Research Article

Universal Electrochemical Technology for Environmental Protection

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ABSTRACT

The article experimentally substantiates the fundamentals of electrochemical synthesis technology and of the subsequent use of metastable substances in various technological processes instead of traditional chemical reagents. It considers the basic features of technical systems for the synthesis of electrochemically activated solutions, purification and conditioning of water, as well as for production of the most important products of the chemical industry, such as chlorine, caustic soda, concentrated hypochlorous acid, persistent acid straight in places of their consumption with examples of the creation and application of appropriate electrochemical systems and technologies, which are the main elements of new environmentally friendly chemical industries.

**Keywords**: *Green chemistry, electrochemical activation, anolyte, catholyte, water*
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INTRODUCTION

The main trend in the development of modern technologies is the approximation to the processes taking place in nature, that is, the processes that occur at the micro level and are characterized by the absence of hazardous waste.

One of the scientific and technical areas which realizes this trend in various fields is the universal technology called electrochemical activation [1-29]. The essence of electrochemical activation consists in the effect of temporary preservation of the properties and parameters of the physico-chemical process that occurs in the double electrical layer of the polarized electrode of the electrochemical system as the replica of the near-electrode medium.

The term "replica" is used because neither extremely large deviations of parameters from equilibrium values nor the ability to retain permanently anomalous reactivity, catalyze chemical and biochemical reactions, influence the structural properties of materials during phase transitions, and other properties cannot completely characterize the whole complex of physico-chemical and energy transformations of a metastable near-electrode substance.

The well-known property of an isolated (removed from the electrochemical system) near-electrode medium is to provide long-term coexistence of antagonist substances, in particular hydrogen peroxide and hypochlorous acid, obtained from a dilute sodium chloride solution (0.5-1.0 g / l) at current densities above 1000 A / m^2 of a polarized inert (exchanging with an electrolyte only electrons) anode [2 - 6]. If modeling this process by chemical measures (mixing solutions of hydrogen peroxide and hypochlorous acid), the neutralization occurs in accordance with the reaction:

$$HClO + H_2O_2 \rightarrow O_2\uparrow + H_2O + HCl.$$
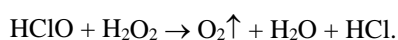
This cardinal difference between the properties of the electrochemically obtained solution and its chemical model becomes understandable when one considers that in the formation of antagonist substances in the double electrical

layer (DEL) of the electrode, in its diffuse and dense parts, where the electric field strength varies from several hundred thousand up to several tens of millions of volts per centimeter, there is an instantaneous hydration in the electric field with the simultaneous formation of structural and energy complexes of protection against mutual destruction. Dense ion-hydrate shells, which retain the structural organization acquired at the time of formation of high tension in an electric field, prevent the interaction of active substances (AS) - antagonists while storing the solution. The relaxation time for this property is calculated in hours and days depending on the conditions of synthesis and subsequent storage. The practical use of the prolonged preservation effect in the dilute aqueous sodium chloride solution of anodic oxidation products, represented by antagonist substances, provides microbiological safety of medical institutions in Russia and other countries, where STEL devices of various modifications and under different trade names have been used for more than twenty years [30]. Fig. 1 shows the first models of STEL devices with Anolyte ANK (commercial name) productivity from 10 to 1000 liters per hour.

Fig. 1. STEL devices of various anolyte productivity, from left to right: 10 l / h (1991), 20 l / h (1992), 60 l / h (1994), 1000 l / h (1995)

Nowadays every hospital in Moscow and St. Petersburg has one or more STEL electrochemical devices that produce environmentally friendly washing, disinfecting and sterilizing solutions which destroy all known types of microorganisms - bacteria, mycobacteria, viruses, fungi, spores, including pathogens of especially dangerous infections - cholera, plague, anthrax, tularemia. This solution is absolutely harmless for macroorganisms, since phagocytic cells of the immune system produce a similar metastable mixture of oxidant antagonists. It should be also noted that Russian medical facilities beginning approximately from 2010 have received mostly fake STEL devices which at the best-case scenario produce hypochlorite solutions which are only formally consistent with the methodological guidelines for the content of active chlorine.

The active substances (AS) of the original electrochemically activated solutions obtained in the original STEL devices are representing the mixture of oxidants equivalent in composition to the one which is formed in the organisms of living beings in phagocytosis (the destruction of foreign substances by phagocytes). In case of degradation, the solution of oxidants of the latest generation (2014, commercial name ANOLIT ANK SUPER) is converted to fresh water with the total mineralization of less than one gram per liter. Electrochemically activated antimicrobial solutions, to which the microflora is unable to develop resistance, are harmless to humans and animals and environmentally friendly, universal and safe for all forms of application (irrigation, immersion, wiping, soaking, aerosol, foam, ice). These solutions are used in many countries in various areas of human activity. For example, at the beginning of the 2000s, the Memorial Institute "Battelle" (USA) developed the decontamination technology with the use of electrochemically activated anolyte for the US Marine Corps Systems Command. It was used when the soldiers leave microbiological or chemical contamination zones. The scientific report of the microbiological laboratory of this Institute states that anolyte ANK with the AS concentration of 0.03% destroys anthrax spores in one second while a sodium hypochlorite solution with AS concentration of 15 times higher requires at least 30 minutes to reach the same results. Russian competent scientific organizations also confirmed these results. Fig. 2 shows the field tests of the STEL device in mobile version with an Anolyte ANK production capacity of 2500 liters per hour.

