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Production of Water with Large Negative Red-Ox Potential.

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ABSTRACT

The possibility was shown to produce and long time conservation of water with large negative red-ox potential by means of introduction in water of molecular hydrogen. The base of process is necessity to keep water with dissolved hydrogen anywhere during time from several hours to one day. The mechanism of process is discussed. Large role in hydrogen activation play background ionizing radiation, including cosmic radiation. The possibility of noncontact water activation is evaluated.

Keywords: negative red-ox potential, hydrogen, oxygen, ionizing radiation

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INTRODUCTION

The main technologies used now to produce water with negative red-ox potential (ORP) are: electrolysis and adding to water a reductant. Variation of ORP in cathode region during electrolysis ΔORP can be written as sum of three addendum:

$$\Delta ORP = \Delta E(H_2) + \Delta E(pH) + \Delta E(X) \qquad (1)$$

Where $\Delta E(H_2)$ – variation of ORP after production on cathode molecular hydrogen and its dissolution in water. The hydrogen dissolution do not affect on pH value.

$\Delta E(pH)$ – variation of ORP owing to variation of pH value. The variation is ~59 mV for $\Delta pH = 1$. When pH is increased the ORP is decreased.

$\Delta E(X)$ – variation of ORP owing to production on cathode in course of electrolysis new chemical compounds X. The value and sign of $\Delta E(X)$ depend on kind of chemical compound X, which is produced in course of electrolysis. For example, when in solution there is NaCl even at very small concentrations, the electrolysis leads to increase of ORP in region of cathode up to high positive value. The electrolysis of aqueous NaCl solution leads to oxidation of Cl^- ions up to ClO^- or Cl_2. Gaseous Cl_2 in water after hydrolysis transfer to ClO^-. Authors observed these phenomena in course of electrolysis various kinds of drinking water.

The water produced in electrolysis can't designate as ecologically pure product as after electrolysis pH value strongly change and it is outside the medical standard, in cathode region pH = 10 ÷ 11, in anode region pH = 3 ÷ 4. Water after electrolysis has abnormally high activity, as all factors affected on ΔpH leads to production of water with pH and ORP values outside the region thermodynamic stability of water [2]. Therefore properties of water after electrolysis can't reproduce by adding in water only any chemicals (oxidant or reductant). The equation (1) is written symbolically, exact equation for ΔpH at electrolysis can be given for specific experiment conditions, including material of electrodes and chemical composition of water. In our work the technology of water production with negative ORP by means of water saturation with gaseous hydrogen was analyzed. The time dependence of ORP after saturation with hydrogen, the condition to reach of negative ORP values, keeping of water with negative ORP during long time and effect of chemicals, dissolved in water on ORP value was investigated.

MATERIAL AND METHODS

Peculiarities of ORP measurement in the case of negative ORP values

The problem is exist when measuring the ORP for negative values which due to absence of reliable and accepted by all scientists standard. Any water solution on air quickly absorbs the oxygen from air. The absorption of oxygen leads to quick and unruled ORP increasing up to positive values. Standard exists only for positive ORP values, were the absorption of oxygen do not play essential role. Comfortable in work and portable devices were made using electrodes, NOW-HOW production of which do not known. The calibration such devices using solution of red $K_3[Fe(CN)_6]$ and yellow $K_4[Fe(CN)_6]$ prussiate for positive ORP values give no guaranty to correct results for negative ORP.

