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Ecological aspects of the extreme purification of water

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ABSTRACT. The influence on the eco-system of the products of the large-scale technology for the preparation of ultra-pure water required for the electronic and radiotechnical industries is examined. The distillation, ion-exchange, and membrane methods are subjected to a comparative analysis. It is shown that the membrane method for the extreme purification of water is ecologically the most desirable. The methods for the elimination of nitrates from drinking water are examined.

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I. Introduction

The preparation of ultrapure water has become one of the most urgent problems in chemistry and chemical engineering in connection with its definite role in the manufacture of electronic devices, integrated circuits, microprocessors, and specially pure substances.

The construction of transistors, integrated circuits, and microprocessors involves a multiplicity of operations with chemical treatment, after which the articles have to be washed with water of the highest purity. There is a direct relationship between the purity of water and the information capacity of integrated circuits. In particular, in order to obtain 64 kbytes of information, the content of organic carbon must not exceed 500 μg litre^{-1} and the attainment of 4 Mbytes requires the use of water in which the concentration of organic carbon is not more than 30 μg litre^{-1}. Even more stringent requirements must be met as regards the content of inorganic substances and micro-organisms. It is therefore not fortuitous that the widely familiar study by Shockley, who first obtained a transistor in 1951, was published simultaneously with the work of Reents and Kahler, who were the first to use a mixed bed of cation-exchange and anion-exchange resins for the extreme purification of water.[1]

The progress in electronic engineering and the synthesis of specially pure chemical and pharmaceutical preparations have helped to convert the ion-exchange technology for the manufacture of specially pure water into a large-scale process. With the aid of this technology, the problem of the conditioning of water for industry can be solved fairly easily. However, it was found subsequently that the ion-exchange method and the ion-exchange technology based on it constitute an "ecological boomerang", since the waste waters from ion-exchange apparatus contain a mass of mineral substances which exceeds by an order of magnitude the mass of impurities extracted from natural waters.

The return to the method of multistage vacuum distillation, developed by Kohlrausch,[2] did not lead to success, although the first impression was that the method and the technology based on it do not involve the discarding of substances into the environment. The paradox of the purification of water by distillation consisted in the fact that the high energy consumption leads to the contamination of the environment not in the region of the operation of the given apparatus but in the regions where there are thermal electric power stations whose gaseous waste is emitted into the atmosphere and spreads over long distances. The results of the ecological analysis of these methods have led to the alarmist attitude for our time.

At the same time, a new aspect of the solution of the ecological problems in the preparation of high purity water has arisen. This is associated with the use of membrane methods for the separation of substances and the membrane technology based on them. Hitherto many specialists have been sceptical about the possibility of replacing distillation and ion-exchange methods for the purification of water by membrane methods, pointing out at the same time the limitations of the baromembrane methods (microfiltration, ultrafiltration, and reverse osmosis), which do not permit the preparation of water purer than distilled water, or of electromembrane methods (electrodialysis with ion-exchange membranes) in view of its limited possibilities in the elimination of organic non-electrolytes with low dissociation constants. However, they failed to take into account the fact that, firstly, there exists a mechanism of the electroosmotic transport of molecules through ion-exchange membranes as a result of the forces arising from the coupling with fluxes of ions (ion–dipole interaction) and, secondly, that there is a possibility of combining various baromembrane and electromembrane methods whereby one can set up a sequence of operations leading to the preparation of ultrapure water. A feature distinguishing membrane purification methods from other procedures is the approximate equality of the mass of the substances entering the liquid waste and the mass of the substances extracted from natural waters when the latter are purified. The ecological usefulness of a particular membrane method also depends on the operating costs, among which the cost of the electrical energy is of main importance. At the present time there are membrane methods, applied under laboratory or even industrial conditions, which permit intensive purification of water with a very low electrical energy expenditure. In the immediate future, there will be a need to increase the information capacity of the integrated

circuits and microprocessors and this will entail both an extensive and an intensive growth of the production of ultrapure water, which has already reached a large scale. The ecological blunders in this kind of technology have therefore become completely inadmissible and this has determined the aim of the present publication. Furthermore, while the problem of the preparation of ultra-pure water is specific, at the same time it has significant general features in common with the solution of other problems in ecological chemistry.

II. The distillation method for the intense purification of water

The purification of water by distillation has been known since ancient times,[3] but interest in the preparation of ultrapure water did not arise until the past century. After G Kwinke observed that the specific conductance of pure water increases on storage, Kohlrausch and Heidweiler[2] applied in the concluding purification stage consecutive vacuum distillations using vessels made of old Jena glass. After 60 days of successive vacuum distillations, water with a specific conductance of 4.2×10^{-8} S cm^{-1} (specific resistance 23.8 MΩ cm) at 18 °C and 6.09×10^{-8} S cm^{-1} (specific resistance 16.4 MΩ cm) at 25 °C was obtained. The preliminary purification was carried out using the freezing out method proposed by Nernst. The principal physical parameters of the water obtained in these experiments are quoted in monographs and textbooks of physical chemistry, although Kohlrausch himself believed that he had not obtained ultrapure water. However, he discovered how to estimate the electrical conductivity of ideal water on the basis of the van't Hoff theory. Calculation showed that ideally pure water should have a specific conductance of 3.8×10^{-8} S cm^{-1} (specific resistance 26.4 MΩ cm) at 18 °C. A novel method for the determination of the physicochemical parameters of ultrapure water without its purification was developed by Harned and Hamer.[4] They measured potentiometrically the ionic product of water using a hydrogen indicator electrode and a silver/silver chloride reference electrode. The electrolyte was a standard solution of potassium hydroxide and potassium chloride. By extrapolating the electrode potentials obtained to zero ionic strength, Harned and Hamer[4] obtained the following numerical value of the ionic product of water:

