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Characteristic traits of hydrochemical processes in continental reservoirs

Traits of hydrochemical processes in continental reservoirs of arid zone, which differ from such gumid districts are displayed.
Kazakhstan continental closed reservoirs Balkhash, Sasykkol and Alakol lakes accumulate river water, ground water and aerial water. Confluence of waters with each other and with the water of these lakes causes both physical mixing and metamorphization processes, causing generation of contemporary saline composition of lake water. Leading role in metamorphization of chemical composition of natural waters plays wind mixing and oxygenation of water layers; alongshore movement of drifts, their flotation (abrasion, segregation), and also saturation of water with colloid-clay substances.
Keywords: hydro chemical regime, hydro chemical processes, continental reservoir, quality of natural water

Introduction

In Balkhash lake and Pribalkhash lakes hydroecological state is changing seriously, mainly under the influence of anthropogenic factor. As a result there are the processes of desertification of huge territories and aggravation of ecosystems. In perspective the situation could be worse, as the water consuming will increase with development of some national economy spheres. Therefore, concern for hydroecological safety of Kazakhstan appears. That's why, by UNESCO proposal, Balkhash lake and other objects are included into the international list of the top line systems, required to be investigated and secured.

Nowadays, negative ecological phenomena have macroregional or zonal-regional importance and their studying is actual.

Continental lakes of Balkhash – Alakol kettle long since attracted attention of investigators, but, from the hydrochemical point of view they started to be investigating in years 1940 – 1950. Summarizing the results of long-term multiple investigations, conducted by the famous scientists and their followers, Strakhov N.M. [1], Sapozhnikov D.G. [2], Konshin V.D. [3], Tarasov M.N. [4], Beremzhanov B.A. [5], Romanova S.M. [6,7], Tursunov A.A.[8], Amirgaliyev N.A. [9] and others, revealing various aspects of regional and applied hydrochemistry (saline balance, formation and dynamics of bottom deposits, forecasts and others) with regard to continental reservoirs, we'll try to show some distinctive features of the leaking chemical processes and water compositions.

Kazakhstan continental closed lakes, Balkhash, Sasykkol and Alakol, accumulate river water, groundwater and aerial water. Mixing with each other and with lake water – is not just a simple physical mixing, but also a chemical process, causing generation of recent saline composition of lake water. These processes are united into the common conception "metamorphization". In metamorphization of chemical compositions of natural water the main role is for: wind mixture and oxygen saturation of water masses; alongshore movement of drifts, their flotation (abrasion, segregation), saturation of water with colloid-clay substances and some other processes.

There are no any investigations, considering processes, stipulating formation of hydrochemical regime and water quality of continental reservoirs of arid zones, affected by anthropogenic factors, as the comprehensive whole, in their interconnection, with their peculiarities and dependence from environment. This fact does not allow obtaining holistic approach

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to the water reservoirs hydrochemistry. It causes necessity in materials systematization and defines the nature of the article.

Materials and investigation methods

Balkhash lake object is chosen for problem solving – typical closed continental water reservoir of arid zone.

Special attention was paid for carbonate generation processes, progressing under the natural conditions and under isothermal evaporation and cooling of waters. Water ability to dissolve or isolate $CaCO_3$ depends on water saturation rate. If the water is not saturated with $CaCO_3$, it cannot dissolve carbon-containing substances. If the water is over-saturated with $CaCO_3$, $CaCO_3$ can precipitate under the definite conditions.

For the investigation period there were organized 10 expeditions for Balkhash lake and 5 hydrochemical surveys of lake water area. For chemical analysis there were taken 1500 samples of lake water from 5-7 kilometers network. Besides, in different years there were conducted observations for regime of chemical composition of instable components of reservoirs water every 2 hours within 2 days. Deep-water sampling was taken by Molchanov Batometer GR-18, and bottom sediments were taken by the Petersen bottom grab DCh-0,025, soil samples were taken by device for basic soil monoliths sampling.

