



Selective Extraction of Salt Ions from Groundwater by Polyamide Membranes

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ABSTRACT:

In this work, problems related to qualitative description and number of parameters of diffusion selective extraction of salt ions in polymer membranes were solved, taking into account the size of membrane pores and pH solutions. The dependence of diffusion coefficient of aqueous solution of salt ions (pH 6.5-7.5) in a range of polyamide membranes with dominant pore radius of less than 6-7 nm has been investigated. The characteristic features of the diffusion coefficient change are compared with the salt ion content within the pH range of the solution. The diffusion coefficients of salt ions in membranes with pore radii of 5 to 8 nm at pH = 6.5-7.5 are generally comparable for salt ions. In the wrong interval between membrane regeneration operations, the efficiency of membrane regeneration operations was reduced, and changes in membrane characteristics could be avoided. The duration of the inter-regeneration period depends on the composition of the source water and its preparation before reverse osmosis. The quality of the water preparation is considered good if the stability of the operation of the desalination apparatus is achieved by periodic dipping them not more than once a month. Features of diffusion of salt ions in PA membranes (exponential dependence of diffusion coefficient on radius of pores of membranes, ν lysine pH) and comparison of the obtained data with the available salts allow to determine prospects and conditions of their separation in PA membranes.

Introduction

Membrane (reverse osmosis) technology for water desalination is being widely introduced throughout the world in various sectors of the national economy. The use of reverse osmosis technology ensures a significant reduction in the consumption of reagents and a reduction in the discharge of saline wastewater [1].

Industrial operation of reverse osmosis units at a number of enterprises has shown that membranes are very sensitive to contamination by heavy metal compounds. Contamination of membranes occurs when the content of corrosion products in the treated water is such that it practically does not affect the operation of ion-exchange water desalination circuits. At the same time, a decrease in the technological performance of reverse osmosis units occurs quickly - in the period from several days to several months.

To ensure stable operation of reverse osmosis units and extend their service life, the following technical solutions are used: acidification of water in retentate chambers, fine filtration of water in filters, supply of pre-purified or softened water to membrane modules, physicochemical methods for cleaning membranes, use of turbulizing mesh between membranes, and finally, chemical cleaning of the membranes.

The desire to increase the productivity of installations by increasing the pressure of incoming water causes pressure on the membranes from the retentate cells, disruption of the distribution of treated water flows and contamination of the membranes. Acidification of the retentate circuit to pH=3M increases the consumption of reagents and complicates the conditions for processing the retentate.



Supplying reverse osmosis devices with softened water practically does not solve the problem of membrane contamination with iron compounds. However, such inclusion of membrane installations practically eliminates one of the main advantages of reverse osmosis - reducing the amount of saline wastewater, and also does not provide a reduction in acid consumption for filter regeneration.

Membrane separation and concentration processes are among the critical technologies for the production and processing of structural and functional materials for water desalination. Supplying reverse osmosis devices with softened water practically does not solve the problem of membrane contamination with salt ions. The material from which the membrane is made must have a high affinity for the solvent (mainly water) and a low affinity for the dissolved component. The selected objects and the subject of the study - the diffusion of water salts on the surface of polyamide (PA) - allow us to count on the possibility of reliable membrane separation of the components of aqueous solutions.

The prospects and advantages of PA membranes are determined by Based on the analysis of the kinetics of membrane separation, the PA membrane is resistant to the studied saline solutions [1; 2]. Calculation of the selectivity characteristics of membrane desalting, based on the basic physicochemical characteristics of the solution, permeate and retant, is a complex task due to the large number of influencing factors [3].

PAs have high selectivity towards salts, but the water flow through them is slightly lower. With a pH range (cleaning pH) of 2.0 – 10 (1-12), PA can withstand processing temperatures up to 100°C without significant changes in the porous structure, allow repeated regeneration, and are resistant to most acids depending on the pH of the environment. PA membranes have a fairly large thickness of up to 150 microns. Such thick membrane films lead to a sharp decrease in the rate of mass transfer. However, this effect is compensated by the extremely high surface of the membrane per unit volume: the specific surface reaches 30,000 m²/m³ [4; 7-9].

Installed [1-3; 10], that the diffusion mobility of ions in PA membranes is generally lower than in free solutions, even in the region of significant pore radii. A decrease in pore size leads to a decrease in diffusion coefficients, associated with the difficulty of moving ions in the near-wall layers of the solution. In this case, the difference between the properties of boundary layers and the properties of bulk solutions is associated with the structuring of water on the polymer surface [1-3; 10; 13; 14]. The orienting effect of the surface OH groups of the polymer leads to restructuring and ordering of the network of intermolecular hydrogen bonds of near-wall water,

limiting the mobility of molecules, and increasing the viscosity of the boundary layers [11-12; 14], to a decrease in the dissolving ability and dielectric constant of water in pores of small radius [13].

Determining the porosity or free volume of the membrane material is one of the most important factors determining the kinetics of membrane processes [5-6]. Thus, the determination of the internal diffusion coefficient in a membrane directly depends on this characteristic [3, 12].

