International Journal of Design & Nature and Ecodynamics
Vol. 17, No. 5, October, 2022, pp. 691-700
Journal homepage: http://iieta.org/journals/ijdne

Chemical Analysis of Groundwater and Wastewater in the Area of the Tengiz Deposit of the Atyrau Region of the Republic of Kazakhstan

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https://doi.org/10.18280/ijdne.170506

Received: 29 July 2022
Accepted: 6 October 2022

Keywords:
Tengiz deposit, groundwater and wastewater, chloride anion, sulfate anion, sodium and potassium ions

ABSTRACT

This article analyzes the content of the chemical composition of groundwater and wastewater of the Tengiz deposit located in the Zhyloy district of Atyrau region of the Republic of Kazakhstan. This analysis is necessary to determine the deposition of inorganic salts in oilfield equipment. The analysis shows that the content of chloride anions and magnesium cations prevails in groundwater and wastewater. Thus, the content of chloride anions exceeds the content of other anions up to 2-3 times of sulfate anions in groundwater and wastewater and up to 2.5-5 times of bicarbonate anions in groundwater and 17-27 times in wastewater. Among the cations, the maximum values are characteristic of magnesium cations, whose content exceeds the calcium content by more than 3.5 times in wastewater and more than 6.5 times in groundwater. In addition, the magnesium content exceeds more than 5 times the content of the sum of sodium and potassium ions. Thus, according to the results of the study, it was determined that the main salts affecting the oilfield equipment at the Tengiz field are magnesium chloride salts.

1. INTRODUCTION

After many years of independent development, Kazakhstan has become one of the world's leading oil producers and exporters, has the richest reserves in the Caspian Sea region and is one of the largest oil producers in the world. It ranks 12th in undiscovered oil reserves and 17th in oil production [1, 2].

A group of oil fields on the northeastern coast of the Caspian Sea, which includes Tengiz, is located in an area that, even without industrial development, belongs to specially protected areas. This is due to the fact that the main landscapes of the area were formed recently, and therefore their ecological balance is easily disturbed by anthropogenic interference.

Administratively, the Tengiz field is located in the Zhylyoy district of the Atyrau region of the Republic of Kazakhstan. The nearest town is Kulsary, located 110 km northeast of the Tengiz field. The regional center – Atyrau is located 150 km away [3].

Geographically, the field is located in the southeastern part of the Caspian basin, in the oil-bearing region of the Southern Emba. The main part of the reserves explored in this area is confined to the subsalt part of the Paleozoic section along the periphery of the basin.

The industrial oil capacity of the Tengiz field was established by the well T 1, in which in 1981, during a short-term testing of the interval 4054-4095 m, an oil inflow with a flow rate of over 100 m^3/day was obtained.

The Tengiz deposit is an isolated carbonate platform consisting of carbonate deposits of early-Middle Carboniferous age located on a common Devonian carbonate base [4]. In stratigraphic terms, the exposed section of the sedimentary strata is represented by sediments from Upper Devonian to Quaternary formations. Tectonically, the Tengiz field is located in the southern part of the Caspian oil and gas province and is confined to the Tengiz-Kashagan seism geological region.

Reservoir waters of oil fields always contain salts, some organic substances and gases dissolved in one or another amount [5]. The salt composition of the waters is characteristic of a certain horizon of this deposit. It should be noted, however, that the salt composition of waters in the oil-bearing horizon is not the same for all parts of the structure (in close proximity to oil and gas, the salt composition of waters is usually different than on the wing of the structure).

During the operation of wells in the field, corrosion of equipment may occur due to the presence of corrosive components in the products.

The research of the mechanism of deposition of poorly soluble inorganic compounds on the surface of oilfield equipment is devoted to the work of many researchers [6, 7]. First of all, it should be noted that the process of deposition of inorganic salts in oilfield equipment is a special case of mass crystallization of insoluble salts from their solutions supersaturated under certain thermodynamic conditions.

According to many researchers, the feeding area of the Tengiz field aquifer complex is the Ural-Mugodzhar mining and folding structure located 320-360 km east of Tengiz Square. The movement of groundwater occurs in the western and south-western directions towards the Caspian Sea. The formation waters of the subsalt part of the section (deposits of carboniferous and Lower Permian age) were studied in the Desert and Karaton areas adjacent to Tengiz, where they are represented by strong brines, the mineralization of which reaches 320 g/l. Hydrogeological data on the Karaton area, characterizing the section from the Tournaisian to the Lower Permian age, indicate the hydraulic connection of this range of deposits [8]. In the stratigraphic section of the Tengiz deposit, two hydrogeological floors are distinguished: the upper one is above–salt and the lower one is below–salt [9]. The upper hydrogeological floor is characterized by relatively low mineralization of reservoir waters, as well as low values of reservoir pressures close to hydrostatic; the lower hydrogeological floor is characterized by abnormally high reservoir pressures, as well as high mineralization of reservoir waters.

Studies on the content of the chemical composition of underground and wastewater will allow you to pay attention to the salinity of soils and high levels of chlorides in the soil to determine the degree of aggressive impact of groundwater and wastewater on the reinforcement of reinforced concrete structures by the content of sulfates and chlorides.

2. MATERIAL AND METHODS

2.1 Study area

The location of geotechnical borings (BH, CPT) has been determined on specified area according to the coordinates on the drawing provided by TCO prior to field investigation commencement.

