Desalination and Water Treatment
www.deswater.com

51 (2013) 930–935
January

doi: 10.1080/19443994.2012.714578

Taylor & Francis
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Selection of nanofiltration membranes as pretreatment for scaling prevention in SWRO using real seawater

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Received 29 February 2012; Accepted 18 July 2012

ABSTRACT

Seawater contains high concentrations of sparingly soluble salts which can cause scaling of membrane surface, limiting the productivity and water recovery of seawater reverse osmosis (SWRO). Nanofiltration (NF) pretreatment of seawater, prevents scaling via preferential removal of scale-forming ions. Several studies have shown that the rejection of scale-forming ions is not the same for various membranes. In a previous study, a selection of the best NF membranes for scaling prevention in SWRO was developed using synthetic seawater. The main objective of this study is to test the same NF membranes using real seawater in order to compare the membrane performance using synthetic and real seawater. The seawater used in this study was collected in El Prat de Llobregat (Barcelona). The results obtained showed that the monovalent ions are less rejected in real seawater than in synthetic seawater. However, the rejection of scale forming ions has been practically the same for all membranes in both types of seawater, obtaining a sulphate rejection higher than 90% for the majority of membranes studied, which is highly important for scaling prevention.

Keywords: Nanofiltration; Scaling prevention; Seawater desalination

1. Introduction

Seawater contains a high concentration of hardness ions, total dissolved solids (TDS) and turbidity, which in turn give rise to three major problems in seawater desalination plants by limiting their water recovery to low values, normally less than 35%. The high degree of hardness constitutes an inherent problem to all forms of desalination, be it thermal or membrane type.

Seawater desalination processes are separation processes in which freshwater is extracted from saline water; this way the salts and hardness ions are left behind in the brine with the effect that both TDS and hardness concentrations are increased. Owing the fact that hardness ions are sparingly soluble in seawater, the increase in their concentration under certain operation conditions can lead to their precipitation on the desalination equipment, causing them to scale.

Depending on the desalination operating conditions, two types of scales can be formed, alkaline soft scale, made of $CaCO_{3(s)}$ and $Mg(OH)_{2(s)}$ and non-alkaline hard scale, consisting of $CaSO_{4(s)}$, or $CaSO_4{\cdot}1/2H_2O_{(s)}$ or $CaSO_4{\cdot}2H_2O_{(s)}$. The formation of this type of scale becomes exaggerated at high temperatures, since the $CaSO_4$ solubility decreases as the solution temperature is increased.

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Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

To prevent and avoid scale formation, certain anti-scalants are added to the feed, e.g. polyphosphate, poly-phosponates or poly-carboxylic acid and H_2SO_4 or HCl, allowing for multi stage flash (MSF) operation without scaling at top brine temperatures of 90, 115 and 120°C, respectively, while anti-scalants are also normally added to prevent seawater reverse osmosis (SWRO) membrane scaling. In spite of this, the product water recovery as the fraction of product to feed remains low, namely, 30–35% [1].

NF was used for the first time by Hassan et al. [1] as a pretreatment of three desalination processes: SWRO, MSF and SWRO rejected in MSF ($SWRO_{reject}$-MSF). In these integrated processes, nanofiltration (NF) minimized hardness, microorganisms and turbidity. Fig. 1 shows the NF rejection results obtained at a pressure of 22 bar. The permeate thus obtained was far superior to seawater as a feed to SWRO or MSF. This enabled a SWRO and MSF pilot plant to operate at a high recovery: 70 and 80%, respectively.

About 10 years ago, a demonstration plant was built at Umm Lujj, Saudi Arabia, consisting of six Spiral-Wound NF modules (8″ × 40″) followed by three SWRO elements, and the results obtained from the demonstration unit confirmed those previously obtained in pilot plant studies [2]. In 2009, Farooque et al. [3] did an autopsy of 6 NF membranes' elements to evaluate their condition after 5 years of continuous operation at the Umm Lujj NF-SWRO plant. Foulant deposits mainly consisted of organic matter that was easily scraped off from the membrane's surface but left stubborn stains difficult to clean, even with strong chemical cleaning agents. It was, therefore, concluded that with a long operation period, these foulants were strongly adsorbed onto the membrane surface and became irreversible in nature. The existence of organic foulants suggests the urgent need and application of a coagulation-filtration pretreatment process using a coagulant such as $FeCl_3$. This can be easily done by replacing the existing antiscalant sodium hexametaphosphate, which is not necessary, because the current pH of the pretreated seawater feed of about 6.2 is sufficient to prevent scale formation on SWRO and NF membranes.

