

Control of microbes in water treatment and medicine: two sides of the same problem

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Recently, in September 2009, at the conference dedicated to the 70-th anniversary of the Institute MosvodokanaNIIproekt, the principal engineer of the Saint-Petersburg Vodokanal noted in his report that, in St. Petersburg, there was the ceremony of removal of the last chlorine container from the territory of the Northern waterworks situated in Zanevka township and that the city became now the first megalopolis worldwide that has completely abandoned the use of poisonous chlorine in the water decontamination process. The essence of the subsequent speech consisted in the fact that the removal of the last chlorine container closed the final chapter on the centenary history of application of the deleterious substance. There are no high-risk locations in the urban water purification system. At present, instead of chlorine, non-toxic sodium hypochlorite, which is not less efficient and, at the same time, non-toxic, is used in all urban waterworks. In addition, he noted that the rate of ultraviolet irradiation of water in the complex process of water decontamination is so high that "this beater knocks all microbes!".

Let's try to analyze whether the technologies extensively proposed in Russia at present are really innovative. Such analysis is seems to be of current concern, since, possibly, it can help in the future to prevent regret due to new false strategic decisions.

The modern Russian special journals are overfilled with information on what reagents and technologies for water decontamination to be used alone or in combination are better: chlorine, sodium hypochlorite, chlorine dioxide, ozone, ultraviolet irradiation, ultrafiltration, reverse osmosis, and then dozens of alternative technologies.

Many monographs, textbooks, research articles, which show the role of each above-mentioned agent used alone or in combination and were published in the period from 1960 to 1990 in different countries worldwide, including our country, are turned out to be forgotten.

The advantages and disadvantages of some agents studied in detail in XIX-XX centuries are briefly shown in Table 1 compiled mainly from the data of classic and fundamental sources of information [1-3].

Table 1

Characteristics of some water disinfection agent

Name and characteristic of disinfectant	Advantages	Disadvantages
Main disinfectants		
<p>Chlorine It is applied in gaseous state, requires observance of rigorous safety precautions</p>	<ul style="list-style-type: none"> ▪ efficient oxidizing agent and disinfectant ▪ effective for removal of unpleasant taste and odors ▪ possesses aftereffect ▪ prevents growth of algae and biofouling ▪ decomposes organic compounds (phenols) ▪ oxidizes iron and manganese ▪ decomposes hydrogen sulphide, cyanides, ammonia, and other nitrogen compounds 	<ul style="list-style-type: none"> ▪ exclusive transportation and storage requirements ▪ potentials health risk in the case of leakage ▪ forms sides disinfection products, viz., trihalomethanes (THM) ▪ forms bromates and bromine organic side products in the presence of bromides
<p>Sodium hypochlorite It is applied as liquid (commercial concentration of solution is 10-12%), may be prepared in the site of application (<i>in situ</i>) by the</p>	<ul style="list-style-type: none"> ▪ Efficient against most of causative microorganisms ▪ relatively safe on storage and when using ▪ when prepared <i>in situ</i>, it does not require transportation and storage of dangerous chemicals 	<ul style="list-style-type: none"> ▪ non-efficient against cysts (<i>Giardia</i>, <i>Cryptosporidium</i>) ▪ ages on long storage ▪ potential hazard of chlorine evolution on storage ▪ forms side disinfection products, including trihalomethanes, particularly, bromoform and bromates in the presence of bromides ▪ when prepared <i>in situ</i>, it requires either immediate applications or, for the purpose of providing possibility of storage, special measures for purification of source

Name and characteristic of disinfectant	Advantages	Disadvantages
electrochemical method.		water and salts from heavy metal ions <ul style="list-style-type: none"> the accumulation of chlorates occurs on storage of NaClO solutions at the concentration of available chlorine more than 450 mg/L and pH > 9
Chlorine dioxide Prepared only <i>in situ</i> At the present time, it is considered as the most efficient disinfectant among chlorine-containing reagents for water treatment at elevated pH	<ul style="list-style-type: none"> works at underdoses does not form chloramines does not promote the formation of trihalomethanes decomposes phenols, which is the source of unpleasant taste and odor efficient oxidizing agent and disinfectant for all kinds of microorganisms, including cysts (Giardia, Cryptosporidium) and viruses does not form bromates and bromine organic side products in the presence of bromides facilitates removal of iron and manganese from water through their fast oxidation and sedimentation of oxides formed 	<ul style="list-style-type: none"> obligatory preparation <i>in situ</i> requires transportation and storage of fire accelerant starting materials forms chlorates and chlorites when combined with some materials and substances, it affords peculiar odor and taste
Chloramine Forms upon the reaction of ammonia with the compounds of available chlorine, used as the long-acting disinfectant	<ul style="list-style-type: none"> possesses stable and long-term aftereffect promotes removal of unpleasant taste and odor have lower level of formation of trihalomethanes and other side organochlorine disinfection products 	<ul style="list-style-type: none"> weak disinfectant and oxidizing agent compared to chlorine and hypochlorite non-efficient against viruses and cysts (Giardia, Cryptosporidium) disinfection requires high dosages and prolonged contact time poses a hazard to the patients that undergo dialysis, since it can penetrate through the dialyzer membrane and damage erythrocytes forms nitrogen-containing side products
Alternative disinfectants		
Ozone Used over few decades in some European countries for disinfection, colour removal, taste improvement, and odour elimination	<ul style="list-style-type: none"> strong disinfectant and oxidizing agent very effective against viruses the most effective against Giardia, Cryptosporidium, as well as against other pathogenic flora promotes removal of water turbidity eliminates foreign flavors and odors does not form chlorine-containing trihalomethanes 	<ul style="list-style-type: none"> forms side products, including: aldehydes, ketones, organic acids, bromates (in the presence of bromides), peroxides, bromoacetic acid requires application of biologically active filters for removal of the side products formed does not provide residual disinfecting action requires the heavy initial costs for equipment requires considerable costs for training operators and equipment maintenance reacts with complex organic compounds, split them into fragments being nutritional medium for microorganisms in the water distribution systems
Ultraviolet The process consists in irradiation of water with ultraviolet light, which can kill different types of microorganisms	<ul style="list-style-type: none"> does not require storage and transportation of chemicals does not form side products efficient against cysts (Giardia, Cryptosporidium) 	<ul style="list-style-type: none"> does not have residual effect requires heavy costs for equipment and maintenance service requires high operational (power) costs disinfecting activity depends on water turbidity, hardness (formation of deposits on the lamp surface), sedimentation of organic pollutants on the lamp surface, as well as on variations in electrical network, which have an effect on wavelength change. no possibility of operational monitoring for the efficiency of water disinfection

