5.6. ELECTROCHEMICAL ACTIVATION: THE KEY TO ENVIRONMENTALLY CLEAN WATER TREATMENT TECHNOLOGIES

The possibility of reagent-free control of the properties of water and aqueous solutions in various technological processes, discovered in the seventies of the last century [1–11], Fig. 5.6.1, is implemented today in hundreds of thousands of different electrochemical systems — from household devices for obtaining "super-reduced" or "superoxidized" (so-called "living" and "dead") water to industrial systems that operate at a wide variety of facilities in many countries and produce electrochemically activated washing, disinfecting, sterilizing, extracting, emulsifying, stabilizing, demulsifying, preserving, bleaching, medicinal and other

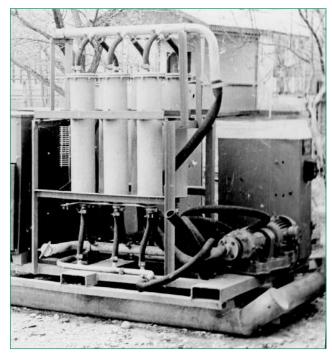


Fig. 5.6.1. UEV-4 [3] device for the production of electrochemically activated water used in the preparation and treatment of drilling mud, water treatment for cooling systems of gas treatment systems, compressor stations of main gas pipelines. Six hydraulically parallel connected flow-through electrochemical reactors with coaxial placement of electrodes and a diaphragm. Anodes are graphite rods with a diameter of 100 mm and a length of 900 mm, a diaphragm is a chlorinated fabric on a vinyl plastic frame. The interelectrode distance is 10 mm. Catholyte productivity is 25000 l/h, anolyte productivity — 5000 l/h, current 1200 A, voltage — 30 V. Kokand plant "Bolshevik" produced more than a thousand such devices in the period from 1977 to 1980.



V. M. Bakhir. Water supply and sewerage, January-February, 2012, p. 89–103.

solutions [12]. This wide variety of technological properties of solutions is explained by the unique combination of pronounced oxidative, reductive, catalytic and biocatalytic activity of electrochemically activated solutions with a disproportionately small concentration of active substances, which fundamentally distinguishes activated solutions from traditional solutions of the corresponding chemical reagents.

The historically established priority of Russia in this no more young, but intensively developing scientific and technical field of applied electrochemistry is supported by the work of scientists and specialists, whose efforts until 2005 were united by informal scientific and technical bonds, and since 2005 — by the scientific informational structure of the Vitold Bakhir Electrochemical Systems and Technologies Institute.

The main principle of electrochemical activation (ECA) is the use of substances in a metastable state in technological processes, which allows for a multifold reduction in the need for chemical reagents.

Technological principles of ECA processes:

- before using in technological processes, water and dilute aqueous solutions of substances are converted into a metastable state by electrochemical unipolar treatment;
- chemically active reagents necessary for technological processes are synthesized at the place of their application, thereby excluding the transportation and storage of hazardous substances;
- industrial high-performance electrochemical systems are formed of autonomous compact highly reliable modular cells — by analogy with the construction of living organisms of individual cells.

The main criterion for the rationality of ECA application:

- multiple savings in energy, labor, time and materials in comparison with traditional technical solutions while increasing the efficiency of the main technological process;
- getting new properties of the final product, new technological effects and results.

The best results in the application of ECA systems and technology can be achieved with an optimal combination of three conditions: rational design of an electrochemical reactor, a flow chart of its use, specified for a certain purpose, and optimal technology for using an electrochemically activated solution or water.

Some aspects of the above conditions are discussed below.

CELLS. Long-term work on the search for the optimal design of an electrochemical reactor, carried out since the mid-70s of the last century, led in 1989 to the creation of a flow-through electrochemical modular cell known as FEM-1 (flow-through electrochemical modular cell, UK patent GB 2253860).

Until that time, in the technical literature, devices for producing electrochemically activated solutions were called either water electrical treatment devices, or electroactivators, or (less often) diaphragm electrolyzers. In the early 90s, the term *electrochemical cell* was introduced into the technical lexicon and its distinctive features were first formulated [13].

An electrochemical cell, unlike its closest analogue, a diaphragm electrolyzer, has much more technological and system degrees of freedom and is designed for the electrochemical transformation of a wide variety of liquids, i.e., not only water or aqueous solutions of electrolytes in a wide range of concentrations - from zero to saturated solutions, but such, for example, as milk, vegetable and mineral oils, solutions of carbohydrates, ammonia, alcohols, surfactants, organic and inorganic fertilizers, herbicides, pesticides and many others. A flow-through electrochemical modular cell combines the physicochemical, electrical and mechanical properties of various structural and auxiliary materials with the geometric dimensions and configuration of electrodes in an optimal way, that is, taking into account the whole variety of processes of movement and simultaneous electrochemical transformation of liquids and gases of different nature and chemical composition, electrode chambers, the entire interelectrode, intra-electrode and intra-diaphragm space. The optimal combination of all the above parameters and factors should be observed practically for each cross-section of the electrode chambers, since the intensity and speed of energy and mass transfer in the reactor vary significantly along the main direction of the interelectrode medium in proportion to the current density, flow rate and strongly depend on the chemical composition and concentration of starting substances, as well as products of electrochemical reactions in each microvolume of the interelectrode space, including the diaphragm.

The first modular cells of FEM-1 were being manufactured for three years (1989–1991) at the experimental plant of the All-Union Scientific Research and Testing Institute of Medical Technology (VNIIIMT).

