Study of seawater alkalization as a promising RO pretreatment method

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Abstract

Inorganic fouling is a major challenge in seawater RO desalination due to its relatively high SO_4/HCO_3 molar ratios. In most of the recorded cases, if not all, calcium sulfate scale is dominating (>90% wt/wt) other scale types such as $CaCO_3$, $MgSO_4$, $MgCO_3$, $MgSiO_3$, SiO_2 and $CaPO_4$. However, the standard pretreatment practice in RO plants depends on the acidification of seawater in order to remove the minor carbonate and bicarbonate. Meanwhile, solubility of the major sulfate species decreases considerably because of acidification. The present study investigated the application of NaOH alkalization on the Red Sea surface water instead. It was found that the method has many technical and economical advantages, such as removal of hard chemical species (i.e. hard carbonate, bicarbonate, sulfate, silicate, phosphate and iron), removal of suspended solids and colloids, bacterial disinfection, cleaning and wetting of a membrane surface, increasing permeate recovery, lower sludge volume of environmentally chemical nature, and the possibility of instant preparation of NaOH in-line by seawater electrolysis. The alkalization method is fast, clean and economic. The proposed model as well as chemical equations are presented in detail.

Keywords: Seawater alkalization; RO pretreatment; Seawater softening; Seawater electrolysis

1. Introduction

Inorganic fouling is a major challenge in RO seawater desalination. Seawater is characterized by high SO_4/HCO_3 molar ratios that lie normally between 11 and 15 [1]. In most of the recorded cases, if not all, calcium sulfate scale dominatied (>90% wt/wt) other species such as $CaCO_3$, $MgSO_4$, $MgCO_3$, $MgSiO_3$, SiO_2 and $CaPO_4$ [2]. However,

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the standard pretreatment practice in RO plants depends on the acidification of seawater (pH~8.3) with concentrated H_2SO_4 to pH 6–6.5 in order to remove carbonate and part of bicarbonate ions. Ferrichloro-sulfate ($FeClSO_4$) usually added as inorganic coagulant-aid (5–10 mg as Fe/l) to remove suspended solids and plankton through flocculation and coagulation during a period of about 60 min. From the chemical point of view, this acidic pretreatment introduces considerable amounts of H^+ and SO_4 ions into seawater. This may accelerate the deposition of $CaSO_4$, which decreases its solubility with acidity and increases with basicity. In addition, iron may redissolve partially from its hydroxide sludge in the presence of excess H^+, which is known as iron-leak, and back to the system again. In order to overcome all these defects, several types of expensive antiscalants are currently used. Practically speaking, it is not a big deal to remove minor carbonate and bicarbonate from seawater via this costly method without any guarantee against the expected sulfate scaling.

The application of other softening methods on seawater is quite limited. An ion exchange softening method could be highly efficient in removal of hardness ions from seawater, but it needs repeated replacement of the expensive resins, in addition to the expected oxidation and degradation of resins because of the high content of dissolved halogens.

Recently, the nanofiltration technique was introduced — on a pilot scale test — in order to remove hardness from the Red Sea water as a pretreatment step before RO membrane desalination [3]. It was reported that satisfactory removal levels were achieved: 89% Ca, 97% Mg, 61% Na, 86% HCO_3, 97% SO_4 and 61% Cl. Some doubts may arise about the feasibility of such a configuration because of the possibility of transferring the scale problem from the RO membrane to the nanomembrane. In addition, the high-pressure nanofiltration system used (>40 bar) should be very costly as compared with other conventional chem-ical softening methods.

Alkalization has been applied for long time for economic softening of domestic drinking water, but no application on seawater is reported. Con-

sidering that hard sulfate is the major inorganic fouling problem in seawater membrane desalination, so alkalization is chemically accepted rather than acidification pretreatment [4]. Alkalization technology comprises three methods, namely: lime, lime/soda–ash and caustic soda softening.

In brief, calcium can be precipitated as $CaCO_3$ from water at a pH of ~9.5 by the addition of hydrated lime $Ca(OH)_2$. Water containing little or no non-carbonate hardness can be softened with lime alone. Soda ash (Na_2CO_3) may be needed to supplement carbonates in water with high calcium hardness: alkalinity ratio. Magnesium is precipitated from water as $Mg(OH)_2$ at pH higher than 10.5. Excess lime is required to increase the pH to >10.6. A practical limit for calcium removal is ~0.8 meq/L, (~40 mg/L $CaCO_3$) of which ~0.5 meq/L (~25 mg/L $CaCO_3$) are colloids and ~0.3 meq/L (~15 mg/L $CaCO_3$) are soluble $CaCO_3$. Most of heavy metals, as well as silica, could be efficiently removed by alkalization too. Lime and lime/soda–ash methods reduce TDS by the amount of hardness removed.

