# Electrochemical Activation of Water and Aqueous Solutions: Past, Present and Future

Electrochemical activation (ECA) is based on a new, previously unknown law of anomalous changes of reactional and catalytic abilities of aqueous solutions subjected to electrochemical unipolar (either anodic or cathodic) treatment.

ECA of solutions is necessarily associated with alteration of their chemical composition, acidity and (or) alkalinity within a wide range. That is why ECA application makes it possible to exclude reagent methods of solution properties' regulation from routine technological processes, to improve production's quality, to reduce the number and duration of technological operations, to decrease their labor-consuming nature, to facilitate and simplify processes of sewage purification.

Unlike well-known electrochemical procedures, in the processes of electrochemical activation initial substances are diluted aqua-saline solutions, fresh or low-mineralized water, i. e. liquids of low electric conductivity. The eventual ECA products are not concentrated chemical substances, but activated solutions, that is, low-mineralized liquids in a metastable state, manifesting increased chemical activity in relaxation period. Synthesis of electrochemically activated solutions is only possible when unipolar electrochemical exposure is combined with treatment of as many as possible microvolumes of liquid in a high voltage electric field of a double electric layer near the electrode's surface.

The above stated conditions of producing activated solutions can be realized only in special technical electrochemical systems.

Some examples of the practical application of electrochemically activated solutions are given below.

**1. Sterilizing solutions in medicine.** Electrochemically activated sodium chloride solution (3g. per 1l) in tap drinking water of 100mg/l oxidant concentration (0.01 %) demonstrates sporicidal activity, whereas sodium hypochlorite solutions, or hypochlorous acid, or alkaline glutaric aldehyde possess no sporicidal activity at a 2 % concentration, i. e. a 200 times higher one.

This fact has been proved many times in many countries, there are numerous test protocols, methodical recommendations on practical application of the technology in question. Today, over 20,000 ECA devices producing such solutions are used in Russian hospitals. An ECA device's recoupment period is no longer than 30 days.

Universal action ability on electrochemically activated biocidal antiseptic solutions, that is, is capable of destroying any large systemic microbial groups (bacteria, fungi, viruses and protozoa), without damaging the tissue cells of man and other higher organisms, i. e. somatic animal cells as a part of a multicellular system.

**2. Swimming-pool water disinfection.** Application of ECA devices in this area began in 1992. Usually anolyte is added to water before a pump, providing water circulation in a swimming pool. Content of active chlorine introduced into a swimming pool with anolyte is calculated from routine chlorine disinfection technology. In the process of wide practical application it was found that replacing chlorine with anolyte contributes to a quick (in 3-4 days) cleaning of filters from microorganisms usually living and proliferating under a layer of fatty and protein deposits on the filtering matter. Even super-large doses of chlorine can't rid swimming-pool filters of microorganisms.

Besides, it turned out that the application of anolyte instead of chlorine renders water ideally transparent, does not irritate skin and eyes, excludes chlorine liberation into the air above swimming-pool surface.

Experts working in swimming-pool service centers, in addition to the above stated benefits, found that operational costs were twice reduced when ECA devices were used instead of chlorine or electrochemical hypochlorite devices.

Now this technology is being actively developed in Russia. ECA devices are installed in many cities, where they are used for swimming-pool water disinfection, there are methodical recommendations approved by authorities.

**3. Drinking water purification.** The process of water purification by ECA devices having no analogues in the world consists of several studies separated in space and time, which are different in their active influence on water and the admixtures it contains. In ECA devices, water purification is based on utilization of oxidation and reduction processes, which help destroy and neutralize all natural toxic substances. In ECA devices natural processes of redox destruction and neutralization of toxic substances are many times augmented due to direct electrochemical reactions, as well as due to participation in purification processes of electrochemically synthesized from purified water itself and salts of highly active reagents dissolved in it, such as ozone monatomic oxygen, peroxide compounds, chlorine dioxide, short living free radicals. It secures high efficiency and ecological safety of water purification with the help of "Emerald" devices as compared to other known methods.

The capacity of ECA devices is from 60 to 1000 l/h specific power consumption from 1 to 2 kWh/$m^3$.

