Electrochemical activation: a key to ecologically pure technologies of water treatment

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Possibility of reagentless directing of water and water solution properties in different technological processes was discovered in the seventies of last century [1-11], fig.1. Now it is realized in thousands various electrochemical systems from domestic devices for production of "superreducing" or "superoxidized" (so called "live" and "dead") water to industrial devices which work at different places in many countries and produce electrochemically activated disinfecting, sterilizing, detergent, extractive, emulsifying, demulsifying, stabilizing, preserving, bleaching, medicinal and other solutions [12]. This variety of technological properties of solutions can be explained by unique combination of the pronounced oxidizing, reducing, catalytic, biocatalityc activity of electrochemicall activated solutions with disproportionately low concentration of active reagents, that fundamentally distinguishes activated solutions from traditional solutions of appropriate chemical reagents.

Historically existing priority of Russia in this not young but highly upcoming scientific and technical direction of applied electrochemistry keep high due to the work of scientists and specialists, whose efforts till 2005 were joined with informal scientific and technical contacts and from 2005 - under scientific and informational structure of Electrochemical Systems and Technologies Institute.

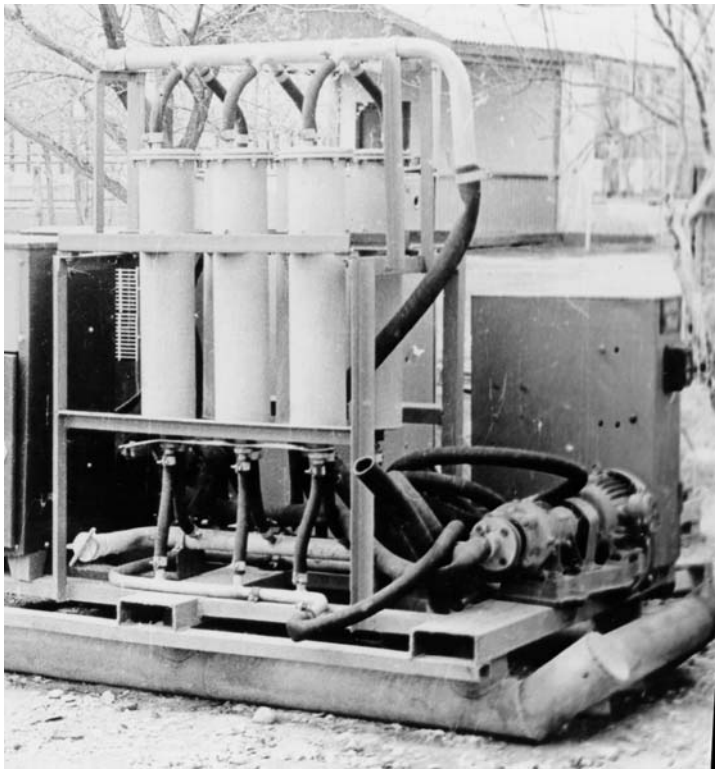

Figure 1. UEV-4 device [3] for production of electrochemically activated water used in processes of preparation and treatment of drilling fluid, water treatment for cooling systems of gas preparation devices, compressor stations of gas-main pipelines. Six hydraulically parallel-connected flow-through electrochemical reactors with coaxial placed electrodes and diaphragm. Anodes are from graphite rod of 100 mm diameter and 900 mm length, diaphragm is from chlorine material at vinyplastic frame. Interelectrode space is 10 mm. Productivity of catholyte is 25 000 l/h, productivity of anolyte – 5 000 l/h, current strength is 1200 A, voltage - 30 V. Kokand factory "Bolshevik" produced such devices more than 1000 from 1977 till 1980-ties.

The main principal of electrochemical activation (ECA) is usage of substances in metastable state in technological processes, that allows greatly to lower need in chemical reagents.

Technological and technical principals of ECA:

- Water and dilute water solutions of substances are changed before its use in technological processes into metastable state by electrochemical unipolar effect;
- Active reagents necessary for technological processes are synthesized at places of its use that helps to exclude transportation and storage of hazardous substances.
- Industrial highly productive technical electrochemical systems are formed from separate compact high-reliability modular reactors – on the analogy of construction of living organisms from separate cells.

The main criterion of rationality of ECA application:

- Multiple saving of energy, labour, time and materials in comparison with traditional technical solutions under simultaneous increase of efficacy of main technological process;
- Attainment of new properties of end product, new technological effects and results.

The best result of ECA systems and technologies application can be achieved under optimal realization of three conditions: rational design of electrochemical reactor, technological scheme of its use specialized for concrete application, and then optimal technology of application of electrochemically activated solution or water.

Some aspects of the above conditions are examined below.

REACTORS. Years of research for optimal design of electrochemical cell started in early 70s of the last century resulted in creation of Flow-through Electrochemical Cell known as FEM-1 (Patent GB 2 253 860) in 1989.