$$K_w\ (25^\circ\mathrm{C}) = [\mathrm{H^+}][\mathrm{OH^-}] = K\cdot[\mathrm{H_2O}] = (1.008+0.001)\cdot 10^{-14}, \quad (1)$$

where K is the dissociation constant of water. With the aid of the Ostwald dilution law

$$K = c\alpha^2/(1-\alpha), \quad (2)$$

where α is the degree of dissociation of a weak electrolyte and C its concentration, it is possible to calculate the degree of dissociation from which the equivalent molar conductance can then be evaluated by means of the familiar Arrhenius relation:

$$\alpha = \Lambda/\Lambda_\infty \quad (3)$$

The values obtained are sufficient to calculate the specific conductance $\varkappa$ and the specific resistance ρ:

$$\varkappa = 1/\rho = \Lambda\cdot c \quad (4)$$

It was found[5] that the specific resistance of ideally pure water at 18 °C is 26.6 MΩ cm^{-1}, while at 25 °C it falls to 18.25 MΩ cm. We shall now introduce the dimensionless specific resistant ρ^*, which is equal to the ratio of the experimental specific resistance ρ to the calculated specific resistance of ideally pure water ρ_{lim}:

$$\rho^* = \rho/\rho_{\mathrm{lim}} \quad . \quad (5)$$

Using calculated resistances for the temperatures at which the experimental measurements were made as ρ_{lim}, we are able to estimate the degree of purity of water which is independent of the temperature of the measurement. In particular, Kohlrausch[2] was able to obtain water having $\rho^* = 0.8947$, which is 89.47% of the specific resistance of ideally pure water.

At the present time the distillation method is used widely to desalinate sea and ocean waters, using various evaporators of the thin-film type improved to achieve instantaneous ebullition, hygroscopic and hydrophobic evaporators, and distillation on membranes. The water obtained by single distillation has an intrinsic cost between 3 and 13 roubles per m^3. A relatively high consumption of metals accompanied by a relatively low quality of the purified water (the content of inorganic impurities is approximately 1 mg litre^{-1} and that of organic substance is approximately 4 mg litre^{-1}) is characteristic of distillation apparatus. An increase in the number of purification stages leads to an exponential increase in the cost of the water, so that multistage distillation is used for the preparation of specially pure water only under laboratory conditions.[6]

The distillation method creates the illusion that it is ecologically clean, since at the site where the apparatus operates no discharge of harmful substances is observed, while in the liquid waste the mass of substances is not greater than the mass of substances extracted from natural waters. Nevertheless distillation must be classified as a harmful technology because of its exceptionally high energy consumption. Therefore in order to analyse the ecological effects of distillation, it is essential to estimate the ecological effects of the production of electrical energy.

Since the fraction of electrical energy generated by thermal power stations is 80%, we shall confine ourselves to the analysis of the gaseous waste in the combustion of a non-renewable organic fuel. It has been established that the generation of 1 kWh of electrical energy by the combustion of coal entails the discharge into the atmosphere of 14 g of slag, 80 g of ash, 1000 g of carbon dioxide, and 14 g of sulphur dioxide (21 g of sulphuric acid).[7] We may draw attention to the production of sulphur dioxide, the discharge of which exceeds the permissible amount for the turnover of sulphur in nature.[8] When the limiting permissible concentration (LPC) of sulphur oxides is exceeded, asthma, bronchitis, and emphysema are contracted.[9] It is also known that sulphur dioxide disturbs the photosynthetic process by decomposing chlorophyll.[9] Acid rain, containing sulphuric acid, destroys forests and fish, increases the corrosion of metals, and destroys ancient monuments.

The discharge of nitrogen oxides into the atmosphere has both positive and negative effects on the eco-system. The positive influence consists in supplementing the store of bound nitrogen, which is formed in limited amounts as a result of the functioning of nitrogen-fixing bacteria (on leguminous plants), fungi, and seaweed and is also derived from the molecular nitrogen in the atmosphere under the influence of electric discharges. However, the negative effect of the discharge of nitrogen oxides into the amtosphere is much more significant. On interaction with hydrocarbons in the presence of sunlight, such oxides give rise to peroxyacetyl nitrate and ozone. The reaction is an example of synergism, where certain contaminants react with one another in the environment and form secondary even more toxic compounds. Both peroxyacetyl nitrate

and ozone induce lachrymation and also exert an irritant effect on the respiratory pathways in man. Furthermore, both products are toxic to plants, since ozone intensifies the respiration of leaves and plants are destroyed through exhaustion, while peroxyacetyl nitrate blocks the Hill reaction in photosynthesis, which also leads to the destruction of plants caused by the low intensity of the synthesis of nutrient substances.[8]

Apart from sulphur and nitrogen oxides, the waste from thermal electric power stations contains also solid waste, slags, and dust and soot particles which nowadays occupy many millions of hectares of land which used to be arable. As the structure of the fuel–energy balance changes, in particular, with increasing contribution by nuclear power, the situation may alter fundamentally.