The analysis of these data allows us to see that there are no ideal disinfectants and technologies among the above-mentioned ones, just as there is no receipt of the "ideal" drinkable water despite the importance of its effect on the human health. It is obvious that the composition and properties of drinkable water are determined by the geographical, geological, climatic,

hydrological conditions and regional differences in the degree and character of economic territory development/ In this regard, the regulation of drinkable water quality in developed countries is based on the valid, scientifically proven standards of its microbiological (priority parameter) and chemical composition from a perspective of safety and harmlessness for humans and determines the procedure for quality control of water fed to peoples that appreciates in the best way the regional formation conditions and the composition of source water, as well as the methods applied for water treatment and water delivery to consumer.

In 2007, the articles dedicated to determination of the rational ways for improving industrial and environmental safety of the water treatment and discharge objects of housing and utilities infrastructure were printed on the pages of the journal "Industrial safety". At bottom, this is a manifesto, which may be conceived as recommendations for development of the water decontamination and purification technologies and engineering in our country.

The important thing in these articles is the conclusion drawn from the analysis of known water decontamination technologies on that the use of ozonizers or devices for ultraviolet irradiation of water must certainly be combined with chlorination, which provides long-term retention of decontaminating effect. In addition, the important and reasonable decision is the abandonment of application of chlorine dioxide as the only biocidal agent. It is safe to say that, when realized, these two conclusions can serve for many years for good of peoples and will allow to save large assets both in the housing and public utility system and in the healthcare system of Russia.

In recent years, the articles, wherein the authors describing some innovative technologies cite information contradictory to the scientific foundations in the corresponding fields of knowledge and to experience gained worldwide, are frequently published in the Russian technical journals.

For example, based on the experimental studies, some authors maintain that sodium hypochlorite have stronger disinfecting effect than chlorine. At the same time, the chemical reactions that prove the total identity of the substances formed on dissolving chlorine or sodium hypochlorite in water are described. However, it is known from formal education that any salt as the reaction product of the corresponding acid and base has a lower chemical activity than its original substances. Sodium hypochlorite is the salt of hypochloric acid and sodium hydroxide and, therefore, inherently, has a much less antimicrobial activity, which is confirmed by thousands upon thousands of the most authoritative studies. In particular, this fact is confirmed in generalized form in [1], which, for example, shows that, in order to achieve the equal effects of drinkable water decontamination using hypochloric acid, sodium hypochlorite, and chloramine at the same concentration of available chlorine (0.1 mg/L), the said reagents require less than 2 minutes, more than 100 minutes, and about 500 minutes, respectively. If water is decontaminated by the equal doses of alkaline metal hypochlorite and acid chlorine water, then, in full conformity with the Le Chatelier principle and mass action law for the chemical reaction rate, which are also known from the school course of chemistry, even at the same final pH values of decontaminated water, the active chlorine compounds will be represented in water with the low-activity hypochlorite ions in the first case and with hypochloric acid in the second case.

All, who proceed or are going to proceed to decontaminating water with solutions of sodium hypochlorite, should be remembered that, along with hypochlorite, an equal (at best) or much more (almost always) amounts of ballast electrolytes, *i.e.*, salt and alkalies, enter to water, which intensifies the pipeline metal corrosion [6-9], causes deposition of mineral sediments on the surfaces of water conduits [10-12], promotes the formation of side chlorination products in much more amounts than those formed on application of chlorine [1]. Also, it must be kept in mind that even imperceptible increase in the water salinity level, which certainly occurs when using hypochlorite, does not favour improvement of its influence on human body [14, 15] and knowingly impairs the ecological balance in environment [16].

The application of sodium hypochlorite for water decontamination necessitates water ammonation, since only the presence of chloramines in water can provide the required by the sanitary norms levels of active chlorine in the extended water conduits where biofilms absorb and deactivate the free chlorine, which is harmful for them, and remain chloramine, the organic

fragment of molecules of which is readily utilized by the most of bacteria. In recent years, the research studies on the effect of chloramines, which are contained in drinkable and waste waters, on a human body and ecosystems were intensified abroad. The damage effect and strong allergenic action of chloramines have been reported in a few score of scientific papers in recent years, for example, in [17-20].