Fig. 2. Marines at the training range deploy the mobile device "Decontamination Generator" with FEM-3 (MB-11) elements, filling the rubber-fabric tanks with anolyte ANK and treatment with anolyte of military personnel, their equipment and weapons in the tent where the shower systems are installed. Atlanta, USA, 2001.

During 1982-1999, the long-term preservation of the replica parameters of the electrochemical process on a polarized electrode in the application to various technological processes was studied on various liquids and gases: distilled water, mineral oil, straight-run gasoline, aqueous and non-aqueous solutions of organic and inorganic compounds, gaseous chlorine, hydrogen, and helium [1-6, 13, 14]. At the same historic period, the ways of practical application of the detected effects in various technologies were determined, including the usage in petrochemical industry (pyrolysis of straight-run gasoline, purification of oil and oil products from sulphur), the metallurgy and mining industry (quenching of steels, extraction of metals from ores and slags), in the engineering industry (the preparation and regeneration of lubricating-cooling liquids, the creation of drainless galvanic plants with the regeneration of chemical agents), etc. However, the electrochemical reactor which is the main tool of the technology at that time was not suitable for widespread usage in industrial production. That is why till the present moment the author has been constantly perfecting the design or reactors. In general, the technology of industrial production is a set of methods, techniques, tools and the sequence of production. This technology ensures the rational use of energy, labor, time and materials. A rational and effective combination of all these components which could be successfully used in thousands of potentially feasible technological processes with the implementation of electrochemical activation is capable of making production safe for nature and people with the smallest financial and time costs while improving the quality of products at the same time. In 2016, electrochemical reactors of a new generation, namely electrochemical systems based on MB elements with the general collective name AQUATRON [30], was created. Fig. 3 shows MB elements of a new generation and an electrochemical reactor consisted of new MB elements.

Fig. 3. MB Elements manufactured in accordance with the technical specifications TU 3614-015-77350578-2016

The technical and technological parameters of the 2016 generation MB elements entirely meet the criteria for broad industrial usage which is confirmed by the first practical tests. As part of the work under the grant of the Russian Science Foundation (RSF) in 2016, a laboratory device AQUATRON-16-500L was designed for the synthesis of electrochemically-activated anolyte and catholyte of distilled water. The AQUATRON -16-500L electrochemical reactor is equipped with MB element of a new generation. Along with biological experiments based on the use of electrochemically-activated substances and the working program under RSF grant, the study of the actual synthesis of

anolyte and catholyte of distilled water was performed and there was an attempt to transfer the obtained results to a wider range of phenomena associated with the creation of artificially induced ion selectivity in inactive ceramic ultrafiltration diaphragms of alumina in alpha form. These diaphragms are the main part of the flow-through electrochemical module MB elements of the 2016 generation.

Long years of experiments [1-14] of the pH study and redox potential (ORP) of distilled water subjected to electrochemical action at the surface of the positive and negative electrodes of the electrochemical system have established that the pH and ORP of anolyte and catholyte of distilled water acquire anomalous values in comparison with the values that are calculated on the basis of the laws of electrolysis, as well as the values obtained by modeling the acid-alkaline properties of anolyte and catholyte by introducing acid and alkali into the initial distilled water. Fig. 4 shows the results of study experiments of the parameters of electrochemically-activated distilled water obtained in the AQUATRON-16-500L system. In all experiments, the initial distilled water was used in accordance with GOST 6709-72 with the following parameters: the mass concentration of the residue after evaporation of the water (samples studied in three different laboratories) mg / dm3, ranging from 3.5 to 4.8 mg / dm3; the specific electrical conductivity at 25° C is from 3.8 to 4.6 μS / cm; pH from 5.8 to 6.2; redox potential measured with a platinum electrode relative to a silver chloride reference electrode, from +215 up to + 340 mV.

The pH and ORP were measured by a pH meter PH FE20 (METTLER-TOLEDO) and the conductivity of the water by a conductivity meter FP-30 - STANDARD (METTLER-TOLEDO).

Unlike the traditional electrochemical systems for the production of anolyte and catholyte of distilled water [1], a flow-through electrochemical module element MB-11T-01 was used in the AQUATRON-16-500L system. The ultrafiltration diaphragm of this element was made of chemically pure alumina in alpha form. The uniformity of the structure and physico-chemical properties of the diaphragm made it possible to exclude the electromigration of the products of electrochemical reactions from the auxiliary to the working electrode chamber of the MB element. It was done due to the same filtration rate for each microspace of the filtering surface under the effect of pressure drop at the diaphragm (0.5 to 1.8 bar) and the electric field that regulates the chemical components of the filtration flow in the diaphragm.

The cooled electrodes of the MB-11T-01 element ensured a constant temperature of the water flowing through the electrode chambers within 22 plus or minus 3° C. In various experiments, the current was maintained in the range from 0.038 up to 0.041 A at a voltage of 360 to 390 volts. The specific amount of electricity spent on water treatment in the cathode or anode chambers of the MB element ranged from 40 to 45 K / l. Basing on the laws of electrolysis, it was more than ten times higher in comparison to the theoretical value required for complete electrochemical conversion of the dissolved in water substances – electrolytes.

