



Nanofiltration process for seawater desalination–salt production integrated system

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ABSTRACT

A performance of three commercial nanofiltration membranes (NF200, NF270 and TFC-SR2 KOCH) was investigated in order to check their ability in the integrated UF-NF-RO-MED–crystallization seawater desalination system. The experiment was carried out using synthetic seawater solution. The TFC-SR2 KOCH membrane showed good separation properties and could be utilized in the integrated seawater desalination system with simultaneous production of evaporated salt. The rejection coefficients were found as follows (%): Ca^{2+} – 65.7, Mg^{2+} – 81, SO_4^{2-} – 95 and Cl^- – 23.7. Based on aforementioned experimental results and industrial plant operation data, the cost of seawater desalination in UF-NF-RO-MED–crystallization system was then estimated. The total water recovery (the sum of RO permeate, MED distillate and condensate from evaporation–crystallization process) was found as high as 78.2%. If 80% NaCl recovery is assumed (as related to MED brine) 17.1 kg of NaCl per 1 m³ of UF permeate is obtained. Assuming \$30/t evaporated salt selling price, the cost of desalinated water has been estimated at \$0.5/m³. The applying of “high boron rejection” RO membranes (boron rejection 93%), and then blending RO permeate with MED distillate (that is practically boron free) may decrease boron content below the value recommended by WHO. To the best of our knowledge, for the unit cost of desalinated water obtained from the system with capacity ca. 50,000 m³/d, no better results are available in the accessible literature.

Keywords: Desalination; Integrated system; Nanofiltration; Salt production

1. Introduction

Increase of worldwide shortage of fresh water resources and recent reduction in cost of desalination technologies have enhanced the interest in potable water production from saline or brackish waters. Generally desalination technologies may be grouped into thermal methods, i.e. multi-stage flash (MSF), multi-effect distillation (MED), and membrane processes, i.e. reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED). Historically, most of installed seawater desalination capacity has

been produced by using thermal distillation processes. Since 1990s 20th century, reverse osmosis membrane systems have become the fastest growing segment of the seawater desalination market. The worldwide desalination capacity increased from 8,000 m³/d in the 1950s to 8,040,000 m³/d in the 1980s and to 26,970,000 m³/d by 2005 [1], the majority of which was produced in the Middle East region, Saudi Arabia, Kuwait and Qatar.

According to Cooley et al. [2], in 2005 the world's installed capacity consisted mainly of MSF and RO processes. These two processes make up about 82% of the total capacity. The remaining 18% is made up of the multi-effect distillation, vapor compression, electrodialysis, and

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others. The cost of desalted water product is different in many countries, and depends on many factors, e.g., water quality, feed water salinity level, energy cost and plant capacity. The cost levels vary with respect to the local conditions, nevertheless there has been a significant cost reduction from the cost of 10 years ago (\$3.00/m³ to \$0.5/m³) [3].

There is no single best method of desalination. In order to reduce or even overcome the limits of single methods and improve performance of a system it is necessary to couple several membrane and thermal processes. Another advantage, which is connected with high performance of desalination systems, can be lower price of desalted water.

The aim of this paper is to give a brief overview of the applications of the nanofiltration process in seawater desalination and present cost estimation for the integrated UF–NF–RO–MSF/MED–crystallization system taking into consideration experimental results and current data concerning membrane and thermal methods.

2. Application of NF in seawater desalination process

Nanofiltration is a relatively new pressure-driven membrane process for liquid phase separation. The most attractive applications for NF are water softening, water treatment, biotechnology and pharmaceutical industry. In seawater desalination process, NF is applied as a pretreatment of seawater feed before its processing by RO or MSF. The NF membrane pretreatment was found to be successful in removal of turbidity, significant removal of residual bacteria, scale forming hardness ions, lowering of the seawater TDS, and reducing energy and chemical consumption [4]. Higher recovery may be then reached when desalting in comparison to traditionally treated water.

For the first time NF membrane pretreatment process was integrated with one of the conventional desalination processes on a pilot plant in Saudi Arabia. This conception was evaluated on NF–SWRO, NF–MSF, and NF–SWRO–MSF pilot plant units using Gulf seawater [5]. The NF process was carried out at pressures 18, 22 and 31 bar. At a pressure of 22 bar, NF removed hardness ions of Ca²⁺, Mg²⁺, SO₄²⁻, HCO₃⁻ and total hardness by 89.6%, 94.0%, 97.8%, 76.6% and 93.3% respectively. Moreover, NF reduced the monovalent ions of Cl⁻, Na⁺ and K⁺ each by 40.3%. The obtained permeate was applied as a feed to SWRO or the make up to the MSF. This made it possible to operate a SWRO and MSF pilot plant at a high recovery: 70% and 80% respectively [5]. The NF recovery in the NF–SWRO was fixed at 65% [6], so the total recovery ratio did not exceed 58%. The use of NF product as a feed to MSF process makes it possible to operate an MSF unit at a high top brine temperature of 120°C without the addition of antiscalant or antifoam

chemicals. In a trihybrid system, the reject from SWRO of the NF–SWRO unit is used as the make up to the MSF unit. This desalination system arrangement should allow increasing the conversion of the NF permeates up to 90%. These integrated desalination systems, combined with a reduction of chemicals and energy, allow to operate the seawater desalination process at a 30% lower cost compared to conventional SWRO [5].

