## PHYSICAL CHEMISTRY
## OF WATER TREATMENT PROCESSES

# The Use of Redox Potential in Water Treatment Processes

## V. V. Goncharuk, V. A. Bagrii, L. A. Mel'nik, R. D. Chebotareva, and S. Yu. Bashtan

*Dumanskii Institute of Colloid and Water Chemistry,*

*National Academy of Sciences of Ukraine, Kiev, Ukraine*

Received January 14, 2009

**Abstract**—The use of redox potential as a control parameter of wastewater treatment processes for characterizing the natural water condition and estimating the antioxidant properties of drinking water has been investigated.

## INTRODUCTION

Redox potential (ORP) is an essential indicator of the properties of natural and waste waters. Its value allows us to estimate the redox mode of water in water bodies (its contamination with decay products of organic matter and with the wastewater of industrial enterprises), and also to control the water treatment process at purification facilities. Natural waters being in contact with the atmosphere are characterized by more positive ORP values unlike the underground subterranean waters interacting with sulfides, silicates, and organic matter (oil, coal, etc.). Low values of ORP for household and industrial wastewaters indicate the presence of reducing agents (ammonia, nitrites, organic substances capable of being oxidized, etc.), while the high values of ORP indicate the presence of oxidizing agents, for example Cr(VI), Mn(VII), oxygen, gaseous chlorine or products of its hydrolysis. The ORP versus pH relationships (Purbe diagrams) make it possible to anticipate the forms of existence of any particular elements or their compounds in solutions. As of today the ORP measurement is the only method available for estimating the antioxidant properties of drinking water.

## OXIDATION–REDUCTION PROPERTIES OF NATURAL WATERS

The reactions occurring in aqueous solutions and involving the transfer and attachment of electrons are called redox reactions. The relationship between the oxidized and reduced forms of a substance in water is characterized by the ORP value. Under the equilibrium conditions ORP reaches its stationary value that allows us to make certain general conclusions regarding the chemical composition of water. Hence, the oxygen and chlorine present in water tend to accept electrons and have a high electric potential, i.e., they are oxidizers, while the hydrogen-type elements readily donate electrons and have a low electrode potential. Oxygen possesses the highest oxidizing ability, while hydrogen has the highest reducing ability, however between them there are other elements present in water that play their part of oxidizers or reducers less effectively.

In multicomponent chemical and biological systems redox couples occur in complex combinations and constantly changing ratios. Values of pH essentially depend on the balance of oxidized and reduced forms and, in turn, affect ORP. The stationary values of each individual redox couple with due regard for the pH factor are determined by the well-known Nernst formula [1].

$$\varphi_{st} = \varphi_n + \{0.06 \log ([Ox]/[Red])\}/n - 0.06 \text{ pH}, \tag{1}$$

where $\varphi_{st}$ is the stationary ORP with due correction for pH; $\varphi_n$ is the normal ORP for the given redox couple with respect to the normal hydrogen electrode (NHE) under the equilibrium of concentrations of oxidized and reduced forms and pH equal to 0. From the formula it follows that as pH increases by unity, ORP decreases by 60 mV (at 25°C). It should be emphasized that in the general case the experimentally measured ORP is not referred to any separate redox couple and represents a compromise for all redox reactions occurring in water.

In laboratory practice the ORP measurements make use of the test platinum electrode in a pair with reference silver–chloride electrode (SCE), the potential of which is by 0.2224 V more positive than that of NHE.

Given the same values of ORP the rate of redox processes depends on standard potentials $\varphi_0$ of the specific electrode reaction. The lower is the standard potential, the easier is oxidized the given substance. For example,

$\varphi_0$ of oxidation reaction $Fe^{2+} \to Fe^{3+} + e^-$ (771 mV) in a strongly acidic medium is much higher than $\varphi_0$ of oxidation reaction $Cu^+ \to Cu^{2+} + e^-$ (167 mV), i.e., given the values of ORP of both reactions are the same or close, univalent copper will be oxidized easier than the divalent iron.

Depending on the ORP one can distinguish several main situations that occur in natural waters [1]. For the sake of convenience below all the specified ORP values are given with respect to SCE.

### Oxidation Situation

(ORP > 100−300 mV) is characterized by the presence in water of free oxygen, and also a wide range of elements with high degrees of valence ($Fe^{3+}$, $Mo^{6+}$, $As^{5+}$, $V^{5+}$, $U^{6+}$, $Cu^{2+}$). This situation is most typical for surface waters. ORP of certain surface and subterranean waters containing free oxygen may reach 700 mV.

### Transient Oxidation−Reduction Situation

(ORP in the interval 0−100 mV) is determined by an unstable geochemical mode and the variable content of hydrogen sulfide and oxygen. In the specified conditions one can observe both the weak oxidation and weak reduction of a wide range of metals.

### Reduction Situation

(ORP < 0 mV). Such situation is typical of subterranean waters where the metals with low degrees of valence ($Fe^{2+}$, $Mo^{4+}$, $Mn^{2+}$, $V^{4+}$, $U^{4+}$) and also hydrogen sulfide are present.

