

**COMPARATIVE STUDY ON THE USE OF ZEOLITE AND PRECIPITATION
AGENTS TO RETARD SCALE FORMATION IN THE SEAWATER
PRETREATMENT PROCESS**

K. Dahmani^{1,2}, M. Belloul¹, D. E. Kherroub^{2,3*}

¹Laboratory of numerical and experimental modelling of the mechanical phenomena, Ibn
Badis University, Mostaganem, 27000, Algeria

²University Centre of Relizane Ahmed Zabana, Institute of Sciences and Technology, BP
Relizane, 48000, Algeria

³Laboratory of Polymer Chemistry, Department of chemistry, Faculty of Sciences, University
of Oran, BP 1524 El'Menouer Oran 31000, Algeria

Received: 14 October 2018 / Accepted: 11 December 2018 / Published online: 01 January 2019

ABSTRACT

The scale formation in heat transfer surfaces in seawater desalination plants by multi stage flash processes (MSF). This scale is formed during the precipitation of salts containing in seawater such as calcium and magnesium carbonates. The pretreatment is based on the removal of the calcium and magnesium cations from seawater, using zeolite as cation exchanger and precipitator agents as: lime, soda ash, and mixture of soda ash with soda. DRX, SEM, and EDX analyses were employed to characterize the zeolite before and after pretreatment so as to demonstrate the change composition on the zeolite surface. The results revealed that the pretreatment by a mixture of soda ash (13g/L) and soda (4g/L) favor the precipitation of calcium and magnesium ions. The calcium and magnesium ion concentrations in seawater were reduced, respectively, from 620 mg/L and 644 mg/L to 5 mg/L and 9.11 mg/L.

Keywords: desalination; calcium carbonate; hydroxide magnesium; soda ash; lime.

Author Correspondence, e-mail: djamaledine.kherroub@yahoo.com

doi: <http://dx.doi.org/10.4314/jfas.v11i1.16>



1. INTRODUCTION

The shortage of drinking water is a problem touched all world countries, the water consumption increase with population growth, and needed of water for various uses and exploitation [1]; with rapid increase of population water shortage is provided to augment around 60% by 2025 [2]. The seawater desalination technology solve the scarcity of water, this technology is mainly divided into two types, thermal and membrane desalination [3], the mostly process used in thermal desalination is multi stage flash (MSF), this process close to 60% of the total world production capacity [4,5], water production quality by MSF characterize by low salts contents because vapor contain a few solids [6]. Therefore, the MSF plants used the thermal energy to produce the fresh water, and usually operate at high temperature range of 120 °C [7]. The seawater composition and operating temperature in the MSF desalination installations are a responsible for scale formation onto heat transfer surfaces, such as; evaporators and brine heated [8,9]. The formation of scale is resulted by deposition of minerals salts of calcium carbonate (CaCO_3) and magnesium hydroxide (Mg(OH)_2), both are called alkaline scale. The non alkaline scale is mainly the deposition of calcium sulfate CaSO_4 .

The formation of alkaline scale of calcium carbonate and hydroxide magnesium depend on temperature, pH, concentration of HCO_3^- , CO_3^{2-} , Ca^{+2} and Mg^{+2} , and also the release of carbonic gas (CO_2). The solubility of CaCO_3 and Mg(OH)_2 decrease with temperature increase [10-14]. The problem of alkaline scaling is to reduce the heat transfer as much as 80% [15], increase of energy consumption and operating costs, loss of production because the factories will need continual cleaning. Several studies were worked for controlled and evaluated of scale formation in MSF installations. The interaction between the decomposition products of the bicarbonate ion of seawater with calcium and magnesium ions produces calcium carbonate and magnesium hydroxide, the inhibition of the decomposition of the bicarbonate ion is the proposed solution to limit this precipitation. The control of scaling in heat transfer surfaces in MSF installations employs various methods: the old method which consists of acid treatment in MSF distillers, additives treatments with organic or inorganic polymeric, and the use of cleaning sponge ball [16-18], but the formation of non alkaline scales in MSF distillers, are controlled by maintain the top brine temperature below 122 °C [13]. Another method of scaling prevention involve softening of seawater before desalination process, using strong cationic resin and zeolite to removal the calcium and magnesium ions [19-21]. A new decalcification strategy has been suggested for precipitating calcium carbonate and magnesium hydroxide using carbonic gas CO_2 and an alkaline source as

precipitators respectively [22-24]. Therefore, the decalcification pretreatment by CO_2 eliminate the major fouling and calcium scaling in seawater desalination installations. In previous work, Ayoub et al [25] evaluated the use of precipitation softening as a pretreatment step for seawater desalination, by the addition of $\text{NaOH}/\text{Na}_2\text{CO}_3$ (2:1) solution, the results showed that precipitation softening at a pH of 11 leading to the removal of a number of scale-inducing materials such as calcium, magnesium, silica, iron, and bacteria.

The novelty of our work is the elimination of calcium and magnesium ions from seawater, using the commercial zeolite z 3125 as cation exchanger and a precipitating agent such as soda ash, lime, and sodium hydroxide. Removal of calcium and magnesium before desalination of seawater minimize the risk of the scale formation onto heat transfer surface. This proposed technique of precipitation and softening by zeolite z3125 is considered as a pretreatment step for seawater desalination.

