Selective separation of seawater Mg^{2+} ions for use in downstream water treatment processes

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ABSTRACT

A nanofiltration-based method is presented for selectively separating soluble Mg(II) species from seawater, with the aim of using the Mg-loaded brine for either enriching desalinated water with magnesium ions or for enhancing precipitation of struvite from wastewater steams. Two 2.4″ commercial NF membranes were tested under varying operational conditions. The membrane that was chosen for further investigation (DS-5 DL, Osmonics) showed lower Cl:Mg and Na:Mg concentration ratios in the brine, and improved performance (with respect to the investigated process) at high recovery values. Since the addition of antiscalants was perceived detrimental to the downstream uses of the brine, the aquatic chemistry program PHREEQC was used to simulate the critical (highest) recovery values at which no CaSO$_4$ would precipitate, assuming two concentration polarization factors. To prevent CaCO$_3$ precipitation at the critical recovery values a theoretical calculation was performed (PHREEQC) to determine the required strong acid dosages to the raw seawater. Using the DS-5 DL membrane at 64% recovery, the attained Mg(II) concentration in the brine was 3500 mg/l. Therefore, for attaining 12.15 mg Mg/l of desalinated water the brine should be dosed to the water at a 1:288 ratio, resulting in additional concentrations of 32.5 mg SO$_4$$^{-2}$/l, 89.3 mg Cl$^-$/l, 39.4 mg Na$^+$/l, 3.3 mg Ca^{+2}/l, and 0.01 mg B/l. The overall cost of the proposed process was estimated at 0.00098 \$/m^3 product water, i.e. approximately five times lower than two assessed alternative processes and more than one order of magnitude cheaper than implementing direct dissolution of chemicals, using either MgCl$_2$ or MgSO$_4$.

1. Introduction

Seawater is characterized by a high Mg^{2+} concentration ($\sim$1430 mg/l in the Mediterranean Sea; 1280 mg/l on average in the oceans) and a relatively high Ca^{2+} concentration (400–500 mg/l). Mg^{2+} ions, if separated selectively from seawater (i.e. if the counter anions are made up predominantly from the relatively non-problematic species SO$_4$$^{2-}$ rather than Cl$^-$) can be used in a cost effective fashion within a variety of water/wastewater treatment processes. Two of these applications, i.e. Mg^{2+} addition to post treated desalinated water; and removal of orthophosphate species from wastewater via precipitation of struvite (MgNH$_4$PO$_4$), a potentially reusable product, are discussed below. However, efficient and low cost separation of Mg^{2+} ions from a solution (seawater) which contains a very high concentration of Cl$^-$ ions ($\sim$20,000 mg/l) and Na$^+$ ions ($\sim$11,000 mg/l), constitutes a challenge. The presence of these two monovalent ions (along with other seawater constituents, e.g. boron) should be minimized since they

are unwanted in the context of both desalinated water and wastewater operations. This work presents a nanofiltration-based method for the separation of Mg^{2+} ions from seawater. Before a detailed description of the process is presented, the main potential uses of Mg-rich solutions from seawater origin are discussed.

1.1. Possible uses for cheap Mg^{2+}-containing solutions within water treatment processes

1.1.1. Addition of magnesium ions to the product water within the post treatment step of desalination plants

The World Health Organization (WHO) has recommended in its recent publications the inclusion of Mg^{2+} and Ca^{2+} ions in desalinated and naturally soft waters [1,2] because of their acknowledged public health beneficial effects. Both ions are welcome not only in drinking water but also in desalinated water designated for irrigation [3] and in treated wastewater from desalinated water origin [4]. From the human health perspective, magnesium ions are recommended by the WHO at a concentration higher than 10 mg Mg/l and calcium ions at a concentration higher than 20–30 mg/l [1,2]. Following this recommendation, the Israeli Ministry of Health is currently promoting a new regulation to add a minimum of 10 mg/l

of Mg^{2+} to desalinated water. In all desalination plants in Israel, Ca^{2+} ions are added as part of the treatment since calcium (and bicarbonate) ions are also required for "chemical stability" purposes, i.e. to reduce the aggressiveness of soft waters to the water distribution systems. Calcium and bicarbonate ions are added to desalinated waters in the "post treatment" step, through the dissolution of solid $CaCO_3$ (quarry limestone), which releases to the water both Ca^{2+} ions and carbonate alkalinity. However, to date, Mg^{2+} ions are not added.

Hitherto, the addition of Mg^{2+} ions to desalinated water could potentially be carried out using one of the following processes: (1) Direct dosage of magnesium salts, such as $MgCl_2$ or $MgSO_4$, to the water, as practiced in Cyprus, for example [5]; (2) dissolution of quarry dolomite ($MgCa(CO_3)_2$) rocks [6]; or (3) a process based on extraction of Mg^{2+} ions from seawater by a cation exchange resin and subsequent release of the Mg^{2+} to the desalinated water in exchange for Ca^{2+} ions, which originate from $CaCO_3$ dissolution [7]. Another option that is sometimes proposed in seawater desalination plants is to blend the desalinated water with ~1% seawater (volume to volume basis) to attain Mg^{2+} concentration of ~13 mg/l. This option suffers from a major disadvantage that in addition to Mg^{2+} other unwanted seawater species, namely Na^+, Br^- and Cl^- ions are added to the water at high concentrations.

