STUDY OF REVERSE OSMOSIS DESALINATION TECHNOLOGY FOR CASPIAN SEA WATER WITH PRELIMINARY NANOFILTRATION SOFTENING

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Abstract

The article presents the results of a study of the technology of reverse osmosis desalination of Caspian water with preliminary nanofiltration softening, carried out using the computer program "ROSA". At the NF stage, the possibilities of the most perfect membrane, NF90-400, were studied. To prevent carbonate scale formation, acidification with sulfuric acid was provided with a decrease in pH to 6,4÷6,6 and with control according to the Stif-Davis criterion. It has been established that when the permeate yield exceeds 55% of the initial water, precipitation of sulfate scale on the membranes is predicted, which, in accordance with the recommendations of the program, makes it necessary to increase the induction period for the crystallization of this salt by introducing antiscale. The possibility of reliable exclusion of the formation of calcium deposits on the membranes of the reverse osmosis stage is substantiated. It is shown that this purification system makes it possible to obtain additional water from the water of the Caspian Sea for heating networks and power boilers of thermal power plants with a pressure of up to 9,8 MPa inclusive. For boilers with a pressure of more than 13,4 MPa, additional cleaning is required in mixed-bed filters or electrodeionization modules.

Keywords: seawater, thermal power plants, desalination, reverse osmosis, nanofiltration, scale formation

1. Introduction

Desalination of saline water is an effective means of solving the problem of ever-increasing shortage of natural fresh water. Of the known desalination methods, the reverse osmosis (RO) method is currently the most widely used: up to 69.2 per cent of desalinated water. The shares of the other methods are: 17.1% - multistage instantaneous evaporation; 6.9% - multistage surface evaporation; 2% - electrodialysis; 1.9 - others [1]. This circumstance makes it urgent to further improve the RO method, including by developing more reliable ways to prevent scaling on membranes, compared to the currently practised methods. According to the publications of recent years, innovative ways of solving this problem include preliminary softening of saline water by nanofiltration (NF) method [2].

In [2] a review of the main works in the field of NF-RO technology integration is given. It follows from the review that most of the studies were carried out on the example of ocean water (35 g/dm^3). According to [3] this system allows desalination process at relatively low pressure (22 bar) compared to single-stage RO using SWRO brand membranes - (60 bar). As a result, the cost of desalinated water is reduced by 27%. High selectivity of nanofiltration membranes for divalent ions is noted: from 89.4% for Ca^{2+} to 97.8 - for SO_4^{2-}. The paper [4] presents data on reconstruction of the operating RO unit by connecting NF. It is shown that in this case the ocean water hardness is reduced to 220 mg/dm^3, which eliminates the danger of calcium deposits formation on RO membranes, allows increasing the desalinated water yield at this stage from 28% to 56% and reducing the power consumption from 9.6 kW·h/m^3 to 5.9 kW·h/m^3. According to [5], on the example of desalination of brackish water of one of Iranian cities, comparative studies of three purification technologies were carried out: nanofiltration with NF270 membrane, reverse osmosis with BW30 membrane and their hybridisation. It was found that the hybrid system requires fewer membrane elements than RO purification. The specific energy consumption is also reduced. The authors of the study [6] have studied the possibilities of NF-RO hybrid system on the example of water with salt content 28.2÷28.7 g/dm^3. It was found that under the traditional scheme of RO with BW-30 membranes and operating pressure of 30 bar it is possible to reduce the salt content of permeate to 3.13 g/dm^3, and under the hybrid scheme this index is reduced to 0.76 g/dm^3. It was recommended to use this water for soil irrigation.

The analysis of the above and a number of other publications shows that the efficiency of the NF-RO system depends to a large extent on the quality of the source water. Studies in this area were mainly empirical in nature. Therefore, quantitative regularities obtained on individual water types cannot be extrapolated to waters of arbitrary composition, including Caspian Sea water. The authors are not aware of any studies on NF-RO treatment of Caspian water, one of the peculiarities of which is a high potential of calcium sulphate deposits formation on membranes. Meanwhile, this technology is of great interest for the Caspian republics in terms of obtaining desalinated water for technical purposes, including supplementary water for thermal power plants (TPS).

The aim of the present research is to evaluate the efficiency of reverse osmosis desalination technology of Caspian Sea water with preliminary nanofiltration softening for the preparation of supplementary water for TPS.