With the improvement of flow-through electrochemical modular cells, the number of electrochemical devices and their use for various applications were growing, so they have served and continue to serve people. Thus, the number of commercially used FEM-1 cells did not exceed 1000, while the number of FEM-2 cells manufactured and sold as part of electrochemical systems was about 80,000, and that of FEM-3 cells — more than a million.

FEM-2 cells (RF pat. No. 2042639) were manufactured by the Emerald Soviet-British joint

venture until 1996 under license. After the license was revoked, the enterprise kept producing FEM-2 cells for some time, but it was forced to stop production due to the appearance on the market of devices with more advanced FEM-3 cells (RF Pat. No. 2078738). Serial production of FEM-3 cells was organized at the Laboratory of Electrotechnology (*LET* LLC) and lasted from 1995 to 2008.

Expanding the range of tasks and the range of technological processes, where electrochemical technologies made it possible to achieve significant economic and technical advantages, led to the emergence of flow-through electrochemical modular cells FEM-7 (RF Pat. No. 2176989) and FEM-9 (RF Pat. No. 3370885). In 2009, based on the generalization and analysis of the experience in the production and operation of FEM-3, FEM-4 cells (RF Pat. No. 2145940) and FEM-9, MB-11 and MB-26 cells (RF Pat. No. 2350692, Bakhir Module) appeared, possessing improved electrochemical parameters in comparison with previously created ones. All of those products were also serially produced by *LET* LLC on the basis of an agreement between the copyright holder and the enterprise.

At the beginning of 2011, scientists and specialists of the Vitold Bakhir Electrochemical Systems and Technologies Institute (www.vbinstitute.org) completed research work, which served as the foundation for the creation of a whole series of fundamentally new designs of MB cells and, accordingly, new technologies — electronic electrochemical systems. At the same time, the LET LLC enterprise was deprived of the right to manufacture products under all the above-mentioned patents because of the raider seizure.

Since July 2011, the only company in which serial production of MB elements of various models has been organized under the control and with the participation of authors and copyright holders is the Vitold Bakhir Institute. The design of the new generation MB cells concentrates previously unknown new technical and technological achievements. Due to this, the productivity of MB elements and RPE cells (flow-through electrochemical cell [13]) of these elements has increased more than twenty times, and the duration of continuous operation — more than fifteen times. The electrical power consumption of new models of MB elements is in the range from 60 to 3000 W. They are used in all electrochemical devices manufactured by the Vitold Bakhir Institute and it's official scientific partners.

TECHNOLOGICAL SCHEMES FOR THE CELLS **OPERATION.** Systems, devices and apparatus with RPE reactors of one or several MB modular elements, equipped with hydraulic systems (piping) of the reactor, represent a higher degree of integration of technical electrochemical systems and, depending on the application, include additional units and hydraulic systems, due to which the reactor operates in a given technological mode. Currently, the most common and well-known are three types of electrochemical systems: EMERALD devices for purification and conditioning of fresh water, STEL devices for the synthesis of electrochemically activated detergents, disinfectants, medicinal and other solutions with various active substances (AS), as well as devices of the AQUACHLOR and ECOCHLOR type for obtaining electrolysis products of concentrated electrolyte solutions in order to replace the corresponding bulky chemical industries with safe compact modular systems close to the places of consumption of the final products. Numerous devices of similar purpose, offered by various companies, are mainly products of unfair copying (borrowing), as well as accompanying descriptions of physicochemical properties, technologies for the production and use of electrochemically activated water and solutions.

EMERALD devices are used for producing water with antioxidant properties and purification of fresh water from microorganisms, organic impurities, ions of heavy metals, iron, manganese, as well as from herbicides, pesticides, surfactants, phenols and oil products.

Disinfection of water by direct electrolysis is a type of oxidative treatment of water, but it differs from common methods of disinfection in that oxidants are produced from the water itself and not brought in from outside and having fulfilled their function return to the previous state. The efficiency of water disinfection by direct electrolysis is higher in comparison with chemical methods. Direct electrolysis does not require metering pumps or reagents. Chlorine necessary to prevent secondary bacterial contamination of water in distribution networks is generated from natural mineral salts in the water passing through the electrolysis tank and immediately dissolves in it. Direct electrolysis breaks down chloramines converting them to nitrogen and salt. The technique and process of direct electrolysis of fresh water began to develop in the sixties of the last century, when relatively inexpensive low-wear metal-oxide anodes appeared [14-16].

The essence of the technology for disinfection and purification of fresh water by direct electrochemical action predetermines the design features of devices in which the entire flow of treated water is subjected to electrochemical treatment for a short period of time. In the Potok and Potok-M electrochemical diaphragmless devices made by the Russian Kommunalnik Plant, as well as in other known devices, all the treated water flows through narrow (no more than 3 mm) gaps between flat plate electrodes of alternating polarity. Water almost always having a small amount of chlorides, is saturated with hypochlorite formed during the mixing of the products of cathode and anode reactions, as well as electrolysis gases, which in some such devices is used in the processes of further flotation purification from suspended particles and organic substances that have coagulated or oxidized under effect of hypochlorite ions and oxygen.