Materials and Methods

PA is a methodology for studying the diffusion transport of solutes across membranes.

In all cases, a single experimental action was used to determine the indicators of diffusion transport. Only the concentrations and pH of the solutes, methods for determining the amount of substances passing through polyamide (PA) membranes and the temperature at which experiments were carried out were converted. The diagram of the laboratory installation is shown in Figure 1

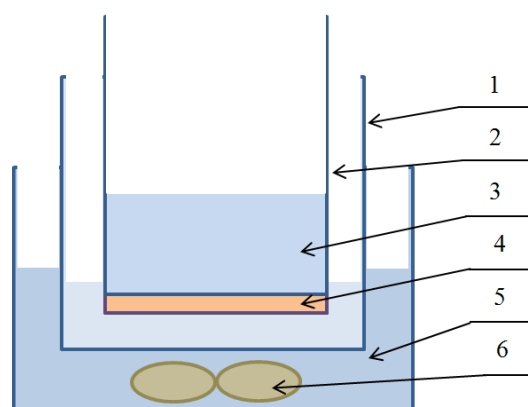


Figure 1. Installation diagram for the study of diffusion transport of substances through PA membranes; 1-receiver cell; 2-Feed Cell; 3-feed cell; 4 - pa membrane; 5-thermostat; 6-mixer.

In the study of diffusion, we placed membranes between two cells, in one (feed cell) of which the subject substance is a solution, and in the other (receiver) – water. We observed the dynamics of diffusion by an increase in the amount of the subject substance in the receiving cell. In a number of experiments, we used the method of discrete analysis of samples. The aqueous-salt solution, which passed through the membrane, was poured into receiving glasses with distilled water, which was replaced at certain intervals. We carried out the experiments under the



conditions of thermostating at 25 ± 1 °C; in individual cases, the study of diffusion was carried out in the temperature range of $25 \div 70$ °C.

As a result of preliminary experiments, it was found that the liquid column in the feed cell with a diffusion transfer rate of 10-20 mm was preserved during the change in height, and this did not have the effect of hydrostatic pressure on the experimental results.

Methods of analytical determination

Obtaining kinetic dependences of diffusion is based on sorting and analysis of samples of receiver cell solutions with period. In order to determine the current concentrations of Ca^{2+} , Ba^{2+} cations, sulfate, nitrate and chloride anions, we used their characteristic absorption in the visible and UV regions of the spectrum. We used the potentiometric method of determining Cl^- anions using selective electrodes during the study of membrane transport of alkali metal chlorides.

Determination of Ca^{2+} and Ba^{2+} ions.

We analyzed the diffusion transport of aqueous solutions of CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, CaSO_4 and BaCl_2 according to photometric determination of the amount of ions that passed into the receiver-cell. We determined Ba and Ca cations at wavelengths of $\lambda_{\text{max}}=510$ nm and $\lambda_{\text{max}}=800$ nm, corresponding to the dd transitions in the spectrum of their aqua complexes recorded using the SF-56 spectrometer; the corresponding spectrum and the implementation of the Lambert-Beer law are shown in Figure 3. The type of spectrum and values of absorption values in the case of calcium nitrate, chloride and sulfate solutions were consistent for all used concentration ranges. The values of the extinction coefficients at the maximum of the absorption bands were 8.011 and 6.274 $\text{mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$ in the case of Ca^{2+} and Ba^{2+} , respectively. The results of CaCl_2 diffusion studies using photometric analysis of cations coincided with the experimental data obtained during monitoring of Cl^- anions (using a chlorine-selective electrode) with an accuracy of 2%. Basically, this means the integration of ion transport, ie preservation of its electroneutrality during the diffusion transport of the solution.

Result and Discussion

Numerous experiments with solutions whose concentration has been modified to enter the membrane have also proven the absence of a registration effect of osmotic water transport from the receiving cell to the feeding cell on the dynamics of diffusion of the subjects.

In many cases, we conducted experiments on diffusion after preliminary retention (saturation) of membranes in the working solution. Accordingly, the

"start point" of diffusion occurred in the negative region of the time scale, and then the output of the analyte to the receiving cell was "delayed" (15-20 minutes) when applying the "pre-saturation" method to the membranes (Figure 2). Also, at this time, the slope of the kinetic straight lines (and the diffusion rates calculated on them) under the specified conditions for conducting the experiment in all the experiments carried out completely coincidentally, which is shown by a separate example in Figure 2.