Using of platinum electrodes and standard reference electrode (for example silver chloride electrode) at first sight can give true result. But in this case large significance has purity of platinum electrode. The measured value is difference of potentials between electrodes. Input resistance of millivoltmeter is large but not endless, it usually equals about 10^{10} – 10^{12} Ω. For ORP = 100 mV current in input circuit of millivoltmeter equals ~ 10^{-13} A or 10^{-13} coulomb per second. The charge of electron is 1.6 x 10^{-19} coulomb. For R = 10^{12} Ω current of input circuit is ~ 10^{6} electrons per second. Let us consider our "electric cell" in which one of electrode is impurities on the surface of platinum, and suppose that "electric cell" can give current during 1 hour. For this time at current 10^{6} electrons per second the "electric cell" gives ~ 10^{10} electrons. Hence the amount of impurities must be not less than $10^{10}/(6.02 \times 10^{23}) \approx 10^{-13}$ mol to give potential 100 mV at input resistance 10^{12} Ω. It means the small impurities with concentration about 10^{-13} mol/l capable during long time affect on indication of device which measure difference of potential. The more is input resistance of millivoltmeter, the fewer amounts of impurities can affect on device indication. Therefore if we measure negative ORP potential, the calibration with solutions of red and yellow prussiate do not give guaranty for correctness of measurements.

In course of experiment we undertake some steps for maintenance of purity for platinum electrode. In the end of every day we insert platinum electrode in aqueous solution of hydrochloric acid (1:5), doubly distilled water was used. Next day before measurements the electrode wet out with doubly distilled water. However, it is impossible to prove that this procedure give pure platinum electrode as there is no standard for negative ORP value.

Method for production of water saturated by hydrogen and measurement of ORP

Hydrogen was produced in electrolytic cell with nickel electrodes. Electrolyte was 30% aqueous solution of KOH. The current of electrolysis was 5 A. Production rate of molecular hydrogen was 2.1 L/h. In industrial experiments hydrogen from high-pressure balloon was used. Some results obtained with electrolytic hydrogen were repeated with balloon hydrogen. For all cases the same results (values ORP) were obtained.

Various kinds of bottles (volume, material) were used in experiment. First of all every bottle was filled with investigated aqueous solution (water) top full, mouth was closed with stopper (cork). Then the bottle bottom up was dip into water bath. In water the stopper was removed and by means of pipe the hydrogen was introduced in bottle. No hydrogen purification was made. The solubility of hydrogen was 1.78 ml in 100 ml of water at 20°C. In volume 0.5 L is dissolved 8.9 ml of hydrogen, therefore to produce a water saturated with hydrogen, in bottle volume 0.5 L must be introduced not less than 9 ml of hydrogen. In bottle 0.5 L hydrogen was introduced so as above liquid surface was bulb not less than 10 ml, after that the bottle was closed with stopper. When hydrogen from balloon was used, the procedure of bottle filling was the same. The bottle filled with liquid and hydrogen was kept bottom up or on the side to avoid hydrogen leakage through the stopper.

After keeping of bottle in that position during previously given time, the bottle made open, the liquid (roughly 250 ml) pour into glass for measuring ORP. ORP was measured by means of standard silver chloride and platinum electrodes. In course of measurements, when electrodes introduce into liquid, the indication of device firstly was decreased, reach minimum and then was increased. The time to reach minimum indication was from 1 up to 30 minutes. The increasing of ORP was essentially slower than it's decreasing. We have in mind that owns ORP of silver chloride electrode (SCE) with respect to standard hydrogen electrode (SHE) according technical manual was 201 mV for 3M solution KCl at 20°C. Minimal indication of millivoltmeter was taken as potential ORP_{SCE}. Hence the $ORP_{SHE}(mV) = ORP_{SCE}(mV) + 201$ mV, were ORP_{SCE} is potential measured by millivoltmeter relative SCE. The concentration of oxygen, dissolved in water, was measured with Clark electrode. All measurements were made with device Expert-001 (Firm Econics, Moscow, Russia).

