"NEFTİN, QAZIN GEOTEXNOLOJİ PROBLEMLƏRİ VƏ KİMYA"
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"GEOTECHNOLOGICAL PROBLEMS OF OIL, GAS AND CHEMISTRY"

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Technology of reverse-osmosis sweetening of seawater with permeate softening
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Abstract

In energy production systems, the allowable concentration of hardness in feed water is 1-10 µg/l to ensure smooth operation of medium and high pressure (3.9-13.4 MPa) steam drum boilers. Calculations show that during reverse osmosis (RO) processing of Caspian Sea water, the hardness of sweetened water (permeate) is higher than required: depending on the prcentage of permeate (50-80%) and the selection of the membrane (99-99.8%), it varies between 0.23 mg/l and 2.1 mg/l. Therefore, softening of the permeate is required. Usually, the Na-cationization method is used for this purpose, and cationite regeneration is carried out with a 3-8% solution of external NaCl salt.

The article shows that in the softening of the permeate, the waste concentrate which is rich in NaCl and Na_2SO_4 salts of the RO process can be used instead of external NaCl salt for the

regeneration of the cationite. Their concentration reaches 3-4%. In this case, the ion-exchange process takes place in equilibrium conditions. Approximately 40% of KU-2 cationite which has total ion-exchange capacity of 1700 mq/l is used in the permeate softening process. The residual hardness concentration of the softened permeate is 0.5-33 µg/l, and when the selectivity of the membrane is taken as 99.4-99.8%, the hardness concentration drops to the required level of 0.5-10 µg/l.

The authors believe that the proposed method can be effective for obtaining softened permeates from ocean and other saline waters.

Research were conducted by analytical method and some simplifying conditions. Therefore, it is planned to verify the obtained results by experimental method in the future.

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1. Introduction

One of the most important problems of modern times is the shortage of fresh water. The reason for this is the increase in the population, the change of the economic situation, the fact that the percentage of fresh water in the Earth's total water is very small (2.5%) and etc. It is known that the main part of natural waters (> 97%) is sea, ocean and other salty waters with a salinity of 3-50 g/l. "Fresh" water means waters with salinity less than 1 g/l [1,2].

Experience shows that one of the main ways to solve the fresh water problem is the desalination of salt water by different methods. This problem is becoming relevant for some regions of the Republic of Azerbaijan. Desalination of the Caspian Sea water has already been put on a practical level by the state.

Although various seawater desalination methods are used, the most widely used method is reverse osmosis (RO - reverse osmosis): 60-65% of desalinated water is processed by this method [1]. The principle of this method is process of filtering sea water through a special (semi-permeable - mainly permeable to water molecules) membrane with a pressure higher than the osmotic pressure. The reasons for the widespread use of the RO method are the following - its simplicity, low energy consumption, less space requirment and are modular, easy automation, etc. The main disadvantages of the method are the high residual water salinity (TDS – Total Dissolved Solids) of the received permeate: in the RO-process of Caspian Sea water (TDS=13 g/l) -100-120 mg/l, RO of ocean water in the process (TDS=35 g/l) - 400-600 mg/l; short service life of membranes (3-5 years), use of complex pre-treatment technologies to RO membranes from various deposits, etc. i. [3].

As a rule, the production of water with different purposes is carried out with the additional processing (post treatment) of the permeat received in RO units [4,5]. Mainly by further processing of RO permeate, water is prepared for the following purposes:

- Drinking water production;
- Production of demin water for heat energy production systems (steam boilers with different pressures, heating networks, etc.);
- for other purposes.

For example, in [6] preparing hot drinking water from RO effluent is considered. It is shown that when additional salts are added to the permeate (remineralization), formation of scale is

observed. İt was observed that water temperature, calcium concentration and two types of inhibitors have effect on formation scale. It was determined that at low water temperatures (20-25^{0}C) and when the concentration of Ca is 40-69 mg/l, scale does not form.