In the oxidizing medium featuring the presence of free oxygen of the air, such elements as sulfur, chromium, and vanadium are present in water in the form of well-soluble compounds, such as sulfates, chromates, vanadates, etc., while ions $Fe^{3+}$ and $Mn^{4+}$ form hardly soluble compounds. In the absence of free oxygen the presence of the trivalent iron is an indicator of the oxidized state of water.

The small content of dissolved oxygen is intrinsic for subterranean waters. The so-called "oxygen surface" is established at a specific depth in these waters, and below the specified surface the water does not contain free oxygen. The depth of this surface under conditions of intensive and long-term water exchange in layers of rocks that do not contain organic matter (oil, coal, etc.) may reach hundreds of meters and in isolated cases − 1 km and more [2]. Subterranean waters related to oil deposits are characterized by the ORP values that are much less than zero, and in places may be up to −500 mV. These conditions give rise to the evolvement of processes of reducing $Fe^{3+}$, $SO_4^{2-}$ and other ions.

The key agents of reduction reactions in natural water are microorganisms decomposing the organic matter. Under conditions of the reducing medium the trivalent iron and four-valence manganese transit into a bivalent form creating well-soluble compounds. In the presence of $H_2S$ metal sulfates transit into hardly soluble sulfides (PbS, ZnS, CuS, $Ag_2S$, etc.). The presence of bivalent iron and the absence of free oxygen represent the main criterion of the reduction environment.

Data on the ORP of natural water makes it possible to assess the migration ability of separate elements and, in particular, the concentration and scattering of the latter. Hence, a low level of ORP in northern bogs and in certain subterranean waters determines the possible migration therein of iron in the form of $Fe^{2+}$. And conversely, hardly soluble minerals of the trivalent iron are formed in oxygenated soil and subterranean waters of grasslands and deserts.

A large number of papers are available that use ORP for estimating the natural water quality together with other indicators. They mostly include pH, electrical conductivity, the content of free oxygen, available chlorine, and ions of heavy metals. Hence, paper [3] presents data on the investigation of a water system including the lake, the river flowing into it, and the subterranean water in the same area by measuring the values of ORP and electrical conductivity (as total pollution indicator). Seasonal fluctuations of these parameters were noted. The average ORP of the lake water was equal to 140 mV, $ORP_{max}$ was 350 mV; ORP of subterranean water was 120−210 mV, the electrical conductivity was 90−160 μS/cm. ORP of the river water was 120−440 mV, while the electrical conductivity was equal to 10−270 μS/cm.

The possible use of ORP measurements for estimating the efficiency of iron removal during the water treatment process for drinking purposes was investigated in paper [4] using a pilot biological filter. It was shown that the ORP measurement makes it possible to estimate the iron concentration in the water subjected to treatment. If ORP does not exceed 300−470 mV, the iron concentration will be more or equal to 3 mg/dm$^3$. At

higher ORP values the residual iron concentration will be less than 0.2 mg/dm$^3$ (the French Standard for drinking water).

An advantage of the ORP indicator is the possibility of real-time operational control of water quality, in particular under the field conditions [5]. Using the measurements of ORP and pH the authors of paper [6] offer to determine the content of ClO, $ClO_2^-$ and / or $HClO_2$ in the drinking water. The measurement of ORP in water decontamination processes makes it possible to automatically control the consumption of the electrolytically generated hypochlorite [7]. Devices for continuous water quality control during the water conditioning process were patented [8, 9]. These devices are equipped with sensors of pH, ORP, salt content, electrical conductivity, temperature, etc. Using additional sensors and units it is possible to determine such parameters as, e.g., the rate of oxygen consumption and the content of different forms of nitrogen. The system is controlled by a personal computer and its power supply is provided from a car battery.

Papers [10, 11] offer the continuous monitoring of water quality at different sources with the transfer of information to special centers by using custom-designed computer networks. The controlled parameters include dissolved oxygen, the concentration of metal ions, concentration of fluorine, pH, ORP, flow rate, etc.

## THE USE OF REDOX POTENTIAL FOR REAL-TIME OPERATIONAL CONTROL OF WATER TREATMENT PROCESSES

Investigations conducted in the Harvard University in 1936 revealed the correlation between the water ORP and the degree of bacteria inactivation in chlorination processes. Later the specified tests were corroborated in other research laboratories all over the world. As a result, the ORP measurement became one of the basic approaches to the standardization of parameters of water disinfection [12]. The main advantage of the ORP measurement technique as a method of disinfection quality control is the possibility of implementing the real-time control as compared with the conventional method based on measuring the concentration of residual chlorine [13–15]. In 1971 the World Health Organization (WHO) adopted the ORP value equal to 700 mV as a standard for disinfection of the drinking water. In 1982 the German Standards Agency adopted the ORP value equal to 750 mV as a standard value for the water in public swimming pools, while in 1988 the National Institute of Swimming Pools in the Federal Republic of Germany (FRG) adopted the ORP equal to 650 mV as the value for public spas [12].

