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Application of pellet softening (PS) as a scale prevention method in seawater desalination plants

Ahmed Al-Ghamdi[a,*], Waid Omar[a,b]

[a]*Chemical Engineering Technology Department, Yanbu Industrial College P.O. Box 30436, Saudi Arabia*
Tel. (+966)4-3946163; Fax: (+966)4-3920213; email: alghamdia@yic.edu.sa
[b]*Department of Natural Resources and Chemical Engineering, Tafila Technical University, Tafila, Jordan*

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ABSTRACT

This research investigates the potential of pellet softening (PS) on calcite particles as a control method to avoid scaling of calcium carbonate from seawater in desalination. Experimental studies were conducted in a 5 L agitated vessel under controlled temperature and agitation. The measured transient calcium ion concentration, salinity, pH, and total alkalinity of seawater during mixing with calcite particles show that the Ryznar Stability index (RSI) increased from 4.3 to 5.7, which means that the status of seawater changed from “high scaling potential ”to “low scaling potential” after being subjected to PS process at 70˚C. The supersaturation of seawater with respect to calcite is reduced from 33.5 to 5.27. The results demonstrate that PS is a feasible and effective pretreatment strategy for thermal and membrane seawater desalination facilities.

Keywords: Scaling; Prevention; Control; Seawater; Calcite; Pellet softening; RSI; Supersaturation; Pretreatment; Particles growth

1. Introduction

The scaling of heat transfer surfaces in desalination processes is of economical importance to achieve low-cost fresh water. It contributes negatively in shortening of the overall life of the heat transfer equipments and reduction of the thermal efficiency due to its insulating characteristics thus, enlarged maintenance and energy costs, and plant shutdowns. The scaling problem can lead to in an increase of up to 6% of the multiple stage flash (MSF) desalination unit costs due the requirement of 20–25% excess design allowance [1] as the heat transfer area makes up around 30%. The same problem occurs in membrane desalination due to membrane fouling. In order to implement efficient and economical thermal seawater desalination, the scale layer formation at the metal surfaces of the heat exchanger tubes must be inhibited or at least the seawater scale forming potential must be reduced to its ultimate minimum level.

There many research efforts conducted to find appropriate techniques for scale control in thermal and membrane desalination systems. Chemical inhibitors are widely used to control the fouling [2–5] in both membrane and thermal units. The efficiency of these scale inhibitors varies depending on the type of mechanism by which they function to control or

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*Corresponding author.

retard scale formation. However, scaling inhibitors are typically not green chemicals and may have a substantial environmental impact [3]. There are many published studies that address the application of nanofiltration as a pretreatment step to reduce the scaling potential of seawater before it is fed to a multi stage flash (MSF) plant [6–13]. Another scaling control technique is proposed by Hasson et al. [14], based on electrochemical principles. Ghernaout et al. [15] studied the application of electrocoagulation for the removal of organic and inorganic matter by electroflotation. The application of magnetic treatment of water to control scaling in tubes and boilers has been reported in the literature by many authors [16,17].

Pellet softening (PS) or seeded crystallization processes can be implemented as promising pretreatment stages for the control of the scaling potential. Application of crystallization methods is a well-known technology for the production of drinking water from non-seawater sources, particularly in the Netherlands and in Belgium. Tran et al. [18] investigated the feasibility of a hybrid system consisting of a pellet reactor and electrodialysis (ED) to treat reverse osmosis (RO) concentrates in which the pellet reactor was used to remove the scaling potential before ED treatment. Precipitation in the pellet reactor showed higher calcium removal up to 95% when the pH was adjusted to 11.5. Van der Bruggen et al. [19] presented a case study for softening of drinking water before distribution using the pellet reactor technique based on precipitation of $CaCO_3$ by NaOH addition. A cost-benefit analysis of central softening for production of drinking water where large-scale investments in this technology was conducted. The results showed that softening is beneficial if water hardness is to be decreased by at least 5°F. Turek and Dydo [20] suggested a hybrid NF/RO/MSF crystallization system. The results indicated that this combination offered a very promising performance with high water recovery (77.2%) and water costs reduced to $0.37/m^3. The idea of using the same technology for scaling reduction of seawater might be an effective, green, and low-cost scale control method [21–23]. The method is based on introducing calcium carbonate particle to supersaturated seawater within the meta-stable zone. The growth of calcium carbonate particles in seawater will lead to a reduction of the amount of the scaling compounds in seawater. There are limited studies which focus on the feasibility and the potential of PS process in reduction of scaling potential of seawater and the parameters influencing the efficiency of this process.