Measurements of pH, ORP and electrical conductivity were made within 2 to 3 minutes after the end of electrochemical treatment. The time of each measurement did not exceed 5 minutes.

Final parameters of the catholyte are the following: pH = 10.3 - 10.5, ORP = minus 795 - minus 800 at a temperature of 20 - 25 ° C. The specific electrical conductivity is 4.8 - 5.6 μS / cm.

Anolyte parameters: pH = 3.8 - 4.0; ORP immediately after receipt - from plus 350 to plus 400 mV; after slight stirring in the flask for 10-15 minutes - from plus 1050 to plus 1100 mV at a temperature of 20-25 ° C. The specific electrical conductivity is 3.2 - 3.5 μS / cm.

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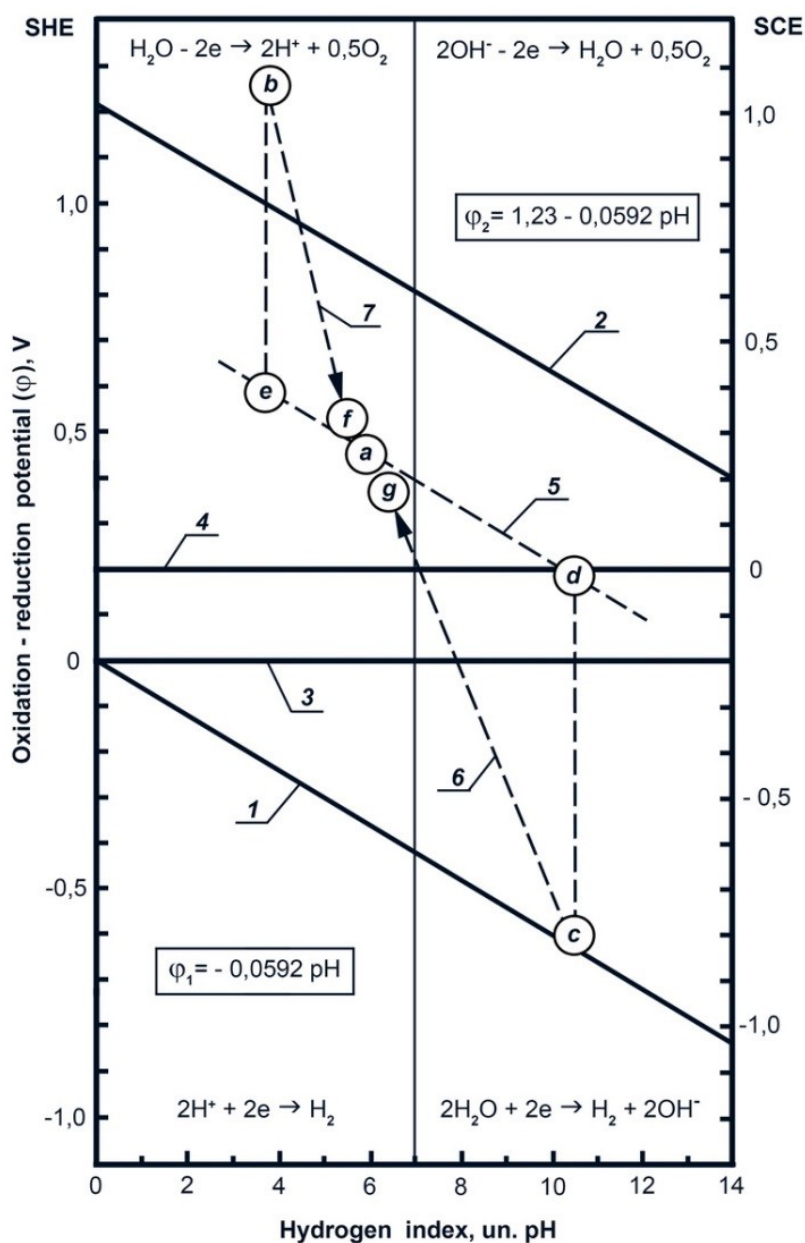
Fig. 4. Ratio of pH and ORP under the electrochemical and chemical regulation of the distilled water parameters. Legend: 1 and 2 – reduction potential of water on an inert cathode ($\varphi 1 = -0.0592$ pH) and oxidation potential of water on an inert anode ($\varphi 2 = 1.23$-0.0592 pH), respectively; 3 and 4 are the zero lines of the hydrogen (SHE) and silver chloride (SCE) reference electrodes; 5 - direction of pH and ORP changes during chemical regulation of distilled water parameters; a - initial values of the parameters of distilled water; b and c - parameters of anolyte and catholyte, respectively; d and e - parameters of chemical models of catholyte and anolyte, respectively; f and g are the parameters of anolyte and catholyte after the end of the relaxation, respectively.

Fig. 4 shows these results. The pH-ORP coordinates show the initial values of these parameters, as well as those obtained as a result of cathodic and anodic treatments. In the upper and lower parts of the graph, chemical reactions of water decomposition are shown which are common for oxidation and reduction processes on inert electrodes

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(exchanging only with electrons with a near-electrode medium) depending on pH. The parameters of anolyte and catholyte are also shown after the end of the relaxation period (about 72 hours in closed flasks). The letters "e" and "d" indicate areas of chemical modeling of the pH of freshly prepared catholyte and anolyte, respectively. Modeling of catholyte was made by introducing micro portions of sodium hydroxide into the initial distilled water in an amount from 6.0 to 6.5 mg / l. To model the anolyte, micro portions of hydrochloric acid were used in the amount of 3.9 to 4.2 mg / l. The replacement of hydrochloric acid by sulfuric acid did not lead to significant deviations. It should be noted that the electro conductivity of model solutions is significantly higher than that of its "analogues": 36-40 μS / cm in the chemical anolyte model versus 3.2-2.5 μS / cm for a real anolyte and 34-36 μS / cm for a chemical model of catholyte against 4.8 - 5.6 μS / cm for real catholyte, respectively.