In spite of the high efficiency and low cost of the lime/soda–ash method, many technical disadvantages must be considered, such as high doses (up to 1300 mg/l) may be required, production of bulky sludge, instability of strength due to absorbing atmospheric CO_2, repeated feeding problems due to moisture, serious air contamination is possible, and large area is normally required for storage and preparation.

Caustic soda (NaOH) method is superior over the lime/soda–ash method in performing precise controlled alkalization over a wide variation of feed water quality. Sodium ion and TDS slightly increased as a result. Caustic soda alkalization produces less sludge than the lime/soda–ash method. Under normal operating conditions, caustic soda does not deteriorate rapidly during storage and allows clean and steady operation.

The aim of the present work is to study and evaluate the application of NaOH alkalization method on the Red Sea surface water as a pretreatment step for removal of hardness in RO membrane desalination process.

2. Experimental work

The objective of experimental work is to collect a suitable typical sample(s) from the Red Sea surface water in order to identify its chemical composition and carry out the alkalization titration with NaOH solution starting from the initial pH-value and up to pH 12. In order to achieve this simple target it was necessary to exert much effort in fieldwork and laboratory as well.

The collection of a technically suitable surface seawater sample is not a simple process. First, it requires to be sure about the origin of the collected sample. All of the installed RO plants on the western Red Sea coastal strip are getting seawater from drilled beachwells at the depths between 30 and 60 m to avoid surface bioactivity load. Such groundwater has different chemical composition than surface seawater, and is usually characterized by higher TDS that could be up to 60,000 mg/l and more [2].

In the first trial, a 20-l sample was collected from the shoreline of a site located 2 km north of Hurghada town, then transferred to Geochemica Laboratories, Cairo within 8 h. The oven-drying salinity test indicated TDS of about 38,000 mg/l, which was lower than expected. It has been decided to carry out bacterial investigation as well as COD measurement in order to detect possible contamination. The fast COD test (~3 h) showed an unusually high result of 546 mg/l that pointed to a possible contamination with organic substances. After a 3-day incubation, the bacterial investigation confirmed the presence of E. coli at a level of 12×10^6 and a total count of 46×10^6 unit/100 ml. It was clear that the selected site lies down the coastal-stream crossing the marina area, which is crowded with yachts all over the year.

After several unsuccessful trials, and under the acknowledged guidance of the Oceanographic Institute in Hurghada, it was possible to collect 4 plastic containers, 10 l each, from the depth of about 2 m under sea level at a location of 7 km from El Hurghada town inside the sea. The field parameters, which included water temperature,

pH-value, alkalinity, and dissolved CO_2 and dissolved oxygen, were measured in site during sampling.

It is interesting to mention that inspite of all possible precautions taken during sampling, transportation and storage, the influence of atmospheric CO_2 was powerful enough to acidify the collected seawater considerably in a short time. The sample pH decreased rapidly from 8.25 to 7.32, and CO_2 content increased from 18.73 to 48.68 mg/l just in less than 36 h.

The same effect of atmospheric CO_2 reflected strongly on the NaOH titration-curve experiments. It was necessary to use a tight plastic cupboard supplied with CO_2-free air via a blower, $Ca(OH)_2$ trap and moisture filter. In addition, a big sample volume (500 ml each) was used in all experiments to minimize possible CO_2 interference. Each alkalization experiment was repeated 3 times, and alkalinity was measured according to the recommended fast-titration method of seawater [6]. A freshly prepared standard solution of ~0.5 M NaOH was used in titration of the Red Sea surface water samples. All samples volumes were corrected for temperature, density and the added volume of standard NaOH solution.

The results below represent the arithmetic mean of 3 runs of each experiment. The general precision and accuracy were lower than ±0.5%, in either experiments or chemical analyses. The ion balance difference between cations and anions of the analyzed water samples was ±0.12%. Chemical analysis and bacterial investigation were carried out according to the standard water and wastewater analysis methods given by the APHA, AWWA and WPC [6].

3. Results and discussion

The chemical analysis and physical properties of the Red Sea surface water are presented in Table 1. The ionic concentration is given in mg/kg after correction of analytical unit (mg/l) for water sample density. Consequently, the corresponding molar ratio was calculated from its molar concen-