Considering space distribution of chemical composition elements in Balkhash lake water, there was used lake water area hydrochemical regionalization by the method of Tarasov M.N. [3]. To find out vertical stratification of the components of water chemical composition there were taken samples in surface (0,5 m) and near-bottom layers.

According to recommendations [10], estimation of instable water components (pH, HCO_3^-, CO_3^{2-}, NO_2^-, NH_4^+, oxidability, O_2, CO_2) was made right after the sampling, and estimation of the rest – in the laboratory after preserving samples with definite reagents.

Usual hydrochemical practical methods were used for identification of chemical water composition components. Verification of the stated methods showed, that percentage of errors didn't increase acceptable errors values. All samples of water and soil were analyzed in 3-4 reiterations at least. Mathematic processing was applied for reliable summary [11].

Near-bottom sampling analysis was made according to the guideline [12]. Calculation of carbonate-calcium balance components was made by the method and recommendations of Alyokin O.A., Moricheva N.P., [13] and author [14] not considering generation of ionic pairs and combinations.

For more precise quantity estimation of salt crystallization there was made laboratory investigation on isothermal evaporation and polythermal cooling of Balkhash lake water. There was used the method, proposed by the scientists of International scientific investigation institute of halurgy and Kazakh National state university named after al-Farabi [15]. In the course of water evaporation out of concentrated solution there was made sampling of liquid phases and separation of sediments. Liquid and solid phases were analyzed on main ions content.

Studying of hydrochemical processes, including salification and salt accumulation, terms and processes of formation and transformation of water composition, affected by various factors, is in close dependence with theoretical basics of hydrochemistry.

Investigating the questions, we were leading by studying of Academician Kurnakov N.S. about physics-chemistry analysis applicable to natural waters, brines and salts, developed by his students and followers both in Russia, Kazakhstan, Kirgizstan, Uzbekistan and in far abroad countries.

As natural waters are essentially the solutions of mineral and organic nature, they are considered as naturally balanced physics-chemical systems, containing water and compounds, dissolved in it. There also applied laws and theories of solutions and individual matters.

The studying of processes of formation and accumulation of salts, conditions and processes of formation, transformation of water content under the influence of different factors is very involved with theoretical principles of hydrochemistry.

To them laws and theories of solutions and individual substances (first of all laws of masses, thermodynamics, heterogeneous equilibriums, equivalents, the theory of strong and weak electrolits, electrolytic dissociation, and also theories of a structure of substances, chemical bond) are applicable.

Peculiarities of hydrochemical processes of arid zones reservoirs

By increasing total water mineralization of Balkhash, Sasykkol and Alakol lakes upon their length, the concentration of individual ions is changing in a peculiar way. The count of chlorine coefficients for Balkhash lake showed, that carbonate ions concentration increases from the west to the east: there are no any in west part, they appear in the region from Tas-aral bay up to the narrow spot between west and east parts of the lake (channel Uzyn-aral or Sary-Esik), and in eastern area the water is intensively enriched with carbonates. Chloric coefficients of bicarbonate and calcium ions are going down continuously. Sulphate and magnesium ions rate is low in west-end area, and gradually increase in eastern direction, achieving high value at the east of Tas-aral and keeping the level over the whole lake length, decreasing a little in east-end. The processes with bicarbonate and calcium ions, causing calcite sediment, can happen even in west part with mineralization about 2 g/l, and the processes with magnesium ion also, contributing to sediment of magnesium carbonate or dolomite, can happen only in eastern stretch, where water mineralization does not increase 5 g/l. Such discrepancy between growth of individual ions concentration and whole mineralization growth can only be the pointer of metamorphization process and is one of the peculiarities of arid lake.

It is well known fact, that in humid lakes, the salts precipitate at high mineralization and concentration of individual ions (higher, than 10 g/l). In World ocean and Caspian sea water with total salt value about 30 g/l, the salt precipitation happens only in deep water of the ocean and Karabogazgol bay with mineralization, much higher, than 50 g/l /8/. In the lakes of arid zone, salt precipitation happens at much lower mineralization and it differs them from humid zones reservoirs.