Until that moment devices for production of electrochemically activated solutions were called in technical literature as devices for electrical treatment of water or electroactivator or (rarely) diaphragm electrolyzers. In the beginning of 90-th term “electrochemical reactor” was put into technical vocabulary and for the first time its distinguishing features were formulated [13]. Electrochemical reactor in comparison to its closest analogue diaphragm electrolyzer has additional technical and technological advantages in electrochemical conversion of various liquids, i.e. water and aqueous solutions of electrolytes with TDS from zero to saturated; milk, vegetable oil, mineral oil, solutions of carbohydrates, ammonia, alcohols, surface active agents, organic and inorganic fertilizers, pesticides, etc. Electrochemical reactor provides optimal conversion of various liquids and gases differing by nature and by chemical composition due to combination of physical-chemical, electrical and mechanical properties of its construction and auxiliary materials, geometry and configuration of electrodes, electrode chambers, inter-electrode space and inside-diaphragm space. Optimal combination of all outlined parameters must be met for each cross-section of electrochemical chambers as intensity and mass transfer are changed significantly along the direction of inter-electrode media in proportion to current density, flows, chemical composition and concentration of initial components and products of electrochemical reactions in every micro-volume of inter-electrode space, including diaphragm.

First FEM-1 elements were produced during 3 years (1989 - 1991) by pilot plant of All-Russian Scientific-Research Institute of Medical Enginering (VNIIIMT), where the inventor, V.M. Bakhir, worked at that time.

FEM elements went through multiple improvements and a number of systems

incorporated FEM elements were increased. Total number of commercially used FEM-1 elements did not exceed 1,000; a total number of FEM-2 installed in electrochemical devices were 80,000 elements; a total number of FEM-3 (Patent RF N2078738, 1994) were over a million elements.

FEM-2 elements (Patent RF N2042639) were produced by Soviet-British enterprise “Emerald” until 1996 based on the licensing agreement from patent holder. Emerald was manufacturing FEM-2 elements for some period of time after license was revoked, but had to stop after improved element, FEM-3, was introduced to the market. FEM-3 elements were serially manufactured by Laboratory of Electrotechnology (LET ltd.) from 1994 till 2008 by agreement between patent holder and enterprise.

New applications of electrochemical processes, which could result in economical and technical advantages in compare to traditional processes, required creation of new electrochemical modules, FEM-7 (Patent RF N2176989) and FEM-9 (Patent RF N3370885). Analysis of production and exploitation of FEM-3, FEM-4 (Patent RF N2145940) and FEM-9 helped to create electrochemical elements MB-11 and MB-26 (Patent RF N2350692, Bakhir’s module) in 2009. MB-11 and MB-26 have improved electrochemical characteristics in comparison to previous generations of elements. All cells were manufactured by LET according to agreement between patent holder and enterprise.

In the beginning of 2011 scientists and experts of Vitold Bakhir Electrochemical Systems and Technologies Institute (www.vbinstitute.ru) have completed research work, which became a basis for creation of new generation of MB elements and new electrochemical systems. Rights for manufacturing of new elements and systems were assigned to company DELFIN AQUA in 2011. Simultaneously LET was deprived of its right to manufacture all goods based on the named patents as well as any other patents of V.M. Bakhir and his co-inventors.

Beginning from July 2011 DELFIN AQUA ltd. (http://www.delfin-aqua.ru) is the only company, which manufactures different configurations of MB elements under author’s control. New generation MB elements have all the latest improvements. Particularly, production capacity is increased more than 20 times, service life of element increased more than 15 times. Power consumption of new elements varies from 60 to 3,000 Watt. All electrochemical systems manufactured by DELFIN AQUA incorporate new elements.

TECHNOLOGICAL SCHEMES OF REACTOR USE. Devices and systems with RPE reactors, composed of one or several modular MB elements and provided with hydraulic systems, are highly integrated technical electrochemical systems and have additional units and hydraulic systems depended on purpose, thanks to which the reactor works in the appropriate technological regime. For the moment there are 3 widespread and well-known types of electrochemical systems: IZUMRUD devices for fresh water treatment and changing of its properties, STEL devices for synthesis of electrochemically activated disinfecting, sterilizing, detergent, medicinal and other solutions with various active substances, AQUACHLOR and ECOCHLOR devices for production of electrolysis substances from concentrated solutions of electrolytes to replace the appropriate bulky chemical factories with safe compact modular systems near the places of end products consumption. Numerous devices of the same destination, which are offered by different firms, are mostly products of unprincipled imitation as well as its accompanied description of physical-chemical properties, technologies of production and application of electrochemically activated water and solutions.

IZUMRUD devices for production of water with antioxidant properties, for treatment of fresh water from microorganisms, organic compounds, ions of heavy metals, iron, manganese.

Water disinfection by direct electrolysis is one of the varieties of water oxidative treatments but differs from widespread disinfecting methods by another principle - oxidants are produced from the same water and are not brought from outside, and after its use oxidants come into the initial state, i.e. water. Efficacy of water disinfection by direct electrolysis is higher in comparison with chemical methods. It does not need dosing pumps and reagents usage for direct electrolysis. Chlorine needed for prevention of second bacterial contamination in water pipes is generated from natural mineral salt of water come through electrolyzer and dissolved in it right away. Direct electrolysis destroys chloramines and transforms it into nitrogen and salt. Technique and technology of direct electrolysis of fresh water began to develop in sixties of last century, when relatively inexpensive low-wearing metal-oxide anodes were appeared [14 - 16].

