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Schemes for salt recovery from seawater and RO brines using chemical precipitation

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ABSTRACT

Disposal of brines from seawater desalination plants affects marine ecology and significant financial burdens. Recovery of salts from brines improves both sides of the problem and avails opportunities for new state of the art desalination/salt production complex. Three important separation processes could be adopted to formulate the corner stones for state-of-the-art salt recovery production line, namely chemical treatment, nanofiltration (NF), and ion exchange. This paper explores the performance of selected precipitants on saline solutions presenting synthetic seawater, natural seawater, and two reverse osmosis (RO) brines obtained from desalination plants located on Mediterranean (B1) and Red Sea (B2) shores. Sodium carbonate enabled 95.5, 89, and 95% recovery of calcium (Ca) seawater, Mediterranean, and Red Sea RO brines, respectively. While, values of magnesium (Mg) recovery from chemically treated schemes lie between 85.6 and 91.3%. Also, phosphate precipitation enabled two-stage recovery of Ca and Mg range from 75 to 98% for Ca and 24 to 47% for Mg. Moreover, analysis of our experimental results and other reported data on chemical softening enabled identification of three integrated salt recovery schemes from seawater and RO desalination brines. The first scheme is basically applicable for new desalting plants or even as stand-alone solution for chemical recovery from seawater. The second scheme could be applied when retrofitting current desalination plants where state-of-the-art NF is introduced and the generated NF brine is subjected to two-stage chemical and ion exchange treatments. The third scheme targets currently operating plants where RO brines could be directed to chemical precipitation for maximum Ca removal and subsequently decalcified streams could be processed for Mg removal using ion exchange. Optimization of the developed schemes is currently underway to identify comparative capital outlays and other relevant financial indicators.

Keywords: Seawater; Brine; Precipitation; Calcium; Magnesium; Chemicals recovery

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1. Introduction

Brine management is one of the challenging problems in most large-scale seawater desalination plants. Conventional techniques such as marine outfall or deep well injection manifest technical, financial, and environmental limitations [1–4]. Sound management practices targeting recovery of chemicals from concentrated brines would provide a cost-effective solution for targeted development and safe utilization of large-scale desalination plants [5–7]. Numerous purification steps are undertaken to precipitate seawater feed for desalination and limited benefits are currently achieved from discharged brines [8,9]. Brine management could also be achieved through physical, chemical, and physicochemical process. Salts recovery methods can be generally classified in the chemical precipitation processes, extraction methods, ion exchange resins, and advanced membrane processes [7,10–13].

Basically, chemical softening as a basic entity in the overall management process had been the subject of numerous endeavors for desalting, softening, deionization, or recovery of chemicals from seawater or brines [14,15]. Ca and Mg are precipitated from seawater and brines by addition of alkali (sodium carbonates, sodium hydroxides, lime, etc.). Both Ca and Mg are in a delicate equilibrium where slight changes in alkalinity and carbon dioxide tension may cause precipitation [16–18]. They have many similar chemical properties which make some difficulties for their separation with high purity. Irving [16] studied the precipitation of Ca and Mg from sea-water using Na_2CO_3 and NaOH in which much more Ca and relatively small amount of Mg were precipitated at pH up to 10. These factors agree with the much greater solubility product of $MgCO_3$, while NaOH precipitated less Ca above pH 10, conforming with the greater solubility of $Ca(OH)_2$ than $CaCO_3$. Robinson et al. [19] patented a simple scheme for recovering Mg from seawater as $Mg(OH)_2$ using lime at pH 10.5. Another patented process for producing MgO with 98% purity was developed from brines and bitterns by Panda et al. [20] using calcined magnesite, dolomite, calcite, or limestone to precipitate $Mg(OH)_2$. Mg phosphates may be precipitated from brines or seawater through the addition of a suitable phosphate salt such as sodium phosphate [21,22]. The produced Mg phosphate could be used for struvite making through reaction with ammonium hydroxide to produce high-purity struvite or addition to ammonium wastewater (e.g. fertilizer industry), as well as addition to municipal wastewater treatment [23–26].

