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CORRELATION BETWEEN GROUNDWATER COMPOSITION AND LITHOLOGY OF THE LOWER PERMIAN SEDIMENTS WITHIN ORCHYKIVSKA DEPRESSION OF THE DNIPRO-DONETS DEPRESSION

КОРЕЛЯЦІЯ ГІДРОГЕОХІМІЇ ПІДЗЕМНИХ ВОД З ЛІТОЛОГІЄЮ НИЖНЬОПЕРМСЬКИХ ВІДКЛАДІВ ДНІПРОВСЬКО-ДОНЕЦЬКОЇ ЗАПАДИНИ В МЕЖАХ ОРЧИКІВСЬКОЇ ДЕПРЕСІЇ

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Correlation between groundwater content and lithology of the Lower Permian sediments within Orchykivska Depression of the Dnipro-Donets Depression has been studied. Groundwater is characterized by considerable variety of salinity, macro- and micro-components content. The main factor of this diversity is the presence of thick strata of the Lower Permian and Upper Devoniant saltbearing rock mass. On determining these hydrochemical «anomalies» formation mechanisms, the evaluation of ground water dynamics and orientation of physical-chemical processes in the «rock-water» system is of fundamental importance. In this regard, maps of salinity izopahits, Na/Cl ratios and other hydrological characteristics of groundwater have been created. Based on analysis of the maps and lithological and paleohydrological data the conditions of groundwater chemical composition in area and in cross-section has been determined as different. On the basis of the constructed maps of the Na/Cl ratio distribution, genetic type's zones of origin, mixed and leaching brines have been distinguished.
Keywords: salt dome structures, groundwater, brine, terrigenious formation, rock salt formation

Досліджено взаємозв'язок гідрогеохімії підземних вод з літологією нижньопермських відкладів Дніпровсько-Донецької западини в межах Орчиківської депресії. Підземні води характеризуються значною мінливістю мінералізації та вмісту макро- і мікро компонентів. Головним фактором цієї строкатості є наявність потужних соляних товщ нижньої пермі та верхнього девону. При визначенні механізмів формування даних гідрохімічних «аномалій» принципове значення має оцінка динаміки підземних вод на фоні широкого розвитку солянокупольних структур, а також спрямованість фізико-хімічних процесів в системі «порода-вода». Виходячи з цього, побудовано карти ізоліній мінералізації, коефіцієнту Na/Cl та інших гідрогеохімічних характеристик підземних вод. На основі аналізу отриманих карт в сукупності з літологічними даними була визначена невитриманість хімічного складу підземних вод по площі і в розрізі, виділено зони генетичних типів розсолів: седиментогенних, вилуговування та змішаного типу.
Ключові слова: солянокупольні структури, підземні води, розсіл, теригенна формація, соленосна формація

INTRODUCTION

Within the Orchykivska Depression groundwater (brines) is characterized by considerable changeability of salinity and content of macro- and microcomponents, due to the presence of powerful strata of the Lower Permian and Upper Devonian salt-bearing rock mass in the context of the sedimentary complex. To determine the mechanisms of formation of the chemical composition of brines the evaluation of groundwater against the background of extensive development of salt tectonics is essential.

These brines are widespread in basins containing salt-bearing formations: Angara-Lenskyi basin of the Siberian Platform (Cambrian); Canning Basin, Australia (Devonian) (Yapaskurt, 2005), Prypiat Basin (Upper Devonian) (Makhnach, 2000); Caspian Basin (Lower Permian) and in several basins of North-Western Europe – Zechstein (Upper Permian), West Turkmenistan (Upper Jurassic); Carpathian (Neogene) and North America – Mississippi and Paradox (Gutsalo, Krivoshiya, 1969, Michael et al., 2003, Spencer, 1987).

Water-bearing complex of Upper Carboniferous - Lower Permian Dnieper artesian basin occurs at considerable depths – over 4000 meters, which explains its insufficiency of study compared with upper bedded horizons. For the last 20 years in this region intensive search of oil and gas of deep strata has been conducted. As a result a large amount of related hydrogeological information was gathered.

Since groundwater of the zone of very slow water exchange is in reduced mobility compared to waters of other hydrodynamic zones, they are essentially connected with the solid phase. Interacting with the mineral part of rocks, they expose physical and chemical changes in the sedimento- and lithogenesis. Therefore, the study of physical and chemical processes in the «water-rock» system, combined with lithological and paleohydrogeological data will settle the following questions: their genesis, the formation of ion-salt composition, migration of many elements and the formation of mineral resources.