Research [4] discusses demin water preparation technologies for steam boilers by combining RO and ion-exchange methods. It is shown that the permeate treatment stage is selected and designed depending on the steam boiler pressure:

- for the preparation of make-up water of boilers of flat-flow and critical-to-high-pressure, as well as high-pressure steam-gas plants, in the first stage, permeate aeration (to get rid of CO_2 gas), in the second stage, complete desalination of permeate is carried out in mixed-effect filters loaded with cationite and anionite. Acidic (H_2SO_4) and alkaline (NaOH) solutions are used for filter regeneration. As a result, the specific electrical conductivity of water reaches the limit of 0.2 µSm/cm (TDS=0.4 mg/l);

- for the preparation of make-up water of boilers of laminar-flow and critical-to-high-pressure, as well as high-pressure steam-gas plants, in the first stage, permeate aeration (to get rid of CO_2 gas), in the second stage, complete desalination of permeate is carried out in exchange filters loaded with cationite and anionite. Acidic (H_2SO_4) and alkaline (NaOH) solutions are used for filter regeneration. As a result, the specific electrical conductivity of water reaches the limit of 0.2 µSm/cm (TDS=0.4 mg/l);

- deep softening (Na-cationization) of the decarbonized permeate is performed instead of complete desalination for the preparation of additional water of low, medium and high pressure drum steam boilers. The essence of the process is the exchange of Ca and Mg ions, which make up the hardness of water and lead to the formation of scale, to Na ions that do not form scale. In the process of Na-cationization, regeneration of the cationite filter is carried out with a 3-8% solution of NaCl salt.

Permeate conventional Na-cationization technology has the following disadvantages:

1. NaCl salt is purchased dry from an external system and requires certain costs.

2. A part of the RO permeate is used for the preparation of NaCl solution.

3. The spent regeneration solution formed in the regeneration process is formed and causes environmental damage as a result of its discharge into the environment.

Considering the indicated disadvantages of RO permeate softening technology due to external NaCl salt, an alternative approach is proposed and investigated in this paper. The essence of the proposal (hypothesis) is that instead of the regeneration solution made from external NaCl salt, the softening of the permeate is carried out using the concentrate of the RO process. As a result of the literature review, the authors did not come across any research work conducted in this direction.

The possibility that the RO process of seawater can be useful as a cationite regenerant comes from the fact that $NaCl+Na_2SO_4$ salts are the main components of all sea and ocean waters, and the concentration of these salts increases to 3-4% in the reverse osmosis process. However, unlike traditional technology, the concentration of hardness in the concentrate of the RO process is high. This worsens the technological performance of the Na-cationization process. But the degree of influence of this factor is not clear. Therefore, it is required to conduct appropriate research by analytical method.

Thus, the aim of the study is to investigate the efficiency of using the waste concentrate of that RO process instead of external NaCl salt as cationite regenerator for the softening of the

permeate formed in the RO desalination process of the Caspian Sea water by the Na-cationization method.

Research Me

Figure 1 shows the technological schemes of the reverse osmosis sweetening system with Na-cationization of the permeate.
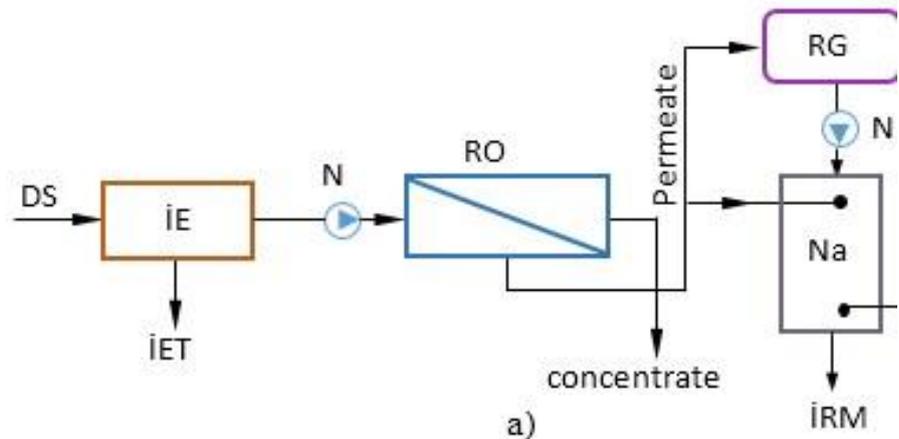
Figure 1. Technological schemes of reverse osmosis sweetening system with Na-cationization of permeate: a) traditional method, b) proposed method: DS-sea water; IE– pre-treatment , IET – waste of primary processing; YP – softened permeate; IRM – spent regeneration solution; RC - regeneration tank; N-pump.