In this study, the potential and the feasibility of PS of calcium carbonate from seawater on calcite particles will be investigated as a scale control method. The role of temperature will be explained. Based on the experimental investigations in a batch vessel, the reduction of supersaturation and the improvement of scale inhibition will be introduced.

2. Experimental methods

The measurements were conducted in a 5 L jacketed, closed, and stirred vessel. The control of temperature was achieved by circulating thermostated water through the jacket of the vessel. A programmable thermostat (Thermo Scientific-AC150) was used to control the temperature inside the vessel with an accuracy of (±0.01°C).

The seawater used in all experiments was artificial standard seawater at salinity of 45 g/kg which was prepared from salts of analytical grade, purchased from Sigma-Aldrich, and deionized water. About 50 L of homogeneous stock seawater solution was prepared at room temperature of 23°C in a closed vessel and used for all experiments. The analysis of the stock feed seawater used in this study is presented in Table 1.

Calcite seeds were prepared from natural calcite rock. After grinding the calcite rock, the particles were sieved using OCTAGON-Digital test sieve shaker for 2 h and the seeds between the sieves 500 μm and 600 μm were collected.

The experiments were conducted in a way that 20 g of calcite seeds were introduced to 4 kg supersaturated seawater under controlled temperature and pH. The initial pH was adjusted to 8.25 using few droplets of Na_2CO_3 (10 Wt.%). The suspension density of calcite particles in the seawater solution was kept constant for all experiments at 5 g/kg seawater and

Table 1
Analysis of the artificial seawater used in the experiments

Ion	Concentration (g/kg)
Mg^{2+}	1.484
K^+	0.478
Ca^{2+}	0.574
Na^+	14.208
Sr^{2+}	0.017
Cl^-	25.135
Co^{3-}	0.036
HCO_3^{2-}	0.122
SO_4^{2-}	3.293
Salinity (TDS)	45.347
pH	7.42
Conductivity (mS/cm)	64.3
Density (g/cm^3)	1.033

the agitation speed was fixed to be constant at 120 rpm. Seawater samples were taken from the vessel for analysis at different time intervals to measure the transient change in seawater scaling parameters such as pH, conductivity, salinity, calcium contents, and total alkalinity.

The pH value of seawater was measured within the accuracy of (±0.01) using the pH meter (WTW-pH 315i). The electrical conductivity of the seawater with different salinities was measured using a conductivity meter (Mettler Toledo S30). Seawater analysis for calcium content was measured by ICP-AES according to standard methods of seawater analysis.

The total alkalinity was determined using the end point potentiometric titration (pH = 4.3) method. The relation used to determine the alkalinity is:

$$\text{Total alkalinity} = \frac{V_T \times N \times 50,000}{V_P} \tag{1}$$

where V_T is the volume of titrate (mL), N is the normality of the titrate (N), and V_p is the volume of probe (mL).

The variation of the salinity of seawater was correlated to the variation of the conductivity. The calibration curves used in this study relating the salinity of seawater to the conductivity at the temperatures 50 and 70°C are given in Fig. 1.

3. Results and discussion

In order to investigate the potential of PS on the reduction of scaling potential of seawater with respect to calcium carbonate, experiments were conducted in which the supersaturated seawater and calcite particles were mixed at a fixed stirring rate, solid particles concentration, and initial pH at 50 and 70°C. The measured variation of calcium ion concentration, salinity, pH, and alkalinity of seawater with time during a120 min batch run is depicted in Fig. 2(A)–(D), respectively.

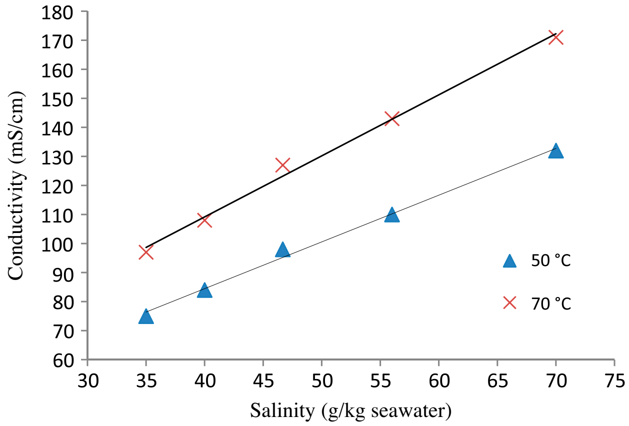

Fig. 1. The calibration curves for measuring the salinity of seawater from conductivity measurements.