**A short list of experimental and prototype engineering and technology articles for electrochemical activation of liquids, found at different stages of development (from laboratory models to experimental and serial articles), which are designed and produced by scientists and experts :**

1. EMERALD(IZUMRUD) - a family of devices for purification of drinking water from microorganisms, organic admixtures and heavy metal ions. Various technological processes of water purification are realized in EMERALD devices. They vary in the succession of technological stages of water purification and are used for purification of drinking water depending on its initial parameters. The capacity of EMERALD devices ranges from 60 to 1000l/h, specific power consumption is 1-2kWh/m3. Domestic water purification appliances EMERALD are wall devices which are hydraulically connected to tap water faucet with the help of constant or temporary joint, and electrically - to a. c. circuit of 220 or 110 V. They are supplied with an infrared flow relay, providing automatic connection of the device when water flows and its disconnection in the absence of flow.

2. STEL - a family of devices for synthesizing electrochemically activated washing, disinfectant and sterilizing solutions. They are mainly used in medical prevention and sanitary-epidemiological institutions. Capacity: from 30-1000l/h, specific power consumption is 4-8 kWh/$m^3$.

3. AQUACHLOR - devices for electrochemical synthesis of gaseous oxidant mixture from sodium chloride aqueous solution. The main components of the oxidant gaseous mixture are molecular chlorine, chlorine dioxide, ozone and oxygen, found at a ratio of 70: 20: 5: 5%, respectively. The given ratio depends on the device's operational regime and may widely vary.

There are several modifications of AQUACHLOR devices: A-50, A-100, A-500, A-1000, whose capacity varies from 50 to 4000 grams of oxidants per hour. An A-1000 device has been designed as a module, making possible to assemble compact devices of any desired capacity.

AQUACHLOR devices can be used to replace routine water chlorination systems at water-purification stations of drinking water supply (they can be used instead of liquefied chlorine bottles), in water decontamination systems of swimming-pools, for decontaminating household, agricultural and industrial waste liquids. Sodium chloride discharge for synthesis of 1g oxidants is 2g. Specific power consumption for oxidant synthesis is 1.8 Wh/g.

**Conclusion.** ECA is a technology of the future and for its development it needs experts who can see faults in the existing system of scientific, technical and technological notions, as well as trying to solve difficult problems of the modern world with the help of new instruments designed for new electrochemical technologies and engineering and based on unique module elements - FEM-3. Transactions of the First International Symposium dedicated to electrochemical activation will undoubtedly play an important role in educating such experts and will contribute to the issue of creating an international community of scientists and experts, having a most important objective in common, that is, achievement of ecologically friendly future on the Earth with the help of the unique technology of electrochemical activation.

## Electrochemical Activation: Theory and Practice

Many years have passed since the first experiments when the author found and investigated the previously unknown regularity: water and diluted saline solutions after electrochemical treatment in anode and cathode chambers of diaphragm electrolyzer (at unipolar electrochemical treatment) transform into metastable state which differs from stable position by abnormal values of physical-chemical parameters, in particular, by the abnormal values of pH and oxidation-reduction potential.

These parameters appear to change spontaneously in time after the end of electrochemical action and achieve stable values much later, that is, the process of relaxation takes place which, in accordance with the determination of classic thermodynamics, is characteristic for the systems, existing in a thermodynamically non-equilibrium position. The liquids in metastable position after unipolar electrochemical reaction were called by the author electrochemically activated, and the technology of their production and use - electrochemical activation (ECA). The very term "Electrochemical activation" was suggested on the analogy of the previously existing terms "Mechanochemical activation", "Magnetic activation", "Barothermal activation" after it had been experimentally determined that the energy spent in the electrolysis process did not fully transform into chemical reaction energy and heat. If the electrochemical reaction is non-equilibrium enough, a part of energy is accumulated in the substance in the form which is impossible to measure with the thermometer, i.e. in the form of inner potential energy.

In the period from 1980 up till now, thousands of investigators and specialists were involved in work with electrochemically activated liquids. In comparably "old" fields of use of activated solutions such as disinfection, sterilization and presterilization purification of medical items, people of medical-preventive institutions already were used to the low concentration of biocide agents in electrochemically activated solutions and accepted their ecological safety as a normal attribute of the current reality. It's quite a normal phenomenon but the task of this article is to answer questions which appear at the attempts to understand the mechanism of synthesis and the nature of differences between activated and non-activated solutions.

