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Research of microelements content in the stratal waters

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The content of trace elements of iodine, bromine in the stratal waters of Chyzhivsk and Bilsk field has been analyzed. Deposits with high content of iodine and bromine ions are studied. The connection has been detected between the high content of iodine in underground water and their mineralization depending on the respected thermobaric conditions. It has been established that stratal waters of Chyzhivsk and Bilsk fields can be attributed to iodine-bromine. The analyzes has revealed that waters of the Chyzhivsk and Bilsk fields can be used for industrial removal of iodine and bromine. Having analyzed the data on the field, it has been determined that ground waters of the disclosed Chyzhivsk and Bilsk field complex cannot be used for amelioration purposes because of their high mineral content.

Keywords: trace element, iodine, bromine, stratal waters, oil basins, thermobaric conditions

Дослідження вмісту мікроелементів у пластових водах

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Відомо, що пластова вода є джерелом цінних мікроелементів, а саме йоду та брому. Підтверджено, що йод і бром – продукт єдиного процесу трансформації органічної речовини, що відбувається при високих температурах і тисках. Для визначення вмісту йоду застосовано йодометричне визначення з використанням гіпохлориту як окиснювача. Цей метод дозволяє визначити кількість іонів йоду з точністю до 0,02 мг в аналізованому об'ємі води без підготовки. Установлено, що пластові води приурочені до пісковиків глибиною від 3 – 14 до 30 м. Води представлено у вигляді розсолів. Визначено, що пластові води Чижівського та Більського родовищ можуть бути віднесені до йодо-бромного типу (бром, який складає щонайменше 25,0 мг/л, йод – принаймні 5,0 мг/л). Згідно з дослідженням вод Серпухівського горизонту Чижівського родовища, виявлено експоненціальну залежність між середнім умістом йоду та вмістом солей у пластових водах свердловин № 39, 50 Чижівського родовища. Вивчено пластові води Більського родовища. Серпухівські відкладення товщиною 200 м представлено щільними пісковиками та алевролітами. У пластових водах свердловин 104 і 105 виявлено бром, йод у кількостях, доцільних для промислового видобутку. Пластова вода має мінералізацію близько176 г л. Дослідження показали, що води Чижівського й Більського родовищ можуть бути використані для промислового вилучення йоду та брому, оскільки вміст йоду перевищує 10 мг/л, а вміст брому досягає 599 мг/л. З'ясовано, що ці пластові води є цінною сировиною для вилучення корисних мікроелементів, які зараз втрачаються.

Ключові слова: мікроелемент, йод, бром, пластові води, нафтові басейни, термобаричні умови

Introduction. It has been found that underground reservoir water can be a source of useful components. Later considerable concentrations of iodine were found in ground waters in nearly all world oil fields. However, in the oil fields waters the iodine content can vary widely. In many world countries industrial ground water is a major source of iodine. Over 70% of bromine production is provided by industrial waters [6, 10, 11]. The main features of iodine and bromine geochemistry were studied by V. Vernadsky. The scholar determined that endogenous rocks, ores and minerals iodine is only contained exceptionally in a dispersed state. The more distant from the sea area is, the higher it is located above its level, the lower the iodine concentration is in the soil, in the water and in the air. The studies were performed by P.M. Bilonizhka, V.I. Knesenko, O.M. Nikipelova [3 – 9] and others.

The study of the potential for iodine recovery from reservoir water has been started not long ago. However, to begin commercial iodine extraction from oil or gas fields waters, it was necessary to analyze the fields where iodine concentration is sufficient enough for industrial production.

The purpose of the research is to provide the content of trace elements in the stratal waters of Chyzhivsk and Bilsk deposits and analyze fields of the deposit with the content of ions iodine, bromine.

The main material of the research. Minerals containing iodine are individual or mixed halides. The sustained cycle of iodine is natural. Iodine is essential for both the biosphere and the noosphere. Its role in industry, medicine is growing every year. Iodine minerals are easily diluted; therefore iodine is easily bloomed out of rocks, carried to the sea, where it is partially accumulated in laminaria (kelp) algae [1].

