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Replenishing Mg(II) to desalinated water by seawater nanofiltration followed by magnetic separation of $Mg(OH)_{2(s)}Fe_3O_4$ particles

Orly Lehmann, Or Eckhaus, Ori Lahav, Liat Birnhack*

Faculty of Civil and Environmental Engineering, Technion, Israel Institute of Technology, Technion City, Haifa 32000, Israel, Tel. +97 2 4 8292627; Fax: +97 2 4 8295696; emails: orlylehmann@gmail.com (O. Lehmann), oreck9@gmail.com (O. Eckhaus), agori@tx.technion.ac.il (O. Lahav), birbirit@tx.technion.ac.il (L. Birnhack)

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ABSTRACT

Magnesium (Mg^{2+}) appears at high concentration in seawater and seawater-reverse-osmosis brines. In contrast, desalinated water is almost completely depleted of Mg^{2+}, a mineral perceived essential for human health and agricultural irrigation. The paper introduces a cost-effective method to enrich desalinated water with an almost pure Mg(II) solution, originating from seawater. The method uses seawater nanofiltration (or nanofiltration of seawater-reverse-osmosis brine) to produce brine characterized by high Mg^{2+} concentration, accompanied by relatively low B, Cl^-, and Na^+ concentrations. Subsequently, Mg(II) is separated from the produced nanofiltration brine by precipitating $Mg(OH)_{2(s)}$ and adsorbing it onto the surface of micro-magnetite particles. Finally, the solid slurry ($Fe_3O_4 + Mg(OH)_2$) is magnetically separated from the brine and the $Mg(OH)_{2(s)}$ is re-dissolved into the desalinated water in a separate reactor. Application of the method results in a relatively pure Mg(II) addition to the desalinated water product. For example, for Mg(II) addition of 10 mg/L (as recommended by the World Health Organization), the following negligible concentrations of unwanted species are added to the water (in mg/L units): Na^+: 0.04, Cl^-: 0.18, Ca^{2+}: 0.05, and B: 0.0094. The cost of adding 10 mg Mg/L was estimated at 0.76 cent $\$/m^3$ of desalinated water, i.e. competitive with previously suggested processes.

Keywords: Magnesium recovery; SWRO; Fe_3O_4, $Mg(OH)_2$; Magnetic separation

1. Introduction

Desalinated water is a rising water source, in which the Mg(II) concentration usually tends toward zero, even after the re-mineralization step. In recent years, the need for magnesium in drinking and irrigation waters has become almost consensual, as manifested, for example, by the World Health Organization's (WHO) recommendation to maintain a minimum Mg(II) concentration of 10 mg/L in all drinking waters [1]. Following the WHO recommendation, the Israeli Ministry of Health decided in 2011 on the replenishment of Mg(II) to desalinated water to a level of 20–30 mg Mg/L [2], dependent on cost-implications derived from a pilot study.

On top of the health-related significance of Mg(II) in drinking water, the need for Mg(II) in irrigation water is also considered unambiguous and in this respect it is noted that desalinated water is increasingly destined for agricultural irrigation either directly or indirectly (i.e. as treated wastewater). A minimum

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*Corresponding author.

Mg(II) concentration in agricultural irrigation water is required in order to minimize the need for application of fertilizers, particularly in case the local soil is low in minerals [3] and no other Mg(II)-containing water sources are continuously available. Yermiyahu et al. [4] concluded that even if water sources rich in minerals are available and planned to be mixed with the desalinated water, to minimize fluctuations in the quality of the supplied water, the mineral content of the desalinated water should approach that of the other sources. Otherwise, the farmer will have to install and operate sophisticated and expensive control systems to level off fluctuations. The addition of adequate concentrations of these minerals to the desalinated water in the desalination plant may circumvent the need for adding them through fertilization.

Unlike Mg(II), the boron concentration in desalinated water is often limited by an upper threshold. From the health aspect, boron limitation is relatively loose: WHO guideline for B(III) concentration in drinking water is 2.4 mg/L [5]. However, in cases where the water is used for irrigation of sensitive crops, the total B(III) concentration should not exceed 0.5 mg/L [6]. In Israel, for example, recent desalination plants bids set a B(III) concentration threshold of 0.3 mg/L [7].

To attain the final desalinated product water composition, a post-treatment (sometimes referred to as re-mineralization) step is invariably applied [8]. Post-treatment processes are often based on calcite ($CaCO_3$) dissolution, enhanced by acidification of the RO permeate water using either H_2SO_4 or CO_2. Both alternatives are followed by pH elevation through dosage of base (NaOH) or CO_2 stripping [8]. Unsurprisingly, these conventional processes do not result in addition of Mg(II), but merely aim at replenishing calcium ions and carbonate alkalinity to the water. Thus, development of a cost-effective method for enriching desalinated water (and other soft water sources) with magnesium is necessary. A successful Mg(II) enrichment method should ensure that the addition of unwanted components (i.e. Na(I), Cl(-I), and B) would be minimal.

Several methods have been thus far suggested for replenishing the Mg(II) concentration in desalinated water: direct dosage of magnesium-salts (either $MgSO_4$ or $MgCl_2$), as practiced, for example, in Cyprus [9]; Magnesia (MgO) dissolution in packed bed reactors [10]; Dolomite ($CaMg(CO_3)_2$) dissolution followed by calcite dissolution [11]; exchange of calcium ions with magnesium ions by means of a specific ion-exchange (IX) resin, loaded with seawater-based Mg(II) [12–14]; dosage of brine rich in Mg(II) produced by nanofiltration (NF) of seawater [15,16]; and dosage of Mg(II)-rich brine originating from seawater RO brine, from which the Mg(II) was extracted by precipitation of $Mg(OH)_{2(s)}$ on the surface of magnetite particles that were subsequently magnetically separated [17]. A thorough comparison, covering various aspects pertinent to the implementation of the previously suggested methods, is provided in Table 1.

The summary given in Table 1 implies that each method has drawbacks (underlined in the Table 1). For example, direct dosage (upper three methods) is preferable from the water quality point of view; it is, however, expensive; on the other hand, the SWNF brine dosage option results in very low TDS addition. However, implementation of this method to enrich the water with 10 mg Mg/L results in elevation of boron concentration by ~0.03 mg/L, which corresponds to ~10% of the Israeli threshold.

The above methods' comparison underlines the necessity for developing a cost-effective Mg(II) replenishment process that would result in minimal addition of unwanted components (namely Na(I), Cl(-I), and B(III)) to the product water. The current work suggests a process that combines two previously suggested Mg(II) separation methods: the nanofiltration-based (e.g. [15,16,19]) and the magnetite-based separation methods. More specifically, in the presented work Mg(II) is first separated from seawater using nanofiltration to produce a Mg(II) rich brine with a low B(III) concentration; thereafter, the Mg(II) present at high concentration in the NF reject brine is further separated using micro Fe_3O_4 particles and magnetic-aided separation. This combination of methods was hypothesized to result in lower Na(I), Cl(-I), and B(III) additions to the desalinated water as result of the Mg(II) dosage. The basis of this assumption is explained in the following paragraph.