The essence of technology of fresh water treatment and disinfection by direct electrochemical influence predetermines constructive features of devices, in which the whole flow of water treated is subjected to electrochemical effect during a short period of time. In electrochemical nondiaphragm devices «Potok», «Potok-M» produced in Russian plant “Kommunalnik” as well as in other known devices all treated water flows through narrow (no more 3 mm) gaps between plate lamellar electrodes of reverse polarity. Water, where almost always there are some chlorides, becomes saturated with hypochlorite which forms under mixing of anode and cathode reactions products and electrolysis gases. It can be used in some processes of following flotation treatment from suspended substances and organic compounds coagulated and oxidized under influence of hypochlorite ions and oxygen.

IZUMRUD devices based on principally different technological scheme were developed in 1990 and protected a year later by two patents of Great Britain (GB 2 253 860, GB 2 257 982) because of absence of Russian patent legislation in that time. ***For the purpose of simplification further links to patents are grouped according to types of electrochemical and devices and put at the end of the article.*** IZUMRUD devices cardinally differ from known analogues with stages of water cathode and anode treatment separated in time and space. Its appearance was possible because of development of flow-through diaphragm electrochemical modular element FEM-1, which resistance provides with current passing with high current density through separating diaphragm under quiet low voltage in fresh water. Flow of fresh water in long narrow tubular gaps between electrode and ceramic ultrafiltration diaphragm in FEM element is under hydraulic low only in current absence. When current flows through FEM element, then character of water flow changes under chemical reactions at electrodes and electric field, under determined combination of flow rate and current density comes into self-organization regime characterized with sharp intensification of energy and mass transfer due to the formation of toroidal structural elements of flow, moving with low rate along the longitudinal axis of electrode chambers. Such a regime provides with the lowest resistance of electrochemical system and the highest possible contact of water microvolumes with electrode surface in a unit if time. Current flow through inert electrodes of FEM elements is determined by taking off electrons from water near anode and bringing of electrons to water near cathode. It is accompanied by various chemical processes both near surface of electrodes and in the volume of water flowing. Volumes of water in electrodes chambers saturated with dissolved and gaseous cathode and anode products of electrochemical reactions do not mix in FEM element because of ultrafiltration ceramic diaphragm, at which surface turned to cathode and anode highly charged layers of anions and cations are correspondingly adsorbed. So electrochemical

FEM reactor allows at the same volume to divide processes of oxidation and reduction in time and space and directionally treat water with either only oxidative or just reduction electrochemical effect.

In natural cleansing processes of water oxidizing-reduction processes play the main role and pass under the influence of solar radiation, physical and chemical processes of interaction with air oxygen, minerals of rock. Usually it is accompanied by another processes - hydration, flotation, sorption, coagulatory, sedimentation ones. Maximum possible use of principal features of natural cleansing processes of water realized with compact high productive modular electrochemical reactors of the distinct functional purpose placed in various order along flow of treated water is the main idea of IZUMRUD devices.

IZUMRUD household devices traditionally from 1991 have productivity of treated water from 40 to 60 liters per hour and energy consumption from to 60 Wt×h. Indeed for such flow rates compact intermediate reactors, where additional water treatment processes are realized, are developed. Driving force of processes in these intermediate "passive" elements of water treatment is self-energy, which is possessed by water in "active" electrochemical FEM elements as a result of non-equilibrium exchange of electrons in FEM elements. In the period from 1991 till 2006 there were developed and commercially realized different technological schemes (technological processes) of water treatment in IZUMRUD devices. General name of devices was kept but subdivided for different models into names of minerals – it were developed such types of the device as IZUMRUD-TOPAZ, -AMETIST, -SAPFIR, -AQUAMARIN, QUARTZ, - RUBIN. When quantity of developed technological processes exceeded quantity of well-known names of clear minerals, types of IZUMRUD device were named as YANTAR, BIRYUZA< AGAT, MALAKHIT.

Figure 2. EMERALD device with productivity of 300 liters per hour. In the device is realized technological process TOPAZ of water treatment. Functional purpose: treatment of water from surface water sources at emergency situation. Power consumption – 800 Wt. Voltage at electrochemical reactor of the device is 24 V. It can be used as a part of mobile complex of water treatment or as a stationary device. Power supply from current source (rectifier) 220/30 V, or from car accumulator. Was produced in 2001 on demand of Department of Defense.

Technological process realized in the first IZUMRUD device consists in three stages: anode water treatment, transformation of chlorine-oxygen oxidants into hydroperoxide ones in catalytic reactor filled with granules of carbon, then cathode water treatment. List of new technological processes was rising according to solution of new tasks.

In the table 1 it is list of technological processes of water treatment developed for IZUMRUD devices.

Table 1.