Stratal water is a valuable source of minerals, bromine and iodine. Stratal water is underground water circulating in rock layers. In oilfield geology, stratal water is water present in the oil stratum (marginal, bottom, middle water). Iodine concentration in Chyzhivske gas condensate field stratal waters is studied. Most of the Poltava Region territory (northern and central) is located within the limits of Dnieper- Donets depression. It has a rather complicated geological structure. Within the Poltava Region territory it includes the southwest relatively smooth slope, separated series of fractures and the lowered central part (palaeorift or Don-Dnieper graben). The border between the south-western slope and the graben of the Dnieper-Donets depression is made along the line of Pyriatyn – Khorol – Bilyk, which roughly corresponds to the depth of the crystalline basement 1500 m. Different depths of hydrocarbons deposits, and hence different pressure, temperature and other geological conditions favored the formation of gas condensate, gas, petroleum, oil-and-gas, gas-and oil, oil-and-gas condensate fields [1].

Chyzhivske oil field is located on the territory of Gadyach and Lokhvitsa districts of Poltava Region, 15 – 20 km to the east of Gnidyntsi oil-and-gas field. In the vicinity of the field the following towns are located: Gadyach, Lokhvytsya, Romney, Glynsk, Pryluky, Bakhmach, Zinkiv, Myrgorod and the villages of Petrivka-Romenska, Krasnoznamenka, Chervonozavodske, Yaroshovka and others. Chyzhivske raise is a complication of Glinsko-Rozbyshivsky shaft, and it is located northwest of Pogarshchynske on the same axis with it, but it is more sunk. Chyzhivske raise is a crypto-diapiric structure with pre-carboniferous deep deposits of Devonian salt core. Chyzhivske raise, in tectonic terms, is located in the central part of the Dnieper – Donets shaft and is confined to the smooth anticline structures belt. To the west of Chyzhivske raise Avdiyevska structure is located, and to the east of it there is Komyshnivska structure. On the south of the structure belt, Lokhvytsko-Yarivsky and Zhadanivsky saggings are adjacent [2].

According to the schemes of detailed seismography and deep drilling, Chyzhivska structure is an anticline fold stretching northwest as to its productive T horizon's roof. In the vault its axis is archwise bent, resulting in the north-west stretching of the structure being changed in the sub-latitudinal direction. The length of the fold on the long axis is 12 km and its width is 9.5 km. The amplitude of the elevation makes 700 m. West pericline is more extended, deepened at angles of 12 – 14°. The south wing is somewhat smoother than the north one, its inclination degree makes 10 – 11°. In the north wing a coherent faults zone is traced, consisting of two tearing faults. According to the structure schemes of the Chyzhivske raise, its Visean deposits preserve all the morphologic features. In the younger sediments ranging from the Middle Carboniferous, the uplift is gradually incurving, and according to the Mesozoic-Cainozoic sediments a sloping northwest stretching monocline is silhouetting.

The Visean layer is divided into the lower and upper sub-layers. The lower part of the sub-layer is formed of dark grey and black argillites bands of limestones, siltstones and mortars. The upper part of the sub-layer is composed of dark grey very dense limestones. The Serpukhov layer consists of the lower and upper sub-layers. The lower one consists of dense dark grey argillites. The upper one is an argillous greenish strata with bands of sandstone, limestone and coal. The Middle Carboniferous section is reaching on the rocks the Lower Carboniferous layers with stratigraphic and angular incoherence and it is presented by the Bashkir and Moscow layers. The Upper Carboniferous section is a chain of argillites and sandstones, sometimes with bands of siltstone and limestone. To characterize the water saturation of the horizons and for qualitative assessment of the aqueous rocks collectors properties, the stratal water flow discharges were calculated for some horizons using the layer recovery curves. The stratal pressure in aqueous horizons was measured by means of the depth gauges. The

stratal temperatures were measured by means of electric thermometers. The water viscosity was determined with account of its temperature and salinity. In the upper part of the section, in the active water exchange zone the aqueous horizons of the Cainozoic and Cynoman Low-Cretaceous sediments are located. Aqueous are loams, anisomerous sands and sandstones with bands of argillous sands and clays. The rock filtration properties vary widely (F_f = 0.6 – 3.6 m/day, according to the experimental pumpings) and are defined by their lithologic composition, homogeneity degree and consistency in length . Aqueous horizons contain fresh water of sodium-hydrocarbonate composition with mineralization of 0.4 – 1.2 g/l, which is widely used for drinking water supply. The lower occurring aqueous strata are located in the zone of slow water exchange. The relative productive horizons of the section include the Moscow and Bashkir layers of the Middle Carboniferous, Visean layer of the Lower Carboniferous and the Turney-Devonian periods sediments confined to sandstone strata. The depth of the aqueous Middle Carboniferous horizons varies from 2 – 5 to 20 – 30 m, the porosity is 20 – 24%. The water content of the complex is high: at testing the Moscow layer deposits in well No. 12, the obtained inflow of stratal water made 214 m^3/day , with the productivity factor of 0.37. The smaller inflows of stratal water were obtained at testing the Bashkir layers, where they are 20 – 34.8 m^3/day.

