materials. If the problem of the manufacture of such a membrane can be solved, then, apart from improving the technical-economical parameters of the operation of the engine, by increasing the oxygen content and reducing the nitrogen level in the air mixture it will be possible also to reduce the ejection into the surrounding atmosphere of the combustion products in the form of hydrocarbons, nitrogen oxides, and solid carbon. The same situation arises also in fuel–energy plants.

Table 4. Membrane gas-separating devices of the MVK series designed for the preparation of air enriched in oxygen directly from the atmosphere.

Principal characteristics	MVK 0.0125	MVK 0.025	MVK 0.3
Productivity, $nm^3 h^{-1}$*	12.5	25.0	300
O_2 concentration, %, not less than	35	35	35
Specific energy consumption, kW h m^{-3}	0.35	0.25	0.14
Starting time, min	1–2	1–2	2–3

*Probably $m^3 h^{-1}$ (Ed. of Translation).

Table 5. Gas permeability coefficients (P) for organosilicon polymers.

Polymer	$10^9 P$, cm^3 cm $cm^{-2} s^{-1}$ $cmHg^{-1}$			
	hydrogen	methane	oxygen	nitrogen
Polyvinyltrimethylsilane	20	1.8	4.4	1.1
Polydimethylsiloxane	65	95	60	28
Polytrimethylsilylpropyne:				
Japan Institute of Petrochemical	690	720	400	200
Synthesis of the USSR Academy of Sciences	700	–	590	280

Thus the possibilities of ecologically clean membrane gas separation processes are associated primarily with the creation of new polymeric materials and membranes with an exceptionally high productivity and selectivity and also with the creation of membrane methods and devices in which the membrane would play not only the role of a separating element but would also be actively involved in the chemical reactions of the substances, i.e. would play the role of a membrane reactor.

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Chemical aspects of a circulating water supply

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One of the most important ecological problems is that of water. Using water from various natural sources in enormous amounts, the human population partly wastes it by evaporation but most of it is returned to nature in the liquid but contaminated form. In the USSR the overall water resources amount on average to 4500 km^3 per year (4/5 corresponds to surface waters and 1/5 to subsoil waters). It is believed that a little more than 110 km^3 of water can be used annually for industrial and agricultural needs and for utilities without harming the water balance in the country. The industrial consumption of water in the USSR runs to many tens of cubic kilometres (from 40 to 60 km^3 according to different data). Approximately the same amount of water is consumed domestically by the population. The manufacture of one tonne of nickel requires on average 800–850 tonnes of water. The bleaching of 1 tonne of cotton requires 280 tonnes of water. One tonne of caustic soda requires 250–300 tonnes of water, etc. Naturally, even in related undertakings, these consumptions differ markedly. Nevertheless they are very large. A similar situation has been observed also in other industrially developed countries. For this reason, the saving of water and the fight against the exhaustion of the water resources of our planet and the contamination of water have now become one of the most important problems facing humanity.

One of the aspects of the solution of this problem involves the conversion of industrial undertakings and heating systems to a circulating water supply. Trends of this kind are characteristic of many branches of industry, but they are perhaps most characteristic of ferrous metallurgy—a large consumer of water.

The water economy in metallurgical undertakings has developed rapidly during the last decades towards the creation of a circulating water supply system.

More than one thousand circulating water supply systems have now been created in the undertakings of the Ministry of Ferrous Metallurgy of the USSR; the fraction of the circulating water supply in the overall water consumption of this branch of industry has exceeded 85%.

The conversion of the water economy of any industry to circulating schemes leads to a gradual impairment of the quality of water in the systems. As a result of the repeated employment of limited volumes of water (with a necessary external supply to make good the losses) in such systems, salts accumulate and dense salt deposits are formed on the equipment.

The formation of salt deposits in circulating water supply systems is now occurring on a wide scale. Industrial undertakings suffer annual additional costs and losses running altogether to several hundreds of millions of roubles. The removal of part of the circulating water to water reservoirs in order to reduce the content of sparingly soluble salts and thus diminish the rate of formation of deposits is used as a palliative solution. It is then necessary to

make good this loss by supplying fresh water to the system, which leads to partial return to open water supply systems. As industrial undertakings are converted into loss-free water utilisation schemes, it becomes urgently necessary to solve the problem of the stabilisation of the possible precipitation of deposits of salts responsible for the hardness of water, i.e. the creation of inhibitors of salt deposition and corrosion.

A similar situation has arisen in non-ferrous metallurgy, in the chemical and petroleum industry, in the systems employed in thermal electric power stations, in heat and power plants, and in other branches of industry. In all cases the organisation of an ecologically favourable circulating or closed water supply is inhibited by the abundant formation of salt deposits, whose periodic removal involves much labour and time. Hence arises the problem of preventing salt deposits, which although difficult is entirely soluble. Thus the solution of a major, one may say global, ecological problem is based on the solution of the more specific problem of inhibiting salt deposition.