II. Technological scheme of hybrid NF-RO desalination system and research methodology

The technological scheme of the investigated NF-RO desalination system is presented in Fig.1.

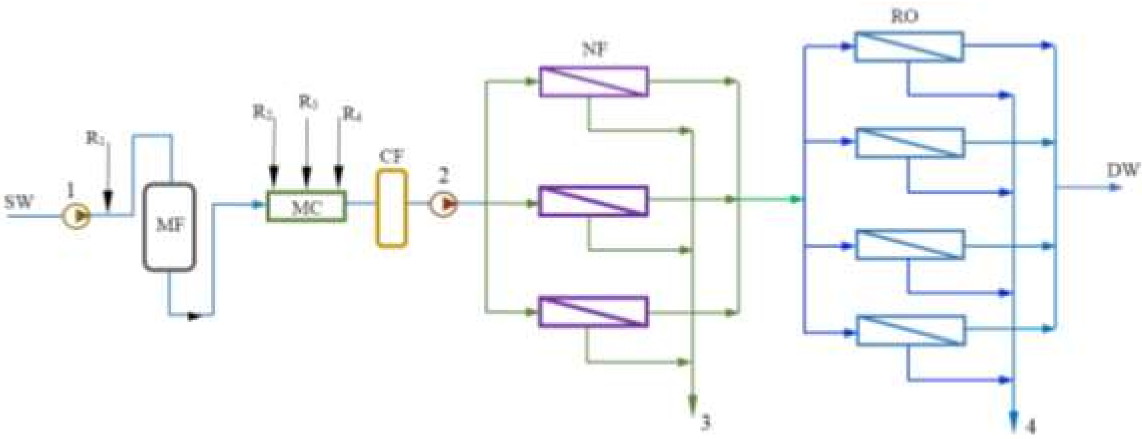


Figure 1: *Technological scheme of hybrid NF-RO seawater desalination system*
SW - sea water; MF - mechanical filter; MC - mixing chamber; CF - cartridge filter; DW - desalinated water; R_1-R_4- tanks for reagents; 1 and 2 - pumps; 3,4 – discharge concentrates.

According to this scheme seawater (SW) after preliminary treatment with sodium hypochlorite ($R_{1)}$ is fed by pump (1) to mechanical filter (MF) where it is cleaned from mechanical impurities. The clarified water enters the mixing chamber (SC), into which three reagents are fed: calcium sulphate solution (R_2), antiscale (R_3) and sodium bisulphide (R_4). The purpose of using each of these reagents is described in detail in the literature, in particular in [7]. The combined goal is to reduce the intensity of organic and calcium fouling on membranes.

After the mixing chamber, the water enters the cartridge filter (CF) with a mesh size of 5 μm for deep cleaning from mechanical impurities, then by a high-pressure pump (2) is fed to nanofiltration modules where it is divided into two streams: permeate passed through the membranes and residual concentrate (3). The latter is discharged or discharged to the wastewater tank of the power plant, and the permeate is fed to the RO modules, where it is also divided into two streams: permeate (desalinated water), used as a target product and concentrate (4). The latter can be discharged or, for reuse, fed to the high pressure pump intake (2).

The work was carried out on the example of Caspian water with qualitative indicators characteristic of the Apsheron coast of the Republic of Azerbaijan: pH=8.2 and ion concentration (mg/dm^3): $S_{Ca^{2+}}$=320.9; $S_{Mg^{2+}}$=729.9; S_{Na^+}=3174.9; S_{Na^+}=5034.3; $S_{SO_4^{2-}}$ =3264.0; $S_{HCO_3^-} = 244{,}0$; TDS = 12768.

