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CORRELATIONS BETWEEN CHEMICAL MACRO COMPOSITION AND REDOX POTENTIAL FOR MINERAL WATERS FROM TRUSKAVETS DEPOSIT

Корреляции между химическим макросоставом и редокспотенциалом для минеральных вод Трускавецкого месторождения

V. Ya. Berezovskyy[1], O. R. Datsko[1], W. Zukow[2]
В. Я. Березовский[1], О. Р. Дацько[1], В. Жуков[2]

[1]O.O. Bogomolets Institute Physiology National Academy of Sciences of Ukraine, Kyiv, Ukraine
[1]Институт физиологии им.А.А. Богомольца НАН Украины, Киев, Украина
[2]Kazimierz Wielki University, Bydgoszcz, Poland
[2]Uniwersytet Kazimierza Wielkiego, Bydgoszcz, Polska

Keywords: oxidation-reduction potential (ORP), potentiometry, chemical macro composition, mineral waters.

Ключевые слова: окислительно-восстановительный потенциал (ОВП), потенциометрия, химический макросостав, минеральные воды.

Abstract

Correlations were researched between chemical macro composition and oxidation-reduction potential (ORP) measured by potentiometry for mineral waters from Truskavets deposit.

It has been shown that mainly ORP values are correlated satisfactorily with hydrogen sulfide content and dissolved oxygen.

Резюме

Исследованы корреляции между химическим макросоставом и окислительно-восстановительным потенциалом (ОВП), измеренным потенциометрически для минеральных вод Трускавецкого месторождения.

Показано, что в основном величины ОВП удовлетворительно коррелируют с концентрацией сероводорода и растворенного кислорода.

INTRODUCTION

The article Sigg L. (2000) [1] noted that the characterization of redox conditions in natural aquatic systems has both scientific and practical importance. Biogeochemical processes in anoxic systems have been studied for many objects in lakes, for sediments (sludge) and groundwater (e.g. [2, 3]). The level of redox processes in groundwater, and the presence of reduced iron ions (II), manganese (II) and sulfides are important from a practical point of view, such as the use of groundwater for households or cleaning (remediation) of polluted areas. In articles [4, 5] redox conditions were described for groundwater that are laden runoff from landfills that emit a large amount of decomposition products, and the dynamics of their degradation. Special attention for degradation processes of oil fields, which are large-scale in space and time. An important place is occupied not only chemical but microbiological processes. This degradation of oil soils underlying the formation of waters Naftusya, which are used for medical treatment on Truskavets resort [6].

The sequence of redox processes is defined by their standard redox potential, in the case of microbial systems, their sequence can be seen in the diagram that is shown in Fig. 1 and was taken from [1]. Oxidants with highest redox potential come first into the reaction, and then oxidants with lower potential will be react. This sequence occurs in the vertical distribution of the components in the lake water which is enriched with nutrients (eutrophication of water) and in closed systems containing an excess of organic matter, such as reactors for anaerobic fermentation [7].

Most reactions occur with the help of microorganisms (excluding reduction MnO_2 and FeOOH (solid residue)), and so they are parallel to environmental sequences of microorganisms: aerobic heterotrophs, microorganisms for denitrification, fermenters, sulfate reducers and then methane bacteria. In addition, it was noted that reactions with higher power yield take precedence over processes with lower power yield [7].

In article [8] the results were presented for research ORP value of mineral waters, their changes during storage without air and under diffusion contact with air samples for samples of mineral water Naftusya from four boreholes of Truskavets mineral waters (21-H, 1-HO, 8-HO, 17-HO) and observation boreholes (16-PK) and six samples of mineral water Skhidnytsia deposits used in balneological practice (Spring №3, №10 (well-room), №18, №2C, №25, №26). Studies, carried out in article [8], showed that mineral waters, extracted from boreholes and springs, have negative ORP that is these mineral waters are formed under anaerobic conditions. Finally ORP value is a reflection of microbiological and hydrogeological environment, in which mineral waters are formed , and chemical composition is product of processes in this environment. At the extraction of mineral water on the surface water sample is in contact with air oxygen and its potential increases going from negative to positive. Thus ORP value of mineral water can be used as an indicator of water nature origin. In article [8] the recommendations was given to preserve the ORP value of mineral water on the way from the well to the consumer.