Hypotheses of genesis, formation of the ground water chemical composition (highly salinity chlorine-calcium brines and porous solutions of weakly permeable strata) and the mechanisms of their inflow in adjacent strata were studied by I.K. Zaitsev (1958), A.E. Babynets (1961), M.G. Valiashko (1968), D.P. Shvai (1973), K.M. Varava (1977), Ye.V. Posokhov (1981), A.O. Makhnach (1989, 2000), Ye.V. Pinneker (1982), V.V. Kolodiy (1983), A.O. Sukhorebryi (1993, 1998), S.L. Shvartsev (1997), J.M. Salvany, A.M. Stueber (1998), G.W. O'Brien (1999), I. Gavrieli, Y. Yechieli, L. Halicz (2001), K. Michael (2003) and others. It was determined by them that the presence of powerful halogen strata in cross-section of sedimentary basins has led to the formation of ground water and brines, essentially different in chemical composition and salinity.

In this regard, the aim was to identify regularities of spatial hydrogeochemical peculiarities and correlation of rocks lithological composition with chemical composition of brines of the Upper Carboniferous – Lower Permian water-bearing complex.

The goal was achieved by solving the following tasks:

- collection and systematization of the actual (fund) material, resulting in the database of chemical composition of groundwater Upper Carboniferous – Lower Permian water-bearing complex;
- summarizing and clarification of lithological peculiarities of research cross-section rocks;
- contraction of brines salinity and Na/Cl ratio contour maps within the study area;
- ascertainment of hydrogeochemical characteristics of brines based on the analysis of the spatial patterns of maps.

RESEARCH AREA, RESEARCH SUBJECT AND METHODS

The Orchykivska depression stretches from Poltava structure to Spivakivskyi highland and it is characterized by extensive development of salt domes structures which are composed by Upper Devonian evaporites (Frasnian stage) (Fig. 1.). Water-containing rock of Upper Carboniferous – Lower Permian water-bearing complex is represented by evaporite and carbonate formations of the Lower Permian and terrigenous deposits of the Upper Carboniferous. Their lithologic and stratigraphic characteristics are given below.

Upper Serious C_3 is presented by interbedding packs of powerful sandstones, siltstones, mudstones. Thickness of individual layers are 5-10 m.

