metallurgical plants in Chelyabinsk, Novolipetsk, Magnitogorsk, and Makeevka. Use of complexones has made the extent of the formation of carbonate deposits many times smaller.

Under the influence of complexones, the previously formed deposits, consisting mainly of calcium carbonate, undergo a change in structure, soften, and are gradually washed out of the system. It has been noted that the combination of IOMS and HEDP gives rise to a positive result even for a high carbonate hardness of the circulating water (35 mequiv. litre^{-1}).

The prevention of salt deposition permitted a reduction of the cost of maintenance by a factor of several tens. Salt deposition and corrosion inhibitors have been introduced in more than 20 metallurgical undertakings.

A second example is provided by the water supply to the gas purification equipment in ferroalloy furnaces. Provision has been made for a circulating water supply. The cooling and purification of the circulating water after gas purification are carried out in the sludge accumulator. During warm seasons, the system is operated continuously. As the temperature of ambient air is reduced during winter an intense increase in salt deposition begins on the impellers of the pumping equipment supplying water to consumers. The water pressure falls and after 5–7 days the pumps have to be switched off to clean the impellers. The cleaning is carried out mechanically by hand. The use of 1 g m^{-3} of FOSFANOL makes it possible to continue the operation without stopping for the removal of the salt deposits.

Mention should also be made of the application of HEDP in chemical factories, in heat exchange systems employing artesian water with a temporary hardness of 5–7 mequiv. litre^{-1}. The employment of polyphosphates to prevent salt deposition proved ineffective. Experience gained in the operation of the water circulation cycle with the cooling water heated to 50 °C and using HEDP demonstrated the high stabilising effect of the reagent and made it possible to abandon frequent stopping of the equipment for cleaning.

It is possible to quote many more examples. Effective results have been obtained using organophosphorus complexones in the water circulating systems of non-ferrous metallurgy, in the coal industry, in the mineral fertiliser industry, in medium- and high-pressure boiler plant, in particular, in more than 20 combined heat and power generating plants, hydroelectric power stations, and atomic power stations, in the water heating boilers of central heating systems, in cooling systems with cooling towers, in hydrotransport apparatus, etc.

The consumption of the organophosphorus complexone in circulating water supply systems is usually approximately 1–3 g m^{-3}. It is noteworthy that sometimes, together with the inhibition of the salt deposition, a diminution in the corrosion of metallic surfaces is also observed. To achieve this effect, anticorrosion additives are usually introduced into the composition.

The effect of organophosphorus complexes and salt deposition inhibitors is normally considered from the standpoint of economic results attained under these conditions: a significant diminution of the cost of prophylactic maintenance, the shortening of the periods during which the equipment remains idle, and the saving of labour, metal, water, etc. The economic effect can then run into tens and hundreds of millions of roubles. However, economy is not the only concern. The use of salt deposition inhibitors permits a very wide scale employment of circulating water supply systems and its ecological effect is hard to overestimate: the saving of water, whose resources are extremely limited, is achieved and the ejection of contaminated and mineralised waters into the environment is prevented.

Naturally, the inhibition of the formation of salts in circulating water supply systems has so far been only initiated. Although a fairly wide range of phosphorus-containing complexones have been created, on the basis of which inhibiting compositions have been developed, much work still remains to be done on the introduction into numerous water consuming industries of circulating water supply systems employing salt deposition and corrosion inhibitors, which may make a major contribution to the solution of ecological problems in our country.

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Biological purification of sewage from chemical plants

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Sewage from chemical plants contains substances both in solution and in the form of suspensions including compounds which constitute explosion hazards. These substances may be present at concentrations many times higher than the maximum permissible concentration for reservoirs, and therefore it is unacceptable for sewage to be discharged without purification. The most satisfactory solution would be to utilise the substances present in the water and the purified water itself in the chemical plant thereby transforming the processes in the plants into operations generating a low level or even no effluent. In the scientific-industrial combine "Soyuz" at Lyubertsy a procedure for the treatment and purification of water and the recycling of water from industrial sewage has been developed and includes the following elements (Fig. 1):