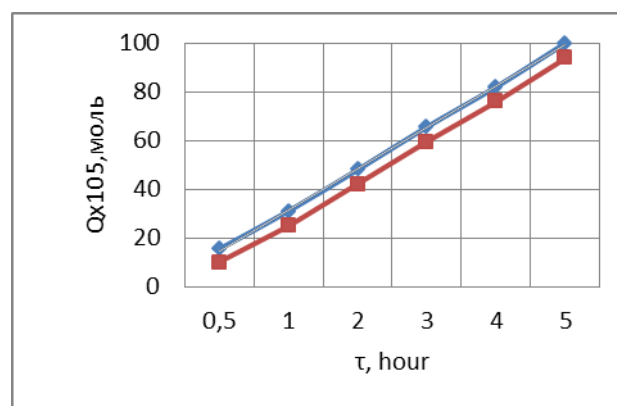


Figure 2. Kinetic dependence of the diffusion of CaCl_2 (0.5 m aqueous solution) in the PA-membrane, the membranes of which are pre-saturated with a solution (1) and without a solution (2) at 25 °C with $\text{GP} = 8 \text{ Nm}$

In all cases, we recorded the preservation of strictly linear kinetic dependencies $Q(\tau)$ during the control time of diffusion flows. This is due to the fact that at the time of the experiment, the concentration of the accumulated melt in the receiving cell was much (3-4 times) lower than the concentration of the filtered melt. Thus, depending on the initial states of the membranes, the stationary diffusion flow through the membranes is actually detected at the beginning or late, and maintained during the time required to obtain reliable kinetic dependencies.

In PA-membranes Diffusion of CaCl , $\text{Ca}(\text{NO}_3)_2$ and CaSO_4 solutions

The study of the diffusion transport of CaCl , $\text{Ca}(\text{NO}_3)_2$ and CaSO_4 aqueous solutions in PA-membranes was carried out in order to determine the forms of analytical dependence of the diffusion coefficients on the radius of the membrane pores, as well as to determine the effect of the anion nature on the mobility of salts, possibility and the very small amount of sorption on the PA membrane surface in an acidic environment, as the main potential factor affecting the value of the diffusion coefficient, makes it possible to allocate the radius of the membrane pores, making it easier to set the tasks and solve them.

The results shown below are obtained under the conditions of thermostating the systems at 25 °C. Diffuse



transport of CaCl, Ca(NO₃)₂ and CaSO₄ solutions in all cases had a stationary character, which was responsible for the implementation of Q(τ) linear dependence of the amount of salts transported through the membrane on time: a set of corresponding kinetic lines is shown in Figure 3.

Thus, the rate of diffusion mass transfer was defined as dQ/d τ.

We considered it correct to use Fick's first law in the case of a stationary process, and according to it, we expressed the diffusion flow through the membrane as follows:

$$dQ/d\tau = D \cdot s \cdot \delta \cdot \Delta c / h \text{ or } D = \frac{dQ \cdot h}{\tau \cdot s \cdot \delta \cdot \Delta c} \quad (1)$$

where D is the diffusion coefficient; s·δ is a free cross-section of the membrane in the form of a geometric area δ with a correction to the porosity value; Δc/h is the drop concentration at the entrance and exit of the membrane of thickness h. Since the concentration of the solution exiting the receptor cell ~10⁻⁴-10⁻⁵ M is slightly lower than the concentration entering the membrane in all experiments, we took the magnitude of the gradient in equation (1) to be equal to:

$$\Delta c / h = (s \cdot \delta - s \cdot \delta) / h \approx c_{ex} / h \quad (2)$$

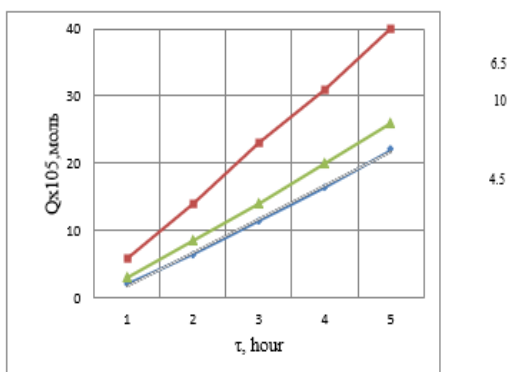


Figure 3. Kinetic dependencies of CaCl₂ amounts transported through PA membranes with a pore radius of 4.5-10 nm. The concentration of melt is 0.5 M; T = 25 °C.

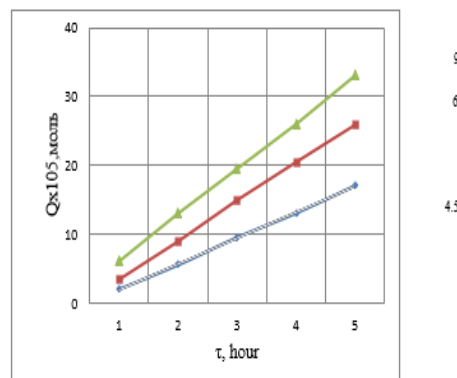


Figure 4. Kinetic dependencies of Ca(NO₃)₂ quantities transported through PA membranes with a pore radius of 4.5-9 Nm. The concentration of melt is 0.5 M; T = 25 °C.

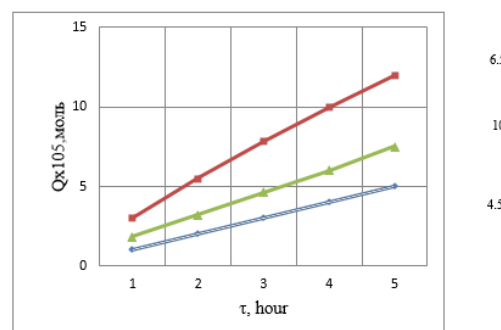


Figure 5. Kinetic dependencies of CaSO₄ quantities transported through PA membranes with a pore radius of 4.5-10 nm. The concentration of melt is 0.5 M; T = 25 °C.