1.1.2. Use of Mg^{2+} salts for recovery and reuse of a phosphorus fertilizer product from wastewater streams

A cheap Mg-rich solution separated from the sea may be also used for intentional precipitation of the crystal struvite ($MgNH_4PO_4 \cdot 6H_2O$) as part of the operation of domestic wastewater treatment plants located near the shore. Struvite, a white crystalline compound, consisting of magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphate (PO_4^{3-}) at equal molar concentrations, is known to precipitate in wastewater treatment plants (WWTP) around the world. Such precipitation is normally unwanted since it gives rise to clogging of pipes and pumps, causing both operational difficulties and increased maintenance costs. However, whereas in WWTP struvite is a recognized operational problem, in agricultural applications it may be considered a desirable product: struvite may be employed as a cheap replacement to slow-release fertilizers or as a component in other commercial fertilizers [8–10], due to its low (but not very low) solubility in neutral pH solutions [11].

In addition, since it has been shown that a significant percentage of the dissolved phosphate in wastewater can be recovered through struvite crystallization if controlled precipitation is applied [10,12,13,14,15], using the recovered phosphorous makes struvite a sustainable product. This is significant as natural phosphorus resources are dwindling worldwide and according to current assessments stocks will reach a critically low point by the end of the century [16]. Struvite precipitation occurs only when at least two of the three species, Mg^{2+}, NH_4^+ and PO_4^{3-} are present at relatively high concentrations. Such combination of concentrations is encountered in WWTP only in the anaerobic sludge treatment line. Thus, deliberate precipitation of struvite is typically located on the pipe which delivers the anaerobic digester supernatants back to the treatment plant. At this point the Mg^{2+} concentration is typically roughly one order of magnitude smaller than that of the total ammonia and phosphate weak acid systems, hence the dosage of external magnesium salts (namely $MgCl_2$ and $MgSO_4$) is required for precipitation of a significant mass of struvite solids [12,17–21]. To date, the high cost of magnesium salts limits the application of this process. Notwithstanding, recovery of phosphate from wastewater streams will become, in the foreseeable future, essential for maintaining appropriate phosphorus supply for food production, all over the world.
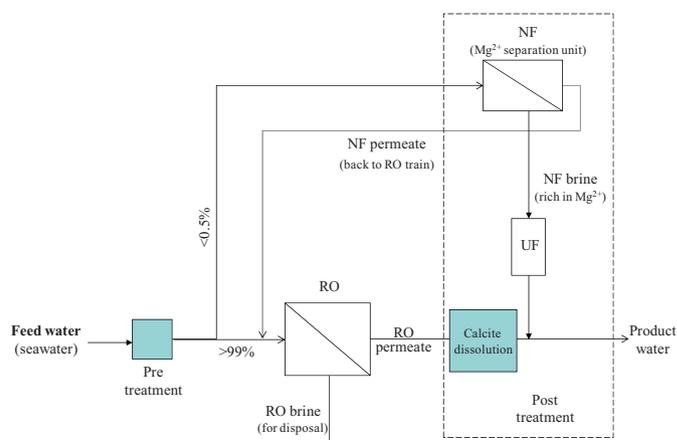

Fig. 1. Schematic of the proposed Mg^{2+} separation process and re-injection of the NF brine to the effluent of the calcite dissolution reactor as part of the desalination post treatment process (indicated by a dashed line).

With respect to this option (similarly to the desalinated water option, described previously) it is noted that addition of unwanted components (Cl^-, Na^+, etc.) to wastewater should also be minimized, particularly in places where treated effluents are reused for agricultural irrigation (e.g. Spain, Australia, Israel, etc.). Another point worth mentioning is that if the Mg^{2+} separation method that is used results also in a high Ca^{2+} concentration, the dosage of Ca^{2+} along with the Mg^{2+} may interfere with the precipitation of a pure struvite product, due to possible competition between struvite and calcium phosphate precipitants. This point, which is not addressed in this paper, requires further investigation.

1.2. The proposed process

This paper introduces a new method for separating Mg^{2+} ions from seawater in a fashion that maximizes the Mg^{2+} concentration in the target solution while at the same time minimizes the addition of the unwelcome species (Cl^-, Na^+, B, Br^-) to the receiving water. The Mg^{2+} separation method is based on passing seawater through a specific NF membrane in a way that (1) enhances separation between divalent and monovalent ions; (2) generates brine with the highest Mg^{2+} concentration possible without using antiscalants which are unwelcome in the receiving water in both discussed alternatives, i.e. desalinated water and struvite precipitation reactors; (3) minimizes the ratio between the unwanted Cl^- and Na^+ ions and the wanted Mg^{2+} ions in the brine. The final NF Mg^{2+}-rich brine can be ultimately used as the solution which supplies Mg^{2+} ions either as part of the post treatment stage in the desalination plant or dosed for enhancing struvite precipitation within the operation of wastewater treatment plants. The proposed process is depicted schematically in Figs. 1 and 2 for the two suggested uses of the brine.