1) Local installations for the purification and recycling of water from industrial sewage in each phase of the manufacturing process as a result of which 70% of the water and up to 90% of useful substances can be returned to the plants (such substances would otherwise have been irreversibly lost and it would have been necessary to purify 100% of the industrial waste waters containing a high concentration of toxic materials);

2) A facility for the purification of industrial sewage in plants in which suspended substances are mechanically removed leaving 30% of the effluents formed by washing of equipment, premises, and pipework, etc.;

3) Biological sewage works in which industrial and domestic waste waters are purified concomitantly so that all toxic components are rendered completely harmless;

4) Secondary purification plant and where necessary the exhaustive purification of biologically purified effluents with the return of this water to the process water of chemical and other plants.

State-of-the-art techniques and modern water purification equipment are used, for example ultra- and hyper-filtration, membrane electrolysers and electrolysers with a three-dimensional cathode, continuously operating self-washing filters, and compact sedimentation tanks.

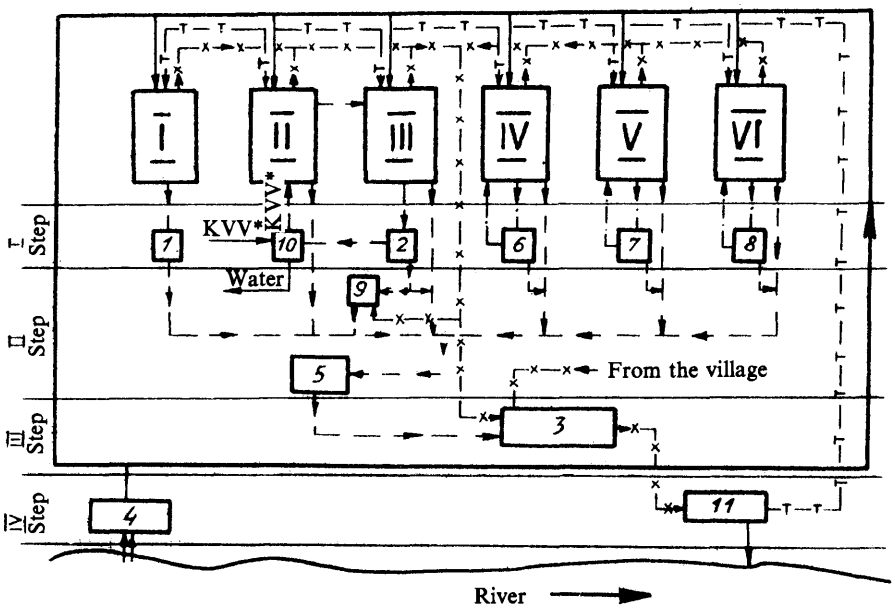


Figure 1. A four-step schematic representation of the treatment and purification of water and the recycling of water from industrial effluents: I–VI, production phases; *1, 2, 6, 7, 8, 10*, local installations for the purification and recycling of industrial wastewaters; *9*, installation for the biological purification of oxygen-containing inorganic compounds; *5*, installation for the mechnical purification of the total sewage from the plant; *3*, biological sewage works; *11*, installation for the secondary purification and exhaustive purification of sewage; *4*, water intake.

*The meaning of this abbreviation is not clear; it may refer to aluminium treatment (Ed. of Translation).

Biofilters with plastic packing, air tanks with a porous aggregate, and also a unique method involving biological reduction of oxygen-containing inorganic compounds including highly toxic hexavalent chromium and the separation of chromium as a precipitate in the form of the hydroxide, Cr(III), are used for biological purification. The latter method has been devised in collaboration with the Institute of Biology of Water Reservoirs, Academy of Sciences of the USSR. Other oxygen-containing inorganic salts of perchloric, nitric, and nitrous acids are converted into harmless chlorides and free nitrogen. This process is achieved with the aid of microorganisms isolated in the Institute of Biology of Water Reservoirs, Academy of Sciences of the USSR. This method is protected by eighteen patents published in the USA, England, France, the Federal Republic of Germany, and Italy, etc.