Numerical values of salt diffusion coefficients calculated according to equation (1) are given in table 1.

Table 1. Diffusion coefficients CaCl, Ca(NO₃)₂ and CaSO₄ in PA-membranes with increasing radius pores

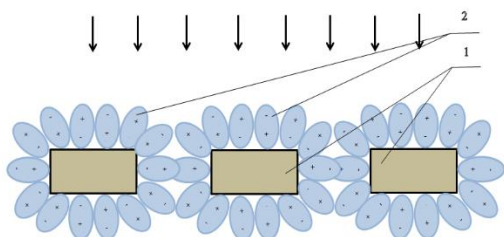
r _p , nm	D 10 ⁶ , cm ² /s	Ca(NO ₃) ₂	CaSO ₄
4.5	2.7060	1.7810	0.6220
6.5	3.6530	2.0640	1.0180
10	4.6440	2.5230	1.4990

First, let's compare the coefficient sizes. In a wide range of pore radii, there is an immediate decrease in the mobility of salts in the order CaCl₂>Ca(NO₃)₂>CaSO₄. The lack of reliable data on diffusion in solutions does not allow comparison of the obtained values of D_c measurements for bulk solutions. In addition, the analysis of available data for aqueous solutions of alkali metal salts [15-18] generally corresponds to the established sequence. The decrease in mobility of nitrates compared to chlorides can be attributed to the increase in anion size, and the low D values of calcium sulfate suggest that the larger divalent anions are more diffusion-limiting than the divalent anions.



In this regard, there is a reason to believe that the type of dependence of $D(rn)$ is related to the limitation of diffusion of ions at the boundary, which has changed compared to the volume and layers of solutions in the membranes. It is difficult to carefully "encrypt" this thesis of common nature, which basically lies in the structuring of water on the polymer surface and the limitation of the mobility of hydrated ions associated with it. The formation of networks of intermolecular hydrogen bonds under the influence of surface forces determines the increase in the viscosity of boundary layers. There is reason to believe that bound water is characterized by a reduced solvent capacity [19-21]: one of the most important reasons for this may be a sudden decrease in its dielectric conductivity (caused by limited motion) [4,8], as a result of which ions dissolved in water are energetically ineffective in its boundary layer. is located. The indicated factors are directly related to the reduction of the observed diffusion coefficient in pores of small radius.

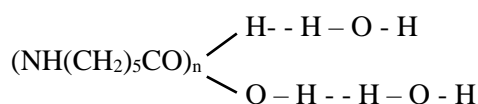
If we assume that the entire free volume of the polymer membrane is evenly distributed among all the structural fragments that make up the substance of the membrane, then we can introduce the concept of free volume per fragment (Figure 6).



1- Polymer membrane, 2 - water molecules

Figure 6. Arrangement of water molecules on the membrane surface

Hydrogen is present on the surface of PA membranes; upon contact with water, a hydrogen ion is formed:



For polymer membranes, the macromolecules of which are built from alternating fragments with a certain mobility, the free volume can be defined as the sum of the free volumes per each fragment of the structure:

$$\bar{V}_f = \sum_i N_i V_{if}$$

Where N_i - number of particles per unit volume.

The formula can also be written as [3]:

$$\bar{V}_f = \sum_i \varphi_i V_{if}$$

Where φ_i - volume fraction of fragments of macromolecules that make up the membrane in its matrix.

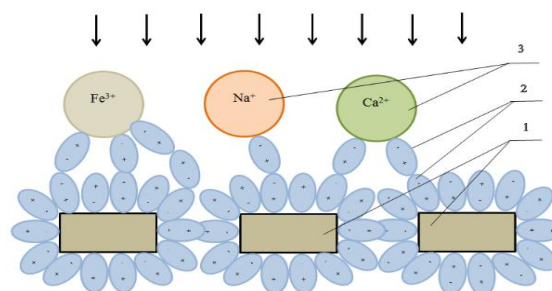
The specific free volume determined in this way per one structural fragment depends on temperature, pressure and the chemical nature of both the polymer substance of the membrane itself and the nature of the substance diffusing in it.

When describing the influence of the molecular weight of the membrane substance on the diffusion properties of the matrix that determines the structure of the membrane, the issues of the formation of the internal structure in the contact zones of macromolecules at the internal and terminal sections of the polymer chains must be separated.

It is known that there are two main ways of organizing macromolecules in the polymer matrix of a membrane [3, 6-11]. In the first case, the ends of the polymer chains are free, and in the second case they are "cross-linked".

Let us consider the case of free ends of polymer chains in the matrix. As follows from statistical physics, in this case the thermal motion of the free end fragments of the polymer chains of the membrane matrix can be considered as undergoing thermal motion in relative independence from the thermal motion of the main part of the chains.