The recent studies [14] corroborate the need of maintaining the water ORP at the level of no less than 650 mV for ensuring the typical antibacterial activity with respect to pathogenic bacteria *E. Colli, Salmonella, Erwinia,* and *Pseudomonas,* as well as other nonsporous microorganisms. Unfortunately, the resistant spore-forming pathogens such as *Cryptosporidium* are highly resistant with respect to chlorine, bromine, iodine, and other strong oxidizers. That is why the detection of the specified pathogens in the process of preliminary microbiological analysis involves the need of using the ozone treatment or high-intensity UV irradiation for water disinfection.

Unlike the disinfection processes based on using chlorine compounds, where ORP measurements have widespread application for controlling the bacteria inactivation, this method of control has not yet found practical application during the disinfection based on using ozone. The reason is the absence of strict correlation between the degree of disinfection and the ORP variation. It has been experimentally found [14] that perceptible changes of the solution ORP occur much later than the time of complete disinfection of water with ozone. This is possibly related to subsequent biodestruction of perished bacteria that is not observed in chlorinated water.

Nowadays the ORP measurements are used for controlling not only the drinking water disinfection process, but also the washing waters produced during the harvesting and  packaging of vegetables and fruit, the processes of underground water conditioning, water demanganization and purification [15], the destruction of cyanides, bleaching, chromium reduction, and metal etching [13, 14].

The concentration of dissolved oxygen and pH and ORP values belong to the number of key parameters of the wastewater treatment, in particular for the optimization of the nitrification–denitrification processes at biological treatment plants [16–21] and also for the determination of the ratio of aerobic and anaerobic processes [22]. These indicators make it possible to promptly control the treatment process using the on-line automatic control systems. This ensures the stability of quality parameters of the discharged wastewater in terms of the nitrogen content and eliminates the excessive electric power consumption for aeration.

Under conditions of wide fluctuations of wastewater flows and their nitrogen content, especially at the biological treatment plants of small and middle capacity, the schemes with fixed volumes of nitrificators–denitrificators are inefficient. It was found out [18] that the schemes of periodic nitrification were promising with

alternating phases of nitrification, using pneumoaeration and mechanical stirrers, and denitrification, where only the stirrers are running.

The automatic control systems with ORP as the main controlled parameter are used for adapting the periodic nitrification systems to fluctuations of the wastewater flow and nitrogen content, and also for ensuring the economy of power consumption on aeration/stirring. As ORP decreases to a specific value, the pneumoaeration system is turned on, the content of ammonium nitrogen decreases, while the content of nitrates increases, respectively. After the ORP value is stabilized pneumoaerators are replaced with stirrers (anoxic/ anaerobic phases) resulting in the implementation of the denitrification phase. The above control principle of the nitrification−denitrification process forms the basis for other plants of wastewater treatment from ammonium nitrogen.

It was shown that the course of aerobic processes occurs in a wide range of ORP values (100−1229 mV), however their progress is most stable at the ORP level of 1229 mV; at ORP ≤ 100 mV anaerobic processes prevail, the products of their activity are carried to the surface resulting in the beginning of $H_2S$ release [23]. In order to ensure the wastewater treatment without the appearance of unpleasant smell, it is necessary to maintain the strongly oxidizing medium at the ORP level of 1229 mV.

Due to the establishment of the optimal range of ORP (150−50 mV) during the medium aeration it is possible to enhance the efficiency of water treatment from Cr(VI) in a modular bioreactor by using the immobilized biocenosis [24]. In this case the reduction rate of Cr(VI) reaches 15 mg/($dm^3$ h) that is much more efficient than implementing the process under the obligatory-anaerobic conditions. Under the periodic cultivation Cr(VI) concentration of 100 mg/$dm^3$ is reduced within 4.5−5 h. In paper [24] the lubricating fluid was used as a source of carbon and donor of electrons.

The ability of bacteria using the oxidized forms of nitrogen as terminal acceptors of electrons to change ORP of the nutrient medium during the metabolism was studied in paper [25]. It was established that nitrates did not affect the ORP dynamics in the culture of denitrifying *Pseudomonas,* while in the presence of nitrites the transition of cells from aerobic to nitrite breathing occurred only after a certain latent period typical of each of strains. The reduction of nitrate nitrogen into the elementary state in the culture of denitrifying *Pseudomonas* occurred in the ORP range from 160 to −100 mV, while that of nitrite nitrogen in the range from 130 to −60 mV.

Data obtained in paper [25] are in agreement with those in paper [26]. According to these data the successful nitrification (oxidation of ammonium to nitrates) requires the maintenance of ORP at the level 100−350 mV while using nitrifying bacteria, and the successful denitrification (reduction of nitrates to the molecular nitrogen) requires the maintenance of ORP at the level 50−(−50) mV [27]. The Biological removal of phosphorus is implemented in two stages. At the first (anaerobic) stage the optimal ORP values amount to (−100)−(−225) mV, while at the second (aerobic) stage these values amount to (−25)−250 mV. The removal of organic impurities using anaerobic bacteria occurs at ORP values in the range 50−250 mV.