The articles describing chlorine dioxide and a mixture of chlorine dioxide with chlorine as the reagents that fully solve problems of water decontamination emerged. However, in all cases of application of chlorine dioxide, there was more problems than solutions, which is evidenced by the publications of foreign researchers having incomparably greater experience in application and investigation of these agents compared to analogous experience and investigations in the CIS countries [21, 22]. In particular, it is no matter from what basic starting material chlorine dioxide is produced: from sodium chlorite or sodium chlorate. All starting materials are dangerous and their production is carried out in specialized electrochemical enterprises, their transportation and storage require special precautions without mentioning the requirement of enhanced accuracy of dosing chlorine dioxide depending on the chemical composition of water decontaminated.

It is often suggested to replace poisonous chlorine for ultraviolet irradiation of water, which is safe for human health. All would be good if water enters from the ultraviolet irradiation area directly to the human mouth rather than travels over long distance along water conduits coated inside with a biofilm infested with microorganisms. These microorganisms stand off ultraviolet light, even if the distance separating them from the lethal irradiation is estimated at millimeters, and do not know that, somewhere, upstream of their position, there is a powerful "beater", which defeats the subjects like them. Conversely, they are glad that there are less "competitors" and more "foods" in the water coming to them.

Let's see what happens in medicine where the control of microorganisms is as urgent as in water treatment.

At first, note that the euphoria due to application of ultraviolet is totally absent among epidemiologists of medicoprophyllactic institutions (MPI) in contrast to the specialists in modern Russian innovative technologies of water treatment. In health care institutions, ultraviolet occupies the strictly limited position corresponding to its capabilities and, in no case, can replace the chemical decontaminating agents play a modest role of aider only in some fields. The understanding that the microworld is much older than our world and microbes possess incredible capabilities (in human terms) of adaptation and survival came to health professionals a long time ago. A health care provider never says that water became sterile due to ultraviolet irradiation. It suffices to remember the contents of labels on drug and food products in order to understand that: any vessel (drug ampoule, preserve can) is infected with microbes in sigma after loss of sealing. The same occurs with water after it escapes from the ultraviolet irradiation zone.

The underlying principles in design of an "ideal" liquid agent for control of microbes in medical practice are as follows:

- antimicrobial agent must possess a wide spectrum of antimicrobial activity, *i.e.*, efficiently exterminate bacteria, mycobacteria, viruses, fungi, and spores regardless of application duration and frequency, which implies the presence of such properties that do not allow microorganisms to produce resistance;
- antimicrobial agent must be safe for human and animals both during its preparation and application and after termination of intended use, *i.e.*, during the period of degradation and destructive changes under the influence of environmental factors or as a consequence of biodegradation processes in the human body; in other words, antimicrobial agent and its natural or artificial degradation products should not contain xenobiotics.

In the context of water treatment technology, these principles are quite topical. The more so, as being realized in medicine long ago, these principles are sufficiently fast distributed over all scopes of human activities. Their realization become possible owing to understanding the mechanism used by the Nature for protection of human and animal bodies from infections, as well as owing to new (according to the current fashion, referred to as "innovative") technical and process

design details, which provide creative copying of technologies created by the Nature for human daily requirements.

Let's consider the mechanism of antibacterial protection created by the Nature and operating in the internal environment of human and animals over millions years without any failing.

It is well known for a long time [23] that the leading role in the bactericidal action of neutrophiles belongs to hypochloric acid (HClO) produced by phagocytes. Upon respiratory distress, up to 28% of the total amount of oxygen consumed by neutrophiles is spent for the formation of HClO. HClO forms in neutrophiles from hydrogen peroxide and chloride ions. The function of catalyst in this reaction is performed by myeloperoxidase (MPO): $\text{H}_2\text{O}_2 + \text{Cl}^- \rightarrow [\text{Cat (MPO)}] \rightarrow \text{HClO} + \text{OH}^-$ [24, 25].

Hypochloric acid dissociates in the aqueous media to form hypochlorite anion and hydrogen ion: $\text{HClO} \leftrightarrow \text{H}^+ + \text{ClO}^-$.

At the close to neutral pH values, the concentrations of HClO and hypochlorite anions ClO^- are approximately equal. Lowering of pH results in the shift of this reaction equilibrium in favour of increase in the concentration of HClO, which, in turn, results in increase in the concentration of hypochlorite anions.

The formation of H_2O_2 and HClO in a short period of time (fractions of a second) in a small volume of the aqueous medium, *i.e.*, in the volume of active phagocytosis area, must be accompanied with the spontaneous decomposition reactions and reactions of the transformation products of these compounds to form active species similar to those that form upon water radiolysis and electrolysis.