In Figure 1,a, process of the RO-Na process with traditional method which use external NaCl salt, is shown. As can be seen from the scheme, sea water (DS) is purified from certain impurities in the initial treatment stage (IE-Pretreatment) and is fed to the RO module under high pressure. Here, seawater is separated into two parts: permeate (sweetened water) and concentrate, which has high salinity. The latter is thrown into the sea. Part of the permeate is fed to the regeneration tank (RC) to prepare the NaCl salt solution. Regeneration of the cationite charged to the Na-cationite filter is carried out by means of that solution. The processed regeneration solution (IRM) is discharged into the sea. In the regeneration process, the cationite changes to the Na-form. In the next step, the rest of the permeate is softened by passing it through a cationite filter: the main part of Ca and Mg ions in the permeate is replaced by Na ions. Softened permeate (YP) is used as make-up water of steam boilers. The second scheme (Fig. 1,b) is based on the proposed new method and, as can be seen from the figure, it is envisaged to use the concentrate of the RO process for the regeneration of the Na-cationite filter.

Analytical method was chosen as the research method of the proposed method. The study of the RO phase was carried out with the modern methodology presented in [3]. The Nikolski equation based on the law of mass effect was used in the study of the Na-cationization process of the permeate [7]. Main issues resolved:

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- Determination of the concentration of Na, Ca and Mg ions in the obtained permeate and concentrate depending on the share of RO permeate and the selectivity of the membrane.

- Derivation of the formula for the specific consumption of Na-ions contained in the concentrate of the RO process (the ratio of the permeate to the hardness).

- Evaluation of the ion exchange capacity of the cationite and the residual hardness of the permeate during the softening process of the permeate.

In order to solve the problems, a computational model of the researched technology (Fig. 1, b) was developed and a computer simulation of this model was carried out. The residual hardness of the softened permeate was compared with the acceptable hardness of the feed water of different pressure steam boilers [8].

1. Nominal pressure at the outlet of the boiler, MPa	3,9	9,8	13,8
2. Total Hardness content of feed water, µg/l:			
for liquid fuel boilers	≤ 5	≤ 1	≤ 1
3. for other type fuel boilers	≤ 10	≤ 3	≤ 1

Researches were conducted on the example of Caspian Sea water (mg-eq/l): Na=136; Ca=16; Mg=60; Cl=140; SO$_4$=68; HCO$_3$ = 4. Total salinity- TDS=12.6 g/l.

2. Calculation Method

The calculation scheme of the RO module is given in figure 2.
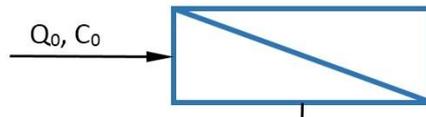
Fig. 2. RO-module calculation scheme

According to the calculation scheme, sea water with consumption Q_0 m^3/h is supplied to the membrane module and is separated into two parts during the treatment process: the permeate passing through the membrane (QP) and the residual concentrate (QK) that does not pass through the membrane. The concentration of salts in seawater is C0, in the permeate - CP, in the concentrate - CK. Then we can write the following material balance equations:

$$Q_0 = Q_P + Q_K \quad (1) \qquad Q_0 \cdot C_0 = Q_P \cdot C_P + Q_K \cdot C_K \quad (2)$$