Nowadays the ORP measurements are used for controlling the fouling of pipe surfaces with microorganisms and waterweeds in heat exchange systems [26]. This is particularly urgent in those cases, when for some reason the use of biocides is undesirable. It was established that the biological activity of microflora could be inhibited by reducing ORP to values (−300)−0 mV that corresponds to the concentration of dissolved oxygen in the range 0.01−0.1 mg/$dm^3$. It was offered to bind the excessive dissolved oxygen with hydrogen synthesized in a special reactor with catalyst.

It is well-known that ORP can be applied for controlling the redox processes of water treatment from heavy metals in the metallurgical industry [28] and for determination of the rate of reactions in organic chemistry [29, 30]. Hence, in paper [29] the kinetic characteristics of hydrochinone oxidation were determined by the redoxometric method, while paper [30] presented a mathematical model of ORP variation in the redox processes of ascorbic acid.

It should be noted that a considerable body of ORP data has been presented in the patent literature [8−10]. This is related to the growing demand on the measuring and analytic equipment for controlling the water pollution. In accordance with paper [31] the volume of sales of the measuring equipment designed for controlling the water quality in countries of Europe had to increase from 311.8 million USD in 1999 to 421.2 million USD in 2005. In this case 43.8% of this turnover falls on instruments for measuring pH, ORP and electric conductivity of water, 15.1%—for measuring BOD, COD, and total organic carbon, and 13.1%—for measuring the content of ammonium nitrogen, nitrates, and phosphates.

The information about the companies producing instruments for water quality control is presented in papers [32−37]. In particular, it is reported [32] about new ECM series instruments produced by Dr. Bruno Lange GmbH (Germany) and intended for measuring temperature, ORP, pH, DpH, conductivity, and oxygen

concentration. JUMO GmbH and Co.KG Company offers a variety of instruments for the determination of pH, ORP and the content of $H_2O_2$, Cl, $ClO_2$, $O_3$, and $O_2$ in water [37]. Paper [38] discusses the design features of different electrochemical sensors intended for the monitoring of natural waters with respect to the content of ammonium, nitrates, pH, ORP, etc. A particular attention was devoted to the long-term stability of such sensors. The authors of paper [39] developed the exact electrochemical sensors for deep-water measurements. These sensors make it possible to measure pH, ORP, $pCO_2$ directly in sea water by the potentiometric method, $O_2$—by the amperometric method, and the salt content by the conductometric method.

## ESTIMATION OF THE ANTIOXIDANT ACTIVITY OF DRINKING WATER

The drinking water quality is determined by national standards. In Ukraine Standard GOST 2874-82 Drinking water is still in force [40], where ORP is included as a nonstandardized indicator.

Upon the recommendations of WHO the drinking water ORP should not exceed 60 mV, while under the current conditions this indicator is generally lies within the limits 100−400 mV. The last statement is valid practically for all kinds of water: tap water, water sold in plastic and glass bottles, and the water purified at membrane−sorption installations.

ORP of the internal environment of a person in health is always below zero in the range from −100 to −200 mV (SCE). That is why from the viewpoint of human health it would be optimal for people to use water having a negative ORP value. However, in everyday life people use water with positive ORP. The adaptation of the ORP of the consumed water to the ORP of human internal environment occurs at the expense of consuming the electric energy of cell membranes, i.e., the energy of the highest level that actually is the end product of the biochemical chain of transformation of nutrients [41, 42]. In the general case, the amount of energy consumed by a human organism for achieving the biocompatibility of water is proportional to its quantity and the difference of the water ORP and the ORP of the human internal environment.

The general direction of transformation processes of water impurities proceeding with participation of live organisms also depend on the ORP value. The exchange processes in wild life occur in a rather narrow interval of pH. The spread of pH values does not generally fall outside the limits of 6−8. Major functional violations appear in the protein-cellular media of mammals at pH < 6 and pH > 9. In the pH range of 3−4 the majority of dissolved proteins are subjected to irreversible coagulation. Aggregation of protein molecules, mostly irreversible, occurs at pH shifts of protein media in the range 9−10. The approximate range of ORP for biological substrates is in the range from −250 to 1000 mV (SCE) [41].

During the life a man is exposed to the impact of various harmful external factors, such as poor ecology, incorrect and often imperfect nutrition, the use of poor quality drinking water, stress situations, smoking, alcohol abuse, the use of medications, diseases and many others. All these factors contribute to the destruction of the oxidation−reduction system of the organism regulation at the cellular level. The direct cause of the cell damage and death may be extremely reactive substances containing oxygen or free radicals: $O_2^{-\bullet}$, $O_2$, $OH^{\bullet}$, $OOH^{\bullet}$, $NO^{\bullet}$, and $H_2O_2$. As noted in paper [43] the oxidative stress represents the state of disbalance due to the formation of excess of free radicals and the reduced activity of the antioxidant protective body system. All oxidizing reactions are a permanent source of potentially cytotoxic active oxygen compounds that play a vital part in live systems. Under the physiological conditions the active oxygen compounds are completely inactivated due to the well-developed cellular and exocellular antioxidant protective system. However, under specific conditions the enhanced generation of active oxygen compounds and/or the reduction of the antioxidant capacity results in the oxidative stress. Hence, pancreatic diabetes is characterized by the increased production of active oxygen compounds, sharp reduction of the antioxidant protection of organism, and variation of the cellular redox status [43]. The oxidative stress is also associated with physiological degeneration that accompanies Parkinson's and Alzheimer's diseases, cardiovascular and oncological diseases, and also aging [44, 45].