Technological processes of water treatment in IZUMRUD devices, technical systems for its realization and short description of processes

№	Name of the process	Technical system for realization of the process	Short characteristic of the process
1	Anode electrochemical water treatment	FEM element (MB), RPE reactor	Microorganisms destruction, oxidizing destruction of organic compounds and microbial toxins
2	Electromigration removal of cations	FEM element (MB), RPE reactor	Current transfer through diaphragm by cations in the process of anode treatment of water
3	Cathode electrochemical water treatment	FEM element (MB), RPE reactor	Transformation of heavy metal ions into colloid substances of hydroxides
4	Electromigration removal of anions	FEM element (MB), RPE reactor	Current transfer though diaphragm by anions in the process of cathode treatment of water
5	Heterophase catalytic destruction of active chlorine compounds	Catalytic reactor of dechlorination E_C	Removal of active chlorine compounds under simultaneous formation of active oxygen compounds
6	Liquid-phase oxidation of organic compounds in medium with catalysts-charge carriers	Reactor of mixing E_T	Oxidation of organic compounds by products of anode electrochemical reactions in a volume with slow flow rate under mixing
7	Microflotation of colloid substances	Floatation reactor E_F	Use of air microbubbles for water treatment from colloid suspension
8	Microelectroflotation of colloid substances	Floatation reactor E_{FE}	Use of microbubbles of electrochemically got hydrogen or oxygen for water treatment from colloid suspension
9	Electrokinetic extraction of colloid substances (electrokinetik fixation)	Electrokinetic reactor E_K	Concentration of colloid substances in electric field of the double electric layer of mineral granules, fixation and dehydration of colloid substances at interphase interface
10	Microelectrophysical water treatment	Catalytic microbubbles reactor of E_D	Electrophysical influence at water and dissolved organic compounds in electrically active gaseous microbubbles in moments of phase change of first type near places of electric and hydraulic medium disturbance

In the process for customers demands satisfaction there were developed IZUMRUD devices of high productivity – till 500 liters per hour. Appearance of new type of electrochemical reactors, development of new universal approaches to technology of water treatment and conditioning, use of new materials and technologies of its use leaded in 2011 to the creation of IZUMRUD devices of the next generation – IZUMRUD-REDOX devices. IZUMRUD-REDOX devices have productivity from 50 to 500 liters per hour and include models in various types of performance – from household to special devices including devices for superheavy working conditions at places contaminated with chemical agents, bacteriological or other toxic pollutants, as well as devices for use in cottages and small settlements.

In general IZUMRUD-REDOX is for production drinking water with antioxidants

properties and additional water treatment from microbes and its toxins, heavy metal ions, iron, manganese, aluminium, harmful organic compounds: herbicides, pesticides, hormones, phenols, surface-active substances, mineral oils. Antioxidant water from IZUMRUD-REDOX device has beneficial effect to the whole organism, antiradiation activity, stimulates metabolism processes, increases immunity.

In IZUMRUD-REDOX devices of water treatment and conditioning main processes are oxidative-reductive reactions upon inert electrodes, i.e. electrodes which exchange only electrons with treated water. Spectrum of physical-chemical reactions proceeded in IZUMRUD-REDOX devices is maximum closer to natural processes of water treatment in the nature under effect of wind and sun as well as to reactions of phagocytosis in organisms of warm-blood including man under destruction of microbes and foreign substances.

In IZUMRUD-REDOX devices in processes of anode oxidation microorganisms, microbe toxins and organic compounds (herbicides, pesticides, phenols) are destroyed. Heavy metal ions change into insoluble hydroxides under cathode reduction and move away by special electrokinetic reactor.

Life time of main elements of IZUMRUD-REDOX devices – electrochemical modular elements (reactors) exceeds 100 000 hours. The device does not contain elements for periodic replacement.

STEL devices for electrochemical synthesis of anolyte ANK.

STEL devices for production of electrochemically activated disinfection, sterilizing and detergent solution – anolyte ANK – strongly entered State Register of medical technique of Russia since 1994. Just every hospital of Moscow, Saint-Petersburg, many other cities of Russia, foreign countries and the former Soviet republics is supplied with STEL devices.

Electrochemically activated detergent and antimicrobial solution – anolyte ANK, synthesized in STEL devices is the only ecologically clean solution in the world officially allowed under the same concentration of active substances both for high level disinfection, sterilization, presterilization treatment of medical instruments including endoscopes, for a wide variety of functions and for medicinal use as a remedy. Anolyte ANK has much more less corrosion activity in dependence with the chlorine content equal to the same chlorine concentrations in hypochlorite solution or chlorine water. Anolyte ANK exceeds the above mentioned analogues with its efficacy. Under water disinfection by anolyte no chlorates are formed, that allows to use anolyte ANK for water disinfection at schools, hotels, hospitals, stomatology clinics even in those countries, where chlorine (hypochlorite) use for water disinfection at such objects is forbidden (Holland, Germany).

Technology of synthesis of anolyte ANK in STEL devices protected with patents of RF and many other foreign countries includes line of important processes. Among its number there are removal of ions of polyvalent metals from initial solution of sodium chloride by rise of its pH to the value providing formation of insoluble hydrates, separation of hydrates of heavy and alkaline-earth metals from the initial solution, saturation of the initial solution by soluble hydrogen, and at last addition of electrochemically synthesized chlorine-oxygen and hydroperoxide oxidants into the prepared solution under pH control.