The present paper focuses on the experimental investigations of chemical precipitation of Ca and Mg from seawater and reverse osmosis (RO) brines using sodium carbonate and sodium phosphate to come up with the most appropriate schemes for selective precipitation of Ca and Mg from seawater and RO desalination brines.

2. Materials and methods

2.1. Materials and analysis

Analytical grade chemicals from Merck and ADWIC were used in this study. Sodium carbonate and sodium phosphate tribasic ($Na_3PO_4{\cdot}12\ H_2O$) were used for alkali treatment and pH adjustment for seawater and brines.

Natural seawater samples were collected from Mediterranean Sea and two RO brine samples were collected from two different desalination plants in Egypt: (B1) from Marsa Matrooh and (B2) from Red Sea. Chemical analysis and physical properties for natural seawater and RO brines (B1, B2) are presented in Table 1.

Simulated seawater samples were prepared from mixing stock solutions of 24 g/l sodium chloride, 4 g/l sodium sulfate, 0.67 g/l potassium chloride, 0.2 g/l sodium bicarbonate, 1.5 g/l calcium chloride, and 10.782 g/l magnesium chloride**.** The main compositions were; Ca^{2+}: 450 mg/l, Mg^{2+}: 1,235 mg/l and Na^+: 14,000 mg/l.

The concentration of metal ions in the filtrate was analyzed using an atomic absorption flame spectrometer (GBC Avanta). pH and conductivity were measured using HANNA apparatus model-211. Selected precipitate samples were individually filtered through Whatman filter paper (no. 44) and dried in a 100℃ oven, and stored for X-ray diffraction (XRD) analysis using Philips X-ray Diffractometer PW/1710 with Monochrom TOR, Cu-radiation at 40 K.V., 35 mA and scanning speed 0.02˚/sec. Scanning electron microscopy (SEM) was conducted using SEM model JEOL: JXA-840A electron probe micro analyzer coupled with energy dispersive analysis by X-ray.

2.2. Methodology

2.2.1. Approach

The adopted approach for effective salt recovery schemes from saline water involves processing of saline solutions from Mediterranean Sea water and RO brine, as well as Red Sea RO brine as follows:

Table 1
Chemical and physical characteristics of Mediterranean Sea water and RO brines

		RO brine	
Parameter	Mediterranean Sea water	Mediterranean (B1)	Red Sea (B2)
Ca^{2+}, mg/l	400	800	690
Mg^{2+}, mg/l	1,460	1920	2,600
Na^{+}, mg/l	11,000	19,000	24,000
Cl^{-}, mg/l	20,000	35,000	40,000
SO_4^{2-}, mg/l	2,700	4,890	5,400
k^{+}, mg/l	500	600	800
CO_3^{2-}, mg/l	20	25	43
HCO_3^{-}, mg/l	90	190	146
Alkalinity, mg/l	110	210	190
TDS, mg/l	36,320	62,640	73,870
Conductivity, μs	57,500	84,000	108,700
pH	7.6	7.48	7.87

(a) Processing of synthetic seawater solutions to identify chemical treatment trends for the selected precipitants.
(b) Performing chemical precipitation using natural seawater based on reported and experimentally identified dosage norms for chemical precipitants.
(c) Experimental investigations on RO brines obtained from RO desalination plants on Mediterranean and Red Sea shores.
(d) Identification of viable salt recovery schemes for new and currently operating RO plants, as well as other plants subjected for phase retrofitting.

The basic information of those schemes depends on the experimental precipitation results in addition to other reported indicators.

2.2.2. *Precipitation of Ca and Mg from seawater and RO brines*

Precipitation of Ca and Mg was investigated for simulated and natural seawater as well as brine samples (B1, B2) using selective precipitants (sodium carbonate and sodium phosphate tribasic) at different pH values. Prepared samples were well sealed after the precipitant addition to avoid CO_2 acidification effect, shaken and sorted for 1 d. The removal of Ca and Mg from the saline solutions is indicated by their concentration difference before and after precipitation.