The balance of the reduction−oxidation system of regulation can be normalized by using antioxidants. The strongest antioxidant is water with negative ORP. Due to its reduction properties such water ensures the following:

− normalizes the microflora of the gastrointestinal tract by stimulating the growth of proper normal microflora (bifidobacteria and lactobacteria) and suppression of pathogenic and opportunistic pathogenic microflora, including *Staphylococcus aureus*, salmonella, *Shigella* (dysentery), *aspergillus*, *Listeria, Clostridia*, *Pseudomonas aeroginosa*, *Helicobacter pylori* (considered to be the cause of peptic ulcer diseases) [41];

− restores and activates the immune system of people with compromised immunity, including that after the exposure to radiochemotherapy [46−48];

− exhibits antimutagenic (anticarcinogenic) properties [44];

— exhibits hepatoprotector properties [49];

— stimulates wound healing and anti-inflammatory processes [50];

— exhibits the antidiabetic effect [43, 51−53];

— suppresses hepatitis C, herpervirus and influenza viruses.

The only method of estimating the antioxidant properties of water is redoxometry. The table below presents the ORP values for the most characteristic types of natural and activated waters, carrot juice and certain biological fluids of human organism.

The substances reducing ORP in the internal environment either produce indirect impact via the oxygen factor, i.e., due to the $pO_2$ reduction or produce the similar effect, irrespective of $pO_2$ changes (such substances include cysteine, glutathione, and vitamin E) [54]. It should be noted that the administration of deoxidizers by itself does not guarantee significant negative ORP shifts in tissues. Anyway, this cannot be achieved by the parenteral administration of glucose, pyruvate, amber acid, valine, alanine, and methylene blue. The administration into the system of such substances as cysteine, cystamine, cysteamine, diethyl propanol, histamine, glutathione, thiourea, sodium nitrite, fructose, ether (during the inhalation narcosis), sodium citrate, and methionine reduce the ORP local value of muscular tissue by 140−170 mV. In the general case, the value of standardized ORP of pharmaceutical preparations cannot be a reliable guide in their application aimed at reducing ORP of living tissues [41].

Redox potential of water and water solutions

| Medium | ORP value, mV |
|---|---|
| Tap water | 220−380 |
| Bottled water | 200−400 |
| Water in wells and springs, and rain water | 200−320 |
| Water from wells (> 100 m deep) | (−50)−50 |
| Water with microhydrin | up to −200 |
| Water passed through any household filter | does not change the initial ORP value |
| "Water of life"—catholyte, pH 7−11 (for medical purposes) | (−1200)−0 |
| "Dead water"—anolyte, pH 1−7 (for disinfection) | 0−1000 |
| Freshly squeezed carrot juice | −70 |
| Oral fluid of apparently healthy person | (−50)−50 |
| Mother's milk | −70 |
| Internal environment of apparently healthy person | −70 |
| Optimal medium for growth of bifidobacteria | (−200)−50 |
| Electrochemically activated water | up to −500 |

The efficient antioxidant properties are intrinsic to certain natural regenerated waters such as Nordenau Spring (Germany, [52]) and Hita Tenryosui (Japan, [48]).

The known techniques of reducing ORP of water by treating such water with kaolinite-bentonite ceramics enriched with magnesium (pH 10−11.5, ORP = (−140)−(−195) mV) [55] and by dissolving the combination of minerals in clean water (pH 10.5, ORP = −200 mV) [44].

Coral Club Company (Vladivostok) offers a technique of activating water with coral stone. When the water is treated by coral calcium, its ORP shifts into the negative region. ORP of the coral calcium in water may reach −200 mV, i.e., if the water before its interaction with the powder had ORP equal to 150 mV, then after the treatment with coral powder its ORP value may drop to −50 mV. Such value corresponds to optimal indicators of ORP for intercellular fluids of body tissues. In this case the body cells would not need to spend an additional amount of energy for ORP leveling and the energy will be directed on intracellular exchange.

The application of microhydrin (nanocarbon) having ORP in the range from −500 to −600 mV is still more impressive. Microhydrin provides an enormous quantity of electrons and, correspondingly, confers antioxidant properties to our diet. As regards this indicator microhydrin definitely is tens and hundred times as good as the most popular state-of-the-art antioxidants. The properties of microhydrin were discovered by American scientists in the 2000s. One tablet per glass of water, milk, coca-cola changes its ORP from 300 to −300 mV that is much higher than that of the freshly squeezed carrot juice (−70 mV) (see the table). Unfortunately, the cost of such tablet is fairly large.