If we take the amount of permeate β = QP / Q0, we can write the following expressions for the amount of Na, Ca and Mg ions:

$$G_{K,Na} = Q_0(1-\beta) C_{K,Na} \quad (3) \qquad G_{P,Ca} = Q_0 \cdot \beta \cdot C_{P,Ca} \quad (4)$$

$$G_{P,Mg} = Q_0 \cdot \beta \cdot C_{P,Mg} \quad (5) \qquad G_{P,Ca+Mg} = Q_0 \cdot \beta \cdot (C_{P,Ca} + C_{P,Mg}) \quad (6)$$

Here $G_{K,Na}$ - sodium in the concentrate of RO, $G_{P,Ca}$; $G_{P,Mg}$ and $G_{P,Ca+M}$ are the amounts of calcium, magnesium and hardness ions in the permeate, mg-eq; $C_{K,Na}$, $C_{P,Ca}$, $C_{P,Mg}$ - is the concentration of the corresponding ions, mg-eq/l. The concentration of each i ion in the concentrate and permeate can be calculated by the following formulas [3].

$$C_{i,K} = C_{i,0} (1- \beta(1-R))/(1- \beta) \quad (7) \qquad C_{i,P} = C_{i,OR}(1 - R) \quad (8)$$

$$C_{i,OR} = 0,5(C_{i,0} + C_{i,K}) \quad (9)$$

Here $C_{i,0}$; $C_{i,K}$ and $C_{i,P}$ are the concentrations of any ions in seawater, concentrate and permeate, respectively, in mg-eq/l; $C_{i,OR}$ is the average concentration of ions in the water flowing over the membrane, mg-eq/l; R is the selectivity of the membrane.

Taking these into account, the formula for the specific consumption ($g_{Na,P}$) of sodium salts in the concentrate of RO and used for softening the permeate can be written as follows:

$$g_{Na,P} = G_{K,Na}/(C_{P,Ca}+ C_{P,Mg}), \quad \text{mq-eq/mq-eq} \qquad (10)$$

If formulas (7)-(9) are taken into account in (10):

$$g_{Na,P} = (1- \beta) C_{K,Na}/ (\beta(C_{P,Ca}+ C_{P,Mg})), \quad \text{mq-eq/mq-eq} \qquad (11)$$

For the ion-exchange equilibrium process, using the relative concentrations for the system of different valence cations, the Nikolsky equation is written as follows [7]:

$$\frac{1-\theta}{\theta^\lambda} = B \frac{1-\varphi}{\varphi^\lambda} \qquad (12)$$

Here θ -is the share of Na ions in cationite; λ is the ratio of hardness and valence of Na ions, $\lambda=2/1=2$; φ is the amount of Na ions in water; $B = K^\lambda /h$, where K is the average value of concentration constants of ion pairs; h is the ratio of the total concentration of cations in water to the total ion-exchange capacity (E_T) of the cationite:

$$\varphi = \frac{C_{Na}}{C_{Ca}+C_{Mg}+C_{Na}} \qquad (13)$$

$$h = \frac{C_{Ca}+C_{Mg}+C_{Na}}{E_T} \qquad (14)$$

As a result of the general solution of formula (12), we get:

$$\theta = \frac{-\varphi^2+\varphi\sqrt{\varphi^2+4B(1-\varphi)}}{2B(1-\varphi)} \qquad (15)$$

Formula (15) calculates the amount of Na ions for the concentrate and permeate of the reverse osmosis unit in the cationite content: $\Theta_{K,Na}$ and $\Theta_{P,Na}$. Based on these, useful ion-exchange capacity of cationite according to hardness ions is determined - E_F:

$$E_F = E_T(\Theta_{K,Na} - \Theta_{P,Na}) = E_{K,Na} - E_{P,Na}, \quad \text{mq-ekv/l}_K \qquad (16)$$

Here, lK is the volume of the cationite, l.