The main component of salt deposits is usually carbonates (mostly calcium carbonate), formed from the hydrogen carbonates responsible for the temporary hardness of water. Procedures for the chemical prevention of salt deposition and for washing the equipment clean have been proposed at different times—for example, the acidification of water and the use of a series of polymeric inhibitors, but best results have been obtained by employing polyphosphates, which form complexes with the cations of the deposited salts. However, polyphosphates are effective only when the content of salts in water does not exceed 3 mequiv. litre^{-1} (however, many waters, especially those from artesian wells, contain a greater amount of salts). Furthermore, in all cases the effective action of polyphosphates is comparatively brief—so long as the content of salts in the circulating water does not rise to the limit indicated above (as a result of the supply of fresh water and evaporation). Finally, polyphosphates gradually hydrolyse. Thus the use of polyphosphates does not exclude measures for the removal of salt deposits. Naturally, in their presence this can be done more rarely but it is nevertheless frequent enough.

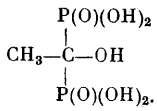
An effective procedure for combating salt deposition involves the binding of metal cations into water-soluble complexes with the aid of complexones. The disodium salt of ethylenediamine-*N,N,N'N'*-tetra-acetic acid (EDTA) (Trilon B) was used initially as a reagent of this kind. Other carboxylic acid complexones have also been proposed. However, subsequently, following the appearance of organophosphorus complexones, they were all to a large extent displaced by the latter, since these are more effective and at the present time organophosphorus complexones are in fact widely employed to inhibit salt formation in circulating and closed water supply systems.

The effectiveness of organophosphorus complexones is based not only on their ability to form stable water-soluble complexes with the majority of cations present in water, but also, and this is particularly important, on their ability to effect inhibition in substoichiometric amounts, the amount of the complexone required being significantly smaller than the amount necessary for the stoichiometric formation of stable complexes. Studies have shown that this is a consequence of the adsorption of complexones on the crystallisation nuclei of the salt, which prevents the growth of the nuclei and the formation of crystals. A supersaturated solution incapable of giving rise to a deposit is formed.

Numerous organophosphorus complexones have been tested. It was found that the most effective complexones are those whose molecules contain several (three or more) phosphonic acid groups.

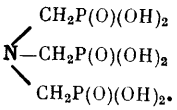
At the present time our industry produces the following organophosphorus compounds for the inhibition of salt deposition.

1. Hydroxyethylidenediphosphonic acid (HEDP):



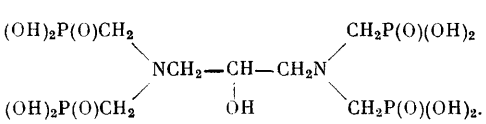
HEDP is obtained from acetic acid and phosphorus trichloride. We investigated its complex forming properties and the methods for its industrial synthesis. HEDP can be used as a salt deposition inhibitor both in a pure form and in different compositions.

2. Nitrilotrimethylphosphonic acid (NTP):



NTP is obtained from ammonium chloride, formaldehyde, and phosphorus trichloride. The extremely effective IOMS combined inhibitor of salt deposition and corrosion has been developed. This preparation contains about 80% NTP, but, since ammonium chloride (a waste product in the manufacture of polyethylenepolyamines) containing an admixture of polyethylenepolyamines is used as the nitrogen-containing starting material, the preparation contains, apart from NTP, also phosphorylated polyethylenepolyamines which have a synergistic effect on NTP. The phosphorus-containing starting material used under these conditions is phosphorous acid (a waste product in the manufacture of lauryl peroxide). This results in the preparation of an extremely cheap and extremely effective salt deposition inhibitor—IOMS.

3. 2-Hydroxypropylene-1,3-diamine-*N,N,N'N'*-tetramethylphosphonic acid (DPP):



DPP is obtained from epichlorohydrin, ammonia, formaldehyde, and phosphorus trichloride. A technical product, obtained from a crude mixture consisting of 80% of 1,3-diamino-2-propanol and 20% of polymeric products of the interaction of ammonia with epichlorohydrin, is manufactured on the basis of DPP. The phosphorylation of such a mixture yields DPP and polycomplexones. This mixture is manufactured under the name DPP-1 or FOSFANOL (a neutral form of DPP-1). The effectiveness of the technical product is higher than that of pure DPP.

Each of the proposed salt deposition inhibitors has its "speciality"—the type of salt deposits which it prevents most effectively.

The use of recipes which include, apart from organophosphorus complexones, also corrosion inhibitors, surfactants, and other ingredients has become very important.

The overall volume of manufacture of organophosphorus complexones used as salt deposition inhibitors amounts at present to several thousand tonnes annually (10 commercial brands are produced). Much experience has accumulated in industry as regards the preparation of organophosphorus complexones for the inhibition of salt deposition, in particular for the stabilisation of water by complexones in circulating gas purification cycles in blast furnaces. Complexone stabilisation of water is used nowadays in the

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.