The spontaneous decomposition of hydrogen peroxide in the aqueous medium is accompanied with the formation of compounds possessing a very high antimicrobial activity (the corresponding chemical reactions are given in parentheses): HO_2^- is the hydroperoxide anion ($\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$); O_2^{2-} is the peroxide anion ($\text{OH}^- + \text{HO}_2^- \rightarrow \text{O}_2^{2-} + \text{H}_2\text{O}$); O_2^- is the superoxide anion ($\text{O}_2^{2-} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^- + \text{OH}^- + \text{OH}^\bullet$); HO_2^\bullet is the hydrogen peroxide radical ($\text{HO}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^\bullet$); HO_2 is hydrogen superoxide ($\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{OH}^-$). In addition, the formation of extremely reactive singlet oxygen $^1\text{O}_2$ can proceed simultaneously: ($\text{ClO}^- + \text{H}_2\text{O}_2 \rightarrow ^1\text{O}_2 + \text{H}_2\text{O} + \text{Cl}^-$). It is found from experiments [24, 25] that the molecular radical ion of oxygen O_2^- is involved in the phagocytosis reactions, one of the ways for the formation of this radical ion may be that described above.

It is known that the formation of the active free radicals ClO^\bullet , Cl^\bullet , HO^\bullet can proceed in the aqueous medium in the presence of HClO and ClO^- : ($\text{HClO} + \text{ClO}^- \rightarrow \text{ClO}^\bullet + \text{Cl}^- + \text{HO}^\bullet$). From the perspective of modern theory of catalytic processes, the formation of intermediate activated complex involving myeloperoxidase as the catalyst is also seems to be not improbable. Decomposition of this complex is accompanied with the formation of the radical O^\bullet , return of catalyst to the initial state, and acidification of the medium: $\text{HClO} + \text{ClO}^- \rightarrow [\text{HClO} \leftrightarrow \text{Cat (MPO)} \leftrightarrow \text{ClO}^-] \rightarrow 2\text{Cl}^- + 2\text{O}^\bullet + \text{H}^+$.

The active hypochlorite radicals ClO^\bullet can be involved in the formation of atomic oxygen (O^\bullet) and hydroxyl radical (HO^\bullet): $\text{ClO}^\bullet + \text{ClO}^- + \text{OH}^- \rightarrow \text{Cl}^- + 2\text{O}^\bullet + \text{OH}^\bullet$. The subsequent chain propagation occurs during the formation of atomic chlorine: $\text{OH}^\bullet + \text{Cl}^- \rightarrow \text{Cl}^\bullet + \text{OH}^-$.

The radicals formed and atomic oxygen are involved in destruction of microorganisms through the reaction with biopolymers capable of oxidation, for example, in accordance with the reactions: $\text{RH}_2 + \text{OH}^\bullet \rightarrow \text{RH}^\bullet + \text{H}_2\text{O}$; $\text{RH}_2 + \text{Cl}^\bullet \rightarrow \text{RH}^\bullet + \text{HCl}$; $\text{RH}_2 + \text{O}^\bullet \rightarrow \text{RH}^\bullet + \text{OH}^\bullet$.

A metastable mixture of compounds formed during the phagocytosis is very efficient agent for destruction of microorganisms, since it have many spontaneously realized possibilities for irreversible damage of vital functions of biopolymers of microorganisms at the level of electron transfer reactions. Metastable species with different values of electrochemical potential have a universal action spectrum, *i.e.*, they can have a damaging effect on all large systematic groups of microorganisms (bacteria, mycobacteria, viruses, fungi, spores) without damaging the tissue cells of human and other higher organisms, *i.e.*, somatic animal cells as part of a multicellular system.

This is caused by the fundamental differences in the structure and living conditions of cells of these living forms. The cells of higher organisms during vital activity, for example, in the oxygenase reactions of functioning of P-450 cytochrome, during phagocytosis upon adhesion and immobilization of microbial cells, produce and use a number of highly active oxidants. These cells have a powerful chemical system of antioxidative protection, which prevents the toxic effect of such substances on vital cellular structures. The antioxidant properties of somatic cells are associated with the presence of the powerful three-layered lipoprotein envelope, which contains the diene conjugates ($-C=C-$) and sulfhydryl groups (SH) possessing electron-donating properties. Microorganisms do not have powerful antioxidative protection systems involving the said chemical groups.

All somatic cells of animal bodies are heterotrophs: their trophism depends on the presence of nutrients in the extracellular medium, such as glucose, amino acids, fatty acids. The biological well-being of a somatic cell depends on the position that it occupies during distribution of the trophic functions of all elements of a multicellular system (one cell supports another one). The functions of trophism of animal cells follow the interchangeability law. If the trophism of one individual cell is damaged, then this damage can be corrected through the neurotrophic regulations, endocrine regulations, functions of neighbour cells, reparative processes, nutritional function of blood *etc.*

All microbial cells are autotrophs and their nutrition depends on their own energetic activity, *i.e.*, upon inhibition of enzymatic processes inside a microbial cell, such a cell dies due to the absence of the compensatory mechanisms. A microbial cell provides all its trophic functions only due to the enzymatic reactions. The interaction between microbial cells in their living environment is not compensatory, *i.e.*, the tender place of a microbial cell is its autonomism.

The maximal use of fundamental differences of living beings of micro- and macrobiological world is ideological basis for the electrochemically activated antimicrobial solutions produced by STEL and AQUACHLOR devices.

To date, there are more than 40,000 STEL devices in the Russian medico prophylactic institutions, which produce the electrochemically activated anolyte ANK from sodium chloride and water. Each Moscow hospital has at least, ten of such devices. STEL devices are operated in the Moscow city clinical hospitals Nos. 15 and 52 from 1989 and 1997, respectively. During this time, no case of emergence of resistant microbial flora was noted in any one of thousands worksites of STEL devices. These data are official and confirmed on many thousands pages of expert reports, protocols, survey reports, analysis reports, scientific reports, procedural guidelines, regulations, manuals.

