International Journal of Geology, Earth & Environmental Sciences ISSN: 2277-2081
An Open Access, Online International Journal Available at http://www.cibtech.org/jgee.htm
2024 Vol. 14, pp. 241-248/Burieya and Zhuraev
Research Article

FEATURES OF THE FORMATION AND DISTRIBUTION OF HYDROGEN SULFIDE WATERS POLEOGENIC DEPOSITS OF THE SURKHAN-DARYA ARTESIAN BASIN

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ABSTRACT
The method of forecasting prospective areas of hydrogen sulfide water formation is described. Geological factors were studied and analyzed in order to clarify the features of the formation of hydrogen sulfide water. Specific natural geological features were identified for the artesian basin. It was clarified that hydrogen sulfide waters are formed due to a biochemical process in the Surkhandarya artesian basins due to a thermochemical process. Promising areas of hydrogen sulfide water formation with a complex of specific natural features are recommended. The perspective areas of the South-Eastern part of the Surkhandarya basin.

Keywords: *Specific Features, Geological Factors, Oxidative Reaction, Water Pressure System, Geostructural Factor, Tectonic Disturbance, Hydrogen Sulfide Waters, Discharge of Reservoir Water, Oil Field*

INTRODUCTION

In health care practice, the role of mineral waters as an important therapeutic and preventive effect on the human body is steadily increasing. Hydrogen sulphide waters occupy one of the leading places among mineral waters. Currently, the only large sanatorium in Uzbekistan, Chimion, operates, which specializes in hydrogen sulphide water from the Fergana Depression (Burieva *et al.* 2019). Identification of promising areas for hydrogen sulphide waters in the rest of the republic is relevant. Currently, there is information about the presence of hydrogen sulphide water in the Fergana, Surkhandarya and Amu Darya oil and gas basins (Khudoiberdiev H.F. *et al* 2022).

The degree of knowledge of the problem. The problem of the origin of hydrogen sulfide in the underground hydro and lithosphere attracted the attention of many researchers. At the end of the last century, hydrogeological scientists A.M.Ovchinnikov, V.V. Ivanov, G.N.Plotnikova, A.I. Rivman studied and analyzed the conditions for the formation of hydrogen sulfide waters in the CIS countries (former USSR) (Zhuraev *et al.,* 2015). In Uzbekistan, DS Ibrahimov studied the hydrogeology of hydrogen sulfide deposits in the southern part of the Fergana artesian basin. L.S. Balashov studied the conditions for the formation of groundwater in the Surkhandarya artesian basin, A.I.Rivman - substantiated the main hydrochemical types of hydrogen sulfide waters of the Fergana and Afghan-Tajik intermountain depressions (Plotnikova, 1981). All researchers analyzed hydrogeochemical factors and identified the main hydrochemical types of hydrogen sulfide water.

Conditions for the formation of hydrogen sulfide. Distribution areas of hydrogen sulfide waters are usually confined to oil and gas bearing (or prospective for oil) basins of platform and folded areas, in the context of which evaporate deposits are developed. The greatest amount of hydrogen sulfide is observed in the waters of open and decaying oil fields, i.e. where there is a connection with surface waters (Zhuraev, 2016).

The ratio and stability of various sulfur-containing compounds in groundwater is determined by the combined effect of Eh and pH. Sulfur migrates in the aquatic environment in the form of sulfate sulfur; in an acidic reducing medium, a stable sulfur-containing component H2S, which with increasing pH changes to HS- (pH ~ 7) and S2- (pH ~ 14) (Ivanov, 1977). The formation of hydrogen sulfide in groundwater, their concentration and dispersion are determined by hydrodynamic and closely related hydro chemical conditions. Its distribution, as a rule, depends on the development of sulfate-reducing bacteria in them, but they have not been found in some hydrogeological closed structures with a high content of hydrogen sulfide. This gave grounds for microbiologists to assert that the process of sulfate reduction is carried out only in the presence of water exchange. In the course of the life of sulfate-reducing bacteria, sulfates of various minerals (gypsum, barite, celestine, etc.) and organic compounds are used (Ivanov, 1977). The reaction goes according to the scheme:

$SO_4^{2-}+2\text{Copг}+2H_2O=H_2S+2HCO^{3-}$ (1)