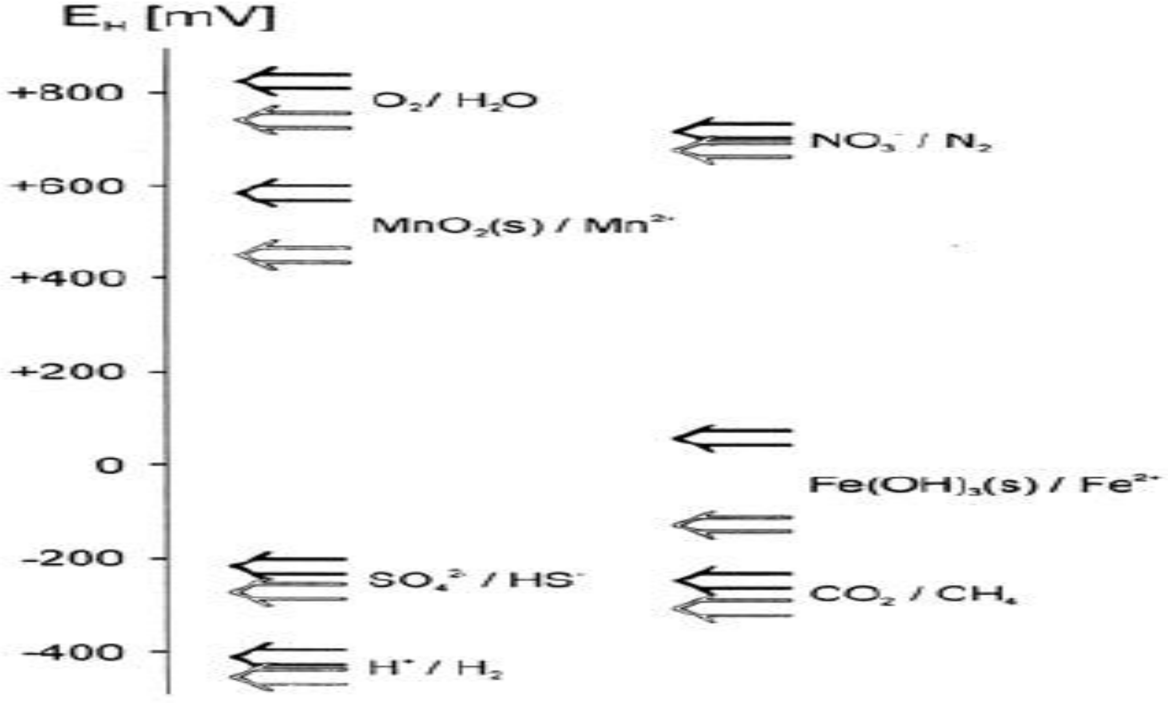

Fig. 1. Redox potentials of some important redox pairs in natural waters at pH 7 (dark arrows) and pH8 (light arrows). Redox potentials are calculated for activities {Red} = 1 and {OX}=1; if it is accepted that for Mn and Fe activity is {Mn2+}=l0-6M and {Fe2 +} = l0-6M. (taken from [1])

In a situation where dissolved oxygen affects on the ORP value it is necessary simultaneously to monitor these values in continuous operation in one and the same sample without air that has not been done in article [8] which were made single determinations of dissolved oxygen by Winkler method and found the correlation between these results and ORP value. At addition, in article [8] measuring cell was open to air access, due to the purpose of this study, which investigated the change for ORP value of mineral water in diffusion contact with air.

In the report [9] there are results of the study during the year for the four wells Truskavets deposit, 21-Н, 1-НО, 8-НО, 17-НО, 16-РК and samples of cold water Naftusya from well-rooms Б1 and Б2. It was shown [9] that hydrogen sulfide content in these samples varies from 0.07 mg/dm^3 to 3.74 mg/dm^3, and the dependence ORP value on the concentration of hydrogen sulfide have a low correlation value of $R^2 = 0,15$. Report [9] noted that in addition to hydrogen sulfide there are additional factors that affect on the ORP value, including one of these factors may be oxygen in the air, which was previously shown in article [8].

Purpose of this article - to study the values of redox potential (ORP) with minimal contact with air for samples of Truskavets deposit of mineral waters those are used in balneologic practice and establishing possible correlations between ORP value with chemical macro composition of mineral waters.

MATERIAL AND RESEARCH METHODS

Objects of research

The objects of study were samples of mineral water from Truskavets deposit taken from wells 5-К, 7-А, 7-К, 9-Б, 16-РК, 61-РГД and sources №11 «Юзя»(Дж-11) and mineral water Naftusya 21-Н, 1-НО, 8-НО, 22-Д.

To measure the redox potential of mineral waters we used glass cell (position 1), which is shown in Figure 2 and has volume 250 cm^3. A cell consists of a tank of liquid capacity of about 200 cm^3, conical neck having grinded sealing surface and glass shell for stable temperature control, which is pumped heat carrier from the thermostat. Closed cell teflon stopper (pos. 2), in which are holes made for electrodes (poses 4,5) and other equipment (poses 3,9,11) needed for experiments. Height of cork (pos. 2) is 35 mm. On top of cork (pos. 2) at a distance of 3 mm from the edge of concavity made about 2.0 mm fluid that acts as hydraulic valve since fluid mixing in the contact electrodes stopper in the vertical direction is difficult.

Mineral water is poured to half of the conical neck of the cell and then covered with a teflon stopper with mounted electrodes. This excess mineral water was displaced by stopper through the device for supplying gas and leaks in the area of electrodes adjoining with teflon. Water displaced is partially remained on the surface of teflon cork in specially made deepening with depth 2 mm, that favours sealing the cell. To measure the temperature served chromel-alumel thermocouple placed in a glass tube with a diameter of 5 mm (position 11). Mineral water pH value was measured by combined electrode Model ЭСК-10603/7 (position 4) connected to a pH meter Model pH-150 (position 6). Redox potential measured by combined electrode Model ЭРП-105 (position 5) connected to a pH meter Model pH-150 (position 7). For the measurement of dissolved oxygen using oxygen meter Model YSI-58 with sensor №5905 (Clark electrode). The mixing of the water sample was carried glass stirrer, a screw of which is located directly about the sensor of oxygen. Information from the ADC goes on a computer's USB port. Manage the collection of information from the ADC was carried out using software Acon administrator version 2.0.15.