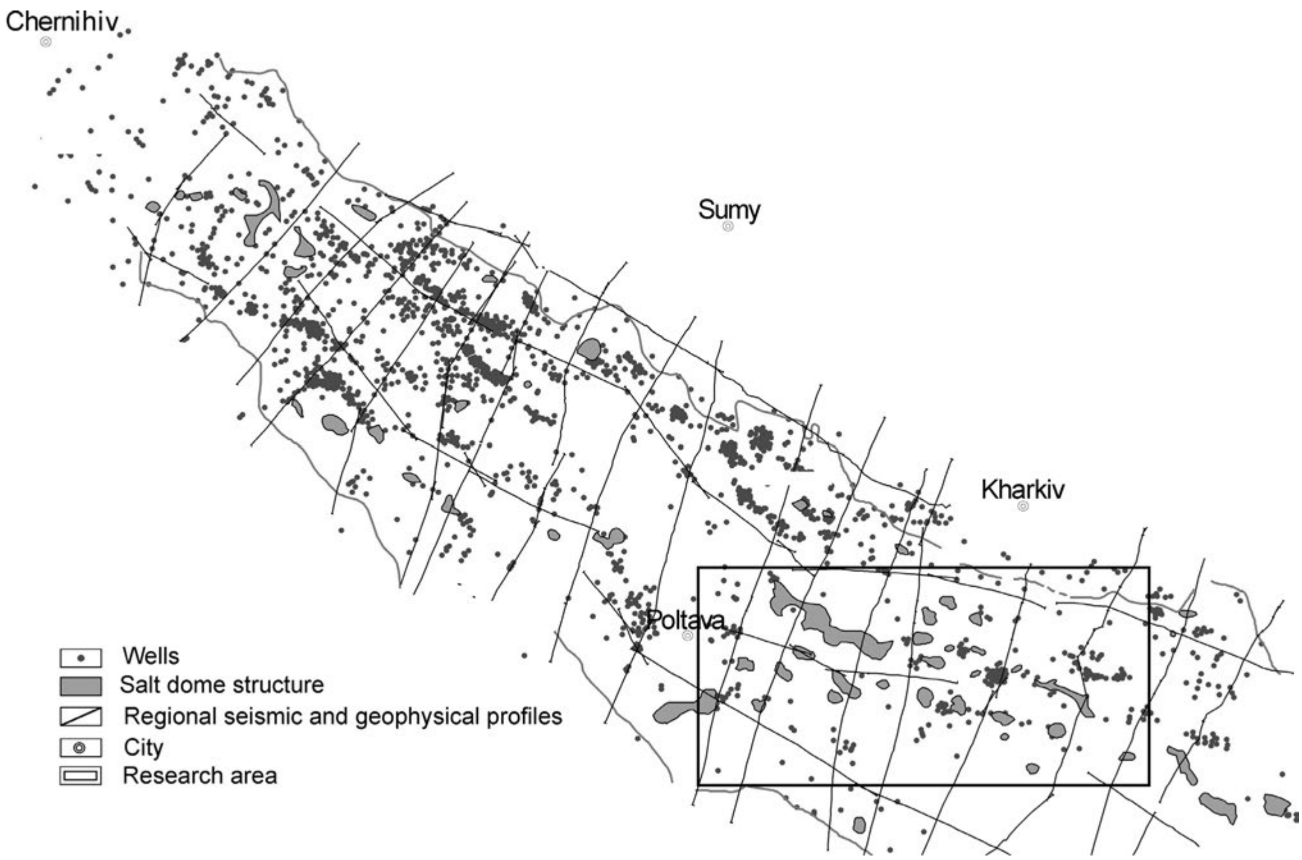

Fig. 1. Distribution of wells, used for GIS-model generation.

Their position in the cross-section is nonmature, they are often completely replaced by siltstones. The total thickness of the Upper Carboniferous is 1530 m (Aizenverg et al., 1988).

Lower Permian complex of angular and stratigraphic inconsistency occurs in Carboniferous deposits. Red terrigenous (kartamyska) formation of Lower Permian is composed of sand and clay deposits – mudstones, sandstones and siltstones; formations continental, transitional and marine facies.

Evaporite formation lies on the red-coloured terrigenous formation with transgressive unconformity. The Lower Permian evaporite formation is divided into two subformations: the salt-bearing Mykytivska, Slovyanska and Kramatorska K-Mg-bearing ones. The salt subformation, which is up to 1200 m thick, is represented by the alternated layers of rock-salt (up to 75 m thick), limestones, mudstones, marls, anhydrites and halopelites. Dronivska suite of the Triassic system lies on the Paleozoic erosion surface with the stratigraphic and angular unconformity.

In terms of hydrogeology research area belongs to the Dnieper artesian basin. The main regional water-resistant is evaporites of Slovyansk and Kramatorsk suite that lie at depths of 500-3500 m and separate the Triassic water-bearing complex from of Upper Carboniferous – Lower Permian one. These strata are the boundary that separates hydrodynamic zones of slow (in some areas – intensive) and very slow water exchange (Babinets, 1961, Shestopalov et al., 2009). The content of the collectors in the context of the complex is almost 50 % and it is represented by sandstones, fractured dolomite, anhydrite and limestone strata with dense waterproof anhydrite, dolomite and rock salt.

Thickness of the complex in the south east is over 1000 m and in the central part is up to 2450 m. The water temperature at depths of 1800-2000 m can reach 45-48˚C (Gutsalo, Krivoshiya, 1969). Reservoir water of Lower Permian sediments is represented by highly salinity chlorine-calcium brines; their salinity reaches 312 g/L. The research strata thickness refers to the zone of difficult water exchange. This zone is characterized by elision mode and low rates of groundwater movement – 0,7 m/year (Babinets, 1961).

The object of the research is brines of Upper Carboniferous – Lower Permian water-bearing complex of Dnieper artesian basin. Data of the chemical composition of brines of over 100 wells have been used (at depths of 691-3997 m within the south-eastern part of Dnieper-Donetsk depression from Poltava structure to Spivakivska highland).

To construct contour maps of salinity, Na/Cl ratio and other hydrogeological characteristics of groundwater, mathematical tools of software system Spatial Analyst, ArcView 3.2a were used. The methodology was based on creating of coherent mathematical models with the usage of initial information by Spline – approximations, as the most effective method of flattening the surface curvature.

RESULTS AND DISCUSSION

Salinity and Na/Cl ratio contour maps have been constructed for clarifying regularities of the spatial hydrogeochemical characteristics and relationship between rocks lithological composition and chemical composition of brines of Upper Carboniferous – Lower Permian water-bearing complex.