At the temperatures studied, a reduction in the calcium ion concentration (Fig. 2(A)) and salinity of seawater (Fig. 2(B)) with time is observed. The measured reduction in calcium ion concentration during 120 min of PS in batch at 50 and 70°C is 0.0043 and 0.00455 mol/l, respectively. Also a gradual lowering of pH (Fig. 2(C)) and total alkalinity (Fig. 2(D)) of seawater was observed. The measured reduction in the concentration of calcium ions, total carbonate, and salinity can be attributed to the reduction of calcium carbonate content in seawater due to its deposition on the surface of calcite particles. Fig. 2(A), (B) and (D) show that the rate of decrease in calcium ion concentration, total alkalinity, and salinity at 70°C is faster than at 50°C.

The temperature has a significant influence on the rate of calcium carbonate deposition from seawater on the calcite particles due to its direct influence on the level of supersaturation of seawater with respect to calcite. Consequently, PS of the scaling material, calcium carbonate, from seawater must be conducted at a high level of supersaturation sufficient to initiate the deposition process.

The supersaturation is the main parameter affecting the deposition rate of calcium carbonate and its value is affected by a complex interrelated parameters. Thermodynamically, the mixing of meta-stable supersaturated seawater and calcite particles over the temperature range 50–70°C will result in PS (mainly as calcium carbonate) on the surface of calcite particles [16]. The seawater has the potential to deposit calcium carbonate only when the value of supersaturation is greater than one and the higher the supersaturation, the stronger the potential of seawater to deposit the calcium carbonate.

The supersaturation of seawater with respect to calcite is temperature dependent and given by the relation [19]:

$$\sigma = \frac{[\mathrm{Ca}^{2+}] \times \mathrm{TA}}{K_{\mathrm{sp,calcite}}(2 + [\mathrm{H}^+]/K_2)} \tag{2}$$

where $[\mathrm{Ca}^{+2}]$ and $[\mathrm{H}^+]$ are the calcium ion and hydrogen ions concentrations (mol/kg), respectively. TA is the total alkalinity as calcium carbonate (mol/kg). The level of supersaturation will be higher for seawaters of higher salinities due to increasing of $[\mathrm{Ca}^{+2}]$ and TA. $K_{\mathrm{SP,calcite}}$ in Eq. (2) is the solubility product of calcium