Then suppose that the type of connection of the terminal fragments with the main part of the chain can be defined as a hydrogen connection with salt ions (Figure 7).



1 - membranes, 2 - water molecules, 3 - ion elements.

Figure 7. Arrangement of water molecules and element ions on the membrane surface.

The effectiveness of membrane filtration is determined by comparing the values of the diffusion coefficients of the separated or extracted components of solutions [9; 12]. After substances are dissolved in water, hydration shells are formed around their particles: ions,



molecules, small associates, micelles (large associates). Those. all particles (with rare exceptions), being charged, tend to attract and orient the dipole water molecules around them, i.e. distort or even destroy the original structure of water. The extent to which this tendency occurs depends on the size of the charge and the configuration of the particle. In this case, a two-layer hydration shell appears around the ions, polar molecules and micelles, consisting of a dense layer of oriented water molecules and a loose layer of semi-oriented water molecules. The dense layer of the hydration shell can be considered to consist of water clusters interconnected by hydrogen bonds, the structure of which is specific depending on the nature of the hydrated particle. This layer is quite strong, strictly ordered under the influence of an electric field, and the water molecules in this layer are, as it were, "frozen." During the electrolysis process, it moves along with the ion. An approximate calculation for solutions with a relatively low concentration (0.1-0.5 M) gives the size of the secondary hydration shell 1.5-2.0 nm (15-20 Å), which is comparable to the pore sizes of semi-permeable PA membranes. The thickness of the layer is determined by the charge density of the ion (particle), i.e.

the ratio of the charge of an ion (particle) to its diameter. The average lifetime of water molecules in a hydration shell depends on the nature of the particle, the concentration of dissolved substances and temperature. The boundary condition for the emergence of such a system (i.e., the concentration of the electrolyte in the solution) was usually called the boundary of complete hydration of an aqueous solution (HHG). For different electrolytes, this concentration ranges from 2.14 to 4.63 mol/l.

After experimental tests, the surfaces of the PA membranes were examined for the content and location of the elemental composition of the concentrate using a scanning electron microscope (SEM) (Figure 8).

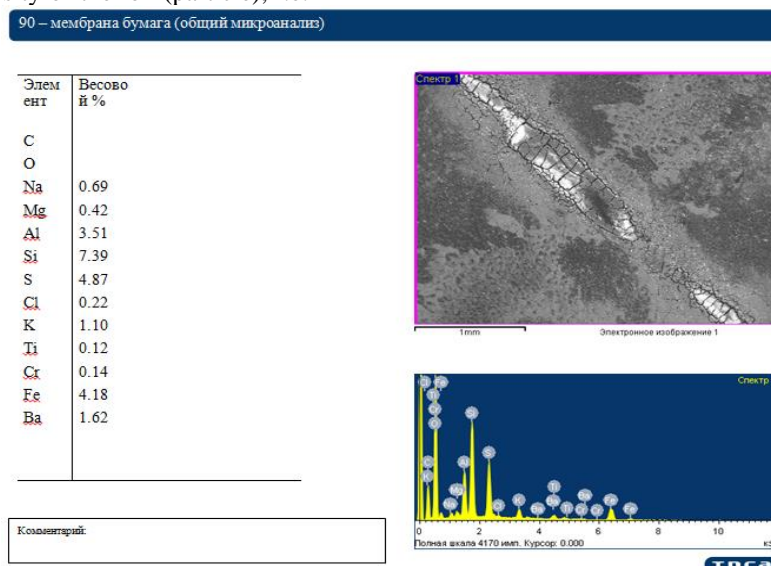
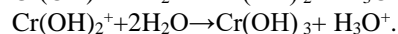
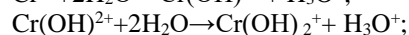
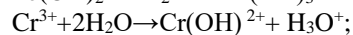
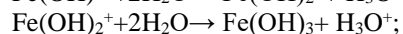
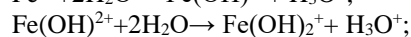
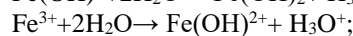
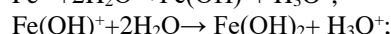
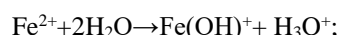
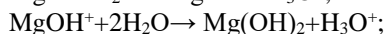
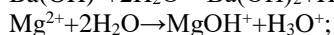
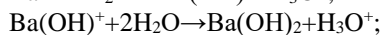
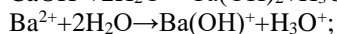
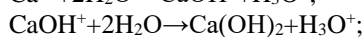
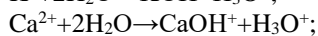
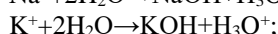
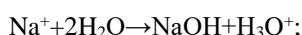


Figure 8. Content and location of the elemental composition of the PA membrane surface concentrate