In bays, seasonally running into Balkhash, where salts sum achieves 16 g/l, there is precipitation of both carbonates and sulphate. And for intensive fall of Aral lake water level and sharp growth of salinity, the simultaneous precipitation of carbonates, sulphates and chlorides appears. Instead of expected hard crust of harmless carbonates there appeared marsh and crust-plump saline lands, easily scattered by wind onto huge distance [16].

The process of fast precipitation of salts in continental lakes is stipulated, most probably, by shallow reservoir, high insolation, arid climate, intensive mixing of water masses, e.i. by morphometric and climate factors.

Considering reasons and content of water chemical composition metamorphization, it is necessary to be guided by significant achievement of Kurnakov N.S. academician about directed change of reservoirs water and brines chemical composition under the metamorphization. The considered reason of lake water metamorphization is a mixing of various types and concentrations of water, and also appearance of colloid clay materials, containing absorbing complex. It is proved, that [4-7] main role in salts precipitating for relatively low mineralization is played by suspengel – the smallest particles of sediments, appearing due to constant turbulent water mixing by wind waves, their flotation in coastal zone, mud and bottom sediment detachment, abrasive aging of huge drifts during alongshore mixing. Besides, suspengels are great sorbents for various macro and micro components, gases; they are also catalysts of a number of chemical reactions, particularly, carbonate formation and they take part on hydrochemical processes. As a result of this process there is a formation of solid salts and relatively clear water, and arid reservoir is cleaning from salification. By other words, self-preservation mechanism comes into effect, when turbid water of arid water reservoir and rivers, containing clay colloid material, through a number of chemical reactions and physical processes clean water from solute mineral and organic substances.

Arid lake contains sulfate, sulfate-carbonate lake waters, (more mineralized, as a rule) carbonate and sulfate waters of underground feeding, and also sulfate and carbonate waters of atmosphere precipitation. These waters are mixing with lake sulfate water. For blending these waters, the leading one is mixing of carbonate and sulfate waters, as a result there are double exchange reactions, leading to hardly reversible change in chemical composition, i.e. waters metamorphization. Composition of carbonate waters (especially groundwaters) includes sodium carbonate. It is generated in result of alkanization, and also of weathering of feldspar, and then it is washed away by groundwater and reacts with calcium and magnesium sulphate from water sulphate. It leads to precipitation of calcium and magnesium carbonates, and Balkhash lake water,

same as Alakol lake water, is being enriched with sodium sulfate.

Influence of underground and ground waters on the hydrochemistry of reservoir is as follows. Special hydrochemical investigations showed, that in shore parts of most arid zones there are quite wide and deep depression of underground waters level [17]. These depressions are caused by «fuse effect», more intensive water evaporation from the surface of ground stream, coming close to the reservoir. It is also found out, that middle-depression water level, with the square, comparable to the western part of Balkhash, is accordingly 7,0 m lower, than Balkhash lake water level. Considerable masses of salt are directed from lake shore zone to the depression side because of such depression and strong filtration stream.

By mind of the Professor Tursunov A.A., this factor is one of the main expenses of salt balance in arid reservoirs. Same depressions appear at the shore of other continental lakes and water reservoirs of Kazakhstan.

In common, the metamorphization way of all types of water and brines, Mr.Balyashko M.G. states as follows:

$$P_1 + P_2 \leftrightarrow P_3 + \text{solid phase},$$

where P_3 – metamorphized water. As Mr. Beremzhanov B.A. proved, such reactions can take place both in arid reservoirs and in rivers and groundwaters at definite conditions.

It is possible, that in slightly mineralized parts of lakes and streams, feeding the lake, these reactions will be much slower, but in result of mixing length, calcium and magnesium carbonates accumulate, and lake water is being enriched with sodium sulphate [5].