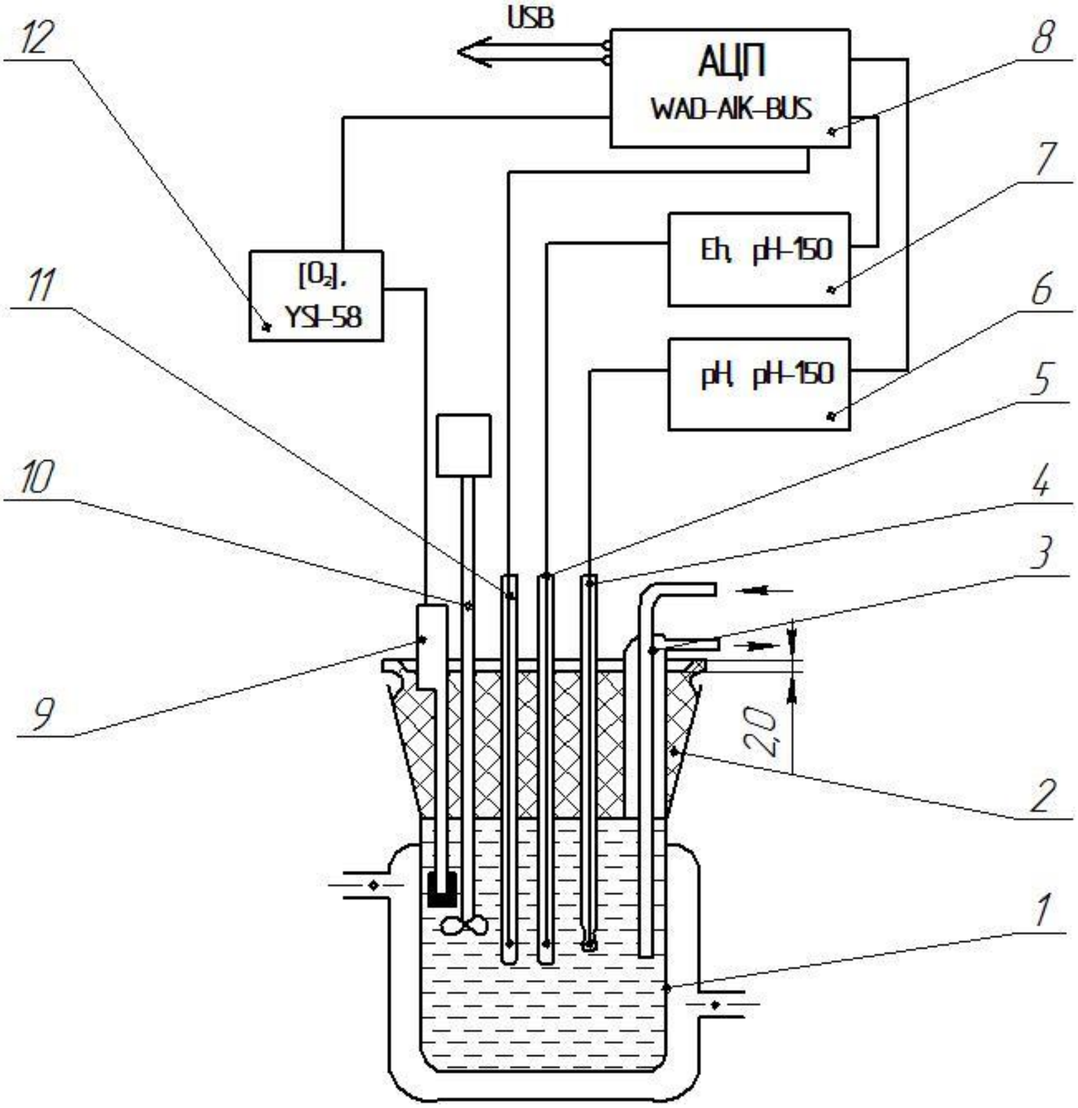

Fig. 2. Instalation for measuring the redox potential of mineral waters: 1 – glass cell; 2 – conical teflon stopper; 3 – device for gas passing in cell; 4 – combined electrode Model ЭСК-10603/7; 5 – combined electrode Model ЭРП-105; 6 – pH meter Model pH-150; 7 – potenciometer Model pH-150 for measuring of ORP; 8 – analog to digital converter Model WAD-AIK-BUS; 9 – oxigen sensor Model YSI №5905 (Clark electrod); 10 – glass stirrer for work of Clark electrod; 11 – pocket with chromel-alumel thermocouple ; 12 – oxigen meter Model YSI-58.

Equipment calibration

pH meter calibrated by standard buffer solution [10]. Equation (1), reflecting the dependence of the pH from potential of combined electrode Model ЭСК-10603/7, is:

$$pH = \frac{367{,}7 - 1000 \cdot E_1}{50{,}546} \qquad (1)$$

where $\boldsymbol{E_1}$ - readings recorded in file by channel #1 of the ADC, Volts.