Heavy-duty vertical filters with a rubble packing are used for secondary purification of the biologically purified mixture of industrial and domestic effluents. Active charcoal is incorporated into the free space between the packing grains in order to achieve a high degree of purification, and the charcoal is regenerated *in situ* by a chemical treatment without the need to unload the filter. After this type of treatment the water quality meets the specifications for the water of fish-farming reservoirs (Five-day biological oxygen demand (BOD_5), 2; quantity of suspended matter, 5; nitrate nitrogen, 0.02; nitrates, 9; petroleum derivatives, 0.05 mg/litre.

The specially designed high-performance and continuously operating filters and equipment for the biological purification of water used in chemical plants have formed the basis for the creation of facilities for intensive fish farming in an enclosed recycling system. These facilities may be operated both in fish farms (for breeding young fish) and in large-scale establishmnents (for fish breeding on a commercial scale). A schematic representation of the installation is shown in Fig. 2.

The installation has a fish production capacity of 200 kg of carp per cubic metre of the reservoir per annum, whereas in fish breeding ponds the value of this parameter is no greater than 200 g/m^3 per annum, i.e. 1000-fold less productive. The installations devised are superior to the best foreign equivalents in regard to quality of recycled water, compactness, and fish production efficiency. These devices are patented in Comecon countries. More than seventeen agreements have been reached for acquiring the intensive fish farming technology designed in the scientific-industrial combine "Soyuz" in Lyubertsy. Thermal power stations have shown a particular interest in these installations.

An essentially novel and ecologically safe method for rendering waste waters harmless by the reduction of oxygen-containing inorganic compounds with open cultures of microorganisms has aroused great interest in regard to the purification of effluents from chemical plants. Waste waters from certain plants are polluted with toxic inorganic salts which are readily soluble in water and which contain bound oxygen in the molecule, for example salts of perchloric, chlorous, nitric and nitrous acids. The maximum permissible concentrations for domestic (in the numerator) and fish farming (in the denominator) reservoirs are as follows: perchlorates, 5/0.08; chlorates, 20/0.35; nitrates, 45/40; nitrites, 3.3/0.08; hexavalent chromium, 0.05/0.001.

Biochemical reduction could be the most straightforward and economical method for purification of water by removal of oxygen-containing inorganic compounds. However this type of process is

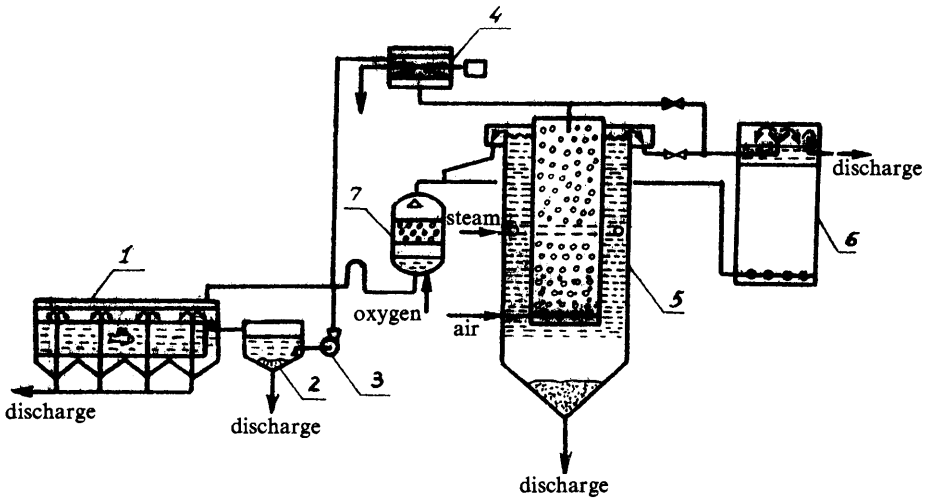


Figure 2. A schematic representation of an installation for intensive fish farming: *1*, fish tank; *2*, dirty water container; *3*, pump; *4*, continuously operating self-washing filter; *5*, aeration tank/sedimentation tank; *6*, denitrifier; *7*, oxygenator.

available for only three classes of compounds, i.e. nitrates (nitrate reduction), sulphates (sulphate reduction), and carbon dioxide (methanogenesis). Each class of compound is reduced only by a specific unique microbial culture under strictly defined conditions essential for the growth and metabolism of the microorganisms. Foreign scientists have been unable to identify microorganisms which have the ability to reduce other oxygen-containing inorganic compounds.