EMERALD devices based on a fundamentally different technological scheme of water treatment, were created in 1990 and a year later protected by two UK

patents (GB 2253860, GB 2257982) due to the absence of Russian patent legislation at that time. The EMERALD devices are fundamentally different from the above analogs by the stages of anode and cathode treatment of water separated in time and space. Their creation became possible due to the invention of the FEM-1 flowthrough diaphragm electrochemical modular cell, with the electrical resistance, when operating on fresh water, allowing a significantly dense current flowing through the separating diaphragm at a relatively low voltage. The flow of fresh water in the long narrow tubular gaps between the electrode and the ceramic ultrafiltration diaphragm in the FEM element obeys the laws of hydraulics only in the absence of current. If an electric current flows through a FEM element, then under the influence of chemical reactions on the electrodes and an electric field, the nature of the flow changes and at a certain combination of the flow rate and electric current density it switches to a self-organization mode characterized by a sharp increase in energy and mass transfer due to the formation of toroidal structural elements of the flow, relatively slowly moving along the longitudinal axis of the electrode chambers. This mode provides the lowest electrical resistance of the electrochemical system and the highest possible contact of microvolumes of water with the surface of the electrodes per unit time. The flow of electric current through the inert electrodes of the FEM element is due to the selection of electrons from the water at the anode and the introduction of electrons into the water at the cathode. This is accompanied by a variety of chemical processes both directly at the surface of the electrodes and in the volume of flowing water. The volumes of water in the electrode chambers saturated with dissolved and gaseous cathode and anode products of electrochemical reactions do not mix in the FEM element due to the presence of the ultrafiltration ceramic diaphragm with highly charged layers of anions and cations adsorbed on its surfaces facing the cathode and anode, respectively. Thus, the FEM electrochemical reactor makes it possible to separate the oxidation and reduction processes in time and space in the same water flow and directly expose water to either only oxidative or only reductive electrochemical treatment.

In the natural processes of water self-purification, redox processes play a dominant role and proceed under the influence of solar radiation, physicochemical processes of interaction with air oxygen, minerals of rocks. They are usually accompanied by other processes: hydration, flotation, sorption, coagulation, sedimentation. The maximum possible use of the fundamental features of natural processes of water self-purification in compact high-performance modular chemical reactors of a certain functional purpose, placed in various sequences along the flow of purified water, is the main idea of EMERALD devices.

Household EMERALD devices traditionally, since 1991, have purified water capacity in the range from 40 to 60 liters per hour and power consumption from 30 to 90 W/h. It is for such flow rates that compact intermediate reactors have been developed, with additional water purification processes carried out in them. The driving force of the processes in these intermediate "passive" elements of water purification is the internal energy that water acquires in the "active" FEM electrochemical elements as a result of the nonequilibrium exchange of electrons in the FEM element. In the period from 1991 to 2006, a variety of technological schemes (technological processes) for water purification in EMERALD devices were developed and commercially implemented. The general name of the systems was retained, however, the names of various technological processes of water purification were also chosen from mineralogy, since the names of minerals are euphonious for speakers of different languages. This is how the EMERALD, TOPAZ, AMETIST, SAPPHIRE, AQUAMARIN, QUARTZ, RUBIN systems appeared.



Fig. 5.6.2. EMERALD device with a capacity of 300 liters per hour. The device implements the TOPAZ water purification process. The device application: water from surface sources purification in emergency areas. Power consumption - 800 watts. The voltage at the electrochemical cell of the device is 24 V. It can be used as part of a mobile water purification complex or in stationary conditions. Power supply from a 220/30-volt current source (rectifier), or from car batteries. Produced since 2001 by orders of the RF Ministry of Defense.

When the number of developed technological processes exceeded the number of widely known transparent minerals, the names of translucent and opaque ones were used: AMBER, TURQUOIS, AGATE, MALACHITE.

The technological process implemented in the first EMERALD device consists of three stages: anode treatment of water, conversion of chlorine-oxygen oxidants into hydroperoxide ones in a catalytic cell filled with granules of carbon material and, finally, cathode treatment of water. The list of new technological processes increased as new tasks were solved. Table 5.6.1 presents a list of water treatment processes developed for EMERALD devices.

In the course of work, in order to meet the needs of various customers, high productivity EMERALD systems were developed — up to 500 liters per hour (Fig. 5.6.2). The emergence of new types of electrochemical reactors, the development of new universal approaches to water purification and conditioning technology, the use of new materials and application technologies led in 2011 to the creation of the next generation of EMERALD systems — EMERALD-REDOX devices. EMERALD-RE

Table 5.6.1

No.	Process name	Process actualization technical system	Brief process description
1	Anode electrochemical water treatment	FEM (MB) element, RPE cell	Destruction of microorganisms, oxidative destruction of organic compounds and microbial toxins
2	Electromigration cation removal	FEM (MB) element, RPE cell	In the anode water treatment process, the transfer of current through the diaphragm by cations
3	Cathode electrochemical water treatment	FEM (MB) element, RPE cell	Conversion of heavy metal ions into colloidal particles of hydroxides
4	Electromigration anion removal	FEM (MB) element, RPE cell	In the cathode water treatment process, the transfer of current through the diaphragm by anions
5	Heterophase catalytic destruction of active chlorine compounds	Catalytic dechlorination reactor E_c	Removal of active chlorine compounds with simultaneous formation of active oxygen compounds
6	Liquid-phase oxidation of organic compounds in a medium with charge transfer catalysts	Mixing reactor E_{T}	Oxidation of organic compounds by products of anode electrochemical reactions in a volume with a slow flow rate during stirring
7	Microflotation of colloidal particles	Flotation reactor E_{F}	Using air microbubbles to remove colloidal suspensions from water
8	Microelectroflotation of colloidal particles	Flotation reactor $E_{\rm FE}$	Using microbubbles of electrolytically produced hydrogen or oxygen for water purification from colloidal suspensions
9	Electrokinetic extraction of colloidal particles (electrokinetic fixation)	Electrokinetic reactor E_{κ}	Concentration of colloidal particles in the electric field of an electric double layer of mineral granules, fixation and dehydration of colloidal particles at interphase boundaries
10	Microelectrophysical water treatment	Microbubble catalytic reactor E _D	Electrophysical impact on water and dissolved organic impurities in electrically active gas microbubbles at the moments of the first kind phase transitions at places of electrical and hydraulic disturbances of the medium