Oxygen meter Model YSI-58 was calibrated according to the manual. The dependence of the dissolved oxygen concentration ($[O_2]$, mg /dm^3) from the $\boldsymbol{E_2}$ (Volts) readings, recorded in file by channel #2 of the ADC, has the form (2).

$$\left[O_2\right] = 19{,}067 \cdot E_2 + 0{,}1903 \qquad (2)$$

Calibration of oxygen meter was performed daily since there were changing ambient temperature, pressure and aging of sensor.

pH meter for measurement of **Eh** potential calibrated by quinhydrone solutions with different pH values, as described in detail in article [8]. The link of **Eh**-potential for the sample with readings was given by the equation (3):

$$Eh = 968{,}26 \cdot E_3 + 204{,}92 \qquad (3)$$

where $\boldsymbol{E_3}$ - readings, recorded in file by channel #3 of the ADC, Volts.
Calibration ORP electrodes for determination was performed every two days.

Chromel-alumel thermocouple calibrated temperature range 25-45ºC taking into account the temperature of the cold ends. The thermocouple was connected directly to the ADC on channel #4. Got equation (4) to calibrate the thermocouple chromel-alumel:

$$t^oC = \frac{1000 \cdot E_4 + 0{,}7669}{0{,}0324} \qquad (4)$$

where $\boldsymbol{E_4}$ - readings, recorded in file by channel #4 of the ADC, Volts.

Experimental part.

The cell (see Fig. 2) was thermostated at 25ºC. The temperature of heat carrier was measured by a mercury thermometer. In cell filled with mineral water included stirrer and registration of measuring parameters in software mode "Oscilloscope". Both openings of device for gas supplying were shut. After one hour of teflon plug with attachments was transferred to the cell with the same neck filled with distilled water and bubbled with air at 1 cm^3/s. This procedure allows to check the calibration of oxygen meter. In the same pot electrodes were kept between experiments. All water samples were tested in the same conditions.

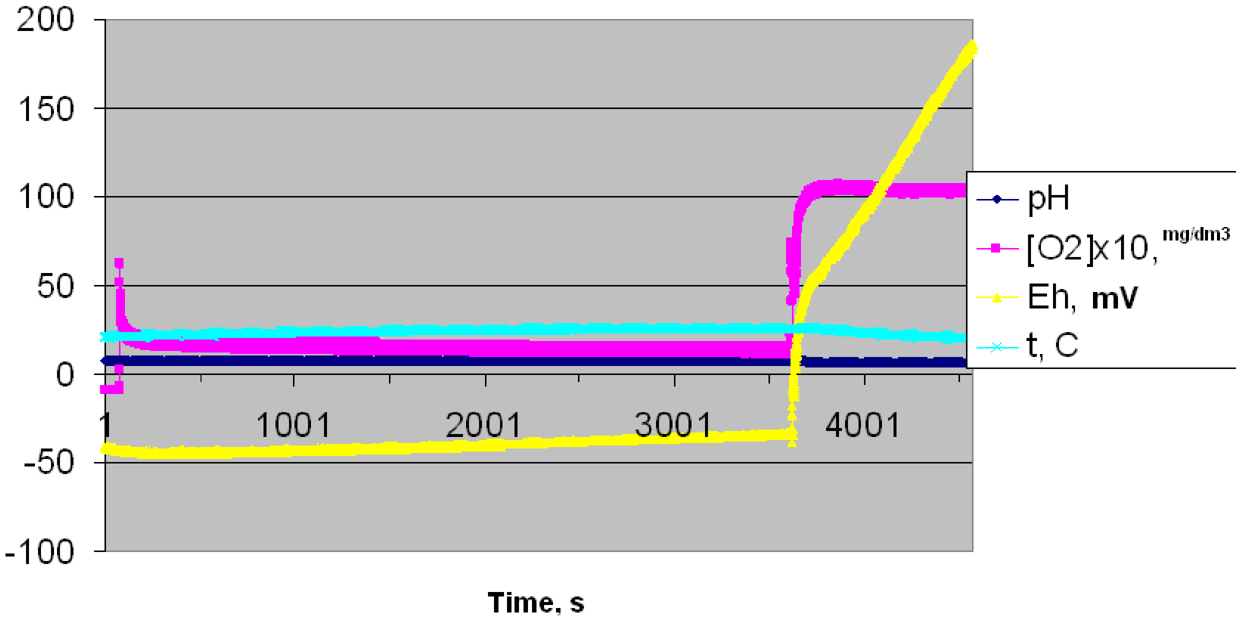

Fig. 3. Characteristic changes for sample of water Naftusya from well 1-HO in studing time.

An example is shown in Fig.3 for the general form of recorded measurements that were obtained in tested water from well 1-HO . Water from this well is characterized by the following parameters: pH=(7,16-7,18); concentration of dissolved oxygen $[O_2]$ = 1,32-1,59 mg/dm^3; standard redox potential (recalculated relative hydrogen electrode) **Eh** = (-39.8…-36.2) mV; measurements were made at temperature (23,6-25,6) °C.