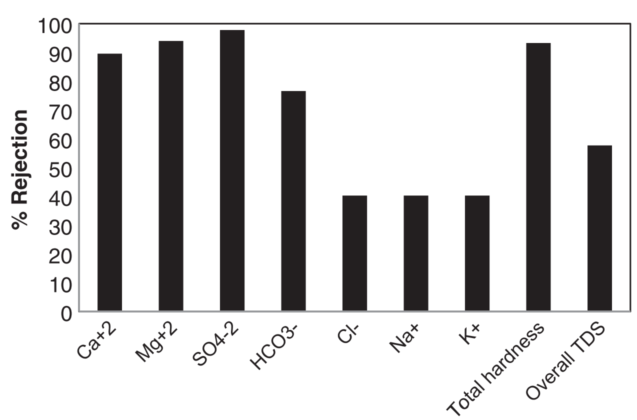

Fig. 1. NF rejection results obtained by Hassan et al. [4] at 22 bar of pressure.

To evaluate the developed configuration of a NF-SWRO system on a commercial scale, a single SWRO desalination plant was converted into a dual NF-SWRO desalination process by introducing an NF membrane pretreatment ahead of the SWRO desalination train [4]. The results showed that the permeate flow from the dual NF-SWRO system was increased to $130\,m^3\,h^{-1}$ compared to the $91.8\,m^3\,h^{-1}$ permeate flow from the single SWRO desalination process.

Al Zoubi [5] reported the use of the NF membrane NF90 in the pretreatment of desalination processes and in partial demineralization. This membrane shows its ability to reject both monovalent and divalent ions of coastal seawater from the Indian Ocean, with concentrations from 38 to 25 g/l using one stage. On the other hand, the NF270 membrane can reject monovalent ions at relatively low values and divalent ions at reasonable values, and reduce water salinity to 33 g/l at a very high permeate flux.

In 2007, Macedonio et al. [6] analysed seven different integrated membrane systems for seawater desalination namely: (1) Only the RO unit; (2) NF-RO; (3) MF-NF-RO; (4) MF-NF-RO and membrane crystalliser module on NF brine; (5) MF-NF-RO and membrane crystalliser module on RO brine; (6) MF-NF-RO and membrane crystalliser module on both, NF and RO brines; and (7) MF-NF-RO, membrane crystalliser module on NF brine and membrane distillation on RO brine. Through the introduction of NF as a pretreatment, the RO permeate increased due to the lower osmotic pressure of the water fed into the RO unit; more importantly, the increase of the water recovery was up to 52%. Furthermore, the cost of desalted water for the process with only RO was $0.61\$\,m^{-3}$, whereas with the addition of NF as a pretreatment, the cost went down to $0.47\$\,m^{-3}$.

To summarize, the NF pretreatment of seawater in desalination plants:

- Prevents SWRO membrane fouling by the removal of turbidity and bacteria,
- Prevents scaling (both in SWRO and MSF) by removing scale forming hardness ions,
- Lowers the required pressure to operate SWRO plants by reducing seawater feed TDS by 30–60%, depending on the type of NF membrane and operating conditions.

From this point it can be concluded that the use of NF membranes for seawater desalination as pretreatment is a very good option for scale prevention. In a recent study, Llenas and co workers [7], studied different commercially available NF membranes in order to find the most suitable ones for this purpose, and they found that NF270 (Dow Chemical), NF99HF (Alfa Laval) and K-SR2 (Koch Membrane Systems), showed good performance for scale prevention in SWRO. However, they used synthetic seawater containing only inorganic salts as feed solution to do their rejection experiments, and the aim of this study is to perform the same experiments but using real seawater. This way, the performance of the membranes can be studied with the real feed water, as in the real desalination plants. Moreover, with this new set of experiments, the membranes' performance can be compared using both feeds, to conclude if the organic matter and other dissolved solids present in real seawater affect inorganic ions rejection.