Since it is virtually impossible to take into account all the factors leading to the contamination of the environment on distillation of water because of their different influences, Mazo[10] suggested that analysis be restricted to the discharge of sulphur and nitrogen oxides, which are converted respectively into sulphuric and nitric acids. Account was also taken of the fact that the generation of 1 kWh of electrical energy leads to the discharge of 0.5 of an equivalent of sulphuric and nitric acids. The coefficient of the contamination of the environment, as a result the purification of water, can be expressed by the ratio of the mass of the acids formed to the volume of water V treated annually:

$$Cd = \sum_i m_i/V + \sum_k m_k/nV \,, \qquad (6)$$

where Cd is the coefficient of the contamination of the environment, m_i the mass of the contaminants entering the environment during the operation of the technological set up, m_k the mass of the contaminants entering the environment during the establishment of the technological set up, and n the duration of operation of the technological cycle. Eqn. (6) expresses the coefficient of the contamination of the environment as a quantity proportional to the rates of the reactions generating the products contaminating the environment. As a result, the contamination coefficient is given by the sum

$$Cd = \sum_i \frac{\partial C_i}{\partial \tau} \,, \qquad (7)$$

in which C_i is the concentration of the harmful substances produced and τ is the reaction time.

In order to be able to compare the different contaminants in the environment, it has been suggested[11] that norms be laid down for the limiting permissible concentrations (LPC). By introducing the dimensionless concentration

$$C_i^* = \frac{C_i}{C_{lim}} \,, \qquad (8)$$

representing the ratio of the concentration of the harmful component to its limiting permissible concentration C_{lim}, we obtain the following expression for the rate of production of the component contaminating the environment:

$$\frac{\partial C_i}{\partial \tau} = C_{lim} \frac{\partial C_i^*}{\partial \tau} \,. \qquad (9)$$

Here one should bear in mind that the product obtained may also react chemically. In one case it is assimilated by the eco-system, being converted into a harmless component or mixture of components, while in another it is converted, like nitrogen oxides, into a component even more dangerous to life (synergism). In both cases, account must be taken of the rate of reaction of the component:

$$\frac{\partial C^*}{\partial \tau} = K_1 - K_2, \qquad (10)$$

where k_i is the rate constant for the reaction leading to the formation of the component contaminating the environment and K_2 is the rate constant for the reaction leading to the consumption of this component. Eqn. (10) was formulated solely for zero-order reactions. For $K_1 \leqslant K_2$, i.e. when the reaction product does not contaminate the environment, it is possible to assess the ecological situation as favourable, because in this case nature fully processes the harmful waste.

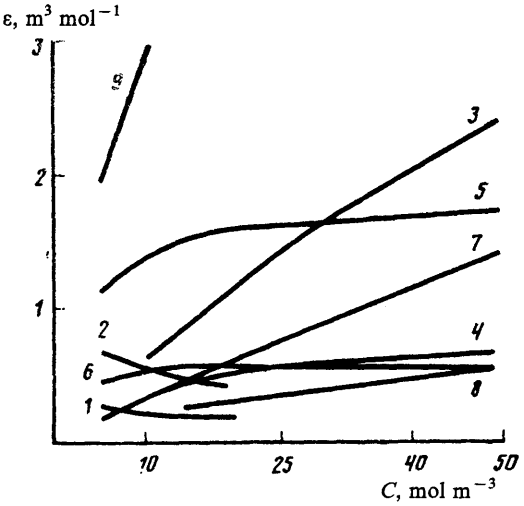


Figure 1. Dependence of the coefficient of the pollution of the environment on the salt content in the initial water subjected to extreme desalination by various methods: *1*, ion exchange (cation exchange–decarbonation–anion exchange–deionisation by a mixed bed); *2*, ion exchange with processing of waste water by electrodialysis; *3*, electrodialysis and ion exchange; *4*, ion exchange softening–electrodialysis–ion exchange; *5*, reverse osmosis–decarbonation–ion exchange; *6*, ion exchange softening–reverse osmosis–decarbonation–ion exchange; *7*, multichamber evaporation–ion exchange; *8*, ion exchange softening–multichamber evaporation–ion exchange; *9*, reverse osmosis–electrodialysis with ion exchange membranes and grains–ion exchange in a mixed bed.[10]

Fig. 1 presents the result of the calculation by Eqn. (7) of the coefficients of the pollution of the environment in the purification of water.[10] Analysis of the data presented in the figure shows that ion-exchange technology is ecologically less desirable than distillation technology, but the quality of water obtained by ion exchange is significantly higher than that produced by distillation.

