Development of Resource-Saving Technologies in the Use of Sedimentation Inhibitors for Reverse Osmosis Installations

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ABSTRACT
The processes of desalination of weakly mineralized waters using a reverse osmosis membrane were studied. The operational efficiency of membranes is limited mainly by membrane contamination. It was shown that the preliminary mechanical water purification helps to increase the productivity and selectivity of the membrane. One of the main causes of membrane contamination is the formation of carbonate deposits on their surface. One way to prevent membrane contamination is to dose antiscalants. It was established that the use of hydrolyzed polyacrylonitrile (HPAN) and hydrolyzed polyacrylamide (HPAA) as a stabilizer of scale formation is effective for concentrates of reverse osmosis desalination of water.

Keywords: reverse osmosis, concentrate, membrane, permeate, productivity, selectivity, antiscalant.

INTRODUCTION
Recently, in industrial densely populated areas, the problem of water pollution and a sharp increase in water mineralization of surface waters has become more acute (Biggs et al. 2015, Radovenchyk et al. 2021, Trus et al. 2017). This is caused by the discharge of mine and industrial wastewater, as well as effluents from thermal power plants (DiGiulio et al. 2015, Abualhaija and Mohammad 2021, Trus and Gomelya 2021). Today, the most highly efficient technologies for water desalination include baromembrane processes (Cohen et al. 2017, Ashfaq et al. 2019, Trus and Gomelya 2021). Reverse osmosis units provide high and guaranteed stable cleaning quality throughout the operation (Miller et al. 2015). The main task today is to achieve the maximum service life of membrane elements. The service life of membranes is determined mainly by the drop in their productivity, and the operational efficiency of membrane water treatment systems is limited mainly by their pollution degree (Da’na et al. 2020, Kucera et al. 2019, Yelemanova et al. 2021).

At present, in water-deficient industrial regions, highly mineralized waters with high hardness are used in cooling systems (Filloux et al. 2015, Croué et al. 2013, Sweity et al. 2013, Trus et al. 2020). These waters are not suitable for use in cooling systems without special treatment (Yelemanova et al. 2021, Remeshevska et al. 2021, Trus et al. 2019). The use of effective stabilizers allows abandoning expensive water softening and deaeration systems, as well as ensuring long-term operation of heat exchange equipment. Despite the large number of studies, the stabilization of such waters to sediments is not a sufficiently explored question (Popov et al. 2019, Ang et al. 2016, Khan et al. 2013). The main factor limiting the widespread use of reverse osmosis (RO) installations in drinking water production and industrial water treatment
is the scaling of sparingly soluble salts (Golovesov et al. 2021, Chaussemier et al. 2015, Shemer et al. 2013).

In order to reduce the scale of gypsum and silicon dioxide, it is necessary to use antiscalants with different functionalities, so when cleaning wastewater containing different types of scale, it is important to select a reagent that provides maximum effect (Yin et al. 2021, Pramanik et al. 2017, Rashed et al. 2016, Mi and Elimelech 2013).

Phosphonate antiscalants are widely used in the processes of reverse osmosis desalination of water to prevent scale formation and improve the quality of purified water. In reverse osmosis desalination of groundwater at a sampling rate of 85% (Ca\(^{2+}\) = 765 mg/L, PO\(_4^{3-}\) = 13–15 mg/L and pH = 7.6), various antiscalants were used to inhibit the formation of calcium phosphate. (Mangal et al. 2021). However, it is desirable to remove them before disposing of the RO concentrate, as the presence of phosphonate antiscalants can prevent the removal of hardness from the concentrates and affect the ecosystem. A highly effective magnetic adsorbent (magnetic La/Zn/Fe3O4@PAC composite) can be used to remove the phosphonate antiscalant (Li, C. et al. 2021).

In (He et al. 2009) it was shown that the K752 antiscalant can significantly extend the induction period for the gypsum nucleation, while the GHR antiscalant extends the induction period for calcite nucleation; even at a dosage of only 0.6 mg/L, they slow down the rate of crystal deposition. In (Qiang et al. 2013) it was shown that scale inhibitor was prepared by modified chrome shavings hydrolyzing collagen and the scale inhibitor had good ability on calcium carbonate scale inhibition.