2. Materials and methods

2.1. Ion rejection experiments

All rejection experiments were carried out in a laboratory scale crossflow module (SEPA CFII, GEOsmonics, France). The flow sheet of the experimental set up is shown in Fig. 2. Flow is delivered to the SEPA CFII membrane cell from the feed tank via a pump (model Hydra-Cell G03-X, Wanner Internation Ltd., Hampshire, UK). The transmembrane pressure was adjusted manually using a needle valve located in the concentrate line, and it was varied between 2 and 20 bars. The crossflow velocity used in these measurements was $0.15\,m\,s^{-1}$ and was recorded using a flow meter (Burkert 8035, Burkert Contromatic S.A., Spain). This value of crossflow velocity is the same as that used in the previous study using synthetic seawater [7], and it was chosen according to data proportioned by Dow Chemical, so this value is between the ones used normally in desalination plants. Conductivity and pH of the permeate stream were measured on-line, using a conductivity cell (Crison 53 92) and a pH electrode (Crison 53 03). The experiments were conducted at 25°C and were controlled by immersion of the feed tank in a thermostatic bath. Finally, the permeate flow was measured via the sample port by mass output taken from a balance (AW-224, Sartorius AG, Goettingen, Germany), and the mass vs. time profile was then used to calculate the volumetric membrane flux.

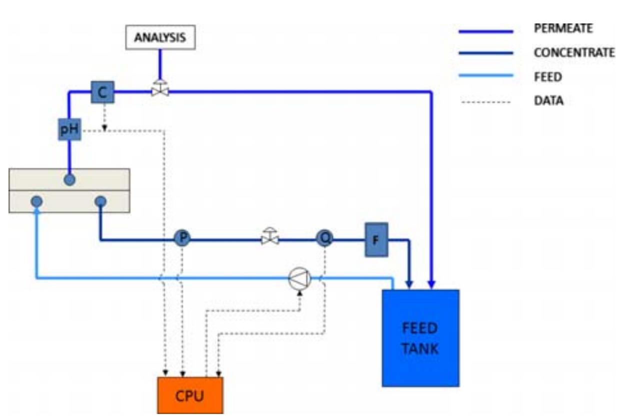

Fig. 2. Experimental system flow sheet.

At each operating pressure, a sample was collected and stored at 4°C until the corresponding analysis was completed. The rejection of solute was calculated using the following equation

$$R = 1 - \frac{C_p}{C_b}$$

where C_p and C_b are the concentration of the permeate solution and the feed solution respectively.

Before starting the experiment, all membranes were pressurized at the maximum pressure for the experiment, 20 bar. The membranes were pressurized for 1 h with deionized water and then for a further hour with the seawater.

2.2. Analytical methods

In order to determine the rejection of all the ions present in the feed water, several analytical methods have been used for the analysis of feed water and permeate samples.

Ion Chromatography (Dionex ICS-2000) was used to analyse anions (Cl^-, SO_4^{2-}, Br^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), a total carbon analyzer (Analytic Jena Multi N/C 3100) was used to analyse inorganic carbon and solute concentrations in the pore size characterization and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Agilent 9500cx, was used to analyse total boron and strontium.

Reference materials and spiked samples were analysed together with samples in each analysis batch, and the recoveries were always between 90 and 110%

2.3. Feed solution and membranes

The real seawater used in this study was collected in the desalination pilot plant of Degrémont, situated in El Prat de Llobregat (Barcelona). Specifically, the

Table 1
Composition of the real seawater collected in El Prat de Llobregat

	$mg\,kg^{-1}$
Cl^-	21,357 ± 1,385
Na^+	13,153 ± 489
SO_4^{2-}	2,944 ± 398
Mg^{2+}	1,505 ± 123
Ca^{2+}	462 ± 13
K^+	449 ± 11
HCO_3^-	26 ± 1
Br^-	86 ± 6
Conductivity ($ms\,cm^{-1}$)	53 ± 4
pH	8.09 ± 0.01

Table 2
Membrane pore size and membrane roughness for the different studied membranes [6]

Membrane	rp (nm)	Rms (nm)
NF270	0.50	5.35
NF200	0.46	7.39
NF90	0.34	103.3
K-SR2	0.69	0.76
ESNA 1-LF2	0.49	49.07
NF99HF	0.46	12.29

water was collected after passing through the ultrafiltration step to avoid suspension solids in the feed water that can cause fouling in the membranes. To do the rejection experiments with different membranes, seawater had to be collected thrice to guarantee that there was no biologic degradation of water.

The raw seawater was analysed each time it had been collected in the pilot plant, and the average composition obtained is shown in Table 1.

The six membranes used in this work were the same ones that were studied using synthetic seawater [7]. Three membranes from Dow Chemical: N270, NF200 and NF90, one from Hydranautics: ESNA 1-LF2, one from Koch membrane Systems: K-SR2, and finally one from Alfa Laval: NF99HF have been the membranes tested, and Table 2 shows the membrane pore size and the membrane surface roughness of the six membranes studied.