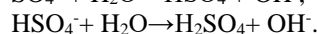
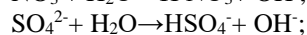
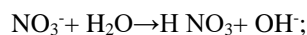
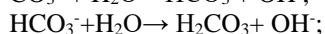
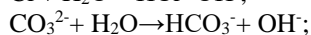
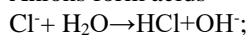
When cations and anions of salts contained in water interact, the following reactions occur:

1) Cations form Hydroxides





2) Anions form acids



It is almost impossible to unambiguously establish the form of existence of particles and their quantitative ratio in aqueous solutions [5]. In the pH region = 6-7, the co-presence of the main charged forms of salt ions is assumed. To prevent precipitation of larger forms, it is necessary to work with solutions diluted in ions in the presence of background electrolytes, which, unfortunately, does not meet the conditions of membrane filtration experiments we accepted. In this regard, we limited ourselves to studying the diffusion of aqueous solutions of salt ions with pH = 6-7, counting on the manifestation in the mass transfer parameters of partial (caused by an increase in pH) di/trimerization of ions, which should be accompanied by a decrease in the measured diffusion coefficient. Thus, based on the results of studying diffusion in membranes, one can judge the possibility of structural transitions in transported systems.

In this work, problems related to the qualitative description and quantitative determination of the parameters of diffusion transport of solutions of salt ions in

polymer membranes, taking into account the pore sizes of the membranes and the pH of the solutions, were solved.

It should be noted, however, that the values of the diffusion coefficients of salt ions in membranes with pore radii from 5 to 8 nm at pH = 6.5-7.5 are generally comparable for salt ions.

In practice, the most widely used methods for cleaning the surface of semi-permeable membranes and restoring their properties are chemical methods, which involve treating the membranes and washing the devices with solutions of various reagents. The effectiveness of such methods is due to the correct selection of the reagent. When choosing a substance for washing the apparatus, it is necessary to know the structure and composition of the contaminants that should be removed, and also take into account the resistance of the membranes in solutions of this substance.

The main technological solutions used for chemical cleaning of membranes are shown in Table 2 [2].

Table 2 Chemical membrane cleaning

Types of Membrane Fouling	Chemical cleaner	Cleaning efficiency
1	2	3
Inorganic salts: calcium carbonate and sulfate (hardness salts)	0.5% hydrochloric acid solution (pH<2.3); 0.5% phosphoric acid solution (pH<2.3); 2.0% citric acid solution	Very good Satisfactorily Satisfactorily
Hydroxides are heavier-bare metals (iron and manganese)	0.5% phosphoric acid solution (pH<2.3); 1.0% sodium hydrosulfite solution	Fine Fine
1	2	3
Inorganic colloids (silt)	0.1% sodium hydroxide solution, 30°C (pH>11); 0.025% sodium dodecyl sulfate solution; 0.1% sodium hydroxide solution, 30°C (pH>11)	Fine Fine Fine
Biological contaminants	0.1% sodium hydroxide solution, 30°C (pH>11); 1.0% solution of sodium salt of ethylenediamine tetraacetic acid (1ChGa2EDTA); 0.1% sodium hydroxide solution, 30°C	Very good It's very good when it also contains inorganic particles
Organic pollution	0.025% sodium dodecyl sulfate solution; 0.1% sodium hydroxide solution, 30°C (pH>11); 0.1% sodium triphosphate solution; 1% solution No. 2ED TA	Fine Fine Fine Fine



<i>Silicic acid</i>	<i>0.1% sodium hydroxide solution, 30°C (pH>11); 1.0% solution No. 2ED TA and 0.1% sodium hydroxide solution, 30°C</i>	<i>Satisfactorily</i> <i>Satisfactorily</i>
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During long-term operation of reverse osmosis devices, the pH value in the retentate circuit should be > 4 . The maximum exposure time to a washing solution with a pH from 2.3 to 4.0 during the operating life of the device should not exceed 100 hours. When using washing solutions with pH from 11.0 to 11.9, the maximum time of exposure of the solution to the membranes is limited to 500 hours for the entire period of operation of the reverse osmosis elements [2].

There is a similarity to the processes of accumulation of deposits on the surface of membranes in reverse osmosis devices.

In reverse osmosis devices in the circuit of retentate calcium-carbonate reaction equilibrium



shifts to the right side due to the non-selectivity of membranes with respect to CO_2 . This leads to both supersaturation of the solution with respect to calcium carbonate, its deposition on the membrane surface, and an increase in the pH of the solution in the retentate circuit. The latter causes the deposition of metal hydroxides (iron, manganese, aluminum, etc.) on the membrane surface.

The results of analyzes of raw water (well collector) of the pilot test revealed the following salt ions presented in Table 3.