2. EXPERIMENTAL

2.1. Materials and methods

Seawater from the KAHRAMA desalination plant (Algeria) was used, its composition as listed in Table 1. The pretreatment process was studied by measuring the following parameters: pH, total hardness concentration, calcium concentration [Ca^{+2}], magnesium concentration [Mg^{+2}], and HCO_3^- , CO_3^{2-} , and OH^- ion concentrations. The samples of used seawater in testing procedures were stored at 22 °C. We observed that the total water hardness is very high 420 °F using EDTA complexometric titration method (Table 1). For this purpose, it is necessary to find a proper pretreatment of seawater before introduced into the MSF distillation evaporators. We considered the elimination of the water hardness using precipitator reagents like soda, soda ash, and lime and used the commercial zeolite z 3125 as cation exchanger. Zeolite z3125 is a zeolite type LTA (A5), the properties of this zeolite is the form ionic Ca, and particle diameter is 10 microns.

2.2. Characterization

The seawater pretreatment method consists of Ca^{+2} and Mg^{+2} ions removal by precipitation using Na_2CO_3 , CaO and NaOH, then a softening process using zeolite z3125. The solutions were filtered and analyzed.

Analyses consisted of measuring the following parameters: pH; conductivity (ms/cm); total hardness TH (mg/L); calcium hardness Ca^{+2} (mg/L); and magnesium hardness Mg^{+2} (mg/L). The pH values of the filtered solutions were measured using an electrode in conjunction with a Starter type 210 pH meter. The conductivity values were measured using Conductivity

Instrument HI 2315 (Romania). Calcium and magnesium ions were measured by EDTA complexometric titration method. All analyses were run at a temperature 22 °C.

Table 1. Composition of the seawater fed to the KAHRAMA desalination plant

Parameters	Value
Total hardness, mg/L	4200
Ca ⁺² , mg/L	620
Mg ⁺² , mg/L	644
Cl ⁻ , mg/L	20412
TA, mg/L	24
TAC, mg/L	90
Conductivity, ms/cm	54.5
pH	8.15
Temperature, °C	22

During the use of Na₂CO₃ and in order to determine the optimum amount of soda ash to use, we introduced different amounts ranging from 0.2 to 1.3 g in 100 mL of seawater. The mixture was stirred well for 10 min at a speed of 100 rpm.

A second test was conducted using CaO; samples of 100 mL of seawater solution were transferred to 125 ml Erlenmeyer flasks in which amounts of 10, 20, 30, 35, and 38 mg of the CaO were added. The samples were stirred for 10 min, at a speed of 100 tr/min, in order to determine an optimal amount of lime.

Finally, to determine optimum conditions for soda ash-caustic soda, we added quantities of caustic soda ranging between 100 and 500 mg to a series of five flasks containing the filtrate of the optimal amount of sodium carbonate 13 g/L, and then the solution was analyzed. In order to explore the composition of raw commercial zeolite before and after treatment, 5.5 g of zeolite were introduced into 125 ml Erlenmeyer flask containing 100 ml of seawater and stirring for 30 minutes at a speed of 100 rpm (55 g/L of zeolite and 30 min were the optimum amount and time respectively).

Moreover, commercial zeolite z3125 was characterized by X-ray diffraction analysis (XRD), scanning electron microscope (SEM), and energy dispersive X-ray (EDX). XRD was used to characterize the zeolite before and after treatment on a Bruker D8 advance X-Ray diffractometer (40 KV, 15 mA) using CuK α radiation at the step size of 2° with a counting time of 1 min of each step. EDX analysis (HIROX SH 400 M, Bruker) was used to determine

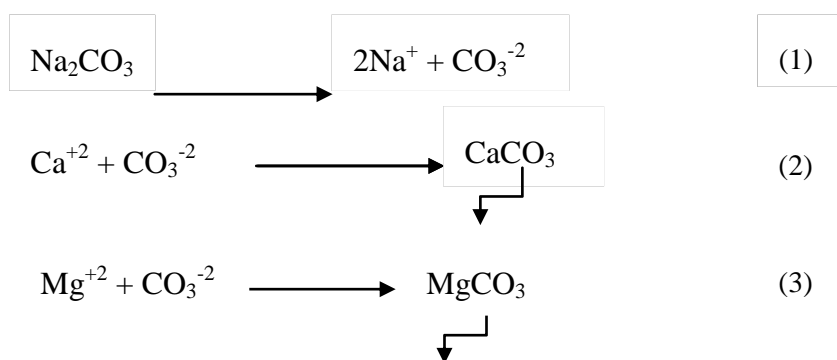
the chemical composition of zeolite. SEM was used to identify the morphology of the zeolite before and after treatment. Accelerating voltage was maintained constant at 20 KV for SEM and EDX analyses.

3. RESULTS AND DISCUSSION

3.1. Effect of added soda ash on Mg^{+2} and Ca^{+2} removal from seawater

The concentration of calcium and magnesium ions in filtered solution decreased after adding various amount of Na_2CO_3 and mixing for 10 minutes (Fig.1a). As the concentration of Na_2CO_3 increased, the concentrations of Ca^{+2} and Mg^{+2} in the filtered solutions declined. For instance, the concentration of Ca^{+2} declined to near 10 mg/L after 13 g Na_2CO_3 was added. This means that the soda ash is a promoter of calcium precipitation. The calcium concentration decreased to near 0 mg/L after adding 0.05 M of Na_2CO_3 with mixing for 30 min at room temperature [26].