The explanation of this fact could be attributed to a change in the forces of the interionic interaction as a result of the nonequilibrium electrochemical unipolar effect. It is known that the value of the interionic interaction forces in aqueous solutions of electrolytes characterizes the coefficient γ in the equation connecting the activity of the α ions in the solution with their concentration with: $\alpha = \gamma \cdot c$. The activity of ions α is the effective concentration of the ion, correspondingly, it participates in all chemical reactions in solution. The activity coefficient γ shows how many times the activity of an ion differs from its true concentration in a solution of a strong electrolyte. In dilute solutions (with $<10^{-4}$ mol / l), to which the distilled water belongs, the ion concentrations are small and the interionic interaction is practically absent, therefore $\gamma = 1$ and the ion activities are very close to their molar concentrations: $\alpha = c$.

A negligible amount of stable electrolysis products in distilled water makes it possible to investigate relaxation processes without their interfering influence, but requires special electrochemical exposure conditions that ensure the contact of as many microflows of water as possible with the electrode surface and the absence of electrochemical reactions from the counter electrode chamber. An increase in the concentration of ions of electrolytes in the initial water from several tens to several hundreds of milligrams per liter greatly increases the "activation" component of the reactivity of the anolyte and catholyte due to a variation in the activity coefficient in the range close to unity, respectively, increasing the technological value of the activated water.

Analysis of the above theoretical data and the results of practical experiment shows that the electrochemical nonequilibrium action is capable of changing the reactivity (activity) of ions in solutions ten times higher without changing their concentration.

The pH values achieved during electrochemical exposure correspond to equilibrium concentrations of alkali and acid many times higher than the salt content in water, from which these alkalis and acids could be obtained. The values of the ORP are beyond the limits of the possibilities of chemical modeling for this electrical conductivity and are therefore unique.

Analyzing these results, which demonstrate the long-persistent abnormally high and anomalously low activity of electrons in water contacted with the surface of the cathode or anode, it can be assumed that in this case the Le Chatelier principle is also valid, in accordance with which in the process of electrochemical exposure the near-electrode medium counteracts physicochemical transformations, but when they are completed, it retains the metastable state achieved for a long time, opposing the transition to state of thermodynamic equilibrium with the environment.

The results obtained on a laboratory device equipped with the electrochemical reactor of a new generation are much higher than previously achieved [1] and this significantly expands the prospects for industrial application of the obtained effects. Below are four examples to illustrate this statement.

Example 1. In 1983, at the TASMA enterprise, there were detected bacteria Pseudomonas aeruginosa (Pseudomonas aeruginosa) in a titanium tank with distilled water of 2000 liters. Periodic treatment of water with hydrogen peroxide and ozone did not produce any effect. An anodic chamber of an electrochemical reactor with glass-graphite electrodes and an alundum diaphragm was turned in a circulating circuit closed in a container with distilled water. In the auxiliary (cathode) chamber, distilled water flowed at a rate of about 1.5 liters per hour and was discharged into the drain. An electrochemically activated anolyte with a maximum ORP value of +870 mV (CSE) was synthesized in flown-through anode chamber of the reactor at a pressure of 0.3 atmosphere and mixed with the volume of water in the tank. The usage of an electrochemical reactor for 1 hour a day in circulation mode ensured the sterility of water from the second day of use.

Example 2. In 1986, for the miliary plant A-7220 in Tashkent one of the authors proposed a method for polishing silicon single crystals with the replacement of a solution of potassium hydroxide in deionized water at pH 8.5 with catholyte of deionized water with pH = 9.3. At that time, this was the maximum pH reached when water was treated in the cathode chamber of a flow reactor with electrodes of glass-carbon and an alundum diaphragm with pore sizes

ranging from 1 to 10 microns. The result exceeded expectations: the polishing rate to one monoatomic layer increased three times while increasing the adhesion of the chemically deposited copper layer to the polished silicon surface by eliminating the possibility of adsorption of potassium ions on silicon.