NF membranes are characterized by an intermediate molecular weight cut-off between 150 and 1000 dalton, i.e. in between RO and UF membranes. Due to a charged surface (typically negative, rarely positive) they can be used for separation of electrolytes according to ionic valences. Many works have attempted to model the rejection of uncharged and charged species by NF membranes (e.g., [22–25]. Negatively charged NF membranes typically reject SO_4^{2-} ions at >99% [23] while positively charged membranes can reject Ca^{2+} and Mg^{2+} at a similar efficiency [26]. A few models have been developed to predict the rejection of ions through NF membranes in the context of multi-component feeding solutions (e.g., [22,25,27,28]). However, with the current knowledge it seems that accurate predictive calculations, which involve combined effects of
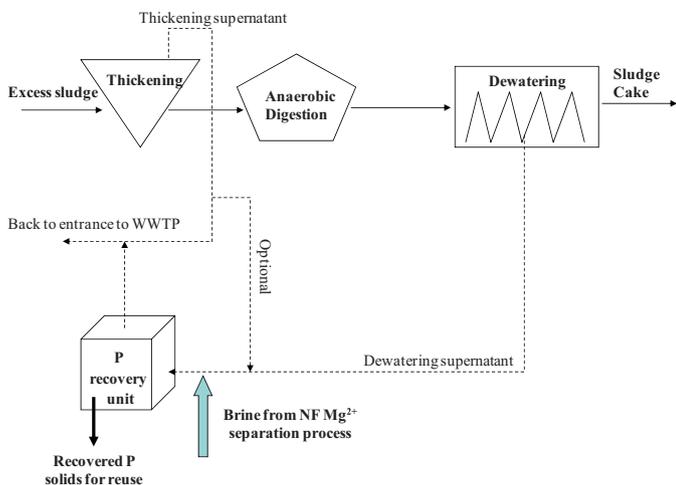
Fig. 2. Schematic of a typical sludge treatment sequence in a municipal WWTP and the point at which struvite may be precipitated with the aid of the NF brine solution.

steric, Donnan and dielectric phenomena are not yet available. This is particularly true for multi-component electrolyte mixtures [25] such as seawater, a fact which makes the task of obtaining empirical data, essential.

From the practical standpoint a considerable amount of work has focused on the use of NF membranes for water-softening purposes (e.g., [29]), seawater desalination pretreatment (e.g., [30]), brackish water pretreatment (e.g., [31,32]), wastewater applications (e.g., [33]), for producing divalent rich brine for agricultural irrigation [34] and other applications (e.g., [35]).

With respect to seawater NF applications: Abdullatef et al. [36] investigated various arrangements of NF membranes (type and manufacturer not reported) for pretreatment for seawater desalination. In general, the results showed high rejection of SO_4^{2-}, Mg^{2+} and Ca^{2+} (99.3%, 94.8% and 82.3% at a recovery of 50%) along with relatively low rejection of Cl^- and Na^+ (8–12%). The brines attained in this application were characterized by Mg^{2+} concentrations of approximately 3140 mg/l accompanied by Cl^- and Na^+ concentrations of 18,740 mg/l and 11,120 mg/l, respectively. In normalized terms, for the addition of 12 mgMg/l in the PT stage ~72 mg/l of Cl^- and ~42 mg/l of Na^+ would be added to the product water. Similarly, for the addition of 10 mM of Mg^{2+} (the approximate dosage required to result in the removal of 90% P, i.e. from a typical concentration of 300 mgP/l to 30 mgP/l, in belt press filtrate lines returning to the WWTP [21]), 1450 mg/l of Cl^- and 860 mg/l of Na^+ will be added to the supernatant. Since the supernatant flow rate is typically about 1% of the overall flow rate of the WWTP, the additions of Cl^- and Na^+ to the WWTP effluents can be estimated to be ~14 and ~9 mg/l, respectively. In places where treated wastewater is used for irrigation, such additional Cl^- and Na^+ concentrations have the potential to limit the use of the water for certain crops, however when no reuse is planned, or when the irrigated crops are less sensitive to these ions, the additional concentrations can be expected to have little or no impact on the wastewater treatment process.

This paper describes experiments conducted with two NF membranes, which were tested for their suitability to the proposed process. Since the presence of antiscalants in the brine is undesirable with respect to both planned downstream uses (in struvite precipitation reactors the presence of antiscalants is expected to slow down struvite precipitation kinetics), a theoretical calculation was carried out to determine the acid dosage required for attaining the maximal recovery value at which the system can be operated safely without precipitating both $CaCO_{3(s)}$ and $CaSO_{4(s)}$.

2. Materials and methods

2.1. Nanofiltration procedure

The experiments were performed with a 2.4″, 40″ long commercial NF membrane elements (effective membrane area 2.6 m^2) in a laboratory scale test cell, using a cross flow module and 50 l of UF-pretreated Mediterranean seawater. Two negatively charged thin-layer NF membranes were used: DS-5 DL (Osmonics, average pore radii between 0.45 and 0.47 nm [37,38]) and NE2540-70 (CSM). Trans-membrane pressures ranged from 4 to 21 bars.

Temperature ranged between 20 °C and 30 °C. Reject streams were returned to the feed tank to resemble a system comprising a few membrane elements operated in series. The permeate stream was removed. Recycled feed flow rate ranged from 60 to 84 l/h m^2.

Solute rejections, r, were defined as $r(\%) = (1 - C_P/C_F)100\%$, where C_P and C_F are the solute concentrations in permeate and in feed streams, respectively. The concentrations of ions in the permeate were either directly measured or calculated indirectly by substituting the measured recovery value and the ion concentrations measured in both the accumulated brine and the initial feed water into mass balance equations". The recovery value, γ, was defined as $\gamma = (V_P/V_F)100\%$, where V_P and V_F are permeate volume and initial feed volume, respectively.

2.2. Analyses

Coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine Mg(II), Ca(II), K(I), Na(I) and SO$_4$ -S concentrations. Cl(-I) concentration was measured by the argenometric method, according to Standard Methods [39].