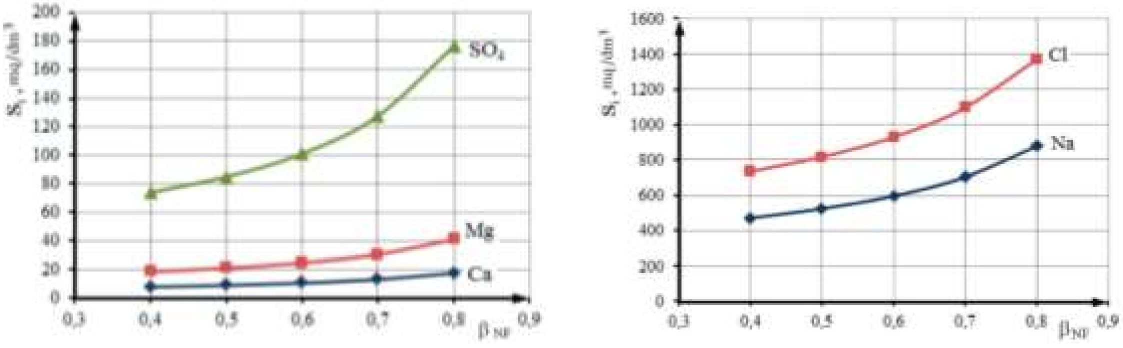
The calculation and analytical method of research with the use of the computer programme "ROSA" (Reverse Osmosis System Analysis) was used in the research. At the NF stage, the capabilities of the most perfect membrane, NF-90, included in the programme package were studied. To prevent carbonate scaling, acidification with sulphuric acid was envisaged with pH reduction to 5.4÷6.6 and control by Steef-Davis criterion. The values of permeate yield -β_{NF} (conversion, hydraulic efficiency), as well as temperature (10÷40^{0}C) were varied within 0.4÷0.8. In the RO stage, the capabilities of two types of membranes, BW30 and SWHR-380, were investigated. Temperature and permeate yield were also varied at this stage -$\beta_{RO.}$

III. Research results.

According to calculations at variation β_{NF} within 0.4÷0.8 there is a significant decrease in concentration of ions in NF permeate, and in the greatest degree - of scale-forming divalent ions. Thus, the concentration of calcium ions decreases to 8.1÷17.8 mg/dm^3, magnesium - to 18.8÷41.2 mg/dm^3, sulphates - to 74.1÷176.5 mg/dm^3 respectively with minimum and maximum values β_{NF}. The investigated membrane is characterised by lower values of selectivities on univalent ions Na^+ and Cl^- that causes relatively high residual concentrations of these ions in the NF permeate: on the average 630 and 920 mg/dm^3, respectively. The character of influence of β_{NF} on the residual concentrations of ions can be judged from the data of Fig. 2. These dependences are close to parabolic. Increase of ion concentrations with growth of β_{NF} is caused by corresponding decrease of concentrate fraction and increase of its salt content.

The result of the decrease in ion concentration is a significant decrease in the salt content of the permeate: from 1.3 to 2.5 g/dm^3, i.e., on average by 85%. Increase of NF leads in the specified range to approximately three times increase of osmotic pressure of concentrate, and working pressure from 12.5 to 21.1 bar.

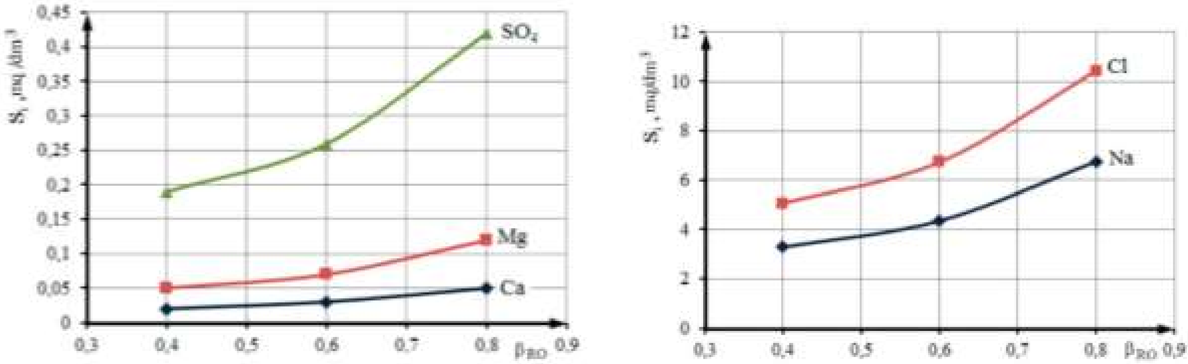
Such deep desalination of Caspian water on one stage of NF using NF-90 membranes creates real prerequisites for obtaining drinking water with salt content less than 1 g/dm^3 in two-stage plants. This issue is the subject of a separate study. As for power boilers of TPS, it is known that to ensure scale-free operation much deeper desalination of sea water is required, and in some cases - complete desalination. The latter is traditionally carried out in mixed action filters, and in modern technologies - in special electrodeionisation modules. To increase the efficiency of such finishing treatment, it is required to minimise the salt content in the source water, which can be achieved by reverse osmosis.



a) b)

Figure 2: *Effect of NF permeate yield on ion concentrations.*
a) for divalent ions; b) for monovalent ions.