This geotechnical report contains the site MMWP 48-1 data (Figure 1). The following types ofgeotechnical surveys have been performed at the site:

- Field works;
- Laboratory works;
- Office works.

The location of geotechnical borings has been set/established by the SRDI Caspiymunaygas JSC Topographic-Geodetic Service.

The numbers, coordinates, marks, depths of engineering-geological wells and the total number of ground water samples taken are presented below, in the form of Table 1.

During the production of engineering and geological exploration, 2 types of water were found within the investigated area: sewage and groundwater.

Wastewater is extracted from trenches and ditches for groundwater dewatering during construction works, and then with the help of sewage collectors it is drained to the projected landfill site. The depth of wastewater in the varietal section is 0.20-0.40 m. above the daytime surface, by chemical composition they belong to the brine group, a subgroup of strong brines.

Groundwater within the investigated area is uncovered by all passed engineering and geological workings (drilling wells). The groundwater level in the range from 0.40 m to 0.80 m. and by chemical composition belong to the brine group, a subgroup of strong brines.

(a) The scale 1:25000

(b) The scale 1:5000

Figure 1. The location of the investigated area

2.2 Methods

The boreholes have been drilled at the sor site MMWP 48-1 by means of all terrain drilling rig “ARDKO” (Country of manufacture - USA). Borehole drillings are supportedwith casings. Drilling diameter is up to 108mm.

Measurements of the steady-state groundwater level (UGV) and sampling of groundwater were carried out using the PE-1220 sampling device.

The groundwater level has been measured at all open boreholes at the time of drilling completion and 24 hours after drilling completion. The values shown on the borehole logs are the ones measured after 24 hours [10].

The groundwater level (GWL) measurement and groundwater sampling have been done by means of PE-1220 sampler [11].

The boreholes drilling were provided during the period from 30.11.2021 to 08.12.2021.

Determination of the content of sulfate andchloride ions was carried out in the geotechnical laboratory of JSC "NIPI "Kaspiymunaygas", according to the following methods: GOST 26426-85. “Soil. Methods for determining the sulfate ion in an aqueous extract” and GOST 26425-85. “Soil. Methods for the determination of chloride ion in an aqueous extract”.

Table 1. The numbers, coordinates, elevations, depths of geotechnical boreholes and total number of groundwater samples

ItemNo.	Borehole No.	Borehole coordinates		Elevations ofborehole, m	Borehole depth,m	Ground water sampling
		E	N			
1	B48-1-04	684626.08	5102679.06	-26.47	10.0	1
2	B48-1-07	684625.96	5102553.91	-26.53	20.0	1
3	B48-1-08	684826.02	5102553.97	-26.51	20.0	-
4	B48-1-11	684826.01	5102429.00	-26.51	20.0	1
5	B48-1-12	685026.04	5102428.97	-26.51	20.0	1
6	B48-1-15	685025.92	5102303.89	-26.46	20.0	1
		TOTAL 6 WELLS			110.0	5

The statistical processing of obtained and collected information is, first of all, based on the Interstate standard “GOST 20522-2012. Soils. Test results statistical processing methods”requirements, and also other fundamental State and Interstate regulations and legislative instruments.

For most simple measurements, the so-called normal distribution law of random errors (Gauss' law) is performed well enough. In this case, the order of calculation of random errors can be taken as follows.

1. Measurements of a given physical quantity are carried out n times under the same conditions.

2. The arithmetic mean value x of the measured value x is calculated:

$$\bar{x}=\frac{1}{n}\sum_{n=1}^{i}x_i \tag{1}$$

3. The absolute errors of each of the n measurements are calculated:

$$\Delta x_i = |\bar{x} - x_i| \tag{2}$$

4. The squares of absolute errors are calculated $(\Delta x_i)^2$ of each dimension.

5. The average quadratic error (also called the mean quadratic deviation) of the arithmetic mean is determined:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} \tag{3}$$

6. The value of the confidence probability *a* is set. (Since random errors are caused by random causes, it is fundamentally impossible to specify exactly the interval in which the measured value is enclosed. This interval can be specified only with a certain probability a, called confidence probability.) In the practice of academic work, the value of a is chosen to be 0.90÷0.95, and in critical cases – 0.99 or more.

7. According to the selected confidence probability *a* and the number of measurements *n*, the student coefficient $t_a(n)$ is determined.

8. The confidence interval *Dx* is determined:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) \tag{4}$$

9. The final result is recorded as:

$$x = \bar{x} \pm \Delta x \text{ with } a = \cdots \quad E = {}^{\Delta x}/_{\bar{x}} \tag{5}$$

Table 2. The measurement error rates (at the level of the water quality standard) of the composition and properties of natural and wastewater [12]

Water quality standard, mg/l	Error rates±$\delta_н$, %
Up to 0.00001	80
From 0.00001 to 0.0001 inclusive	70
Over 0.0001 to 0.001	60
From 0.001 to 0.01	50
From 0.01 to 0.1	40
From 0.1 to 1	35
From 1 to 10	30
From 10 to 100	25
From 100 to 500	20
From 500 to 1000	15

The measurement error rates (at the level of the water quality standard) of the composition and properties of natural and wastewater are given in Table 2.

3. RESULTS AND DISCUSSION

An artificial waterlogging of the territory because of huge volume of water leaked from damaged utilities and other water using facilities within the boundaries of large industrial areas, oil field areas, service-utility facilities, unregulated discharge of waste water, irrigation of planted land, etc. is more powerful nutrition source of water bearing stratum over the last ten years due to intensive industrial development of the Caspian Sea (Peri-Caspian) area [13]. This phenomenon results in a considerable rise of GWL, reduction of its mineralization, deterioration of the geological and environmental conditions [14]. An impermeable stratum as clayey soils that occurs at the shallow depth may facilitate the rapid rise of the water table (GWL) and formation of “perched water table”.