Note that since ion pairing effects are significant in seawater brines, the terminology Mg(II) (for example) is used throughout the manuscript to denote the overall magnesium concentration, i.e. free Mg^{2+} plus ion pairs such as $MgSO_4^0$ and $MgCl^+$.

Alkalinity (with reference species $H_2CO_3^*$ and $B(OH)_3$) was determined using the Gran titration technique [40].

2.3. Calculations

Theoretical calculations related to gypsum and aragonite precipitation potentials (PP), as well as determination of total $HCO_3(-I)$ concentrations were performed using the PHREEQC software [41]. The database selected in all PHREEQC calculations for estimating activity coefficients was the Specific Interaction Theory (SIT) [42].

3. Results and discussion

3.1. Membrane selection

The first goal of the study was to identify appropriate commercial NF membranes characterized by a high rejection of multivalent ions (particularly Mg(II)) and at the same time low rejection of monovalent ions (especially Cl(-I) and Na(I)). Two types of NF membranes were selected for testing, based on a literature review: NE2540-70 and DS-5 DL. Since the ratio between Cl(-I) and Mg(II) and also the ratio between Na(I) and Mg(II) were perceived important on top of the brine Mg(II) concentration itself, the rejection performances of both membranes were evaluated empirically at varying operational conditions. It is stressed that the two membranes shown in this paper are not necessarily "optimal" for the particular use described in the paper, and it is almost inevitable that other NF membranes exist that would result in higher Mg(II) rejection and lower rejections of unwanted species. However, the purpose of this paper was to introduce the concept rather than to optimize it.

Table 1
Rejection percentages of the main seawater ions as a function of the type of membrane used and trans-membrane pressure (experimental conditions: $\gamma = 50\%$; $T = 20$–$22\,^\circ$C and $T = 28$–$30\,^\circ$C for the NE2540-70 and DS-5 DL experiments, respectively).

Membrane type	P (bar)	Cl(-I) (%)	Na(I) (%)	K(I) (%)	Ca(II) (%)	Mg(II) (%)	SO$_4$(-II) (%)
NE2540-70	6.0	2.7	4.6	10.3	27.5	45.7	88.4
NE2540-70	8.5	5.8	2.8	7.8	29.4	48.0	89.0
NE2540-70	11.0	8.6	7.3	12.0	37.2	57.5	91.5
NE2540-70	14.0	8.9	2.7	7.8	35.3	56.3	91.7
DS-5 DL	8.0	7.9	0.4	0.2	48.2	75.1	98.2
DS-5 DL	11.0	9.6	−2.5	1.2	48.0	79.8	97.8
DS-5 DL	14.0	10.4	−1.8	9.8	56.0	83.8	98.2
DS-5 DL	16.5	10.0	−4.3	−0.6	50.7	82.3	97.7

The performances of the membranes were first evaluated at a constant pressure (14 bar) and 50% recovery. Table 1 lists the rejection values and brine compositions obtained from the operation of the two membranes under these conditions (4th and 7th rows). The DS-5 DL membrane showed significantly higher rejections towards divalent ions than the NE2540-70. For example, Mg(II) was rejected at 83.8% and 56.3%, respectively. The rejections of Cl(-I) and Na(I) by the DS-5 DL membrane were lower than the rejections observed with the apparently looser NE2540-70 membrane. Consequently, the ratios between the concentrations of Cl(-I) and Na(I) and the concentration of Mg(II) in the DS-5 DL brine were approximately 25% lower than those recorded in the brine generated by the NE2540-70 membrane, rendering the DS-5 DL membrane more appropriate for the proposed process at the conditions tested in this experiment.

3.2. Effect of trans-membrane pressure

The effect of the applied trans-membrane pressure (range: 6–16 bar) on the rejection of the main seawater ions was tested using both membranes while maintaining the permeate flux through the membranes constant. Results are shown in Table 1. Based solely on the hydrated ion radii [43], the theoretical rejection sequence for the dominant ions could be expected to be Mg^{2+} > Ca^{2+} > SO$_4^{2+}$ > Na$^+$ > Cl$^-$ ≈ K$^+$. Indeed, both membranes showed higher rejection towards divalent ions than towards monovalent ions. However, since the actual rejection sequences were: SO$_4$(-II) > Mg(II) > Ca(II) ≫ K(I) > Cl(-I) > Na(I) (NE2540-70) and SO$_4$(-II) > Mg(II) > Ca(II) ≫ Cl(-I) ≫ K(I) ≈ Na(I) (DS-5 DL), it was clear that a combination of steric and Donnan exclusion effects were involved in determining the actual rejections, e.g. the high SO$_4$(-II) rejection was mostly due to the fact that both membranes were negatively charged. It is also noted that at the high species concentrations in the brine, formation of ion pairs is significant, and their radii are different from the radii of the free ions. With regard to the NE2540-70 membrane, increasing the trans-membrane pressure up to ~10 bar resulted in an increase in the rejection of Cl(-I), SO$_4$(-II), Mg(II) and Ca(II), however elevating the pressure to beyond 11 did not result in further increase in rejections. With regard to the DS-5 DL membrane, increasing the pressure from 8 to 14 bar resulted in increased rejection values for Cl(-I), Ca(II), Mg(II) and K(I). Again, further pressure increase did not result in elevated rejection values. The rejection values of the other ions did not show a noteworthy pressure effect. Similar trend of rejection dependence on pressure was reported by Cuartas-Uribe et al. [38] and Hilal and Al-Zoubi [44].