Production of water for experiment, chemicals

The tap water purified to could plasma by means of device BER-49-M "Pilimin" series was used [3, 4]. Water during the treatment was purified from organic compounds. The organic compounds were destroyed up to CO_2 and H_2O. ORP_{SCE} of water in one day after treatment (before beginning to saturate of liquid by hydrogen) was 150 ÷ 250 mV, pH = 7.3 ÷ 7.4. Permanganate water oxidability was not more than 1 mg O/L. The water in course of treatment was disinfecting by ozone, that produce under could plasma. The tap water after could plasma treatment contains 0.3 mg/L of ozone, it provide the disinfections of glass and chemicals, introduced in solution. In control experiments doubly distilled water was used. To use for experiments more purified water (Milli-Q) there is no reason as investigated processes have duration not less than one day. And it is known that the resistance of water Milli-Q on air is decreased more than 10 times during 1 hour as water absorb the carbon dioxide. After absorption of carbon dioxide from air the quality of Milli-Q water is the same as doubly distilled water.

The plastic and glass bottles from drinking water 0.5 L volume with metal stopper and plastic sealant were used. The chemical, solution of which want to investigate, was introduced in bottle first. The bottle pours with water directly from BER-49-M device. After dissolving of chemical and ozone decay on second day in bottle introduce hydrogen. We have used pure grade chemicals: NaOH and Na_2SO_3.

RESULTS AND DISCUSSION

The properties of water, saturated with hydrogen, and keeping of water with negative ORP in closed volumes

The dependence of ORP from duration of bottle keeping after hydrogen saturation up to moment of bottle opening for plastic and glass bottles is in Figures: Figure 1 – initial region (small time) for glass bottles; Figure 2 – for glass and plastic bottles up to keeping time 67 days. The amount of introduced in bottle hydrogen was 40 – 50 ml. Minimum time keeping was 2 minutes. In this time value of potential ORP$_{SCE}$ was –(200 ÷ 250) mV. In one hour ORP$_{SCE}$ is decreased up to –400 mV. This value not varied during 4 ÷ 5 hours (see Fig. 1). Then ORP$_{SCE}$ reach value about – 600 mV in 12 ÷ 15 hours after hydrogen introducing. The dependence of ORP$_{SCE}$ from initial up to – 600 mV during first 15 days was the same both plastic and glass bottles (see Fig. 2).

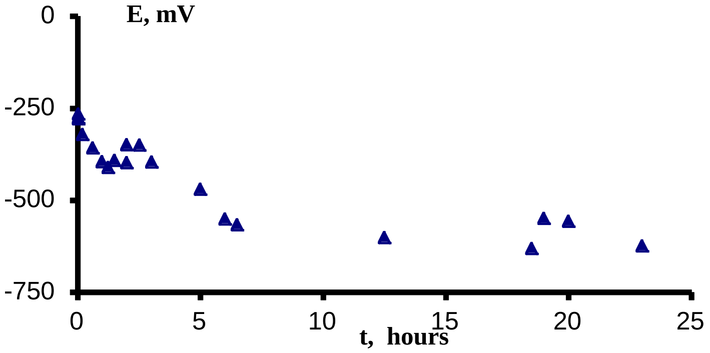

Figure 1: First points of time dependence for ORP$_{SCE}$ (E) of water in glass bottles for times starting from hydrogen saturation up to bottles opening and measuring of potential (t, hours).

When keeping duration is more 15 days, between plastic and glass bottles there are no distinct difference. In glass bottles ORP$_{SCE}$ is retained on the same level – 600 mV up to 3 months of observation (see Fig. 2, curve 1). In plastic bottles after 15 days keeping ORP$_{SCE}$ begin to increase (see Fig. 2, curve 2), there are strong dispersion of experimental points, and after keeping during about month ORP$_{SCE}$ increase up to 0 ÷ (–50) mV.