The groundwater and wastewater samples chemical analysis results are shown below in the Figures 2-17.

Chemical analysis of groundwater

Figure 2 shows the composition of the chloride anion in groundwater in 5 wells.

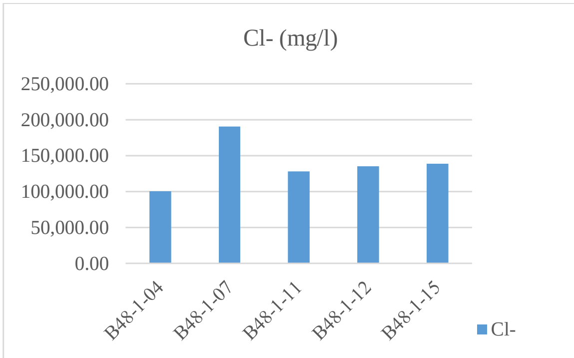

Figure 2. The content of chloride anions in the groundwater wells of the Tengiz field

As can be seen from this diagram, the highest indicator for chloride anions in groundwater was observed in well B48-1-07 (190594.3 mg/l). If we compare the maximum permissible concentration (MPC) of chloride anion (350 mg/l) in drinking water, this indicator exceeds 534 times [15]. The lowest indicator was observed in the well B48-1-04 (100 495.2 mg/l or 287 MPC). In the remaining 3 wells within 130000 mg/l of chloride anions (128 218.0-138 614.0 mg/ l or 366-396 MPC).

Calculation of the error of chloride ions:

For 5 data $\bar{x}$=138614.04 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 65379.80$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {}^{65379.8}/_{5 \cdot 4} = 3268.99$$

Choose *a*=0.95, *n*=5 and determine the student coefficient $t_a(n)$=2.8. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 2.8 \cdot 3268.99 = 9153.1728$$

Recording the final result:

$$x=138614.04\pm9153.1728$$
$$E = \Delta x/_{\bar{x}} = {9153.1728}/_{138614.04} \cdot 100\% = 6.6\%.$$

Thus, the random error in the content of chloride ions is 6.6%.

Figure 3 shows the composition of the bicarbonate anion in groundwater in 5 wells.

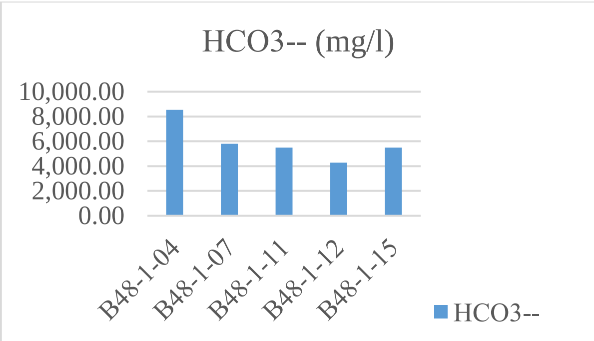

Figure 3. The content of the bicarbonate anion in the groundwater wells of the Tengiz field

In this figure, the highest indicator was observed in the well B48-1-04 (8540.0 mg/l). If we compare the content of bicarbonate anion in drinking water (400 mg/l) with the maximum permissible concentration (MPC), then this indicator exceeds 21 times [16]. The lowest indicator was observed in the well B48-1-12 (4270.0 mg/l or 10 MPC). In the remaining 3 wells within 5000 mg/l of bicarbonate anions (5490-5795 mg/l or 13-14 MPC).

Calculation of the error of bicarbonate anions:

For 5 data $\bar{x}$=5917 mg/l. $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 3157.9$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {3157.9}/_{5 \cdot 4} = 157.9$$

Choose *a*=0.95, *n*=5 and determine the Student coefficient $t_a(n)$=2.8. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 2.8 \cdot 157.9 = 442.1$$

Recording the final result:

$$x=5917\pm442.1$$
$$E = \Delta x/_{\bar{x}} = {442.1}/_{5917} \cdot 100\% = 7.4\%$$

Thus, the random error in the content of bicarbonate anions is 7.4%.

Figure 4 shows the composition of the sulfate anion in groundwater for 5 wells.

In this figure, the highest indicator was observed in the well B48-1-04 (60860.9 mg/l). If we compare the content of sulfate anion in the well at 48-1-04 with the content in drinking water, which is 500 mg/ l, then this indicator exceeds 121 times [17]. In the remaining 4 wells, the content of sulfate anions exceeds 35000 mg/l (35183.30-39668.60 mg/l or 70-79 MPC).