The efficacy of scale inhibitors for a reverse osmosis desalination plant has been developed and evaluated (Chesters et al. 2009, Pervov & Andrianov 2017). Adding antiscalants into the solution slows down the scale on the membrane, as evidenced by membrane flux, morphology and layer thickness (Chen et al. 2021).

Management of scale formation can be achieved at the design stage by the inclusion of unit processes to the scale forming constituents or by the application of the antiscalants that delay the onset of nucleation (Antony et al. 2011).

The developed methods of softening of a scale deposit mainly do not depend on membrane materials, whereas expediency of creation of the scale-resistant membranes is specified but is not reached in full in the literature. Accordingly, potential design strategies and issues related to the development of new membrane materials with improved scale resistance are discussed, and future research needs are proposed (Tong et al. 2019).

Modification of the membrane surface and development of a new material can be an effective strategy to reduce the scaling of the membrane (Baoxia et al. 2010, Du et al. 2018, Kang et al. 2012). The methodology for predicting scaling by membrane distillation (MD), which considers the thermodynamics, kinetics and mechanics of the liquid, was developed and experimentally confirmed using calcium sulfate (Rahman 2013, Warsinger et al. 2017, Kavitskaya et al. 2000).

This review describes in detail the various contaminants and contamination mechanisms in the membrane distillation process, their possible mitigation and control methods, and characterization strategies that can help in understanding and minimizing the contamination problem (Tijing et al. 2015, Litynska et al. 2019). Despite the significant amount of research and publications, the development of effective scale stabilizers is very important and relevant.

Thus, the development of methods for effective stabilization water treatment will reduce corrosion and scale formation in heat exchange equipment, as well as allows switching to closed systems of water consumption and rational use of water (Gomelya et al. 2020, Vorobyova et al. 2019). The development of scientific bases of resource-saving technologies will increase the level of ecological safety of objects, region and country.

**MATERIALS AND METHODS**

The processes were studied using a Filmtec TW30-1812-50 low pressure reverse osmosis membrane cassette. A low-mineralized solution, similar in composition to the water from Toretsk: (H = 10.3 mg-eq/dm\(^3\), C (Ca\(^{2+}\)) = 3.4 mg-eq/dm\(^3\), C (Mg\(^{2+}\)) = 6.9 mg-eq/dm\(^3\), L = 4.6 mg-eq/dm\(^3\), C (SO\(_4^{2-}\)) = 15.0 mg-eq/dm\(^3\), C (Cl\(^-\)) = 3.1 mg-eq/dm\(^3\), pH = 8.47) was used as a medium. After filtering the solution, the turbidity decreased from 50.0 mg/dm\(^2\) to 0.0 mg/dm\(^2\); chromaticity - from 90.0 degrees Pt/Co up to 22.0 degrees Pt/Co.

The process of reverse osmosis desalination of water was carried out using 10 dm\(^3\) of model solution. By means of a pump, water was fed into a cassette with a reversed osmosis membrane. The concentrate was returned to the container.
with the initial solution, the permeate was taken in a separate container. The pressure in the system was maintained by a valve that regulates the selection of concentrate. After sampling each dm$^3$ of purified solution, the permeate and concentrate were analyzed for chlorides, sulfates, hardness ions and alkalinity was determined. The degree of permeate selection was varied from 10 to 90%. Sulfates were determined by using the photometric method, chlorides with the Moore method, whereas alkalinity and hardness by means standard methods.

Membrane performance (transmembrane flow rate) was determined by the formula:

$$J = \frac{\Delta V}{S \cdot \Delta t}$$

where: $\Delta V$ is the volume of permeate (dm$^3$) that passed through the membrane with area $S$ (m$^2$) during the sampling $\Delta t$ (h).