Table 3. The results of analyzes of raw water (well collector) of the pilot test revealed the following salt ions

ANIONS			CATIONS		
	mEq/l	mg/l		mEq/l	mg/l
HCO_3	4,8	292,89	Ca	4,5	90,18
Cl	0,56	20	Mg	2,0	24,32
SO_4	1,87	90	Na	0,76	17,48
NO_2	----	----	Fe		0,074
NO_3	0,03	2,4	pH	7,5	
Humates	0,1				
SiO_2	0,55	16,5			0,005
PO_4	0,025	2,4	Suspended solids		0.2
C/C		410.2			
Oxidability		0.32			
CO_2		6.6			

During the operation of membrane plants, there is a gradual decrease in their productivity and selectivity, due to contamination of the membranes by deposits of poorly soluble salts and microparticles formed on the surface [3-5]. Dense deposits on the surface of the membranes create a barrier that prevents the supply of treated water to the semi-permeable membrane, reducing the filtering surface and leading to a decrease in membrane performance. When the membrane surface is contaminated, the pressure in the apparatus increases, and concentration polarization intensively develops, since the thickness of the boundary layer increases by the

thickness of the sediment. Contaminants formed in reverse osmosis devices may also include corrosion products of metal pipelines, fittings and other elements of installations (compounds of iron, copper, nickel, etc.).

The rate of formation and the nature of contamination of semi-permeable membranes are largely determined by the hydrodynamic conditions in the apparatus. An increase in the concentration of all ions near the membrane surface compared to their concentration in the bulk of the solution accelerates the process of supersaturation of solutions with poorly



soluble compounds. Contamination of the apparatus affects the uniformity of solution distribution in the pressure chamber and, as a consequence, the salt retention of semi-permeable membranes. Unevenness in the movement of liquid along the pressure channel, due to imperfections in the design of the installation or technological deviations in its manufacture, can also cause intense contamination of semi-permeable membranes and their permeability. One of the types of occurrence of uneven distribution of flows is that in a very narrow (for example, 0.02mm) channel even insignificant (about 0.01mm) the misalignment causes a significant redistribution of the flow along the membrane. A stagnant zone is formed, in which favorable conditions for sedimentation are created. In the

extreme case, the flow redistribution can be so significant that the salt content of the filtrate coming from stagnant zones is equal to the salt content of the treated water. Another type of uneven distribution of the flow of desalted water is the difference in flow rate through parallel-connected devices or chambers of filter-press devices. This unevenness may be due to defects in the design of the apparatus or deficiencies in the manufacture and adjustment of the desalting installation.

After experimental tests, the surfaces of the PA membranes were examined for the content and location of the elemental composition of the concentrate using a (SEM) scanning electron microscope (Figure 9).

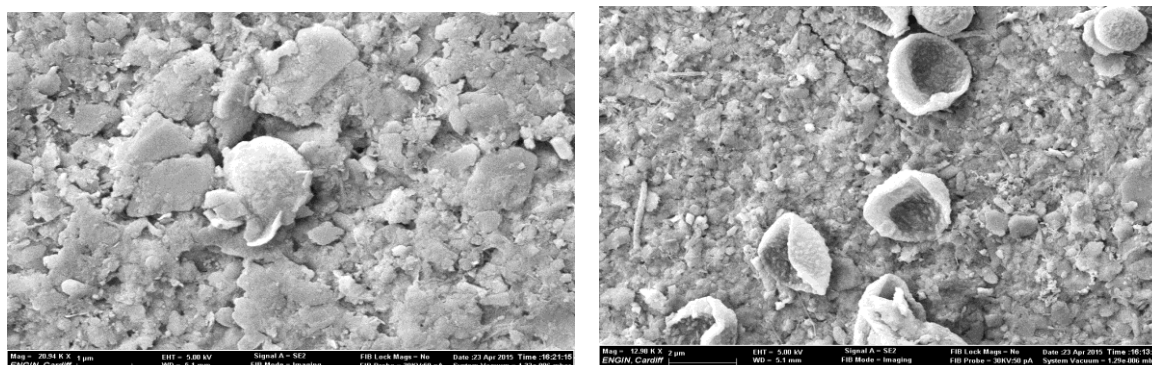
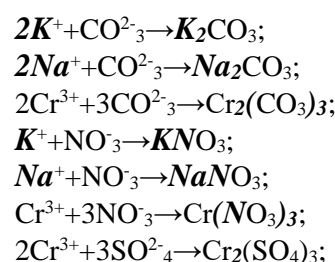
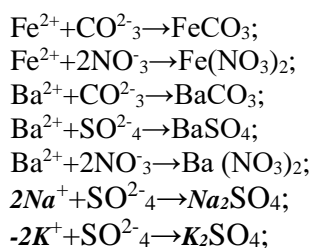
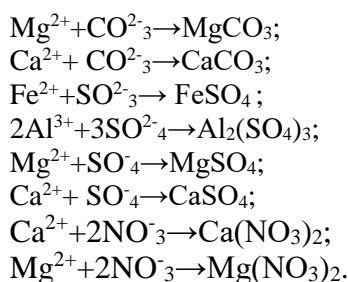


Figure 9. Location of the elemental composition of the concentrate on the surface of PA membranes

Contamination of the pressure channel in some cases can lead to failure of the reverse osmosis device. Thus, contamination of the devices affects almost all elements and processes occurring during the desalination of water by reverse osmosis, ultimately causing a decrease in the useful performance of the devices and a deterioration in

the quality of the permeate, while forming the following salts on the surface of the membranes below:



When filtering under pressure, both the structure of the membrane changes due to its deformation and the individual pores of the membrane become clogged with water molecules. The set of all processes associated with membrane deformation (changes in membrane structure, fluidity of the polymer matrix, decrease in membrane thickness, etc.) under the influence of pressure is called

membrane creep. Due to the fact that hydraulic resistance increases during creep, this process is to a certain extent accompanied by a decrease in membrane selectivity. However, creep manifests itself most strongly in a drop in performance.