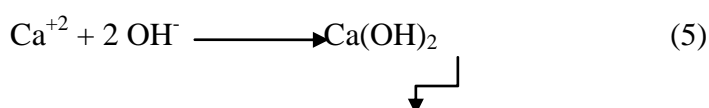
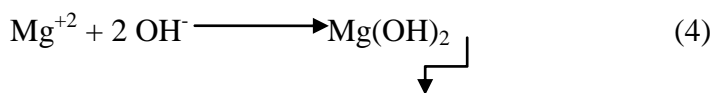
When soda ash is added to seawater, it dissolves and produces two sodium ions [Na^+], and one carbonate ion [CO_3^{-2}] for each unit of soda ash (Equation 1). The carbonate of soda ash reacts with the calcium and magnesium ions existing in seawater for give the insoluble precipitates of calcium carbonate [$CaCO_3$], and magnesium carbonate [$MgCO_3$], respectively (Equations 2 & 3).



3.2. Influence of caustic soda added on filtered seawater solution of soda ash

The concentration of Ca^{+2} and Mg^{+2} in filtered solution of 13 g/L of soda ash after adding various amount of NaOH and stirred for 10 min, were indicated in Fig.1b. As the amount of NaOH added increased, the concentration of Ca^{+2} and Mg^{+2} in the filtered solution decreased. The concentration of Ca^{+2} and Mg^{+2} in the filtered solution decreased to 5 mg/L and 9.11 mg/L, respectively, after adding 400 mg of NaOH. Beyond this concentration, the calcium and magnesium levels in seawater remained constant. So, the combination of soda ash and caustic soda gave the best result for pretreatment of seawater.

The change of Ca^{+2} and Mg^{+2} concentrations in filtered solution is clearly remarkable, because the addition of NaOH has led to an increase in the concentration of OH^- , which react with Mg^{+2} to form $\text{Mg}(\text{OH})_2$, and with Ca^{+2} to form $\text{Ca}(\text{OH})_2$. The existence of a sufficient amount of the OH^- ions, provided by NaOH has led to the precipitation of calcium and magnesium ions (Equation 4 & 5) [27].



After softening by soda ash of 3000 mg/L at pH 11.3, and adding the optimum amount of sodium hydroxide, the calcium and magnesium were decline below 15 mg/L and 1 mg/L respectively.

3.3. Impact of lime added on Mg^{+2} and Ca^{+2} concentration in seawater

Fig.1c explains the variation of calcium and magnesium concentrations as function of the lime concentration. In order to determine the optimal amount of lime, we noticed that the concentration of magnesium was reduced from the 643.95 mg/L to 157 mg/L after added an amount of 350 mg/L of lime, but the calcium concentration was increased. The lime is a promoter of magnesium precipitation that has led to the formation of magnesium hydroxide. The increase in the concentration of Ca^{+2} ions was due to the amount of Ca^{+2} released during dissociation of CaO in water.

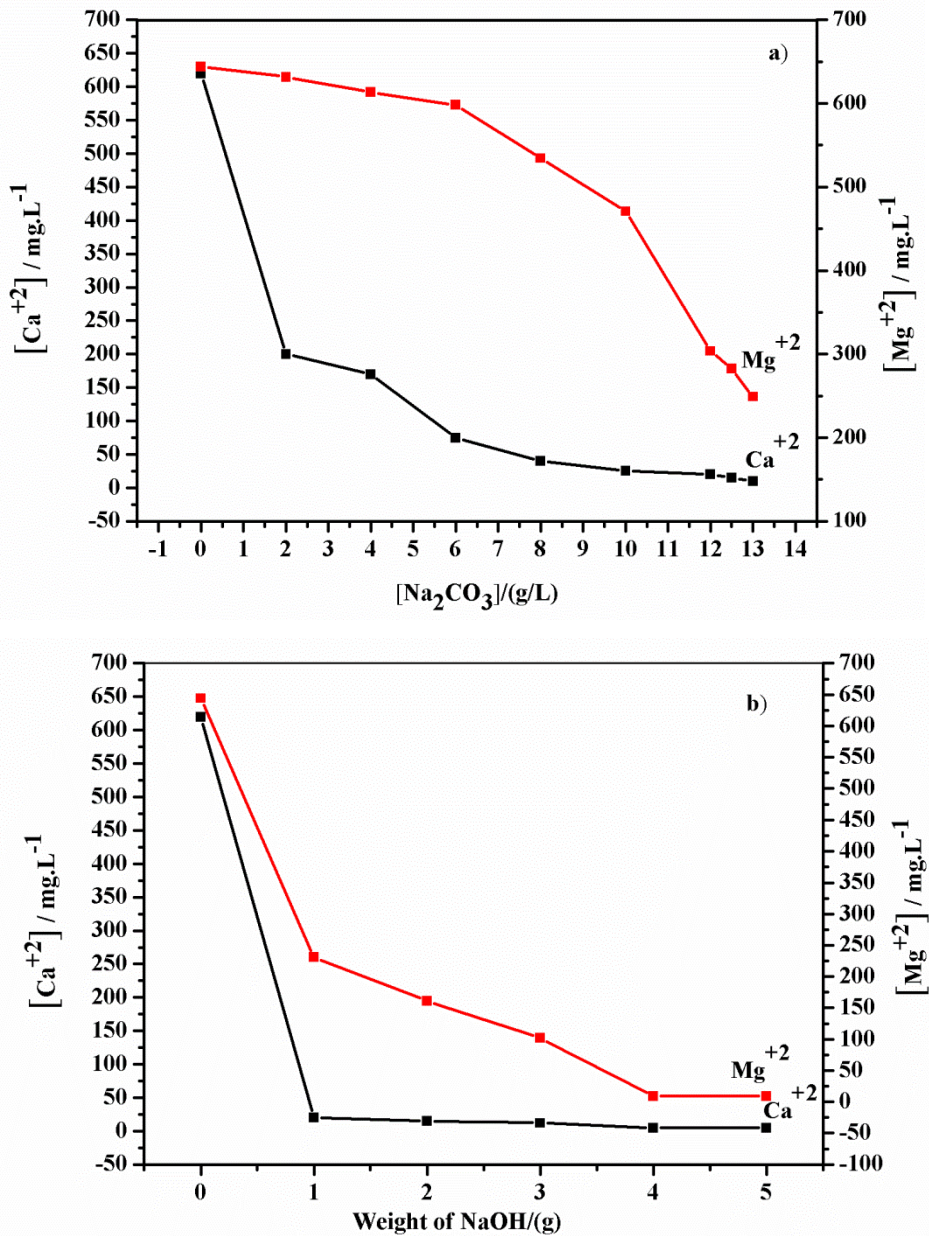
The pH and concentration of HCO_3^- , CO_3^{2-} , and OH^- in raw seawater solution and in filtered solution of 13 g/L of soda ash, after adding various amount of sodium hydroxide and mixing for 10 min of 100 rpm were shown in Fig.2.