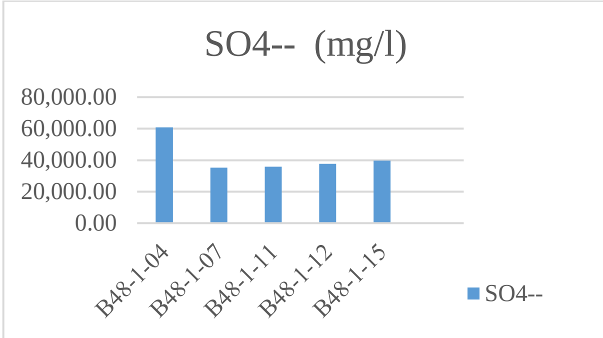

Figure 4. The content of sulfate anions in the groundwater wells of the Tengiz field

Calculation of the error of sulfate anions:

For 5 data $\bar{x}$=41833.1 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 21560.1$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {21560.1}/_{5 \cdot 4} = 1078.0$$

Choose a = 0.95, n = 5 and determine the student coefficient $t_a(n)$=2.8. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 2.8 \cdot 1078.0 = 3018.4$$

Recording the final result:

$$x=41833.1\pm3018.4$$
$$E = \Delta x/_{\bar{x}} = {3018.4}/_{41833.1} \cdot 100\% = 7.21\%$$

Thus, the random error in the content of sulfate anions is 7.21%.

Figure 5 shows comparative indicators of anions in groundwater.

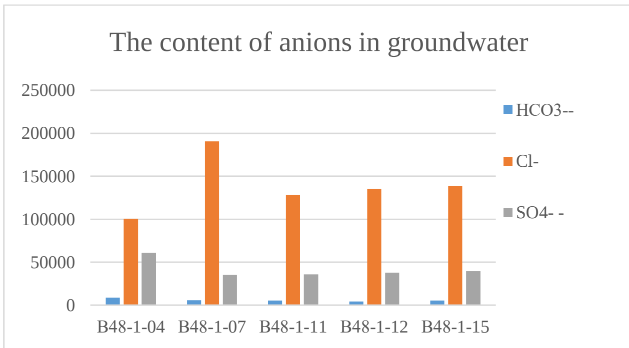

Figure 5. Comparative indicators of anions in wastewater wells of the Tengiz field

As can be seen from Figure 5, the highest indicator for anions in groundwater is observed in chloride anions (100495.2 – 190594.3 mg/l). Minimal arrows are typical for hydrocarbonates. (4270.0-8540.0 mg/l). High values in B48-1-04 are observed in bicarbonate and sulfate anions. Only chloride anions showed a low indicator. In addition, in the well B48-1-07 chloride anions are higher, and sulfate anions and bicarbonate anions are lower. In the other 3 wells, all indicators are the same.

Figure 6 shows the composition of calcium cation in groundwater in 5 wells.

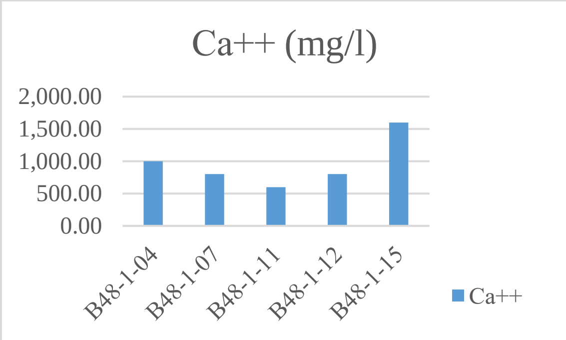

Figure 6. The content of calcium cations in the groundwater wells of the Tengiz field

In the figure above, the highest indicator was observed in the well B48-1-15, i.e. the maximum indicator was 1600.0 mg/l. If we compare the content of calcium cation in drinking water (180 mg/l) with the maximum permissible concentration (MPC), then this indicator exceeds 8.8 times [18]. The calcium cation index in wells B48-1-07 and B48-1-12 is the same amount (800.0 mg/l or 4.4 MPC). The lowest indicator among wells is b48-1-11 (600.0 mg/l or 3.3 MPC), which is 1000.0 mg/l less or 2.7 times less than the maximum indicator.

Calculation of the error of calcium cations:

For 5 data $\bar{x}$ =960 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 769.41$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {769.41}/{5 \cdot 4} = 38.47$$

Choose *a*=0.95, *n*=5 and determine the student coefficient $t_a(n)$=2.8. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 2.8 \cdot 38{,}47 = 107.718$$

Recording the final result:

$$x = 960 \pm 107.718$$
$$E = {\Delta x}/{\bar{x}} = {107.718}/{960} \cdot 100\% = 11.22\%.$$

Thus, the random error in the content of calcium cations is 11.22%.

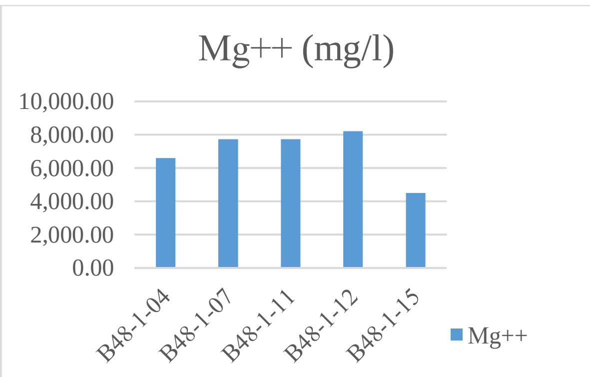

Figure 7. The content of magnesium cations in the groundwater wells of the Tengiz field

Figure 7 shows the composition of magnesium cation in groundwater in 5 wells.

As can be seen in the diagram in Figure 7, we see the highest indicator for magnesium cations in groundwater in the well B48-1-12 (8220.0 mg/l). If we compare the maximum permissible concentration (MPC) of magnesium cation in drinking water (50 mg/l), then this indicator exceeds 164 times [19]. The lowest indicator was observed in the well B48-1-15 (4500.0 mg/l or 90 MPC), which is 3720 mg/l less than the maximum indicator. In the other two wells, the index of magnesium cations is the same (7740.0 or 154 MPC).