In order to assess the possibility of achieving the biochemical reduction of oxygen-containing anions of perchloric, chromic and other acids, the present authors have made a thermodynamic calculation of the change in the isobar-isothermal potential of the biochemical reactions occurring during the oxidation of organic substances.

It has been shown that in these reactions a whole series of oxygen-containing substances generate energy and they may be ranked in the following order of decreasing energy yield:

$$ClO_4^-,\ ClO_3^-,\ NO_3^-,\ NO_2^-,\ Cr_2O_7^{2-},\ Cr_2O_4^{2-},\ \text{and}\ SO_4^{2-}.$$

However, this does not imply that in addition to the denitrifiers and sulphate reducers there are microorganisms with the ability to reduce other anions of interest.

Nevertheless Soviet scientists in the Institute of Biology of Water Reservoirs, Academy of Sciences of the USSR, have isolated microorganisms, which have the ability to utilise the bound oxygen in salts of perchloric acid (i.e. *Vibrio dechloraticans Kusnezovi*) and also chromates and bichromates [*Bacterium dechromaticans (Rom)*][1,2].

Processes, equipment and installations for the purification of waste waters to remove these compounds with the aid of these unique strains have been developed (Fig. 3).

Optimal media have been developed for the strains discovered by V I Romanenko[3] and the morphological, cultural, and biological characteristics and sugar relationships have been studied, and the conditions required for maximum viability have been determined. The present authors have been able not only to elaborate a process but also to enhance the process in which water is rendered safe by removal of these compounds.[4]

The profile of the biochemical reduction of oxy-anions and the effect of physicochemical factors (temperature, redox potential, pH, organic substrates, etc.) on these processes have been studied in laboratory, semi-industrial and pilot-plant devices.

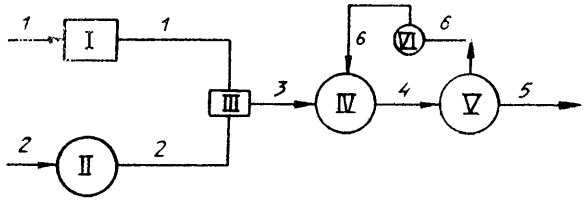


Figure 3. A schematic representation of the removal of hexavalent chromium from effluents; I, neutraliser; II, V, sedimentation tanks; III, mixer; IV, biological regenerator; VI, pump; *1*, chromium-containing waste waters; *2*, domestic waters; *3*, a mixture of chromium-containing and domestic waters; *4*, purified waters with a specific sludge and chromium hydroxide; *5*, purified effluent; *6*, specific sludge.

The process of biochemical reduction of oxy-anions can be described by a system consisting of three differential equations characterising the relationship between the rate of utilisation of the nutrient substrate, $dZ/d\tau$, the kinetics of the utilisation of chemically bound oxygen, $dE/d\tau$, and the rate of increase (or decrease) in viable specific bacteria, $dX\delta/d\tau$. By resolving this system of equations and taking into account the material balance for continuous cultivation and batch cultivation devices it was possible to obtain an equation

for the technical calculations for the installations in which salts of perchloric acid could be rendered harmless (converted to harmless chlorides) and nitrites and nitrates could be converted to free nitrogen. The nutrient substrate consisted of readily oxidisable organic substrates present in domestic effluents, surplus activated sludge, processed biofilm from normal biological sewage works, effluents from meat-packing plants, and others.

The biological method for the purification of effluents by removal of Cr(VI) devised in the scientific-industrial combine Soyuz in Lyubertsy is now being used in various branches of the national economy, since waste waters containing this harmful toxicant occur extensively not only in the chemical industry but also in a wide range of other industries (especially in the electroplating industry).