These questions can be quickly formulated in the following way: are there any blank areas on the map under the name "Electrochemical activation"? What is the degree of prediction and reproductivity of the results of the use of electrochemically activated solutions?

Answering the first of raised questions, it's necessary to say that despite great experience accumulated by scientists and specialists in the field of the practical use of electrochemically activated solutions, these solutions appear to be very complicated for investigation.

There are some factors responsible for the properties of electrochemically activated solutions.

1. Electrochemically synthesized alkalis in catholyte and acids in anolyte. Their concentration is proportional to water mineralization and specific consumption of electricity in the process of synthesis. The presence of alkalis in catholyte and acids in anolyte explains the long preservation of correspondingly low and high pH values of anolyte and catholyte.
2. Superactive metastable compounds with high oxidental (in anolyte) or reduction (in catholyte) ability. These compounds, during the solutions' preservation, gradually pass to a stable stage as a result of some spontaneous structural energetic and chemical conversions. In the process of practical use of the solutions they quickly disappear, playing the role of catalyzers, initiators and reagents in several chemical reactions. Metastable compounds sufficiently increase the revealing of acid and oxidizing properties of anolyte, alkali and reducing - of catholyte. It is impossible to receive such metastable compounds in water by the way of diluting chemical reagents because of unique conditions of electrochemical synthesis.
3. Electrically active microbubbles of electrolytic gases stabilized by non-compensated electric charges, concentrated on the interface of phases: "gas-liquid". The size of these bubbles ranges from 0.2 to 5 mm, the concentration may achieve 106-107 ml-1. In electrochemically activated solution microbubbles don't float up as their even distribution in the contents is also stabilized by Coulomb interaction forces. They represent a very electrically and chemically active component of electrochemically activated solution.
4. The metastable structure of water and water solutions which appear under the influence of an electric field with high intensity ($10^4$ -$10^6$V/cm)

in double electric layer at the electrode surface. Catholyte preserves for a long time (up to several dozen hours) the structural changes received at electrochemical cathode reaction and reveals the properties of the electron-donor environment. Anolyte, correspondingly, reveals electron-acceptor properties. In activated solutions water molecules possess an additional degree of freedom due to the broken hydrogen links under the action of the electric field. This factor greatly influences fine physical-chemical and biological reactions. It determines a raised capability of activated solutions and water to penetrate into intermolecular spaces of different substances and also through biological membranes, to extend hydrate jackets around separate ions and molecules and on the interface of phases, to increase the solubility of barely soluble compounds, to intensify the extraction activity of solutions and water.

5. The factor which is responsible for preserving and sending information about electrochemical reaction reveals at the non-contact influence of electrochemically activated solutions or water on biological objects.

In the period when distinguished scientists from the former USSR started to get acquainted with works in the ECA field, only the first from the above mentioned factors has not been a subject to doubt. As for the second one, it has its own story. One investigator who was highly erudite and really devoted to science met with the author many years ago (1982), and the results of the following experiment were discussed: tap water with 0.87 g/l mineralization was passed by two flows through anode and cathode chambers of a diaphragm electrochemical reactor. As a result, at the reactor's output the anolyte with oxidation-reduction potential (ORP) = +1200 mV (with respect to comparison chlorine silver electrode - CSE) and catholyte with ORP = - 800 mV were obtained. With this the water mineralization practically didn't change. The scientist declared that it was principally theoretically impossible, and that it was necessary to check the apparatus thoroughly to avoid artefacts.

Nowadays, the second factor has received a great many theoretical and experimental corroborations, altough the study of the chemical composition of highly active particles in water is very complicated and demands the use of some special research equipment which is not used for routine analises.

We found the third factor (microbubbles) with the help of a specially constructed apparatus, based on the optical observations of electrochemically active hydrophilic and hydrophobic surfaces of conductors with electronic and hole conductivity and regulated potential, which were put into the investigated medium.

The fourth factor is extremely complicated for "pure" research because at the present level of knowledge about water structure and water solutions it is difficult to form an opinion about the correlation connection of electrochemical treatment type (cathode, anode) or water properties after unipolar electrochemical treatment (catholyte, anolyte) with the observed results of physicochemical reactions with its participation.