Calculation of the error of magnesium cations:

For 5 data $\bar{x}$ =6960 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 2997.6$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {2997.6}/{5 \cdot 4} = 149.88$$

Choose *a*=0.95, *n*=5 and determine the Student coefficient $t_a(n)$=2.8. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 2.8 \cdot 149.88 = 419.66$$

Recording the final result:

$$x = 6960 \pm 419.66$$
$$E = {\Delta x}/{\bar{x}} = {419.66}/{6960} \cdot 100\% = 6.03\%.$$

Thus, the random error in the content of magnesium cations is 6.03%.

Figure 8 shows the composition of the compound of sodium and potassium cations in groundwater in 5 wells.

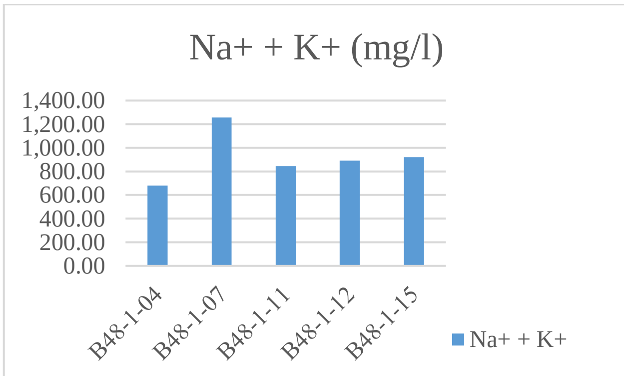

Figure 8. The content of the compound of sodium and potassium cations in the groundwater wells of the Tengiz field

According to the bar above, the amounts of sodium and potassium cations are also different in 5 wells. The maximum indicator is observed in the well B48-1-07 (1255.77 mg/l) [20]. The lowest indicator is observed in the well B48-1-04, the content of which is 678.98 mg/l. The indicators of the sum of sodium and potassium cations in the remaining three wells are 846.27-921.51 mg / l. The MPC of potassium is 20 mg/l. The MPC of sodium is 200 mg/l. For process water with a hardness from 0 to 1.00, the optimal values of the sum of potassium and sodium cations are 12-60 mg/l. Thus, the results of the sum of potassium and sodium in all wells show high parameters.

Calculation of the error of the compound of sodium and potassium cations:

For 5 data x̄=918.726 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 420.829$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)} = {420.829}/{5 \cdot 4}} = 21.04$$

Choose a=0.95, n=5 and determine the Student coefficient $t_a(n)$=2.8. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 2.8 \cdot 21.04 = 58.91$$

Recording the final result:

x=918.726 ±58.91

$$E = {\Delta x}/{\bar{x}} = {58.91}/{918.726} \cdot 100\% = 6.41\%.$$

Thus, the random error in the content of the compound of sodium and potassium cations is 6.41%.

Figure 9 shows comparative indicators of cations in groundwater.

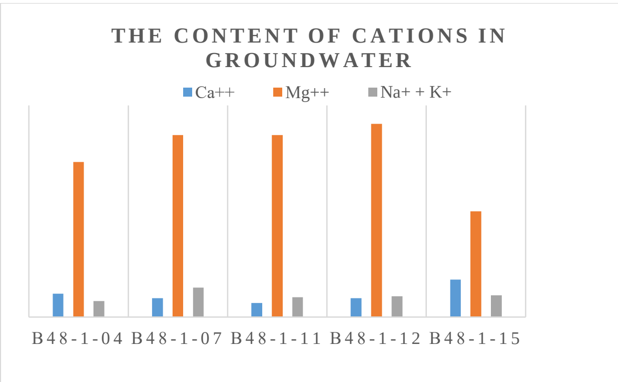

Figure 9. Comparative indicators of cations in wastewater wells of the Tengiz field

As can be seen in Figure 9, the maximum indicator for cations in groundwater is observed in magnesium cations (4500.0 – 8220.0 mg/l). And the indicators of the remaining calcium compounds (600.0-1600.0 mg/l) and sodium and potassium cations (678.98-1255.77 mg/l) in significantly lower amounts. Although magnesium cation (4500.0 mg/l) in well B48-1-15 is relatively the maximum amount, calcium cation (1600.0 mg/L) is the highest among wells.

Chemical analysis of wastewater No. 1

Figure 10 shows the composition of bicarbonate anions in wastewater from 3 wells.

Based on the above diagram, we observe the maximum values in the same amount of B48-1-1 and B48-1-3 (6100.0 mg/l). The maximum permissible concentration (MPC) of bicarbonate ions in drinking water is 60 mg/l. If we compare the content of bicarbonate anion in drinking water with the maximum permissible concentration (MPC), then this indicator exceeds 101.7 times. At the B 48-1-2 well, the indicator of bicarbonate ion is 5795.0 mg/l, which is slightly lower and close in value to the other two wells and exceed the MPC by 96.5 times.