What is the anolyte ANK? It is an environmentally friendly solution with a wide spectrum of antimicrobial activities, which possess multi-purpose action: it can serve as a detergent, disinfecting and sterilizing agent, as well as an efficient drug for local or external administration (according to the corresponding monograph). The process for preparation of the ANK anolyte have not changed from the moment of its design: an initial water and water-salt solution are saturated with the dissolved hydrogen and alkalized by mixing with the cathodic reaction products, the heavy and alkaline-earth metal ions are transformed into the insoluble hydroxides, which are removed together with the excess of hydrogen into the drainage in the foam reactor, and then the anodic oxidation products of solution referred to as oxidant mixture are introduced into the medium treated in such a way.

In the ANK anolyte having a neutral pH value, active compounds (AC) are represented predominantly by hypochloric acid, small amount of the hypochlorite ions, chlorine dioxide, ozone, hydrogen peroxide and singlet oxygen. It is impossible to prepare such an oxidant mixture chemically, however, it forms in the human body during phagocytosis due to the electrochemical reactions in the cytochrome P-450 enzyme and exists for a very short time by solving the task of infection control. The specific conditions for the electrochemical synthesis in the electrochemical reactors of STEL devices can create conditions for a long-term (from a few days to two-three months) coexistence in a solution of metastable antagonist species. Compared to the conventional disinfecting agents, the anolyte ANK (neutral anolyte with a prior cathodic treatment) is a crucially

new object similar to the cold plasma, in contrast to hot plasma, for example. In both cases, there are metastable species, for which microorganisms cannot produce resistance, on principle, and the chemical composition of these species cannot be dissected in order to study extensively each individual component. This is precisely why the ANK anolyte exterminates the spores of Siberian plague at the concentration of active substance 0.03% in a matter of seconds, while using a solution of sodium hypochlorite at the 15-fold concentration of active substance, the same result is achieved for 30 minutes. These data are cited from the scientific report of the Battelle Memorial Institute (USA), however, they are confirmed in one form or another in more than 50 countries, including Russia. The ANK anolyte is certified long ago under different brand names in many countries (more than 30) and included in the European list of agents approved for treatment of endoscopes (European Society of Gastrointestinal Endoscopy Nurses and Associates – ESGE Guidelines Committee). The ANK anolyte that is produced in the devices equipped with the reactors patented by the Russian inventors is successfully used in Netherlands for drinkable water decontamination (there is a certificate for it) and in USA for the improvement of preservation of food products (greens on grocery shelves, meat, fish, and seafoods). The field of application of electrochemically activated solutions is continuously expanded [27-64]. The major difference of electrochemically activated solutions of oxidants from common solutions of chlorine, sodium hypochlorite, hydrogen peroxide, chlorine peroxide is what antagonists can coexist in these solutions for a long period of time, but enter into the neutralization reactions and so annihilate each other in common solutions.

The STEL devices was applied up to date mainly in medicoprophyllactic institutions. However, in Russia, a new device for generation of the ANK anolyte was now prepared for batch production, which is referred to as STEL-ANK-PRO and has oxidant productivity up to 0.5 kg/h. The ANK anolyte produced in this device has the same active substances as discussed above, but differs by a very low salinity level comparable with that of fresh water at the neutral pH value. This gives to it a number of new qualities and makes it irreplaceable for water disinfection in water abstractions of any capacity and for decontamination of water in swimming baths and waste water of infectious diseases hospitals. The absolute advantage of the STEL-ANK-PRO device against all systems known worldwide is what it produces the ANK anolyte having pH from 6 to 7 and discharges a small amount of the water that has pH from 8.5 to 9.0 and virtually the same salinity level as the original water. This water, pH of which is somewhat increased, but falls within the limits of standard specifications, can be directed to the delivery point before the filters of water purification plant and added directly to the decontaminated water flow prior to the feed point of the ANC anolyte. Thus, the STEL-ANK-PRO device solves completely a problem of "excess" sodium hydroxide production.

Compared to the STEL-ANK-PRO device, the AQUACHLOR device is less sophisticated in terms of construction and technology. A solution of oxidants produced by the AQUACHLOR device comprises also a mixture of the same oxidants, which, in contrast to the process for preparation of the ANK anolyte, is introduced into water without additional treatment (there are no steps of hydrogen saturation and removal of heavy and alkaline-earth metal ions from water). Therefore, the pH of oxidant solution prepared in the AQUACHLOR devices is no more than 3.0. In fact, the AQUACHLOR devices are industrial modular systems for water decontamination with a mixture of oxidants (chlorocaustic mini-plants). They provide not only the production of oxidants, but also the production of the second product, *viz.*, a concentrated solution of sodium hydroxide (150-170 g/L), which can be used in a water treatment technology (for dissolving coagulants and for batch purification of sand-gravel filters from deposits), as well as a detergent sanitizer (the content of sodium hypochlorite in a hydroxide solution is from 1 to 3 g/L) in primary wool washing plants, meat-packing plants, battery farms for washing of equipment *etc.*

The pooled data from the scientific reports in the past decade on the properties of an oxidant solution produced in the AQUACHLOR devices are given in Table 2.