The Japanese scientists [56, 57] offered a technique for obtaining the antioxidant water including the electrolytic production of hydrogen and the addition to water of the colloid of platinum, palladium, rhodium, iridium, ruthenium, gold, silver, rhenium or their compounds, or hydrogenase enzyme for the reduction of hydrogen released. This technique makes it possible to stabilize the negative value of water ORP, however, the use of precious metals rules out its application in practice.

Nowadays electrolysis is the main technique of obtaining water with negative ORP. It is customary to assume that the main processes leading to the ORP reduction occur at the boundary with the cathode surface, where high strengths of electric field are possible. In this case the activated structures are formed in the extremely thin (only 50–60 nm) layer of the solution near the electrode surface. In accordance with paper [54] the catholyte obtained as a result of the electrochemical treatment of relatively small intensity (pH < 9, ORP > −400 mV, SCE) is ineffective. The catholyte obtained in the mode of intensive electrochemical treatment (pH > 9.5, ORP < −400 mV, SCE) can act as a regulator of metabolism.

The molecular hydrogen released at the cathode is a strong reducer. That is why one can assume that the negative value of catholyte ORP is determined by dissolving hydrogen in water. The analysis of the hydrogen release process in [58, 59] involved the consideration of the following reaction:

$$2H^+ + 2e \rightarrow H_2, \tag{2}$$

the standard potential of this reaction with respect to NHE at pH 7 is equal to 414 mV [60]. This is much less than the ORP value observed in experiments and equal to about 600 mV. As was shown in paper [61], the saturation of water with hydrogen (at concentration of $\sim 8 \times 10^{-4}$ mol/dm$^3$) may yield the ORP values in the range (500–700) mV. The reaction that ensures such potential (standard potential with respect to NHE amounts to 828 mV) can be written in the form

$$2H_2O + 2e \rightarrow H_2 + 2OH^-. \tag{3}$$

Thus, the ORP value achieved during electrolysis is determined by the release of hydrogen in accordance with reactions (2) and (3) and subsequent dissolution and diffusion of hydrogen over the entire volume of liquid.

As noted in paper [62], hydrogen is an ideal trap for active compounds of oxygen: $O_2^{-\bullet}$, $O_2$, $OH^\bullet$, and $H_2O_2$. At the same time a more detailed study of the mechanism of hydrogen action revealed [48] that hydrogen reduced only most toxic radicals $O_2^{-\bullet}$ and $OH^\bullet$ rather than all active forms of oxygen. In the specified paper it is also noted that hydrogen is capable of rapid migration through biological membranes contributing to the enhanced antioxidant effect.

The results of experiments dealing with contactless activation of water in a container made of different materials and placed into the catholyte with negative ORP [54] can be also explained by the dissolution and diffusion of hydrogen. Hence, according to paper [61] the reduction of the water ORP in a container placed into the catholyte was observed, when the glass was made of thin plastic or water was kept in a polyethylene bag. The reduced ORP values were explained by the diffusion leakage of hydrogen through the container walls. Under the same conditions ORP variations in glass containers were not observed. When these containers were placed into a solution with negative ORP, the contactless activation of solutions in hermetically sealed glass containers did not occur.

The authors of papers [42, 63] claimed to develop a technology for maintaining in a metastable condition of low mineralized (0.01–0.5 g/dm$^3$) activated aqueous solutions and water-containing raw materials with negative ORP. The license on the author's patent [42] allowed Redox Technologies Company to organize the production of a drink under the name "Vashe Zdorov'e" (Your health) with the storage life of no less than one year (the water produced now by using household electrochemical activators preserves its properties no more than 5–6 h). The information presented in papers [42, 63] requires corroboration, because from the patents published by the authors the mechanism of stabilization of negative ORP value of water is not clear.

## CONCLUSIONS

The data presented in this paper indicate that ORP is a vital indicator of the natural water condition and one of the main control parameters of wastewater treatment processes. The drinking water ORP affects the metabolism processes of living tissues. The more negative is ORP value, the higher are antioxidant properties of water. There is still no universal method for obtaining water with a stable negative value of ORP. Since ORP reflects integral redox processes in aqueous solutions without regard to their chemical composition (the same ORP values may correspond to different chemical compositions), it cannot unambiguously characterize the water quality. For this reason the standards of WHO, US EPA, EC and SanPiN (Sanitary Regulations and

Standards in Russia) do not include the ORP value as a mandatory parameter. Nevertheless, the ORP value is vital for the estimation of physicochemical properties of water, since it allows us to reasonably approach the issue of selection of the optimal scheme of water treatment and regulation of its antioxidant properties.

## REFERENCES

1. *Voda pytna. Normatyvni dokumenty* (Drinking Water. Regulatory Documents), Lviv: NTTs Leonormstandart, vol. 2, 2001.

2. Nikanorov, A.M., *Gidrokhimiya* (Hydrochemistry), Leningrad: Gidrometeoizdat, 1989.

3. Williams, J.B., Williams, L., Baldwin, N., et al., *Proc. Nat. Conf. on Environ. Sci. and Technol.,* (*Greensboro, N.C., September 8−10, 2002*), Columbus (Ohio): Richland Battelle, 2003.