Technological water purification processes in EMERALD devices, technical systems for their actualization and brief process descriptions

DOX devices have a capacity of 50 to 500 liters per hour and include models in various versions — from domestic to special ones, including extra-heavy-duty devices for areas contaminated with chemical warfare agents, bacteriological or other toxic pollutants, as well as devices for use in cottages and small villages.

In general terms, the EMERALD-REDOX device is designed to obtain drinking water with antioxidant properties and additional purification of water from microbes and microbial toxins, ions of heavy metals, iron, manganese, aluminum, harmful organic compounds: herbicides, pesticides, antibiotics, hormones, phenols, superfactants, oil products. Antioxidant water from the EMERALD-REDOX device has a beneficial effect on the entire body, stimulates metabolic processes, has a radioprotective effect, strengthens the body's immunity.

In EMERALD-REDOX water purification and conditioning devices, the main processes are redox reactions on inert (exchanging only electrons with the water being purified) electrodes. The spectrum of physicochemical reactions occurring in the EMERALD-REDOX devices is as close as possible to the natural processes of water purification caused by wind and sun activity, as well as to the reactions of phagocytosis in the body of warmblooded animals and humans during the destruction of microorganisms and foreign substances.

In EMERALD-REDOX devices, microorganisms, microbial toxins and organic compounds (herbicides, pesticides, phenols) are destroyed in the course of anode oxidation reactions. Heavy metal ions are converted to insoluble hydroxides as a result of cathode reduction and are removed using a special electrokinetic reactor.

The duration of operation (the resource) of the main elements of the EMERALD-REDOX device — electrochemical modular elements (cells) — exceeds 100 thousand hours. The device does not include elements requiring periodic replacement.

STEL devices for electrochemical synthesis of Anolyte ANK

STEL devices for the production of electrochemically activated washing, disinfecting and sterilizing solution — Anolyte ANK — have been firmly entrenched in the State Register of Medical Equipment of Russia since 1994. Almost all health care institutions in Moscow and St. Petersburg, many other cities of Russia, countries of near and far abroad are equipped with them.

Electrochemically activated detergent and antimicrobial solution — Anolyte ANK, synthesized



Fig. 5.6.3. STEL devices in a 1000-bed tuberculosis hospital in Tbilisi, 2004. Anolyte ANK produced by the devices, is fed from the storage tanks to the wastewater flow in a proportional amount, automatically controlled by a system of valves and level sensors. The devices operate in automatic mode, providing a constant maximum level of Anolyte ANK in storage tanks.

in STEL-type devices, is the only environmentally friendly solution in the world that, at the same concentration of active substances (AS), is officially approved not only as a high-level disinfectant for a wide range of applications, pre-sterilization cleaning and sterilization of medical devices, including endoscopes, but also as a medicinal product. Anolyte ANK, having a significantly lower corrosive activity in comparison with solutions of hypochlorite or chlorine water equal in the concentration of active chlorine, is a very effective means of water disinfection, much superior to the above analogs. When water is disinfected with anolyte, chlorates are not formed, which makes it possible to use Anolyte ANK to disinfect water in schools, hotels, hospitals, dental clinics, even in those countries where the use of chlorine (hypochlorite) for water disinfection at such facilities is prohibited (Holland, Germany).

The Anolyte ANK synthesis technology in STEL devices, protected by patents of the Russian Federation and many foreign countries, includes a number of important processes. Among them, the removal of polyvalent metal ions from the initial sodium chloride solution by increasing its pH to a value ensuring the formation of insoluble hydrates, the separation of heavy and alkaline earth metal hydrates from the initial solution, saturation of the initial solution with dissolved hydrogen, and finally the introduction of electrochemically synthesized chlorine-oxygen and hydroperoxide oxidants into the solution prepared this way with control of its pH.

The active ingredients in Anolyte ANK is a mixture of peroxide compounds (HO[•] — hydroxyl radical; HO_2^- peroxide anion; ${}^{1}O_2^-$ singlet molecular oxygen; O_2^- superoxide anion; O_3^- ozone; O^{\bullet} atomic oxygen) and chlorine-oxygen compounds (HClO — hypochlorous acid; ClO⁻ — hypochlorite ion; ClO[•] — hypochlorite radical; ClO₂ — chlorine dioxide).

Such a combination of active substances ensures the absence of adaptation of microorganisms to the biocidal action of the Anolyte ANK, and the low total concentration of active oxygen and chlorine compounds guarantees complete safety for humans and the environment during its long-term use.

The loss of antimicrobial properties of Anolyte ANK during storage is due to the reactions of mutual neutralization of most metastable chlorine-oxygen and hydroperoxide oxidants, which have the higher rate, the higher the total mineralization of Anolyte ANK. Reactions of this type, in particular, include the processes of interaction of hypochlorous acid with hydrogen peroxide (HClO + $H_2O_2^{\rightarrow}O_2^{\uparrow} + H_2O + HCl$), of hydrogen peroxide with ozone $(H_2O_2 + O_3 = 2O_2^{\uparrow} + H_2O)$ and a number of others.