Ground water of Upper Carboniferous – Lower Permian water-bearing complex is represented by brines with salinity that ranges from 55,86 g/L (Balakleiska well no. 6) to 312,61 g/L (Riabukhynska well no. 208). The brines are mainly of calcium chloride type (by genetic classification of V.O. Sulin, 1948) of sodium chloride composition (Fig. 2).

According to A.Ye. Babynets (Babinets, 1961) and V.V. Kolodiy (Kolodiy, 1983) investigations, salinity of groundwater increases to Lower Permian evaporites, but it reduces in the carboniferous deposits. However, as it can be seen from the results, salinity maximal values (256,65-312,61 g/L) are observed in areas adjacent to the salt domes (Kopylivskyi, Chutivskyi, Rozpashnivskyi, Lannivskyi, Sosnovskyi, Riabukhynskyi, Shebelynskyi and Spivakivskyi), indicating the impact of leaching brine directly through the contact area and/or the possibility of hydraulic connection between permeable layers even under very difficult water exchange conditions. The minimal values of salinity (55,86-112,0 g/L) are confined to space between salt domes and/or fractured anhydrite brines.

Brines with sulphate high content, from 301,22 mg/L (Kopylivska well no. 39, 2744 m) up to 2687,24 mg/L (Riabukhynska well no. 208, 3440 m) and the $(rSO_4*100)/rCl$ ratio varies widely 0,0075-0,45, occur in areas of gypsum and anhydrite distribution. The (Cl-Na)/Mg coefficient varies from 2,06 (Shevchenkivska well no. 304, 1980 m) to 21,3 (Rozpashnivska well no. 81, 3628 m). Value of the Ca/Mg ratio varies from 1,5 to 3,5.

The question of the origin of high salinity calcium chloride type brines is still controversial. For the reason that salt rock formation containing calcium carbonate and anhydrite, when in contact with sodium chloride oversaturated brines, produced conditions for the calcium chloride accumulation and concentration – saline with the highest solubility. First the brine becomes sodium chloride → sodium-calcium → calcium-sodium, and then it becomes of calcium-chloride type. Carbonates are the source the calcium, but the leading role belongs to calcium transition from anhydrite (Shvartsev, 1997). Calcium transition is also possible from terrigenous rocks, such as plagioclase albityzation (Alekseyev et al., 2005).

Sulphates are removed from the solution in the form of gypsum and magnesium is removed in the form of dolomite. It leads to a calcium chloride relational concentration. V.I. Gurevich, A.I. Osipov, Yu.S. Kormilets, A.O. Makhnach and others stated on the possibility of the dolomite catagenetic origin in connection with the calcium-chloride type brines formation. Cation exchange may also be the reason for the increased calcium content. Liquid phase enriches by strontium, barium and other elements in the presence of other sulphate minerals in the rocks. The indispensable conditions for brines concentration are considered to be the following: period for geological time scale, reducing medium and thermodynamic conditions relevant to the zone of difficult water exchange (Gavrieli et al., 2001, Wallace, 1990).

Brines differ by bromine high content – up to 1549 mg/L (Melekhivska well no. 8, depth – 2180 m), the minimum recorded value is 44,23 mg/L (Alekseevska well no. 4, depth – 2500 m). Bromine, according to its distribution in the halogenous saline (halite, sylvite and carnallite) can transit into the liquid phase in large quantities. It must be taken into consideration that the bromine compounds solubility greatly increases with the temperature and pressure growth. The value of the Cl/Br ratio ranges from 64-3046 mg/L, pH ranges from 4,5 (Kopylivska well no. 32, depth – 2922 m) to 8,6 (Riabukhynska well no. 208, depth – 3440 m).