For example, it was quite impossible to predict theoretically that the cathodely electrochemically activated distilled water, used in the pyrolysis process of directly distilled gasoline, contributes to yield increase of pyrolysis target products - ethylene, propylene, divinyl and benzene. But after the discovery of this fact (1982) some scientific hypotheses immediately appeared, explaining the process mechanism from the positions of physical chemistry.

Similar situations were also observed in other cases. For example, it was impossible to expect theoretically that in the same pyrolysis process, anodely activated distilled water encourages quick purification of the pyrolysis oven coil from sediments of pyrocarbon.

Cathodely and anodely electrochemically activated distilled water greatly influences the processes of dielectric chemical metallization, crystals growth, epitaxial films and many others.

The mechanism of these processes has not been studied but this does not prevent the practical use of electrochemically activated distilled water because technologically useful effects caused by its metastability are characterized by a high-level of reproducibility.

The fifth factor is more complicated for study though many cases of its use are known. For example:

1. Water moistened plant seeds are put into souldered ampoules which are placed for 12 hours into vessels with catholyte, anolyte, initial water, alkali and acid control solutions. The results of seed germination and catalase force in leaves of germinated plants are compared. The differences characterize the specifics of information exchange between the seeds in the period of germination and the medium where the test tubes were placed.

2. Open Petri dishes, filled with sugar or salt solutions, are placed on flat glass lids of vessels completely filled with catholyte, anolyte, initial water, alkali and acid control solutions. Comparing the size and shape of formed crystals, one can watch manifestations of different informational backgrounds during the period of the crystals' growth.

3. The souldered ampoules with the distilled water are placed into vessels with catholyte, anolyte, initial water, alkali and acid control solutions. In three-four hours pH and oxidation-reduction potential of water from ampoules are measured. The differences are caused by the non-contact water interaction in and out of ampoules.

All three experiments are carried out under identical outside conditions: at the same temperature, pressure, mineralization of catholyte, anolyte, initial water, etc.

Their theoretical substantiation is, probably, possible under the Fundamental Field Theory (FFT), created by the outstanding Russian physicist I.L. Gerlovin.

In accordance with FFT, the information about physical effect, to which the substance was subjected during the activation process, is preserved in it for a long time if it is not subjected to some other, stronger effect. In this case, the overlap of information takes place, which may lead to its mutual destruction. The information about physical effect forms a field in a Physical Vacuum (PV), which means that for its perception direct contact with an activated substance is not necessary, although the less the distance is between the transmitter and the receiver of information the better the link conditions are between them. Information transmission from activated substance and its perception by other substances doesn't mean at all that the information is always able to change their properties or evidently reveal in any interactions. The information contained in activated substances may have influence only on the self-organizing processes and the closer are informative codes of transmitting and receiving systems the stronger is the influence.

It's necessary to mark that the absence of deep theoretical concepts of the processes connected with electrochemical activation of water and water solutions doesn't prevent its practical application. The selection principles of the best use of ECA use are quite simple. In proportion to the mineralization decrease of electrochemically activated solution, the degree of theoretical unpredictability of the results of its interaction with different substances or the degree of its behavior unpredictability in following physicochemical interactions and reactions increases.

Proceeding from the experience of the use of electrochemically activated water and solutions one may distinguish three fields of results prediction depending on the concentration of inorganic compounds:

1 - (difficult to predict but in future, well reproducible results) - less than 100 milligrams in 1 liter (the above given examples refer to this very field);
2 - (well predictable and reproducible results) - from 100 to 1500 milligrams in 1 liter;
3 - (fully predictable and reproducible results) - from 1500 to 5000 milligrams in 1 liter.

In reality, this division is rather conditional and such sharp gradations do not exist. They are rather precise depending on concrete physicochemical processes in which the properties of electrochemically activated water reveal.

For the first field of concentrations a detailed experiment is necessary, copying real conditions of investigated technology in main (principle) items.

For the second and third fields of concentrations the choice principles are simplified. For example, if traditionally used technologic solution contains oxidants and/or acids, then the activated solution, which replaces it, must be anolyte with pH from 2 to 7 and clearly defined oxidation properties. Similarly, if traditionally used technologic solution contains alkalis and/or reducers, the replacing activated solution must be catholyte with pH from 7.5 to 12 and clearly defined reduction properties. As a rule, the replacement of a traditionally used solution by an activated one leads to the sufficient decrease or full exclusion of chemical reagents, to the increase of the solution's action efficiency (improvement of the technology product's quality, the elimination of the formation of waste water subject to purification before disposal), etc.