STEL-10N-120-01 type devices ensure the production of Anolyte ANK of the first generation, with the total mineralization not exceeding 5 g/l and being approximately 9–10 times higher than that of oxidants. Chlorine-containing disinfectant solutions with the total mineralization exceeding 5 g/l, are not activated, even if they are obtained in electrochemical devices according to the above Anolyte ANK production technology. Within a few hours, such solutions lose their activity turning into a saline solution of hypochlorite and hypochlorous acid. Such a solution is antimicrobial, but, unlike electrochemically activated one, it does not have sporicidal activity, has a characteristic chlorine odor and, when used for water disinfection, forms chlorination byproducts, in particular, chloroform.

Low total mineralization of Anolyte ANK obtained in STEL-ANK-PRO or STEL-ANK-PRO-M devices, developed in 2009–2011, with a high specific content of oxidants determines the high stability of the molecular complexes with hydrogen bonds present in the solution, which can have not only molecules in the ground state as components, but also ions, free radicals, molecules in an excited state (exciplexes), which in turn are hydrated (the phenomenon of distant hydration), turning into electrically neutral aqua complexes.

The increase in the stability of aqua complexes and the decrease in the charge density of metastable particles are the more noticeable, the lower the concentration of ions in the solution. The difference in the properties of Anolyte ANK, depending on its total mineralization, is shown in Table 5.6.2. The explanation of the seemingly unusual, at first glance, properties of the Anolyte ANK obtained in STEL-ANK-PRO and STEL-ANK-PRO-M devices, presented in Table 5.6.2, is associated with the ratio of ballast substances (sodium chloride ions) and active substances (metastable oxidants) in Anolyte ANK.

STEL devices for electrochemical synthesis of Anolyte ANK

An increase in the salt concentration in the electrochemically activated anolyte contributes to a shift in the equilibrium towards the formation of molecular chlorine, thereby increasing the corrosive activity of the solution, its destructive effect on polymeric materials and metals, giving the solution a characteristic chlorine odor.

On the contrary, a decrease in the salt content in the electrochemically activated anolyte leads to an increase in the proportion of reactions of the formation of active oxygen in the process of electrochemical synthesis, a significant decrease in the corrosivity of the solution, a decrease, up to complete disappearance, of chlorine odor. Comparison of the properties of Anolyte ANKs of different mineralization shows the advantage of low-mineralized solutions in preventing biochemical corrosion. This is primarily due to the synergistic effect of the antimicrobial action of hypochlorous acid against the background of the oxidative activity of dissolved oxygen and leads to the removal of old bio-sediments, as well as to the prevention of the growth of new biofilms while simultaneously reducing corrosion and biocorrosion. Almost complete elimination of corrosive activity of low-mineralized Anolyte ANK obtained in STEL-ANK-PRO and STEL-ANK-PRO-M devices, can be achieved by adding trisodium phosphate in the amount of 0.1 g/l to the prepared solution. Anolyte ANK with this additive can last as long as without it, that is, for at least 30 days.

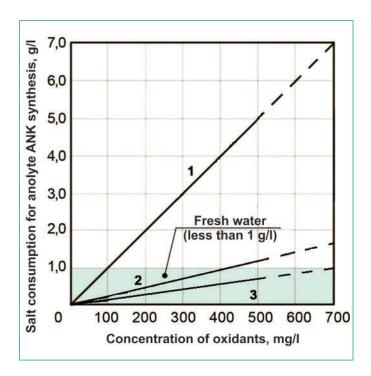
One of the most important directions of technical improvement of STEL devices is to reduce the content of ballast substances (sodium chloride ions) in the Anolyte ANK whose active substances are a mixture of metastable oxygen-chlorine and hydroperoxide oxidants. The appearance in 2011 of the third generation Anolyte ANK marked the achievement of a theoretically possible ratio of ballast and active substances in Anolyte ANK.

The third generation Anolyte ANK, named Anolyte ANK SUPER, is characterized by the absence of ballast substances and is produced in STEL-ANK-SUPER devices. Anolyte ANK with an oxidant concentration of 500 mg/l contains no more than 0.9 g/l of dissolved electrolyte ions, i. e., it is ballast-free (see Fig.5.6.4).

Indicators and properties of Anolyte ANK	TEL-10H-120-01 Device	STEL-ANK-PRO (STEL-ANK-PRO-M) Device
Total dissolved solids, g/l	3.0-5.0	No more than 1.0
Concentration of oxidants, mg/l	No more than 500	No less than 500
Storage time, days	No more than 5	No less than 30
Possibility of dilution with fresh water to the required concentration of oxidants	No	Yes
Corrosive activity	High	Moderate
Chlorine smell	Weak	Very weak
Possibility of introducing anti-corrosion additives without reducing antimicrobial activity	No	Yes
Degradation products	Low-mineralized water	Fresh water
Traces on smooth surfaces after drying	Yes	No
Antimicrobial activity against all pathogenic microorganisms	Yes	Yes
Increased antimicrobial activity due to the osmotic transfer of active metastable compounds into the internal environment of microorganisms (reduction of treatment time)	No	Yes
Improvement of detergent properties due to increased hydration activity	No	Yes

Properties of Anolyte ANK from the first and second generation STEL devices

AQUACHLOR devices for the synthesis of a solution of oxidants used for the disinfection of drinking water, waste water, and swimming pool water



Over the past three years, about 400 AQUACHLOR-500 (A-500) devices have been put into operation at the drinking water, wastewater, and swimming pool

Fig. 5.6.4. The ratio of the amount of salt consumed for the synthesis of 1 liter of Anolyte ANK and the concentration of oxidants in the Anolyte ANK obtained in STEL devices.