III. The ion-exchange method for the preparation of ultrapure water

Ion exchangers are solid or liquid substances containing ions capable of exchanging with other ions of the same charge sign present in the solution where the given ion exchanger is insoluble.[12] Ion exchange was first used for the treatment of water with the aid of modified activated charcoals,[13] but, owing to their low stability in alkalies, the technology did not come to be widely employed. Furthermore, the natural and synthetic inorganic ion exchangers had a comparatively low exchange capacity. After Adams and Holmes[14] established in 1935 that the phenol-formaldehyde resin obtained by polycondensation has a much higher capacity compared with the known ion exchangers, commercial production of cation exchangers for the purification of water was organised in Germany. Less than a decade was needed to synthesise phenol-formaldehyde cation exchangers with sulpho-groups. D'Alelio[12] synthesised a sulphonated copolymer of styrene and diviylbenzene—the first monofunctional highly acid cation exchanger. Anion exchangers of the weakly basic and strongly types were soon synthesised. The present stage of the use of ion exchange for the purification of water began from that moment. The preparation of ultrapure water begins with cation exchange. The initial highly acid cation exchanger must be in the acid form and the cation exchange reaction then leads to the formation of the corresponding acids:

$$RH+NaCl=RNa+HCl\ ,$$
$$2RH+Ca(HCO_3)_2=R_2Ca+2CO_2+2H_2O\ ,$$
$$2RH+MgSO_4=R_2Mg+H_2SO_4\ .$$

The reactions are carried out so long as the cation exchanger in the acid form remains in the column. After the conversion of the cation exchangers into salt-forms, they must be regenerated. Chemical regeneration of cation exchangers with acids is usually employed in technology. The reason for the ecological undesirability of ion exchange for the intensive desalination of water arises from the necessity for the ion exchanger chemical regeneration reactions:

$$RNa+HCl=RH+NaCl\ ,$$
$$R_2Ca+2HCl=2RH+CaCl_2\ ,$$
$$R_2Mg+2HCl=2RH+MgCl_2\ .$$

Cation exchangers with the ionogenic sulpho-group have the maximum affinity for multicharged ions. The reason for this is both the direct and stronger electrostatic interaction of the multicharged counterions with the fixed ions and the strengthening of the hydrogen bond formed by the molecules of the water of hydration, the counterions, and the fixed ions. The sorbability series is as follows:

$$Fe^{3+}>Ca^{2+}>Mg^{2+}>Na^{+}>H^{+}\ .$$

The desorption of calcium and magnesium ions, the absorption of which is described by a convex isotherm, requires an appreciable excess of acids for regeneration. The complete regeneration of the cation exchanger in the sodium-form requires a 2.5-fold excess of acids. The desorption of doubly charged ions from an ion exchanger requires an even greater excess of acid and the regeneration is therefore carried out without restoring fully the capacity of the acid-form,[15] although this does not eliminate the need for the use of an excess of acid. As a result, the waste water from cation-exchange columns contains after regeneration an appreciable excess of acids together with sodium, calcium, and magnesium salts.

After cation exchange, the water is decarbonated to remove carbon dioxide, which is followed by anion exchange. The anion exchange process is carried out successively, initially on weakly basic and then on highly basic anion exchangers. The weakly basic anion exchangers contain primary, secondary, or tertiary amines as ionogenic groups which function effectively only in an acid medium. Therefore anion exchangers of this type sorb strong acid anions:

$$R'OH+HCl=R'Cl+H_2O\ ,$$
$$2R'OH+H_2SO_4=R_2'SO_4+2H_2O\ .$$

The necessity to use weakly basic anion exchangers is associated with the ease of their regeneration (the consumption of alkalies on the regeneration process is greater than the stoichiometric amount by a factor of 1.2–1.5). However, weakly basic anion exchangers hardly sorb weak acids, in particular silicic acid. An important feature is that highly basic anion exchangers function virtually in any pH range and sorb silicates from natural waters. On the other hand, highly basic anion exchangers are much more difficult to regenerate (the consumption of reagents is 5–10 times greater than the stoichiometric amount).

An exceptionally important step in the development of the ion-exchange method in the technology for the preparation of highly desalinated water was the application by Reents and Kahler[1] and almost simultaneously by Kunin and McGarvey[16] of a mixed bed of granulated cation and anion exchangers. The following reaction takes place in this case:

$$RH+ROH+NaCl=RNa+RCl+H_2O\ .$$

The proximity of heteropolar ion exchangers and the presence of a product with a low dissociation constant lead to a virtually irreversible reaction, which permits the complete demineralisation of water. Both a strongly acid cation exchanger and a strongly basic anion exchanger must be used for the complete demineralisation.

Since the electrochemical regeneration of a mixed bed of ion exchangers[17] has not come to be widely used, an obligatory stage is the separation of the components of the mixed bed. This operation is usually carried out by supplying water in the direction from below upwards. The cation exchanger, which is more dense, then settles downwards, while the anion exchanger forms the upper layer. After this, the cation exchanger and the anion exchanger are regenerated with acid and alkali respectively, the amounts consumed exceeding the stoichiometric amount by a factor of 2–3.