3. Results and discussion

3.1. *Effect of pH on Ca and Mg precipitation using sodium carbonate*

3.1.1. *Simulated seawater*

Fig. 1 represents the removal efficiencies of Ca and Mg at different pH values (8.1–10.4) after precipitation from simulated seawater. The data show that the removal of Ca is higher than Mg and preference of Ca removal (almost 100%) over Mg removal (about 58%) is revealed in the pH range (9–9.5).

3.1.2. *Natural seawater*

Fig. 2 represents the removal efficiencies of Ca and Mg at different selected pH values (9–9.5) after precipitation from natural seawater using sodium carbonate.

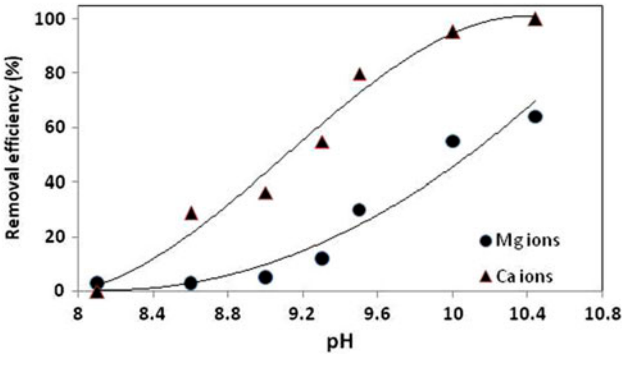

Fig. 1. Effect of pH on Ca and Mg removal efficiencies from simulated seawater using sodium carbonate.

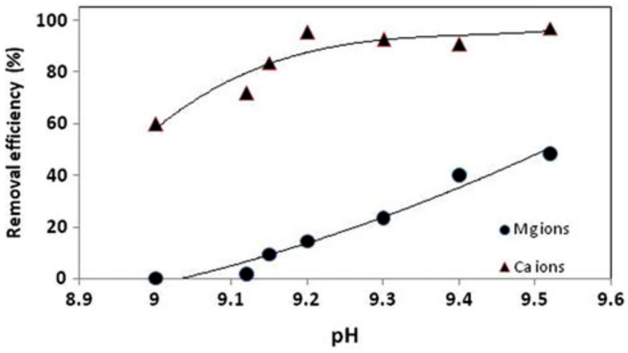

Fig. 2. Effect of pH on Ca and Mg removal efficiencies from natural seawater using sodium carbonate.

Same trend of Ca and Mg removal is attained for both simulated and natural seawaters. It is worth mentioning that Ca removal values in natural seawater are higher than simulated seawater at pH range (9–9.4). Preference of Ca removal (95%) over Mg removal (14%) is attained at pH value of 9.2.

3.1.3. RO brines (B1 and B2)

Fig. 3 represents the removal efficiencies of Ca and Mg after precipitation from Mediterranean and Red Sea RO desalination brines (B1 and B2) using sodium carbonate at selected pH range (9.1–9.6). The data show almost similar trends of the two brines in the tested pH range. Higher removal values for Ca and Mg were achieved for the more saline RO brine (B2). In both RO brines, the selected pH values are 9.32 and 9.2 to attain maximum Ca and minimum Mg removal (89% for Ca and 11.5% for Mg) and (95% for Ca and 8.7% for Mg) for B1 and B2, respectively. It may be concluded that, from process design point of view, Ca removal ranged from 89 to 95.5%, while Mg removal ranged from 8.7 to 14%.