It has already been shown that relatively pure Mg(II) rich solutions can be produced from SWRO brine by precipitation of $Mg(OH)_{2(s)}$ on micro Fe_3O_4 (magnetite) particles [17] (bottom row in Table 1). Lehmann et al. [17] showed that the purity of the produced Mg(II)-rich brine with respect to Na(I) and Cl(-I) was high (>97%). However, since boron species are adsorbed as $B(OH)_4^-$ on the surface of both the magnetite particles and the $Mg(OH)_{2(s)}$ precipitant [17,20,21], most of the boron that was present in the source solution, found its way to the Mg(II)-rich product solution. Thus, to reduce B(III) additions to the product water, an NF step is now added before the magnetite separation step. This way, a reduction in the boron concentration is expected in the solution fed to the magnetite step, and consequently also in the product water.

This work also introduces another optional process for Mg(II) addition to desalinated water, which is

Table 1
General comparison of the currently suggested methods for Mg(II) addition to desalinated water. The drawbacks of each method are underlined

Method	Maximum Mg(II) in product water	Cl^- and Na^+ to Mg^{2+} additions	Ratio of boron to Mg^{2+} additions	Water quality flexibility[a]	Cost	Footprint	Refs.
	mg/L	mg:mg	mg:mg				
$MgCl_2$ dosage	No limit	$Cl^-:Mg^{2+} \approx 2.93$	None	High	High [15]	Very small	
$MgSO_4$ dosage	No limit	Negligible	None	High	Very high [15]	Very low	
MgO dissolution	~20	Negligible	None	Moderate. Effects alkalinity and pH	High	High	[10]
Dolomite-calcite dissolution	~12	Negligible	None	Low	Moderate	Moderate	[11]
IX	~20	Negligible	None	Moderate (mainly effects Ca^{2+})	Moderate	Moderate	[12]
SW dosage	No direct limit	$Cl^-:Mg^{2+} \approx 14.6$ $Na^+:Mg^{2+} \approx 8.52$	$\sim 1.8 \times 10^{-3}$	High	Very low	Very low	[18]
SWNF-brine dosage	No direct limit	$Cl^-:Mg^{2+} \approx 3.5$ $Na^+:Mg^{2+} \approx 1.32$	$\sim 4.4 \times 10^{-4}$	High	Low	Low	[15,16]
SWRO-brine-magnetite	No limit	$Cl^-:Mg^{2+} \approx 0.036$ $Na^+:Mg^{2+} \approx 0.019$	$\sim 2.7 \times 10^{-3}$	High	Moderate-low	Low	[17]

[a] Influence of Mg(II) addition on alkalinity, pH, Ca^{2+} concentration, stability etcetera.

based on separation of Mg(II) from SWRO brine using nanofiltration membranes.

1.1. The suggested processes

Two alternatives for enriching desalinated water with Mg(II) are presented. Both alternatives are aimed at minimizing the addition of unwelcome components (namely Cl(-I), Na(I), and B). The main developed process is an enhancement of the process described in [17]. The new process, described schematically in Fig. 1, utilizes either SWRO brine or SW as the Mg(II) source. These two alternatives are denoted Process 1 and Process 4, respectively. The first process step consists of acidification of the raw solution, followed by aeration, with the aim of stripping almost all (>95%) the dissolved inorganic carbon from the original solution (i.e. either SW or SWRO brine), to prevent $CaCO_3$ scaling in the following step. In the next step, the decarbonated original solution is nanofiltered to produce a Mg(II)-rich brine that is also characterized by relatively low boron concentration. After passing through a UF step to remove microorganisms, the produced brine flows into a fully mixed $Mg(OH)_{2(s)}$-precipitation-adsorption reactor. pH is raised by dosage of strong base (preferably CaO, being the cheapest base) until practically all the Mg(II) precipitates as $Mg(OH)_{2(s)}$ on the surface of the magnetite (Fe_3O_4) particles while other ions remain in the dissolved form. The solids slurry (Fe_3O_4-$Mg(OH)_{2(s)}$) is then separated from the Mg(II) depleted brine by applying a magnetic field, and further by vacuum filtration. The separated Fe_3O_4-$Mg(OH)_{2(s)}$ mixture is optionally rinsed, depending on the required purity of the final solution. The $Mg(OH)_{2(s)}$-coated-magnetite-particles are then contacted with desalinated water, in order to enrich it with Mg(II) while at the same time elevate its alkalinity, pH, and calcium carbonate precipitation potential (CCPP) values, as required [22].

The Mg(II) replenishment process is integrated with the conventional post treatment (PT) process which is commonly applied in desalination plants, i.e. calcite dissolution. In the conventional PT process, NaOH is added to the calcite dissolution reactor (CDR) effluents to reach a small positive CCPP (or Langelier saturation index) value. In the developed process, $Mg(OH)_{2(s)}$ is added to the effluents of the CDR (stream #3 in Fig. 1). Therefore, $Mg(OH)_2$ dissolution is used both as means of Mg(II) supply and for pH elevation, replacing costly NaOH dosage. Nevertheless, the required $Mg(OH)_{2(s)}$ dosage (e.g. to attain 10 mg Mg/L in the product water) is much higher (in equivalent units) than the conventionally required NaOH dosage (aimed only at achieving the CCPP requirement). Thus, prior to Mg(II) dissolution, strong acid must be dosed to avoid surpassing the pH and

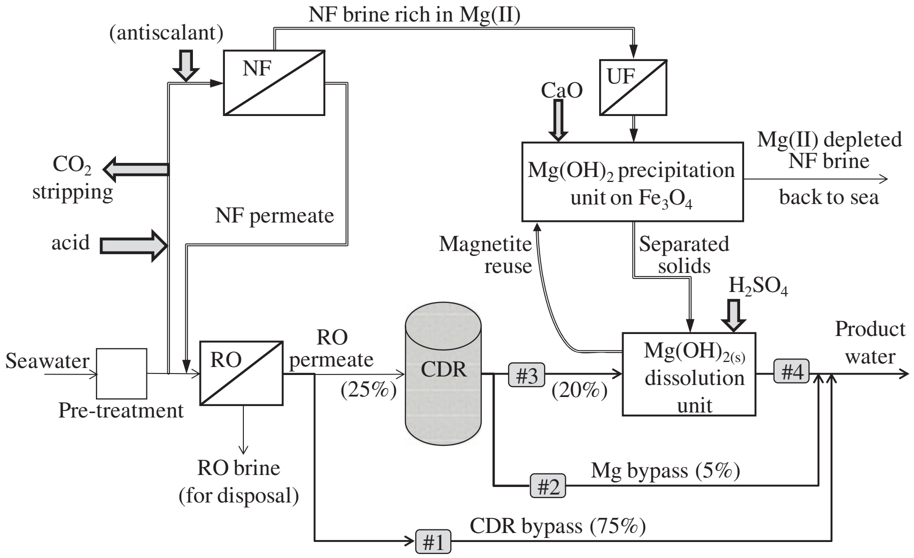

Fig. 1. Schematic illustration of the main suggested process. Stream numbers are indicated on the arrows. Numbers in brackets represent the percentage of flow rate out of the total RO permeate flow rate. The percentages represent Scenario A.