Hydrogen sulfide is a colorless poisonous gas formed by the combination of sulfur and hydrogen. The origin of hydrogen sulfide is associated with the biogenic or chemical reduction of sulfate minerals, as well as with magmatic activity. In near-surface conditions, magmatic hydrogen sulfide is oxidized to form SO_2, SO_3, H_2SO_3, H_2SO_4, sulfates, sulfur metals, and native sulfur. Oxide sulfur compounds in a favorable geochemical environment can be generators of hydrogen sulfide. The highest H_2S contents are observed in underground waters of oil and gas regions. Its maximum concentrations in waters reach 3500-10000 mg/l. Several main processes of biogenic formation of hydrogen sulfide are known. In the underground hydrosphere, the most common is microbiological oxidation of organic matter due to the reduction of sulfates [3,4].

Figure 1: Overview map.

In recent years, various experiments have been carried out on the reduction of sulfate compounds under conditions of high temperatures and pressures. The experiments of S.M. Grigoriev (Ivanov, 1977) in an autoclave showed that at t 100 - 150 ° C and pressure up to 10 atm. the interaction of methane and sulfate salts is the formation of hydrogen sulfide by the reaction:

$$CaSO_4 + CH_4 = CaCO_3 + H_2O + H_2S$$

$$Na_2SO_4 + CH_4 = Na_2CO_3 + H_2O + H_2S$$

Sakai (Ivanov, 1977) proved the formation of hydrogen sulfide as a result of the chemical reduction of methane sulfate at a temperature of about 500 ° C. Of great interest are the experimental works of Malinin and Khitarov (1969), who conducted research on the reduction of sulfur under hydrothermal conditions and showed that at a temperature of about 200 ° C there is a reduction of sulfate sulfur with hydrogen. Experimental data on natural conditions can be reasonably assumed that hydrogen sulfide superheated brines (170–200 ° C) opened in Ciscaucasia (well, Perekrestnaya, Galyugaevskaya, Malgobek, etc.) at depths of 4200 - 5250 meters in sulfate-containing and bituminous Jurassic deposits and chalk, have a thermochemical origin (Plotnikova, 1981).

Search criteria for the formation of hydrogen sulfide waters. The regular relationship of the distribution of hydrogen sulfide waters with sulfate-containing and petroleum-bearing sedimentary complexes

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Centre for Info Bio Technology (CIBTech) 39 determines the main search criteria for hydrogen sulfide waters and the selection of promising areas. Among natural factors and conditions, the decisive importance in the process of forming hydrogen sulfide waters are: 1) the lithofacial composition of water-bearing rocks (primarily the presence of sulfatecontaining sediments) and the oil and gas content of the sedimentary sequence; 2) geological and structural conditions; 3) hydrogeochemical environment; 4) hydrodynamic and geothermal conditions (Ivanov, 1977).
Below are considered and analyzed lithofacial factors associated with the formation of hydrogen sulfide water in the oil and gas fields of the Surkhandarya artesian basin.

RESULTS AND DISCUSSION

Distribution of sulphide (hydrogen sulphide) waters in the Surkhandarya artesian basin. Sulfide waters have been identified in the Termez, Dzharkurgan, Shurchin, Altynsay, Kumkurgan and Denau districts in the following areas: Uchkyzyl, Dzhayrankhana, Khaudag, Lalmikar, Kokayty, Navbahor, Shorbulak, Khodja-ipak, Yuzhny and Severny Kurganchi, Dzharkurgan, Dalan and others. Within the Surkhandarya region, sulfide waters are tapped by wells at depths from 100 m to 2956 m. Well flow rates are from 1 to 10 l/sec with spontaneous discharge. Depending on the depth of tapping and well flow rates, the water temperature at the wellhead varies from 30 to 50oC. The concentration of hydrogen sulfide in water ranges from 10 to 800-1207 mg/l, in most cases 200-500 mg/l.
In the north-eastern part of the Surkhandarya artesian basin, hydrogen sulphide waters are opened by deep wells in the areas: Dalan, northern and southern Kurgancha and are opened at a depth of 640-650 m in limestones of the Alay horizon of the Paleogene. Well flow rates do not exceed 1 l/sec. The chemical composition of the water is sodium chloride-sulphate with a mineralization of 20 g/l. The concentration of hydrogen sulphide is 16-20 mg/l. Underground waters confined to limestones of the Bukhara horizon are opened by wells at a depth of 1036-1200 m. Well flow rates reach up to 12 l/sec during self-flow. The chemical composition of the water is sodium sulphate-chloride with a mineralization of 35-47 g/l. A well 2130 m deep was drilled 5 km north of the Jeyranhan Physiotherapy Hospital, which opened up hydrogen sulphide waters in the limestone of the Alay horizon. The water flow rate from the well is 3 l/sec with spontaneous flow. The water temperature is 600C at the wellhead. The opened mineral waters are slightly