1 — Anolyte ANK of the first generation, obtained in STEL-10N-120-01 devices. The ratio of salt consumption to the concentration of oxidants: 5.0:0.5 = 10. The quantity of ballast substances is approximately 10 times more than AS. 2 — Anolyte ANK of the second generation, obtained in STEL-ANK-PRO devices. The ratio of salt consumption to the concentration of oxidants: 1.0:0.5 = 2. The amount of ballast substances and AS is approximately equal. 3 — Anolyte ANK of the third generation, obtained in STEL-ANK-SUPER type devices. Salt consumption to oxidant concentration ratio: 0.6: 0.5 ≈ 1. No ballast.



Fig. 5.6.5. AQUACHLOR-500 devices at the Balakovo water treatment system. In total, the system uses 76 A-500 devices, including standby ones. The daily productivity of the system in molecular chlorine equivalent is more than 900 kg.

water treatment facilities in many Russian and foreign cities, with the oxidant capacity of A-500 devices mounted at one facility (the capacity of a single system) having already exceeded 900 kg per day in the equivalent of active chlorine (Balakovo) (Fig. 5.6.5).

The AQUACHLOR device is a compact modular chlorine-caustic system, which surpasses large chlorinecaustic systems in all specific technical and economic parameters. The AQUACHLOR device is safe for people and the environment, since all the gaseous chlorine produced in it with a small amount of chlorine dioxide, ozone and hydroperoxide radicals (a gaseous mixture of oxidants) enters the ejector mixer built in the device and immediately dissolves in the flowing water, which thus turns into a solution of oxidants with the same concentration of dissolved chlorine as in chlorine water formed in typical chlorinators with molecular chlorine dissolved in water.

Further, this solution of oxidants is mixed with the main flow of the treated water according to the existing technological chlorination schemes, using the same hydraulic lines, in a ratio that allows obtaining a concentration of oxidants in the disinfected water that meets the requirements of the current sanitary norms and rules. Studies carried out in recent years by a number of reputable scientific organizations in Russia, Ukraine, Germany, the United States have shown that, unlike ordinary chlorine water, the oxidant solution produced by the AQUACHLOR device is a stronger disinfecting agent (destroying viruses, spores, biofilms), and can prevent the formation of chlorination by-products. This is due to the fact that the solution contains a mixture of oxidants (chlorine, acid, hypochlorous chlorine dioxide, ozone, hydroperoxide compounds), and not just one monosubstance, as in the well-known traditional chemical disinfection technologies. A mixture of freshly prepared dissimilar oxidants in solution has a synergistic effect in the processes of oxidative destruction of organic compounds. Very similar processes of the simultaneous formation of a heterogeneous mixture of oxidants take place in all living warm-blooded organisms during

phagocytosis, when, under the influence of an electric field created in the phagocyte structure, an electrochemical synthesis of hypochlorous acid, hydrogen peroxide, ozone, singlet oxygen from blood plasma (sodium chloride solution with a small amount of organic and inorganic substances) in a microscopically small volume comparable to the size of a foreign object (microorganism, cell fragments, etc.). It is the similarity of the processes that ensures the harmlessness of the mixture of oxidants for the human and animal body and the lack of the ability of microorganisms to adapt to the metastable mixture of oxidants. The unique properties of the oxidant solution obtained in the AQUACHLOR devices make it indispensable for the disinfection of drinking water, waste water and swimming pool water.

A fundamentally new technological process is implemented in AQUACHLOR devices - ion-selective electrolysis with a diaphragm, which provides complete separation of the initial salt solution with a concentration of 180 to 250 g/l in MB-26 modular cells in one treatment cycle (without returning to regeneration anolyte, without salt freezing from catholyte, without returning salt to the process, without adding acid to the anode circuit, without high-quality cleaning of brine, etc.) into a wet mixture of gaseous oxidants (chlorine, chlorine dioxide, ozone) and sodium hydroxide solution with a concentration of 150-170 g/l at a salt conversion rate of 98 to 99.5% and electricity consumption in the range of 2-3 kW/h per kilogram of gaseous mixture of oxides. These indicators are very close to theoretically possible, therefore AQUACHLOR devices have no competitors among the well-known electrochemical systems and technologies.

The advantages of AQUACHLOR devices in comparison with liquid chlorine and hypochlorite are as follows. AQUACHLOR devices allow obtaining two products from a sodium chloride solution at the point of consumption—chlorine and caustic soda in the required amount at any time. Since freshly obtained chlorine contains small amounts of other oxidants (chlorine dioxide, ozone), chlorination by-products in water, such as chloroform, are not formed.

Also, a solution of oxidants, unlike traditional chlorine water, effectively removes biofilms from the inner surface of water pipelines, which eliminates the need for ammonization, reduces the corrosion rate of water pipelines (it is known that the rate of biocorrosion is several times higher than that of chemical one), gives the water excellent sensory properties. The AQUACHLOR device is a small-sized chlorine and caustic soda solution generator combined with a chlorinator.