Since the calculation of the residual hardness of softened permeate by analytical method is a very complicated matter – [7], with some simplifications (taking into account the activity coefficient of ions in water and cationite, etc.) and taking into account that $C_{Ca+Mg, YP} \ll C_{Ca+Mg, P.}$, softened permeate residual hardness - $C_{Ca+Mg, YP}$ (C_{YP}) can be calculated from the following formula:

$$C_{Ca+Mg, K}/(C_{Na, K})^2 = C_{Ca+Mg, YP}/(C_{Na, P}+(C_{Ca+Mg, P}- C_{Ca+Mg, YP}))^2 \qquad (17)$$

A program in Pascal language was developed to conduct the computer simulation of the calculation model. amount of permeate $\beta= 0.5-0.8$; the selectivity of the membrane was changed in the range of R= 0.990-0.998 (99-99.8%). The full ion exchange capacity of KU-2 cationite ET=1700 mg-eq/l was considered

3. Analysis of Results

Image. Figures 3 and 4 show the influence of the amount of permeate and the selectivity of the membrane on the concentration of Ca, Mg and Na cations in the permeate and concentrate obtained in the RO process.
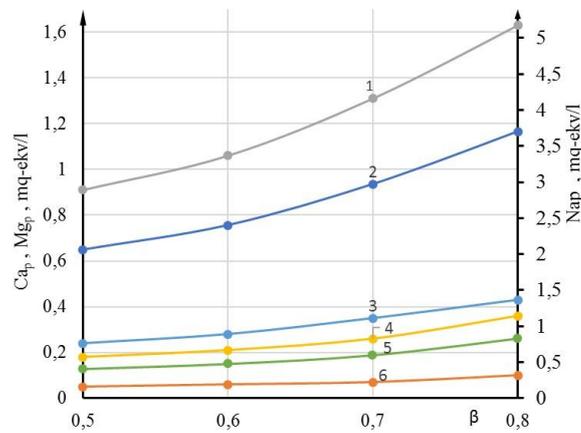

Fig. 3. Dependence of the concentration of cations in the permeate on the amount of the permeate and the selectivity of the membrane:
1,4- Mg$_P$; 2,5-Na$_P$; 3,6-Ca$_P$; 1,2,3 – R=99%;
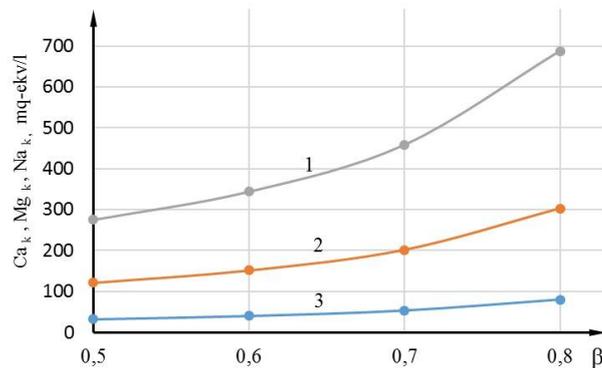4,5,6 – R=99,8%

Fig. 4. Dependence of the concentrations of cations in the concentrate on the amount of the permeate and the selectivity of the membrane: 1- Na$_K$; 2- Mg$_K$; 3- Ca$_K$; R=99,6%

Analysis of the first graph shows that increasing the amount of permeate (β) leads to an increase in the concentration of all three cations in the permeate at both levels of membrane selectivity. At values of β greater than 0.7, concentrations increase more rapidly. At 99% value of R, the total hardness of permeate increases from 1.2 mg-eq/l to 2.6 mg-eq/l. The concentration of sodium ions increases from 2.1 mg-eq/l to 3.7 mg-eq/l. This increase is explained by the fact that the increase in β decreases the amount of the concentrate, and since the amount of salts is constant, the salinity of the concentrate flowing over the membrane increases. Since the permeate is taken from that concentrate, the concentration of ions passing through the membrane, including cations, increases.