Since the rejection of Mg(II) increased while the rejection of Na(I) remained roughly constant or even dropped (Table 1) at the higher pressure range (for both membranes), the ratio between the concentrations of Na(I) and Mg(II) in the brine dropped from 6.41 to 5.87 mol/mol for the NE2540-70 operation and from 4.71 to 4.31 for the DS-5 DL. The Cl(-I) to Mg(II) concentration ratio in the DS-5 DL brine dropped when the pressure was elevated from 8.0 to

14.0 bar, however it slightly increased when the pressure was further increased. In contrast, no significant change was observed in the Cl(-I) to Mg(II) concentrations ratio in the brine generated by the NE2540-70 membrane, due to the fact that both ion rejections increased almost similarly when the pressure was increased.

Throughout the investigated pressure range it was observed that the concentrations ratio between the main unwanted ions (i.e. between Cl(-I) and Na(I)) and the required ion, i.e. Mg(II)) were lower when the DS-5 DL membrane was used, due to significantly higher rejections values for Mg(II) and a lower rejection value for Na(I). Consequently, all further investigations were performed using the DS-5 DL membrane.

Based on the results presented thus far it can be concluded that increasing the external pressure up to 14 bar (for the DS-5 DL membrane) results in increased Mg(II) concentration in the brine and in a slightly decreased Na(I):Mg(II) and Cl(-I):Mg(II) ratios. Beyond 14 bar no improvement was observed with respect to the Cl(-I):Mg(II) ratio.

3.3. Effect of recovery on Mg(II) rejection and Na/Mg and Cl/Mg concentration ratios in the brine

The performance of the DS-5 DL membrane was studied as a function of the recovery and a constant pressure of 14 bars, and the results are shown in Table 2. The rejection values for SO$_4$(-II) were >98% in all the examined recoveries (results not shown). Increasing the recovery resulted in decreased rejection values for all the ions, except for SO$_4$(-II). Similar results with respect to the effect of recovery on rejections of seawater ions in NF were observed by others, e.g. [36]. However, while the rejection of Cl(-I), K(I) and Na(I) decreased significantly (e.g. the rejection of K(I) decreased from 9% at $\gamma = 40\%$ to 3% at $\gamma = 78\%$) the decrease in the rejection of Ca(II) and Mg(II) was much less pronounced (a decrease of ~30%).

Irrespective of the mechanism that led to the relative ion rejections at the higher recovery, the net result was that the molar ratios between Cl(-I) and Mg(II) as well as between Na(I) and Mg(II) in the brine decreased considerably as the recovery went up, as shown in Fig. 3. For example, the molar ratio between the concentrations of Na(I) and Mg(II) in the brine dropped from 4.6 (at $\gamma = 50\%$) to 2.58 (at $\gamma = 78\%$) molNa/molMg and the molar ratio between the concentration of Cl(-I) and Mg(II) in the brine dropped from 6.47 (for $\gamma = 50\%$) to 4.00 (for $\gamma = 78\%$) molCl/molMg. Since the aim of the separation step was both to produce a brine rich in Mg(II) but also with as low as possible Na(I) and Cl(-I) concentrations, a clear incentive exists for operating the process at high recovery values.

3.4. Prevention of chemical fouling at high recovery values without the use of antiscalants

Since the advantage of operating the process at high recovery values was apparent from the results, the issue of chemical fouling

Table 2
Rejection values recorded for the main seawater ions, as a function of the recovery (membrane type: DS-5 DL, pressure: 14 bars, feed flow rate: 60 l/h m^2; temperature range: 25–27 °C; permeate flux range: 19.2–18.0 l/h m^2).

Recovery (%)	Cl(-I) (%)	Na(I) (%)	Ca(II) (%)	Mg(II)) (%)	K(I) (%)	HCO$_3$(-I) (%)
10	28.4 ± 4.0	4.3 ± 2.6	100.0 ± 0	100.0 ± 0	32.7 ± 12.5	37.7 ± 0.9
40	14.2 ± 0.1	2.0 ± 1.5	60.7 ± 5.1	98.2 ± 2.5	9.1 ± 7.1	37.7 ± 0.5
50	11.7 ± 0	2.6 ± 1.4	58.3 ± 1.1	98.2 ± 0.2	4.8 ± 0.5	36.4 ± 2.2
55	10.6 ± 0	1.6 ± 0.6	58.2 ± 6.1	92.6 ± 3.8	4.7 ± 2.3	35.6 ± 1.8
60	10.2 ± 0.4	3.1 ± 1.5	54.6 ± 0	92.9 ± 0.2	6.1 ± 1.9	33.8 ± 1.6
63	9.6 ± 0.3	1.8 ± 0.3	49.7 ± 0.8	95.0 ± 7.1	5.7 ± 1.3	33.7 ± 1.5
66	9.3 ± 0.2	1.3 ± 0.7	46.4 ± 3.7	89.5 ± 1.3	5.6 ± 1.0	32.6 ± 0.1
69	9.1 ± 0.5	1.4 ± 0.1	47.0 ± 0.5	91.4 ± 8.7	4.9 ± 1.5	30.0 ± 1.5
72	8.5 ± 1.3	1.1 ± 0.3	45.1 ± 1.3	89.2 ± 4.0	4.4 ± 1.2	30.2 ± 1.9
75	8.3 ± 0.6	0.4 ± 0.8	41.8 ± 1.3	83.4 ± 5.4	4.1 ± 2.2	31.2 ± 5.9
78	6.5	0.8	38.8	71.5	3.1	21.6

had to be addressed. Since the addition of antiscalants could not be considered for both planned uses of the brine, chemical fouling became the limiting factor for operating the proposed system at the high recovery values. To overcome this problem a critical recovery value (below which no precipitation would occur) was calculated based on the ion concentrations measured in the brine, assumed concentration polarization (CP) factors and thermodynamic data.