Fig. 5.6. 6. AQUACHLOR-500M device with MB-26-100 cells operating in self-cleaning mode. Designed in 2011.

Therefore, it is possible to place AQUACHLOR devices without performing design and the device operation in the existing chlorination rooms, using the existing hydraulic and electrical networks. In 2011, the serial production of new generation AQUACHLOR devices was launched, named AQUACHLOR-M (Fig.5.6.6). Table 5.6.3 presents the comparative characteristics of the A-500 and A-500M devices.

From the middle of 2012 the serial production of automated AQUACHLOR devices has been started in the Vitold Bakhir Institute. The devices function in full or partial (depending on the Customer's wishes) cycle of a complex operation scheme [17]..

Table 5.6.3

S. No.	Technical parameters and operations	A-500	A-500M
1	Oxidant capacity (in terms of chlorine) when operating in nominal mode, g/h	500	500
2	Oxidant capacity (in terms of chlorine) when operating in maximum mode, g/h	520	600
3	Time of continuous work in maximum mode, h	6	24
4	Salt consumption for the production of 1 kg of oxidants (in terms of chlorine), kg	2.0	1.8
5	Concentration of additional product - sodium hydroxide solution, g/l	150-170	160–180
6	Time of continuous work (before flushing) of the electrochemical cell when operating on a solution of food salt "Extra", prepared on tap drinking water, h.	40–50	260–280 The latest models use self- cleaning MB elements
7	Break time in the operation of the device cell when flushing with a 10% solution of hydrochloric acid, min.	30	5
8	Control of the start time of the device cell flushing operation	By the operator	Automatically
9	Performing the operation of flushing the device cell	Manually, by the operator	Automatically
10	Possibility of connecting a module for the production of hydrochloric acid solution	No	Yes
11	Possibility of connecting to external power sources of various types	No	Yes
12	Monitoring the parameters of the device operation	Periodically, by the operator	Automatically, continuously
13	Possibility of automatic regulation of the productivity of oxidants depending on the concentration of active chlorine in the treated water	No	Yes
14	Number of failures per 1000 hours of continuous operation (probabilistic estimate)	3	0,1
15	Device design	Open frame, monoblock	Case, block-modular

Comparative characteristics of AQUACHLOR-500 and AQUACHLOR-500M devices

A BRIEF LIST OF ELECTROCHEMICAL SYSTEMS IN MASS PRODUCTION IN THE VITOLD BAKHIR INSTITUTE FROM THE BEGINNING OF 2012

- Flow-through electrochemical modular cells FEM and MB, flow-through electrochemical cells RPE from FEM and MB elements — universal flow-through electrochemical compact cells in accordance with RF patents No. 2042639, 2063932, 2078738, 2096529, 2141454, 2145940, 2153474, 2176989, 3370885, 235069 Great Britain GB.2253860, certificates for utility model RF 20513, 20514.
- 2. EMERALD, EMERALD-REDOX devices for obtaining water with antioxidant properties, purification of fresh water from organic impurities, microorganisms, heavy metal ions. A distinctive feature of EMERALD devices from other known water purification devices lies in the fact that after treatment in EMERALD devices, purified water acquires a redox potential (ORP), which characterizes the activity of electrons in water, close to the ORP of the internal environment of the human body (from minus 200 to minus 300 mV). EMERALD and EMERALD-REDOX devices are manufactured in accordance with RF patents Nos. 2038322, 2038323, 2056364, 2090517, 2091320, 2096337, 2040477, 2149835, 2207982, 2322395, 2322394, 2350692, UK patents Nos. 2253860, 2257982 utility models of the Russian Federation No. 3599, 3600, 3601.
- 3. STEL devices for electrochemical synthesis of Anolyte ANK SUPER. Anolyte ANK SUPER is a universal environmentally friendly antimicrobial solution of a wide spectrum of action and application, which is produced from an aqueous solution of sodium chloride by introducing chlorine-oxygen and hydroperoxide oxidants into water saturated with free hydroxyl groups and dissolved hydrogen, previously purified from heavy metal, iron, manganese, magnesium, calcium ions. The optimum proportion of a mixture of chlorine-oxygen and hydroperoxide oxidants in Anolyte ANK SUPER is 500 mg/l. The mineralization of Anolyte ANK SUPER does not exceed 0.9 g/l (0.5 g/l at a concentration of oxidants of 500 mg/l), which ensures its most high efficiency, environmental friendliness and shelf life up to 6 months. The maximum possible salinity of the Anolyte ANK of the first generation is limited to 5 g/l, the minimum salinity achieved in STEL

devices models of 2011–2012 (STEL-ANK-SUPER) and equal to theoretically possible, being 0.5 g/l. STEL devices are manufactured in accordance with RF patents No. 2033807, 2038322, 2076847, 2088539, 2155719, 2207983, 2208589, 2322397, 2321681, 2350692.

4. STEL-PEROX devices for electrochemical synthesis of Anolyte PEROX and catholyte. STEL-PEROX devices produce a unique antimicrobial solution, the active ingredient of which is percarbonic acids and sodium or potassium peroxocarbonates. Anolyte PEROX is produced from an aqueous solution of sodium or potassium carbonate or bicarbonate.

Anolyte PEROX is environmentally friendly, does not possess corrosive activity, and has pronounced antimicrobial properties. The total dissolved solids of Anolyte PEROX does not exceed 0.6 g/l. Simultaneously with anolyte, STEL-PEROX devices produce electrochemically activated Catholyte K, which has excellent detergent properties that exceed those for detergent solutions. STEL-PEROX devices are manufactured in accordance with RF patents No. 2329335, 2329197.