Table 2

Characteristics of new alternative water disinfectant – an oxidant solution from the AQUACHLOR device

Name and characteristic of disinfectant	Advantage	Disadvantages
<p>A solution of oxidants from the AQUACHLOR devices</p> <p>Prepared by the electrochemical synthesis of a wet gas mixture of oxidants, such as chlorine, chlorine dioxide, ozone, hydroperoxide compounds, from a solution of sodium chloride</p>	<ul style="list-style-type: none"> ▪ efficient at underdoses ▪ does not promote the formation of trihalomethanes ▪ decomposes phenols, which is the source of unpleasant taste and odor ▪ efficient oxidizing agent and disinfectant for all kinds of microorganisms, including cysts (Giardia, Cryptosporidium), viruses, mycobacteria, spores, and microbial toxins ▪ does not form bromates and organobromine side products in the presence of bromides ▪ facilitates removal of iron and manganese from water through their fast oxidation and sedimentation of oxides formed ▪ promotes removal of water turbidity ▪ eliminates foreign flavors and odors ▪ does not require storage and transportation of dangerous chemicals 	<ul style="list-style-type: none"> ▪ requires the presence of electric energy, water-supply pressure line ▪ requires a small consumption of hydrochloric acid for cleaning electrodes when using a low-quality salt (with a large contents of the calcium, magnesium, and iron ions) or systems for chemical softening (for example, using sodium bicarbonate) of a starting solution of sodium chloride <p>However, a technology and technical means for the preparation of hydrochloric acid from chlorine and hydrogen synthesized by the AQUACHLOR device have been developed in 2008.</p>

In order to not overcharge the paper with the data from numerous reports and approval documents of various countries, we cite a fragment from the application instruction for a solution of oxidants produced by the AQUACHLOR devices that was approved by the chief public health physician of the Russian Federation in the beginning of 2009 [65]. This Instruction is based on a great number of official documents and characterizes in brief the main aspects of application of an electrochemically activated solution of oxidants for water decontamination.

1. GENERAL INFORMATION ON THE "AQUACHLOR" devices

1.1. The AQUACHLOR devices are intended for the preparation of a solution of oxidant mixture from a aqueous solution of sodium chloride. The devices are made by the "Laboratory of Electrotechnology" ltd. as modular units with the productivity from 30 to 500 grams of a gaseous oxidant mixture per hour in accordance with the technical specifications TU 3614-037-44464870-2005. The AQUACHLOR devices use a new technological process for the electrolysis of a solution of sodium chloride, *viz.*, ion-selective diaphragm electrolysis, which provides the conjunction of the high cost effectiveness with the complete operational safety. For the preparation of 1 kg of an oxidant mixture in terms of molecular chlorine, the AQUACHLOR device consumes no more than 2.0 kg of sodium chloride and from 1.8 to 3.5 kWh of electric energy.

From a solution of sodium chloride, which is introduced as certain doses to a reactor of the AQUACHLOR devices by means of a diaphragm pump, a wet gaseous mixture of oxidants is synthesized under the pressure from 0.8 to 1.2 kgf/cm² in anodic chambers of compact flow modular units with the zirconium oxide-based ceramic diaphragms and mixed immediately after formation with water to form an analogue of chlorine water. The active substances in an aqueous solution of oxidants having pH from 2.0 to 3.5 are presented by hypochloric acid and molecular chlorine.

1.2. The AQUACHLOR devices are an alternative compact high-productivity source of an oxidant mixture and can be used as a replacement for cylinders and containers with liquid chlorine and, as such, as chlorinator in domestic water purification plants, local plants for water purification, domestic and industrial waste water purification plants, purification systems for water of swimming baths in the form of both singular moduls and group of moduls combined in the integrated hydraulic system with a specified oxidant productivity from 30 gramms to hundreds kilograms per houer.

1.3. The safe operation of the AQUACHLOR devices and the absence of intoxication risk for operating personnel and environment due to the non-controlled discharge of a gaseous mixture of oxidants are guaranteed by a small volume of gaseous electrolysis products (less than 100 mL in

one module of AQUACHLOR-500), which during operation of device enter under the pressure from 0.8 to 1.2 through fluoroplastic pipes to a pressure controller and dissolve in flow water by transforming into an aqueous solution of oxidants at their concentration of 0.5 – 3.5 g/L. The process for synthesis of a gaseous mixture of oxidants in the AQUACHLOR device eliminates the possibility of its accumulation and storage. The loss of sealing in the reactor of the AQUACHLOR device results in immediate termination of production of gaseous oxidants.

The design of the AQUACHLOR device contemplates its automatic shutdown in the case of termination of water passage from pressure water supply plant through the device. In addition, the device control block has a hub for connection with the sensor of device shutdown signal that is received from any danger warning system, such as smoke detector, signalizer of dangerous level of chlorine in a room and the like.

1.4. As a starting solution of sodium chloride, an aqueous solution of non-iodized dietary salt, e.g., according to the GOST R 51574, is used in the AQUACHLOR devices. The conversion degree of sodium chloride contained in a starting solution at the concentration of 200 – 250 g/L achieves 99% in the AQUACHLOR device; therefore, one kg of the salt consumed affords approximately 0.5 kg of a mixture of gaseous oxidants presented by chlorine (95 – 96%), chlorine dioxide (3 – 4%), ozone (0.5 – 1.0%), as well as by hydroperoxide compounds (hydrogen peroxide, singlet oxygen, superoxide radicals) contained in the water minidroplets (0.2 – 0.5%). At the same time, it affords approximately 0.7 kg of sodium hydroxide (NaOH) as a solution with the concentration of 120 – 150 g/L (4.0 – 7.0) L/h) and about 17 g of hydrogen, which is removed outside of a room where the AQUACHLOR device is mounted.