In seawater fed membranes chemical fouling may occur mainly due to precipitation of three minerals: gypsum (CaSO$_4$·2H$_2$O), calcite and aragonite (CaCO$_3$). These solids, separately or together, may become the limiting factor for operation at high recovery values.

The CaCO$_{3(s)}$ precipitation potential (PP) can be reduced by acid dosage and consequent reduction in feed water pH. On the other hand, the PP of gypsum is not pH-sensitive at the close-to-neutral pH range. Therefore, in order to avoid the precipitation of both solids it was first required to identify the critical recovery value, above which the PP of gypsum was positive and thereafter to calculate the acid dosage required for disallowing CaCO$_3$ from precipitating at this recovery value.

Under various operational conditions (e.g. pressure, feed concentration and cross flow velocity) applied to spiral wound NF membranes the CP factor has been reported to range from less than 2% [45] to a maximum of ∼13% [46]. Table 3 lists the predicted PP values of gypsum calculated using the PHREEQC software simulating the conditions near the membrane surface. The ionic composition recorded in the brine at the various recovery values was used in this calculation, modified for CP values of 5% and 13%.

According to the results shown in Table 3 the maximal possible recovery value to avoid gypsum precipitation is 64% (assuming CP = 5%) and 60% (for CP = 13%).

With regard to CaCO$_{3(s)}$ precipitation, the calculations were performed under the assumption that both aragonite and calcite could potentially precipitate and foul the membrane [47]. Since calcite is less soluble than aragonite, in the current calculation
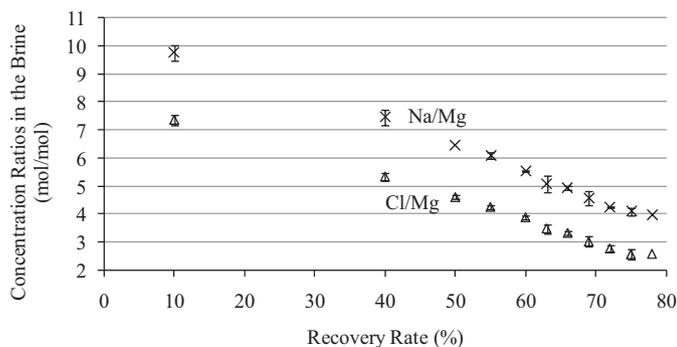
it was assumed that maintaining a negative PP for calcite (by strong acid dosage) would safely prevent CaCO$_3$ (i.e. both minerals) from precipitating on the membrane surface. Note that the steady state PP values of aragonite and calcite in seawater are positive, i.e. 0.269 mM and 0.321 mM, respectively, as calculated using PHREEQC, based on the seawater composition given by [48]. Thus, by maintaining a PP < 0 a further safety factor is applied.

At the operational conditions chosen to avoid gypsum precipitation (i.e. either CP = 5% and γ = 64% or CP = 13% and γ = 60%) CaCO$_3$ precipitation is bound to occur since the PP of calcite is positive, and higher than the value in natural seawater (0.703 mM for γ = 64% and CP = 5% and 0.748 mM for γ = 60% and CP = 13%, both values calculated assuming feed seawater pH of 8.22 – the "natural" pH of seawater). The calculations regarding the required strong acid dosage to prevent CaCO$_3$ precipitation under the conditions prevailing in the DS-5 DL brines as a function of the CP and recovery values reveal that the pH value of the brine should be reduced to pH 7.041 and to pH 7.018 (for CP = 5% and CP = 13%, respectively) to avoid the precipitation of CaCO$_3$ at the respective "critical" recovery values. This can be achieved, in each of the addressed cases, by dosing 7.3×10^{-4} and 6.7×10^{-4} M of H$^+$ (via HCl addition, for example) thereby reducing the pH of the feed water from 8.22 to pH values of 6.777 (assuming γ = 64% CP = 5%) and 6.849 (assuming γ = 60% and CP = 13%).

Calculating the strong acid dosage required to prevent CaCO$_3$ (aragonite) precipitation under the critical gypsum precipitation conditions prevailing in the DS-5 DL brine (i.e. assuming the two above described critical combinations of CP and recovery values to avoid the risk of gypsum precipitation) was carried out using the PHREEQC program. The acid dosage calculation procedure was carried out in three steps: the pH for which the CCPP value in the brine equaled zero mmol/l was first identified. The concentration of HCO$_3$(-I) (i.e. total bicarbonate species concentration) at this pH value, calculated for the specific brine composition, was defined as the maximal allowable concentration (denoted $C_{B\text{-Max}}$(HCO$_3$(-I))). In the next calculation step $C_{B\text{-Max}}$(HCO$_3$(-I)) was used along with the predetermined rejections values of HCO$_3$(-I) and the two assumed CP values for calculating the maximal allowable feed

Fig. 3. Concentration ratios between Na(I) and Mg(II) and between Cl(-I) and Mg(II) in the brine as function of the recovery (membrane type: DS-5 DL, pressure: 14 bar).