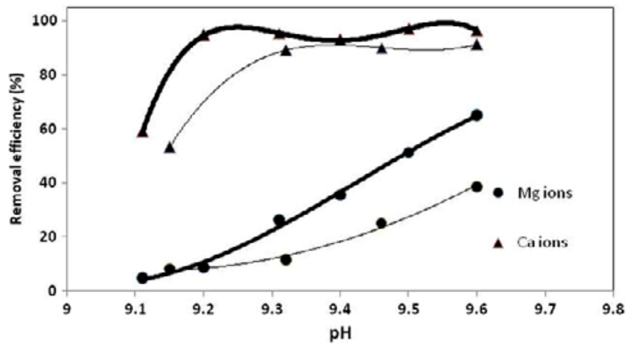

Fig. 3. Effect of pH on Ca and Mg removal efficiencies from RO brines B1 (–) and B2 (–) using sodium carbonate.

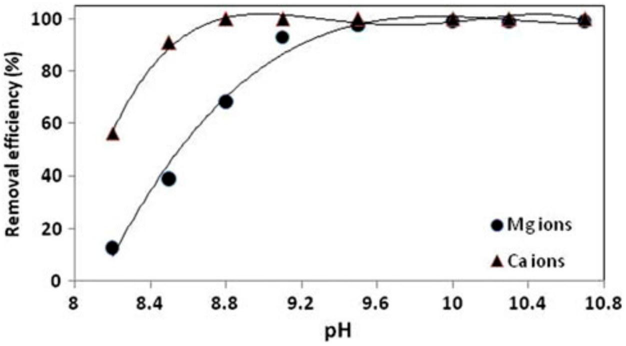

Fig. 4. Effect of pH on Ca and Mg removal efficiencies from simulated seawater using sodium phosphate.

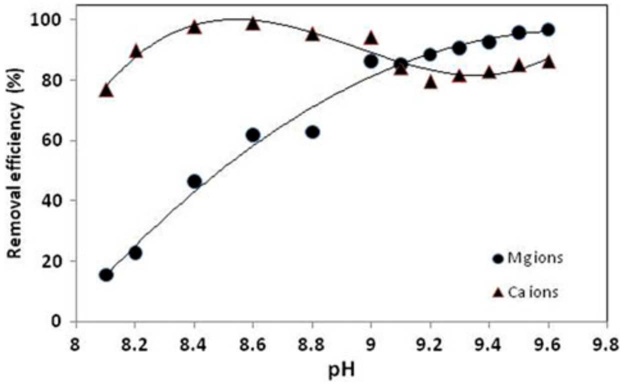

Fig. 5. Effect of pH on Ca and Mg removal efficiencies from natural seawater using sodium phosphate.

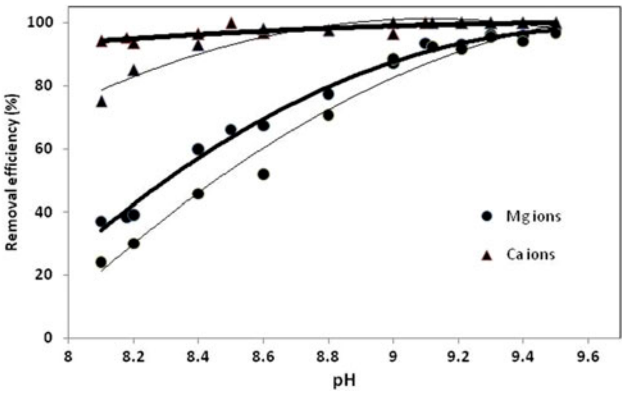

Fig. 6. Effect of pH on Ca and Mg removal efficiencies from RO brines B1 (–) and B2 (–) using sodium phosphate.

Table 2
Selected experimental conditions for targeted precipitation of Ca and Mg from saline solutions

				Concentration (mg/l)					
				Ca		Mg		Removal (%)	
Source	Precipitant	(g/l)	pH	Initial	Effluent	Initial	Effluent	Ca	Mg
(1) Natural seawater	Na_2CO_3	3.5	9.2	400	20	1,460	1,250	95.5	14.4
(Mediterranean)	$Na_3PO_4 \cdot 12\ H_2O$	13.2	8.4	400	10	1,460	780	98	47
(2) RO brine (B1)	Na_2CO_3	5	9.32	800	88	1,920	1,700	89	11.5
(Mediterranean Sea)	$Na_3PO_4 \cdot 12\ H_2O$	6	8.1	800	200	1,920	1,460	75	24
(3) RO brine (B2) (Red Sea)	Na_2CO_3	4.2	9.2	690	36	2,600	2,375	95	8.7