The second demonstration plant was built at Umm Lujj, Saudi Arabia [7,8]. The results obtained from the demonstration unit confirmed the results obtained from the pilot plant study.

Another integrated system (NF–RO–MC) was proposed by Drioli et al. [9] where MC is a membrane crystallizer. The presence of the NF unit in this arrangement allowed an increase in water recovery of the RO unit up to 50%. Moreover, according to the authors' opinion, introduction of an MC led to a 100% recovery and elimination of the brine disposal problem.

Pontié et al. [10] proposed direct application of NF in order to obtain partial demineralization of seawater (raw water from Biarritz, France). They used two successive NF stages. The treated water could be used in the field of human health (e.g., preparation of nasal sprays, medical dietetics and hot mineral springs).

Turek et al. [11,12] suggested the following system: UF–NF–RO–MSF–crystallization. In this system the highly concentrated MSF brine might be used as a possible by-product, e.g. for obtaining salt. Salt obtaining may improve the economics of the system and then decrease the total cost of water desalination. As pre-concentration by RO is cheaper than by MSF in the range of relatively small salt concentration values, cost reduction of the desalination–salt production process can be achieved by introducing RO before the MSF unit. Authors proposed to use NF membranes with high rejection coefficient of calcium, magnesium and sulfates but relatively low rejection of chlorides. They applied Desal 5-DL (Osmonics) membrane. The rejection coefficients were found as follows (%): Ca²⁺ – 63.0, Mg²⁺ – 75.7, SO₄²⁻ – 95.0, Cl⁻ – 15.9, which allowed the authors to estimate the composition of process streams of NF and water desalination cost in integrated UF–NF–RO–MSF–crystallization system. They found that the aforementioned integrated system offered a very promising performance: high water recovery (77.2%) and water cost as low as \$0.37/m³. The integrated UF–NF–RO–MSF–crystallization system offered also high reduction of the waste quantity that lead to a lower environmental impact.

To solve ecological problems caused by saline coal mine waters in Poland, Turek et al. [13,14] proposed NF–evaporation system for their utilization. It was found that NF–evaporation combination should set down the unit costs of the concentration of coal mine waters below those of mere evaporation.

3. Unit cost estimation of desalination–salt production system

Taking into account current data concerning industrial membrane and thermal plants, cost estimation for UF–NF–RO–MED/MSF–crystallization system was renewed. In this system NF membranes with high rejection coefficients of calcium, magnesium and sulfate but low rejection coefficients of chloride ions were required. Thus, a performance of three commercial nanofiltration membranes (NF200, NF270 and TFC-SR2 KOCH) was investigated in laboratory. The experiment was carried out with model seawater solution, containing (g/L): 18.67 Cl⁻, 2.68 SO₄²⁻, 1.48 Mg²⁺ and 0.39 Ca²⁺ at 14 bar. Retention coefficients are presented in Table 1.

The TFC-SR2 membrane showed good separation properties and could be utilized in the integrated seawater desalination system with simultaneous production of evaporated salt. Comparing TFC-SR2 membrane with mentioned Desal 5-DL it can be observed that TFC-SR2 membrane has higher rejection coefficient of calcium and magnesium. Moreover, TFC-SR2 membrane has at about 37% higher permeate flux than Desal 5-DL, that may decrease both NF operating and maintenance costs. Based on the aforementioned experimental results, the concentrations of Ca²⁺, Mg²⁺, SO₄²⁻ and Cl⁻ ions in NF permeate may be calculated using the following formula [13]:

$$C_p = C_0 \frac{1 - \left(1 - \frac{V_p}{V_0}\right)^{1-R}}{\frac{V_p}{V_0}} \quad (1)$$

It was assumed that open ocean water pretreated by UF is used as NF feed and 80% NF recovery is obtained. Seawater treated by UF (UF permeate) and NF permeate compositions are given in Table 2.

The UF pretreatment cost calculated by Glueckstern et al. [15] is in the range of \$0.048/m³–\$0.057/m³. In our estimations, the cost of UF pretreatment is set to \$0.05/m³. Further, it was assumed that cost NF equals to \$0.18/m³. As small value as \$0.18/m³ in NF process was assumed because the pretreatment cost was considered separately as UF cost. MSF process is recommended for seawater plants with the capacity greater than 25,000 m³/d. For plants capacities in the range of 10,000–25,000 m³/d the MED process is suggested [16]. According to A. Ophir [17] the total water cost for MED with a capacity of 14,400 m³/d equals to \$0.75/m³. This value is given when seawater is applied as MED feed. Instead, if UF–NF–RO–MED–crystallization system is considered RO retentate constitutes the feed to MED plant and the final brine is close to sodium chloride saturation. Thus, its vapour pressure value was predicted as 1.15 times lower than seawater one [18], and the corresponding increase in the MED unit cost to \$0.86/m³ was assumed.