3. Results and discussion

3.1. Membrane permeabilities

Fig. 3 shows the permeabilities of the six membranes studied using real seawater together with the

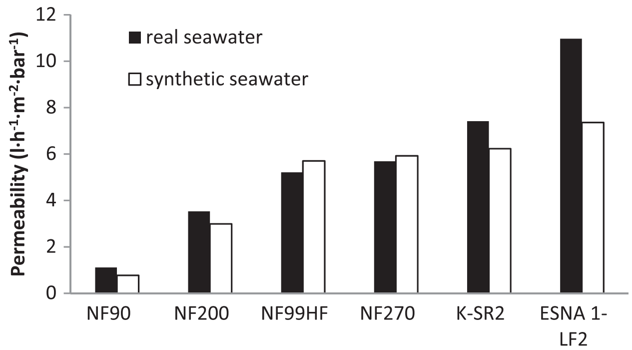

Fig. 3. Membrane permeabilities with real seawater compared with the values obtained using synthetic seawater [6].

values obtained using synthetic seawater in the study performed by Llenas and co-workers [7].

Looking through the data presented in Fig. 3, it can be observed that the NF90 is the least permeable membrane, whereas energy saving nanofiltration membrane from hydranautics (ESNA 1-LF2) is the membrane with the highest permeability.

Comparing these values with the ones obtained in the previous work [7], it can be concluded that for the majority of membranes permeability with real and synthetic water is similar. The only exception is the case of ESNA 1-LF2, which presents a higher permeability using real seawater. The differences between the permeabilities observed in both studies, can be attributed to the use of different feed solutions, but they can also be associated because of using two different membrane samples and the experimental error associated with carrying out two different experiments.

3.2. Ion rejection using real seawater and comparison with synthetic seawater results

The rejection results obtained for the main ions present in seawater are shown in Fig. 4(a–g).

First of all, talking about the rejection of monovalent ions, it can be observed that most of the membranes studied present rejections lower than 20% for chloride, potassium and sodium. The only membrane that shows quite higher rejections for these three ions is the NF90 membrane, and that is because this membrane has properties similar to reverse osmosis membranes.

The rejection of bicarbonate is higher than the rejection of the other monovalent ions, for some membranes it reaches values of 60%, and most membranes reject up to 40% of this ion. That is important for the scale prevention because $CaCO_3$ is one of the most important scalants in SWRO.