At computer simulation of the RO stage, the conditions of feeding this stage with nanofiltration permeate with different values of β_{NF} were modelled. At the same time, the yield of permeate of the RO stage was varied - β_{RO}=0.4÷0.8. Fig.3 shows graphs of dependence of ion concentrations in permeate of OO stage at feeding with NF permeate corresponding to β_{NF} = 0.8.



a) b)

Figure 3: *Effect of the permeate yield of RO and on ion concentrations at β_{NF}=0.8.*
a) for divalent ions; b) for univalent ions.

As follows from the graphs, the character of dependences remains the same, the average concentrations of calcium, magnesium and sulphate ions are 30, 70 and 260 μg/dm³, respectively; sodium and chloride - 4.4 and 6.6 mg/dm³, and total salt content - 11.4 mg/dm³. At minimum acceptable conversion values equal to 0.4 the cation concentrations are 10, 20, 70 μg/dm³ and salt content is 3.9 mg/dm³ respectively.

The influence of permeate outputs on the salt content of the permeate and specific consumption of electrical energy can be judged from the data of Fig. 4.

As can be seen from the graph, the increase in outputs leads to an increase in the salt content of permeate RO from 3.9 to 8.2 mg/dm³, at β_{NF}=0.4 and from 8.8 to 18 mg/dm³, at β_{NF}=0.8. At the same time, increasing β_{RO} reduces energy consumption almost twofold: from 1.35 to 0.62 kW·h/m³ on average.

In the process of research it was found that at β_{NF}>0.55 precipitation of $CaSO_4$ is expected on NF membranes in connection with which the programme recommends the use of antiscaling. The possibility of precipitation of this salt on SO membranes is completely excluded at any values of β_{RO}: at the permissible degree of concentrate saturation <100%, the actual value of this indicator was less than 1%.

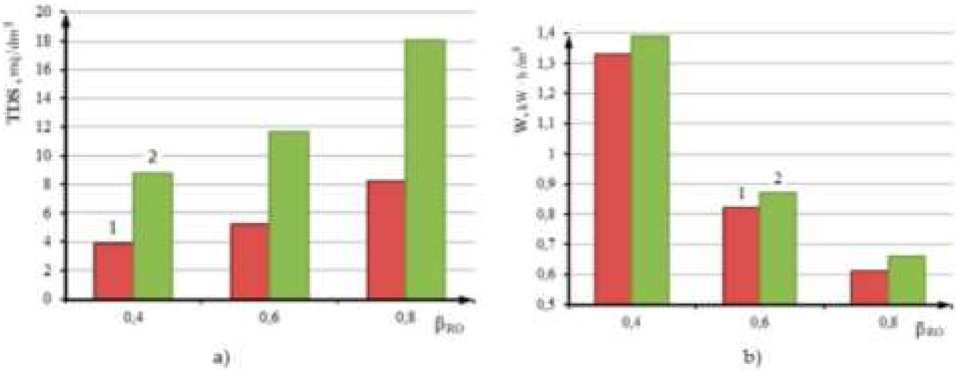


Figure 4: *Effect of RO permeate yield on its salt content (a) and specific energy consumption (b).*
(1-β_{NF}=0.4; 2-β_{NF}=0.8)

It is known, that at TPS treated water can be used as make-up water of heating networks and boiler make-up water of various parameters. Each of these systems imposes certain requirements to the quality of treated water. Comparison of these requirements with the quality of water obtained from the Caspian under the investigated scheme shows that the NF stage permeate can be used for heating network make-up water, as it is characterised by a very low value of carbonate index. Assuming the condition that the quality of boiler make-up water should be not worse than the quality of feed water, the permeate of the RO stage satisfies the norms of feed water quality for boilers with pressure up to 9.8 MPa inclusive. For boilers with pressure of 13.8 and 23 MPa the required quality is not provided by hardness and specific electrical conductivity.