The significant inflows of stratal water from the wells, where the Middle Carboniferous sediments were tested indicate that gas deposits confined to this complex are under the conditions of highly active hydrodynamic system. In the oil and gas fields a slight overpressure is traced, exceeding hydrostatic pressure by 0.5 – 1.9 MPa.

Developed under the Turney-Devonian conditions, thermodynamic water-pressure systems normally have limited contact with the gas deposits. The rocks water saturation in gas contour areas of the productive horizons is not very high, although their capacity and filtration parameters within the gas content loop are significant enough. The water obtained from this facility is a highly metamorphized, practically sulfate-free solution (SO_4^{2-} content makes 16 mg/l) of calcium-chloride type with the level of mineralization making 232 g/l. It its salt composition the abnormally high iodine (50.8 mg/l) and bromine (39.43 mg/l) concentrations are observed. The obtained data may indicate the possibility of the stratal waters ingress through the tectonic shift from the Devonian intersalt sediments, characterized by a high content of the above trace elements [2].

Also the stratal water in the Bilske fields are studied. The bilgeous gas condensate field is administratively located in Zinkivsky district of the Poltava region and Ohtira district of the Sumy region. In orygrography, the Bilske fields is in the midst of the Vorskla rivers in the east and Grun in the west.

Among the most representative in hydrogeological terms, directly in the field, are wells 105 and 104, where from the early coal deposits deposits of stratal water. Serpukhov deposits with a thickness of 200 m are represented by densely packed sandstones and siltstone with low gas saturation. Of the microcomponents are bromine, iodine and boron, the content of which is respectively 224 mg/l, 12 mg/l and 17 mg/l. Stratal water is calcium-chloride type, with mineralization – 176 g/l.

To analyze the deposits, no special studies have been conducted in the field. The actual material has been accumulated in the course of testing productive horizons of coal deposits. In the process of obtaining the water inflow the following activities were exercised: a) determination of the layer recovery curve to the static position; b) measurement of stratal pressure and temperature; c) water sampling for chemical analysis and sampling of water-soluble gas. Water sampling for chemical analysis was performed either in the mouth or at self-filling by means of depth samplers. In addition to the chemical composition of waters, the gas concentration and water-soluble gases composition were determined. In most cases, iodine in the field stratal waters is contained as a simple anion (I^-).

However, in the mineralized ground waters, iodine occurs partly in the form of free iodine (I_2). To determine iodine in the hydro-chemical practice the colorimetric method has been used for a long time, basing on the iodine ions oxidation by sodium nitrite to the final I_2 and extracting the latter with chloroform. This method gives satisfactory results only with the waters free from reducing agents (organic matter, H_2S, Fe_2 +, etc.).

The waters of Chyzhivske field contain ions of iron, therefore this method was not used (Tab. 1). The most convenient and accurate method of determining iodine and bromine is iodometric determination of iodine using hypochlorite as the oxidant [2]. This method can determine the amount of 0.02 mg I- in the analyzed volume of water without any preparation. Electrometric determination of iodine and bromine gives quite accurate results for a wide range of concentrations, but this method is time-taking and labor-consuming.

For the analysis of stratal water samples the following reagents were used: methyl orange (Fig. 1), sulfuric acid, potassium phosphate, potassium hypochlorite, sodium formate, potassium iodide, starch 1% (if a sample has changed its color to dark blue (Fig. 2), there is iodine present in it). To determine the amount of iodine, the solution was titrated. The aqueous system is located under this layer, including aqueous strata, confined to the sandstone bands with the depth from 3 – 14 to 30 m. The waters are represented as high salinity brines. The chemical composition of the water is calcium-sodium chloride. The temperature range of the system bedding is 110 – 120 °C [2].