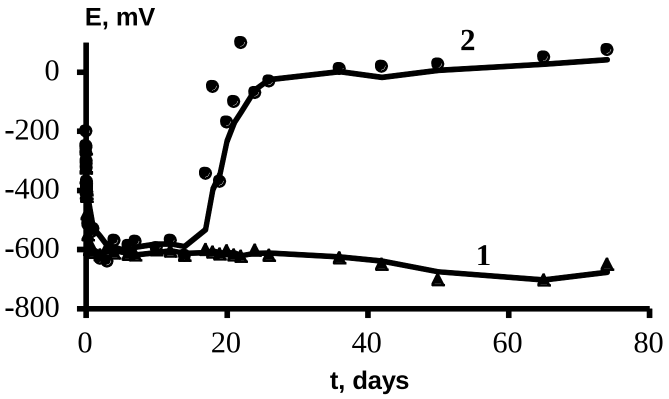

Figure 2: Time dependence for ORP$_{SCE}$ (E) water in bottles for times starting from hydrogen saturation up to bottles opening and measuring of potential (t, hours): 1 – glass bottles; 2 – plastic bottles.

Gaseous bubble in glass bottles during all observation time stay the same. Gaseous bubble in plastic bottles gradually decreases, and when it disappeared, ORP$_{SCE}$ value increase up to zero mV. When gaseous bubble in plastic bottles disappeared, the bottles are compressed. Dispersion of experimental points in Figures

1 and 2 do not due to experimental errors of measurements, but due to unregulated potential variations in different samples. In special experiment the glass bottle was closed on device for productions of aerate water (fizzy water), where balloon hydrogen and special cork from beer bottles were used. In this case the bottle may be keeping in any position (not only bottom up) and ORP_{SCE} during year stay on the level – 600 mV.

On the base of these data we can be stated, that observed potential due to not only reaction of catalytic decomposition molecular hydrogen on platinum electrode, but due to equilibrium:

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \quad (E = -0.828 \text{ V at pH} = 14) \qquad (2)$$

In neutral water, saturated by hydrogen, at pH = 7.4 value ORP_{SHE} with respect to standard hydrogen electrode (SHE) can be approximately – 450 mV. Potential ORP_{SCE} in this case is – 650 mV.

Evaluation of possibility for noncontact water activation

Variation of water ORP in vessel, submerged into catholyte with negative ORP was investigated. The decrease of water ORP_{SCE} was observed when vessel was polyethylene sack or thin-walled plastic beaker. When the glass beaker was used, the variation of ORP not found. These phenomena can be explained as hydrogen diffusion through thin plastic layer. Diffusion of hydrogen through glass is essentially less probable, than through plastic, therefore variation of water ORP in glass beaker submerged into liquid with small ORP (catholyte) do not observed.

The addition experiments with water, saturated by hydrogen, were made. Polyethylene beaker having thickness of wall 0.3 mm and 150 ml volume was set in glass having volume 330 ml with saturated by hydrogen water (ORP_{SCE} = – 560 mV). The time dependence of ORP_{SCE} in polyethylene beaker is in Figure 3, curve 1.

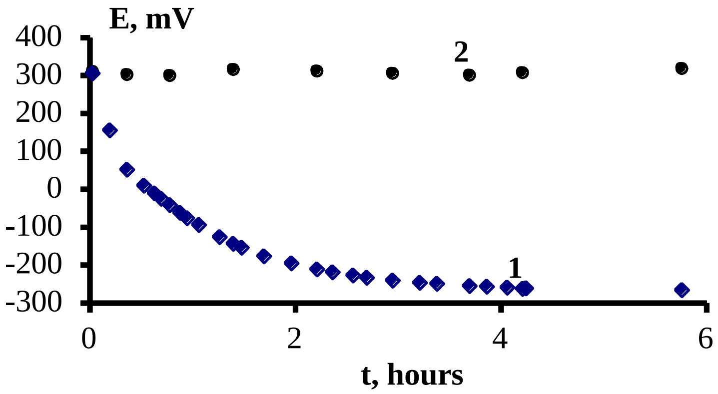

Figure 3: Measurements of ORP_{SCE} (E) in thin plastic beaker: 1 – beaker is submerged in water, saturated by hydrogen, ORP_{SCE} = – 560 mV; 2 – the same beaker submerged in solution of Na_2SO_3, ORP_{SCE} = – 490 mV (see text).