Figure 3. STEL devices in tubercular hospital for 1000 beds in Tbilisi, 2004. Anolyte ANK is produced in devices and dosed from storage tanks into sewage flow proportionally in volume regulated automatically using system of valves and level sen-

sors. STEL devices work in automatic regime, that provides constant maximum level of anolyte ANK in storage tanks.

Active substances in anolyte ANK are mixture of peroxide compounds ($HO^{\bullet}$ – hydroxyl radical; HO_2^- – peroxide anion; $^1O_2$ – singlet molecular oxygen; O_2^- – superoxide-anion; O_3 – ozone; $O^{\bullet}$ – atomic oxygen) and chlorine-oxigen compounds (HClO – hypochlorous acid; ClO^- – hypochlorite ion; $ClO^{\bullet}$ – hypochlorite radical; ClO_2 – chlorine dioxide).

Such a combination of active substances provides with absence of adaptation of microorganisms to biocide effect of anolyte ANK, and small total concentration of active oxygen and chlorine substances guarantees absolute safety for human beings and environment under its use in a long period.

Reduction and lost of antimicrobial properties of anolyte ANK at storage can be explained by reactions of mutual neutralization of the most metastable chlorine-pxygen and hydroperoxide oxidants, and the more total mineralization of anolyte ANK is, the faster reactions pass. One can refer to such type of reactions processes of interaction of hypochlorous acid with hydrogen peroxide ($HClO + H_2O_2 \rightarrow O_2\uparrow + H_2O + HCl$), hydrogen peroxide and ozone ($H_2O_2 + O_3 = 2O_2\uparrow + H_2O$) and some others.

STEL-10N-120-01 devices provide with production of anolyte ANK of the forst generation, which mineralization is no more than 5 g/l and approximately 9-10 times higher than oxidants concentration. Chlorine-content disinfection solutions with mineralization of nomore than 5 g/l are not activated even in case of production from electrochemical devices according to the above mentioned technology of anolyte ANK production. Such solutions lose its activity during several hours and turn into a salt solution of hypochlorite and hypochlorous acid. This solution has antimicrobial properties but in comparison with electrochemically activated solution it has no sporicidal activity, it has typical chlorine smell and forms chlorine by-products, chloroform in particular, under its use for water disinfection.

Low total mineralization of anolyte ANK at high specific concentration of oxidants from STEL-ANK-PRO and STEL-ANK-PRO-M devices developed in 2009-2011determines high stability of molecular complexes with hydrogen bond, which components are both molecules in a base state and ions, free radicals, molecules in a set state (exciplexes), which are hydrated (phenomenon of long-distance hydratation) and become electroneutral aquacomplexes.

Increase of stability of aquacomplexes and reduction of charge density of metastable compounds in the higher, the lower ions concentration in the solution is. Distinctions of anolyte ANK properties depending on its total mineralization are shown in the table 2.

Table 2.

Anolyte ANK properties from STEL devices of first and second generation

Characteristics and properties of anolyte ANK	STEL-10N-120-01 device	STEL-ANK-PRO (STEL-ANK-PRO-M) device
Total mineralization, g/l	3,0 – 5,0	No more than 1,0
Oxidants concentration, mg/l	No more than 500	No less than 500
Storage time, days	No more than 5	No less than 30
Possibility to dilute to necessary concentration of oxidants by fresh water	No	Yes
Corrosiveness	High	Temperate
Chlorine smell	Weak	Almost absent
Possibility of add of corrosion-preventive	No	Yes

compounds without lose of antimicrobial activity		
Products of degradation	Low mineralized water	Fresh water
Traces at smooth surfaces after drying	Yes	No
Antimicrobial activity against all pathogenic microorganisms	Yes	Yes
Increased antimicrobial activity because of osmotic transfer of active metastable substances into internal environment of microorganisms (reduction of exposition time)	No	Yes
Improvement of detergent properties due to increase of hydration activity	No	Yes

Unusual properties, at first sight, of anolyte ANK from STEL-ANK-PRO and STEL-ANK-PRO-M devices can be explained by ratio of ballast substances (sodium chloride ions) and active substances (metastable oxidants) in anolyte ANK.

Increase of salt concentration in electrochemically activated anolyte leads to balance displacement to formation of molecular chlorine, that increase solution corrosiveness, its destruction activity to polymers, metals, brings characteristic chlorine smell.

On the contrary, reduction of salt concentration in electrochemically activated anolyte brings increase of part of reaction of active oxygen formation during electrochemical synthesis, considerable reduction of solution corrosiveness, reduction of chlorine smell till its total disappearance. Analysis of properties of anolytes ANK of various mineralization shows advantages of low mineralized solutions in prevention of biochemical corrosion. It is caused by synergetic effect of antimicrobial influence of hypochlorous acid in presence of oxidative activity of dissolved oxygen and leads to removal of old biofilms, prevents new biofilms appearance at simultaneous decrease of corrosion and biocorrosion. Practically total absense of corrosiveness of low mineralized anolyte ANK from STEL-ANK-PRO and STEL-ANK-PRO-M can be achieved by addition of 0,1 g/l of trisodium phosphate into anolyte ANK. Anolyte ANK with this addition can be stored as long as without this addition, i.e. no less than 30 days.