Example 3. The work that opened the way to the creation of IZUMRUD (EMERALD) electrochemical systems for the purification of drinking water was BAZEKS systems, intended for electrochemical disinfection and conditioning of water purified for hemodialysis, i.e. preparing water with not more than 0.07 g / l of dissolved salts [31]. Before entering the hemodialysis systems and mixing with the concentrate, water was supplied under pressure to the BAZEX system, where it was subjected to anodic electrochemical treatment in a reactor consisting of ten flow-through electrochemical modular elements with ceramic (oxide-zirconium) diaphragms in the 150-200 K / l mode for disinfection and oxidation of organic impurities (pyrogens). After the separation of the coagulated organic compounds on a five-micron filter from porous titanium, water passed into the cathode compartment of another reactor. The cathodic electrochemical treatment was effected in the regime of 250-500 K/ l to change the oxidation-reduction potential and to make the ORP of water close to the internal environment of the human body, that is, close to the patient's blood purified in the dialyzer (from minus 100 to minus 170 mV, SCE). The dialysis solution prepared on this water with optimal pH and oxidation-reduction potential values passed into the dialyzer of an artificial kidney. Clinical tests of the device were conducted on the instructions of the Ministry of Health of the USSR in the hemodialysis center of state hospital in Moscow (State Clinical Hospital No. 50). The BAZEX system was tested in the process of hemodialysis on five patients. The test took 3 months. Due to the full biocompatibility of the dialysis solution with the patient's blood and the acceleration of the transmembrane transport of creatinine and urea through the dialyzer membranes (the effect of preliminary electrochemical treatment), the duration of the dialysis process according to the analysis results of the patient's biochemical parameters of blood was reduced by 1-2 hours (according to individual data) for each of five patients. During the tests, it was noted that the use of the BAZEX device normalizes high arterial blood pressure (ABP) of patients and does not change the blood pressure of patients, if it is normal. The elimination of dermatoses and a general subjective feeling of "softer" dialysis were also pointed out by all patients. The BAZEKS system was made for the first time from a flow-through electrochemical reactor (RPE) consisting of ten FEM-1 elements. The BAZEX system was a prototype, on the basis of which in 1990 - 1991 several technological processes of water treatment were developed, which were later named EMERALD, CRYSTAL and SAPPHIRE. In the same period, basing on BASEX system, new trial systems for the production of a highly effective antimicrobial water solution without the addition of any chemical reagents were created which was practically tested for termination of blue-green algae in fountains, as well as for elimination of the pathogens of Legionnaires' disease in the air conditioning system [1].

Example 4. In 2014 together with the Institute of High Technologies (IHT) of the national atomic company Kazatomprom in the Republic of Kazakhstan, new researches were conducted so as to effect the electrochemical regeneration of a solution for underground drillhole in situ leaching (ISL) of uranium from carbonate ores. For these goals the OXITRON system [30] was used which provided the synthesis of persulphuric and sulfuric acids, as well as hydrogen peroxide, ozone in a relatively low-mineralized spent leach solution. It was shown that the use of OXITRON systems will allow to double the uranium extraction with complete refusal from reinforcing of the solution for underground drillhole ISL with sulfuric acid. According to the IHT, the result of using electrochemical synthesis of persulfuric acid in the technology of underground uranium leaching proves the possibility of reducing extraction costs by 5-6 times.

In researches performed in 2016 with the use of AQUATRON-16-500L systems and the systems described above much higher pH and ORP values were achieved due to perfected design of the main instrument for the synthesis of electrochemically activated anolyte and catholyte which is the electrochemical reactor represented by the MB element. Therefore, one can be sure that much better results should be expected from the use of such reactors in technologies where desalted or slightly mineralized water is used.

Moreover, the new generation of electrochemical elements can be used with greater efficiency in systems for purification and conditioning of drinking water called EMERALD [20, 21], with the passed through water mineralization usually in the range 0.1-1 g / l. The processes of electrochemical oxidation and reduction in MB elements during the treatment of drinking water are conducted under voltage of 12 to 24 volts. EMERALD systems were developed in the early nineties of the XX century. They provide the purification of water due to oxidative destruction of all types of microorganisms and microbial toxins, destruction of organic compounds, including hormones, antibiotics, antidepressants, elimination of water color caused by the presence of humic acids, organic and

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bacterial iron, the removal of heavy metal ions by converting them into insoluble hydroxides with further elimination on filters, oxidation of bivalent iron and manganese. There are about a hundred of different technological schemes for water purification in EMERALD systems. The principles of purification consist in the combination of oxidation and reduction processes that are optimal for each type of water and which take place in active electrode cells which are functioning at constant energy supply, (it is electrochemical, flotation, electro sorption reactors) with passive elements (filters, sorption, catalytic reactors). A typical scheme consists of water flow treatment in the anode chamber of the flowing electrochemical module MB with electricity consumption from 150 to 350 K/l which provides the destruction of microflora, oxidation of organic compounds, oxidation of divalent iron and manganese ions, flotation elimination of coagulated organic compounds with ozone bubbles and oxygen, filtration, catalytic removal of excess chlorine-oxygen oxidants on carbon granules with combination of water treatment in a cathode to convert the ions of heavy metals into hydroxides with their following filtration.

All in all, during the period of 1991 - 2016 more than 300 000 authentic household EMERALD systems with productivity of 50 - 60 liters per hour were manufactured.

In Fig. 5 and 6, different EMERALD systems of various productivity and historic period are shown.

Fig. 5. EMERALD devices for water purification and conditioning, from left to right: 1993 model with built-in high-voltage power source, 50 liters per hour; 2006 model with a remote low-voltage power source, 50 liters per hour; EMERALD EXTREM device for water treatment in emergency situations, 500 liters per hour, 2009; EMERALD System for water purification in a country cottage, 500 liters per hour, 2012

During the last 15 years the number of fake EMERALD systems has increased dramatically as well as the number of systems for production of so-called "ionized", "hydrogen", "alkaline-living" water for medical treatment. The benefits of the commercial use of counterfeits will support their proliferation until consumers become well aware of the technical and technological characteristics of devices. One of the most difficult aspects in the technology of synthesis of electrochemically activated water and solutions is to ensure the processing of each conditionally isolated microvolume of liquid in the DEL and to prevent the premature neutralization of the most active products of electrochemical reactions by the same active electrode of the opposite polarity.

