanium, rubidium and lithium, suggesting that non-sulfate water does not meet on its way geochemical barriers for thesr elements, directly discharging in the source.

5. By geochemical properties strontium is analogue of barium and calcium. In the first case, strontium content is controlled by sulphat, so deep chloride waters are rich in it (Essentuki number 17, Essentuki number 4, Lipetsky Byuvet). Waters of the Alpine region are arranged in series in the temperature regime for barium and strontium. In the second case the strontium and calcium contents are correlated as shown by the example of Narzan. Apparently, an active leaching by glacial melt waters of igneous (granodiorite and diorite) and sedimentary rocks based on calcite (limestone of the Jurassic and Cretaceous) dissolves calcium and contained in them celestite ($SrSO_4$).

6. Low concentrations of manganese are typical for waters Suzdalskye Napitki and Serebrany Sokol, which is a consequence of the high content of dissolved oxygen; a similar situation with waters of the Alpine region. A different situation is with the waters of the Caucasus region: Essentuki number 4, Essentuki number 17 and Rychal-Su are characterized by relatively low concentrations of manganese – the presence of hydrogen sulfide in the hydrogeological systems. Mineral water Narzan shows the maximum concentration of manganese, regardless of the high degree of dilution by melt water, which is associated with the manganese mineralization area. Process of manganese migration is possible from igneous rocks in limestone that make up the lithological basis of extraction area, then its accumulation in carbonate rocks, followed by the removal by aqueous solutions from rocks by analogy with strontium. The high concentration of manganese in the Lipetsky Byuvet underlines the transport function of the ancient faults inherent in the element migration from the deep geological structures into the upper strata.

Conclusions

The method proposed by the authors on the basis of a comprehensive approach integrates qualitative and quantitative parameters in a single table. This form of the material arrangement allows us to make a causal chain and establish a number of important regularities. The regularities of macro-ingredients are identified between content and trace elements in conjunction with the factors of the formation of natural mineral waters. The study confirmed the indicator properties of elements Br, I, In, Ge, Rb, Li, Ba, Sr, Mn, corresponding geochemistry environments of formation waters.

Conclusions based on the summary table, made by the authors serve as preliminary findings, as the range of investigated mineral waters does not exceed ten items. For more accurate findings more statistical data is required, therefore the established regularities for the indicator properties of each element are in the order of discussion.

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Application of New Biotechnologies in the Remediation of Black Soil with Mixed Pollution

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Abstract. During remediation of black soil with mixed pollution we assessed the environmental and economic efficiency of new biotechnologies for the PJSC Tatneft. They included biological preparation «Lenoyl SKhP» based on strains of hydrocarbon-oxidizing microorganisms (development of the Institute of Biology of the Ufa Scientific Center of the Russian Academy of Sciences); complex biological preparation – destructor of oil pollutions «DNZ»; joint introduction of nanosorbents and effective indigenous hydroc arbon-oxidizing microorganisms (development of the Tatar Research Institute of Agrochemistry and Soil Science); and «Gumaks» (development of the LLC «Center Spas») and potassium humate. Experiments were carried out over two field seasons on leached and typical agricultural black soils contaminated due to the spill of Devonian watery and sour oil. Based on the data about dynamics of oil content in soils, results of agrochemical and microbiological monitoring over two seasons we evaluated the efficiency of new biotechnologies and developed recommendations for production.

Keywords: admissible residual oil content; methods of bioremediation of contaminated land; indigenous microorganisms-destructors; humate

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Introduction

Currently there are many new biotechnologies suggested in the literature and Internet resources to remedy the fertility of oil-contaminated soils. But in practice, when depressurising oil pipelines on the fields at the late stage of development with watered oil, oilfield fluid that enters the soil leads to a mixed type of pollution: salt and oil. Therefore, remediation activities should be aimed at the restoration of soil parameters, ensuring their fertility, including their desalinization and bringing the oil etconcentration in the soil to a value of admissible residual TPH in soil (Ibatullin et al., 2006; Shaydullina, 2006; Malykhina et al, 2012;. RD 153-39.0-716-11 ..., 2010).