CCPP upper limits and also in order to enhance the $Mg(OH)_{2(s)}$ dissolution rate and avoid $CaCO_3$ precipitation. To conclude, in the presented process, a $Mg(OH)_{2(s)}$ dissolution step (accompanied with H_2SO_4 dosage) is applied at the end of a conventional calcite dissolution or lime dissolution post treatment process (see Fig. 1).

After dissolving the predefined mass of $Mg(OH)_{2(s)}$, the Fe_3O_4 particles are magnetically separated from the enriched stream. The Fe_3O_4 particles can now be reused in the next adsorption cycle [17]. Finally, the Mg-enriched stream (stream #4 in Fig. 1) is merged with the untreated desalinated water bypass stream (stream #1 in Fig. 1, denoted "CDR bypass") and with the CDR effluent that was not enriched with Mg(II) (stream #2 in Fig. 1, denoted "Mg bypass") to achieve the final water quality.

Another option for enriching soft waters with magnesium is also presented: instead of contacting the $Mg(OH)_{2(s)}$-Fe_3O_4 mixture with CDR effluents, the solid mixture can be mixed with H_2SO_4 acidified water (similar to the dissolution procedure detailed in [17]) so that Mg(II) is re-dissolved for producing a relatively pure and concentrated $MgSO_4$ solution. This final product can be dosed to any soft water, in order to enrich it with Mg^{2+} and SO_4^{2-}.

Dissolution of $Mg(OH)_{2(s)}$ into the effluent of a CDR is advantageous over producing a $MgSO_4$ solution and dosing it, since in the former option less acid and base are required (considering the overall PT process), which is economically favorable and also better from the water quality point of view (as less sodium is added to the water).

Finally, an alternative was also investigated: nanofiltration of SWRO brine (denoted Process 2). Note that this alternative differs from previous SWNF studies in the sense that instead of using SW as the raw stream from which Mg(II) is separated, SWRO brine is used.

2. Materials and methods

2.1. Theoretical calculations

Theoretical calculations related to water chemistry (e.g. strong base and acid dosages, CO_2 stripping and precipitation potential (PP) determination) were performed using the PHREEQC software [23]. The Pitzer approach for concentrated solutions was applied by the use of "pitzer.dat" database, embedded in the program.

The limitations of dissolving $Mg(OH)_2$ into the CDR effluents were also assessed using the PHREEQC software. In all calculations, thermodynamic equilibrium was assumed.

2.2. NF experiments

NF experiments were carried out using a pilot-scale seawater desalination unit comprising one 4´´ spiral wound NF module. The unit is described in detail in [15]. The membrane used was DL4040F1020, stinger (Osmonics), and the applied pressure was

18 bar. Two source solutions were used in the experiments: (1) Filtered Mediterranean seawater (~1,300 mg Mg/L) and (2) first stage SWRO brine produced in the same pilot-scale seawater desalination unit, using Mediterranean seawater as the feed solution and SW30-HRLE4040 by DOW Filmtec membrane and applied pressure of 65 bar. The Mg(II) concentration in the SWRO brine was ~2,400 mg Mg/L. In both cases, prior to being introduced to the NF step, the feed solutions were acidified and over 95% of the carbonate concentration (in the form of CO_2) was stripped out of them. The NF brine produced from SWRO brine was assessed for use both "as is" i.e. direct dosage to desalinated water for Mg(II) enrichment, and as the raw material introduced to the magnetite aided Mg(II) separation unit.

2.3. Magnetite aided $Mg(OH)_{2(s)}$ precipitation and separation

Mg(II) was extracted from the two types of NF brines in a laboratory-scale experimental apparatus, applying the procedure described in [17]. The operational conditions applied in the current study were chosen based on the conclusions drawn in [17]: (1) A base (KOH) was slowly dosed at a stoichiometric ratio, aiming at separating all of the Mg(II) present in the source solution as a $Mg(OH)_2$ precipitant adhered to the magnetite particles; (2) Fe_3O_4 concentration was 4.17 g Fe/g Mg precipitated; (3) Solid settling was enhanced by applying an external magnetic force (Magnet: Neodymium 80 mm × 80 mm × 20 mm); (4) The separation step consisted of vacuum separation via a sintered glass filter porosity grade 4, followed by rinsing the solids with a 20 ml distilled water per g solids ($Fe_3O_4 + Mg(OH)_2$) and a second, final vacuum separation step.

2.4. Dissolution of $Mg(OH)_{2(s)}$

Two alternatives were examined for dissolving Mg(II) out of the produced $Fe_3O_4 + Mg(OH)_2$ solid mixture: (a) mixing with H_2SO_4 acidified distilled water (requiring an acid dosage equivalent to the $Mg(OH)_{2(s)}$ to be dissolved), to produce a concentrated $Mg(II)/SO_4^{2-}$ product solution for dosing it into soft waters; (b) dissolution into simulative solution representing CDR effluents: 280 ml of CDR effluents solution was prepared by dissolving analytical grade $CaCl_2$ and $NaHCO_3$. The CDR effluent sample was carefully poured into a Metrohm sealed beaker (beaker: 6.1415.250, lid: 6.1414.010). The sealing of this beaker, which contains five optional lid openings for electrodes or tubes, ensured no $CO_{2(g)}$ stripping to the atmosphere ($CO_{2(g)}$ stripping had to be avoided since it leads to unwanted pH elevation and consequent reduction in the $Mg(OH)_2$ dissolution potential). A pH electrode was inserted through the beaker lid, and pH was constantly measured. Next, the simulative CDR effluents were acidified using concentrated H_2SO_4 (dosage determined according to final water quality requirements and based on PHREEQC simulations). A weighed mass of the solid mixture ($Fe_3O_4 + Mg(OH)_2$) was immediately immersed into the acidified CDR. A peristaltic pump was used to recirculate the two phases in the beaker, in order to ensure homogenous mixture. Two sealed ports of the beaker's lid were used as inlet and outlet tubes, required for the recirculation. The 280 ml sample filled the beaker and the tubes completely, minimizing headspace to which CO_2 could be stripped. Solution circulating was halted when the pH value reached a value implying that the required mass of $Mg(OH)_2$ had dissolved. Samples were taken before dissolution of $Mg(OH)_2$ and at the end of the dissolution. When mixing was stopped and dissolution was completed, the beaker was placed on a magnet, to enhance settling of solids. Once the solids settled, samples were taken for turbidity measurements, as well as for determining ionic composition.

2.5. Analyses

Samples were characterized by ICP-AEP (1CAP6300 Duo, Thermo Scientific) for determination of the following species concentrations: Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, and B. Chloride concentrations were determined using the Argenometric method, according to Standard Methods [24]. The turbidity of the produced water was measured using a Portable turbidimeter (2100Q, HACH).

3. Results

The results section is divided in two: (a) theoretical calculations, aimed at determining the thermodynamic limitations and effect thereof on the process. The same calculations were used for defining favorable operational conditions to be applied in the experiments; and (b) experimental results of both the NF step and the $Mg(OH)_2$ precipitation and dissolution steps.

3.1. Theoretical calculations

Theoretical calculations (PHREEQC) were aimed at investigating various options for dissolving $Mg(OH)_{2(s)}$ into CDR effluents. There are numerous scenarios for implementing the $Mg(OH)_2$ re-dissolution step. The theoretical calculations served two purposes: first, the set of thermodynamic and kinetics-based limitations of the process were understood, and their effects on the process was studied; next, within the thermodynamic and kinetic boundaries of the process, several operational parameters were altered to investigate their influence on the process results.