With the aid of the method recommended for the purification of chromium-containing effluents it is possible to achieve a three-five-fold reduction in expenditure on the construction of installations and engineering equipment and a five-seven-fold reduction in operating costs depends on the flow-rate of the effluents, the chromium concentration, and the required degree of purification (for each cubic metre of chromium-containing water which may be decontaminated) in comparison with the less expensive installations for the chemical removal of Cr(VI) from effluents. The cost of purifying one cubic metre of chromium-containing industrial effluent in a mixture with domestic waste water is no greater than 5–10 kopeks.

It has been confirmed by reliable medical sources that the microorganisms, which reduce Cr(VI) to Cr(III), are harmless and are not causative agents of diseases. An installation for the biological purification of water to remove Cr(VI) by a batch process has been operating trouble-free since 1974 in the scientific-industrial combine Soyuz in Lyubertsy. A facility for the continuous purification of effluents to remove Cr(VI) has been in operation for ten years in the metal-coating workshop at the "Kommunar" automobile factory in Zaporozhe providing a cost savings of 65,000 roubles. An installation for the continuous purification of ground water in order to remove Cr(VI) operating at an efficiency of 8000 cubic metres per day is now in the second year of operation in the Aktyubinsk Chromium Compound Plant (ACCP). The purified water and the chromium hydroxide obtained are used in industrial processes. A cost savings of 4.4 million roubles has been achieved. A batch process facility is being installed in the Moscow factory "Frezer". It is intended to introduce additional facilities for the removal of Cr(VI) from effluents in the automobile factory "Kommunar" and ACCP. Work will be carried out within the guide-lines of the All-Union programme "Biotekhnika" (Biotechnology) in collaboration with the Institute of Biology of Water Reservoirs, Academy of Sciences of the USSR, on the development of techniques for the removal of Cr(VI) from effluents in different branches of industry and for the reprocessing of chromium-containing dumps in ACCP which amount to five million tonnes.

An economical justification study for constructing installations in the Lyubertsy aeration station for decontaminating treated chromium-containing solutions by a biological method for 900 factories in Moscow and the Moscow district and utilising the extracted chromium is currently being carried out. The anticipated cost savings is 30 million roubles per annum. In 1988 an agreement was reached with the Italian firm Olivetti to introduce the method for biological removal of Cr(VI) in Italy. Three Italian firms are currently expressing an interest in acquiring a license.

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The determining role of the redox process in the formation of the quality of the aqueous environment

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One of the factors determining the adverse effect of man on the environment is the imbalance of redox processes in water reservoirs involving oxygen and hydrogen peroxide, agents which play a key role in the determination of water quality in the natural environment.

In recent years numerous articles have appeared in the literature on the determination of the content of hydrogen peroxide in different water systems, seas, and oceans[2,3] rivers and lakes,[4–7] and in rain and snow[8,9] and even in mineral ice samples in Greenland and in Antarctica.[10] All authors arrive at the same conclusion. Hydrogen peroxide is an inherent component of the natural aqueous environment. It can even be demonstrated that before the intervention of man the evolution of aerobic life on Earth occurred not only in the presence of oxygen and water but also in the presence of hydrogen peroxide.

Hydrogen peroxide in an aqueous environment may arise from four main sources: 1) entry from the atmosphere; 2) formation as a result of catalytic processes for oxidation involving oxygen; 3) formation as a result of photochemical reactions in the presence of sunlight, and 4) formation as a result of biological emission.

When the atmosphere becomes polluted there is an abrupt curtailment of the influx of hydrogen peroxide "from the sky" to the Earth's surface. In environmentally clean regions snow and rain contain $10^{-5}-10^{-4}$ M hydrogen peroxide, whereas according to the data obtained by the present author and co-workers hydrogen peroxide may be totally absent from regions subjected to atmospheric pollution. In turn this leads to a deterioration in the condition of soil ecosystems.

The present author has shown that the presence of hydrogen peroxide in moisture in the soil (in irrigation water) significantly enhances seed germination and plant growth, shortens the duration of the vegetative period, and increases the yield of agricultural crops.