Table 1
Chemical analysis and properties of the Red Sea surface water sample

Ion	mg/kg	mMol/kg	Water description	
Sodium (Na^+)	11,178	486.195	Water density, gm/cc	1.0299
Potassium (K^+)	496	12.697	Water temperature, °C	23.5
Calcium (Ca^{2+})	565	14.108	pH–value in site	8.25
Magnesium (Mg^{2+})	3198	131.571	pH–value in Lab.	7.32
Barium (Ba^{2+})	0.70	0.005	Dissolved CO_2, mg/Kg	18.73
Strontium (Sr^{2+})	10.74	0.123	Conductivity, μmhos	69,000
Chloride (Cl^-)	24181	682.064	Molar ratios	
Bicarbonate (HCO_3^-)	181	2.971	(SO_4/Alk*)	14.308
Carbonate (CO_3^{2-})	40	0.669	(SO_4/Cl)	0.076
Hydroxyl (OH^-)	0.00	0.000	(Alk*/Cl)	0.005
Sulfate (SO_4^{2-})	5003	52.082	(Alk*/SiO_3)	359.770
Silica (SiO_3^{2-})	0.63	0.0083	[(Na+K)/(Ca+Mg)]	3.425
Iron (Fe^{3+})	0.04	0.0007	(Na/Cl)	0.711
Manganese (Mn^{2+})	0.00	0.000	(K/Cl)	0.019
Phosphate (PO_4^{2-})	0.05	0.0005	(Ca/Cl)	0.021
Sum	44,854.16	1382.4945	(Mg/Cl)	0.192
Total alkalinity*	221.4285	3.6400	(Ca/SiO_3)	1709
Ionic strength, eq/kg	1.0346		(Ca/PO_4)	26,018

*Alk = Total alkalinity = $OH + CO_3 + HCO_3$

tration that is expressed in mMole per one kg of water solution (mM/kg) as illustrated in the equation:

$$mM/kg = (mg/l \div d) \div MW \qquad (1)$$

where d is density @ NTP (25°C and 1 atm.), and MW is molecular weight.

The Red Sea water is characterized by higher salinity (TDS = 44854 mg/kg, IS = 1.0346 eq/kg) than the oceanic water (TDS = 36,096 mg/kg) and the Mediterranean Sea (TDS = 38,791 mg/kg). This high salinity was not acquired through natural evaporation but due to the strong effect of the active volcanic rifting tectonics that release huge amounts of hot brine and salt deposits into the middle bottom of the sea. The relative molar ratio (SO_4/alkalinity) of the Red Sea water (14.308) is higher than that of the Mediterranean (11.381) and the Gulf (11.964), which has higher salinity (49,078 mg/kg). In addition, the Red Sea water has an exceptionally high molar ratio (Mg/Cl = 0.193), which is twice that of the Gulf Sea (0.099). There-

fore, the sulfate scaling potential is quite high in the Red Sea water [7]. The alkalization experiments carried out on a 500-ml sample volume of the Red Sea surface water with a standard solution of sodium hydroxide (0.5009 M NaOH). The obtained titration curve is illustrated in Fig. 1. These experiments were executed under controlled conditions in order to minimize the effect of the atmospheric CO_2. However, in the first trials it was not possible to avoid CO_2 interference during the first sludge separation. Therefore, this titration curve was constructed from the data of a continuous addition of NaOH solution to pH 12 without sludge separation. Two equivalence points were obtained at a dissociation equilibrium of $pK_a = 9.65$ and $pk_a = 10.75$ with corresponding 0.5009 M NaOH volume of 13.85 and 19.20 ml/500 ml sample respectively. The carbonate precipitation started at pH 9.3 and ended at pH 10.0, while hydroxide deposition started at pH 10.5 and completed at pH 11. For practical uses, the amount (in mg/kg) of NaOH should be calculated at the endpoint of precipitation, and not at the
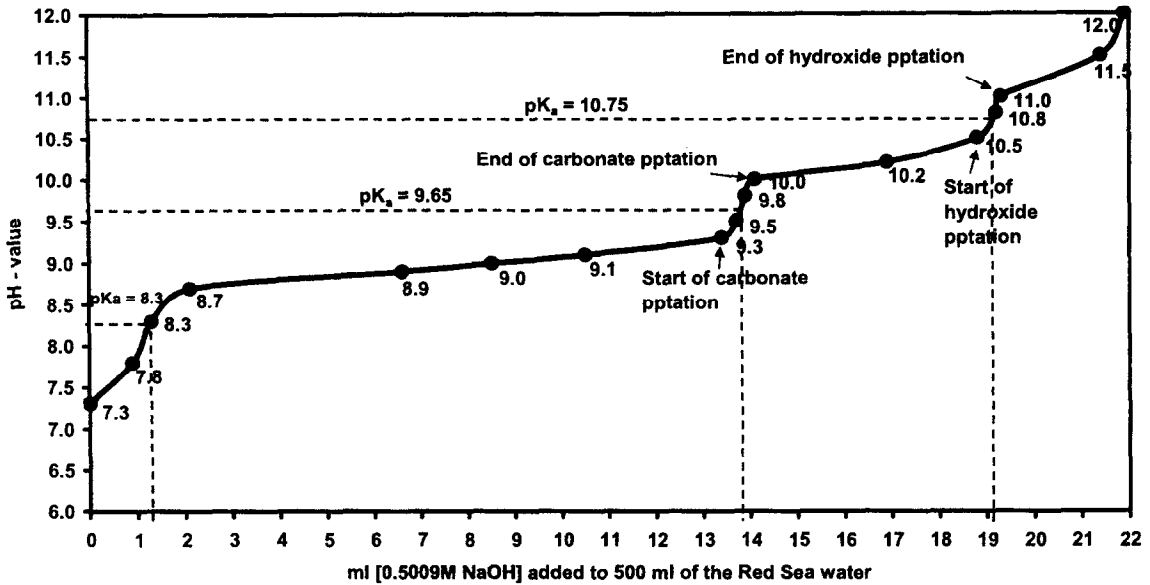
Fig. 1. The relationship between pH value and added 0.5009 M NaOH volume, Red Sea water.