Generally, the following process parameters can differ from one case to another: (a) type of PT applied (e.g. H_2SO_4 based calcite dissolution; CO_2 based calcite dissolution or $Ca(OH)_2$–CO_2 dissolution); (b) the final water quality goals; (c) fraction of flow rates out of the total RO permeate flow rate: %splits #1, i.e. the fraction of flow rate of stream #1 (denoted "CDR bypass", Fig. 1) from the total flow rate of RO permeate; %split #2, i.e. the fraction of flow rate of stream #2 (denoted "Mg bypass", Fig. 1) out of the total flow rate of the RO permeate; and finally, (d) acid dosage into the Mg dissolution reactor. Clearly, altering any of these parameters would affect the re-dissolution step, from both the economic and water quality aspects.

First, two thermodynamic and kinetic considerations that should be met were determined: (1) Unwanted $CaCO_3$ precipitation, which might occur at the end of the $Mg(OH)_2$ dissolution step due to the high Ca(II) concentration and elevated pH value prevailing at this stage (i.e. in stream #4). The kinetics of calcite precipitation is relatively slow and is known to be hindered at high concentration of dissolved Mg(II) [25]. Nevertheless, at high CCPP values unwanted calcite precipitation might occur, hence, the operational parameters should be such that the CCPP value following $Mg(OH)_2$ dissolution would not exceed ~70 mg/L as $CaCO_3$. In addition, in order to avoid calcite precipitation, the retention time in the $Mg(OH)_2$ dissolution reactor should be as short as possible, and merging the treated water (stream #4) with the bypass streams (i.e. stream #2 and #3) should be quick, since the CCPP of the merged stream is reduced, as compared to stream #4 (Fig. 1); (2) The second consideration relates to $Mg(OH)_{2(s)}$ dissolution: in order to ensure relatively high reaction rate in the $Mg(OH)_2$ dissolution reactor, the water entering the reactor should have a potential to dissolve $Mg(OH)_2$ that is considerably larger than the total mass of $Mg(OH)_2$ planned to be dissolved in it, i.e. when the water leaves the reactor it should still have a significant negative PP toward $Mg(OH)_2$ (i.e. <−100 mg/L). On top of these two constraints, the following guideline should also be considered: after merging the Mg(II) dissolution reactor effluent with the CDR bypass (stream #1) and Mg bypass (stream #2) the desired CCPP and pH values should be attained.

In order to comply with these limitations, several manipulations can be applied on the operational parameters. Listed here are three such alternatives. Note that the first two alternatives act to decrease both the CCPP and $Mg(OH)_2$-PP of stream #4, as required, while the third alternative decreases $Mg(OH)_2$-PP and increases the CCPP of stream #4: (a) the first and simplest optional scheme is to elevate the acid dosage into the Mg dissolution unit; (b) the second option is to reduce %split #2, i.e. to decrease the flow rate of the Mg(II) bypass (Fig. 1). Such action would result in a decreased $Mg(OH)_2$ dissolution goal; (c) Finally, it is optional to elevate %split #1, i.e. reduce the flow rate of the CDR bypass stream (stream #1 in Fig. 1). This would result in elevated calcite dissolution goal in the CDR, i.e. higher buffer capacity in the CDR effluents (stream #3 in Fig. 1). Thus, as $Mg(OH)_2$ dissolves into the CDR effluents the increase in pH value is expected to be hindered (due to the higher buffer capacity), and therefore the PP of $Mg(OH)_2$ will be lower. However, this would also lead to higher Ca(II) concentration and therefore elevated CCPP. Looking for the best operational alternative, theoretical simulations were conducted to define operational conditions under which minimum acid and base dosages would be required. The simulations were examined for compliance with the following limitations: high $Mg(OH)_2$ dissolution potential (i.e. above 100 mg/L) and low $CaCO_3$ PP (i.e. below 70 mg/L) in stream #4, and minimal reactor dimensions. Two main alterations were examined in the simulations: (1) reduction of the flow rate into the Mg dissolution reactor in order to reduce its size. This can be achieved by elevation of %split #2 (i.e. decreasing the percentage of CDR effluents entering the Mg dissolution reactor); and (2) decreasing the H_2SO_4 dosage prior to Mg(II) dissolution. Reducing the dosage of acid is clearly economically beneficial. On the other hand, too high %split #2 or too low acid dosage would result in an excessively high pH value at the end of the $Mg(OH)_{2(s)}$ dissolution step, which might lead to unwanted precipitation of $CaCO_3$ and/or to too low $Mg(OH)_2$ dissolution potential, which might limit the dissolution due to kinetics considerations.

In order to exemplify the effect of altering the operational conditions, four PT scenarios (out of numerous potential options) are presented in Table 2. In all the scenarios, the product water is enriched with 10 mg Mg/L by dissolving $Mg(OH)_2$ into the CDR effluent (stream #3). Scenarios A (shown in Fig. 1) and C are based on PT process comprising calcite dissolution enhanced by H_2SO_4 dosage, as practiced, for example, at the desalination plant in Ashkelon, Israel. The assumed final water quality goal (with respect to

Ca(II), pH, alkalinity, and CCPP thresholds) was the water quality currently produced in the 115 M m^3 y^{-1} Ashkelon desalination plant. The final water quality goals of the other three scenarios were set as close as possible to the water quality attained in Scenario A. However, some differences are an inevitable outcome of the use of different acids in the CDR step [8]. Scenarios B and D simulate another common PT process, in which CO_2 is used to dissolve calcite [8]. Note that in the developed $Mg(OH)_{2(s)}$ re-dissolution step, Mg(II) and OH^- ions are simultaneously released to the CDR effluents in the reaction occurring in the Mg dissolution reactor. The added hydroxide ions substitute the need for the conventional addition of costly NaOH dosage; therefore, the $Mg(OH)_{2(s)}$ dosage has a dual use. As a result, in scenarios A and C no NaOH dosage is required, as final pH and CCPP values are elevated as an outcome of the $Mg(OH)_2$ dissolution. On the other hand, in conventional CO_2-based calcite dissolution PT processes, final pH adjustment is frequently achieved through CO_2 stripping, rather than base dosage. Thus, in scenarios B and D, the $Mg(OH)_2$ dosage cannot completely replace the need in CO_2 stripping. Consequently, in the merged stream of scenarios B and D stripping of 10.5 and 15.0 mg CO_2/L are required, respectively, in order to elevate the pH from 7.20 to 7.77, and from 7.06 to 7.80, respectively. The pH increase is accompanied by CCPP elevation to 1 mg/l as $CaCO_3$ (both cases). Such CO_2 stripping is kinetically and thermodynamically feasible, in the investigated scenario since the solution is far enough from equilibrium with atmospheric CO_2.

Table 2 shows that the proposed process is theoretically feasible as a Mg(II) enrichment process for two of the examined PT alternatives, i.e. Scenario A and B. Scenarios C and D are expected to require smaller reactor sizes. However, it is clear that these scenarios are not recommended because of the high CCPP values attained within them in stream #4.