In investigating lake waters there is calcium hydrocarbonate. Until now, metamorphization effect of calcium hydrocarbonate was related to various reactions of double exchange:

1. Valyashko reaction:

$$Ca(HCO_3)_2 + MgSO_4 \leftrightarrow CaSO_4 + Mg(HCO_3)_2$$

$$\downarrow \qquad \downarrow$$

$$CaSO_4 * 2H_2O \quad x\,Mg(OH)_2 * y\,MgCO_3 * z\,H_2O + CO_2$$

2. Gaidinger reaction:

$$2Ca(HCO_3)_2 + MgSO_4 \leftrightarrow Ca, Mg(CO_3)_2 \downarrow + CaSO_4 * 2H_2O + 2CO_2$$

3. Marinyack reaction:

$$2Ca(HCO_3)_2 + MgCl_2 \leftrightarrow Ca, Mg(CO_3)_2 \downarrow + CaCl_2 + 2H_2O + 2CO_2$$

4. $2Ca(HCO_3)_2 + MgSO_4 + Na_2SO_4 \quad Ca\,Na_2(SO_4)_2 + Mg(HCO_3)_2$

$$x\,Mg(OH)_2 * y\,MgCO_3 * z\,H_2O + CO_2$$

Special investigations of the authors showed, that all these reactions really happen, but by the quantity of solid phases the leading place is for Valyashko reaction. Gypsum and basic magnesium carbonate are of 99% of newly-generated sediment. When the concentration of magnesium sulphate in solution is small, the reaction does not happen, and only calcium hydrocarbonate decomposition happens. But in main mass, in Balkhash water, because of high concentration of hydrocarbonate and carbonate ions by definite binding calculation there are a little ions of magnesium sulfate; and therefore here simple decomposition of calcium hydrocarbonate takes place.

As it was stated above, waters, coming into the lakes, usually bring high quality of suspended

mineral substances, including cation exchangeable particles. River and ground waters of carbonate type bring colloid-clay particles, their absorbing complex is characterized by abundance of calcium. The absorbing complex, contained in colloid-clay particles, comes to the waters mixture and can provoke cation exchange, leading to the settle of sparingly soluble salts and growth of relative concentration of sulfates. Therefore, metamorphization of water, caused by ion-exchange reactions, also leads to calcium carbonate settling.

Speaking about lake water metamorphization, so-called "off-shore metamorphization", it should be taken into account, as it directly affects the change of lake water composition (term «offshore» metamorphization was first proposed by Beremzhanov B.A.). Balkhash has very irregular shore with lots of bays. Due to periodical fluctuations of lake water level, when it sinks, the bays, lakes and lagoons, separated from Balkhash, get their own life. Water in them is heating quicker and stronger and evaporation layer is higher here, than in open reservoir. In this relation, lake water, naturally the saline, gradually concentrating, interact with air carbon dioxide, with shore and bottom rocks and coming in surface and ground waters. Concentration gradient appears, and, due to molecular effects, it provokes higher salt migration from central parts of water area into the shore zones. When wind direction changes and water set-down, huge squares of shallow water dry, hydrocarbonates transform into carbonates, due to the «fuse» effect, salts come to the surface, and dry, generating white coating. Wind makes it job by «Aeolian desalination». All these processes lead to water metamorphization in separated lakes.

At next growth of Balkhashe water level, the separated lakes sink and the salts dissolute in them. But the main lake water doesn't get the salts, that separated from it. Reuniting, they affect Balkhash water methamorphically, in dependence with depth of processes, taking part in separated lakes, and with the time length, during which they were separated, changing their type.

Colloid clay material, accumulated in separated lakes and absorbing complex, containing in them, mixing with Balkhash water, also metamorph it through cation exchange.