Fig. 6. EMERALD device (trade name IZUMRUD-V3) with MB elements of the new generation, providing the best of the achieved quality of purification and conditioning of drinking water, 60 l / h, 2017.

Electrochemical systems manufactured without this fact in mind are usually not effective. In particular, it is impossible to obtain the results described in this paper with their help. Practically all industrial, laboratory and household devices manufactured by unauthorized manufacturers allow to obtain only small or trace quantitative and qualitative effects due to the metastable state of the near-electrode medium. For this reason, the evidence of efficiency of electrochemically activated water and solutions usage are more evident taking into account the results of many foreign researchers who have used the simplest and far from perfect technical electrochemical systems [32-84]. It should be pointed out that foreign scientific publications in the field of electrochemical activation appeared only 10 years after the publication of the first reports in the Soviet Union, that is, in the late eighties. Nowadays due to the rapid dissemination of information, the speed and quality of foreign researches has been increasing dramatically, even despite the fact that the technical instrument for synthesize of electrochemically activated substances remain predominantly at a low level. The problem of effective (ion-selective) chemical isolation of the working chamber of the electrochemical reactor from the auxiliary one is solved by finding the optimal design of the reactor and the corresponding regime of its operation in each technological scheme.

The next successful step in solving this problem was made in 2016 with a creation of a new generation of electrochemical reactors in accordance with [30].

The results of intensification of electrochemical influence on water due to the electric field that regulates the chemical constituents of the filtration flow in a porous medium which was also used in electrochemical cells of the new 2016 generation in experiments with distilled water are universal, since here we could observe the transformation of an inactive ceramic ultrafiltration diaphragm into an ion-selective membrane regardless of the concentration of electrolyte ions.T

he following illustrations explain this effect called ion selective electrolysis with a diaphragm [14].
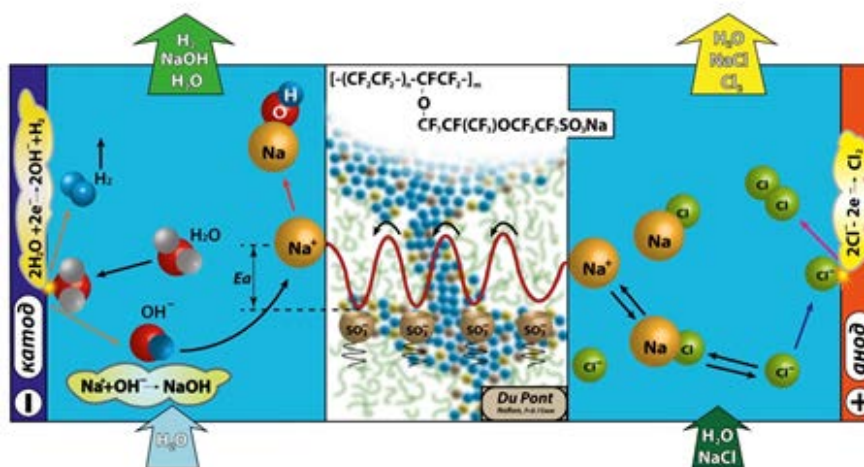
Fig. 7. The parameters of the process of charge transfer through the membrane are determined by the very low electromigration velocity of cations in the polymer electrolyte. The pressure drop across the membrane is absent. The process does not ensure complete decomposition of the sodium chloride solution entering the anode chamber, requires the injection of distilled water into the cathode chamber

Fig. 7 depicts schematically the process of industrial chlorine electrolysis with a cation-active membrane. Modern industrial electrolyzers are a package of flat electrochemical cells (elements) consisting of electrodes and an ion-selective polymer membrane developed by DuPont which is separating them. Nafion membrane is made in the form of thin (no more than 200 microns) film of tetrafluoroethylene and perfluorinated vinyl ether with sulfo groups. The area of the working surface of the membrane in a separate element could be up to 3 square meters. Membranes are sensitive to contaminates in the initial solution of the salt such as ions of polyvalent metals and organic substances. The membranes cannot work at an alternating pressure drop, with a constant pressure difference of more than 0.1 bar. Due to this fact chlorine and hydrogen in membrane electrolyzers are produced and transported at a pressure close to atmospheric. Being once moistened, membranes lose ion-selectivity when re-wetted after drying. All industrial electrolyzers operate with constant chemical composition and concentration of the initial solution, therefore, require