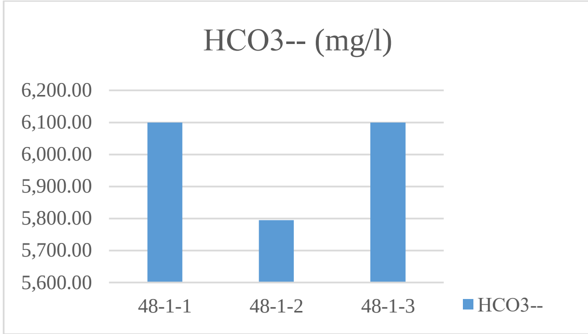

Figure 10. The content of bicarbonate anion in wastewater wells of the Tengiz field

Calculation of the error of bicarbonate anions:

For 3 data x̄=5998.33 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 178.93$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)} = {178.93}/{3 \cdot 2}} = 29.82$$

Choose a=0.95, n=3 and determine the Student coefficient $t_a(n)$=4.3. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 4.3 \cdot 29.82 = 128.234$$

Recording the final result:

x=5998.33 ±128.234

$$E = {\Delta x}/{\bar{x}} = {128.234}/{5998.33} \cdot 100\% = 2.1\%$$

Thus, the random error in the content of bicarbonate anions is 2.1%.

Figure 11 shows the composition of chloride anions in wastewater from 3 wells.

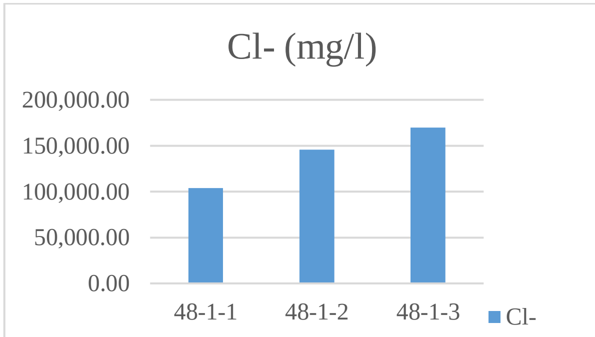

Figure 11. The content of chloride anions in wastewater wells of the Tengiz field

In the figure below, the smallest indicator between wells is observed in the well B48-1-1 (103960.5 mg/l). If we compare the maximum permissible concentration (MPC) of chloride anion in drinking water, this indicator exceeds 259 times. This maximum indicator is 169802.2 mg/l less than the content of chloride anions in the well 48-1-3. The third well in the amount of 145544.7 mg /l.

Calculation of the error of chloride anions:

For 3 data x̄=139769.13 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 47091.4$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {47091.4}/{3 \cdot 2} = 7848.57$$

Choose *a*=0.95, *n*=3 and determine the Student coefficient $t_a(n)$=4.3. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 4.3 \cdot 7848.57 = 33748.84$$

Recording the final result:

x=139769.13±33748.84

$$E = {\Delta x}/{\bar{x}} = {33748.84}/{139769.13} \cdot 100\% = 24.1\%$$

Thus, the random error in the content of chloride anions is 24.1%.

Figure 12 shows the composition of the sulfate anion in wastewater from 3 wells.

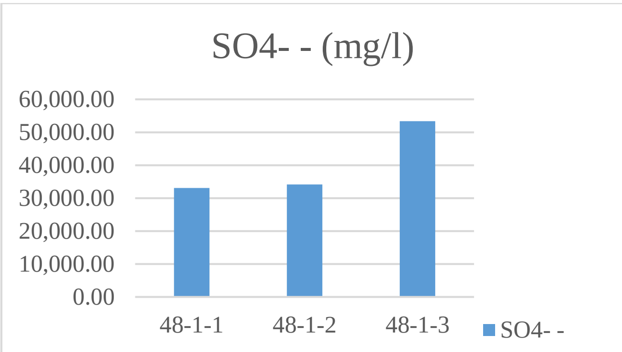

Figure 12. The content of sulfate anions in the wastewater of wells of the Tengiz field

In the above figure, the lowest indicator between wells is observed in the well B48-1-1 (33084.6 mg/l) and it is near of the well B48-1-2, it is 34154.5 mg/l. If we compare the maximum permissible concentration (MPC) of chloride anion in drinking water, this indicator exceeds 66 times. This maximum indicator is 53412.7 mg/l, the content of chloride anions in the well is less than 48-1-3.

Calculation of the error of sulfate anions:

For 3 data x̅=40217.27 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 16178.74$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {16178.74}/{3 \cdot 2} = 2696.46$$

Choose *a*=0.95, *n*=3 and determine the Student coefficient $t_a(n)$=4.3. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 4.3 \cdot 2696.46 = 11594.76$$

Recording the final result:

x=40217.27 ±11594.76

$$E = {\Delta x}/{\bar{x}} = {11594.76}/{40217.27} \cdot 100\% = 28.8\%.$$

Thus, the random error in the content of sulfate anions is 28.8%.

Figure 13 shows the content of anions in wastewater from 3 wells.

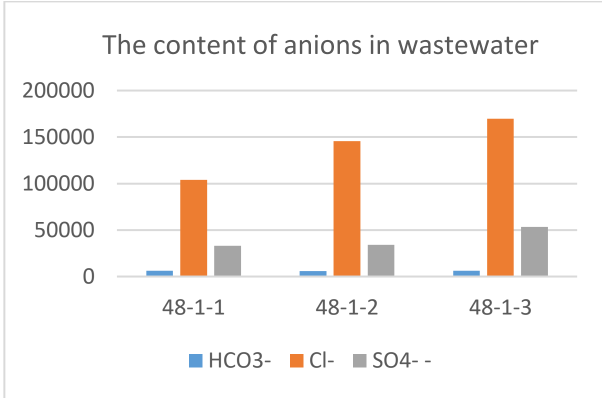

Figure 13. Comparative indicators of anions in wastewater wells of the Tengiz field

As can be seen in Figure 13, the maximum indicator for anions in wastewater is observed in chloride anions (103960.50 – 169802.20 mg/l). And the indicators of the remaining bicarbonate anion (5795.0-6100.0 mg/l) and sulfate anions (33084.6-53412.7 mg/l) in significantly lower amounts. In the well 48-1-3, all indicators of anions, bicarbonate anions (6100.0 mg/l), sulfate anions (53412.7 mg/l) and chloride anions (169802.20 mg/l) in relatively maximum quantities. Based on the above diagram, we observe the maximum values of bicarbonate anions in the same amount of B48-1-1 and B48-1-3 (6100.0 mg/l). The minimum values for chloride anions (103960.50 mg/l) and sulfate anions (33084.6 mg/l) are observed in well B48-1-1.