It is also important to draw attention not only to the necessity for an excess of the regeneration reagents but also for the necessity to double the mass of the reagents relative to the mass of the impurities extracted from natural water, because the cation and anion exchangers are regenerated separately. The cations of each electrolyte are sorbed on the cation exchanger and the anions are sorbed on the anion exchanger. They are regenerated in the same way. Altogether this leads to an increase in the mass of inorganic substances in waste waters by a factor of 3–15 depending on the quality of the initial water and the required degree of desalination.

Ultrapure water cannot be obtained by ion exchange without the preliminary sorption of organic susbtances.[15] Activated charcoals or anion exchangers of the macroporous and isoporous type are used for this purpose. Best results in the sorption of humates and fulvates from natural waters are obtained by the successive employment of weakly basic and highly basic anion exchangers. In particular, their successive adsorption on the USSR-produced anion exchangers IA-1 and AB-17P in the preliminary purification stage makes it possible to avoid the poisoning of the ion exchangers by humates and fulvates.[18] As a result of this, the principal units in the technology for the production of ultrapure water involve preliminary purification specific to a particular type of natural water, the adsorption of organic substances, cation exchange, decarbonation, anion exchange, and ion exchange in a mixed bed of cation and anion exchangers. Some of these operations can be repeated several times.[15]

After all these purification stages, the water is characterised by the lowest concentrations of impurities, approaching ideality in this respect. In the Soviet literature, a single term has not been established for the limiting quality of water and the concepts of ultrapure, specially pure, and highly pure water are used together with the term "deeply" desalinated water. The very term ultrapure water arose in the French language literature (l'eau ultrapure), while in the English language literature two terms exist—ultrapure water and high purity water. We have given preference to the term ultrapure water because it is most widely used in the world's scientific literature.

The question arises what characteristics shoudl utlrapure water possess? In view of the absence of a Government Standard (GOST) for ultrapure water, use is made of OST 11 029.003-80, where brands A, B, and C are distinguished in terms of their quality. The highest quality water of brand A must have a specific resistance not less than 18 MΩ cm at 20 °C, a permanganate oxidisability less than 0.5 mg O_2 litre^{-1}, a silicic acid content less than 0.01 mg litre^{-1}, iron and copper contents less than 0.002 mg litre^{-1}, not more than 2 microparticles per ml, and not more than 1 colony of microorganism. In the USA, the type 1 ASTM standard corresponds to water with a maximum specific conductance of 0.06 μS cm at 298 K (specific resistance 16.67 MΩ cm), a content of organic substances not more than 1 mg kg^{-1}, a content of dissolved gases not more than 200 mg kg^{-1}, a residue after evaporation not greater than 0.1 mg litre^{-1}, the absence of a positive response to the test for silicates, a maximum content of heavy metals of 0.01 mg kg^{-1}, and not more than 150 particles in 1 kg.

The development of the ion-exchange technology ensuring the preparation of water of the very highest quality by the most economical method, involving simple apparatus and permitting the attainment of virtually any required productivity of the latter, for a long time created the illusion that the problem of the preparation of ultrapure water has been solved. Difficulties arose when an attempt was made to organise a waste-free circulating water supply, which in our time has become absolutely essential, since the general ecological situation has become very much more acute. From the standpoint of the protection of nature the question arose whether or not the ion exchange technology transfers impurities to pure rivers and water-containing areas and whether or not the soil, air, and subterranean waters suffer as a result. It is known that water (rain and snow) precipitated on the surface of the soil in the active water exchange zone, where waste is in fact mainly stored, enters river water after approximately 17 years. Calculations show that in the immediate future the amount of chlorides of anthropogenic origin will exceed by a factor of 4 the natural background. By the end of the century, the antropogenic concentration of sulphates will exceed by a factor of almost 7 the concentration in 1980 and the LPC for commercial water-containing areas. The conversion of organic contaminants into mineral ones in the course of the biological purification of water does not in essence alter the fundamental situation. As a consequence of this, the discharge of mineralised waters, including regenerators of ion-exchange filters, is forbidden in the comparatively water-deficient Ukraine and individual sections of the Northern Donets and the Dneper.

We draw attention to the fact that, since the mass of mineral substances in the liquid waste from ion-exchange apparatus after chemical regeneration is more than three times greater than the amount of such substances extracted from natural waters, the degree of mineralisation of subterranean and river waters will increase after a certain time. Since the initial water will become more mineralised, this will entail the consumption of a greater mass of chemical reagents for regeneration. This will lead in its turn to an even greater pollution of the environment and ultimately to an additional increase in mineralisation. The reaction producing mineral substances will change from a zero-order process to a first-order process; since the production of mineral substances under such conditions is proportional to the concentration, we have

$$\frac{\partial C_i}{\partial \tau} = K_i C_i \,, \tag{11}$$

and this leads to an exponential increase in the concentration of mineral substances in subterranean waters and rivers:

$$C_i = C_{0,i} \cdot \exp(K_i \tau) \,. \tag{12}$$

Such a system may be characterised as an ecological boomerang, since not only an increase in the productivity of the devices using the ion-exchange method but also their functioning with a constant productivity entails a continuous impairment of the quality of the initial water and an exponential growth of the waste discharged as a function of time. The creation of the ion-exchange technology can be regarded nowadays as an ecological mistake with unforseeable harmful consequences involving a change in the environment, which vitiates the planned benefit and generates more problems than it solves. This entails a double tragedy, since it will be necessary to seek means not only for the liquidation of the waste discharged into natural waters but also for the solution of all the new problems arising in this connection (human diseases, destruction of fish farming, etc.). The "unpredictability" of the pernicious consequences is due to the inadequacy of the preliminary research and the underestimation of the impact on the environment and human beings.[8] Fig. 1 shows why ion exchange is an ecologically undesirable technology for the extreme purification of water.

IV. The membrane method for the extreme purification of water

The ecological undesirability of distillation and ion exchange necessitated the search for alternative methods leading to the solution of the problem of the preparation of ultrapure water. We shall consider the possibility of using membrane methods for the solution of the problem. Membrane is the term which has come to

be applied to a body whose extent in terms of two coordinates significantly exceeds its extent in terms of the third (a one-dimensional disperse system). The word membrane comes from the latin word meaning pellicle, shell, or partition. When generalised thermodynamic forces are applied to a membrane, mass fluxes arise.[19] Transport processes following the application of a chemical potential gradient (dialysis), a pressure gradient (microfiltration ultrafiltration, reverse osmosis), and an electric potential gradient (electrodialysis) are distinguished.

Baromembrane methods can be most usefully applied in the first stage of the purification of water. Natural water is initially filtered to remove coarsely dispersed impurities, after which it is subjected to microfiltration to remove finely dispersed impurities and bacteria.[20] In the next stage, colloid impurities, high molecular-weight and oligomeric compounds, and viruses are eliminated by means of ultrafiltration.[21,22] Using UAM-100 and UAM-150 ultrafiltration membranes, it was possible to remove about 80% of organic substances from water.[23] Next, reverse osmosis is used to purify water.[21,24]

In particular, when filter elements of the rolled up type with the MGA-95 cellulose acetate membranes are used, reverse osmosis makes it possible to obtain water with a specific resistance of 0.02–0.07 MΩ cm containing 0.25 mM silicate, exhibiting a permanganate oxidising capacity not more than 3.1 mg O_2 litre^{-1}, and showing the complete absence of microflora. On the other hand, one should immediately abandon the illusion that reverse osmosis makes it possible to obtain ultrapure water directly. Studies have shown that by this procedure it has not yet been possible to attain the state of distilled water formed after a single distillation and having a specific resistance of 0.1–0.3 MΩ cm. On the other hand, the role of reverse osmosis in increasing the ecological compatibility of the purification of water is so great that even its combination with ion-exchange deionisation by means of filters containing a mixed bed of granulated ion exchangers has come to be widely used.[25,26]

Extreme desalination of water treated by reverse osmosis can be achieved by electrodialysis using ion-exchange membranes. This can be best carried out in two steps. In the first step of the electrodialysis, the aim is to obtain water with a specific resistance of about 1 MΩ cm, while in the second the aim is to achieve a specific resistance of the order of 18 MΩ cm. Several versions of the procedure can be selected for the preparation of water with such a specific resistance. The first version represents electrodialysis employing ion-exchange membranes and a small distance between the membranes.[27] The intermembrane distance of 0.5 mm used by Tezikov and Saldadze makes it possible to obtain water in the required condition but at a relatively high coefficient of hydraulic resistance, requiring additional expenditure of electrical energy. The reason for the increase in the efficiency of desalination with decrease in the inter-membrane distance was investigated by laser interferrometry[28] and it was shown that the overlap of the boundary diffusion layers of the solution at the interfaces with the membranes plays a decisive role. For large intermembrane distances, there remains a zone in the middle of the desalination section in which no concentration changes occur. The second version, electrodialysis with the desalination section between the membranes filled with a mixed bed of granulated ion exchangers, was proposed by Walters, et al.[29] Glueckauf[30] investigated the function of the grains in electrodialysis with an ion-exchanger filled intermembrane section and found that heteropolar contacts between the anion-exchange grains and the cation-exchange membrane, on which water undergoes irreversible dissociation with formation of hydroxide ions migrating along the circuit and regenerating continuously the ion exchanger, play the main role. Subsequently anion exchange takes place between the hydroxide-form of the anion exchanger and the impurities in the water. Correspondingly water also decomposes the contacts between the cation-exchange grains and the anion-exchange membrane, hydrogen ions migrating along the chain of cation exchanger grains, regenerating them continuously. This is followed by ion exchange between the cationic impurities in the water and the hydrogen ions. Complete deionisation takes place because the desorption products (hydrogen and hydroxide ions) recombine to water—an electrolyte with a low dissociation constant. The impurity cations and anions migrate respectively along the chains of grains to equipolar membranes and are removed through them by the electric current to adjoining sections where the concentration takes place. In their study of the mechanism of transport through pairs of equipolar $\overrightarrow{C-C}$ and $\overrightarrow{A-A}$ grains (C and A denote cation-exchanger and anion-exchanger grains respectively and → indicates the direction of the direct current from the anode to the cathode) and also through heteropolar $\overrightarrow{C-A}$ and $\overrightarrow{A-C}$ grains, Gnusin and Grenenyuk established a series of fundamental features of the mass transfer.[31] They believe that equipolar contacts do not introduce significant changes into the distribution of local concentrations in the solution, whereas the C–A contacts concentrate the electrolyte in capillary gaps. The electrolyte concentrated in the capillary gaps is distributed by convection throughout the bulk of the solution in the desalination section, reducing fundamentally the efficiency of the process. This is the reason for the attempts to find a way of eliminating the C–A contacts. A solution was found using monolayers of alternating cation- and anion-exchanger grains placed in an inert grid.[32] The replacement of the inert grid by an ion-conducting grid makes it possible to reduce the energy expenditure to 0.2 kW h m^{-3}.[33]