strictly prescribed and unchanged operating conditions. Nevertheless, the periodic replacement of membranes is required at least once in 3 years or more often if there are any small deviations from optimal operating conditions. The diaphragms replacement requires complex equipment, the mandatory availability of special lifting devices (crane beams), moreover, replacement work is performed only by authorized staff of the manufacturer. To replace even one defective membrane, the long procedure of electrolyzer stopping is required. Anolyte and catholyte after leaving the electrode chambers of the membrane electrolyzer and removing chlorine from the anolyte are conditioned in the external system of the electrolysis process devices to normalize the chemical composition, and only then are returned to the electrolyzer.
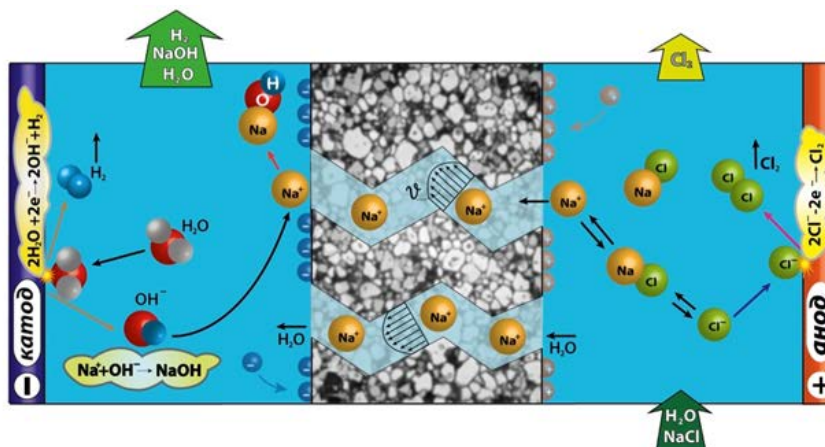
Fig. 8. A ceramic inactive DIAPHRAGM with pore sizes from 0.01 to 0.1 μm is converted into a cation-active MEMBRANE by the superposition of the pressure field (from the anode to the cathode) and the electric field. The parameters of the process of charge transfer through the diaphragm are determined by the of filtration flow velocity of the electrolyte solution in a porous medium, represented by inert metal oxides. The process provides continuous and complete electrolytic decomposition of sodium chloride solution to chlorine, caustic soda solution and hydrogen.

Fig. 8 shows the same process of chlorine electrolysis effected in an MB element with a ceramic ultrafiltration diaphragm. In MB elements one could observe a complete transformation of the initial saline solution into gaseous chlorine, sodium hydroxide and hydrogen. This technology does not require auxiliary operations typical for membrane electrolysis processes such as tapping and dechlorination of the anolyte, enriching it with sodium chloride, introducing distilled water into the cathode chambers of the reactor. The chlorine made in the anode chambers of MB elements is under pressure from 1.5 to 3.0 bar (the pressure gradient is directed from the anode to the cathode) and occupies a volume of several milliliters. Chlorine and hydrogen transportation to the places of use or discharge is carried out by fluoroplastic tubes, designed for high pressure. A diaphragm made of chemically resistant material (alumina in alpha form) insensitive to any pollution works in the MB element under pressure drop of 1.5 to 3.0 bar and provides the mass transfer of sodium cations together with the solvent (water) into the cathode chamber thanks to the electric field in a porous medium with a strength of 1 to 3 V / cm.

In this case, the electric field blocks the filtration transfer of chlorine anions and the filtration flow through the diaphragm with a pressure gradient of 6-10 bar / cm in its turn blocks the penetration of hydroxyl anions from the cathode chamber to the anode chamber. Thus, the ceramic diaphragm becomes cation-active and ensures complete decomposition of the sodium chloride solution (chlorine, caustic soda, hydrogen) entering into the reactor without external costs for conditioning and returning to the reactor operations. Moreover, this technology does not require a system for the removal of electrolysis gases since both hydrogen and chlorine are transported in the pressure lines.

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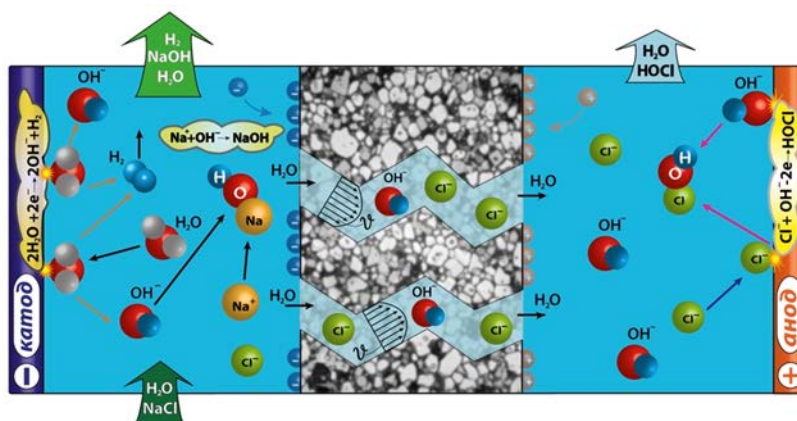
Fig. 9. A ceramic inactive DIAPHRAGM with pore sizes from 0.01 to 0.1 μm is converted into an anionic MEMBRANE by the superposition of the pressure field (from the cathode to the anode) and the electric field. The process provides the production of caustic soda, hydrogen and hypochlorous acid with a concentration of up to 30% from initial concentrated sodium chloride solution

Fig. 9 shows the process of obtaining a concentrated (up to 30%) solution of hypochlorous acid in a membrane element with a ceramic diaphragm. At the same time in the same MB element, the ceramic ultrafiltration diaphragm becomes anionic when the direction of the pressure field gradient reverses from the cathode to the anode. It should be noted that the mass transfer rate (electromigration plus filtration) is thousand times greater than the rate of diffusion of ions in the polymer membrane. The high selectivity of the diaphragm in the regime of ion selective electrolysis does not decrease in the presence of impurities in the electrolyte and is ensured by a balance between the current strength (the amount of electricity flowing per unit time) and the rate of input of the initial substances in the solution into the electrochemical reactor. Practical use of this process will enable one to fundamentally solve the problem of disinfection of drinking water, sewage, swimming pool water by replacing chlorine (reacts with water and form hydrochloric and hypochlorous acid) and sodium hypochlorite solution (reacts with water and form an inactive ion hypochlorite, contains ballast substances such as salt and sodium hydroxide) to an aqueous solution of hypochlorous acid only.