Regarding the effect of membrane selectivity, it can be seen from the graph that increasing this indicator from 99% to 99.8% decreases the concentration of cations. For example, at the

maximum value of β, the concentrations of Ca, Mg and Na ions decreases approximately the same level respectively 4.3, 4.5 and 4.6 times. Thus, the minimum and maximum values of permeate hardness in the study area are 0.23 and 2.1 mg-eq/l, respectively: the average is 1.16 mg-eq/l.

According to calculations, the selectivity of the membrane has little effect on the concentration of cations in the concentrate. Therefore, the graph of the corresponding dependence was brought for the average value of R (99.6%) - Fig. 4. According to the graph, the concentration of Na ions increases from 280 mg-eq/l to 700 mg-eq/l. If we convert these salts to equivalent NaCl salt, we get 1.6-4.1%. But the hardness of this solution is very high and on average it is 260 mg-eq/l.
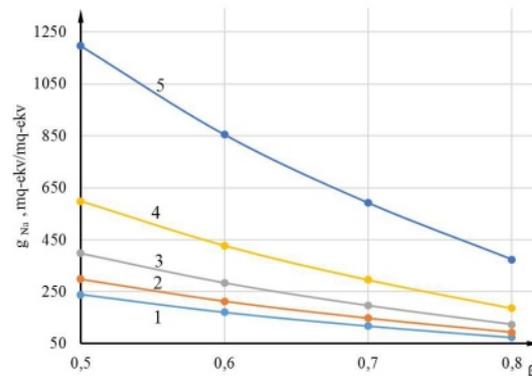

Fig. 5. Dependence of the specific consumption of Na-salts on the share of the permeate and the selectivity of the membrane: 1-R=99%; 2-99.2%; 3 -99.4%; 4-99.6%; 5- 99.8%

As shown above, the ratio of the amount of Na ions in the RO process concentrate to the sum of the amount of Ca and Mg ions in the permeate indicates the specific consumption of Na ions (g_{Na}) in the softening process. As can be seen from Fig. 5, the numerical value of this indicator depends on β and R. An increase in β decreases the specific consumption of Na ions, and an increase in R increases it.

Analysis of the graph shows that the increase of β, regardless of the value of R, reduces the specific consumption of Na ions by 3.2 times. The main result is that the absolute values of the specific consumption of Na ions are very high in all cases. Even minimal values (75-375 mg-eq/mg-eq) are on average 18 times higher than required (10-15 mg-eq/mg-eq in the conventional method). This is an indicator that the ion-exchange process is in equilibrium.

Graphs of the effect of β and R indicators on useful ion-exchange capacity of cationite and residual hardness of softened permeate are given in figure 6.

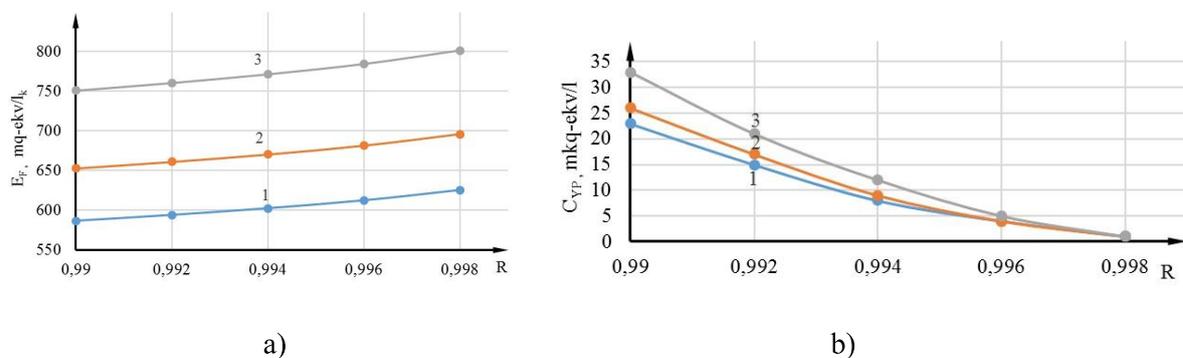a)   b)

Fig. 6. Influence of permeate fraction and membrane selectivity on useful ion exchange capacity (a) and residual hardness of softened permeate (b): β=0.6(1); 0.7(2); 0.8(3).