1.5. A solution of oxidants obtained in the AQUACHLOR device is fed to the treated water flow by a conventional ejector pump or direct input (through an existing line for input of chlorine water, a specially buried pipeline made of polyvinyl chloride, polyethylene, and polypropylene) or through collection bowl equipped with an automatic or manual metering system.

A solution of sodium hydroxide (caustic soda), hereafter referred to as catholyte, obtained in the AQUACHLOR device can be used for the preparation of coagulant solutions, as an efficient detergent, for the pH control of water (drinkable, waste water and water of swimming baths), pH control a solution of oxidants by mixing catholyte with a solution of oxidants in different ratios. Upon mixing of the total amount of catholyte with a solution of oxidants, a solution of sodium hypochlorite having pH from 8.5 to 9.0 is produced. This solution can also be used for water treatment, although it is less efficient disinfecting agent compared to a solution of oxidants.

1.6. A solution of oxidants produced by the AQUACHLOR device is more efficient antimicrobial and oxidizing agent than a solution of single substances in water, which form upon dissolving of chlorine, chlorine dioxide or ozone alone in water, since the chemical reactions involving it follow the regularities of synergism and the presence of a small amount of more powerful oxidizers than chlorine prevents the formation of trihalomethanes upon treatment of water containing a large amount of humic compounds.

Thereby, the Directorates of the Rospotrebnadzor for the constituent entities of the Russian Federation is recommended to perform periodical amendment for the total concentration of oxidants in treated water that is needed for water decontamination downwards compared to the current specifications.

1.7. The total concentration of oxidants in a solution produced by the AQUACHLOR devices can be determined by any method set forth in the Appendix 1 provided that the sample is taken in accordance with the procedure used upon manufacturer testing of the AQUACHLOR devices.

The concentration of oxidants in the decontaminated water should be determined in accordance with the standard procedures prescribed and approved as appropriate by the corresponding regulatory documents.

1.8. It is recommended to operate the AQUACHLOR devices in the standard chlorinator room or in any heated space equipped with the combined extract-and-input ventilation with single air replacement per hour. The presence of water pressure line, sewage runoff, 220 V appliance receptacle of "Europe" type with a power capacity of 1.2 kW (for one module of the

AQUACHLOR-500 device) is obligatory. The hydrogen formed upon the preparation of a solution of oxidants should be discharge outside of the room using a hose connected with a gas remover of the AQUACHLOR device.

2. DECONTAMINATION OF WATER IN THE DOMESTIC WATER SUPPLY SYSTEMS

Decontamination of domestic water with a solution of oxidants produced by the AQUACHLOR devices is carried out in accordance with the sanitary regulations and norms SanPin 2.1.4.1074-01 "Drinkable water. The hygienic requirements for the quality of water in the centralized drinkable water supply systems. Quality control.", according to which the contents of residual chlorine in water after clean-water reservoirs should be within the range indicated in Table 1.

Table 1.

Residual chlorine	Concentration of residual chlorine, mg/L	Minimum time required for the contact of chlorine with water in minutes
1. Free	0.3 – 0.5	30
2. Fixed	0.8 – 1.2	60

For the preparation of a solution of oxidants, a drinkable water from water pump line with a pressure of 2-6 atm is used.

The control of the content of residual chlorine in water is performed by the laboratory personnel of organization that operates the device. The control of water condition prior to its supply to a consumer is performed at the discretion of the Directorates of the Rospotrebnadzor for the constituent entities of the Russian Federation in accordance with the SanPiN 2.1.4.1074-01 in all water treatment steps. If the free and fixed chlorines are simultaneously present in water, then their concentration should not be greater than 1.2 mg/L. In some cases, upon the epidemiologic risk, the increased concentration of residual chlorine in water is allowed at the directions of the Directorates of the Rospotrebnadzor for the constituent entities of the Russian Federation or by agreement with them. When the control of epibioses in the water-supply network is needed, the delivery and dosage points of chlorine are agreed with the Directorates of the Rospotrebnadzor for the constituent entities of the Russian Federation. In the step of under-control operation of certain water-supply systems, the chlorine dose delivered to the distribution system is identified, which ensures the final operational benefit: decontamination of water up to the regulatory value in accordance with the standards SanPiN 2.1.4.1074-01 "Drinkable water. Hygienic requirements for the quality of water from the centralized drinkable water supply systems. Quality control".

Determination of the free and fixed chlorines in water is performed by the titrimetric method according to ISO 7393-1 (at the total concentration of chlorine less than 5 mg/L) and ISO 7393-2 (at the total concentration of chlorine more than 5 mg/L), the iodometric titration method according to ISO 7393-3 or the colorimetric method according to ISO 7393-2.

3. DECONTAMINATION OF DOMESTIC AND INDUSTRIAL WASTE WATER

Waste water is characterized by a high degree of organic overload. The empiric values of decontaminating concentration of active chlorine in waste water can achieve 15 mg/L. Accordingly, a solution of oxidatns from the AQUACHLOR device with the oxidant content of 1 g/L must be diluted in a ratio of 1 : 66 upon its introduction to waste water. In order to prepare a solution of oxidants, treated waste water is used.