Figure 14 shows the composition of calcium cation in wastewater from 3 wells.

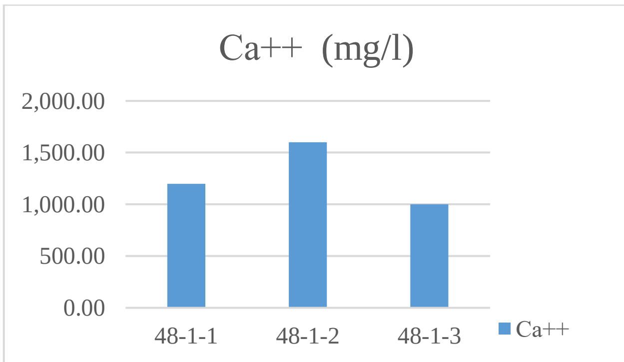

Figure 14. The content of calcium cations in wastewater wells of the Tengiz field

If you look at the data in the diagram, you can see that the content of calcium cations in well 3 is the maximum value in well 48-1-2 (1600.0 mg /l). If we compare the content of calcium cation in drinking water with a pre-permissible concentration (MPC), then this indicator exceeds 8.8 times. This is 600.0 mg/l less compared to the minimum dose in the well 48-1-3.

Calculation of the error of calcium cations:

For 3 data x̅=1266.67 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 432.06$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {432.06}/{3 \cdot 2} = 72.01$$

Choose a=0.95, n=3 and determine the Student coefficient $t_a(n)$=4.3. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 4.3 \cdot 72.01 = 309.64$$

Recording the final result:

x=1266.67 ±309.64

$$E = {\Delta x}/{\bar{x}} = {309.64}/{1266.67} \cdot 100\% = 24.4\%.$$

Thus, the random error in the content of calcium cations is 24.4%.

Figure 15 shows the composition of magnesium cation in wastewater from 3 wells.

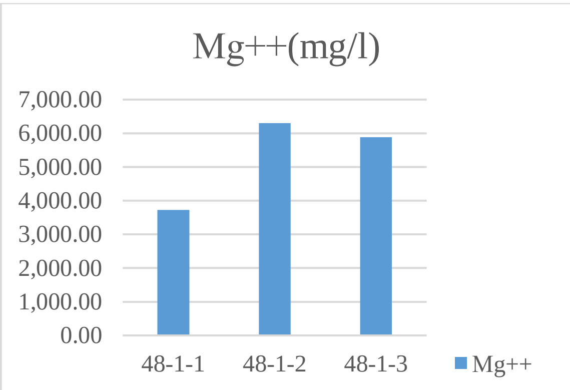

Figure 15. The content of magnesium cations in wastewater wells of the Tengiz field

As can be seen in the diagram in Figure 15, we see the highest indicator for magnesium cations in wastewater in the well 48-1-3 (6300.0 mg/l). If we compare the maximum permissible concentration (MPC) of magnesium cation in drinking water, this indicator exceeds 126 times. The lowest indicator was observed in the well 48-1-1 (3720.0 mg/l or 74 MPC), which is 2160 mg/l less than the maximum indicator.

Calculation of the error of magnesium cations:

For 3 data $\bar{x}$=5300 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 1957.75$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {1957.75}/{3 \cdot 2} = 326.29$$

Choose *a*=0.95, *n*=3 and determine the Student coefficient $t_a(n)$=4.3. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 4.3 \cdot 326.29 = 1403.05$$

Recording the final result:

x=5300 ±1403.05

$$E = {\Delta x}/{\bar{x}} = {1403.05}/{5300} \cdot 100\% = 26.4\%$$

Thus, the random error in the content of magnesium cations is 26.4%.

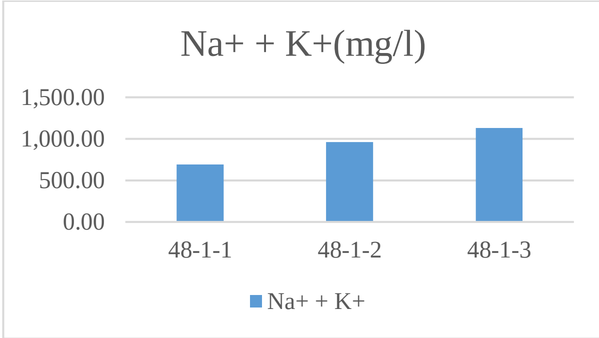

Figure 16. The content of compounds of sodium and potassium cations in wastewater wells of the Tengiz field

Figure 16 shows the composition of the compound of sodium and potassium cations in groundwater in 3 wells.