equivalence point, as follows:

$$\text{NaOH}_{1st}, \text{mg/kg} = [(V_{eq} + a) \times \\ \times (M \times MW/1000) \times (1000/V_s)]/d \qquad (2)$$

$$\text{NaOH}_{2nd}, \text{mg/kg} = [(V_{eq} + b) \times \\ \times (M \times MW/1000) \times (1000/V_s)]/d \qquad (3)$$

where V_{eq} is the NaOH volume in ml to the 1st or 2nd equivalence point; a is the difference between NaOH volume at the first equivalence point and the first end point of precipitation; b is the difference between NaOH volume at the second equivalence point and the second end point of precipitation; M is the morality of NaOH solution (0.5 M); MW is the NaOH molecular weight (39.997); V_s is the Red Sea sample volume (500 ml); d is the density of Red Sea water (1.0299 mg/cc at NTP). The consumed amount from 100% NaOH in the 1st pH 10 and 2nd pH 11 stages reactions are given below:

Consumed NaOH_{1st}
$= [(13.85+0.25)(0.5009 \times 39.997/1000)(1000/500)]$
$/1.0299$

$= 548.57$ mg/kg
$= 0.54857$ kg per one ton of the Red Sea water.

Consumed NaOH_{2nd}
$= [(19.2 + 0.1)(0.5009*39.997/1000)(1000/500)]$
$/1.0299$
$= 750.88$ mg/kg
$= 0.75088$ kg per one ton of the Red Sea water.

It should be remembered that the resultant NaOH titration curve is based on the initial pH 7.3 due to the unavoidable effect of atmospheric CO_2, therefore, the amount of consumed NaOH is expected to be considerably lower when alkalization is applied directly on seawater in a site where pH is about 8.3.

The difference in consumed NaOH between pH 10 and pH 11 is relatively high (~36%) as compared with the 1st stage (549 mg NaOH/kg) consumed over pH 7.3 to pH 10. This reflects the presence of a strong buffering effect characteristic of a complex reaction system. In order to determine the removal percentage and study the mechanism of involved reactions, it was necessary to carry

out a series of 2-stage alkalization experiments to separate solids from solutions, and then all products (solids and solutions) were subjected to detailed chemical analysis. It should be noted that during these long bulky experiments it was not possible to avoid the influence of atmospheric CO_2. Table 2 presents the analytical arithmetic mean results of three alkalization experiments carried out on the Red Sea surface water with sodium hydroxide solution considering the precipitation of hardness salts. Several tests had been carried out to select the most suitable NaOH solution that can perform precipitation effectively in the shortest time via the fast-addition method. It was found that a solution of 2 mole/l of pure NaOH salt is able to form the 1st stage stable condensed sludge (at pH 10) from a 500 ml sample in less than 1 min and could be separated volumetrically by suction

after 15 min. In the 2nd stage, the sludge was compacted enough to settle down within 10 min, a volumetric correction was made for the removed 1st stage sludge as well as the added NaOH volume solution. In all experiments, both solution and sludge had been subjected to chemical analysis separately. The analytical results given in Table 2 represent the net change percentages in individual ion concentration found in the solution after sludge settling. The result differences were less than ±2% whether between solution and its generated sludge or the repeated experiments. The obtained analytical results indicated the following:

1) The 1st stage sludge contains an unusual amount of magnesium ion (1865 mg/kg) associated with the formed carbonate sludge at pH 10. It was surprising that from the total Mg removal percentage (74%) a major part of 58% was precipitated within

Table 2
Analytical results of NaOH alkalization experiments on the Red Sea surface water

Ser.	Parameter	Initial conc., mg/kg	1st stage at pH 10		1st and 2nd at pH 11	
			mg/kg	Change %	mg/kg	Change %
1	Sodium (Na)	11,178	11,492	2.81	11,608	3.85
2	Potassium (K)	496	496	0.00	496	0.00
3	Calcium (Ca)	565	351	−37.88	262	−53.63
4	Magnesium (Mg)	3198	1333	−58.32	818	−74.42
5	Barium (Ba)	0.70	0.45	−35.71	0.19	−72.86
6	Strontium (Sr)	10.74	6.65	−38.08	2.03	−81.10
7	Silica (SiO_3)	0.63	0.26	−58.73	0.00	−100.00
8	Iron (Fe)	0.04	0.03	−25.00	0.00	−100.00
9	Hydroxide (OH)	0.00	12.00	>100	18.00	>100
10	Carbonate (CO_3)	40	0.00	−100.00	0.00	−100.00
11	Bicarbonate (HCO_3)	181	0.00	−100.00	0.00	−100.00
12	Chloride (Cl)	24,181	24,181	0.00	24,181	0.00
13	Sulfate (SO_4)	5003	3647	−27.10	2670	−46.63
14	Phosphate (PO_4)	0.05	0.03	−40.00	0.00	−100.00
	Sum	44,854.16	41,586.42	−7.29	40,122.22	−10.55
15	Sludge volume (15 min.), ml/l		114		87	
16	Sludge volume (30 min.), ml/l		63		41	
17	Sludge density (30 min.), gm/cc		1.214		1.107	
18	Nonionic polymer settling time, min		8		6	
19	Cationic polymer settling time, min		10		8	
20	Anionic polymer settling time, min		11		9	
21	Silt Index, after non-ionic addition	2.3	<0.01		<0.01	
22	Bacterial count/ml	2.3×10^3	—		—	