The most important direction of technical improvement of STEL devices is decrease of content of ballast substances (sodium chloride ions) in anolyte ANK with active substances presented by mixture of metastable chlorine-oxygen and hydroperoxide oxidants. With the appearance in 2011 of anolyte ANK of third generation it is achieved theoretically possible ratio of ballast substances and active substances in anolyte ANK.

Anolyte ANK of third generation is characterized by absence of ballast substances and produced by STEL-ANK-SUPER devices. Anolyte ANK with oxidants concentration 500 mg/l contains no more than 0,5 g/l of dissolved ions of electrolytes, i.e. free of ballast (see fig. 4).

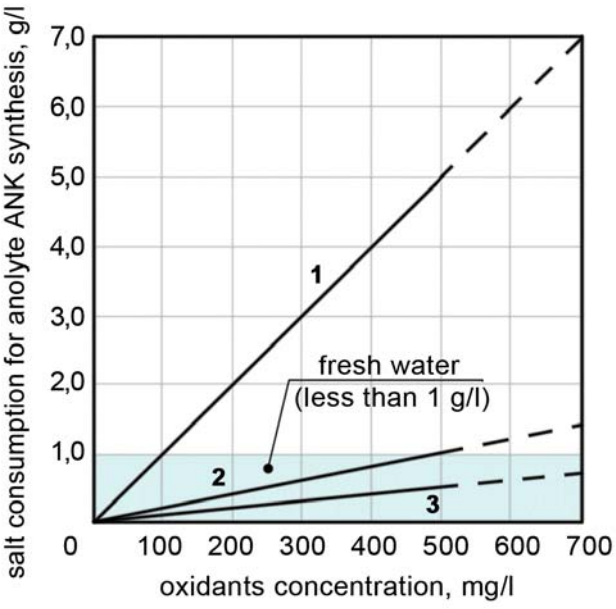

Figure 4. Ratio of salt used for synthesis of 1 liter of anolyte ANK and oxidants concentration in anolyte ANK produced by STEL devices
1 – anolyte ANK of 1st generation produced by STEL-10N-120-01 devices. Ratio of salt consumption to oxidants concentration: 5,0 : 0,5 = 10. Bal-

last substances exceed active substances more than 10 times.
2 – anolyte ANK of 2nd generation produced by STEL-ANK-PRO devices. Ratio of salt consumption to oxidants concentration: 1,0 : 0,5 = 2. Concentration of ballast substances is equal to active substances concentration.
3 – anolyte ANK of 3rd generation produced by STEL-ANK-SUPER devices. Ratio of salt consumption to oxidants concentration: 0,5 :0,5 = 1. Ballast substances are absent.

AQUACHLOR device for synthesis of oxidants solution used for disinfection of drinking water, sewage, water of swimming pools

During last three years about 250 AQUACHLOR-500 devices (A-500) were put in work at places of treatment of drinking water, sewage, water of swimming pools in many Russian and foreign cities. Productivity of oxidants from A-500 (productivity of single system) has already exceeded 900 kg per day in equivalent of active chlorine (Balakovo city).

AQUACHLOR device is a compact modular chlorine-caustic mini-plant, which specific technical-economical parameters exceed the same parameters of big chlorine-caustic factories. AQUACHLOR device is safe for people and environment as all produced gaseous chlorine with small content of chlorine dioxide, ozone, hydroperoxide radicals (gaseous mixture of oxidants) goes into ejector mixer of the device and dissolves immediately in flowing water, which becomes an oxidant solution of the same concentration of dissolved chlorine as chlorine water produced by typical chlorinators at molecular chlorine dilution into water.

Figure 5. AQUACHLOR-500 devices at water treatment station, Balakovo. There are 76 A-500 devices at station including reserve ones. Daily productivity of system in equivalent of molecular chlorine – more than 900 kg.

Then oxidants solution mixes with flow of treated water in present technological chlorination systems using existing hydraulic lines in ratio, which allows to get oxidants concentration in disinfected water, that meet the demands of sanitary code in force. Last researches carried out in a number of scientific organizations in Russia, Ukraine, Germany, USA showed oxidants solution as more effective agent (against viruses, spores, biofilms) than usual chlorine water and absence of chlorination by-products formation under water disinfection by oxidants solution. It can be explained by the fact that solution contains mixture of oxidants (chlorine, hypochlorous acid, chlorine dioxide, ozone, hydroperoxide substances) and not just a mono-substance as it is used in traditional chemical technologies of disinfection. Mixture of fresh various oxidants in solution has synergism effect in processes of oxidative destruction of organic compounds. Similar processes of simultaneous formation of mixture of oxidants take place for all warm-

blood organisms during phagocytosis, when electrochemical reactions of formation hypochlorous acid, hydrogen peroxide, ozone, singlet oxygen from blood plasma (sodium chloride solution with some organic and nonorganic substances) in microscopical volume are similar to formation of analogous substances at electrochemical activation. This similarity of processes provides safety of oxidants mixture for organisms of man and animals and absence of microorganisms resistance to metastable oxidants mixture. Unique properties of oxidant solution from AQUACHLOR device make it indispensable for disinfection of drinking water, sewage and water of swimming pools.