Earlier we have conducted joint testing of biotechnologies on leached black soils with the release of native strains of hydrocarbon-oxidizing microorganisms in conjunction with nanobentonite (FBGNU Tatar NIIAHP of the Russian Agricultural Academy) and using humic preparation – "Gumaks" (developed by LLC "Center Spas" and LLC "NPP") on the artificially contaminated beds with different types and doses of entering oilfield environment. The traditional method was used as a controlling mean, including manure and planting of soil improver. It has been shown that recommended biotechnologies are economically safe for the adjacent natural environments, as well as less expensive compared to conventional soil remediation option (Shaydullina et al., 2015).

The aim of this work was to identify on promising conditions for the PJSC Tatneft of environmentally friendly and cost-effective methods of black soil biological remediation with a mixed type of contamination on areas with spilled Devonian watered and sour oil. Based on the literature reviewed we selected the following: biotechnology on the basis of biological preparations of hydrocarbon-oxidizing microorganism strains "Lenoyl SKhP", "DNZ"; biotechnology with the release of native strains of hydrocarbon-oxidizing microorganisms in combination with nanobentonite (FBGNU Tatar NIIAHP of the Russian Agricultural Academy) (Yapparov et al, 2011.); biotechnology with humic substances "Gumaks" (proposed by LLC "Center Spas") (TU 2458-001-09265941-2,012.2012) and potassium humate of brand BP 20 (TU 2189-004-54775950-2000). The traditional method of remediation of oil-contaminated soil lies in the manure introduction in the amount of 60 t/ha and phosphogypsum as a soil improver in the amount of 10 t/ha and periodically loosening of the soil.

Materials and methods

The works were carried out for two seasons on the experimental plots after the spill of watered sour oil (the type of soil – leached black soil) and watered Devonian oil (type of soil – typical black oil).

Plots located near the place of laying the field studies with no visible signs of land violations were selected as background.

Plots with spill of watered sour and watered Devonian oil were divided into 6 plots where the following remediation options were investigated: "Native strains + bentonite", "DNZ", "Lenoyl SKhP", "Gumaks", "Potassium humate" in comparison with the traditional method. In addition, control plot with exclusively farming practices was laid in each of the test sites.

Working aqueous suspensions of biological preparations were introduced into the soil by sprinkling.

Working suspensions "Lenoyl" and "DNZ" before introduction were intensified in the nutrient solution for one day. When using the method of FBGNU Tatar NIIAHP on the surface of oil-polluted soil we added agromineral bentonite as nanosorbent and ammonium nitrate at the rate of 0.15 t/ha; further during the growing season we performed twofold treatment of oil-contaminated beds by biologic liquid hydrocarbon-oxidizing microorganisms (titer of inserted community 1.4-1011 CFU/ml), diluted with tap water (1:1) in combination with conventional agronomic activities. In the first season, plowing was carried out 3 times. In the second season, only farming practices were held and sowing of wheat on the field with the Devonian oil spill. In the area of sour oil spill observations were made for the field of the dominant species of vegetation.

When testing the effectiveness of remediation biotechnologies in oil-contaminated soil, an integrated approach was used. Environmental biotechnology efficiency was evaluated by the results of the survey for two field seasons by agrochemical, microbiological characteristics of the averaged samples of tested soil, their phytoproductive and reduction dynamics of petroleum products in the soil; cost-effectiveness was evaluated by calculating the costs of applied methods.

Experimental studies to assess the effectiveness of the considered technologies conducted by the accredited laboratories TatNIPIneft and the Kazan Federal University, as well as FBGNU Tatar NIIAHP.

Field survey, sampling and sample preparation to the analysis were carried out by conventional methods (GOST). Determination of the mass fraction of oil in the soil were determined by spectrometry at the PC device KN-1 (Measurement procedure ..., 1998).

Indicators of biological activity, phytoproductivity of soil, agrochemical and microbiological characteristics of soils were assessed using accepted in the practice monitoring methods (GOST, RD, PNDF et al.). All laboratory experiments were performed at least in triplicate.

The statistical data processing was carried out using Statistica 8.0 software package. The significance of differences was evaluated with the results obtained using the Student factor (P = 95%), the characteristics of a random error component were calculated by the conventional scheme (Korn, Korn, 1978).