As can be seen from Fig. 6,a, the increase of input variables increases the useful ion-exchange capacity of cationite in the range of 580-800 mg-equiv/lK, which is 34-47% of the full ion-exchange capacity. But at a constant value of the amount of permeate, the absolute value of the increase in E_F is small - about 50 mg-eq/lK. The increase in EF is related to the fact that as the β and R indicators increase, the TDS of the RO concentrate, including the concentration of Na-salts, which is its main part, increases. It is known from the theory and practice of ion-exchange that as the concentration of the regenerant increases, the ion-exchange capacity increases and the residual hardness of softened water decreases. As can be seen from Fig. 6, b, the residual concentration of softened permeate (C_{YP}) varies in the range of -0.5-35 μg-eq/l. The smallest values are obtained at the maximum value of R, regardless of β. At small values of R, the increase of β decreases the residual hardness of softened permeate, for example, when R=99.2%, hardness decreases by 5 μg-eq/l. It can be seen from the figure that the selectivity of the membrane used in the RO unit is greater than 99.4% to ensure the residual concentration of the softened permeate in the range of 1-10 μg-eq/l. Permeate with a higher hardness value can be used in low-pressure steam boilers and medium-pressure boiler-utilizers.

If we compare the results presented in the last graph and the norm indicators of feed water of different pressure steam boilers, it can be seen that by choosing the selectivity of the membranes used in the RO process and the proportion of permeate, the required hardness of the permeate can be ensured.

5. Conclusion

1. On the example of Caspian Sea water, analytical studies show that the concentrate produced in this process can be used instead of external NaCl salt to soften the permeate obtained in the RO process by the Na-cationization method. With this method, it is possible to prepare make-up water for steam boilers operating at a working pressure between 3.9 and 13.4 MPa, which provides a scale free and has a concentration of less than 10 μg-eq/l. It is considered that the quality indicators of make up water of steam boilers should not differ from feed water.

2. From an economic and ecological point of view, this method is more convenient, because: a) costs incurred for the purchase of external NaCl salt are eliminated; b) a part of sweetened water is not used to prepare a working solution from dry salt; c) no additional salts are thrown into the environment, they consist only of seawater salts.

3. The authors believe that the permeate softening method of the RO process using its own concentrate can be used for the treatment of other saline waters, including standard ocean water with TDS=35 g/l.

4. Analytical research and number of simplifed conditions require experimental verification of the obtained results and are planned by the authors.

Conflict of interest
The authors declare that they have no conflict of interest in relation to this research.

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Engineering solutions optimization aimed at mitigating risks

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Abstract

Current Facilities for unloading, storage, preparation, transportation and offloading as a rule have design life to last of over 30 years, often 50 years. In reality very often facilities require life cycle extension as being still in demand after expiry of design life. Such an approach has become more in demand during recent decades as modern engineering more and more aims at optimizing the overall costs while engineering values, to achieve higher efficiencies.

During latest periods the occurring disastrous events are being observed with the aging facilities, like fires, explosions etc., which sometimes are ascribed to conspiracies, which however often are due to inadvertent attitudes to facilities and hazards those facilities may conceal. Risks are not properly identified and addressed, thus leading to artificial higher cost efficiency missing critical assessment criteria for brownfield engineering solutions.

This Article aims at structuring the approaches to safer engineering by dividing the process into stages each having its weight in consideration of extension of facility's longevity. Such approach will significantly minimize risks of hazardous events during exploitation of facility beyond their design life. This will be through staged approach, evaluation of threats at each stage and developing solutions at various levels of approach.

Keywords: oil and gas, optimization, design life, hazards identification, risk assessment, critical parameters, efficiency engineering

1. Introduction

The contemporary situation with the industrial facilities and their engineering systems being under operation, requires a significant change in the attitude to their upgrades and maintenance. This is the result of the quick progresses in engineering fields and very often the crucial and sometimes step