- 5. STEL-UNIVERSAL devices for electrochemical synthesis of electrochemically activated anolyte and catholyte from fresh water and solutions of various electrolytes. The devices allow synthesizing Anolytes ANFOS, ALOX-M. Anolyte A, the active ingredients of which are, respectively, electrochemically activated perphosphoric, peracetic acids or a mixture of oxidants obtained from fresh water or water-salt solution. The total content of dissolved substances in both anolytes and catholyte does not exceed 1.0 g/l. STEL-UNIVERSAL devices are manufactured in accordance with RF patents Nos. 2204530, 2148027, 2157793.
- 6. AQUACHLOR-M devices for electrochemical synthesis of oxidants solution are the world's most advanced compact modular systems for converting sodium chloride solution into oxidants solution used in the processes of water disinfection and purification, and concentrated electrochemically activated caustic

soda solution, at the degree of salt conversion. solution above 99.5%. AQUACHLOR devices are manufactured in accordance with RF patents No. 2088693, 2270885, 2176989, 2350692, USA — 7,897,023.

- ECOCHLOR devices for electrochemical synthesis of gaseous chlorine and concentrated caustic soda solution are compact safe modular chlorine-caustic systems that have no analogues in the world. The capacity of a single module varies from 1 to 10 kg/h of chlorine gas. ECOCHLOR devices are manufactured in accordance with RF patents Nos. 2270885, 2350692.
- 8. HYPOCHLOR devices for the synthesis of highly purified sodium hypochlorite solution are compact devices that have no analogues in the world, generating an electrochemically activated concentrated sodium hypochlorite solution with a minimum content of ballast substances, i. e sodium chloride and hydroxide. The degree of use of sodium chloride in the process of conversion of the starting solution is up to 95%. HYPOCHLOR devices are manufactured in accordance with RF patents Nos. 2157793, 2148027, 2145940.
- 9. OXITRON-M devices for the synthesis of electrochemically activated hydrochloric acid used in the leaching of non-ferrous, precious and rare metals from dumps of mining and processing systems, blast furnace slag, ore, non-ferrous and rare metals scrap. They have no analogues in the world. OXITRON-M

devices are manufactured in accordance with RF patents Nos. 2079575, 2270885, 2350692.

- 10. OXITRON-K devices for the synthesis of hydrochloric acid from chlorine and hydrogen are unique devices that have no analogues in the world. The process of synthesis of hydrochloric acid does not require preliminary purification of source gases from moisture, the safety of the process is guaranteed by the new principle of supplying gases to the reaction chamber. OXITRON-K devices are manufactured in accordance with RF patents Nos. 2176989, 2079575, 2270885, 2350692.
- 11. ROSTOK devices for producing a solution of electrochemically activated nitrogen and phosphorus fertilizers in irrigation water without changing its mineralization. In ROSTOK devices, ordinary irrigation water is converted into an analogue of water after a spring thunderstorm, which has a beneficial effect on the growth and development of plants. Chlorides, sulfates and carbonates of ions of alkali and alkaline earth metals, which make up the natural mineralization of this water, are converted into nitrates and phosphates of these metals. The process is completely controllable in all parameters and allows you to create conditions for plant nutrition with selectively specified fertilizers, choosing their optimal concentration corresponding to the phases of plant development. ROSTOK devices are manufactured in accordance with RF patents Nos. 2063932, 2079575, 2207982.

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Bakhir V. M., Panicheva S. A., Prilutsky V. I., Panichev V. G.

345 ELECTROCHEMICAL ACTIVATION: INVENTIONS, SYSTEMS, TECHNOLOGY

The book considers theoretical concepts and hypotheses about the nature of the phenomenon of electrochemical activation of substances discovered by Vitold M. Bakhir in the seventies of the last century. It provides information on the most significant inventions in the field of electrochemical activation and the results of the practical implementation of inventions in various fields of science, engineering and technology. It describes various electrochemical systems for producing liquids with an abnormally high activity in oxidation-reduction, catalytic and biocatalytic processes.

Based on the experience of engineering and practical use of electrochemical systems for production environmentally friendly, safe for humans and animals electrochemically activated detergents, disinfectants and for production of the environmentally friendly sterilizing solutions, the authors predict further development of electrochemical activation technology. Various examples show that the role of electrochemical activation in the near future will steadily increase not only in the field of drinking water disinfection and purification, wastewater and swimming pool water treatment, food industry and agriculture, but also in chemical, petrochemical and mining industries to save raw materials, time and energy, while improving environmental safety and efficiency of the processes.

The book is intended for a wide range of specialists and students interested in the application of electrochemical technologies in various fields of human activity.

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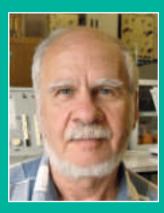
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VITOLD BAKHIR — the creator of new scientific and technical field — electrochemical activation (ECA). Doctor of Technical Sciences, Professor, Scientific Director at Electrochemical Systems and Technologies Institute. The author of more than 400 inventions with copyright certificates of the USSR and patents of the Russian Federation, USA, Canada, Great Britain, Germany, Switzerland, Italy, Japan, China, South Korea. The above-mentioned inventions are implemented in several hundred thousand various electrochemical devices in many countries. The author of 7 monographs and more than 300 scientific articles.



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