It should be said, that except long-terms cycles there are some short-term periodic level ups and downs inside these cycles. Besides, on the lake there are spring tides ups and downs. All these long- and short term separations of some Balkhash water in form of big and small lakes lead to the whole or partly metamorphization, hereinafter called as offshore metamorphization of lake water. Special investigations of year 1986, made by the article author showed, that in one of half-separated bay of 5 km length, mineralization increased from 4,2 g/l up to 9,9 g/l. That time water mineralization of separated bays from Balkhash achieved 76,1 and 88,3 g/l. The same phenomena observed also in other arid reservoir, Chany lake. Here water salinity is continuously increasing by distance from Malyi Chany lake (1,17 ‰) up to Yaroslavskiy stretch (7,85 $\%_o$, Yu.D. Mikhailov). Salts sulfate fall out in water deep layers by such mineralization values. Thank to such phenomena, many Balkhash lakes served and serve as natural salt source. Perceptiveness of Balkhash lake was pointed by Grokhovskiy L.M. in year 1963, he counted total reserve of mirabilite and tenardite in lakes, it is equal to about 10 mln.t. [18].

Such metamorphization cannot be neglected, as up to 7 % of water or more, than 2 mln. tons of Balkhash lake salt annually consumed for separation and infiltration into the shores [4].

Bottom salts sediments, particularly, calcium and magnesium carbonate in arid and humid lakes behave in different ways. In relatively deep humid zone reservoirs, where evaporation layer does not increase precipitations, in depth and at the bottom, quite high concentration of carbon dioxide, biocenosis vital activity product, accumulates. Settling insoluble carbonate, coming to the bottom, interacting with carbon dioxide, transforming into the soluble hydrocarbonates. Concentration of the latter can grow gradually.

In arid zone reservoir the situation is different. Zoobenthos and other types of biocoenosis here accumulates not at the bottom, but in shallow water, well protected from wind and damaged straight sun beams. These water areas contain a little carbon dioxide. Besides, because of strong wind mixing of water, degassing of carbon dioxide happens. In this connection, calcium and magnesium carbonates, other salts, freely achieving bottom, can stay in bottom sediments for a long time. The proposal is proven experimentally.

In result of sulfate and carbonate interaction of water and ion exchange, peculiar for continental reservoirs only, there was generated salt composition of the contemporary water of Balkhash and Alakol

lakes. The abovementioned proves, that composition of these lakes water should have characterizing peculiarities. One of water composition peculiarity is relatively small content of common salt. Its content in Balkhash and Alakol water is twice lower, than of Caspian and Aral sea, and in comparison with Black sea and Ocean water – it is almost 2,5 times less. Along with low content of common salt, the water has high value of sulphate-chlorine – chloric coefficient SO_4^{2-} /Cl^-. The value of this coefficient for Balkhash water is 1.5 times higher, than for Aral water, is 2,5 times higher, than Caspian water, 10 times higher, than ocean and Black sea water, and for Alacol water it is much higher.

The other very interesting peculiarity of arid zone lakes water is content of magnesium ion, which has approximately same sum of ions, as in Caspian and Aral seas, but content of magnesium sulfate in Balkhash water is two times less, and in Alakol water it is 8 times less.

One more peculiarity in the studying lakes water is absence of dissolved calcium sulphate (gypsum).

For the period from year 1956 till year 2007 total mineralization of water of Balkhash closed lake increased from 2,43 till 4,02 g/l, that take the lead over prediction values [7]. For the lake the typical horizontal differentiation of mineralization is constant (growth by more than 4 times), vertical stratification appears very rare in connection with strong wind mixing of water masses. There was found close interrelation between concentration of main ions and mineralization, allows to finding components of water chemical composition by calculating annual water content.

As it was stated above, one of the unique features of Balkhash lake is well-expressed metamorphization of water chemical composition, favour salification and salt accumulation. The process of carbonate generation in Balkhash lake is 10 times intensively, than in other closed water reservoirs of arid zones. The water is oversaturated with calcium, oversaturation is unequal and is increasing along the eastern area in various years (1941-2001) from 3,00 up to 32,7. Balance calculation of magnesium and calcium carbonates for year 1985 showed, that annually in lake water 4,47 mln t. precipitates, 2,46 – in the western part and 2,01 mln. t. in eastern part.