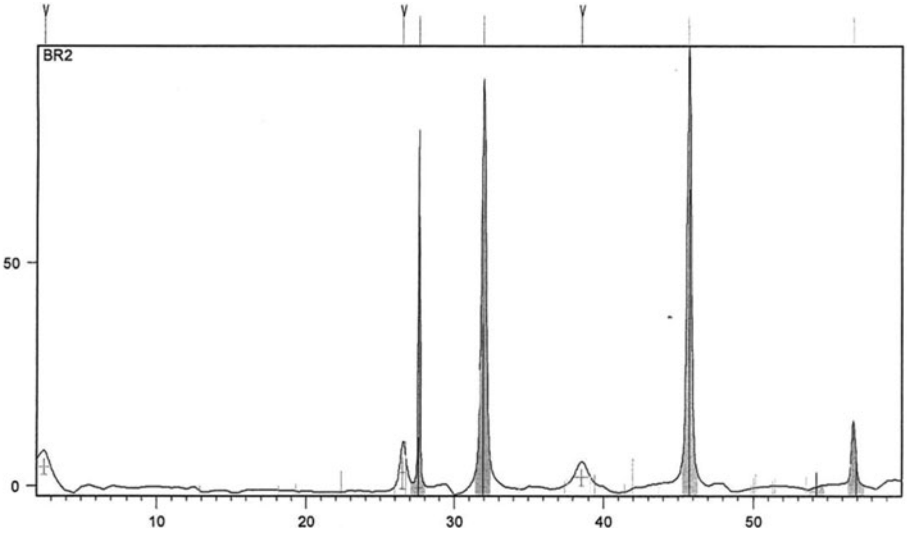

Fig. 7. XRD pattern of Red Sea brine (B2) precipitate using sodium carbonate at pH 9.2.

3.2. Effect of pH on the precipitation of Ca and Mg using sodium phosphate tribasic

3.2.1. Simulated seawater

Fig. 4 represents the removal efficiencies of Ca and Mg at different pH values (8.2–10.8) after precipitation from simulated seawater using sodium phosphate tribasic. Precipitation of Ca and Mg started at pH 8.2 and increased till achieving almost complete removal of both Ca and Mg at pH values higher than 9.5. Removal of Ca is higher than Mg till pH 9.5 and this result agrees well with the results of Golubev et al. [26]. It is observed that preference of Ca removal over Mg removal falls in the pH range (8.1–8.5).

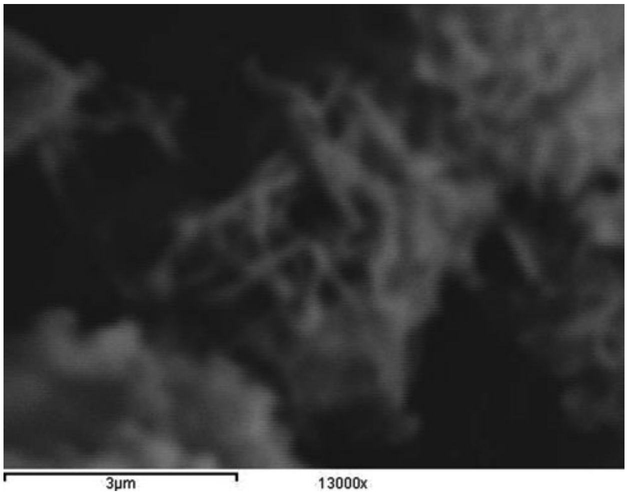

Fig. 8. SEM image of Red Sea brine (B2) precipitate using sodium carbonate at pH 9.2.