Results and discussion

Agrochemical monitoring includes determining the particle size distribution, pH of salt extraction, cation exchange capacity, pH of aqueous extraction, solid residue of the aqueous extract, hydrolytic acidity, chlorides, sulfates, available phosphorus, organic matter, hydrolyzable nitrogen.

Analysis of the results showed that for the area of Devonian oil spill in all cases with the use of microbial technology, the total carbon content was reduced more rapidly than in case with traditional method. For a plot a sour oil spill, the greatest value of total carbon content recorded for the options "traditional" and "control".

According to the complete analysis of soil water extraction, the type of salinity in the studied areas belongs to the "chloride". According to the SNIP 2.06.03-85 "Reclamation constructions and facilities" for chloride type of salinity, the upper limit of the amount of toxic salts has to be 0.10%, sulfate ions – 0.02%, chlorine ions – 0.03%. Maximum allowable concentration of sulfate ions in the soil is 160 mg/kg of soil (SanPiN 42-128-4433-87,1987). In the area of Devonian oil spill by the end of the first season, all biotechnologies, except from the option "Lenoyl-SKhP" were better than the traditional and "control" options as a result of reducing the content of chloride ions in the soils. The traditional method and normal farming activities (option "control") to the beginning of the second season failed to reduce the content of chloride ions to the desired level of SNIP 2.06.03-85. The laboratory results are shown in Table 1.

By the end of the second season in soils contaminated with Devonian oil, a slight excess of sulfate ions was observed only for the plots treated with potassium humate (0.026%), the traditional method (0.025%) and biological preparation "Lenoyl SKhP" (0.026%). For soils contaminated with sour oil, all plots to the beginning of the second season met the requirements of SNIP 2.06.03-85 on the content of chloride ions, but on the content of sulfate ions in the topsoil, plot with the traditional option remained contaminated (0.046%).

For a plot with spill of Devonian oil in the option of 'traditional method' content of dry residue of water extraction in soil samples by the end of the second season was 0.458%, which is above the established limits. For the area of sour oil spill content of dry residue of water extraction has a slight excess for option "Lenoyl SKhP" (0.115%).

For other agrochemical indicators the research results for all options were comparable.

Thus, by agrochemical parameters according to the data obtained for the site with Devonian oil spill, remediation options: "native strains + nanosorbent", "Tumake", "DNZ" are the most preferred. For site with spill of sour oil – all the methods are preferred except the "traditional" method and "Lenoyl SKhP".

Microbiological monitoring consisted in determination of the amount of hydrocarbon and heterotrophic microorganisms, microscopic fungi, total microbial biomass, basal respiration of soil microbial community.

Technology	27.05.13	07.10.13	14.05.14	07.08.14
Native strains + bentonite	0,1960	0,0487	0,013	-
DNZ	0,2230	0,0602	0,012	
Lenoyl SKhP	0,2320	0,1560	0,023	-
Gumaks	0,2010	0,0398	0,019	-
Potassium humate	0,1860	0,0657	0,012	-
Traditional method	0,1560	0,1010	0,052	0,0186
Control	0,1560	0,1028	0,04	0,0159
Background	0,0030	0,003	0,016	-

Table 1. The content of chloride ions in the topsoil 0-15 cm, % (experimental site with Devonian oil spill).

The number of hydrocarbon-oxidizing (HOM) and heterotrophic microorganisms in contaminated soil is an important diagnostic parameter, because the soil microflora is actively involved in the natural process of hydrocarbons degradation. For a plot with Devonian oil spill for the first season HOM were most actively developed in the first selection (after the spill) in the options "native strains + nanosorbent", "Gumaks", "DNZ", "traditional method", "Lenoyl-SKhP" (0.25 million/g). However, these figures were much lower than in soils of background areas (0,025 million/g). The second soil sampling was conducted in 1.5 months. It showed for all options a sharp decrease in the relevant indicators (0.025-0.00025 million/g). For the third selection carried out in the end of the season (after 2 months), the amount of HOM increased by about an order of magnitude (0.25-0.025 million/g). In all options, except for "Lenoyl SKhP" (0.025 million/g), the amount of HOM was comparable with the value for the background regions.

The number of heterotrophs in all experimental options during the first selection, except "Lenoyl SKhP" (16.0 million/g) was comparable to background plots typical to the soil (10.8 million/g). After 1.5 months an increase was revealed in their numbers by 3.8-6.3 times. Values were similar in all experimental options. By the end of the season their number was minimal (8.8-10.3 million/g).