When conducting the studies to assess the effectiveness of scale stabilizers a thermostat was used. The samples of 100 ml were kept at a temperature of 60 °C for 6 hours. The choice of temperature is due to the fact that real water circulation systems operate at a temperature of 40–60 °C. As inhibitors were used hydrolyzed polyacrylamide (HPAA) after ozonation of its 5% solution for 1 hour, hydrolyzed polyacrylonitrile (HPAN) after ozonation of 5% solution for 1 hour and HPAN after sonication of 1% solution for 20 minutes. Improvement of the efficiency of reagents is achieved by ozonation or physical modification with low-frequency sound waves (USB). Doses of these reagents were 0.5–15.0 mg/dm$^3$. After cooling, the samples were filtered, and the residual water hardness was determined.

The stabilizing effect was calculated by the formula:

$$SE = \left( 1 - \frac{\Delta H_i}{\Delta H} \right) \cdot 100\%$$

where: $H$, $\Delta H$ – hardness in the experiment with a scale inhibitor, mg-eq/dm$^3$; $H_{res}$ – residual hardness in the blank, mg-eq/dm$^3$; $H_i$ – residual hardness in the sample with a stabilizer, mg-eq/dm$^3$.

RESULTS AND DISCUSSION

Improving the quality of used water reduces its discharge to purge systems, which reduces the water intake from natural sources and discharge of mineralized water into reservoirs, which leads to their pollution. Development of effective scale stabilizers allows developing the resource-saving technologies of water use.

The methods of combating salt deposits are aimed at preventing the loss of salts or removing the formed salt deposits (Amjad and Demadis 2015, Chauhan et al. 2015). The classification of these methods is presented in Figure 1.

There are several impurities that significantly reduce the service life of membranes (Rueengruehan et al. 2020, Gomelya et al. 2014). The first group includes insoluble solids, suspended and colloidal particles. The second group includes the compounds, the presence of which in water leads to the formation of solid inclusions (Kassymbekov et al. 2021, Sevostianov et al. 2021). It is possible to remove the substances belonging to the first group at the expense of mechanical methods, besides preliminary clarification of water on the filter leads to increase in productivity of a membrane (Polyakov et al. 2019). When filtering the model solution at a pressure of 0.3 MPa, the productivity of the installation decreases gradually (Fig. 2, Table 1) as the mineralization of the concentrate increases with increasing degree of selection of permeate. Pre-clarification of water (curve 2) leads to an increase in installation productivity and has little effect on its selectivity for chlorides, sulfates, hardness ions and hydrocarbons.

In this case, the decrease in membrane productivity with increasing degree of permeate selection is due to the increase in osmotic pressure along with the salt content in the concentrate. However, in general, the decrease in the productivity of membrane installations by 95–97% is determined by the contamination of the membrane surface and only by 3–5% by the compaction of their capillary-porous structure. Fundamentally dangerous compounds that promote
sedimentation on membranes include hardness salts – compounds of calcium and magnesium in the form of carbonates, bicarbonates and sulfates (Sharma et al. 2020). One of the promising ways to prevent membrane contamination is the adding of antiscalant (sedimentation inhibitor).

Since under the actual conditions at room temperature, the carbonate deposits on the membrane are formed rather slowly, the effectiveness of antiscalants was assessed using the express method. It was based on determining the stability of concentrates of reverse osmosis water purification.

Figure 1. Classification of methods of combating salt deposits

Figure 2. The dependence of the performance of the reverse osmosis filter on the degree of selection of permeate during desalination of the model solution
Studies were performed in the presence of an antiscalant and without an antiscalant. During the desalination of the model solution at a sampling rate of ~80%, a concentrate is formed with the following characteristics: H = 50.0 mg-eq/dm$^3$, A$^2$ = 23.0 mg-eq/dm$^3$, SO$_4^{2-}$ = 75.0 mg-eq/dm$^3$, Cl$^-$ = 15.0 mg-eq/dm$^3$, pH = 8.71.

The use of highly mineralized waters leads to intensive sedimentation, especially at elevated temperatures, resulting in the failure of pipelines and equipment. Therefore, it is necessary to use sediment inhibitors.