According to these principles, the data on the complexity level of different technologies based on the use of electrochemical activation are given in the table below.

**Scale of complexity for the processes based on the use of technique and technology of electrochemical activation**

| Category of complexity | Name of technology |
|---|---|
| 0-1 | Synthesis of electrochemically activated sterilizing, detergent and disinfecting solutions of A, K, AN, ANK types with the rate of mineralization from 2.5 to 5 g/l and technologies of their practical use (treatment of equipment, instruments, apartments, hospital linen, decontamination of drinking water, water in swimming pools, purification of waste water, disinfection and washing in poultry and livestock farming, forage production including fodder ensilage. |
| 1-2 | Synthesis of electrochemically activated sterilizing, detergent and disinfecting solutions of AN, ANK, KN types with the mineralization rate less than 2.5 g/l and the technologies of their practical use. |
| 2-3 | The technologies of drinking water decontamination without the increase of its mineralization (without introducing the electrochemically activated biocide solutions with higher mineralization rate); synthesis of electrochemically activated sterilizing solutions in which peracetic acid, percarbonates of alkali metals are the main biocide agents. |
| 3-4 | The technologies of drinking water purification from the ions of heavy metals, herbicides, pesticides, detergents, phenols, trihalomethanes; powder production technology; mirror polishing technologies for lasers made with the use of silicon monocrystal. |
| 4-5 | The technologies of drinking water purification from |

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| | suspended particles, oil products, resinous and humus substances; paper production technologies; ceramic, glass and cut glass ware production technologies; technologies of cement and concrete solutions preparation; plant technologies of chlorine, chlorine dioxide, sodium hydroxide, oxygen, hydrogen, hydrochloric acid production. |
| 5-6 | The technologies of drinking water softening and freshening; technologies of increasing efficiency of water freshening by ionic change, reverse osmose; technologies of increasing the sensitivity of roentgen and photo films; intensification of the synthetic rubbers production processes; technologies of ECA use in paper production, in flotation method of gold and diamond extraction, in the processes of underground uranium leaching. |
| 6-7 | The technology of hemosorbent sterilization for the treatment of disseminated atherosclerosis; technology of obtaining and using the solutions for contact lens sterilization; intensification technologies of hydrocarbon raw materials pyrolysis; technologies of dielectric chemical metallisation in the processes of printed circuit boards production; technologies of ECA use in the processes of microelectronics production; technologies of electrochemical cold production. |
| 7-8 | The technologies of synthesis and use of nitric fertilizers from air and water; technology of non-contact regulation of the infusion medical solutions (INFUSTAT process) pH and ORP; technology of the cod-liver oil, culinary fat and vegetable oil conditioning. |
| 8-9 | The technologies of a dialysis solution pH and ORP regulation in the hemodialysis process; technologies of air regeneration in a closed space (spaceships, submarines); technology of cotton plant defoliation; technology of sterile apyrogenic water production. |
| 9-10 | The technology of biocide dye and varnish covers production; technologies of production and use of biocide ecologically pure solutions for the white flies, gallic nematodes and other plants' pests and diseases control; technologies of lignin utilization with benzene production. |

## Electrochemical Activation for Solving Problems of Labor Protection and Occupational Hygiene

In 1996 the Executive Committee of the General Council of FITUR (Federation of Independent Trade Unions of Russia) passed "The Program of FITUR actions for 1996-2000 for improvement of labor conditions and protection, nature conservation and in social defense of citizens suffered from the accident at the Chernobyl AES and from other radiation accidents".

The program serves to further realize the rights which were left to trade unions by the Foundations of Russian Federation legislation for labor protection, the Law "For nature conservation" and other laws and normative acts.

As it's known, article No.1 of the Foundations of Russian Federation legislation for labor protection defines the labor protection as a system of guaranteeing the safety of the life and health of workers in process of labor including legal, social-economic, organization-technical, sanitary-hygienic, medical-prophylactic, rehabilitation and other arrangements.