Similarities of microcomponent composition of brines and salt rock formations indicate inflow of many elements from rocks (not only Ca, Mg, K,

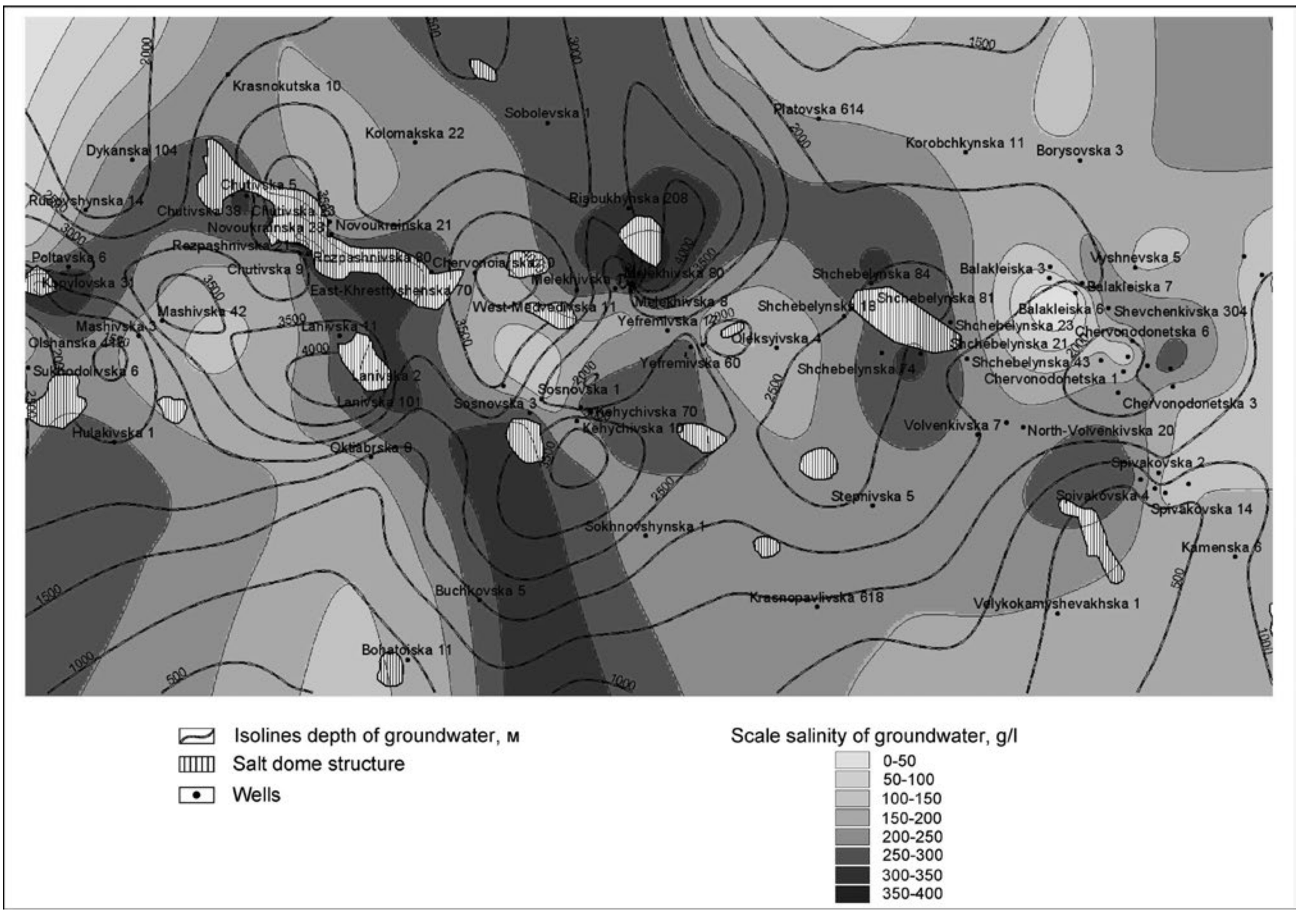

Fig. 2. Upper Carboniferous – Lower Permian water-bearing complex brines salinity contour map.

A and Br, B, Li et al.). Brines iodine negligible concentration – 3,1 mg/L (Spivakivska well no. 11, depth – 560 m) is easily explained by its low content in rocks. The maximum values of iodine reach 113,41 mg/L (Rozpashnivska well no. 81, depth – 3900 m) and 130,0 mg/L (Melekhivska well no. 74, depth – 2548 m). Elements transition from rock salt into solutions at considerable depths is due to molecular diffusion, while raising the temperature and pressure can lead to selective dissolution of individual elements in quantities much greater than in brine (Stadnichenko, 2010).

Combined brines genesis dominates in the Upper Carboniferous - Lower Permian water-bearing complex. They are the mixtures of the origin brines, burial-inflow water and lithogenic water. Underground condensation water and mixtures of strata brines of the hydrogeochemical background occur as local occurrence (Kolodiy, 1983).