The carbonate ions concentration increased with the successive addition of NaOH, but the bicarbonate ions concentration were dropped to zero after added amount of 1 g/L of soda as shown in (Fig.2a and Fig.2b), this concentration of bicarbonates ions remained constant with the continuous addition of NaOH.

The curve of pH (Fig.2c) showed that the pH in filtered solution of soda ash increased with the continuously addition of NaOH. The pH was 9.84 before adding the amount of NaOH. Then, the pH reached 10.80 after adding a quantity of NaOH equal to 4 g/L. Thus, removal rates for both calcium and magnesium ions at pH 10.80 were heavily elevate. The addition of NaOH led to an increase in pH and provided more OH^- which bound to the remaining

magnesium ions in the filtered solution. This effect induced the precipitation of carbonate and magnesium hydroxide.

The filtered solution of 13g/L of soda ash contain 7000 mg/L of CO_3^{2-} and 400 mg/L of OH^- (Fig.2a and Fig.2d), after adding NaOH the both concentrations of carbonates and hydroxides increased. The carbonates ions were reacted with calcium remaining in the filtered solution to induce the precipitation of calcium carbonate or calcium hydroxide. Also, the hydroxide ions were reacted with magnesium to produce the magnesium carbonate or magnesium hydroxide.



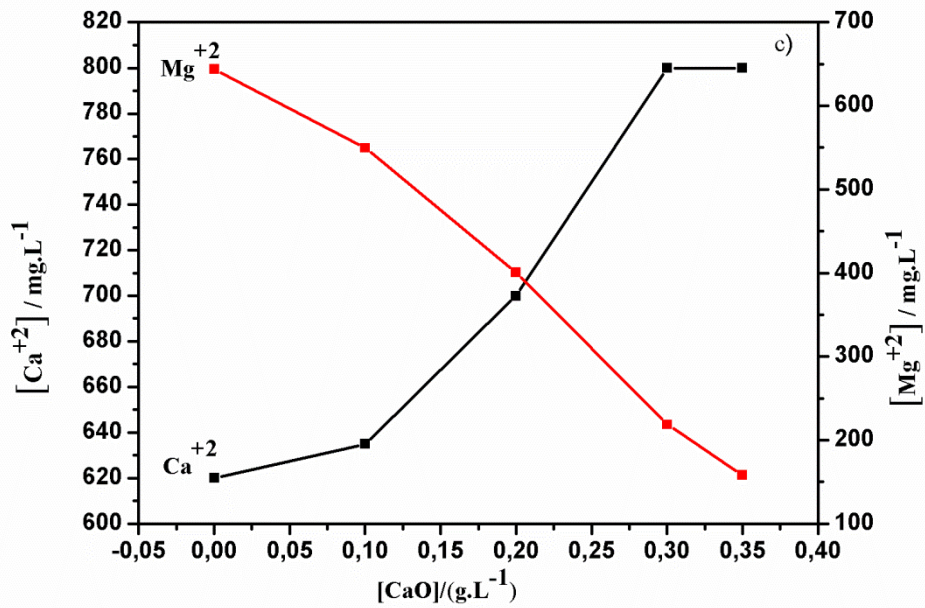


Fig.1. Ca and Mg removal by addition of different precipitator reagents: (a) Na₂CO₃, (b) NaOH added in filtered solution of 13g/L of Na₂CO₃, (c) CaO from seawater