3.2.2. Natural seawater

Fig. 5 represents the removal efficiencies of Ca and Mg at different pH values (8.1–9.6) after precipitation

Table 3
Target salts from the developed salt recovery schemes

	Unit operation			
	Scheme (I)	Scheme (II)	Scheme (III A) RO brine	Scheme (III B)
Target salt	Mediterranean Sea water		Mediterranean	Red Sea
Divalent ions (e.g. Ca, Mg, Ba, etc.)	–	NF	–	–
$CaCO_3$ and $MgCO_3$	Precipitation (IC)	Precipitation (IIC)	–	Precipitation (IIIC)
$MgSO_4{\cdot}7H_2O$	–	Ion exchange	Ion exchange	Ion exchange
$Mg_3(PO_4)_2$	Precipitation (IP)	–	Precipitation (IIIP)	–
Struvite	Mixing	–	–	–
NaCl	Evaporation pond	Evaporation pond	Evaporation pond	Evaporation pond
Produced water	RO	RO	–	–

Table 4
Typical performance indicators for each process of the developed schemes [32–42]

	Removal efficiency (%)						
Unit	Precipitation*			Membrane separation		Ion exchange	Evaporation pond
operation item	(I)	(II)	(III)	NF	RO		
Ca^{2+}	96% (IC) 90% (IP)	90% (IIC)	95% (IIIC) 75% (IIIP)	83	99.4	90	
Mg^{2+}	14% (IC) 80% (IP)	10% (IIC)	9% (IIIC) 24% (IIIP)	85	99.4	90	
Na^+				35	99.4		40
Cl^-				35	99.4		
Water recovery (%) (seawater and brines)				65	50 (I and II)		50

*Carbonate and phosphate precipitation at pH 9.2, 8.1, respectively.

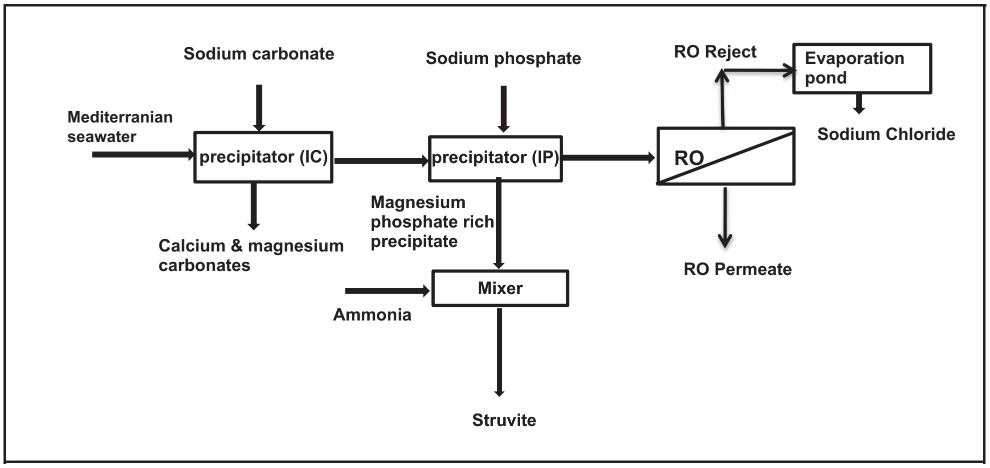

Fig. 9. Developed scheme (I): salts recovery from new RO desalination plants.

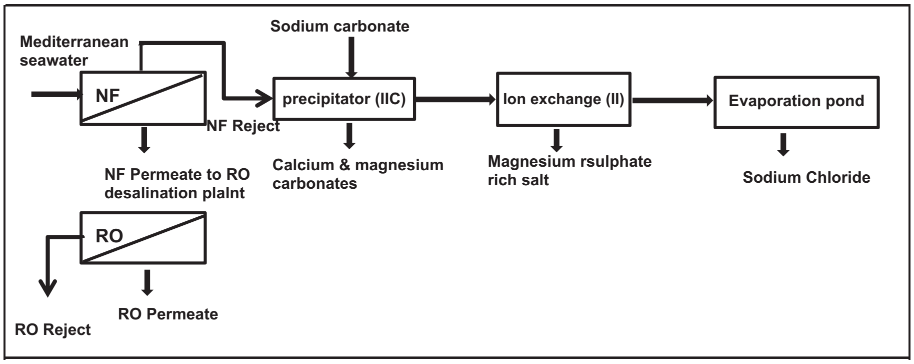

Fig. 10. Developed scheme (II): salts recovery from retrofitting RO desalination plants.