Table 3
Precipitation potential of gypsum calculated in the NF brine for several recovery values, assuming two concentration–polarization factors.

Recovery values (%)	PP (CaSO$_4$·2H$_2$O) (mM)	
	CP = 5%	CP = 13%
60		−0.58
61		+0.01
62		+0.56
63	−0.94	+0.91
64	−0.41	
65	+0.31	

Table 4
Concentrations of the main constituents in the DS-5 DL brine at $\gamma = 60\%$ and $\gamma = 64\%$.

Recovery (%)	Concentrations in brine							
	Cl(-I) (g/l)	Na(I) (g/l)	SO$_4$(-II) (g/l)	Mg(II) (g/l)	Ca(II) (g/l)	K(I) (g/l)	Sr(II) (mg/l)	B (mg/l)
60	25.4	11.6	8.5	3.1	0.9	0.6	12.20	2.57
64	25.7	11.4	9.4	3.5	1.0	0.6	12.38	3.05

HCO$_3$(-I)($C_{\text{F-Max}}$(HCO$_3$(-I))) concentrations. In other words, considering the $C_{\text{F-Max}}$(HCO$_3$(-I)) values, the known HCO$_3$(-I) rejections and the CP values, the ultimate concentration of HCO$_3$(-I) in the brine would equal $C_{\text{B-Max}}$(HCO$_3$(-I)). Finally, the software was used in order to evaluate the acid dosages to be added to the feed to obtain HCO$_3$(-I) feed concentrations equal to $C_{\text{F-Max}}$(HCO$_3$(-I)) at the two critical conditions. This evaluation was conducted assuming that the original feed pH, as well as the original pH in the brine, was 8.22.

Note that as acid is dosed to the feed a fraction of the HCO$_3^-$ ion concentration is converted to the H$_2$CO$_3^*$ species. Recalling that this zero charged species (composed mainly from CO$_{2(aq)}$) is hardly rejected by the membrane, it is clear that the dosage of acid results in a brine that is invariably characterized by a proportionally lower C_T (total inorganic carbon concentration) value. As a result, maintaining the calculated $C_{\text{B-Max}}$(HCO$_3$(-I)) by adding the calculated acid dosage would manifest itself in a lower CCPP than the calculated value of 0 mmol/l, which was calculated assuming a higher C_T (the C_T which is the outcome of no acid dosage). In other words, the calculated acid dosage includes an additional safety factor (on top of the one resulting from maintaining a slightly negative CCPP instead of the CCPP naturally present in seawater).

To sum up this part, it appears that an acid dosage of ~24 mg/l will eliminate the propensity for CaCO$_3$ fouling in the proposed application up to a recovery of 60% (assuming CP = 13%).

According to the above calculations it seems that a safe operational recovery with the DS-5 DL membrane should be between 60% and 64%. Table 4 lists the concentrations of the main ions encountered in the brine assuming $\gamma = 60\%$ and $\gamma = 64\%$.

3.5. Discussion regarding the two potential applications of the obtained NF brine

With respect to the use of the brine to add Mg^{2+} to desalinated water: considering the values listed in Table 4 it can be seen that for attaining a Mg^{2+} concentration of 1 meq/l (i.e. 12.15 mg/l) in the product water the dilution ratio of the NF brine with the RO permeate should be 1 to 288 ($\gamma = 64\%$) or 1 to 259 ($\gamma = 60\%$). As a result, the additional concentration of the other ions to the product water would be (for $\gamma = 64\%$): [SO$_4^{-2}$] = 32.5 mg/l; [Cl$^-$] = 89.3 mg/l; [Na$^+$] = 39.4 mg/l; [Ca^{+2}] = 3.3 mg/l; and [B] = 0.01 mg/l.

It is noted that the conditions at which these results were obtained were not strictly optimized with respect to pressure, membrane pore size, membrane surface charge, etc. It is likely that further experimentation and development of tailor-made membranes (and perhaps tailor-made antiscalants) for the proposed application will result in lower additions of Cl$^-$ and Na$^+$ for a given Mg^{2+} addition to the product water and also in higher recovery values, without the risk of chemical fouling. Note that if 78% recovery was used (the highest value tested in the experiments), a target of 12 mgMg/l in the product water would result in increasing the chloride and sodium ion concentrations by merely 64.2 and 29.3 mgCl$^-$/l and mgNa$^+$/l, respectively. To do this, agreed-upon food grade antiscalants will have to be used to prevent CaSO$_4$ from clogging the membrane. Assuming a typical antiscalant concentration of 3 mg/l in the feed water, the antiscalant concentration in the product water (after dilution) would be lower than 0.008 mg/l.

In cases where the additional concentrations of Cl$^-$ and Na$^+$ are problematic, this may be the preferred option.

The alternative of using the Mg-rich NF brine to enhance struvite precipitation is different in three main respects from the option of dosing MgCl$_2$ or Mg(OH)$_2$ chemicals, which is typically implemented for this purpose. The first difference is that in the NF-brine based option Ca^{2+} ions are also added to the water with the brine, albeit at a much lower concentration than the Mg(II) addition. This might enhance precipitation of Ca-phosphate solids (e.g. hydroxyapetite) and might detract from the purity of the attained struvite mineral [21]. A second difference is that Mg^{2+} addition through NF brine results in dilution of the ammonium and phosphorus concentrations in the wastewater, and as a result in a slight decrease in the struvite precipitation potential, relative to the scenario of pure chemical addition. The third difference stems from an increase in the ionic strength of the wastewater stream, which again acts to slightly reduce the PP of struvite. Due to these effects, the Mg(II) concentration added to the wastewater stream must be increased relative to the concentration typically implemented in direct chemical dosage applications, in order to attain a similar P removal and a given mass of struvite precipitate.