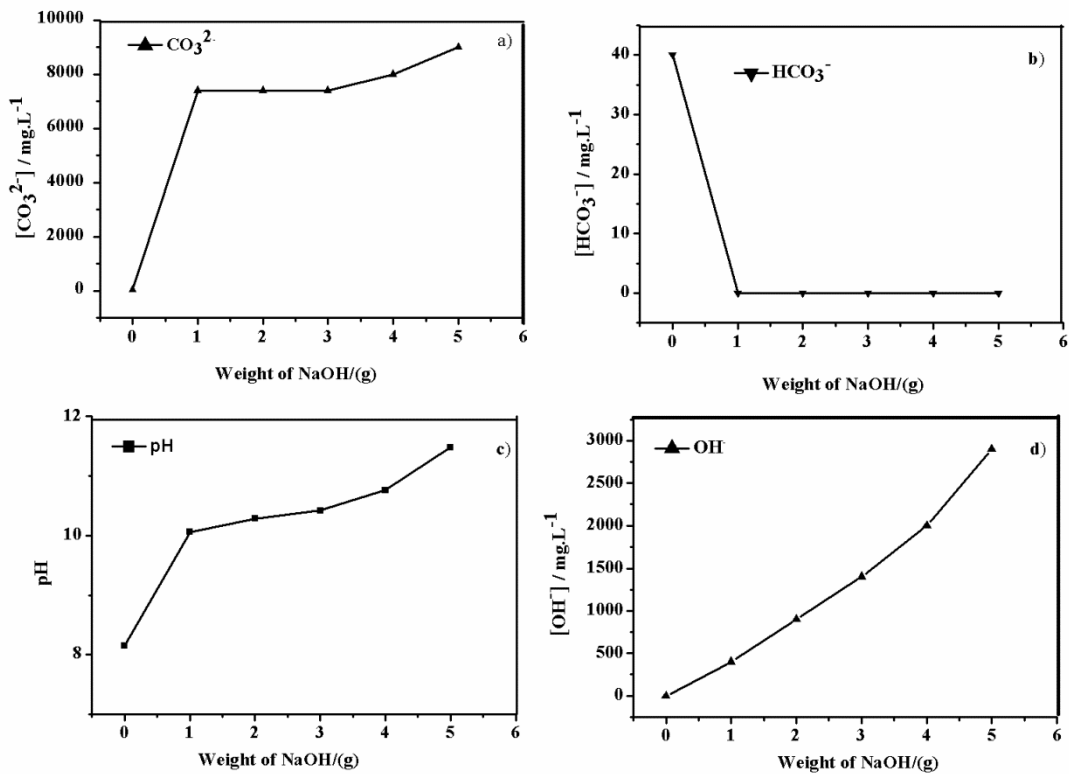


Fig.2. The pH and concentration of HCO₃⁻, HCO₃²⁻, and OH⁻ in filtered solution after adding various amounts of soda (NaOH) at a concentration of soda ash of 13g/L

4. Seawater softening using commercial zeolite z3125

The composition of commercial zeolite z3125 before and after treatment was analyzed using XRD and SEM-EDX. XRD spectra are shown in Fig.3. As seen in the XRD pattern of the zeolite at two different time: 0 min and 30 min; the zeolite before treatment at 0 min is a pure LTA zeolite crystals of form Ca [28]. After 30 min of pretreatment, the RDX spectrum indicates the appearance of a new dominant peak at 2θ of 6° corresponding to the presence of MgO (magnesium oxide) impregnated in zeolite z3125. SEM and EDX were used to confirm the presence of Mg in the zeolite z3125. Fig.4 shows the SEM image of the crude A5 zeolite before (Fig.4a) and after pretreatment (Fig.4b). After 30 min of the contact with seawater solution, the surface of zeolite A5 appears clearly charged resulting in the appearance of a new element, this change of form of the agglomerates on the surface of the zeolite indicates was due to the fixing of magnesium.

Fig.5 and Fig.6 show the EDX spectra of the zeolite before and after treatment respectively. The EDX results indicate that the zeolite before treatment was composed of 0% magnesium, 28.53% of oxygen, and 71.47% of calcium, and after pretreatment its composition became 40.14% of magnesium, 35.96% of oxygen and 23.90% of calcium. The zeolite z3125 adsorbed the existing magnesium ions in the seawater solution. The removal rate of magnesium by the zeolite z3125 was 40.14%, which corresponds to the elimination of 258.50 mg/L of seawater containing 644 mg/L before treatment. The results obtained by EDX analysis corroborate those obtained by SEM.