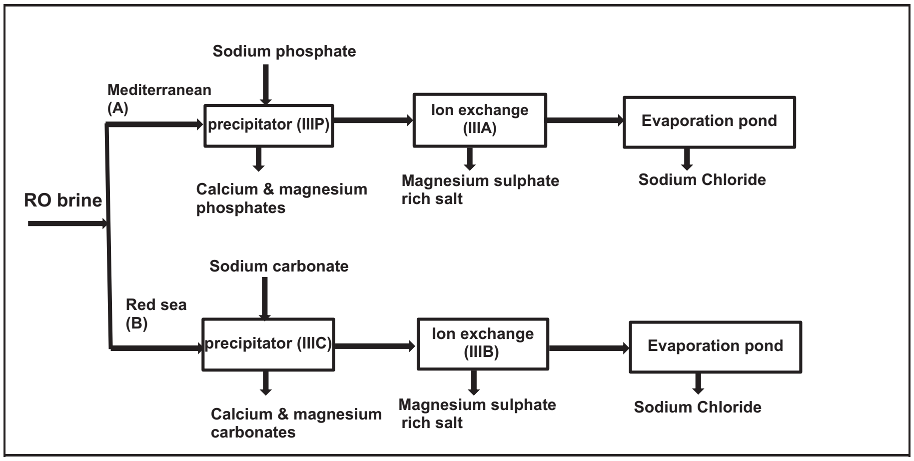

Fig. 11. Developed scheme (III): salts recovery from current RO desalination plants.

from natural seawater using sodium phosphate tribasic. Removal efficiencies for Ca and Mg for natural seawater are higher than those of simulated seawater. Maximum Ca removal (98%) was accompanied with 47% Mg removal at pH 8.4.

3.2.3. RO brines (B1 and B2)

Fig. 6 represents the removal efficiencies of Ca and Mg at different pH values (8.1–9.5) after precipitation of RO desalination brines (B1 and B2) using sodium phosphate tribasic. Higher initial Ca and Mg removal efficiencies were obtained at lower pH values as compared to precipitation using sodium carbonate shown in Fig. 3. The selected pH value for the maximum Ca precipitation and minimum Mg precipitation is 8.1 for both RO brines. The achieved Ca removal efficiencies at this pH value were 75 and 94% for B1 and B2, respectively, and the corresponding Mg removal efficiencies were 24 and 37% for B1 and B2, respectively. Selected results from chemical precipitation experiments representing the highest Ca removal and lowest Mg removal for further development of the integrated schemes are summarized in Table 2. The highest Ca removal and the lowest Mg removal were obtained from RO brine B2 using sodium carbonate at pH 9.2. The XRD pattern of this sample is shown in Fig. 7, which shows that the precipitate is consisted mainly from sodium carbonate in the form of calcite and aragonite. Aragonite is represented by its main peaks at 2 theta of 26.5, 27.5, and 45.5, while Calcite is represented by its main peek at 2 theta of 32 [9,27,28]. Aragonite may be considered to be in lower amount where one of its main peek intensity is lower than the standard intensity at 2 theta of 26.5. The presence of calcite and aragonite at the studied [Mg]/[Ca] molar ratio of 6.3 agrees with Pokrovsk, 1998 [29] for [Mg]/[Ca] molar ratios higher than 3. This result is confirmed by SEM image as shown in Fig. 8, where blend of aragonite and calcite is represented by a flaky nature of aragonite accompanied with cubic crystals of calcite, which agrees with Tréhu et al. [30] and

Nahdi et al. [31]. Dolomite is present with minor amounts as a low intensity peak is observed at 2 theta of 29.5 considered as its main peak [30,31].