Table 2 also presents the water quality attained in a conventional PT process, assuming that a Mg(II) enrichment process is not applied, that is, the water quality attained assuming calcite dissolution enhanced either by H_2SO_4 dosage or CO_2 dosage (corresponding to Scenario A and B, respectively). Dissolved calcium and CCPP values were similar regardless of the Mg(II) replenishment. The small difference in pH and alkalinity values is shown in brackets. Note that apart from the welcome increase in Mg(II), there is practically no difference in water quality.

From the operational conditions point of view, comparing Scenario A and B shows that the main difference between them is the required additional H_2SO_4 dosage: 29.4 and 14.7, respectively. This difference stems from the lower buffer capacity of stream #3 in Scenario A. Due to the low buffer capacity, a lower initial pH is required in order to dissolve the required $Mg(OH)_2$ concentration.

To conclude, according to the theoretical examination the process can be combined with two commonly applied PT processes to result in improved water quality. Based on these theoretical results the process was experimentally examined to conclude whether the kinetic assumptions were feasible, and what is the extent of product purity that can be attained.

Table 2
Theoretical results of the suggested PT process applied for enriching desalinated water with 10 mg Mg/L. Water qualities attained at stream #4 and at the product water. In brackets: the water quality attained in the conventional PT, i.e. without the Mg(II) addition step. In bold: water quality surpassing the recommended limitations

Operational parameters				Extra H_2SO_4 dosage	Quality of Mg dissolution effluent (stream #4)			Product water quality			
Scenario	Split #1 %	Split #2 %	Type of Acid used in CDR –	g/m^3 RO product	pH –	CCPP mg/L as $CaCO_3$	$Mg(OH)_2$ PP mg/L as $Mg(OH)_2$	pH –	Ca mg/L	Alk mg/L as $CaCO_3$	CCPP mg/L as $CaCO_3$
A	25	20	H_2SO_4	29.4	8.69	57	−123	8.29 (8.27)	36	46.4 (45.5)	0.86
B	30	25	CO_2	14.7	7.38	70	−281	7.77^a (7.96)	36	116 (90)	1.03^a
C	25	5	H_2SO_4	28.9	10.47	**336**	−182	8.42	36	46.9	1.79
D	25	10	CO_2	19.6	8.69	**119**	−182	7.80^b	36	111	1.04^b

[a,b] Water quality attained after CO_2 stripping of 10.2 and 15.0 mg/L, respectively.

3.2. Experimental results

Experimental results of the two developed process steps are presented. First, results of applying NF on SWRO brine are described. Then, the results of applying the combined NF—magnetite separation process on SWRO brine and on SW are shown. The aim of the second process was to produce and separate $Mg(OH)_{2(s)}$ that can then be re-dissolved either directly into the acidified CDR effluent or into acidified water. Note that applying the NF step on SW at various operational conditions has already been reported [15,16], hence this topic was not further examined in the current work.

3.2.1. NF separation step: effect of recovery ratio on brine quality

The effect of the recovery ratio on the produced NF brine was recorded with respect to two brine characteristics: the concentration ratios between unwanted components and Mg(II), and the concentration of Mg(II). Fig. 2 presents ratios between the concentrations of unwanted components (i.e. Na(I), Cl(-I), and B(III)) and magnesium in the NF brine produced when SWRO brine was used as feed. The concentration ratios are shown as a function of the recovery ratio. It is evident that the ratios decreased as the recovery ratios increased, thereby improving the brine quality. Considering that the produced NF brine is mixed (either directly or indirectly) with soft waters, it is clear that at a higher recovery ratio is preferable.

Determining the optimal operational recovery ratio in the NF step is a function of both operational cost and the required water quality.

As expected, it was also observed that the Mg(II) concentration in the produced brine increased at the higher recovery ratios: 2733, 3215, and 4198 mg Mg/L were measured at recovery ratios of 21, 35, and 63.5%, respectively. The rejection of Mg(II) was 76, 73, and 62% at recovery ratios of 21, 35, and 63.5%, respectively. Higher Mg(II) concentration is considered advantageous since it enables decreasing equipment size required in the next separation step (i.e. in case Mg(II) purity is further elevated by applying the magnetite-aided separation step). However, a higher recovery ratio also corresponds to a reduction in the mass of magnesium extracted from the raw solution (the SWRO brine) since, by definition, the volume of the permeate increases as the recovery ratio increases, and since Mg(II) rejection was below ~80%, the permeate contained a significant mass of Mg(II).

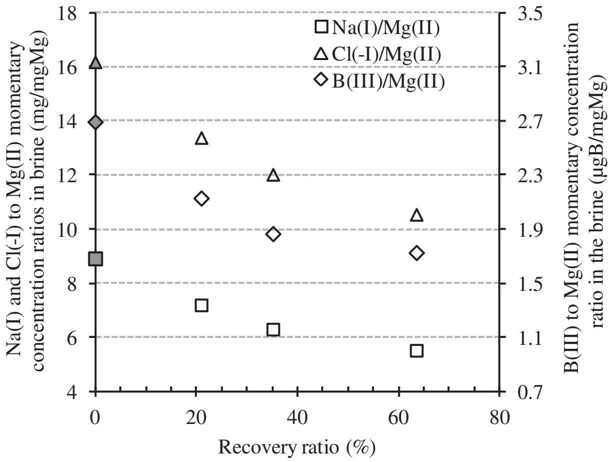

Fig. 2. Characteristics of NF brine produced from SWRO brine at a pressure of 18 bars: ratios between concentrations of unwanted components and concentration of magnesium as a function of recovery ratio. Full signs represent feed concentration ratios.

The practical recovery ratio is ultimately limited by gypsum ($CaSO_4{\cdot}2H_2O$) precipitation. NF experiments on SWRO brine were stopped at a recovery ratio of 63.5% due to experimental system technical limitations. The brine's PP toward gypsum at this point (i.e. 63.5% recovery ratio) was calculated to be: −2.54 g $CaSO_4\ L^{-1}$ (PHREEQC results), taking into account a concentration polarization factor of 5%. That is, the brine was indeed under-saturated with respect to gypsum. Thus, a higher recovery ratio could have been applied, even in the absence of antiscalants. Note that avoiding antiscalant dosage is optional due to the fact that the carbonate system had been removed from the feed prior to the membrane filtration step (see Fig. 1). The produced brine was first assessed as the source solution for the $Mg(OH)_2$-magnetite-based process (denoted “Process 1” in this work; results of this option appear in Section 3.2.2). Then, it was assessed as a source of Mg(II) without any further processing; i.e. dosage of this brine directly to the soft water (denoted “Process 2” in this work). As mentioned, a significant characteristic of the brine is the ratios between concentrations of components of interest and the magnesium concentration. The attained ratios are listed in Table 3. The concentration ratios of all considered processes are given, as well as the ratios of two reference processes: Process 0, which is the process described in [17], consisting of magnetite separation step applied on SWRO brine, and Process 3, which is based on SWNF brine dosage.

Table 3 also lists the results of applying an NF step (at a 63.5% recovery ratio) on SWRO brine (Process 2). As can be directly calculated from the values listed in Table 3, applying Process 2 for enriching soft water with 10 mg of Mg(II) is inherently associated with the addition of 42.9 mg Na(I), 87.1 mg Cl(-I), 0.015 mg B(III), and 2.7 mg Ca(II).