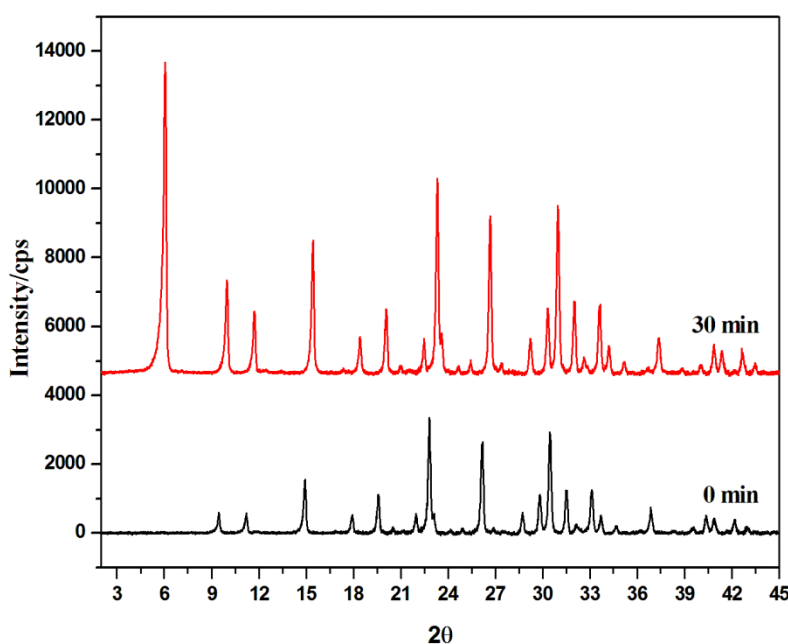


Fig.3. XRD patterns of commercial zeolite z3125 before (black) and after contact with seawater solution (red)

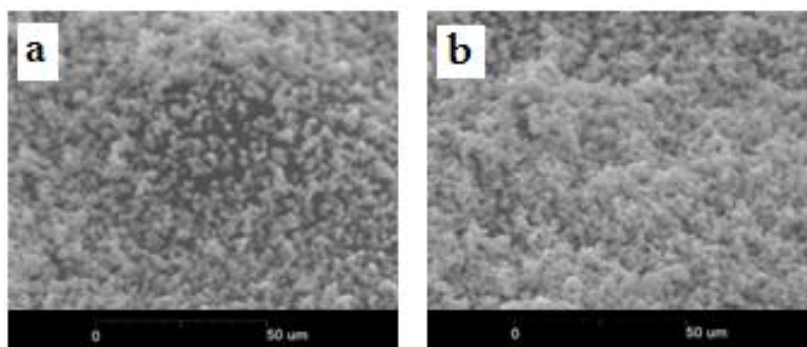


Fig.4. SEM images of zeolite z3125 before (a) and after treatment (b)