The initial value of water ORP_{SCE} in polyethylene beaker was 300 mV. The ORP_{SCE} began to decrease after submergence to hydrogen-saturated water and approximately in 5 hours reach steady state value – 280 mV. For that time the water ORP_{SCE} in volume 330 ml increase was not essential, from – 560 to – 530 mV. This result can be explained as hydrogen diffusion through plastic wall of beaker and reach of steady state between diffused in beaker and volatilized of hydrogen through open liquid surface. If we use not thin-walled plastic beaker but glass beaker with thickness of wall 0.5 mm, no variation of ORP_{SCE} in glass beaker was found.

We observed and reverse process, when in glass vessel of 3 L volume with water, having ORP_{SCE} = 310 mV, was introduced plastic vessel 500 ml volume with water saturated by hydrogen. Vessel of 3 L volume after introducing into liquid plastic vessel was closed by glass cover and keep bottom up during 2 days. In this condition the hydrogen diffusion from plastic vessel 500 ml through wall in 3 L vessel was possible. After keeping during 2 days in glass 3 L vessel ORP_{SCE} = – 100 mV. In plastic vessel 500 ml, initially saturated by hydrogen, ORP_{SCE} = – 210 mV. The decreasing of ORP_{SCE} in 3 L vessel (310 → – 100) mV is due to hydrogen diffusion from vessel 500 ml.

We have investigated the possibility of ORP variation in plastic vessel for the case, when potential is determined by introduced chemicals (reductant), not hydrogen. The setup of experiment was the same as for the case when vessel (breaker) was dipped into liquid, saturated by hydrogen, but now there was no hydrogen.

The negative value of ORP can be produced using chemicals not contain hydrogen. We have used the next chemicals: solutions of Na_2SO_3 250 g/L (2M) and NaOH 40 g/L (1M, pH =14). The equation for potential of neutral (platinum) electrode that is submerged in solution containing both oxidant and reductant is the next:

$$E(\text{мВ}) = \varphi_0 + \frac{59{,}15}{z}\lg\frac{[\text{ox}]}{[\text{red}]} \qquad (3)$$

Where [ox] and [red] – concentrations of oxidant and reductant,

φ_0 – standard electrode potential (mV) for reaction:

$$\text{ox} + z e^- \rightarrow \text{red} \qquad (4)$$

z – is number of electrons in one red-ox act.

Oxidants and reductants always there are in water, that is H^+ and OH^-. ORP value of pure water was determined by equilibrium:

$$O_2 + 2H_2O + 4e = 4OH^- \qquad \varphi_0 = 401 \text{ mV} \qquad (5)$$

The calculated ORP value for alkali solution with pH = 14 is the next:

$$E(\text{mV}) = 401(\text{mV}) + \frac{59{,}15}{z}\lg\frac{[H^+]}{[OH^-]} = -427 \text{ mV} \qquad (6)$$

We really obtained for 1M NaOH solution ORP_{SCE} = – 400 mV, and for solution Na_2SO_3 ORP_{SCE} = – 490 mV. No variation of ORP_{SCE} for polyethylene beaker, submerged into these liquids, during 7 hours of observation was detected. This result confirms that main factor determined ORP of water is chemical composition: presence of oxidants and reductants. Chemicals NaOH and Na_2SO_3 cannot diffuse through walls of beaker and cause the change of ORP value in another vessel. The hydrogen can diffuse through plastic (polyethylene) wall of beaker; therefore if in vessel, which is in contact with beaker, there is dissolved hydrogen, the ORP value in plastic beaker is decreased. There is no activation in the case, when hydrogen or another reductant do not pass from one solution to another.