alkaline with a mineralization of 14 g/l with a chloride-sodium composition. The hydrogen sulphide content in them is 26 mg/l.
In the western part of the Surkhandarya artesian basin, hydrogen sulphide springs with a low content of hydrogen sulphide concentration (from 1 to 100 mg/l) with mineralization from 1 to 10 g/l, suitable for use in the treatment of various diseases, are widespread. Such sources of hydrogen sulphide waters include a group of springs such as Khodja-ikan, Shakarlik-Astana, Obi-Zhalil, Farhad, etc. Here, hydrogen sulphide waters are sodium chloride, chloride-sulphate and calcium-sodium with mineralization of 1-10 g/l. The content of hydrogen sulphide ranges from 10 to 24 mg/l.
The results of the studies conducted within the Surkhandarya region showed that the hydrogen sulphide waters of the region, according to the concentration of sulphides, belong to the following groups (According to V.V. Ivanov);

Table 1. The main criterion for assessing ore medicinal water in Uzbekistan (by hydrogen sulfide type)

Water mineralization norm	Division mg/l	Name of water,
10 mg/l	10,5-50,0	Weakly sulfidic
	50,0-100,0	Medium sulfidic
	100,0-250,0	Strongly sulfidic
	250,0 -500,0	Very strongly sulfidic
	500,0-3 000,0	Ultra strongly sulfidic

Hydrogen sulphide waters for balneotherapy are used in concentrations from 10 to 250 mg/l. In diseases of the cardiovascular system (ischemic heart disease, hypertension, heart defects), low concentrations (25-100 mg/l) are more often used, while in diseases of the peripheral vessels, nervous system, musculoskeletal system, gynecological, skin, higher concentrations (up to 250 mg/l) are used.
Within the Surkhandarya region, sulphide in the Termez, Jarkurgan, and Sherabad districts are of interest for medicinal use. In addition, as was indicated above, many other areas of sulphide have been identified that are of practical interest for their use for medicinal purposes.
Analysis of Paleogene water-bearing rocks of the Surkhandarya megasyncline to study sulfate-containing rocks. Oil is formed in the Bukhara and Akzhar layers of the Paleogene deposits of the Amu Darya, Kokaytinsky, Khaudag, Lalmikarsky, Koshtarsky and Mirshadinsky oil fields. The main water-bearing rocks of the Bukhara-Akzhar layer are limestones and dolomites with gypsum and anhydrite interlayers. To compare the areas of distribution of hydrogen sulfide waters in oil and gas-bearing territories and halogen formations, a map of the main areas of distribution of hydrogen sulfide waters within the Surkhandarya megasyncline was compiled.
The map shows the areas of established development of hydrogen sulfide waters and their boundaries corresponding to the distribution of evaporite sediments of Paleogene water-bearing rocks, outlined by developed and active oil and gas fields promising for hydrogen sulfide waters. Sulfate-containing strata are present in all regions of the depression. Sulfate-containing rocks are in contact with aquifers. As can be seen from the map, the distribution of hydrogen sulfide waters is closely related to the areas of joint development of halogen rocks and oil and gas complexes. The oxidation reaction occurs due to the leaching of sulfate-containing strata, and in the oil-bearing strata a reduction reaction occurs with hydrogen and the participation of sulfate-reducing bacteria. In the absence of one of the necessary conditions (sulfates or oil organics), high-concentration hydrogen sulfide waters are not formed (Fig.2).
Clarification of geostructural factors. It has been experimentally established that during infiltration water exchange over a long geological period, dissolved free oxygen penetrates to significant depths (up to 2 km or more) and spreads along permeable layers over a distance of up to tens of kilometers (Burieva S.R. *et al* 2019)]. In oil fields where hydrogen sulfide waters are formed, the productive horizon lies close to the

earth's surface, which provides it with oxygen and enhances the sulfate reduction process due to the penetration of infiltration waters through tectonic faults. The roof of the productive (Bukhara) layer of the Paleogene lies at a depth of -200 m (Uchkyzyl) to -1700 m (Djayrankhana) at absolute marks. Hydrogen sulfide water is formed in this layer in the Surkhandarya megasyncline. Each oil field is crossed by a longitudinal tectonic fault. The Bukhara layer lies at a depth of up to 2 km (Zhuraev, 2016).