The investigation of the presence in the soil of micromycetes is of considerable interest. They are a group of microorganisms, universal in their significance for the formation of soil fertility. In addition to the background soil, small number for a site with Devonian oil spill was observed only in three experimental options (1.0-5.0 million/g). In the second selection all experimental options showed an increase in their number (40.0-80.0 thousand/g). In the third selection, the number of fungi decreased in 3.2-5.2 times and amounted to 10.0-20.0 thousand/ha.

The microbial biomass and respiratory activity are integral indicators of soil. During the second selection, the maximum values of microbial biomass for the area of Devonian oil spill were reported in versions "native strains +nanosorbent" and "Gumaks" (50.6-56.0 mg Cmic/r), slightly lower figures have been experienced in other variants (22.8-41.4 mg Cmic/r). At the end of the season, this figure was lower (9.8-21.4), while in the background the soil it was 34.1 mg Cmic/r.

Basal respiration during the first selection was the lowest in option "potassium humate" (2.8 mg CO_2/(100g*24 hours) and the highest – in the option "DNZ" (17.8 CO_2/(100g*24 hours). In the second selection in all experimental variants respiratory activity was 22.3-31.4 mg CO_2/(100g*24 hours) and decreased to 12.0-18.1 mg CO_2/(100g*24 hours) to the end of the season.

From the combination of all parameters studied to remedy soil fertility in option with Devonian oil, the best picture is marked for the first season in options "native strains + nanosorbent" and "Gumaks".

In the second year of studies microbiological parameters were determined by the end of the season. In two options – "native strains + bentonite" and "DNZ" – the number of HOM was not changed in comparison with the characteristic of the first year. In "Lenoyl SKhP" the number of HOM decreased by 5.2 times.

Heterotrophic microorganisms actively grew in the options "DNZ", "potassium humate" and "control". In these samples their number increased almost twice compared with the number in the first year. The best indicators were registered in variants "native strains + bentonite" (31.5 million/g) and "Lenoyl SKhP" (29.0 million/g of soil). Only in two samples – "Gumaks" and "traditional" – the number of these organisms remained at the level of the first year.

In all the options we observed an increase in the growth of microscopic fungi. The highest rates were recorded for the option "traditional" (55.0 thousand/g). Composition of micromycete species was studied. In the option "potassium humate" we found phytopathogenic soil fungi (the genus Altemaria). It should be noted that the micromycetes of genus Trichoderma were detected only in "native strains + bentonite" and "control". This is a positive fact, as members of this genus have a high antagonistic activity to phytopathogenic fungi. During the second season on the site with Devonian oil the microbiocenosis condition improved markedly. Proof of this are the indicators of microbial biomass and respiratory activity, which in all experimental variants have increased several times.

For plot with sour oil spill at the first sampling, the maximum number of HOM (2.5 million/g) was observed in the variant "native strains + nanosorbent". The second selection showed a decrease in their numbers for all experimental options, but by the end of the season it slightly increased or remained at the level of the second selection.

Number of heterotrophs in the experimental variants was also not significantly different in the selection of a particular date. However, we should highlight options "Lenoyl SKhP", "DNZ", "potassium humate", "control", in which a few big figures obtained over time.

It must be noted that after the contamination, sour oil had a depressing effect on microscopic fungi. Only at the end of the first season the number was almost the same as in the soil of background portion.

Dynamics of microbial biomass is as follows: the first and third selections have shown comparable results, only rates of the second selection were slightly higher (45.1-66.8 mg Cmic/r).

In the study of basal respiration, rates in the first and third selection were 27.1-47.5 and 18.3-42.4 mg CO_2/(100g*24 hours), respectively. The exceptions were options "traditional", "DNZ", "native strains + nanosorbent", "Gumaks" during the second selection, in which the respiratory activity decreased (15.5-29.1mg CO_2/(100g*24 hours).

In the second season, the number of hydrocarbon-oxidizing microorganisms increased in the variants "native strains + bentonite", "Gumaks" and "control". The decline of this indicator is noted in options "Lenoyl SKhP" and "traditional". In options "DNZ" and "potassium humate" their number is compared with the first-season data.