The system is very dynamic and rapidly responds to any changes. Since the peak of the curve the concentration of oxygen at 180 seconds corresponds switching on mixer and change parameters at 3600 seconds (1 hour) was caused by measurement of distilled water, according to the methodology of the experiment.

As can be seen from Figure 3 the first 300 seconds one can observe transients associated with switching on system and then parameters were stabilized. On the curve, corresponding to the

ORP values, one can observe a stabilized minimum after 500 seconds. This is the minimum value of **Eh** and pH value, temperature and dissolved oxygen concentration, corresponding to this potential, we considered as parameters of the sample. These data together with chemical analysis results are shown in Table 1.

RESULTS OF RESEARCH AND THEIR DISCUSSION

We have shown that the ***Eh*** value for mineral water Naftusya, which are formed during sulfate-reducing processes in anaerobic conditions, increases at the exit to the surface due to atmospheric oxygen, at this situatiob the hydrogen sulfide acts as a buffer [7, 8]. However ORP measurements were conducted in an open cell, that could not affect the results of research. It is therefore advisable to consider the dependence of **Eh** value of water samples from the concentration of dissolved oxygen (Figure 4), where ORP measurements were carried out in a closed cell with the lowest possible effects of the air. From Figure 4 one can see that with increasing concentration of oxygen increases the redox potential of mineral water samples, but there is no clear dependence because all correlation $R^2 = 0{,}514$. At excluding from correlation data for wells 7-A correlation markedly increases to $R^2 = 0{,}749$.

The effect is more pronounced (Figure 5) for hydrogen sulfide on the ORP value of samples . At low concentrations of hydrogen sulfide (less than 0.3 mg /dm^3), the value of **Eh** potential does not depend on its concentration varies from 50 mV to 350 mV, depending on the sample of mineral water. In the presence of hydrogen sulfide (0,3-2,3 mg/dm^3) ORP value is reduced to -50 mV for water samples, which are used for medical treatment. This dependence is described by another equation and it is typical for samples of mineral water Naftusya (wells 1-HO, 8-HO, 21-H, 22-Д). So, we can say that the concentration of hydrogen sulfide in the mineral waters of more than 0.3 mg/dm^3 of ORP value is not growing as fast as hydrogen sulfide at low concentrations (less than 0.3 mg/ dm^3).As well as dissolved oxygen increases the **Eh** potential, hydrogen sulfide has a buffer effect, apparently by reaction with it. On of the data shows that water with less than 50 mV ORP necessarily contain hydrogen sulfide than 0.3 mg/ dm^3. It should be noted that therapeutic mineral water from wells 1-HO, 8-HO, 21-H, 22-Д Truskavets deposit are standards for water of Naftusya, they are used to treat patients with kidney stone disease. On the other hand waters that are claiming to belong to the class of Naftusya, the so-called "Naftusya-type" obviously must contain hydrogen sulfide at least 0.3 mg/dm^3, and their **Eh** potential must be less than 50 mV.

As you know forming mineral water Naftusya is by sulfate-reducing processes is therefore appropriate to consider the relationship between the content of sulfate (sulfate ion) and hydrogen sulfide in the studied waters Fig. 7. When the concentration of hydrogen sulfide less than 0.3 mg / l some water containing almost 2000 mg sulphate ion per liter, the concentration of hydrogen sulfide than 0.3 mg/dm^3 sulfate content does not exceed 50-60 mg/dm^3.

At the same time distinct relationship between the content of sulfates and ***Eh*** potential of mineral waters are observed (Figure 8). The highest content of sulfates (1835 mg/dm^3) has a well 9-Б, and all other mineral water with concentration of sulfate ions in the range of 30 to 350 mg/dm^3, where the majority of points along the interval ORP values, that is, at a certain imaginary horizontal line, which further confirms the lack of relationship between the content of sulfates and Eh potential.

Table 1. Physico-chemical characteristics for studied water samples.

Well	$Na^+ + K^+$, mg/dm^3	Ca^{+2} mg/dm^3	Mg^{+2} mg/dm^3	Fe (total) mg/dm^3	Cl^- mg/dm^3	HCO_3^- mg/dm^3	SO_4^{-2} mg/dm^3	Salinity, mg/dm^3	$[O_2]$ mg/dm^3	Eh мВ	pH	H_2S mg/dm^3
5-К	36,1	130,3	66,9	1,91	141,8	475,8	85,0	935,9	0,81	70,3	7,04	0,068
7-А*	758,4	80,2	30,4	2,36	709	512,4	532,8	2623,4	3,20	342	7,13	0,068
7-К	714,3	80,2	31,6	2,22	664,9	524,6	495,7	2511,3	1,70	44,2	7,41	0,068
9-Б	2903,6	200,4	127,7	0,84	3546	524,6	1834,8	9137	3,36	111,0	7,45	0,068
16-РК	7,8	104,2	60,8	1,73	3,5	561,2	59,5	797,0	6,10	180,1	6,90	0,170
61-РГД	190,1	160,3	73,0	2,68	354,6	488,0	203,6	1469,6	2,21	51,4	7,15	0,068
ДЖ-11	17,4	92,2	48,6	0,01	12,4	500,2	38,7	709,5	6,03	285,0	7,21	0,136
1-НО	17,4	122,2	43,8	0,67	16,0	500,2	86,9	786,5	1,59	-39,7	7,17	2,120
8-НО	18,6	96,2	48,6	0,07	10,6	475,8	72,4	722,2	2,25	54,1	7,17	0,281
21-Н	8,0	112,2	48,3	0,02	24,8	488,0	60,0	741,6	1,29	77,6	7,17	0,280
22-Д	15,4	108,2	43,8	0,25	12,4	486,4	63,2	731,0	0,72	-46,2	7,08	2,070