Table 1 – Chemical composition of stratal waters fields

Field	Mean depth of the deposit location, m	Iodine content, mg/l	Bromine content, mg/l	rNa/rCl
Chyzhivske	3950 (C-5)	15.86 – 34.90	289 – 373	0.82 – 0.83
Chyzhivske	2980 (B-6)	7.2 – 17.98	250	0.77 – 0.79
Bilske	4470 (B-16) well 104	40.18	599	–
Bilske	4465 (B-16) well 105	27.49	125.21	–

Figure 1 – Adding methyl orange to the water samples to determine the content of iodine

Figure 2 – Titration of the water samples taken to determine the content of iodine

The highest concentrations of iodine and bromine are observed in the chloride- sodium waters of extra salinity (Fig. 1, 2). Iodine-bromine mineral waters tend to be located in the tearing faults zones, which serve as path ways for deep ground waters [5].

Iodine and bromine are also the products of the single process of organic matter transformation taking place at high temperatures and pressures. Then carbohydrate solutions and their accompanying deep sodium chloride solutions containing iodine and bromine move through the zones of large tectonic shifts into the higher areas of the Earth crust to the depths where lithologic structural conditions are favorable for the formation of oil, gas and the accompanying iodine-bromine waters accumulations. The latter are localized in artesian basins confined to large tectonic structures.

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The latter are localized in artesian basins confined to large tectonic structures. Thus, according to the Serpukhov horizon's waters study, the exponential correlation was revealed between the mean iodine content and the stratal waters salinity in wells No.39, 50 of Chyzhivske field according to the data obtained in 2012 – 2013 as shown in Fig. 3:

$$M = 12047e^{0.0071I}$$

where M – stratal water salinity, mgEq/l;
I – iodine content in stratal water, mg/l.

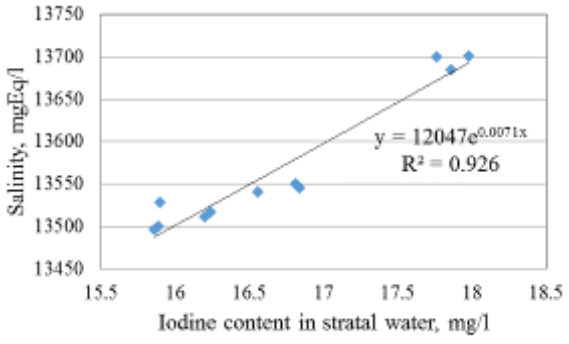

Figure 3 – Diagram of the iodine content mean values correlation with mineralization of wells No. 36, 50 of Chyzhivske field in 2012 and 2013

The correlation is constructed considering the reliability degree of R2 approximation, which is the highest (0.92. Thus, the iodine concentration values of about 18 mg/l are peculiar for well No.50, and the values from 16 to 16.8 mg/l are specific for the stratal waters of well No.36 of Chyzhivske field. The water of well No.50 are having greater mineralization of about 13750 mgEq/l. That is, in the analyzed wells, the iodine concentration grows with the stratal waters' salinity increase. The formation of ground waters with high content of iodine was significantly affected by the powerful sedimentary strata and the respective thermobaric conditions.

It is determined, that the lower temperature limit of iodine evaporation from organic-mineral complex of sedimentary rocks and its accumulation in ground waters is 35 – 50°C. However, the most intensive processes of the iodine containing organic compounds destruction take place at temperatures above 125 – 150o C [3].

Conclusions. Stratal water is a source of valuable micro-elements, namely iodine and bromine. It is determined, that the stratal waters of Chyzhivske and Bilske fields can be attributed to the iodine-bromine type (bromine making at least 25.0 mg/l, iodine – at least 5.0 mg/l) [2]. Thus, according to the Serpukhov horizon waters study, the exponential correlation was revealed between the mean iodine content and the stratal waters salinity in wells No.39, 50 of Chyzhivske field according.

The research has shown that waters of the Chyzhivske field horizons can be used for industrial extraction of iodine and bromine, because the iodine content exceeds 10 mg/l and the bromine content reaches 599 mg/l. Due to the low temperatures on the surface and the unspent water absorption of deposits, they can not be used for heat-energy purposes. However, these stratal water is a valuable raw material for the extraction of useful micronutrients that are now lost.

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