According to the diagram above, the amounts of sodium and potassium cations are also different in 3 wells. The maximum indicator is observed in the well 48-1-3 (1131.32 mg/l). The lowest indicator is observed in well 48-1-1, its content is 692.81 mg/l. The content of sodium and potassium cations in well 48-1-2 is 961.08 mg/l, which is 170.24 mg/l less than the maximum indicator.

Calculation of the error of compounds of sodium and potassium cations:

For 3 data $\bar{x}$=928.4 mg/l, $\sqrt{\sum_{i=1}^{n}(\Delta x_i^2)} = 312.64$. Then according to the formula 3:

$$S_{\bar{x}} = \sqrt{\frac{\sum_{i=1}^{n}(\Delta x_i^2)}{n(n-1)}} = {312.64}/{3 \cdot 2} = 52.11$$

Choose *a*=0.95, *n*=3 and determine the Student coefficient $t_a(n)$=4.3. Calculate the confidence interval by the formula 4:

$$\Delta x = t_a(n \cdot S_{\bar{x}}) = 4.3 \cdot 52.11 = 224.06$$

Recording the final result:

x=928.4 ±224.06

$$E = {\Delta x}/{\bar{x}} = {224.06}/{928.4} \cdot 100\% = 24.1\%.$$

Thus, the random error in the content of compounds of sodium and potassium cations is 24.1%.

Figure 17 shows comparative indicators of cations in wastewater.

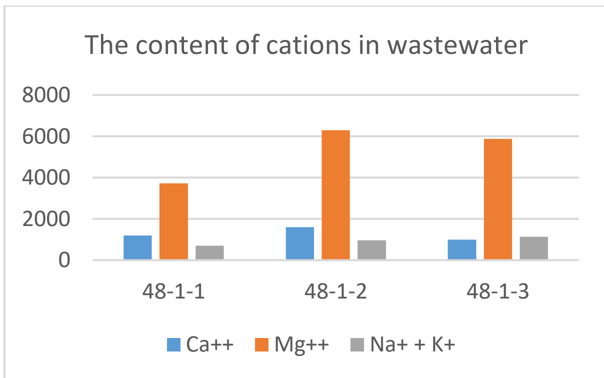

Figure 17. Comparative indicators of cations in wastewater wells of the Tengiz field

As can be seen in Figure 17, the maximum indicator for cations in wastewater is observed in magnesium cations (3720.0 – 6300.0 mg/l). And the indicators of the remaining calcium compounds (1000.0-1600.0 mg/l) and sodium and potassium cations (692.81-1131.32 mg/l) in significantly lower amounts. In the well 48-1-2 magnesium cation (6300.0 mg/l) and calcium cation (1600.0 mg/l) in relatively maximum amounts.

Thus, according to anions, the maximum content in groundwater is generally characteristic of chlorides, the content of which is 2-5 times higher than bicarbonate ions and 2.5-3 times higher than sulfate ions. In terms of cations, magnesium cations predominate in groundwater, the content of which is 5-7.5 times higher than the content of the sum of sodium and potassium cations and 6.5 times higher than calcium ions.

The same pattern is observed for wastewater anions and cations. The content of anions is characterized by an excess of chloride ions by 3 times of sulfates and 17-27 times of hydrocarbonates. In terms of cations, the excess is also characteristic of magnesium cations by 3.7-3.9 times of calcium cations and 5.3-5.5 times of the sum of sodium and potassium cations.

4. CONCLUSIONS

In conclusion, it should be noted that the process of deposition of inorganic salts in oilfield equipment is a special case of mass crystallization of supersaturated insoluble salts from their solutions under certain thermodynamic conditions. Therefore, it is necessary to determine the content of the chemical composition of groundwater and wastewater on the territory of the Tengiz field [21].

Analysis of the content of anions and cations showed that the maximum values for anions in both types are characteristic of chlorides 100495.2 – 190594.3 mg/l and 103960.50 – 169802.20 mg/l, respectively, for groundwater and wastewater, the contents of which are almost 2-3 times higher than the anions of sulfates 35183.30-60860.9 mg/l and 33084.6-53412.7 mg/l in ground and wastewater . With a large difference, the content of hydrocarbonates is exceeded, so in groundwater it is exceeded up to 2.5-5 times (4270.0-8540.0 mg/l), and in wastewater up to 17-27 times (5795.0-6100.0 mg/l).

For cations, there is an increased content of magnesium ions 4500.0 – 8220.0 mg/l and 3720.0 – 6300.0 mg/l, respectively, for groundwater and wastewater. This content exceeds the content of calcium ions by about 6.5 times and 3.7-3.9 times (600.0-1600.0 mg/l and 1000.0-1600.0 mg/l, respectively, for groundwater and wastewater) and the sum of sodium and potassium ions 5-7,5 and 5.3-5.5 times (678.98-1255.77 mg/l and 692.81-1131.32 mg/l is appropriate for groundwater and wastewater).

Calculation of errors of anions and cations shows that for groundwater they are 6.03-11.22%, and for wastewater 2.1-28.8%. All these data do not exceed the measurement error rate (at the level of the water quality standard) of the composition and properties of natural and wastewater according to Table 2.

Thus, the main chemical elements in the groundwater and wastewater of the Tengiz deposit are magnesium chloride salts, in second place are salts containing sulfates, represented by calcium, sodium and potassium sulfates and least of all salts of hydrocarbonates.

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NOMENCLATURE

TCO	Tengizchevroil
MPC	maximum permissible concentration
SPT	Standard penetration test
CPT	Cone Penetration Tests