the 1st stage sludge, which is even much higher than 1st stage calcium (38%). These surprising results contradict the well-known lime/soda–ash and caustic soda models used in removing hardness from drinking and industrial waters.

2) The total removal of both 1st and 2nd stage calcium (54%) and magnesium (74%) are less than expected as compared with the published data of lime/soda–ash and caustic soda methods that normally remove more than 90% of Ca and Mg from hard brackish water.

3) Barium and strontium followed calcium in chemical reaction of the 1st stage (Ca 38%, Ba 36% and Sr 38% removal), but they differentiated considerably during the 2nd precipitation stage.

4) All of CO_3^{2-}, HCO_3^-, SiO_3^{2-}, PO_4^{2-} and Fe^{3+} ions were totally removed through chemical precipitation at the pH 11, while SO_4^{2-} was only 47%.

5) As expected, sodium and hydroxyl ions increased in solution after alkalization, while potassium and chloride ions stayed unchanged. The apparent limited change in sodium (+2.8 and +3.9%) is attributed to the added Na to the initial high concentration in the Red Sea water (Na = 11178 mg/kg).

6) The total dissolved solids (TDS) is surprisingly lowered with 7% at pH 10 and 11% less at pH 11, which indicated that the amount of precipitated chemical species is greater than the added NaOH. This cumulative result confirms that the NaOH alkalization pattern of seawater is quite different from the normal low-salinity water softening.

7) In order to increase the sludge settling rate, limited precipitation experiments were carried out on a separate group of samples after addition of 2.5 mg/kg of anionic, cationic and non-ionic commercial coagulant-aid polymers. It was found that the non-ionic polymer achieved the best results. Silt Index (SI) lowered to less than 0.01, and bacteria was totally removed as shown in Table 2. The powerful oxidation effect of the hydroxyl group (OH⁻) on bacteria in water with alkalinity higher than pH 9 is well known [8].

Due to the differences found between the present seawater alkalization and other alkalization (i.e. softening) methods currently used for hardness removal from low-salinity water, the reaction pattern of the present case must be discussed. In order to understand the possible major reactions, it was necessary to obtain the probable dissolved chemical species of the investigated Red Sea water. First, the USGS PHREEQC software version 2 [9] used for the aqueous geochemical calculations. All of the obtained results were quite lower than expected and confusing, for example: $MgSO_4$ 7.663 and $CaSO_4$ 0.5986 mM/kg, while the major $MgCl_2$ was missing. These results do not even match the standard mean oceanic water (SMOW), which acquires lower salinity (TDS~36000 mg/kg). It is clear that the extended Debye–Huckel model used needs further evaluation when being used with high salinity waters. Table 3 presents the

Table 3

The probable salt combination of the Red Sea surface water

Ser.	Dissolved salt	mMole/kg	mg/kg
1	$CaCO_3$	0.126122	6.31
2	$MgCO_3$	1.211367	51.07
3	$BaCO_3$	0.000047	0.00
4	SrCO3	0.001129	0.08
5	$Ca(HCO_3)_2$	0.419823	22.69
6	$Mg(HCO_3)_2$	4.032283	196.69
7	$Ba(HCO_3)_2$	0.000156	0.01
8	$Sr(HCO_3)_2$	0.003757	0.26
9	$CaSO_4$	9.813750	668.03
10	$MgSO_4$	45.555041	2741.70
11	$BaSO_4$	0.003654	0.43
12	$SrSO_4$	0.087834	8.07
13	Na_2SO_4	73.054903	3458.98
14	$CaCl_2$	25.765234	953.17
15	$MgCl_2$	320.531888	10172.66
16	$BaCl_2$	0.009592	0.67
17	$SrCl_2$	0.230586	12.18
18	$NaCl$	874.982980	25568.08
19	KCl	25.393012	946.54
20	$CaPO_4$	0.001084	0.07
21	$MgSiO_3$	0.016514	0.83
22	FeO_3	0.001055	0.17
23	MnO_2	0.000000	0.00
	Total	1381.241812	44808.70

probable salt combination of the Red Sea water that was manually calculated according to the simplified model described by El-Manharawy and Hafez [7]. The ion-pair stoichiometric calculations showed that the accuracy of distribution of dissolved ions for the obtained probable dissolved salts is better than 99%.