As observed from Table 3, except for the Ca(II) concentration, all ion additions are greater when SWRO brine nanofiltration retentate (i.e. Process 2) is dosed than when seawater nanofiltration retentate is used (i.e. Process 3). Thus, using SWRO brine as feedwater for the NF step is disadvantageous in this respect.

3.2.2. *Water quality achieved in the combined NF-$Mg(OH)_{2(s)}$-magnetite process*

As explained before, in order to enhance the purity of the Mg(II) added to the soft water an additional step was applied on the NF brine: precipitation of $Mg(OH)_{2(s)}$ on magnetite particles that are afterwards separated, and the $Mg(OH)_{2(s)}$ precipitant is re-dissolved into the CDR effluent. The magnetite aided precipitation step was examined using both SWRO–brine–NF–brine and SWNF–brine as feed solutions. Results are shown in Table 3 (Process 1 and 4, respectively).

Note that Process 1 is similar to Process 0, except that the SWRO brine is nanofiltered prior to the magnetite separation step. Comparing these two processes (Table 3), it is obvious that the NF separation step reduces the ratio between boron and Mg(II) in the produced solution, as required. Similarly, the effect of applying the magnetite separation step can be examined by comparing Process 1 to Process 2 and Process 4 to Process 3 (since each of these couples of processes differs from each other only in the presence of the magnetite separation step). Such a comparison demonstrates that adding the magnetite-aided precipitation step dramatically reduced the ratios between the concentrations of Na(I) and Cl(-I)) and the concentration of Mg(II), from several mg per mg Mg(II) in Processes 2 and 3 to only several μg per mg Mg(II) in Processes 1 and 4. However, the B(III) to Mg(II) concentration ratio is practically unaffected by the magnetite-aided separation step, due to the fact that virtually all the B(III) in the brine is adsorbed as $B(OH)_4^-$ onto the magnetite-$Mg(OH)_2$ particles in the precipitation step and is then re-dissolved with the Mg(II) into the product solution.

In order to assess which solution is preferred as the Mg(II) source solution, SWRO brine or SW, the following processes were compared: Process 2 with Process 3 and Process 1 with Process 4. This comparison shows that using SW is advantageous, since lower concentration ratios were achieved in Processes 3 and 4 as compared to Processes 2 and 1, respectively. However, differences were rather small.

To conclude, from the water quality point of view, it appears that the following alternative is preferable: nano-filtration of SW followed by magnetite-aided separation, i.e. Process 4. However, it should be noted that in all alternative processes in which magnetite separation aided is applied, the overall additions of unwanted components are very low. For example, considering a target Mg(II) concentration of 10 mg/L by applying Process 1, the additions of Na(I), Cl(-I), and B(III) are 0.08, 0.22, and 0.011 mg, respectively; This in comparison to 0.04 mg Na(I), 0.18 mg Cl(-I), and 0.009 mg B(III) added in Process 4, assuming the same Mg(II) dissolution target.

3.2.2.1. Implementation of the developed Mg separation process into the PT process. As explained above, Mg(II) enrichment can be achieved by direct dissolution of the precipitated $Mg(OH)_2$ into acidified CDR effluent (see Fig. 1).

Table 3
Average ($n = 3$) ratios between concentrations of components of interest and concentration of magnesium in five possible processes for enriching soft waters with magnesium

		Process 0 [17]	Process 1	Process 2	Process 3	Process 4
Process characteristics	Source solution	SWRO brine	SWRO brine	SWRO brine	SW	SW
	NF step	No	Yes	Yes	Yes	Yes
	Magnetite step	Yes	Yes	No	No	Yes
Product concentration ratios (mg/mg)	B/Mg	$2.5 \times 10^{-3} \pm 5 \times 10^{-5}$	$1 \times 10^{-3} \pm 1 \times 10^{-4}$	$1.5 \times 10^{-3} \pm 3 \times 10^{-4}$	$9 \times 10^{-4} \pm 8 \times 10^{-5}$	$9 \times 10^{-4} \pm 2 \times 10^{-4}$
	Na/Mg	0.016 ± 0.001	0.008 ± 0.002	4.29 ± 0.07	2.28 ± 0.178	0.004
	Cl/Mg	0.036 ± 0.001	0.022 ± 0.007	8.71 ± 0.45	2.3 ± 0.044	0.018 ± 0.002
	Ca/Mg	0.002 ± 0.000	0.005 ± 0.0008	0.27 ± 0.01	0.25 ± 0.023	0.005 ± 0.0007

The results of contacting acidified CDR effluent with $Mg(OH)_2$-Fe_3O_4 solid mixture produced according to Process 4 were further examined, since this process was found to result in the purest Mg(II) addition. The experiments simulated the following conditions: %split #1 = 25%; %split #2 = 20% (Fig. 1); water quality target: alkalinity > 45 mg/L as $CaCO_3$, $[Ca^{2+}] > 80$ mg/L as $CaCO_3$, CCPP > 0 mg/L as $CaCO_3$, $[Mg^{2+}] > 10$ mg/L and pH < 8.5. This scenario corresponds to line 1 in Table 2, which simulates integration of the suggested process into the PT process currently applied in the Ashkelon desalination plant, Israel. This experiment was aimed at validating the kinetic assumptions (related to $CaCO_3$ precipitation and to $Mg(OH)_{2(S)}$ dissolution) on which the theoretical calculations were based (Section 3.1). In this scenario, final pH and alkalinity adjustments by additional base dosage are not required as in conventional PT processes.

Assuming that 20% of the RO permeate passes through the Mg(II) dissolution reactor (Fig. 1), the Mg(II) dissolution target in the reactor is 10/0.2 = 50 mg/L. The experimental results showed that after ~4 min 45.2 ± 2.3 mg/L Mg dissolved ($n = 3$); i.e. 90.4% of the 50 mg/L Mg dissolution target. A pH of 8.7 was measured at this point in all three repetitions; this value is close to the expected value (Table 2). This indicates that most of the pH elevation had occurred due to $Mg(OH)_2$ dissolution, and not due to CO_2 stripping. In order to separate the magnetite particles from the desalinated water, a magnetic field was applied at the bottom of the beaker, and solid settling was allowed. It was found that the turbidity of the desalinated water was reduced to below 1 NTU after 23.7 ± 9.8 min on the magnet. This initial result is sufficient, taking into consideration that the dissolution reactor effluent is further diluted when it is merged with the bypass streams. The results of this examination show that the concentration ratios detailed in Table 3 remain the same regardless of the dissolution procedure, i.e. whether a $Mg(II)/SO_4^{2-}$ rich solution is dosed or $Mg(OH)_{2(s)}$ is directly dissolved into the desalinated water. The measured Ca(II) concentrations before and after the Mg(II) dissolution remained practically the same: 120 mg/L vs. 124 ± 3 mg/L. this indicates that $CaCO_3$ precipitation did not take place during the $Mg(OH)_2$ dissolution, probably due to the short retention time and high Mg(II) concentration.