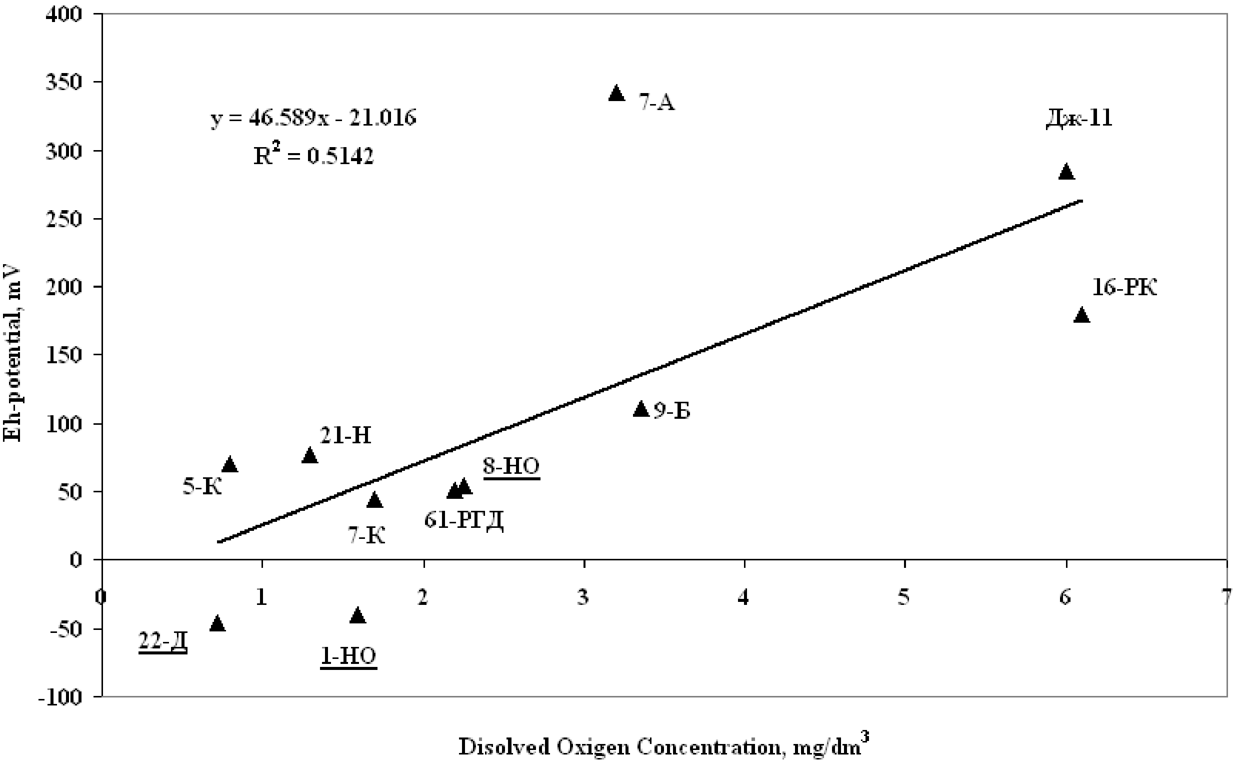

Fig. 4. Dependence for *Eh* potential from disolved oxigen concentration for mineral waters of Truskavetc deposit.