Similarly, the number of heterotrophic organisms changed in the second season. Only in the "traditional" version number of this group remained at the level of the first season, and in the "control" version fell slightly.

Number of microscopic fungi increased in most options. The maximum rate is obtained in the "control" (130.0 thousand/g). The value remained almost unchanged compared to the first season in the version "Gumaks". Thus, the inhibitory effect of sour oil on micromycete leveled. Micromycete species composition was also studied. In the two variants – the "traditional" and "control" we found phytopathogenic soil fungi (of the genera Fusaiium and Altemaria).

The microbial biomass and respiratory activity in most of the investigated variants increased. In two versions – "potassium humate" and "control" – with an increase in microbial biomass indicators of basal respiration remained at the level of the first season.

Thus, for the samples contaminated both with sour and Devonian oil, according to microbiological parameters studied for the first season in the majority of variants comparable data were obtained. For the second season in most experimental options microbial cenosis condition improved significantly. In options using alternative biotechnologies "native strains + bentonite" and "Gumaks" we revealed a higher level of hydrocarbon degradation processes.

By changing the content of petroleum products in the soil for the first season we could not highlight the advantage of any method, the monitoring required for a second season. The visual condition of the soil at the end of the season did not differ from the soil state to the background area and had no odor of oil, which is due to volatilization and degradation of light, but the most toxic for plants hydrocarbons.

In the second season, compared with the results obtained at the end of the first season, more active reduction of petroleum products in the area of Devonian oil spill (soil type – the typical black soil) was recorded for the options "native strains -1-bentonite" (by 56%), "Gumaks" (by 54%). The lowest value of the petroleum products content was identified for option "native strains + bentonite" (5700 ± 1425 mg/kg), which exceeds the norm of admissible residual TPH-in-soil for typical black soil (3100±310 mg/kg) (On approval of regional standards..., 2012).

According to the change dynamics of oil content in soils contaminated with sour oil (soil type – leached black soil), for the second season there was a noticeable decline in the oil concentration for variants "traditional method" (by 71%), "Gumaks" (by 72%), "Native strains + bentonite" (by 56%). By value, close to the norm of admissible residual TPH-in-soil for leached black soil of Tatarstan (2900 ± 290 mg/kg), oil content was achieved for versions "native strains + bentonite" (3341 ± 835 mg/kg), "Gumaks" (4071±1018 mg/kg).

Phytoproductivity is a complex indicator, revealing chronic phytotoxicity, which was proved by our previous studies at the development of standards of admissible residual TPH-in-soil (Ibatullin et al., 2006; Malyhina et al, 2012; RD 153-39.0-716-11 ..., 2010).

Determination of phytoproductivity of contaminated soil after the remediation measures for Devonian oil spill was conducted in the first season for wheat germ (Triticum L.), grown at the experimental plots after harvest taken from uncontaminated area. From each plot 15 plants were investigated. We have studied their appearance, average height and dry phytomass per plant. The results revealed the lowest result of development and growth of plants in options "control" (11.7 cm) and "traditional method" (13.6 cm), the highest in option – "indigenous strains + nanosorbent" (19 cm).

By the magnitude of phytoproductive the plot "indigenous strains+nanosorbent" (0.0471 g) was the best, the worst – "control" (0.0229 g), "Lenoyl-SKhP" (0.0224 g), "traditional" (0.0280 g). On the unspoiled area (background) indicators of average height of wheat plants reached 23.7 cm, and a biomass – 0.1325 g.

Furthermore, to determine phytoproductivity in laboratory conditions we set an experiment in vegetative pots (volume 500 cm3) with soil samples from experimental plots, the exposure time 3 weeks. As test objects we used two types of plants: monocotyledon – spring wheat (Triticum vulgare L.) of varieties Ekada-97 and duocotyledon plant – pea (Pisum sativum L.), of varieties Varne. The choice of these species was due to the high economic importance for the Republic of Tatarstan.

Data analysis by vegetative pot experiments in the laboratory for areas with spill of Devonian oil showed the worst development of plants for the test object peas – in a version "control" (0.0384 g), wheat – in the version "traditional method" (0.0091 g). The best development of plants on the peas was in the variant "DNZ" (0.0663 g), wheat – "potassium humate" (0.0130 g). The value of phyto-mass in the pots with background soil for peas was 0.0591 g, for wheat – 0.0107 g.