Investigation of salt crystallization during the process of water concentrating in continental lake Balkhash by the method of isothermal evaporation (298o K) allowed us to precisely define and supplement the before stated [15] order of precipitation and accumulation of magnesium and calcium carbonate, which differs from the sea way. The quantity of calcium carbonate, precipitating due to evaporation, is insignificant (50 and 126 thousand t.) and for Western (WA) and Eastern (EA) lake areas is equal to 0,11 and 0,05 % accordingly from the total salt volume [7]. Polythermal cooling in water of WA causes generation of 0,20 mln.t. (0,12 %) $CaCO_3$, and EA – sum of $CaCO_3$ and $MgCO_3$ of 0,27 mln.t. (0,46 % from the total volume of salts). Due to that, for the salt balance of the lake it is required to consider precipitating carbonates for both evaporation period and freeze-up period. Ice cover of Balkhash lake, containing dissolved substances (0,25-5,03 g/l), contributes to some growth of mineralization of under-ice water and affects hydrochemical and hydrobiological processes.

There was defined participation of bottom sediments (mean salt alkaline lands and sludges) of Balkhash lake in salification process. In the systems «Balkhash lake water– bottom sediments», «water -clay» there are complex physics-chemical processes (cation exchange, hydrolysis, oxidation – reduction, exchange reactions, leaching and others), causing precipitation of calcium carbonate and raised over-carbonation (up to 26 %). It leads to some water desalination. Quantity of CaCO3, generated through cation exchange, is small (0,45 %) in comparison with its total concentration in sludge (10,5 %) [19-21].

The investigations made have practical application. The results of a number of works are included into the Hydrochemical information Bank of Kazakhstan and Russia, Yearbook on Quality of surface waters and effectiveness of the activities on the territory of Kazakhstani UGKS for years 1987-1990 and State Water Cadastre «Annual data on quality of ground waters».

Conclusion

1. Pointed peculiarities of water composition in accordance with other features should stipulate specific character of hydrochemical rate and water quality of drainless water basins of arid zones, and also composition of salt lakes, made of this water.

For Balkhash lake, accumulating flow of water of various types and concentrations, in long-term cycle (years 1958-2007) characterized horizontal mineralization stratification is constant (4-7 times

growth) and ionic composition (unequal growth (2-15 times), and for Ca^{2+} ions 2-4 times decrease). Vertical stratification appears very seldom due to strong wind mixing of water masses, saturated with oxygen and colloid particles. Other unique feature is sharply expressed metamorphization of chemical composition, leading to various-type processes with evident participation of all the main ions, except Na^{+} and Cl^{-}. Carbonate formation is especially intensive (10 times stronger, than in other basins of arid zones). During year 1985 there was precipitated from water about 4,47 mln.т of calcium and magnesium carbonates, keeping on the basin bottom, in insignificant presence of free carbon dioxide or in absence of it. Metamorphization processes didn't lose their intensity even under the strong anthropogenic influence.

2. By the isothermal evaporation method (298^0K) of Balkhash lake water, the process of calcium and magnesium carbonates precipitation was specified and complemented. Quantity of these salts, precipitating through evaporation, is 0,11 for WA and 0,05% for EA, and precipitating through polythermal cooling - accordingly, 0,12 and 0,46% from total salts reserve.

3. There was stated a line of complicated physics – chemical processes in the systems «water – sludge of Balkhash lake», «water-clay», some of them cause $CaCO_3$ precipitation. So, cation exchange causes, accordingly precipitation of about 0,45% carbonates. Biochemical reactions cause precipitation of 0,8 g of carbonates from 1 l. of lake water.

4. Shallow arid reservoirs, intensive wind mixing of water masses, influence of solar radiation in many cases favors absence of vertical stratification of almost all components of chemical composition, that differs them from humid areas basins.

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