4. Tremblay, C.V., Beaubien, A., Charles, P.N., and James, A., *Water Sci. and Technol.,* 1998, vol. 38, no. 6, pp. 121−128.

5. Wregglessworth, D., *Metal Finish*, 2004, vol. 102, no. 5, pp. 6−7.

6. Gottard, W., Patent Application no. 19960275 (Germany), IPC[7] G 01 N 27/416, Publ. June 21, 2001.

7. Nakamura, Sh., Tarasuka, K., and Okuda, A., Patent no. 6235188 (USA), IPC[7] C 02 F 1/461, Publ. May 22, 2001.

8. Khan, S., Patent no. 6340431 (USA), IPC[7] B 01 D 17/12, Publ. January 22, 2001.

9. Blauwitz, U., Patent Application no. 19808412 (Germany), IPC[6] G 01 N 33/18, Publ. September 2, 1999.

10. Navarro, P., Patent no. 6657546 (USA), IPC[7] G 08 B 21/00, Publ. December 2, 2003.

11. Li, X., Qi, J., and Wang, Y., *J. Harbin Univ. Giv. Eng. and Archit.*, 2002, vol. 35, no. 3, pp. 68−70.

12. *Oxidation−Reduction Potential (ORP)/PEDOX*, *Application Bulletin*, Myron L. Company, 2007.

13. Suslow, T.V., *Introduction to ORP as the Standard of Postharvest Water Disinfection Monitoring,* US Davis Vegetable Research and Information Center, http://vric.ucdavis.edu/veginfo/foodsafety/orp.pdf.

14. Bergendahl, J.A. and Stevens, L., *Environ. Progress*, 2005, vol. 24, no. 2, pp. 214−222.

15. Shakhmetova, S.G., *Bashkir. Khim. Zhurn.,* 2007, vol. 14, no. 2, pp. 118−120.

16. Misier, M.O., *Eau; ind., nuisances*, 2006, no. 288, pp. 57−58.

17. Bongards, M., Patent Application no. 19702951 (Germany), IPC[6] C 02 F 3/30, Publ. July 30, 1998.

18. Bauman, P., Hansen, J., and Richert, J., *KA—Abwasser, Abfal.,* 2005 vol. 52, no. 12, pp. 1352−1358.

19. Fuerhacker, M., Bauer, H., Ellinger, R., et al., *Chemosphere*, 2001, vol. 44, no. 5, pp. 1213−1221.

20. Gao, D.W., Peng, Y.Z., Liang, H., et al, *J. Environ. Sci. and Health*, 2003, vol. 38, no. 12, pp. 2933−2942.

21. Chen, K.C., Chen, C.Y., Peng, J.W., et al., *Water Res.*, 2002, vol. 36, no. 1, pp. 230−238.

22. Teble, F. and Keiser, D., *Umweltpraxis,* 2002, vol. 2, no. 4, pp. 35−36.

23. Reggi, R., *World Leather*, 1996, vol. 9, no. 7, pp. 47−48.

24. Dmitrenko, G.N. and Ereshko, T.V., *Khimiya i Tekhnologiya Vody,* 2005, vol. 27, no. 4, pp. 392−398.

25. Dmitrenko, G.N., *ibid.,* 2001, vol. 23, no. 3, pp. 329−337.

26. Imaoki, T., Hirochi, M., Sugiyama, I., et al., Patent Application no. 1038839 EPO, IPC[7] C 01 F 1/70, Publ. September 27, 2000.

27. Gerardi, M.H., *Oxidation−Reduction Potential and Wastewater Treatment*, *New England Interstate Water Pollution Control Commission, Publication and Resources,* Interstate Water Report, 2007, http://www.neiwpcc.org/iwr/reductionpotential.asp.

28. Meierling, L., *Wasserwird−Wassertechn.*, 2003, no. 5, pp. 36−39.

29. Aizenshtadt, A.M., Bogdanov, M.V., Bogolitsin, K.G., and Abrosimova, A.A., *Izv. Vuzov. Lesn. Zhurn.,* 2006, no. 3, pp. 91−97.

30. Makar', A.V., *Elektron. Obrabotka Materialov,* 2003, no. 2, pp. 80−83, 101.

31. Meß—und Analysegeräte zum Einsatz in der Wasserverschmutzungskontrolle zunehment gefragt, *Galvanotechnik*, 2000, vol. 91, no. 5, p. 1430.