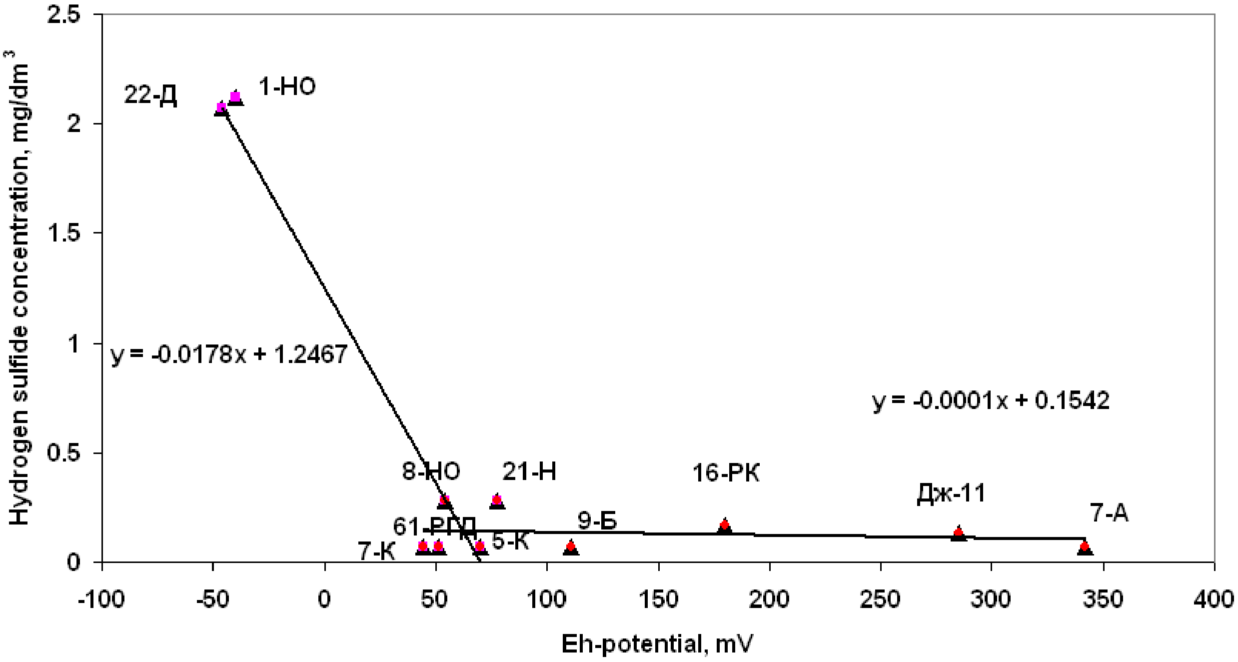

Fig. 5. Dependence for *Eh* potential from hydrogen sulfide concentration for mineral waters of Truskavetc deposit.

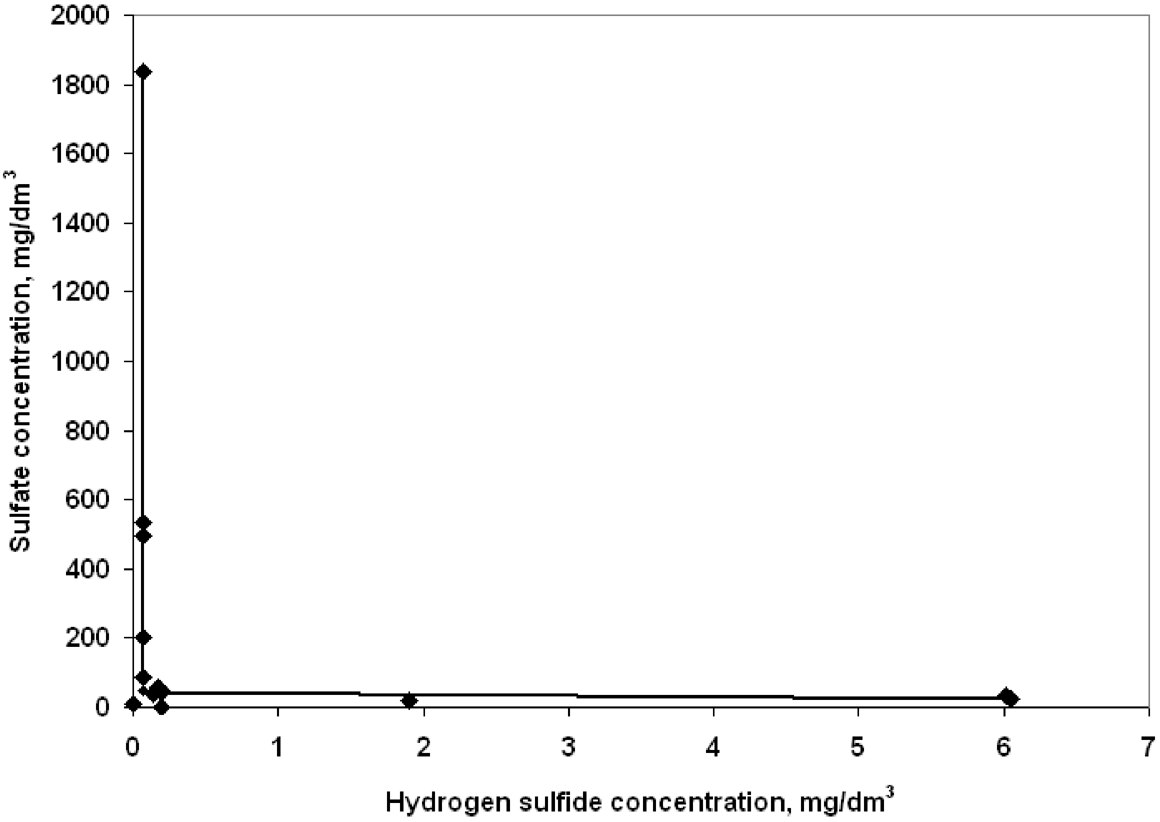

Fig. 6. Relationship between sulfate content and hydrogen sulfide concentration for mineral waters of Truskavetc deposit.