There are geochemical criteria which allow to determine origin brines, leaching and interjacent mixed genetic type. Dependence between Na/Cl and Cl/Br ratios, reflecting the natural processes of concentration in modern seawater lagoons and salt leaching processes is commonly used as the main criterion for the distribution of brines genesis (according to classification of K.M. Varava, 1977) (Varava et al., 1977). For example, high salinity calcium-chloride type brines are common in the undersalt stratum of Permian Basin of West Texas and Oklahoma, (Na/Cl <0,8; salinity >300 g/L), while sodium chloride leaching brines (Na/Cl> 0,9; salinity <290 g/L) were found in the area of subsalt deep aquifer Wolfcampian stratum (Bein, Dutton, 1993, Stueber, Walter, 1991).

On the basis of the constructed maps of the Na/Cl ratio distribution (Fig. 3), we have identified areas of brines: origin, leaching and mixed type.

Origin brines are spread in the north-western and south-eastern parts of the research area, Na/Cl ratio varying from 0,46 (Kopylivska well no. 31) to 0,79 (Spivakivska well no. 5).

Mixed type brines are spread from the south-west to north-east, Na/Cl ratio varying from 0,80 (North Holubivska well no. 5) to 0,89 (Chervonodonetska well no. 4).

Leaching brines are distributed locally and are mainly adjacent to salt domes, Na/Cl ratio varies from 0,94 (Melykhivska well no. 1) to 1,09 (Shebelynska well no. 53).