The statistical correlation between these data and the analytical results in Table 2 indicated the following:

1) The 1st stage alkalization at pH 10 precipitated all of carbonate, bicarbonate and sulfate of Ca, Mg, Ba and Sr, in addition to a limited part of $MgCl_2$.

2) Experimentally, an amount of 37.43% of Ca, Ba and Sr was removed at the 1st stage alkalization. This is in a good agreement with the theoretical removal (37.20%).
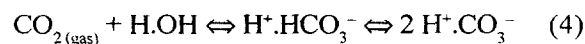
3) At the end of the 1st stage there is no excess sulfate anion available for Ca, Ba and Sr cations. The remaining amount of Ca, Ba and Sr ($\leq$ 62.80%) should be in soluble chloride form.

4) At the 2nd pH 11, the experimental removal was 53.75%, which indicates additional precipitation as a result of chloride alkalization. After precipitation, an amount of 9.05% (of Ca, Ba and Sr) is still in solution as chloride at this high pH value.
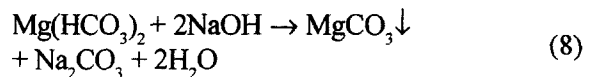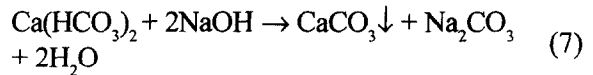
5) The behavior of Mg is different from the rest of alkaline earth cations. The theoretical stoichiometric calculations showed that 18.74% of total molar concentration of Mg is removed with its carbonate, bicarbonate and sulfate at the 1st stage precipitation. The experimental results revealed that 58.32% of Mg (in mM/kg) had been removed at the 1st precipitation, 16.11% at the 2nd stage, and 25.57% remained in the solution as $MgCl_2$.

Regardless of other non-hardness major and minor seawater species, it was possible to define the chemical reaction types that may influence the alkalization of the Red Sea water by NaOH solution, and are as follows.
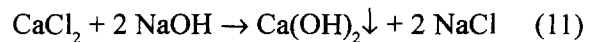
Initial condition at equilibrium (to pH 8.3)

$$CO_{2\,(gas)} + H.OH \Leftrightarrow H^+.HCO_3^- \Leftrightarrow 2\,H^+.CO_3^- \quad (4)$$

$$Ca^+ + 2HCO_3^- \Leftrightarrow Ca(HCO_3)_2 \Leftrightarrow 2H^+.CaCO_3^- \quad (5)$$

$$Mg^+ + 2HCO_3^- \Leftrightarrow Mg(HCO_3)_2 \Leftrightarrow 2H^+.MgCO_3^- \quad (6)$$

1st addition of NaOH (to pH 10)

$$Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3\downarrow + Na_2CO_3 + 2H_2O \quad (7)$$

$$Mg(HCO_3)_2 + 2NaOH \rightarrow MgCO_3\downarrow + Na_2CO_3 + 2H_2O \quad (8)$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4 \quad (9)$$

$$MgSO_4 + Na_2CO_3 \rightarrow MgCO_3\downarrow + Na_2SO_4 \quad (10)$$

2nd addition of NaOH (to pH 11)

$$CaCl_2 + 2\,NaOH \rightarrow Ca(OH)_2\downarrow + 2\,NaCl \quad (11)$$

$$MgCl_2 + 2\,NaOH \rightarrow Mg(OH)_2\downarrow + 2\,NaCl \quad (12)$$

At the initial condition, all mentioned chemical species are present in equilibrium with their products as shown in Eqs. (4)–(6) both of barium and strontium group with calcium reaction(s) and not with magnesium as discussed earlier.

The addition of hydroxyl ion [OH⁻] will shift the three reactions to the right direction, either towards bicarbonate and/or carbonate. The three reaction rates depend mainly on the continuous diffusion of atmospheric CO_2 into the solution during alkalization process. Therefore, it is recommended executing alkalization in a very short time with minimum stirring.

The initial hydrogen ion (H^+ or H_3O^+) is relatively low in the surface seawater (pH > 8) and may be neglected. However, some sea-related groundwater may acquire acidic pH value (<7), in this case acidity must be considered and measured experimentally due to the fact that most of thermodynamic equations are not applicable at seawater of high salinity.

Eqs. (7)–(10) illustrate the 1st stage precipitation of calcium and magnesium carbonates from the corresponding dissolved bicarbonate and sulfate. Sodium carbonate is intermediately formed in the

reaction of NaOH with bicarbonate in a stoichio-metric amount, which in turn reacts with sulfate to form carbonate sludge. When there is a shortage in sulfate, Na_2CO_3 will add residual alkalinity to water. Therefore, it should be clear that any softening calculation based on alkalinity would be misleading.