The synthesis process of pure hypochlorous acid by the method described above is used in practice by our colleagues from Blue Safety company (Germany). The introduction hypochlorous acid solution into the supply line of tap water which is going to the medical facility in an amount regulated by sanitary and hygienic standards for residual chlorine allows to ensure the absence of biofilms on the internal surfaces of the water-diluting lines after reverse osmosis filters which is unattainable under the standard water supply system.

Ceramic diaphragms are used in the electrochemical elements of MB which were patented in the technologically advanced counties and they are perfect for the work even with the organic impurities, polyvalent metal ions in the initial solution, pressure drops, changes in chemical composition and concentration of initial solutions, repeated drying and moistening. These characteristics distinguish them from membrane electrolyzers and that is the reason why they are called electrochemical reactors, i.e. devices which are able to work in a wide range of concentrations, fluid flow rates, pressures and temperatures (like the majority of various chemical reactors). As for ion selective conductivity which is the most important characteristic of membranes, it should be mentioned that due to the ion selective electrolysis with a diaphragm, the ceramic diaphragm acquires the properties of an effective ion-selective barrier while operating in an electric field in superposition with a filtration field set by the pressure drop.

This principle is used in AQUACHLOR and ECOCHLOR systems with the single productivity (the amount of chlorine produced per day per unit of production area including passageways) reached 360 kg of chlorine per day per square meter, which is higher than in large chlorine-caustic plants. Fig. 10 shows the AQUACHLOR and ECOCHLOR devices with productivity of 600 to 4000 grams of chlorine gas per hour.

The average parameters of AQUACHLOR and ECOCHLOR devices are as follows: salt consumption for production of 1 kg of chlorine - 1.8 kg; electricity consumption for the production of 1 kg of chlorine - 2.5 - 3.5 kW; the concentration of sodium hydroxide in the catholyte is 250 g / l.

Fig. 10 shows the models of AQUACHLOR and ECOCHLOR devices of various years of previous generations as well as modern devices based on the new generation MB elements.

Replacement of chlorine plants with compact modular high-performance devices for electrolysis of sodium chloride solution used at each local application site of chlorine, can avoid the transportation and storage of liquefied chlorine at consumer enterprises and can also provide an opportunity to safely solve the problems of using chlorine in the production process not only for large consumers (5 and more tons of chlorine per hour), but also for enterprises which consume chlorine from one to hundreds of grams per hour or tens of kilograms per hour.

Fig. 10. AQUACHLOR and ECOCHLOR devices, from left to right: AQUACHLOR-500 (A-500) with a capacity of 500 grams of chlorine gas per hour, requires frequent cleaning of the electrochemical reactor with hydrochloric acid, 2005; installation of A-500M, 500 grams of chlorine gas per hour, equipped with self-cleaning reactor, manual control of working parameters, 2012; A-600 and ECOCHLOR-3000 (E-3000) devices with a capacity of 600 and 3000 grams of chlorine gas per hour, reactors with the MB elements of a new generation, semi-automatic control, 2016; A-800 and E-4000 devices with chlorine gas capacity of 800 and 4000 grams per hour, self-cleaning reactors, remote monitoring and control, 2017.

CONCLUSION

The laboratory device AQUATRON-16-500L which is a technical electrochemical system for electrochemical regulation of properties and parameters of distilled water was developed within the work under the grant of the Russian Science Foundation. In the electrochemical MB element of this device, cathodic and anodic electrochemical treatment of distilled water is carried out using the technology of ion-selective electrolysis with a diaphragm. The properties of the cationic and anionic diaphragm are induced in an inactive ultrafiltration ceramic diaphragm of alumina in alpha form by superposition of the filtration pressure filed and electric field. The pH, electrical conductivity and oxidation-reduction potential of the initial water, metastable anolyte, and catholyte of distilled water were measured at the time of onset and at the end of the relaxation changes.

During the studies, the abnormal values of the oxidation reduction potential measured with a platinum electrode relative to a silver chloride reference electrode have been achieved for the first time. Such ORP values go well beyond the boundaries of thermodynamic stability of water during its oxidation at the anode and are equal to the maximum limit of thermodynamic stability after reduction at the cathode. These parameters exceed previously reached and known values and allow to predict a significant increase in the efficiency of all previously developed processes for the practical usage of metastable solutions and water. The principal features of the technology of ion-selective electrolysis with a diaphragm are considered. The spheres of possible usage of dilute and concentrated metastable aqueous solutions of electrolytes are shown on real examples, as well as the real life usage of distilled, purified for hemodialysis and fresh drinking water. Moreover, the prospects of applying the new data obtained in the synthesis and subsequent use of environmentally friendly electrochemically activated solutions for disinfection and sterilization in medicine, food industry, water treatment, metallurgy, mining and other fields of human activity are also shown. The key economic parameters of technologies with the use of electrochemically activated water and solutions as well as technologies for industrial electrochemical synthesis of hazardous substances at the site of use are presented in the article, demonstrating their huge economic efficiency in comparison with traditional processes.

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