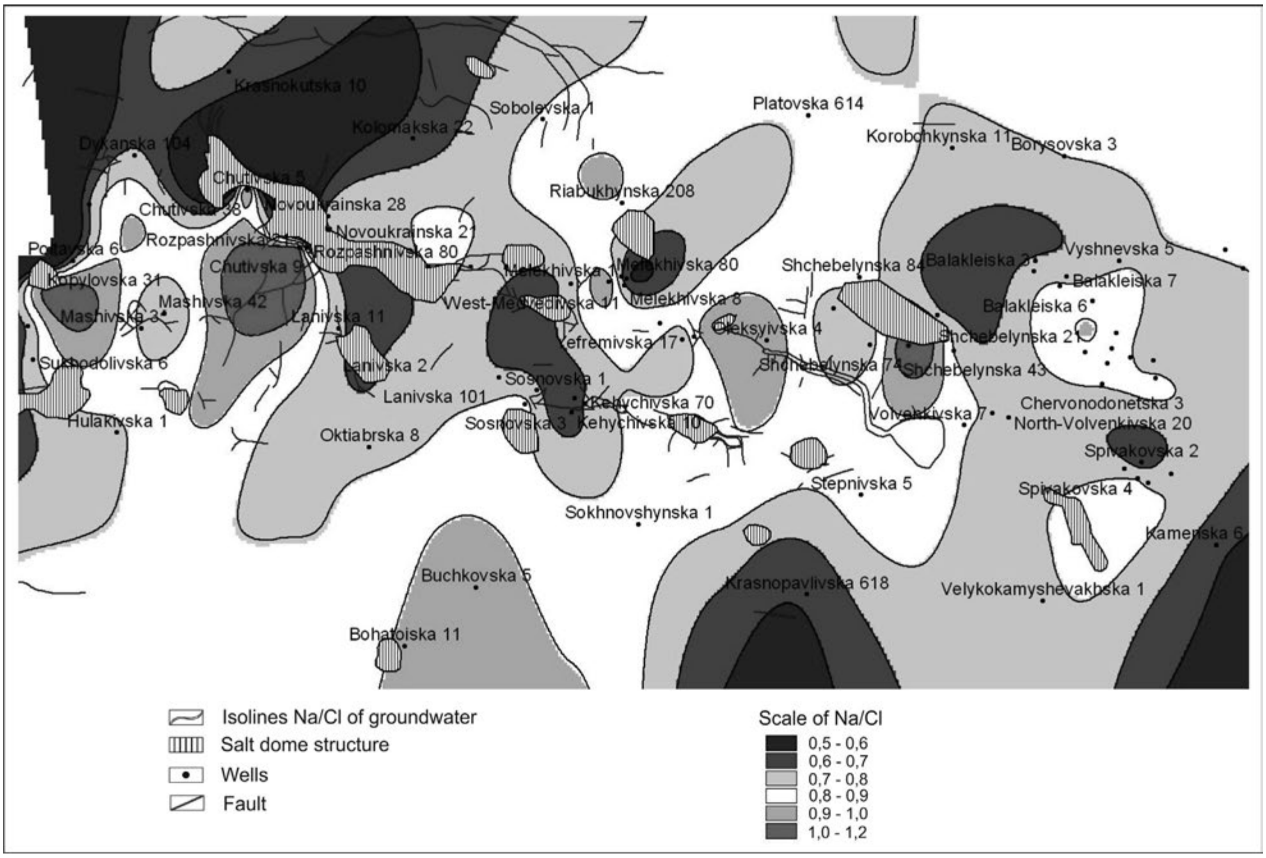

Fig. 3. Na/Cl ratio contours map: < 0.8 – origin brines; 0.8-0.9 – mixed type brines; > 0.9 – leaching brines (according to classification of K.M. Varava, 1977, etc.).