In creating such a system the introduction of concrete technologies of electrochemical activation (ECA) of water and water solutions is becoming constantly more meaningful. Devices produced for water cleaning of the type "Emerald" using the ECA principle allow us to receive water possessing increased biological value, what in particular helps to correct oxidation-reduction potential of biological liquids in an organism.

In the methodical recommendations "Diagnostic of chronic fatigue syndrome medical treatment" passed by Russian Federation Ministry of Health it is mentioned that electrochemically treated water is one of the important factors for complex medical treatment and prophylactic of chronic fatigue syndrome of people who took part in the liquidation of the Chernobyl accident effects. "Emerald" devices were applied in combination with medical starvation, with a dose of a new plant micro-element remedy "Biosenso" and homeopathic remedy "Sandra". Applied therapy was effective for 85% of this patients group.

Given biotechnological complex "Emerald"-"Biosenkos"-"Sandra" attracted the attention of the Commission for Chernobyl Accident Problems of General Trade

Unions Confederation, which recommended it to Heads of Trade Union Centers of Independent States and to International Sectional Trade Union Associations for use in practical work.

The analysis of the ECA practical usage in industry branches applying technologies with the use of water and water solutions shows that the ECA based devices are intended to be incorporated into any existing technology and so convert it to being ecologically clean and effective. In this case, the equipment involved in the technological process practically is not changed, the consequence of technological operation is not changed also. But the time from start to finish of the technological process is decreased; chemical reagents consumption is reduced considerably; production of waste water which requires special treatment (cleaning, neutralization, disinfecting) before release into the environment is reduced abruptly or absolutely excluded; the technology output quality is increased and as a rule the labor conditions are improved.

For instance a water preparation technology by the ion exchanging method for electric power stations and boiler works using the ECA allows us to exclude completely the consumption of chemical reagents, exclude waste water output, expand the degree of softening and desalinization of water, decrease its corrosion activity and correspondingly greatly improve labor conditions.

The cleaning of metallic, plastic, glass surfaces from different types of pollution using cleaning agents based on electrochemical activated solutions provides an increase in the quality and speed of cleaning, the use of expensive, dangerous and flammable reagents (alcohol, acetone, acids, alkalis, oil) are excluded, the safety of cleaning operations is increased considerably for people and the environment. It should be mentioned that the speed at which glassy alkali silicates dissolve in the activated catholite is 30-40% higher than in the non-activated chemical analogues.

The application of ECA in technologies of anti-corrosion pipelines defense, obtaining biocidic paint and varnish covers, preparing and treatment of lubricating and cooling liquids, intensification of secondary methods of oil production improves considerably the labor conditions.

From the point of view of labor protection and occupational hygiene the meaning of ECA in printed cards production technologies should be specially mentioned. This allows us to exclude totally the use of surface-active substances at the stage of degreasing, decrease quantity of alkali by a factor of 3 with simultaneous improvement of surface quality, decrease abruptly content of chromic anhydride (to 50mg/l) and sulfuric acid (to 50 g/l) in etching electrolytes with conservation of demanded quality of surface etching and improvement of solution hydrophilic properties, increase stability of chemical copper plating electrolytes by a factor of 4. It also allows the exclusion of waste water environmental pollution and provides the regeneration of technological solutions.

An ECA application in agriculture has the greatest perspectives. For example, the storage technology for vegetables (carrot, sugar-beet, cabbage, potato) and fruits (mandarines, cherries, apples, grapes) with use of ECA-solutions as disinfecting and conserving agent allows the exclusion of xenobiotic chemical reagents, increase for 50-300% duration of fruit and vegetable products storage (in comparison with the known best ways of storage), save the vitamin content and saccharinity, suppress the growth of fungous and virus sicknesses of fruits, increase storing product resistance against adverse storage conditions.

In plant growth, the ECA successfully provides growth and evolution stimulation, plant harvest increase by seed treatment before sowing, grain disinfection, fight against insect pest, virus and fungus sicknesses of plants using ecological clean solutions.

In cattle breeding and veterinary the ECA lightens considerably labor conditions at cleaning and disinfection of milk lines, milking devices and other equipment.

The examples of successful application of ECA technologies in medicine, agriculture, industry can be continued but it should be noticed that in spite of its high social meaningfulness the introduction of such technologies goes quite slow. The task of our symposium is to attract attention of ministries, heads of factories to the problems of the quickest introduction of electrochemical activation achievements.