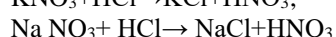
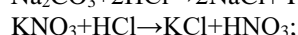
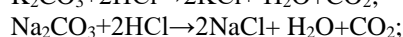
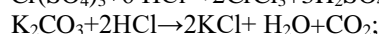
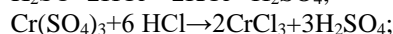
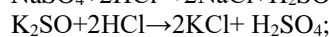
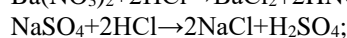
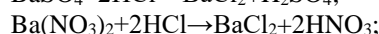
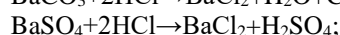
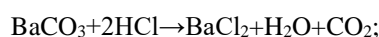
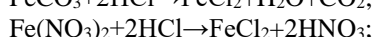
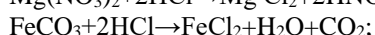
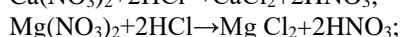
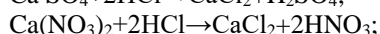
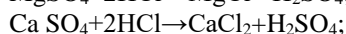
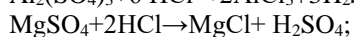
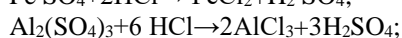
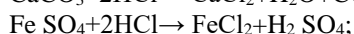
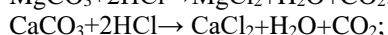
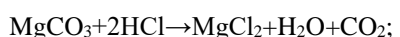
For cellulose acetate membranes, with increasing temperature, permeability initially increases in inverse proportion to the viscosity of the liquid. Then the permeability decreases and drops to zero at a temperature of approximately 85°C. This effect can only be explained by shrinkage and complete contraction of the membrane pores during the process of polymer structuring, which ends at the specified temperature, which is confirmed, in particular, by the irreversible change in the properties of these membranes after operation at temperatures above 50°C. The selectivity of cellulose acetate membranes first increases with increasing temperature and then remains approximately constant.

When demineralizing natural waters, reverse osmosis devices are usually not used when the salinity of the treated water is more than 50g/l (taking into account concentration in reverse osmosis devices), and the pH of the water remains in the range from 5.5 (with preliminary acidification) to 8.5. In such solutions, almost all industrially produced reverse osmosis membranes are chemically resistant. The most common in our country are membranes made of cellulose acetate, which can work stably when desalting water with pH values = 5-8. In a more acidic environment, cellulose acetate undergoes hydrolysis, and in an alkaline environment, it

undergoes saponification. Membranes made of aromatic polyamide are much more resistant in acidic and alkaline environments. They can work for a long time without changing their properties in the pH range from 2 to 11. It must be taken into account that cellulose acetate membranes are unstable in the environment of such polar organic solvents as acetone, dimethylformamide, etc. Membranes made of aromatic polyamides allow desalting water while simultaneously significantly concentrating salts

To restore the original performance of the membrane filter, chemical regeneration (washing) of membrane filters with special acidic and alkaline reagents must be carried out several times a year to remove accumulated contaminants.

To wash membrane filters, you can use plain water, a solution of Trilon B (chelating reagent), citric acid or 1% hydrochloric acid. The frequency of regeneration (washing) of the membrane filter is determined by the degree of contamination of the source water. To regenerate the surface of polyamide membranes, we used 1% hydrochloric acid and obtained the following reaction below.



Conclusions

Many years of experience in operating a large number of desalination stations have shown that with the correct choice of technological scheme and modes of water preparation before desalination, reverse osmosis devices remain operational for more than 5 years. It should be borne in mind that reliable operation of installations for many years can only be achieved if the entire set of operating requirements is met.

If the interval between membrane regeneration operations is incorrectly selected, their efficiency decreases, and changes in membrane characteristics may be irreversible. The duration of the inter-regeneration period depends on the composition of the source water and the technology of its preparation before reverse osmosis. The quality of water treatment is considered

good if the stability of the desalting apparatus is achieved by periodically washing it no more than once a month.

1. The analogy of the conditions for the formation of deposits in reverse osmosis devices is substantiated.

2. The use of periodic regeneration of the membrane surface from deposits ensures the preservation of stable performance of reverse osmosis units.

3. Technologies for membrane regeneration from deposits using chemical reagents have been identified.

The identified features of the diffusion of salt ions in PA membranes (the exponential dependence of the diffusion coefficient on the radius of the membrane pores, the pH value) and the comparison of the obtained data with the available salts make it possible to determine the prospects and conditions for their separation in PA membranes.



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Conflict of Interest

The authors declare no conflict of interest.

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