Using more selective membranes SWHR-380 reduces calcium concentration to almost zero values, magnesium - to 8÷10 μg/dm^3. In other words, the limitations on hardness of supplementary water for boilers with pressure of 13.8 MPa are removed. However, salt content of permeate remains rather high: 2÷3 mg/dm^3, against standardised 0.15 mg/dm^3 according to TPS technical operation rules. Changing the temperature of treated water within the range of 10÷ 40^{0}C leads to a 5-6-fold increase in ion concentrations in the NF permeate and a 30 % decrease in specific power consumption, which is obviously explained by an increase in the membrane pore size (Table 1).

Table 1: *Effect of temperature on nanofiltration performance (β_{NF}=0.6)*

Indicators	t=10^{0}C	t=20^{0}C	t=40^{0}C
Ca, mg/dm^3	3,1	5,92	17,87
Mg, mg/dm^3	7,2	13,74	41,39
Na, mg/dm^3	189,7	344,7	875,89
Cl, mg/dm^3	295,6	537,52	1367,9
SO_4, mg/dm^3	27,9	53,38	162,9
HCO_3, mg/dm^3	5,0	9,1	25,61
TDS, mg/dm^3	528,6	964,4	2491,5
W, kWh/m^3	1,16	1,04	0,82

The character of temperature influence on the RO process parameters is similar regardless of the type of membrane used (Table 2).

It is noteworthy that despite the possibility of deeper purification, the use of high-pressure SW membranes is associated with a twofold increase in specific energy consumption.

Table 2: *Effect of temperature on reverse osmosis performance (β_{RO}=0.6)*

Indicators	t=10⁰C	t=20⁰C	t=40⁰C
Ca, mg/dm^3	0,01/0	0,02/0	0,05/0,01
Mg, mg/dm^3	0,02/0	0,04/0,01	0,12/0,02
Na, mg/dm^3	1,18/0,56	2,26/0,98	7,26/2,74
Cl, mg/dm^3	1,82/0,85	3,48/1,51	11,2/4,22
SO_4, mg/dm^3	0,06/0,01	0,12/0,01	0,39/0,04
HCO_3, mg/dm^3	0,13/0,12	0,15/0,12	0,27/0,15
TDS, mg/dm^3	3,23/1,54	6,06/2,64	19,2/7,19
W, kWh/m^3	1,52/3,96	1,01/2/57	0,53/1/33

Note: Numerator - BW; Denominator - SW.

However, even in this case the salt content of permeate considerably exceeds the permissible one for feeding boilers with pressure of 13.8 MPa and higher, i.e. there is still a need for additional additional desalting, for example, in mixed action filters, although there is a possibility to reduce the consumption of acid and alkali for regeneration of ionite mixture. In this connection the necessity of optimization studies is not excluded.

IV. Conclusions

1. Using the computer programme "ROSA" the conditions of preparation of additional water of TPS by reverse osmosis desalination of water of the Caspian Sea with preliminary nanofiltration softening excluding calcium deposits on membranes of the reverse osmosis stage are established. On the example of NF-90 membrane it is shown that by acidification of initial water the calcium carbonate deposits are excluded, and the most problematic calcium sulphate deposits can be formed on nanofiltration membranes at the value of permeate yield exceeding 55% of initial water. For operation modes with higher yields, in accordance with the programme recommendations, the use of antiscaling agents is suggested.

2. Along with scale-forming ions, the possibility of a sufficiently deep reduction in the salt content of Caspian water has been demonstrated: to 1.3÷2.5 g/dm^3, against the initial level of 12.8 g/dm^3. It has been shown that, according to such indicators as the hardness and salt content of feedwater for thermal power plant boilers, the NF-RO hybrid system allows obtaining water for boilers with a pressure of up to 9.8 MPa inclusive. For boilers with higher pressure, additional desalination in mixed-action filters is required.

3. The main directions of further, more in-depth research of the considered system of supplementary water treatment include study of possibilities of bypassing and recirculation between NF and RO stages, as well as issues of optimisation of the system as a whole and assessment of technical and economic efficiency of hybridisation.

4. We believe that the results of the above studies may be of interest to engineers and researchers engaged in research and design of water treatment plants of thermal power plants located on the Caspian coast.

CONFLICT OF INTEREST.

Authors declare that they do not have any conflict of interest.

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