New technological principle is realized in AQUACHLOR devices – ionselective electrolysis with diaphragm provided total separation of initial salt solution with concentration from 180 to 250 g/l in modular reactors MB-26 within one cycle of treatment (without anolyte return to regeneration, freezing salt out of catholyte, salt return to the process, acid addition to an anode circle, without high quality treatment of the initial salt solution, etc.) to wet mixture of gaseous oxidants and sodium hydroxide solution with concentration 150 – 170 g/l at conversion level of salt from 98 to 99,5 %% and power consumption 2 – 3 kilowatt-hour per 1 kg of gaseous mixture of oxidants. These characteristic are quite closer to theoretically possible characteristics, that is why AQUACHLOR devices have no competitors among known electrochemical systems and technologies.

Advantages of AQUACHLOR devices in comparison with liquid chlorine and hypochlorite are following. AQUACHLOR devices allows to get two products from sodium chloride solution – chlorine and hydrate of sodium in required quantity at any time at places. As freshly produced chlorine contains small amount of another oxidants (chlorine dioxide, ozone), then by-products of water chlorination, such as chloroform, are not generated.

Figure 6. AQUACHLOR-500M device with reactors MB-26-100 worked in self-cleaning regime. Developed in 2011.

Oxidants solution also effectively removes biofilms from inner surface of water pipes, that excludes necessity of ammonization, reduces of rate of corrosion of water lines (it is known that rate of biocorrosion exceeds chemical corrosion in several times), brings to water perfect organoleptic properties. AQUACHOLR device is a small generator of chlorine combined with chlorinator. That is why one can place AQUACHLOR devices without planning and installation works at existing places of chlorination rooms using existing hydraulic and electric lines. In 2011 serial production of AQUACHLOR devices of new generation named as AQUACHLOR-M devices was organized. In table 3 it is shown comparative characteristics of A-500 and A-500M devices.

Table 3.

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

№	Technical parameters and operations	A-500	A-500M
1	Productivity of oxidants (in chlorine equivalent) at work in nominal conditions, g/h	500	500
2	Productivity of oxidants (in chlorine equivalent) at work in peak mode, g/h	520	600
3	Time of continuous running in peak mode, h	6	24
4	Salt consumption for production of 1 kg of oxidants (in chlorine equivalent), kg	2,0	1,8
5	Concentration of by-product - sodium hydroxide solution, g/l	150 – 170	160 – 180
6	Time of continuous running (until cleaning) of electrochemi-	40 - 50	260 – 280

	cal reactor at work with solution prepared with white salt “Extra” and drinking water (tap water), h		In last models there are MB elements with self-cleaning function
7	Break time in reactor work during acid cleaning by 10% hydrochloric acid solution, min	30	5
8	Control of time of the beginning of reactor cleaning	By operator	Automatically
9	Carrying out of reactor cleaning	Manually by operator	Automatically
10	Possibility to add module for production of solution of hydrochloric acid	No	Yes
11	Possibility to connect to external power supplies of various types	No	Yes
12	Control of parameters of work of the device	Periodically by operator	Automatically, continuously
13	Possibility of automatic regulation of oxidants productivity depending on concentration of active chlorine in water disinfected	No	Yes
14	Amount of failures at 1000 hours of continuous work (probabilistic estimate)	3	0,1
15	Design of the device	Open framework, monoblock	Frame, unit construction

From the middle of 2012 “Delfin Aqua” ltd. plans to begin serial production of automated AQUACHLOR-M devices worked on total or partial cycle (depending on desire of customer) of complex scheme of exploitation [17].

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Short list of technical electrochemical systems, which production has been started in "Delfin Aqua" ltd. from the beginning of 2012

1. Flow-through electrochemical modular elements FEM and MB, flow-though electrochemical reactors RPE of FEM and MB elements - universal flow-through electrochemical compact reactors according to patents of RF №№ 2042639, 2063932, 2078738, 2096529, 2141454, 2145940, 2153474, 2176989, 3370885, 2350692, Great Britain GB.2 253 860, certificates of utility model RF 20513, 20514.

2. IZUMRUD devices for production of water with antioxidant properties, fresh water treatment from organic compounds, microorganisms, heavy metal ions. The distinctive feature of IZUMRUD devices is in redox potential of water treated in

IZUMRUD characterizing electrons activity closer to redox potential of internal media in human organism (from – 200 to – 300 mV), that differs IZUMRUD from any other devices for water treatment. IZUMRUD devices are produced in accordance with patents RF №№ 2038322, 2038323, 2056364, 2090517, 2091320, 2096337, 2040477, 2149835, 2207982, 2322395, 2322394, 2350692, patents Great Britain №№ 2 253 860, 2 257 982, certificated of utility models RF №№ 3599, 3600, 3601.