The effectiveness of scale inhibitors depends on the quality of the source water. This water is unstable to scaling, because when heated, the hardness decreases from 50 to 38 mg-eq/dm$^3$ at a temperature of 60 °C.

If the polyphosphates are used long-term, the hydrolysis to orthophosphates occurs. As a result of this polyphosphates lose their activity. In addition, phosphorus is a biogenic element that leads to increased biofouling in buildings and communications. HPAN is a stable substance, so it does not decompose chemically in water at temperatures in the range of 0–100 °C. This reagent is an effective inhibitor of scaling of highly mineralized waters at temperatures up to 100 °C when used in concentrations of 0.5–15 mg/dm$^3$.

Evaluation of the effectiveness of sediment inhibitors was carried out by changing the hardness of mineralized water when heated to a temperature of 60 °C in the presence of inhibitors. The results are shown in Tables 2, 3.

The stabilizing effect of HPAN and HPAA without treatment in highly mineralized waters at a dose of 1–15 mg/dm$^3$ is 39–43%. Ultrasonic or ozonation treatment of these reagents can increase the stabilizing and anti-scale effects.

As it can be seen from Table 3, the HPAN in concentrations of 0.5–5.0 mg/dm$^3$ appeared ineffective; however, an increase of a dose to 5–15 mg/dm$^3$ showed rather high stability of water in relation to scaling.

The stabilizing effect when using HPAA reached 16.7% at a dose of 1 mg/dm$^3$ and 45.8% at a dose of 2 mg/dm$^3$. When increasing the dose of HPAA to 5.0 mg/dm$^3$, this inhibitor provided 100% water stability (Fig. 3).

HPAN at a concentration of 5 mg/dm$^3$ for highly mineralized waters provides a stabilizing effect of 99.8%, and the anti-scale effect of 99.2% (Fig. 4). Therefore, the obtained results indicate the potential of the selected reagents as stabilizers of scale formation.

<table>
<thead>
<tr>
<th>Z, %</th>
<th>R, %</th>
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<tr>
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<tr>
<td>20</td>
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Table 1. Dependence of membrane selectivity on the degree of permeate selection during filtration of model solution (I) and solution after filtration (II)

<table>
<thead>
<tr>
<th>Доза, мг/дм$^3$</th>
<th>N, mg-eq/dm$^3$</th>
<th>H$_{max}$, mg-eq/dm$^3$</th>
<th>ΔH, mg-eq/dm$^3$</th>
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<td>49.9</td>
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<td>99.2</td>
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</table>

Table 2. The dependence of the stability of the concentrate on the dose of HPAA after ozonation at 60 °C
CONCLUSIONS

It was established that pre-purification of the model solution before reverse osmosis desalination helps increase the productivity of the membrane and has little effect on its selectivity for chlorides, sulfates, hardness ions and bicarbonates. Evaluation of the efficiency of using HPAN and HPAA as a stabilizer of scale formation for concentrates of reverse osmotic desalination of water (highly mineralized waters) was performed. HPAA at a concentration of 5 mg/dm$^3$ for the waters with $H = 50$ mg-eq/dm$^3$ at $T = 60$ °C and $t = 6$ h provides a stabilizing effect at the level

<table>
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<tr>
<th>Доза, мг/дм$^3$</th>
<th>$H$, mg-eq/dm$^3$</th>
<th>$H_{res}$, mg-eq/dm$^3$</th>
<th>$\Delta H$, mg-eq/dm$^3$</th>
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<td>46.7</td>
<td>3.3</td>
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<td>47.1</td>
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<td>75.8</td>
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Figure 3. The effect of HPAA dose at 60 °C on water stability; 1 – anti-scale effect; 2 – stabilizing effect
of 37.5–50%, and the anti-scale effect at 85–88%. With increasing reagent concentration to 15 mg/dm$^3$, the anti-scale effect reaches 72.5–75.8% and the stabilizing effect 93.4–94.2%. Direct proportion of residual hardness to dose was found for HPAN. HPAN was shown to be a highly effective scale inhibitor at a dose of 5.0 mg/dm$^3$, with a stabilizing effect of 99.8%.

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