The results of pot experiment conducted in the laboratory for areas with spill of sour oil were comparable for all variants. On both test objects, options "Lenoyl SKhP", "traditional", "DNZ", "native strains + nanosorbent", "Gumaks", "potassium humate".

Thus, based on the above stated for the first season, we may conclude of the effectiveness of all biotechnologies. The process of reclamation using the agrotechnical measures covers the lower horizons of the contaminated soil, where non-volatile heavy hydrocarbons remained. In many ways, if you prefer full-scale field study, methods "native strains + nanosorbent", "Gumaks" have some advantage.

Parameters of plant development in the second season for the area of Devonian oil spill were evaluated on appearance, color, height, weight of fresh-cut plants, and ears of wheat (Table 2). On average phytomass of a single plant, a single ear, height, color and plant growth parameters the best reclamation was shown by technologies "native strains + bentonite" and "Gumaks", the traditional method is inferior. The lowest values, as we would expect, were obtained for option "control".

For the plot with sour oil spill, the best phytoproductive performance on the test object Tripleurospermum inodorum (L.), comparable to phytoproductivity in the background section, were obtained for the variants "native strains + bentonite", "Gumaks" (Table 3). For the test object Lotus comiculatus L. the best phytoproductive figures were recorded for the options "native strains + bentonite", "Gumaks", "potassium humate" (Table 3).

The options "native strains + nanosorbent" (4070 rub./Ha), "Gumaks" (from 4200 to 5400 rub./Ha), "potassium humate" (5900 rub./ Ha) are the most effective from an economic point of view. The rest of the discussed technologies are much more expensive than the traditional method (31000 rub./Ha). Since agricultural activities cost is about the same, in the calculation we took into account

Technology	Color (11.07.14)	Average height of 1 plant, sm (11.07.14)	Average weight of 1 plant, g (11.07.14)	Weight of 1 ear, g (11.07.14)	Weight of 1 ear, g (14.08.14)
Native strains + bentonite	green	94	17,6	2,0	4,86
DNZ	green with yellowish patch	72	5,4	1,0	2,34
Lenoyl SKhP	yellow-green	66	6,2	1,1	2,36
Gumaks	green	78	17,3	2,0	3,5
Potassium humate	green	67	8,6	1,1	2,28
Traditional method	yellow-green	62	3,6	1,0	1,82
Control	yellow-green	52	3,2	0,9	1,64
Background	green	95	27,1	2,4	4,9

Table 2. The results of the phytoproductivity study on the test object wheat (Triticum L.), (section with Devonian oil spill, 2nd season).

Technology	Color	Average height of 1 plant, sm Tripleurospermum inodorum (L.)	Average weight of 1 plant, g Tripleurospermum inodorum (L.)	Average height of 1 plant, sm Lotus comiculatus L.	Average weight of 1 plant, g Lotus comiculatus L.
Native strains + bentonite	bright-green	73	230,0	30	8,6
DNZ	yellow-green	36	70,0	21	4,4
Lenoyl SKhP	yellow	60	77	17	2,23
Gumaks	bright-green	73	180,0	33	11,3
Potassium	green	60	50,0	31	16,1
Traditional method	yellow	39	23,33	20	5,7
Control	yellow	43	30,0	16	2,3
Background	bright-green	73	180	30	8,5

Table 3. Research results of phytoproductivity (section with spill of sour oil) for test objects Tripleurospermum inodorum (L.) and Lotus comiculatus (L.) (11.07.2014).

only the costs associated with the application of fertilizers, soil improver and drugs.

Thus, within the framework of these studies, the recommended technologies to remedy the black soil contaminated by the oilfield fluid are methods "Native strains + nanosorbent" and "Gumaks".

Recommendations for the production

To remedy the black soil of mixed type of pollution in the Republic of Tatarstan we propose to use:

1) Method using "Gumaks" proposed by LLC "Center Spas", environmentally and cost-effective method, easy to use;

2) Method developed by FBGNU Tatar NIIAHP with the release of native strains of hydrocarbon-oxidizing microorganisms in combination with bentonite.

When using the traditional method, rotted manure (humus) should be used to accelerate the recovery of soils.

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