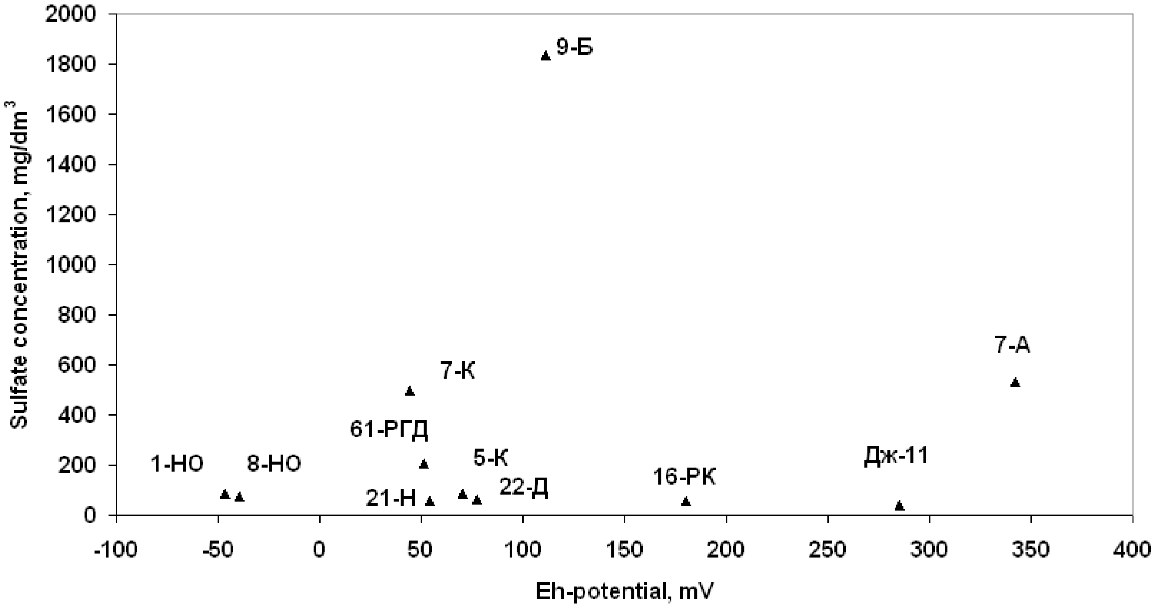

Fig. 7. Relationship between sulfate content and Eh potential for mineral waters of Truskavetc deposit.

All studied by us waters containing a particular amount of iron ions that are also involved in redox processes in their formation. However, a pronounced effect on the value of **Eh** from iron ions potential we not see (Fig. 8).

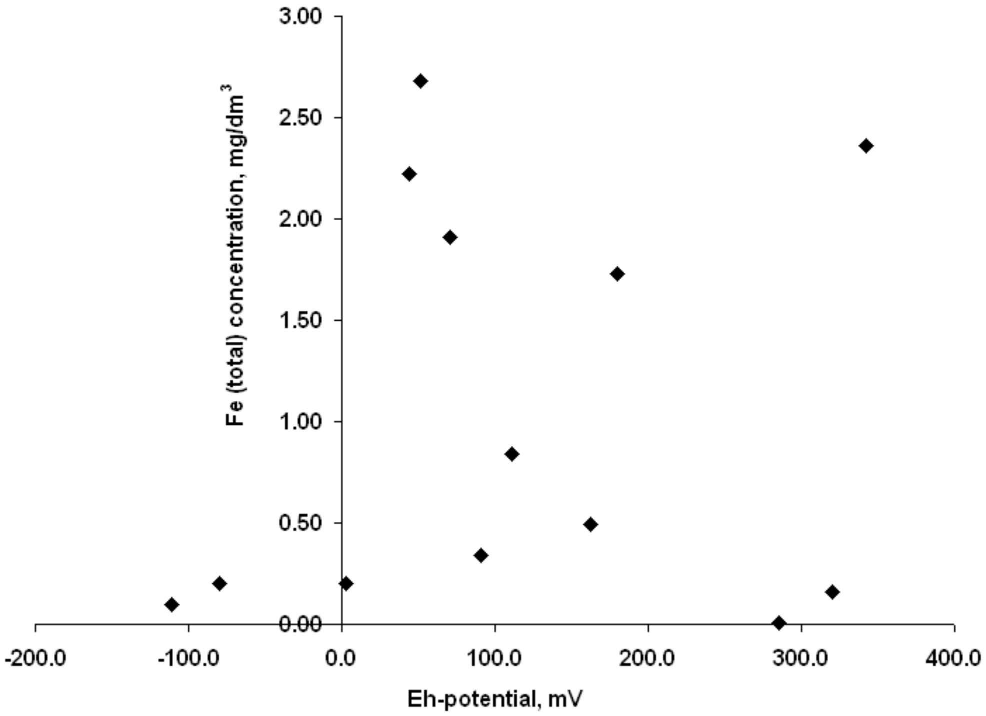

Fig. 8. Relationship between Fe content and Eh potential for mineral waters of Truskavetc deposit.

CONCLUSIONS

Our studies show that for mineral water from Truskavets deposit the ***Eh*** potential varies widely from -50 mV to 300 mV.

ORP values of water samples that do not contain hydrogen sulfide, or include hydrogen sulfide in residual amounts (less than 0.3 mg/dm^3) is positive (more than 50 mV) .

For waters, containing hydrogen sulfide more than 0.3 mg/dm^3, ORP values are less than 50mV, these include mineral water Naftusya for medical treatment.

Eh value, which is formed during sulfate-reducing processes under anaerobic conditions at the exit to the surface, increases due to oxygen, while hydrogen sulfide acts as a buffer.

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