Only electrodialysis with ion-exchange membranes and with the desalination sections between the membranes filled with a mixed bed of granulated ion exchangers can be used for the membrane preparation of ultrapure water in the final stage: in the regime with periodic circulation[34] and in the direct-flow continuous regime.[35] Many years after these investigations similar studies were performed in the USA by the Millipore Corporation[36] and in France.[37] As in the earlier studies,[34,35] the attainment of a specific resistance close to the limiting value was noted.[36,37] However, in addition to what was already known, it was stated[36] that the secondary contamination of water by solid particles is not observed. Thus the sequence of steps in the preparation of ultrapure water by membrane methods consists of filtration, microfiltration, and ultrafiltration stages, reverse osmosis, electrodialysis with ion-exchange membranes and a layer of granulated ion exchangers, and electrodialysis with ion-exchange membranes and the intermembrane space filled with a mixed layer of granulated ion exchangers.

In the membrane purification of water, there is no increase in the mass of substances in waste water compared with the mass of the extracted impurities. In the concentration sections, the mass is doubled and the concentration of inorganic substances is equal to the mass extracted, which imparts to membrane methods appreciable advantages over ion exchange and distillation. To some extent the future of membrane methods, which have been officially declared to be technologies for the XXIst century,[38] depends on the fraction of electrical energy which they consume. Estimation of the ecological compatibility of combined membrane methods yields the lowest coefficients of the pollution of the environment (Fig. 1), which

enables one to predict their successful development. On the other hand, we may draw attention to the large amount of scientific labour required by membrane methods[19] and also the necessity for qualified staff to use them. Theoretical studies in the field of mass transfer through membranes, which make it possible to create mathematical models optimising the membrane technology, have become particularly urgently required.

V. Removal of nitrates from natural waters

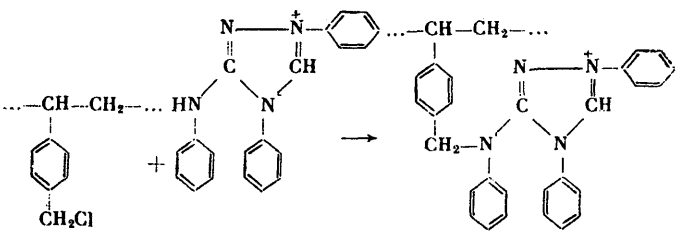
Apart from the tasks involving the general extreme purification of water, there are those concerned with local elimination of components which constitute a risk to human health. Among the problems which have given rise to particularly great alarm in society is that of the removal of nitrates from drinking water. Nitrates enter water as a consequence of the large-scale use of mineral fertilisers containing them. Mineral fertilisers began to be employed after Leibig developed in 1840 the theory of the mineral nutrition of plants, according to which man irreversibly extracts nitrogen compounds from the soil but their deficiency can be made good by nitrogen-containing inorganic salts (nitrates). The nitrates not assimilated by plants enter natural waters, which leads to two types of illness. The first is methaemoglobinemia induced by the oxidation of haemoglobin to methaemoglobin, which is incapable of chemisorbing oxygen. It has been established that an increase in the content of nitrates, nitrites, aniline, and nitrobenzene leads to methaemoglobinemia. Methaemoglobinemia is particularly dangerous for embryos and suckling infants, whose blood contains up to 85% of foetal haemoglobin, which is more susceptible to the action of nitrates than the haemoglobin of an adult human being. The second type of illness is caused by the reduction of nitrates to nitrites in the intestine followed by the reaction with amines, which converts them into carcinogenic nitrosamines. The content of nitrates in natural waters used for drinking has therefore been limited to 50 mg litre^{-1} in the countries of European Economic Community and in 1994 it is planned to reduce the limiting permissible concentration to 30 mg litre^{-1}.