The reason for increasing of ORP in open volume

Negative ORP values observed in our work are determined by reductant that is dissolved hydrogen. In course of water saturation by hydrogen the ORP_{SCE} is decreased by 400 mV (from 200 mV up to – 200 mV) during 2 minutes. The reverse process, i.e. increasing of ORP by hundreds mV in open volume must have the same duration (about 2 minutes), as ORP value is due to hydrogen dissolution. The hydrogen is very movable gas, and it must quickly diffuse from water. The time dependence of ORP_{SCE} value for water previously saturated by hydrogen in open vessel is in Figure 4. We prepare two kind of water, saturated by hydrogen: tap water and distilled water purified by filter with 0.1 μ pores. Before saturation by hydrogen both kinds of water were air decontaminated in vacuum –0.9 bars by means of water-jet pump. The hydrogen saturation was made for pressure 4 bars. From Figure 4 it is seen that in distilled purified water ORP_{SCE} value is increased essentially more quickly than in tap water. The samples of water were studied by means of microscope. The bubbles of gas were observed in every sample. In tap water the solid microscopic particles to which is adhered gas bubbles was seen. In distilled purified water were no solid particles and the number of gas bubbles was essentially less. Liquid in open vessel was kept on air until ORP_{SCE} increase up to positive values, after that in water there are no bubbles.

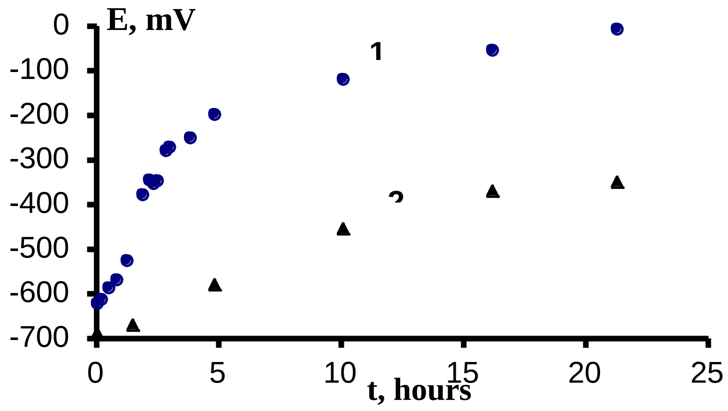

Figure 4: The increasing of ORP_{SCE} (E, mV) for saturated by hydrogen samples of water: 1 – doubly distilled water; 2 – tap water (see text); time keeping with open surface, t, hours.

Evaluation of hydrogen activation mechanism

The relation between oxygen concentration in water and impact of ionizing radiation from radioactive sources was investigated. Water temperature was 4 ÷ 5 °C (in winter). The water was saturated by atmospheric oxygen up to limit of solubility for given temperature, oxygen concentration was ~ 13 mg/L. The water was filled in bottle so as no air bubble stay in volume and after that the bottle was closed. In closed vessel the oxygen concentration was stay the same (~13 mg/L) during long time after heating of water up to room temperature (~20 °C). The reason for this phenomenon as in the case of hydrogen saturation is accumulation of oxygen bubbles into liquid. Oxygen bubbles were seen in liquid sample by microscope examination.

The concentration of active species (oxidants) in water was determined by means of KI solution according standard method. The long living active species produced under cold plasma treatment are ozone and hydrogen peroxide. The concentration of oxidants in water immediately after cold plasma treatment expressed in term of ozone concentration was 0.3 ± 0.02 mg O_3/L. After keeping in closed vessel during one day the concentration of active species is decreased up to 0.05 ± 0.02 mg O_3/L. Active species fully disappeared (up to limit of measurement method sensitivity) after keeping in closed vessel during 7 days. The fresh water prepared for experiment (immediately from output of BER-49-M device) has the next properties: ORP_{SCE} = 570 mV, $[O_3] = 0.3 \pm 0.02$ mg/l, $[O_2] = 13$ mg/L, T = 4 ÷ 5°C. The water treated to could plasma was filled in glass bottles.