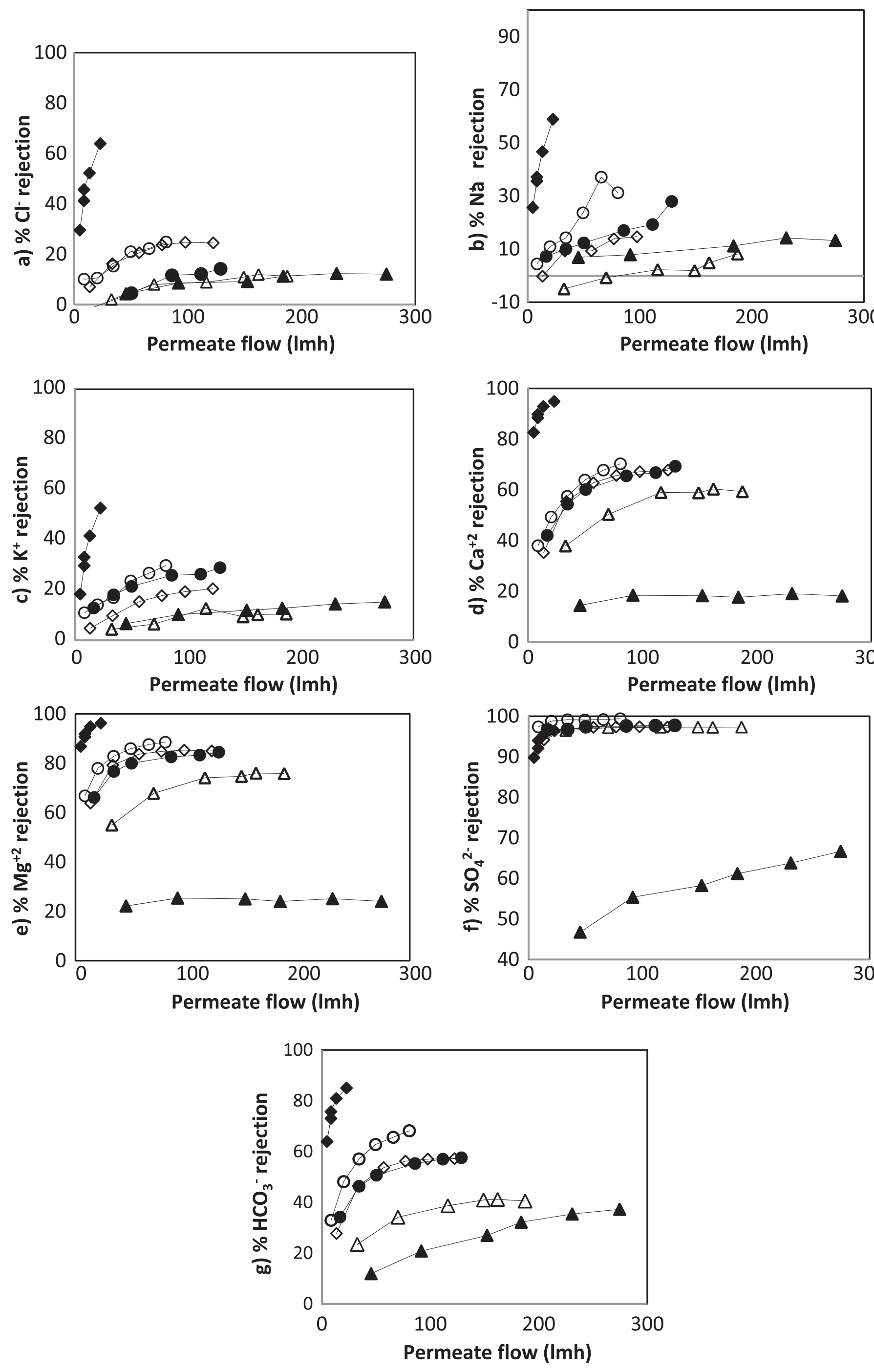

Fig. 4. (a–g) Observed rejections for the main ions present in seawater (•: NF270, ○: NF200, ◆: NF90, ◇ NF99HF, ▲: ESNA 1-LF2, △: K-SR2).

Looking through the obtained results for the other scale forming ions, the results show that sulphates are practically totally rejected for all the membranes studied, excepting ESNA 1-LF2, which presents a sulphate rejection around 60%. Regarding the scale forming cations, calcium rejection ranges from 20 to 95%, being the rejection for the majority of the membranes around 60%. Regarding magnesium, it is better rejected than calcium, rejection being around 80% the most typical value for the majority of membranes studied. As for the sulphates, ESNA 1-LF2 membrane presents very low rejection values for both, calcium and magnesium. Due to that, this membrane is not a good candidate for scale prevention in SWRO.

Comparing the rejection results obtained in this study using real seawater (Fig. 4) with the ones obtained for synthetic seawater [7], it can be observed that monovalent ions are in general less rejected in the case of real seawater feed. For example, in the case of the NF90 membrane, which clearly has higher rejections of monovalent ions, thanks to its similar properties to reverse osmosis membranes, when using synthetic seawater, it presents chloride rejections between 60 and 90%, and in the case of using real seawater, the rejection of this membrane decreases to 30–70%. Regarding the other membranes, they also present lower rejections of the monovalent ions when using real seawater.

On the other hand, the rejection of scale forming ions is practically the same for all membranes in both cases. Hydrogen carbonate rejection is about 20 and 60% for most of the membranes studied in both, real and synthetic seawater; calcium rejection lies between 40 and 60% for four of the six membranes in both feed waters; magnesium also is rejected by a similar amount for real and synthetic seawater between 80 and 60% for four of the six membranes; and sulphates are practically completely rejected by five of the six membranes.

From the obtained results, it can be concluded that there is no significant difference in the rejection of scale forming ions when using real seawater instead of synthetic seawater. This study, therefore, corroborates that NF270, NF99HF and K-SR2 are three very good membranes to be used as pretreatment for scale prevention in SWRO desalination plants.

4. Conclusion

Six different NF membranes have been studied in order to choose which ones can be suitable for the scaling prevention in SWRO. Real seawater was filtered in a laboratory-scale plant and the rejection of different ions was analysed. The obtained results show that the rejection of divalent ions is high in all the membranes tested, which is highly important for scaling prevention.

The conclusion about which would be the more suitable membranes for scale prevention in SWRO is the same when using synthetic or real seawater. An overview of the obtained results concludes that the most suitable NF membranes for anti-scaling pretreatment are: NF270 (Dow Chemical), K-SR2 (Koch Membrane Systems) and NF99HF (Alfa Laval). These three membranes have been selected due to their high rejections of scale forming ions as well as their high permeate flux.

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