Table 1

Retention coefficients of magnesium, calcium, chloride and sulfates ions determined at 14 bar

Membrane	Retention coefficient, %			
	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻
TFC-SR2 KOCH	81.0	65.7	23.7	95.0
NF 270	65.7	50.0	13.0	84.0
NF 200	58.9	50.2	24.3	66.0

Table 2

Composition of UF and NF process streams at 80% NF recovery

Component	Concentration, g/L	
	UF permeate	NF permeate
Ca ²⁺	0.39	0.20
Mg ²⁺	1.48	0.49
SO ₄ ²⁻	2.68	0.26
Cl ⁻	18.55	16.91

The RO unit cost was estimated based on the data given by Wittholz et al. [16]. The authors developed a method of unit cost estimation by analyzing cost database of 300+ plants in a wide range of capacity. Thus, interpolation of data presented by Wittholz et al. for SWRO plants in the range of 10,000–50,000 m³/d, comprising both capital and operating costs as well as plant: capacity, availability, and life costs led us to assume \$0.77/m³ as the RO unit cost for 35,657 m³/d plant capacity. The RO stage recovery was set to 65%. The cost of further evaporation accompanied by salt crystallization was assumed to be \$8/t of salt obtained [12]. Cost estimation for this process is presented in Table 3.

Table 3

Cost of desalination–salt production in the UF–NF–RO–MED–crystallization process

Item	Cost, \$		
	Unit cost	Per 1 m ³ of UF permeate	Per 1 m ³ of UF permeate
UF	0.05/m ³	0.05	—
NF	0.18/m ³	0.144	—
RO	0.77/m ³	0.400	0.520
MED	0.86/m ³	0.181	0.210
Crystallization	8/t	0.137	0.052
Total		0.912	0.782

The total water recovery, i.e. the sum of RO permeate, MED distillate and condensate from evaporation–crystallization process, was found as high as 78.2%.

Vapor compression evaporation coupled with salt crystallization was assumed in the evaporated salt obtaining step. When analyzing the salt crystallization in this system it was found that the presence of magnesium ions negatively influenced its performance. High concentration of magnesium decreased the stability of gas compressor work. Limited resistance of crystallizer construction materials was also reported. Thus, the salt crystallizer should work with magnesium concentration not exceeding 1 kmol/m³ [19]. Therefore, maximum NaCl recovery was set to 80% (as related to MED brine) and 17.1 kg of NaCl per 1 m³ of UF permeate can be produced. Assuming \$30/t evaporated salt selling price, the cost of desalinated water was estimated at \$0.5/m³. This cost is higher by about \$0.13/m³ than that reported by Turek et al. [12]. It is due to the fact, that the cost estimation by the authors mentioned was done based on large-scale plant data.

Besides promising desalination cost reduction in the aforementioned integrated system, another important advantage may be noticed concerning the question of boron presence in drinking water. World Health Organization (WHO) has recommended 0.5 mg/L boron content in drinking water as its permissible value. Applying “high boron rejection” RO membranes with boron rejection of 9% (manufactured by Toray), and then blending RO permeate with MSF distillate (that is practically boron free) may decrease boron content below the value recommended by WHO. Such variant of water desalination will decrease the production cost of water by elimination of additional boron removal step that is necessary in traditional SWRO desalination plants. Thus, additional desalination cost reduction by avoiding the need of boron removal may be assumed as another UF–NF–RO–MED–crystallization system advantage.

4. Conclusions

Applying NF membranes with high rejection coefficients of scale forming ions as a pretreatment in seawater desalination opens the possibility for significant increase of water recovery in both RO and MED processes, and results in the pronounced increase in overall water production in the integrated system. From the presented economical analysis, it is seen that salt obtaining as a valuable product leads to decrease of the total unit cost of desalted water. Moreover, salt production causes reduction of waste products, thereby making the process more friendly to the marine environment. The process evaluation confirms that the proposed integrated system offers high water recovery (78.2%) and water unit cost

equals to \$0.5/m³. One can see that the unit cost value found is still much better than mere RO (\$0.77/m³) or MED (\$0.75/m³) included in the above system and is as low as achievable in mega-plants only until now. To the best of our knowledge, for the unit cost of desalinated water obtained from the system with capacity ca. 50,000 m³/d, no better results are available in the accessible literature.

Symbols

C_0	—	Concentration of the component in the feeding water
C_p	—	Concentration of the component in the permeate
R	—	Rejection coefficient
V_0	—	Flow rate of the feeding water
V_p	—	Flow rate of the permeate

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