3.3. Process design implications

Tables 3 and 4 represent the expected products and the typical performance indicators of the individual developed treatment scheme processes based on reported data [32–42] and the experimental precipitation results conducted in this paper, respectively.

In view of the reported and current results of this work, it is apparent that chemical treatment route for recovering carbonate and phosphate salts of Ca and Mg produced from seawater and brines could be used as chemical products. This can form a corner stone for chemicals recovery from seawater or RO brines. Three obvious salt recovery schemes could be identified for recovery of chemicals from saline solutions as follows:

(a) *Scheme (I):* A staged chemical treatment of seawater via carbonate and phosphate treatment in which softened seawater could be directed to RO desalination unit followed by sodium chloride recovery using evaporation pond as shown in Fig. 9. This scheme is particularly applicable for new desalting plants or even as stand-alone solution for chemical recovery from seawater.

(b) *Scheme (II):* Current desalination plants could be retrofitted to replace conventional pretreatment by state-of-the-art nanofiltration (NF) softener as shown in Fig. 10. The expected Ca and Mg in brines are 1.09 and 3.85 g/l, respectively, for 64% NF recovery [10]. The NF brine is directed to chemical precipitator by optimized carbonate treatment where Ca recovery approaches 95–97%. The Mg-rich brine could be directed to the ion exchange for Mg removal or to advanced crystallization by membrane crystallizer [9].

(c) *Scheme (III):* RO brine could be directed for chemical treatment, where 75% of Ca could be removed from RO brine (B1) using sodium phosphate (III-A) and 95% Ca removal from RO brine (B2) could be achieved using sodium carbonate (III-B) as shown in Fig. 10. Chemically treated brine is directed to ion exchange system for Mg recovery and subsequently to sodium chloride evaporation pond as shown in Fig. 11. This scheme could be implemented in current desalination plants which enables maximum chemicals recovery from RO brines. It is noted that the Red Sea RO brine could also be processed with sodium carbonate where Ca ion recovery approaches 89%. Selection between the two precipitants depends entirely on market demand and further optimization.

4. Conclusions

Partial softening of seawater and RO brines have been investigated using sodium carbonate and sodium phosphate as precipitants for recovering Ca and Mg salts at selected pH values. Seawater and RO brine softening using sodium carbonate caused maximum Ca concentration reduction from 400 to 20 mg/l and from 690 to 36 mg/l, respectively. Further, the corresponding Mg concentration reduction was from 1,460 to 1,250 mg/l and from 2,600 to 2,375 mg/l for seawater and RO brine, respectively. The weight of calcium and magnesium deposits are 1.43 and 2 kg/m^3 for each kilogram of sodium carbonate used for seawater and RO brines softening, respectively.

Phosphate precipitation of Ca and Mg has been explored and the initial results confirmed the recovery of Ca from seawater and RO brines by about 98 and 75%, respectively. The corresponding Mg recovery values were 47 and 24%, respectively.

Results of chemical pretreatment of seawater and RO brines enabled the identification of three process design schemes for recovery of Ca, Mg, and sodium salts. The identified schemes incorporate chemical precipitation as a terminal intervention (up or down stream) with membrane/thermal processing and ion exchange as intermediate and salt recovery technologies. The first scheme (I) is basically applicable for new desalting plants or even as stand-alone solution for chemical recovery from seawater. The second scheme (II) could be applied when retrofitting current desalination plants where state-of-the-art NF is introduced and the generated NF brine is subjected to two-stage chemical and ion exchange treatments. The third scheme (III) targets currently operating plants where RO brines could be directed to chemical precipitation for maximum Ca removal and subsequently decalcified streams could be processed for Mg removal using ion exchange. Studies are currently underway to optimize the three identified schemes to identify comparative capital and other relevant financial indicators.

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