According to the present model, it is possible to predict the amount of NaOH required to remove hard salts from seawater. This model depends on the reaction of NaOH with initial hardness-forming ion-pairs, i.e. $M^{2+}CO_3^{2-}$, $M^{2+}(HCO_3)_2^-$ and $M^{2+}SO_4^{2-}$. As a rule, barium and strontium will follow all calcium reactions in the same order. Table 4 presents a comparison between the theoretical estimation and experimental results of NaOH used in alkalization of the Red Sea surface water to pH 10 (1st stage precipitation) and pH 11 (2nd stage precipitation). The following can be noted:

1) Dissolved calcium and magnesium carbonates [Eqs. (5,6)] do not react with NaOH to precipitate, change in pH towards alkalinity (>9) can do the job. Theoretical estimation of the 1st stage is in agreement with the experimental results.

2) Dissolved calcium and magnesium bicarbonate [Eqs. (7),(8)] react with NaOH to form solid carbonate and generate Na_2CO_3 which in turn reacts with Ca and Mg sulfates to form perceptible

carbonate [Eqs. (9),(10)], i.e. NaOH is consumed once per two successive reactions. Theoretical estimation of the 1st stage is in agreement with the experimental results.

3) The difference was found in the dissolved Ca and Mg chlorides [Eqs. (11),(12)]. Theoretically, it was expected that dissolved Ca and Mg chlorides react with NaOH to form their hydroxide at pH higher than 10, i.e. at the 2nd stage. Analytical results proved that a considerable amount of Ca and Mg hydroxides (equivalent to 0.393% $CaCl_2$ and 0.715% $MgCl_2$) had precipitated within the 1st stage consuming excess NaOH as shown in Table 4. The 2nd stage sludge (at pH 11) was totally formed of hydroxides resulted from 13.161% $CaCl_2$ and 1.812% $MgCl_2$.

In brief, it is possible to conclude the obtained experimental results as follow:

- 1st stage alkalization (pH 10) resulted in:
  - – 100% removal of dissolved Ca, Ba, Sr and Mg carbonates
  - – 100% removal of dissolved Ca, Ba, Sr and Mg bicarbonates
  - – 100% removal of dissolved Ca, Ba, Sr and Mg sulfates
 - – 0.393% removal of dissolved Ca, Ba and Sr chlorides

Table 4
Comparison between theoretical estimation and experimental results of NaOH requirement for alkalization of the Red Sea Water

Ser.	Dissolved salt type	Conc., Mol/kg	Conc., g/kg	Equivalent NaOH, g/g salt	Theoretical estimation		Experimental results	
					1st stage Required NaOH, g/kg	2nd stage Required NaOH, g/kg	1st stage Consumed NaOH, g/kg	2nd stage Consumed NaOH, g/kg
1	$CaCO_3$	0.000130	0.0130	0.00	0.00	—	0.00	—
2	$Ca(HCO_3)_2$	0.000431	0.0699	0.4934	0.0345	—	0.0345	—
3	$CaSO_4$	0.010079	1.3721	0.00	0.00	—	0.00	—
4	$CaCl_2$	0.026580	2.9500	0.7208	—	2.1263	0.0084	0.2798
5	$MgCO_3$	0.001208	0.1018	0.00	0.00	—	0.00	—
6	$Mg(HCO_3)_2$	0.004021	0.5884	0.5466	0.3217	—	0.3216	—
7	$MgSO_4$	0.045427	5.4680	0.00	0.00	—	0.00	—
8	$MgCl_2$	0.320740	30.5378	0.8402	—	25.6574	0.1835	0.4649
					0.3562	27.7837	0.5480	0.7447

 – 0.715% removal of dissolved Mg chloride

• 2nd stage alkalization (pH 11) resulted in:
 – 13.161% removal of dissolved Ca, Ba and Sr chlorides
 – 1.812% removal of dissolved Mg chloride

At hydroxide alkalinity of pH 11, a percentage of 86.446% from Ca, Ba and Sr chloride each, in addition to 97.473% of $MgCl_2$, are still in solution.

In fact, the partial precipitation of alkaline earth chlorides (Ca, Mg, Ba and $SrCl_2$) at the 1st stage (pH 10) is not well understood; the obtained titration curve does not indicate clearly the continuation of their deposition at higher OH concentrations. This may lead us to think about the existence of another intermediate hydrated form of chloride, for example, magnesium hydroxychloride Mg(OH)Cl, which may dissociate in the presence of the bulk sodium chloride of seawater as suggested:

$$Mg(OH)Cl + NaCl \Leftrightarrow MgCl_2 + [Na^{1+}.OH^-]\ (13)$$
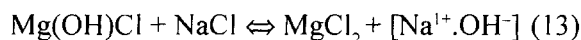
We think that this chemical equilibrium could be responsible, in part, for the steady anomalous seawater alkalinity, which is not explained enough by the well-known carbon cycle. The concentration of organic carbon in seawater is normally less than 1/30 of inorganic carbon, which limits greatly its minor effect towards the aggressive atmospheric CO_2.