When comparing the suggested Mg(II) enrichment options, two aspects are of major importance: process cost and unwanted ion additions. Clearly, reduction in acid and base dosages leads to reduction in process costs. Regarding ion additions, it is noticeable that ions originating from the source solution (either SW or SWRO brine) are added to the desalinated water at the same (insignificant) concentrations in both alternatives (i.e. whether $Mg(OH)_2$ is dissolved directly into the CDR effluents or when Mg(II) is dosed through the production of Mg(II) rich solution). In case $Mg(OH)_2$ is dissolved directly into the CDR effluent, the need for base dosage as in the conventional calcite dissolution PT process [8] is eliminated; Thus, further unwanted Na(I) ions addition is avoided. With regard to the acid dosage, using the CDR effluent reduces the amount of required acid to re-dissolve $Mg(OH)_{2(s)}$ into water. In this case, the acid dosage was determined according to the kinetics limitations of calcite precipitation and $Mg(OH)_2$ dissolution. When producing a $Mg(II)/SO_4^{2-}$ rich solution to be dosed to the water, acid demands are higher: one equivalent of acid is required for dissolving each equivalent of Mg(II) (i.e. 40.3 mg H_2SO_4 for 10 mg Mg/L enrichment). In light of this, and based on the acid dosages presented in Table 2, the savings associated with dissolving Mg(II) directly to the CDR effluents are 10.9 and 25.6 g H_2SO_4 per m^3 desalinated water, for the process presented on line 1 and on line 2 of Table 2, respectively.

3.3. Cost assessment

Table 4 presents a detailed cost assessment of the three developed options for enriching desalinated water with 10 mg Mg/L. The cost assessment is divided in two: (1) the NF process and (2) $Mg(OH)_{2(s)}$ precipitation on magnetite.

Four Mg(II) addition options are compared: (1) dosing the SWRO–brine–NF–brine (64% recovery ratio), i.e. Process 2; (2) dosage of Mg^{2+}/SO_4^{2-} rich solution, produced from SWRO brine and applying both the NF and magnetite steps (i.e. Process 1); (3) dosage of Mg^{2+}/SO_4^{2-} rich solution, produced from seawater and applying both the NF and magnetite steps, i.e. Process 4; and (4) direct Mg(II) dissolution into desalinated water, assuming that the Mg(II) was separated from SW by applying Process 4.

Although from the water quality point of view it was concluded that Process 4 is preferable, since in all suggested processes the unwanted component additions were very low (except in Process 2), the economic aspects of other processes were also looked into. Process 2 was evaluated from the cost point of view, although it was apparently inferior from the water quality point of view, because it was assumed to be considerably less costly.

In all cost calculations a desalination plant of 100 Mm^3 per year was assumed, as well as required addition of 10 mg Mg/L; hence, 1,000 tons of Mg(II) should be separated annually.

Table 4
Estimated cost breakdown associated with the presented processes, for three different processes (cents$ per m^3 of desalinated water for a 10 mg Mg/L addition), and the total cost given in bold font in the last raw

	Parameter	Units	Mg rich solution added to desalinated water		
			NF brine of SWRO brine (Process 2)	NF brine of SWRO brine + Magnetite (Process 1)	SW NF brine + Magnetite (Process 4)
Step I NF brine production	OPEX				
	NF energy[a]	cent$/m^3 desalinated water	0.022	0.022	0.050
	UF energy[b]		1.7×10^{-3}	1.7×10^{-3}	1.59×10^{-3}
	H_2SO_4		–	0.036	0.035
	Antiscalants		3.5×10^{-3}	–	–
	Total OPEX		0.027	0.060	0.087
	CAPEX		0.016	0.016	0.037
	Total cost- step I		0.043	0.076	0.123
Step II $Mg(OH)_{2(s)}$ precipitation on Magnetite	Chemical demands				
	CaO H_2SO_4 for Mg $(OH)_2$ dissolvent	ton chemical/ton Mg(II) produced	–	2.654	2.654
			–	4.036	4.036
	OPEX				
	Chemicals[c]	cent$/m^3 desalinated water	–	1.15	1.15
	Labor, electricity, water, magnetite replenishment, maintenance[d]		–	0.13	0.13
	Total OPEX			1.28	1.28
	CAPEX	cent$/m^3 desalinated water	–	6.42×10^{-3}	6.42×10^{-3}
	Total Cost-step II	cent$/m^3 desalinated water	–	1.29	1.29
	CAPEX + OPEX				
Total Cost: step I + II		cent$/m^3 desalinated water ($/ton Mg(II))	0.043 (43.2)	1.37 (1,366)	1.41 (1,413)
CAPEX + OPEX					

[a] Operating at a pressure of 18 bars, assuming electricity price of 0.068 $/(kW h) and electricity consumption of 0.0278 kW h bar^{-1} pumping m^{-3} of feed.

[b] UF filtrate cost of $0.8 cent per m^3 of the filtrate.

[c] Calculated based on: H_2SO_4 $170/ton; CaO 176$/ton.

[d] Labor cost calculated as 10% of total OPEX. Also included are 10% annual magnetite replenishment at 5,350 $/ton$_{\text{Magnetite}}$ (0.24 ton magnetite per year), i.e. 1.28×10^{-3} cent$/m^3 desalinated water for a 10 mg Mg/L dosage.

3.3.1. Cost assessment of the NF step

The main cost component in the NF process is the energy required in the NF step. The energy required for the subsequent UF step applied on the produced brine (Fig. 1) is lower by one order of magnitude. The cost of the energy required in the NF step was estimated by taking into account operation at a pressure of 18 bars, electricity price of 0.068 $/(kW h) (http://www.eia.gov/electricity/monthly/epm_table_grapher.cfm?t=epmt_5_6_a), electricity consumption of 0.0278 kW h per bar per pumping of 1 m^3 feed and pump efficiency of 90%. This cost component was calculated to be much lower for Processes 1 and 2 than for Process 4. These differences stem from the different brine Mg(II) concentrations attained in each alternative and the different recovery ratio applied (i.e. recovery ratios of 64.3% when SWRO brine is filtered and ~85% when SW is filtered). The cost of the UF step was calculated based on the average UF filtrate cost of $0.8 cent per m^3 of the filtrate [26].

Note that it was assumed that 3 mg/L of antiscalant are added to the SWRO brine fed to the NF step in Process 2, while no antiscalants were used in the other processes. The reason for this difference is that the NF brine produced in Process 2 is dosed as is to the soft water. Therefore, there is no need for removing the inorganic carbon (C_T) from it (as no pH elevation is applied in the next step). On the other hand, in case the magnetite aided step is also applied (Processes 1 and 4), C_T removal is obligatory; therefore, addition of antiscalant becomes redundant. On the other hand, the cost of the NF step in Processes 1 and 4 includes the cost of dosing a small amount of H_2SO_4 in order to avoid $CaCO_3$ scaling. Scaling of $CaSO_4$ is not expected under the conditions tested in these scenarios (i.e. recovery ratios of 64.3% when SWRO brine is filtered and ~85% when SW is filtered). In any event, even if antiscalants are dosed (for example if the NF step is operated at higher recovery ratios) the antiscalant dosage cost corresponds to less than 10% of the total NF step cost (based on an antiscalant price of $2 per kg). Taking into account that the cost of the NF step corresponds merely to ~3% of the total cost of Processes 1 and 4, it can be concluded that from the economic point of view the addition of antiscalant is negligible.