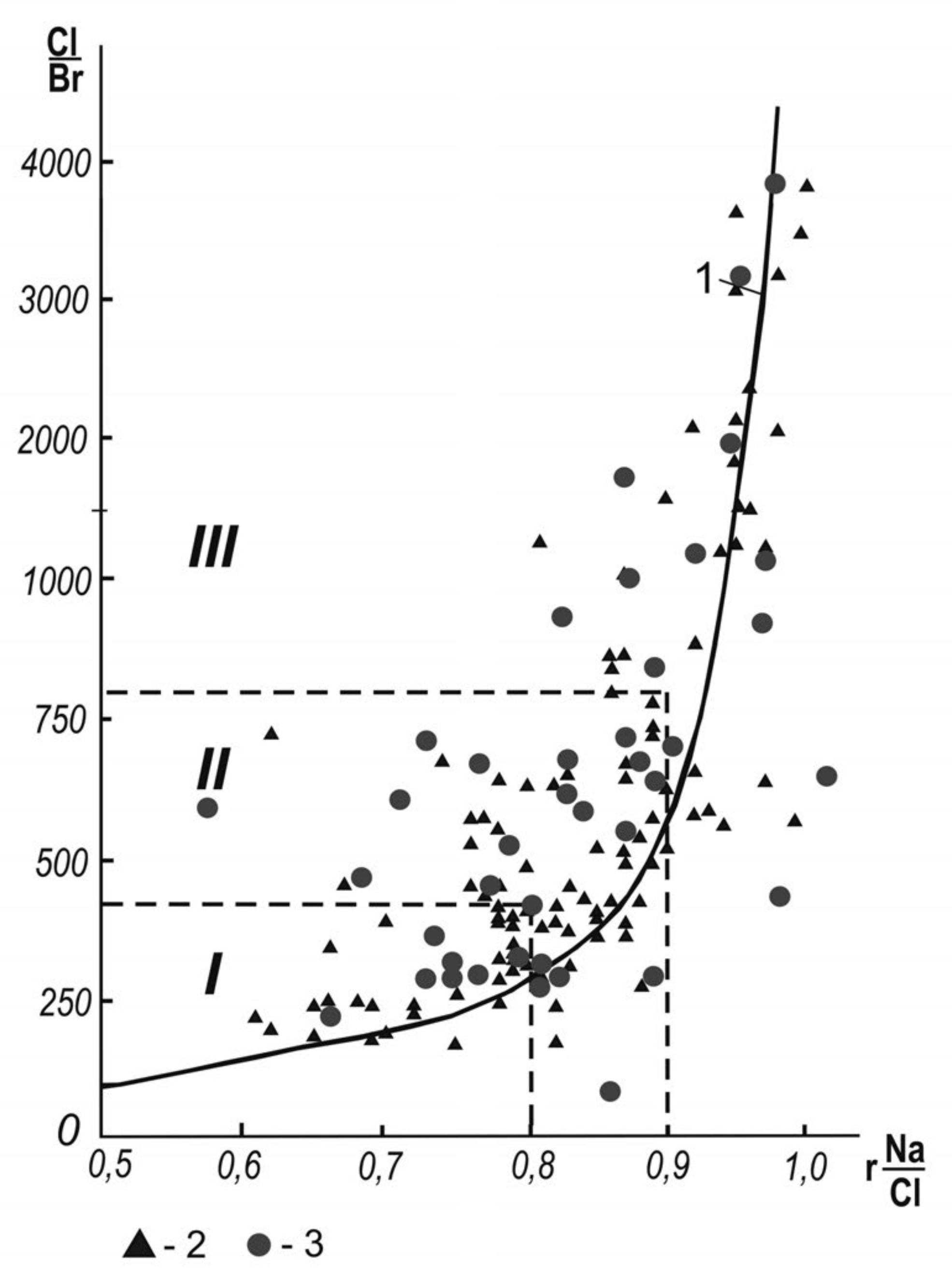

Fig. 4. Brines genetic separation graph of Lower Permian sediments of the Dniprovsky Artesian Basin:
1 – line of average values for the Lower Permian Cl/Br and Na/Cl coefficients; 2 – the actual value of the Cl/Br and Na/Cl Lower Permian waters coefficients (according K.M. Varava, 1977 [15]); 3 – the actual value of the Cl/Br and Na/Cl coefficients (according to data compiled by the authors); I-III – fields of genetic types of brines: I – origin, II – mixed, III – leaching.

As a result of the comparison of the total salinity and Na/Cl ratio there are two brines groups, in which Na/Cl ratio decreases (Rozpashnivska and Melyhivska area) or increases (Kopylivska, Chutivska, Bohatoiska, Riabukhinska, Shebelynska area) with salinity increasing.

Mixed type brines dominate within research area. As it can be seen from the ratio graph between Cl/Br and Na/Cl coefficients, mixed type brines dominate (Fig. 4).

Redistribution and solution mass of brines is made by mixing brines of different stages of generation among themselves and with connate brines and dehydration waters (catagenetic transformation of clay minerals and gypsum-anhydrite transition reactions) (Yapaskurt, 2005). The basic mechanisms of groundwater inflow into subsalt and intrasalt layers are gravity seepage of heavy brines down and lighter water upwards (through pores, cracks, fractures and contact zones of salt dome structures) (Makhnach, 2000).

As a result, different genesis brines inflow into the subsalt and adjacent deposits causes geochemical balance violation within «fluid (brine)-rock» system, which leads to changes of the oxidation-reduction conditions, thermal balance, enhance of the processes of diffusion, dissolution, leaching, precipitation, ion exchange (exchange adsorption), osmosis, redox reactions, thermobarogeochemical transformation of organic-mineral complex with the release of sediments into groundwater and withdrawal of other substances from water solutions and others (Babinets, 1961, Gutsalo, L.K., Krivoshiya, 1969, Shvartsev, 1997). The combination of these processes against the background of diverse lithology of accommodative rocks and halotectokinetic activity causes groundwater chemical composition inconsistency within research area.

CONCLUSIONS

Consequently, regularities of spatial hydrogeochemical peculiarities and correlation of rocks lithological composition with chemical composition of brines of the Upper Carboniferous – Lower Permian water-bearing complex have been established. Inconsistency of chemical composition of groundwater in the area and cross-section has been determined.

Groundwater of Lower Permian sediments is represented by highly salinity 55,86-312,61 g/L mainly of chloride calcium-chloride type, sodium chloride composition. Salinity maximal values (256,65-312,61 g/L) are observed in areas adjacent to the salt domes (Kopylivskyi, Chutivskyi, Rozpashnivskyi, Lannivskyi, Sosnovskyi, Riabukhynskyi, Shebelynskyi and Spivakivskyi), indicating the impact of leaching brine directly through the contact area and/or the possibility of hydraulic connection between permeable layers even under very difficult water exchange conditions. The minimal values of salinity (55,86-112,0 g/L) are confined to space between salt domes and/or fractured anhydrite brines.

On the basis of the constructed maps of the Na/Cl ratio distribution, zones of origin, mixed type and leaching brines have been distinguished. Origin brines are spread in the north-western and south-eastern parts of the research area, Na/Cl ratio varying from 0,46 to 0,79. Mixed type brines are spread from the south-west to north-east, Na/Cl ratio varying from 0,80 to 0,89. Leaching brines are distributed locally and are mainly adjacent to salt domes, Na/Cl ratio varies from 0,94 to 1,09.

Therefore, violation of geochemical balance in the «fluid (brine)–rock» system is a result of different genesis brines inflow into the subsalt and adjacent strata: which leads to changes of the oxidation-reduction conditions, thermal balance, enhance of the processes of diffusion, dissolution, leaching, precipitation, ion exchange (exchange adsorption), osmosis, redox reactions, thermobarogeochemical transformation of organic-mineral complex with the release of sediments into groundwater and withdrawal of other substances from water solutions and others. The combination of these processes against the background of diverse lithology of accommodative rocks and halotectokinetic activity causes groundwater chemical composition inconsistency within research area.

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