Consequently, due to the identified longitudinal tectonic disturbances, hydrodynamic processes occur, and infiltration waters seep into oil-bearing horizons. The following specific natural features are necessary for the formation of hydrogen sulfide waters: longitudinal tectonic disturbance, occurrence of the productive layer near the earth's surface (up to 2 km), discharge of formation waters due to tectonic disturbance of the oil and gas field, as well as occurrence of aquifers with a gentle slope from the feeding area to the oil and gas field. Discharge of thermal waters into the oil structure is carried out along tectonic faults. In evaporite (limestone and gypsum) rocks, an oxidation reaction occurs, which is carried out due to the erosion of sulfate-containing strata. In oil-bearing strata, a reduction reaction with hydrogen occurs with the participation of sulfate-reducing bacteria. As a result, hydrogen sulfide waters are formed.

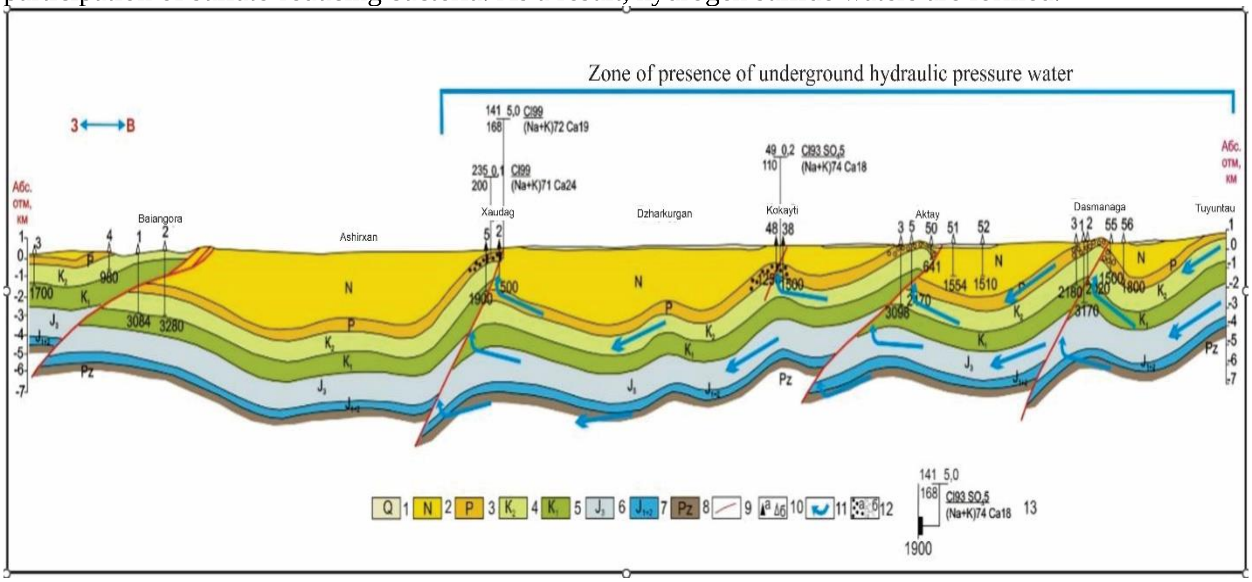

Fig. 2. Schematic section of the process of hydrogen sulfide water formation based on the hydrodynamic factor (hydrogeological profile of the Tuyuntauskaya-Bayangora site). System: 1 - Quaternary, 2 - Neogene, 3 - Paleogene. Cretaceous system, section: 4 - upper, 5 - lower. Jurassic system, section: 6 - upper, 7 - lower and middle sections undivided; 8 - Paleozoic system; 9 - tectonic faults; 10 - oil wells: a - production, b - exploratory; 11-direction of formation water flow; 12-spread of hydrogen sulfide water - a, supposed spread of hydrogen sulfide water - b; 13 - well, top - number, bottom - depth, m. Zones of main water inflows. Left: numerator - mineralization, g / l; denominator - hydrogen sulfide concentration, mg / l. On the right: in the numerator – flow rate, l/s and chemical composition of water.