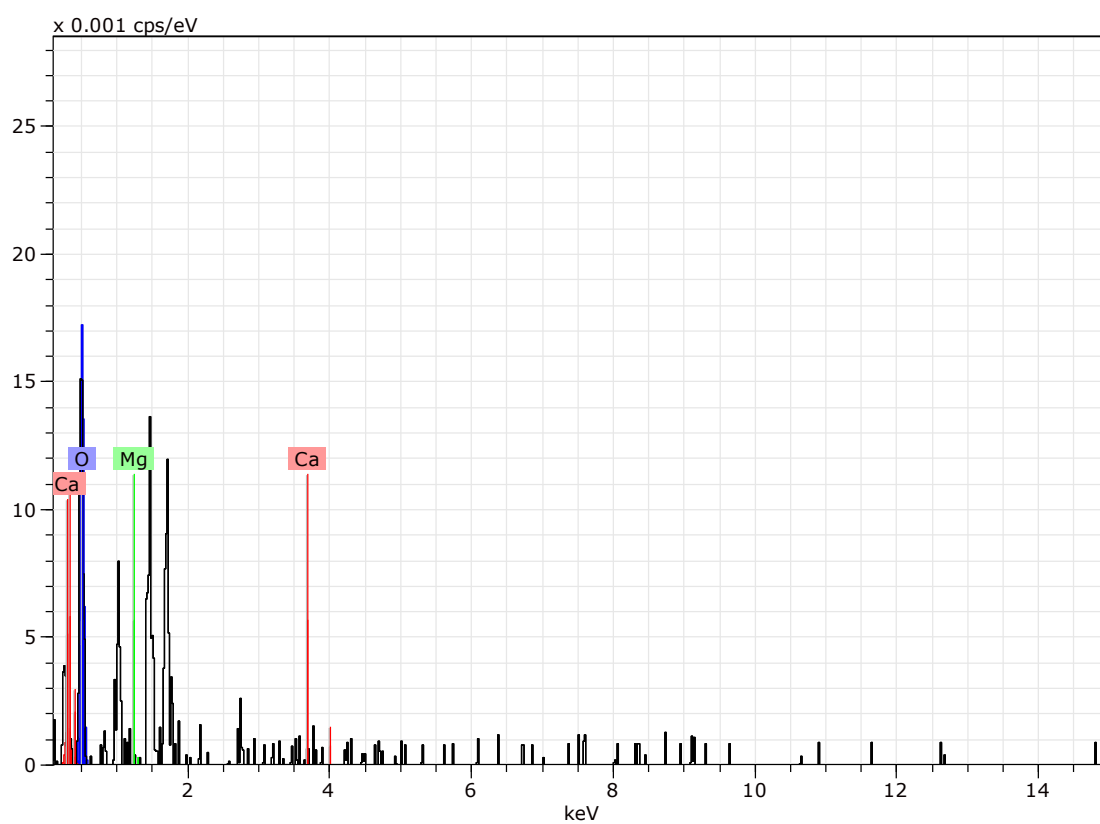


Fig.5. EDX analysis of zeolite z3125 before treatment

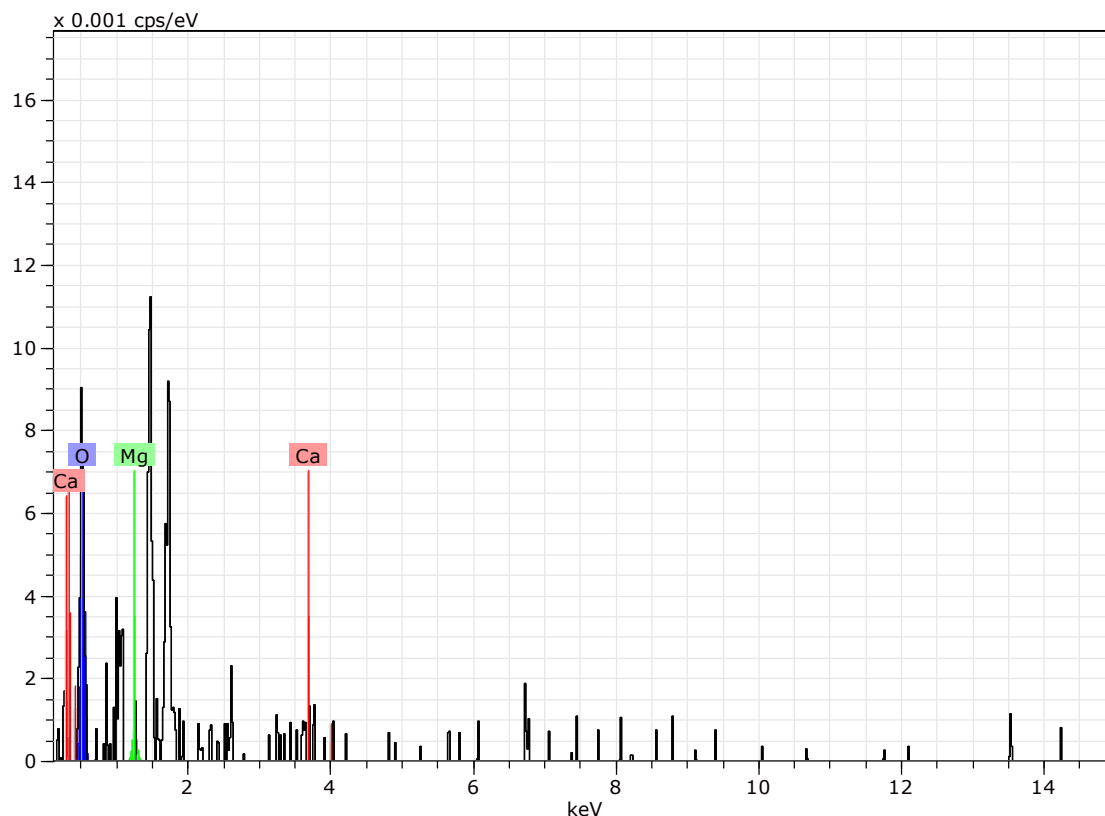


Fig.6. EDX analysis of zeolite z3125 after treatment

5. CONCLUSION

The seawater pretreatment by removal calcium and magnesium using zeolite as cation exchanger and by lime, soda ash, and soda ash-soda as precipitation agents was studied. Softening pretreatment using zeolite is effective for removal magnesium ions from seawater, the DRX, SEM, and EDX analyzes demonstrated the presence of a large amount of magnesium oxide in zeolite after 30 min of the contact with seawater.

The precipitation technique using sodium carbonate is useful for reducing calcium, but not for reducing magnesium. The mixture of sodium carbonate and soda could simultaneously reduce the content of the calcium and magnesium ions in seawater with the rates of 99.19% and 98.58%, respectively. The use of lime is promising for the removal of magnesium from seawater; its rate has been reduced from 644 mg/L to 157 mg/L.

Pretreatment by a mixture of soda ash (13 g/L) and soda (4 g/L) gave the best results. The calcium and magnesium ion concentrations in seawater were reduced from 620 mg/L and 644 mg/L to 5 mg/L and 9.11 mg/L respectively.