Unfortunately the use of nitrates can no longer be avoided, since this would require a threefold increase in the arable land. It is therefore essential to determine nitrogen-containing substances in the soil in order to introduce fertilisers in controlled amounts. The use of a large mass of fertilisers, which cannot be immediately assimilated by soils and plants, is particularly dangerous. The membrane method for the controlled release of substances is therefore especially promising.[39] The Rose-Nelson pump, consisting of three sections separated by one semipermeable membrane and one impermeable elastic membrane, may serve as the simplest example of the use of this method. One of the three sections contains water, whilst the other, adjoining section contains the salt. The osmotic flux through the semipermeable membrane into the salt-filled section increases the osmotic pressure in the latter and, in the presence of the elastic membrane, leads to an increase in the volume of the section. The elastic membrane slowly forces out of the section the fertiliser solution or any preparation, including therapeutic preparations. One may foresee the wide scale future employment of this membrane method for the introduction of fertilisers into the soil. In the introduction of nitrate fertilisers, it is very important to select an appropriate time for this purpose. The best time for the feeding of plants is the vegetative period. Unfortunately at the present time the necessary agrochemical expertise involving the use of fertilisers is lacking and this leads to the limiting permissible concentration being appreciably exceeded in the drinking water in many regions, which require special methods for the elimination of nitrates from natural waters.

We shall consider the possibility of the elimination of nitrates from natural waters by biological and biotechnological methods. For the microbiological removal of nitrates, it is essential to create anaerobic conditions, which is in principle possible directly in the soil but requires not only the participation of bacteria but also of organic substances. For example, under laboratory conditions the anaerobic elimination of nitrates is carried out in the presence of ethanol and sodium phosphate. Such requirements cannot be satisfied in practice. The biotechnological method, in which bacteria convert nitrates into molecular nitrogen, has already found an application and has been proposed by the name Biodenit by the "Energy Equipment for Heidelberg Joint Stock Company". However, the application of this method leads to the production of a large amount of biomass and side products, which is also unacceptable for the conditioning of water in order to obtain drinking water yet alone for its intense purification. The ion-exchange method for the removal of nitrates from drinking water has come to be widely used. Its effective application required anion exchangers selective with respect to nitrates. There are two versions of the synthesis of selective ion exchangers. The first involves the introduction into the polymer of an ionogenic group with a specific strong interaction with a particular ion. The classical example is provided by the synthesis of the potassium-selective cation exchanger by Scogside,[12] who obtained it by introducing into the polymer hexanitrodiphenylamine (dipicrylamine), which is used as a reagent for the precipitation of potassium.

The second procedure involves the regulation of the properties of the polymers, promoting an increase in selectivity. For example, the introduction of the cross-linking agent diphenylbenzene in the polymerisation of styrene increases the selectivity of the ion exchangers as a result of the decrease in the water content. The reduction of the water content is accompanied by a decrease in the number of water molecules between the fixed ion and the counterion in the ion exchanger and an intensification of the electrostatic interaction. Electrostatic interactions involving ions of different radius and bearing different charges differ fairly markedly, whereas the energies of the hydrogen bonds formed by water molecules between the fixed ion and the counterion are similar.

A nitrate-selective anion-exchanger was obtained by the reaction of the chloromethylated styrene-divinylbenzene copolymer with 1,4-diphenyl-2-phenylaminodihydrotriazole (nitrone):[40]

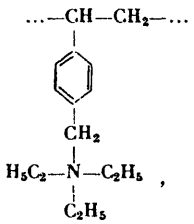


The isotherms of the exchange of chloride and sulphate ions for nitrate ions obtained by Frölich and Weber[40] show the high selectivity of the above anion exchanger in relation to nitrate ions. The nitrone anion exchanger is regenerated chemically with a 5% solution of sodium chloride. After many repetitions of these cycles,

no losses in exchange capacity were observed. The traditional type of highly basic anion exchanger made of the styrene-divinylbenzene copolymer and comprising the benzyltrimethylammonium elementary unit (AV-17) exhibits a higher selectivity in relation to sulphate ions. The selectivity sequence is as follows:

sulphate > nitrate > chloride > bicarbonate

The replacement of methyl groups in the fixed ion by ethyl groups alters the selectivity sequence in the anion exchanger



and the latter becomes more selective in relation to nitrates.

The membrane methods for the removal of nitrates from natural waters are ecologically more promising. However, the membranes synthesised at the present time exhibit a selectivity of 86% with respect to nitrate ions, while the selectivities with respect to chloride and sulphate ions are 94 and 90% respectively. Furthermore, in reverse osmosis the membranes retain also cations. In particular, the selectivity with respect to calcium ions reaches 96%.[42] Therefore reverse osmosis makes it possible to demineralise water at the present time but does not allow the selective extraction of nitrates from it.

Electrodialysis with ion-exchange membranes is especially promising for the removal of nitrate from drinking water.[42] The use of a mixed layer of ion exchangers for the filling of the desalination sections permits the intense elimination of nitrates from water, but, as in reverse osmosis, it is not possible to achieve the selective removal of nitrates from water. Therefore the membrane method has still not solved the problem of the selective transport of nitrates through membranes and the ion-exchange extraction of nitrates with the aid of the nitrate-selective ion exchangers is most useful.

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