Clarification of hydrodynamic processes. Schematic models of sections where the process of hydrogen sulfide water formation occurs have been compiled. The deposits of the Mesozoic-Cenozoic complex lie with a slight slope from the east to the central part of the megasyncline. The presence of tectonic disturbances creates a hydrodynamic barrier on the oil fields, which are located in the eastern part. The hydrodynamic pressure of groundwater in the eastern part of the megasyncline is present due to the presence of tectonic disturbances and a slight slope of the deposits. In the zone of hydraulic pressure water between the eastern peripheral part and the central part, the Paleozoic and Cretaceous-Jurassic formation waters are discharged upwards. A slowdown in the water exchange process in the crest part of the western wing of the oil fields has been established. As a result, microbes (organic substances) are excited in the oil layer, i.e.

sulfate-reducing processes occur and, as a consequence, hydrogen sulfide waters of the Paleogene are formed.

Geothermal environment. The average temperature of the formation water of the productive horizon of the oil-bearing deposits of the Surkhandarya artesian basin, where hydrogen sulphide waters are formed, is from 28 to 70oC. In this temperature regime, conditions are created for biochemical processes suitable for the formation of hydrogen sulphide water, i.e. an oxidation-reduction reaction is carried out.

Hydrogeochemical environment. Consequently, thermal waters are discharged into the oil structure along tectonic faults. In evaporite (calcareous and gypsum) rocks, an oxidation reaction occurs, which is carried out due to the washing out of sulfate-containing strata. In the oil-bearing strata, a reduction reaction with hydrogen occurs with the participation of sulfate-reducing bacteria. As a result, hydrogen sulfide waters are formed.

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Forecasting promising areas for the formation of hydrogen sulphide waters of the Surkhandarya artesian basin based on identified specific natural features.

The formation of sulfurous water requires the presence of the following specific natural factors: longitudinal tectonic disturbance, allocation of the product layer near the surface of the earth (up to 2 km), loading of plastic water behind the tectonic disturbance layer of the oil field, and also allocation of water deposits with a gradual slope from the supply area to the oil field. The tectonic solution and the petroleum structure are