One half of prepared bottles were saturated by hydrogen, second half of bottles stay without alteration. After keeping during fixed time the bottle was open. Values of ORP_{SCE} and dissolved oxygen concentration were measured. Value pH in all experiments stay constant and was pH = 7.2 ÷ 7.3.

For every experiment condition 6 samples of water were prepared. Results of water characteristics measurement are in Table 1. The error of results in Table 1 is due to dispersion of measured values in different samples. The concentration of dissolved oxygen in water samples without hydrogen during 40 days decrease from 13 to 7.9 mg/L, value of ORP_{SCE} decrease from 570 to 120 ÷ 150 mV. In water samples saturated by hydrogen the concentration of oxygen was rapidly decrease and after 40 days there was no oxygen in solution, value ORP_{SCE} decrease up to – 350 mV.

Table 1: Concentrations of dissolved oxygen [O_2] (mg/L) and ORP_{SCE} values (mV) for different samples of water.

t, days	Without hydrogen		With hydrogen	
	[O_2], mg/l	ORP_{SCE}, mV	[O_2], mg/l	ORP_{SCE}, mV
0	13 ± 0.5	570 ± 50	13 ± 0.5	570 ± 50
0.041	12 ± 0.5	490 ± 20	10.2 ± 0.5	140 ± 40
0.21	11.2 ± 0.4	370 ± 15	9.6 ± 0.3	50 ± 20
0.75	10.2 ± 0.4	245 ± 20	6.4 ± 0.3	-120 ± 20
1.83	10.8 ± 0.4	210 ± 20	5.4 ± 0.3	-140 ± 20
3	10 ± 0.4	110 ± 20	5 ± 0.5	-200 ± 20
7	9.7 ± 0.4	135 ± 15	4 ± 0.7	-250 ± 50
11	8.7 ± 0.4	155 ± 15	2.1 ± 0.7	-260 ± 40
17	8.2 ± 0.4	155 ± 15	0.75 ± 0.2	-350 ± 50
40	7.9 ± 0.4	120 ± 15	0.2 ± 0.1	-350 ± 40

So it is seen that strong decrease of ORP take place at low concentrations of oxygen in water. Molecular hydrogen and oxygen are low active species. They not interact one another at room temperature. The ORP value cannot decrease until in water there is high oxygen concentration. The reaction of hydrogen oxidation $O_2 + H_2$ (consumption of oxygen) must be activated by external factors. Water from BER-49-M device contain active oxygen forms (ozone and hydrogen peroxide) which can activate $O_2 + H_2$ interaction. Oxygen consumption is partially due to its impact.

Additional (and main) factor of activation can be external ionizing radiation (first of all cosmic radiation). For evaluation of this factor the experiment was made, in which volumes with water, saturated by hydrogen, was irradiated by radioactive source Cs^{137} with activity 10^5 Bq. It was stated that values of ORP_{SCE} for irradiated to Cs^{137} during 15 ÷ 30 minutes volumes is 100 ÷ 200 mV less than in control not irradiated samples. It confirms the assumption that cause of water activation, saturated by hydrogen, can be ionizing radiation. The activation can due to radiation background in room, if radioactive source do not used.

CONCLUSION

The saturation of water by gaseous hydrogen allow to decrease of ORP_{SCE} up to values $-(600 \div 700)$ mV after keeping of water saturated by hydrogen during not less than one day.

The decreasing of ORP takes place after consumption of dissolved oxygen in reaction with hydrogen. The reaction $O_2 + H_2$ is initiated by external ionizing radiation.

The hydrogen dissolved in water can diffuse through plastic wall of vessel; there is no hydrogen diffusion through glass wall. Therefore the water with negative ORP, produced by hydrogen saturation, can keep during long time only in glass vessel.

In open volume the ORP of water saturated by hydrogen is slow (not quickly) increase as hydrogen there is in water as bubbles, which adhered to hydrophobic micro admixtures of water. These admixtures not allow of hydrogen bubbles quickly come to the surface and volatilize.

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