Capital expenses (CAPEX) were calculated based on a cost of $2,500 per m^3 feed per h; under the conditions of Processes 1 and 2 (SWRO brine as source solution) the NF plant capacity should be 211,000 m^3 brine y^{-1} (corresponding to treating a feed of ~579,000 m^3 y^{-1} by the NF plant). Finally, 5% interest rate and a 20-year serviceable lifetime were assumed.

3.3.2. *Cost assessment of the $Mg(OH)_{2(s)}$ precipitation on magnetite process*

Processes 1 and 4 include a second step comprising of a $Mg(OH)_2$ precipitation and separation process. This second step is the main cost component in these scenarios, contributing to over 90% of the total cost of the Mg enrichment process.

The main cost component in this step is the chemical consumption: CaO used to precipitate $Mg(OH)_2$; and H_2SO_4 used to re-dissolve it in the final stage. This cost was calculated considering a magnesium recovery efficiency of 85% (i.e. 1 mol of CaO was used to recover 0.85 mol of Mg(II), as observed in the laboratory experiments). In other words, only 85% of the Mg(II) was recovered from the NF brine. Note that this low efficiency was probably a consequence of an analytical error. Chemical prices were assumed to be \$170/ton H_2SO_4; 176\$/ton CaO. Cost differences between Processes 1 and 4 were insignificant (on the order of 10^{-4} cents). The cost of labor, electricity (including the required energy for CO_2 stripping that is estimated at under 3×10^{-3} cent\$/m^3 desalinated water), water consumption, 10% annual magnetite replenishment, and maintenance were estimated to be 10% of total OPEX of this step.

Capital expenses comprise mainly of stirred reactors, magnetic separators, synthesis of the initial magnetite mass required in the process, and construction costs (see elaboration in [17]), and packed bed stripping towers, whose cost was estimated to be of the same order of magnitude as stirred reactors. Taking into account a 35% safety margin, the overall capital costs amount to a total of $80,000. The normalized CAPEX was found to be lower than 0.4% of the total cost of this step, i.e. its effect on the overall cost is very low.

According to our results, it can be concluded that in case of stringent water quality requirements applying Process 4 is advantageous. This conclusion is based on the observation that the additional cost of Process 4 (compared to the cost of Process 1) is small (Table 4), while the improved water quality attained when applying this process is significant, especially with respect to Na(I) and Cl(-I) additions (Table 3).

While from the water quality point of view Process 2 is inferior to the other processes tested in this work (Table 3), from the cost point of view Process 2 is preferable (Table 4), amounting at 0.043 cent\$/m^3 desalinated water for addition of 10 mg Mg/L. Whereas adding the same amount of Mg through the production of Mg(II) rich brines according to Processes 1 or 4 (that is, processes that include a second step of $Mg(OH)_2$ precipitation on magnetite) is almost two orders of magnitude more expensive (Table 4).

Table 5 presents the estimated cost of the various methods for enriching desalinated water with 10 mg Mg/L. The methods compared in Table 5 are either previously proposed methods (i.e. methods 1–5), or methods developed in the current work i.e. method 6 which corresponds to Process 1, and methods 7a and 7b, which correspond to Processes 4). Methods 7a and 7b differ from each other only in the way $Mg(OH)_{2(s)}$ is re-dissolved. That is, either by mixing the $Mg(OH)_{2(s)}$-Fe_3O_4 particles with H_2SO_4 acidified water, to produce Mg/SO_4 rich solution (option 7a) or by contacting the $Mg(OH)_{2(s)}$ with the CDR effluents, as shown in Fig. 1 (option 7b). As mentioned, the latter option can be implemented in numerous sub-scenarios, differing in the acid used to dissolve calcite in the CDR step, in the distribution of flow rates between the streams (i.e. %splits applied), and in the required product water qualities. The cost presented in Table 5 is an example, assuming Scenario A detailed in Table 2 and shown in Fig. 1, in which

Table 5
Cost assessment comparison between methods of enriching desalinated water with 10 mg Mg/L

Mg(II) addition Method			Cost (cent$/$m^3$ RO)	
1	$MgCl_2$ dosage		1.18	$MgCl_2$~$300 ton chemical [15]
2	$MgSO_4$ dosage		2.06	$MgSO_4 \cdot 7H_2O$ ~$275 ton chemical [15]
3	Dolomite-calcite dissolution		0.53	Estimation of adding 12.15 mg Mg/L [11]
4	Ion exchange		0.51	Estimation of adding 12.15 mg Mg/L [12]
5	SWNF brine dosage		0.053	[15]
6	SWRO brine-NF brine dosage		0.039	(Process 1 Table 3)
7a	SWNF brine	Mg rich solution dosage	1.41	(Process 4 Table 3)
7b	magnetite	$Mg(OH)_2$ dissolution to CDR effluent	0.75	NaOH 500$/ton [27] H_2SO_4 170$/ton

H_2SO_4 is used to enhance dissolution of calcite, 25% of the desalinated water flow is assumed to be treated in the CDR (i.e. %split #1 = 25%) and 80% of the CDR effluent are introduced into the $Mg(OH)_2$ dissolution reactor (i.e. %split #2 = 20%).

The Mg(II) separation procedure of method 7a and 7b in Table 5 relates to Process 4 (Table 3), as it was found to result in the best water quality at only slightly elevated cost (Table 4). The cost of option 7b was calculated by comparing the cost of the conventional PT process, (comprising of H_2SO_4 based $CaCO_3$ dissolution, followed by NaOH dosage) with the cost of the suggested PT process, in which an additional H_2SO_4 dosage is required, however, no NaOH is dosed (see Fig. 1). Therefore, the cost of NaOH dosage was subtracted from the OPEX of Process 4, presented in Table 4. Comparing the cost of process 7a and 7b reveals that dissolving the $Mg(OH)_2$ directly to the CDR effluent results in a 47% cost reduction, emerging from the elimination of the need to dose 8.7 mg/L NaOH and reduction in the overall requirement of H_2SO_4 (10.9 mg/L less acid is required due to the $Mg(OH)_2$ dissolution potential of the CDR effluents).

It must be noted that the comparison of method costs presented in Table 5 can merely give an indication of the cost aspect, but does not reveal the complete picture since each method produces slightly different water quality (as implied in Table 1). For example if dissolution of dolomite is applied, it is difficult to distinguish between the cost of adding Mg(II) and the cost of providing Ca(II) and alkalinity to the water [12].

4. Summary and conclusions

(1) The developed process for replenishing desalinated water with Mg(II) (based on magnetite-aided $Mg(OH)_{2(S)}$ precipitation from the brine of a SWNF process) was shown to be feasible from the economic and water quality aspects.
(2) The process enables adding Mg(II) to desalinated (soft) waters with practically no additions of Na(I), Cl(-I), and B(III).
(3) The introduced processes are modular and can be added directly to an existing SWRO PT process.
(4) CDR effluent can be used to re-dissolve $Mg(OH)_2$, thus reducing chemical demands in the PT step.
(5) Cost analysis revealed the NF-magnetite method to be competitive for adding Mg(II) to RO water: ~1.4 cent$ per m^3 of desalinated water, enriched with 10 mg of Mg(II) per L.
(6) From the water quality point of view, the use of SWRO brine as the Mg(II) source solution for nanofiltration was found to be slightly less attractive than the use of seawater.

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