Example. A solution of oxidants with the concentration of 1.0 g/L (1000 mg/L) was obtained from the AQUACHLOR device. To prepare the active chlorine dose of 5 mg/L using this solution, 1 L of a solution of oxidants should be added per 200 L of waste water (1000 : 5). Upon calculation of the active chlorine dose needed for treatment of contaminated water, one should take into account the level of its chlorine absorption, which is determined in accordance with the requirement of the standard ASTM D 1291-89.

The active chlorine dose must exceed the specific value of chlorine absorption by water in such a way that the resulting concentration of active chlorine in water would provide the required operation benefit (decontamination rate, water clarification rate *etc.*).

Upon addition of a solution of oxidants from the AQUACHLOR device, the waste water is partially clarified due to coagulation of organic compounds, after which it should undergo incubation in settling wells. After test of treated waste water for the parameters of bacteriological contamination, it enter to the second stage water sumpbags where it can undergo secondary decontamination by the method as described above. The issue on the waste water disposal after decontamination must be solved in each specific case by agreement with the Directorates of the Rospotrebnadzor for the constituent entities of the Russian Federation in full conformity with the standards SanPiN 2.1.5.980-00 "Hygienic requirements for the surface water protection".

As for the methods for determination of the free and fixed chlorine upon decontamination of domestic and industrial waste waters, please see above in Chapter 2 "Decontamination of water in the domestic water supply systems".

4. DECONTAMINATION OF SWIMMING POOL WATER

For decontamination of swimming pool water, it is necessary to introduce continuously or periodically a solution of oxidants from the AQUACHLOR device to the pool basin. In order to prepare a solution of oxidants, as such, the water of basin is used in this case. The concentration of chlorine in water of swimming basin should be in the range of 0.3 – 0.5 mg/L. For examples, to achieve the concentration of active chlorine of 0.5 mg/L in the basin with the water volume of 100 m³, 50 L of a solution of oxidants with the concentration of 1 g/L should be introduced. In the first three days after injection of water into a basin, the delivery rate of a solution of oxidants must be increased by 20 – 50%. In this case, a stable content of residual chlorine in water at the level not less than 0.3 mg/L is achieved. Feeding of a solution of oxidants is operated into the recirculation system of basin from intermediate storage container. The prophylactic "shock" action on water by a solution of oxidants from the AQUACHLOR device is performed overnight once or twice a month. The amount of the solution added must be such that allow increasing the level of residual chlorine in water up to 1.0 – 1.5 mg/L. For example, in the case of 100 m³ basin, this amount will be 100 – 150 L.

Application of a solution of oxidants from the AQUACHLOR device in such mode does not increase the water pH. The optimal pH values of water in the pool basin are \approx 6.0 – 6.5.

In each specific case, prior to commissioning the water-treatment system of a basin with the application of a solution of oxidants from the AQUACHLOR device as a disinfectant, it is advised to perform the following measures:

1. Washing of filtration and recirculation systems of a basin with water having the oxidant content not less than 3 – 5 mg/L. Upon this procedure, a slow ejection of biogrowths from pipelines and filters to pool basin is observed. Such purification is performed for 6 – 24 hours depending on the cumulative previous operating lifetime of a basin.
2. Optimization of flow process diagram of feeding of an oxidant solution to a basin, which involves all changes in the operational modes of equipment depending on the variable operating conditions of a basin (loading with swimmers, overheat of water, lighting program, duration of the period between complete replacements of water in a basin).
3. When benthal deposits appear in the pool basin, it is recommended to remove them using an aspirator.

To date, about 300 AQUACHLOR-500 devices are operated in Russia. The largest group of modules (40 devices) is mounted in the municipal unitary enterprise "Balakovo-Vodokanal". They occupy the area of about 40 square meters and produce 480 – 490 kg of oxidants per day based on the chlorine equivalent. At the same time, the daily production of catholyte containing 150 – 170 g/L of sodium hydroxide is 6000 – 7000 L. The catholyte is used for the in-house needs of water purification plant in accordance with the Instruction whose fragment is cited above. The most long-running group of the AQUACHLOR devices with a productivity of 9 kg of oxidants per hour is mounted in the water and wastewater treatment plant of the Shymkent city (Kazakhstan). To date, they have been operated in a discontinuous mode more than 8 years. However, the most of the

AQUACHLOR and STEL devices produced in Russia are exported abroad. Among countries whereto the devices are supplied, there are Germany, Austria, Poland, Czech Republic, Slovakia, Netherlands, Finland, Ireland, England, India, Vietnam, Korea, Mexico, USA, and a number of other countries.

The number of the foreign scientific papers in the field of application of electrochemically activated solutions in various kinds of human activities grows like an avalanche during the last five years and, to date, it has risen beyond one hundred thousand. One can find more than million references *via* the Internet to the works in the field of investigation and application of electrochemically activated solutions (under different trade and brand names). In the Russian press, the list of serious studies in this tremendous field of science and engineering, which began to develop virtually in the recent years, is fitted on 20 pages typed in Arial 12. In addition, all these studies are performed by the efforts of enthusiasts without any state support. This results most likely in the necessity for purchasing the AQUACHLOR and STEL-ANK-PRO devices from abroad .

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