6. REFERENCES

- [1] Shannon M A, Bohn PW, Elimelech M, Georgiadis J G, Marinas B J, Mayes AM. Science and technology for water purification in the coming decades. *Nature.*, 2008, 452(7185), 301–310.
- [2] El-Dessouky H .T, Ettouney H. M. *Fundamentals of Salt Water Desalination*. Amsterdam, the Netherlands, 2002, pp. 1-691.
- [3] Voutchkov N, Sommariva C, Pankratz T, Tonner J. Desalination process technology. In J. Cotruvo (Ed.), *Desalination technology*. Florida: CRC press, 2010, pp. 21–90.
- [4] El-Dessouky H T, Ettouney H M, Al-Roumi Y. Multi-stage flash desalination: present and future outlook. *Chem. Eng. J.*, 1999, 73(2), 173-190.
- [5] El-Dessouky H T, Ettouney H M, Al-Juwayhel F, Al-Fulaij H. Analysis of Multi stage Flash Desalination Flashing Chambers. *Chem. Eng. Res. Des.*, 2004, 82(8), 967-978
- [6] Al-Hengari S, El-Bousiffi M, El-Mudir W. Performance analysis of a MSF desalination unit. *Desal.*, 2005,182(1-3), 73-85.
- [7] Al-Anezi K, Hilal N. Scale formation in desalination plants: effect of carbon dioxide solubility. *Desal.*, 2007, 204(1-3), 385–402.
- [8] Mizuno H, Kansha Y, Kishimoto A, Tsutsumi A. Thermal seawater desalination based on self-heat recuperation. *Clean. Techn. Environ. Policy.*, 2013,15(5), 765–769.
- [9] Khawaji A D, Kutubkhanah I K, Wie J M. Advances in seawater desalination technologies. *Desal.*, 2008, 221(1-3), 47-69.
- [10] Al-Rawajfeh A E, Glade H, Ulrich J. Scaling in multiple-effect distillers: the role of CO₂ release. *Desal.*, 2005,182(1-3),209-219.
- [11] Chong T C, Sheikholeslami R. Thermodynamics and kinetics for mixed calcium carbonate and calcium sulfate precipitation. *Chem. Eng. Sci.*, 2001, 56(18), 5391–5400.
- [12] Glade H, Ulrich J. Influence of solution composition on the formation of crystalline scales. *Chem. Eng. Technol.*, 2003, 26(3), 277–281.
- [13] Al-Sofi M A. Fouling phenomena in multi-stage flash (MSF) distillers. *Desal.*, 1999, 126(1-3), 61–76.
- [14] Al-Anezi K, Johnson D J, Hilal, N. An atomic force microscope study of calcium carbonate adhesion to desalination process equipment: effect of anti-scale agent. *Desal.*, 2008, 220(1-3), 359–370.
- [15] Al-Rawajfeh A E. Modeling of alkaline scale formation in falling film horizontal-tube multiple-effect distillers. *Desal.*, 2007, 205(1-3), 124-139.

- [16] Ghani S, Al-Deffeeri N S. Impacts of different antiscalant dosing rates and their thermal performance in Multi Stage Flash (MSF) distiller in Kuwait. *Desal.*, 2010, 250(1), 463–472.
- [17] Al-Hamzah A A, Fellows C M. A comparative study of novel scale inhibitors with commercial scale inhibitors used in seawater desalination. *Desal.*, 2015, 359(0), 22–25.
- [18] Shams El Din A M, El-Dahshan M E, Mohammed R A. Inhibition of the thermal decomposition of HCO_3^- A novel approach to the problem of alkaline scale formation in seawater desalination plants'', *Desal.*, 2002, 142(2), 151-159.
- [19] Hoffmann H, Martinola F. Selective Resins and Special Processes for Softening Water and Solutions. *React. Polym.*, 1988,7(2-3), 263–272.
- [20] Xue Z, Li Z, Ma J, Bai X, Kang Y, Hao W, Li R. Effective removal of Mg^{2+} and Ca^{2+} ions by mesoporous LTA zeolite. *Desal.*, 2014, 341(1), 10–18.
- [21] Barba D, Giacomo G D, Evangelista F, Tagliaferri G. High temperature distillation process with sea water feed decalcification pretreatment. *Desal.*, 1982, 40(3), 347–355.
- [22] Zhao Y, Zhang Y, Liu J, Gao J, Ji Z, Guo X, Liu J, Yuan J. Trash to treasure: Seawater pretreatment by CO_2 mineral carbonation using brine pretreatment waste of soda ash plant as alkali source. *Desal.*, 2017, 407 (0), 85–92
- [23] Zhao Y, Yuan J, Zhang J, Xie L, Ji Z, Su M, Chen J. A different approach for seawater decalcification pretreatment using carbon dioxide as precipitator. *Desal.*, 2013, 322(0), 151–158.
- [24] Zhao Y, Cao H, Xie Y, Yuan J, Ji Z. Mechanism studies of a CO_2 participant softening pretreatment process for seawater desalination. *Desal.*, 2016, 393(0), 166–173.
- [25] Ayoub G M, Zayyat R M, Al-Hindi M. Precipitation softening: a pretreatment process for seawater desalination. *Environ. Sci. Pollut. Res.*, 2014, 21, (4), 2876-2887. <https://dx.doi.org/10.1007/s11356-013-2237-1>
- [26] Jeldres R I, Arancibia-Bravo M P, Reyes A, Aguirre C E, Cortes L, Cisternas L A. The impact of seawater with calcium and magnesium removal for the flotation of copper-molybdenum sulphide ores. *Mine. Eng.*, 2017, 109(0), 10–13.
- [27] Subramani A, Cryer E, Liu L, Lehman S, Ning R Y, Jacangelo J G. Impact of intermediate concentrate softening on feed water recovery of reverse osmosis process during treatment of mining contaminated groundwater. *Sep. Pur. Tech.*, 2012, 88(0), 138–145
- [28] Zhou D, Tang B, Lu X H, Wei X L, Li K, Xia Q H. Co^{2+} -exchanged MOR and 5A zeolite as efficient solid catalysts for the epoxidation of styrene with air. *Cat. Com.*, 2014, 45(0), 124–128.

How to cite this article:

Dahmani K, Belloul M, Kherroub DE. Comparative study on the use of zeolite and precipitation agents to retard scale formation in the seawater pretreatment process. *J. Fundam. Appl. Sci.*, 2019, *11(1)*, 245-258.