4) The consumed amount of NaOH (i.e. 0.5480 and 0.7447 g/kg) shown in Table 4 represents only the equivalent for Ca and Mg, while those mentioned earlier (0.54857 and 0.75088 g NaOH/kg) are equivalent for all dissolved chemical species reacted with NaOH and precipitated totally or partially. The difference is less than 0.5%, which is used in precipitation of other minor species (for example: Ba, Sr, PO_4, SiO_3, etc.) and neutralization of initial water acidity as well.

4. Evaluation of the sodium hydroxide alkalization method

From the RO scaling point of view, it is clear

that the 1st stage alkalization of the Red Sea water by sodium hydroxide to pH 10 is quite successful in removing all hardness chemical species (i.e. hard carbonate, bicarbonate, sulfate, silicate, phosphate and iron) effectively.

The higher 2nd stage alkalization at pH 11 is not necessary, as the remaining species exist in the solution as a stable chloride form and/or soluble hydroxide of non-hardness types that will not contribute in scale formation during RO membrane separation process.

The amount of NaOH required for the 1st stage pH 10 alkalization (~0.55 kg/t) is only 42% of the total amount required to reach pH 11 (~1.30 kg/t), which is a big saving in materials consumption. On field application, the required NaOH is expected to be lower because the initial pH on seaside will be around 8.3, which is higher than laboratory pH 7.3.

The method is fast, clean and accurately controlled. It produces a limited compacted sludge volume. After a short exposure to atmospheric CO_2, the collected sludge will be easily stabilized as Ca-Mg-carbonate form, with very low traces from silicates and phosphates (<0.001%) that could be safely used in land application or other industrial uses due to its high purity.

The precipitation of the 1st stage is mostly formed from a very fine carbonate suspension with some dense gel hydroxide, this mixture provides a uniform coagulation pattern and rapid settling velocity. The obtained results showed that more than 99.99% of suspended particulate was collected and removed. The addition of 2.5 mg/kg non-ionic coagulant polymer enhanced settling rate greatly.

It had been proved that the presence of a high concentration from hydroxyl ion (at pH 10) is capable of limiting bacterial growth effectively as shown from the bacterial investigation. The prechlorination process could be eliminated or minimized.

The alkaline feed water will neutralize the static electric charges that are usually found on the membrane surface, as the hydroxyl ion is a strong wetting agent. This will minimize greatly

the surface tension and facilitate the sliding movement of organic and inorganic fouling matters. Therefore, alkaline water will keep the membrane surface always clean and wet. Under these favorable conditions, it would be possible to increase permeate recovery from less than 30% to more than 45% easily.

The corrosion rate of construction materials in contact with the highly alkaline seawater will be decreased effectively, and less expensive materials may be used instead.

It is expected that the product water will be of alkaline nature (pH~9). Recarbonation, either by atmospheric carbon dioxide or by pure CO_2 gas, is effective and economic for neutralization of the product water to pH~7.5. The carbonation process allows the formation of controlled amounts of carbonate and bicarbonate, which provides a valuable addition for human use and for the distribution system as well.

Sodium hydroxide can be added as a concentrated solution (~40%) without storage or feeding problems. The price of pure NaOH ranges widely between $250 and $350 per ton, however, its cost is compatible when one considers technical and economic problems arising from heavy sulfate scaling and shortening of membrane life as a result.

Seawater electrolysis is the best economic choice for preparation of fresh reactive sodium hydroxide either in a site or directly in-line. Roughly estimated, the cost of seawater electrolysis is typically less than 30% of the purchasing, storage and dosing cost of NaOH. The diaphragm and membrane electrolysis cells are commercially available in wide range capacities. The pure nascent chlorine gas produced as by-product in seawater electrolysis, could be used locally for disinfection purposes.

5. Conclusions and recommendations

The alkalization of the Red Sea water by sodium hydroxide to pH 10 was found to be a valuable substitution of the acidification process used for RO pretreatment. The method has many

technical and economical advantages in a single process, such as removal of hard chemical species (i.e. hard carbonate, bicarbonate, sulfate, silicate, phosphate and iron), removal of suspended solids and colloid, bacterial disinfection, cleaning and wetting of the membrane surface, increasing permeate recovery easily, decreasing corrosion rate, low sludge volume of environmentally chemical nature, and the possibility of instant preparation of NaOH in-line by seawater electrolysis. The alkalization method is fast, clean and economic. It is recommended to upgrade the present laboratory study to a pilot-scale in order to update the obtained results on a larger scale, evaluate the technoeconomic pre-feasibility, and determine the detailed engineering parameters required for the full-scale design. It is also recommended installing the pilot plant on the Red Sea side to avoid the rapid interaction of atmospheric CO_2 that will cut the cost effectively. A more detailed laboratory investigation may be needed for better understanding of the proposed model and associated chemical equations, which is basically different from other chemical softening models.

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