32. Neu bei Dr. Lange: Die ECM—Familie, *ibid.,* 1997, vol. 88, no. 6, p. 2052.

33. Redox−Industrieregler, *ibid.*, 1999, vol. 90, no. 3, pp. 734−735.

34. Starkes Wachstum durch neu Leitfähigkeitssensoren, *ibid.,* 2003, vol. 94, no. 2, pp. 402−403.

35. Datenlogger für Kontrollmessungen, *Chem.-Ing.-Technol.*, 1999, vol. 71, no. 12, pp. 1350.

36. Analesenmesstechnik für die Wasseraufbereitung, *Galvanotechnik,* 2005, vol. 96, no. 4, pp. 891.

37. New patented four−beam turbidity sensor, *Int. Environ. Technol.*, 2001, vol. 11, no. 6, pp. 16.

38. Oelbner, W., Hermann, S., Schwarz, J., and Koden, H., *Chem.-Ing.-Techn.*, 2000, vol. 72, no. 1/2, pp. 98−101.

39. Schindler, W., *Incom'98, Düsseldorf (Düsseldorf, 1998)*, 1998.

40. *GOST* (State Standard) *2874−82: Woda pit'evaya. Gigienicheskie trebovaniya i kontrol' za kachestvom* (Drinking Water. Hygienic Regulations and Quality Control), Put into effect on January 1, 1984.

41. Prilutskii, V.I. and Bakhir, V.M., *Elektrokhimicheski aktivirovannaya voda: anomal'nye svoistva, mekhanizm biologicheskogo deistviya* (Electrochemically Activated Water: Anomalous Properties, the Mechanism of Biological Activity), Moscow, 1997.

42. Dvornikov, V.M., *Tekhnologiya sokhraneniya metastabil'nogo sostoyaniya nizkomineralizovannoi aktivirovannoi vody* (Technology of Maintaining the Metastable Condition of Low Mineralized Water), http://www.gepatitunet.ru/nauch_obos.htm.

43. Kim, M.J. and Kim, H.K., *Life Sci.*, 2006, no. 79, pp. 2288–2292.

44. Lee, K.J., Park, S.K., Kim, J.W., et al., *J. Int. Soc. Life Inform. Sci.*, 2004, vol. 22, no. 2, pp. 302–305.

45. Yasunori, S., Shizuo, K., Akiko, A., et al., *Biochem. and Biophys. Res. Commun.,* 2008, vol. 375, no. 3, pp. 346–350.

46. Kokichi, H., Dongxu, S., Richard, L., et al., *Biophysical Chemistry*, 2004, no. 107, pp. 71–82.

47. Hanaoka, K., *J. of Applied Electrochemistry*, 2001, no. 31, pp. 1307–1313.

48. Ikuroh, O., Masahiro, I., Kumiko, T., et al., *Nature Medicine*, 2007, no. 13, pp. 688–694.

49. Huang, K, Yan, C, Lee, K., et al., *Kidney Int.*, 2003, no. 64, pp. 704–714.

50. Yuping, L., Tomohiro, N., Kiichiro, T., et al., *Cytotechnol.*, 2002, no. 40, pp. 139–149.

51. Dan, J., Sung, H.R., Hyun, W.K., et al., *Biosci. Biotechnol. Biochem.*, 2006, vol. 70, no. 1, pp. 31–37.

52. Gadek, Z., Li, Y, and Shirahata, S., *Animal Cell Technol.: Basic and Appl. Aspects*, 2006, no. 3, pp. 377–385.

53. Kajiyama, S., Hasegawa, G., Asano, M., et al., *Nutrition Res.*, 2008, no. 28, pp. 137–143.

54. Leonov, B.I., Prilutskii, V.I., and Bakhir, V.M., *Fiziko-khimicheskie aspekty biologicheskogo deistviya elektrokhimicheski aktivirovannoi vody* (Physico-Chemical Aspects of the Biological Effect of Electrochemically Activated Water), Moscow: VNIIIMT, 1999.

55. Chetkovic, V.S., Purenovic, J.M., and Jovicevic, J.N., *Appl. Clay Sci.*, 2008, no. 38, pp. 268–278.

56. Ryuhei, N., Kiichiro, T., Yoshinori, K., et al., *Cytotechnol.*, 2005, no. 47, pp. 97–105.

57. Yanagira, T., Sato, B., and Syudo, T., Patent no. 2004101402 A (Russia), IPC[7] C02F 1/70, 1/30, Publ. in *byul. no. 13*, May 10, 2005.

58. Petrushanko, I.Yu. and Lobyshev, V.I., *Biofizika,* 2001, vol. 46, no. 3, pp. 389–401.

59. Petrushanko, I.Yu. and Lobyshev, V.I., *ibid.,* 2004, vol. 49, no. 1, pp. 22–31.

60. Dobosh, D., *Elektrokhimicheskie konstanty* (Electrochemical Constants), Moscow: Mir, 1980.

61. Piskarev, I.M., Ushkanov, V.A., Likhachev, P.P., and Myslivets, T.S., *Okislitel'no-vosstanovitel'nyi potentsial vody, nasyshchennoi vodorodom* (Oxidation–Reduction Potential of Hydrogenated Water), http://zhurnal.ape.relarn.ru/articles/2007/023.pdf.

62. Shirahata, S., Kabayama, S., Nakano, M., et al., *Biochemical and Biophysical Research Communications*, 1997, no. 234, pp. 269–274.

63. Bagley, D., Patent no. 20060273030 (USA), IPC A 23 J 7/00*,* A 23 J 007/00, Publ. December 7, 2006.