Another by product of this process will be the increase in concentrations of certain ions in the wastewater treatment plant effluents, namely Cl$^-$, SO$_4^{2-}$, Br$^-$ and Na$^+$, as explained in the Introduction section. However, the main advantage would be the much lower cost of Mg(II) addition, as shown in the next paragraph.

3.6. Cost assessment and conclusion

The cost of the proposed process was assessed and compared with the costs of alternative means and processes for Mg^{2+} supply to desalinated water. This ultimate use of the brine was chosen for pricing over the struvite recovery alternative because it was perceived more straightforward in its implementation. CAPEX and OPEX estimations of five Mg(II) supply alternatives were considered: Alternative #1: a process based on dolomite dissolution [6]; Alternative #2: a process based on calcite dissolution followed by ion-exchange (IX) [49]; Alternatives #3 and #4: direct dosage of either MgSO$_4$ or MgCl$_2$; and Alternative #5: the currently proposed NF based process (assuming a CP of 13% and thus a maximum recovery of 60%). All the costs were normalized for the addition of 12 mg/l of Mg^{2+} to 1 m^3 of desalinated product water in the post treatment stage of desalination plants, assuming production of 100 M m^3 desalinated water per year.

The five addressed alternatives focused on Mg^{2+} addition, along with meeting quality criteria for alkalinity, Ca^{2+} and CCPP concentrations. As a result, the cost of Mg^{2+} addition in Alternatives #1 and #2 could not be easily distinguished from the cost of the overall post treatment processes. However, in the other three alternatives (i.e. the proposed NF method and the two chemical dosage methods) the cost of Mg^{2+} addition could be separated from the overall post treatment cost, and these were shown in Table 5. The cost of the Mg^{2+} addition step in alternatives #1 (dolomite dissolution) and #2 (calcite dissolution + IX) was determined almost directly from the discussion part in the relevant references ([6] and [49], respectively) and only small adjustments were made to the calculation of the cost quoted in the references, such as equating the

Table 5
Estimation of the operational and capital costs ($/m^3 product water) of the direct dosage alternatives and the NF alternative.

		Alternative #3 MgSO$_4$ dosage	Alternative #4 MgCl$_2$ dosage	Alternative #5 proposed process (NF)
OPEX	HCl	–	–	0.00005
	MgSO$_4$	0.03009	–	–
	MgCl$_2$	–	0.0071	–
	Energy	→0	→0	0.00065
Subtotal OPEX		0.03009	0.0071	0.00070
CAPEX	Assuming 6% interest and 20 y serviceable life	→0	→0	0.000281
Total cost		0.03009	0.0071	0.00098

Remarks: energy cost 0.12 $/kW h; HCl cost = 200 $/ton; NF CAPEX calculated based on the following rule of thumb: 6000 $ per m^3/h of brine; Required energy for the NF alternative was calculated based on a rule of thumb of 40 W h per bar per m^3 and brine recovery of 40%.

prices of chemicals in the two alternatives, considering a Mg^{2+} concentration of 12.15 mg/l in the product water in both alternatives and updating/adding the estimated capital costs for each alternative. The prices of the chemicals considered in this paper for the two alternatives were: 150 $/ton (H$_2SO_4$), 40 $/ton (CaCO$_3$), 50 $/ton (CaMg(CO$_3$)$_2$) and 400 $/ton (NaOH). The resulting overall costs for the addition of 12 mg/l of Mg^{2+} in alternative #1 and #2 were estimated at 0.53 and 0.51 cent/m^3 of product water, respectively. Note that the processes differ somewhat from each other in the final water quality so a straightforward cost comparison is not advised. Irrespectively, the cost of the Mg^{2+} addition in both alternatives is almost identical.

Table 5 lists the OPEX and CAPEX estimated for the three other alternatives. Naturally, the cost of the methods based on direct chemical addition is heavily dependent on the price of the chemicals, which were estimated at 500 and 300 $/ton for MgSO$_4$ and MgCl$_2$, respectively. In contrast, the cost of the NF process depends significantly on the CAPEX and to a lesser degree on the energy and strong acid (HCl) requirements, which practically constitute the OPEX. The energy required for the NF process was estimated at 1.4 kW h/m^3 brine, assuming operation at 14 bar pressure and 60% recovery.

Considering the cost of Mg^{2+} addition to 1 m^3 product water in all the considered alternatives it transpires that the cost of the NF option is by far the cheapest: approximately five times lower than the cost of the methods described in [6] and [49,50] and one order of magnitude lower than the cost estimated for the direct chemical dosage methods. Clearly, the cost of each of these processes is affected by the chosen prices of chemicals and other local conditions and may probably deviate by 20–30% from the estimation presented here, however, the inevitable conclusion from this cost estimation is that if the addition of the described concentration of unwanted species, namely Cl$^-$ and Na$^+$, to the product water is perceived acceptable, the proposed NF alternative is by a large amount the most cost effective option for the addition of magnesium ions to desalinated water and probably also to other treatment uses, such as removal and reuse of phosphorus from wastewater streams as a valuable struvite product.

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