3. STEL devices for electrochemical synthesis of anolyte ANK. Anolyte ANK is universal ecologically clean antimicrobial solution of wide spectrum of activity and application, which is produced from sodium chloride solution by input of chlorine-oxigen and hydroperoxide oxidants into water saturated with free hydroxyl groups and dissolved hydrogen and pretreated from ions of heavy metals, iron, manganese, magnesium, calcium. Optimal concentration of mixture of chlorine-oxygen and hydroperoxide oxidants in anolyte ANK is 500 mg/l. Mineralization of anolyte ANK does not exceed 1,0 g/l, which provides with high antimicrobial activity, ecological compatibility and shelf life of no less than 6 months. Maximum possible mineralization of anolyte ANK is no more than 5 g/l, minimal mineralization reached in models of 2011 of STEL devices is equal to theoretically possible and is about 0,5 g/l. STEL devices are produced in accordance with RF patents №№ 2033807, 2038322, 2076847, 2088539, 2155719, 2207983, 2208589, 2322397, 2321681, 2350692.

4. STEL-PEROX devices for electrochemical synthesis of anolyte PEROX and catholyte K. STEL-PEROX devices produce unique antimicrobial solution with percarbonic acids and sodium or potassium peroxocarbonates as active substances. Anolyte PEROX is produced from water solution of sodium or potassium carbonate or hydrocarbonate. Anolyte PEROX is ecologically clean, has no corrosiveness, has pronounced antimicrobial properties. Total mineralization of anolyte PEROX is no more than 0,6 g/l. Simultaneously with anolyte STEL-PEROX devices produce electrochemically activated catholyte K with perfect detergent properties exceeded analogous characteristics for known detergents. STEL-PEROX devices are produced in accordance with RF patents №№ 2329335, 2329197.

5. STEL-UNIVERSAL devices for electrochemical synthesis of electrochemically activated anolyte and catholyte from fresh water and solutions of various electrolytes. Devices produce anolytes ANPHOS, ALOX-M, A with active substances correspondingly presented by electrochemically activated perphosphoric, peracetic acids or mixture of oxidants got from fresh water or water-salt solution. Total concentration of dissolved substances both in anolytes and catholytes is no more than 1,0 g/l. STEL-UNIVERSAL devices are produced in accordance of RF patents №№ 2204530, 2148027, 2157793.

6. AQUACHLOR devices for electrochemical synthesis of oxidants solution are the most perfect in the world compact modular systems for transformation of sodium chloride solution into oxidants solution used in water treatment and disinfection and concentrated electrochemically activated solution of hydrate of sodium under salt solution transformation more than 99,5 %. AQUACHLOR devices are produced in accordance with RF patents №№ 2088693, 2270885, 2176989, 2350692, USA patents – 7,897,023.

7. ECOCHLOR devices for electrochemical synthesis of gaseous chlorine and concentrated solution of hydrate of sodium are compact safe modular chlorine-caustic plants, which have no analogues in the world. Productivity of one module is from 1 to 10 kg/h of gaseous chlorine. ECOCHLOR devices are produced in accordance with RF patents №№ 2270885, 2350692.

8. HYPOCHLOR devices for synthesis of high-purity solution of sodium hypochlorite have no analogues in the world, compact and produce electrochemically activated concentrated solution of sodium hypochlorite with minimal concentration of ballast substances, i.e. sodium chloride and hydroxide. Level of conversion of sodium chloride in the process of transformation of the initial solution achieves 95 %. HYPOCHLOR devices are produced in accordance of RF patents №№ 2157793, 2148027, 2145940.

9. OXITRON-M devices for synthesis of electrochemically activated hydrochloric acid used in processes of leaching of nonferrous, precious and less-common metals from dumps of mining-concentrating plants, slag from blast-furnace, minerals, scrap of non-ferrous and less-common metals. No analogues in the world. OXITRON-M devices are produced in accordance with RF patents №№ 2079575, 2270885, 2350692.

10. OXITRON-K for synthesis of hydrochloric acid from chlorine and hydrogen is unique device, which has no analogues in the world. Process of synthesis of hydrochloric acid does not require preliminary treatment of initial gases from moisture, safety of the process is guaranteed by new principal of gas supply to the reaction chamber. OXITRON-K dvices are produced in accorgance with RF patents №№ 2176989, 2079575, 2270885, 2350692.

11. ROSTOK devices for production of solution of electrochemically activated nitric and phosphoric fertilizers in the irrigation water without changes of its mineralization. In ROSTOK devices ordinary water for irrigation changes into analogue of water after spring thunderstorm, that beneficially influences at growth and development of plants. Chlorides, sulfates, carbonates of ions of alkaline and alkaline earth metals formed natural mineralization of this water change into nitrates and phosphates of these metals. Process is totally controlled according all the parameters and allows to provide with conditions for plants nutrition selectively for mentioned above fertilizers by changing its optimal concentration according to stage of plants growth. ROSTOK devices are produced in accordance with RF patents №№ 2063932, 2079575, 2207982.