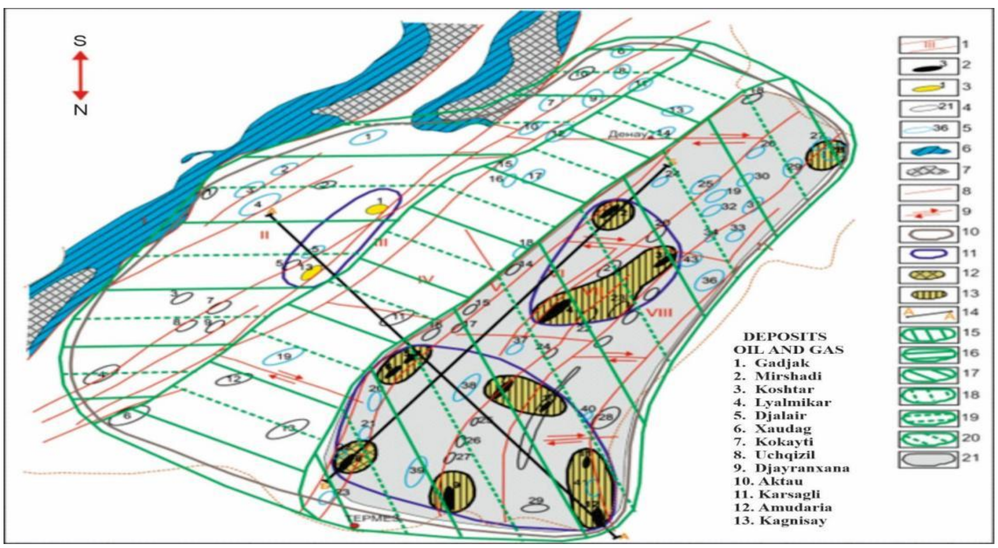

Fig. 4. Schematic forecast map of hydrogen sulfide water formation in the Surkhandarya artesian basin based on specific natural factors. 1 – tectonic block and its number. Field: 2 – oil, 3 – gas, 4 – promising, 5 – identified; 6 – Jurassic deposit outcrops; 7 – Paleozoic formation outcrops; 8 – faults; 9 – shifts and boundaries of latitudinal steps (blocks) in ancient deposits. Boundaries: 10 – distribution of evaporite sediments, 11 – depleted and operating oil and gas fields. Hydrogen sulfide water development areas: 12 – identified, 13 – promising; 14 – geological profile. Water pump system: 15 – more active, 16 – weak, 17 – insignificant. Territories by depth of occurrence of productive horizon: 18 – up to 2 km, 19 – more than 2 km, 20 – deep; 21 – territories with potential for hydrogen sulfide waters.

responsible for the discharge of the thermal water. In evaporite (izvestkovisty and gypsum) products, an oxidative reaction occurs, which cools thanks to the washing of sulfate-containing fibers. In the oil-bearing fiber, a restorative reaction occurs with hydrogen, which is partly sulfate-reducing bacteria. As a result, hydrogen peroxide forms.

Therefore, it is possible to make a schematic forecast map of the formation of hydrogen sulphide waters of the Surkhandarya artesian basin based on the developed methodology. All identified specific natural features necessary for the formation of hydrogen sulphide water are plotted on the base map (tectonic map) (Fig. 3).

The map shows the outlines: developed and active oil and gas fields, dated to the Paleogene, located in the southern part of the basin (Uchkyzyl, Dzhayrankhana, Amu Darya, Korsagly, Aktau, Kokayty, Khaudag, Jalair), the central part (Gajak and Kagnysay) and the eastern part (Lyalmikar, Koshtar and Mirshadi); territories of established development of hydrogen sulfide waters and their boundaries (in order to identify hydrogen sulfide water, detailed prospecting and exploration hydrogeological work was carried out, dated to the Paleogene deposits at the Uchkyzyl oil field in the period 1985-1987, and as a result, the presence of highly hydrogen sulfide water was clarified and reserves were calculated);

oil and gas fields where hydrogen sulphide waters have been discovered (in the southern part – Uchkyzyl, Dzhayrankhana, Amu Darya, Korsagly, Aktau, Kokayty, Khaudag, Jalair; in the eastern part – Lalmikar, Koshtar, Mirshadi and the identified anticline structures of Shorbulak and Kurgancha);

territories where sulfate-containing rocks are distributed (evaporite rocks are distributed throughout the basin).

Oil and gas fields and identified prospective structures for oil and gas, which consist of an asymmetric anticlinal fold of north-eastern strike with a longitudinal tectonic fault, as well as where the productive horizon lies close to the surface (the outlined territories are located on the south-eastern and north-western sides of the edge);

Territories that are distinguished by the nature of hydrodynamic systems (in the south-eastern part of the basin – more active, in the north-western – weak and insignificant in the central part);

Prospective territories for hydrogen sulphide waters are predicted based on the identified features of the formation of hydrogen sulphide water accumulations. All specific natural features are present in the south-eastern part of the Surkhandarya artesian basin.

CONCLUSION

The formation features of promising accumulations of hydrogen sulfide waters in the Surkhandarya basin have been clarified. The Bukhara-Akzhar stage contains limestones and dolomites with gypsum and anhydrite interlayers. Oil and gas are formed in the Paleogene deposits (V, VII, VIII layers). Oil and gas fields, in which hydrogen sulfide waters are formed, have an anticline asymmetric structure and longitudinal tectonic faults. The productive oil-bearing formation responsible for the formation of hydrogen sulfide waters occurs at a depth of -400 to -2000 m; Hydrogen sulfide waters are formed at Eh – -40 – -450 mV; pH 6,5-8,5; M=49-235 g/l; pH_2S=40-550 mg/l. The discharge of formation waters occurs due to tectonic disturbances in oil and gas fields, as well as the gently sloping occurrence of a complex of deposits between the oil and gas field and the area of groundwater supply. The temperature of the productive horizon varies from 28 to 52^{o}C.

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