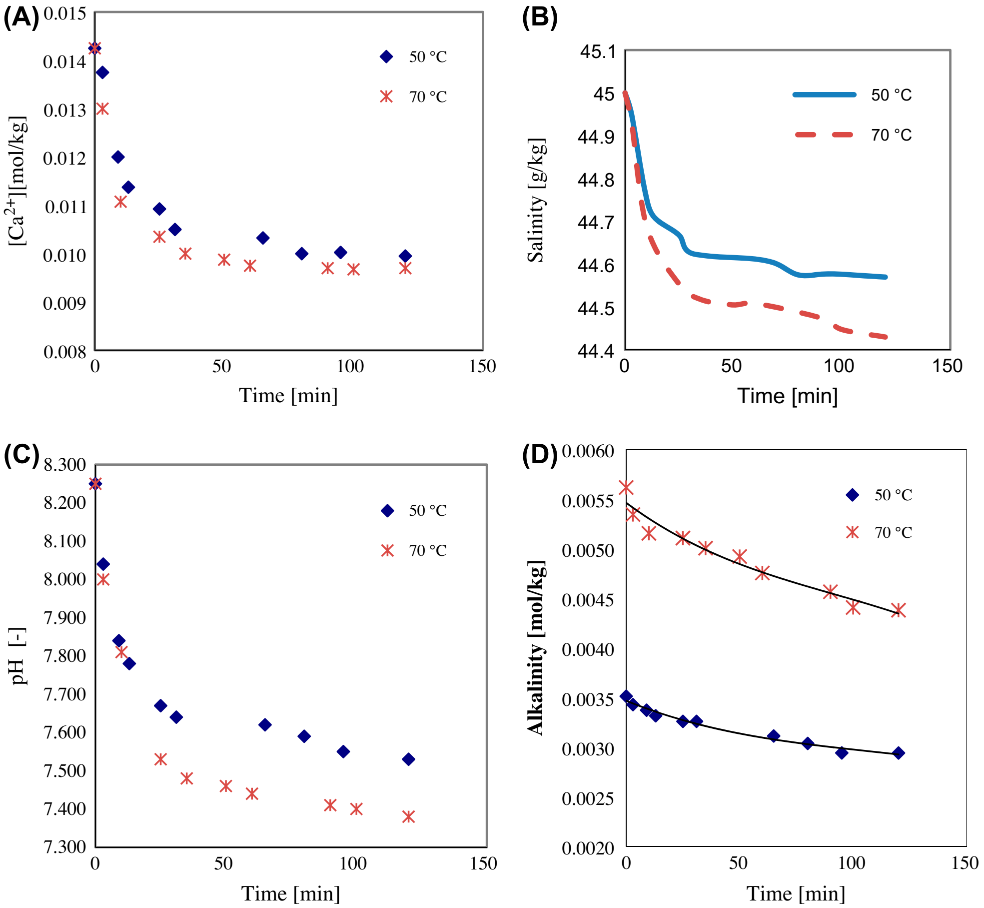

Fig. 2. The measured transient A-calcium ion concentration, B-salinity, C-pH, and D-total alkalinity of seawater during mixing with calcite particles in 5 L agitated vessel (initial salinity = 45.347 g/kg, stirrer speed = 120 RPM, particles concentration = 5 g/kg, particles size = 560 μm, initial pH = 8.25).

carbonate (mol^2/kg^2) with respect to calcite and dependent significantly on the temperature and salinity of seawater. It is described by the solid–liquid chemical equilibrium reaction:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \overset{K_{sp,calcite}}{\longleftrightarrow} CaCO_3(s) \tag{3}$$

K_2 in Eq. (2) is the equilibrium constant for the dissociation of bicarbonate ions to carbonate ions in seawater (mol/kg). It is dependent on the temperature and salinity of seawater, and it is defined by the following liquid equilibrium reaction:

$$HCO_3^-(aq) \xleftrightarrow{K_2} CO_3^{2-}(aq) + H^+(aq) \tag{4}$$

K_2 value is an important parameter affecting the deposition of calcium carbonate on the calcite particles due to its influence on the concentration of carbonate ions.

The temperature influences the level of supersaturation by its direct effect on the values of $K_{sp,calcite}$, K_2, and total alkalinity. Table 2 summarizes the initial values of seawater supersaturation with respect to calcite at the temperatures 70 and 50°C. The supersaturation is calculated from Eq. (1) using the estimated values of $K_{sp,calcite}$ and K_2 from the empirical relation developed by Mucci [24] and Millero [25], respectively. The empirical relations are based on values that are experimentally determined for temperatures up to

Table 2
Effect of temperature on the initial level of supersaturation of seawater with respect to calcite

Seawater parameter	Temperature	
	50°C	70°C
TA (mol/kg)	0.00351	0.00561
$[Ca^{+2}]$ (mol/kg)	0.01425	0.01425
$K_{sp,calcite}$ (mol^2/kg^2)	8.3761E−07	7.45297E−07
K_2 (mol^2/kg^2)	3.25782E−09	4.67443E−09
σ	16.0515787	33.5357363

Table 3
The scaling potential of seawater related to the Ryznar stability index

RSI	Properties of seawater
<5.0	High scaling potential
5.0–6.0	Middle to small scaling potential
6.0–7.0	Equilibrium state
>7.0	No scaling potential

45°C and for salinities up to 50 g/kg. In this work, the values are approximated by extrapolation to the temperatures 70 and 50°C.

Obviously, increasing the temperature from 50 to 70°C will increase the initial level of supersaturation of seawater with respect to calcite. This explains the faster rate of decay of calcium ion concentration, salinity, and total alkalinity at higher temperature. On the other hand, increasing the temperature influences the total alkalinity of seawater by its direct effect on the carbonate bicarbonate ratio in seawater. Table 2 shows higher K_2 value at elevated temperature; therefore, the conversion of bicarbonate to carbonate ions will be higher and consequently enhanced calcium carbonate deposition due to the increased concentration of carbonate ions.

The measured pH decay in Fig. 2(C) is attributed to the reduction of carbonate ion concentration in seawater due to the calcium carbonate deposition. Consequently, more $[H^+]$ ions will be generated according to the equilibrium reaction (Eq. (4)).

The results obtained indicate that PS can be implemented to reduce the scaling potential of calcium carbonate in seawater. The RSI provides the possibility to determine the affinity of seawater to scaling qualitative as well as quantitative. The Ryznar index is defined as:

$$\mathrm{RSI} = 2\mathrm{pH_s} - \mathrm{pH} \tag{5}$$

where $\mathrm{pH_S}$ is the pH value of water in the state of equilibrium with $CaCO_3$. It can be expressed in the following equation:

$$\mathrm{pHs} = \mathrm{p}K_2 - \mathrm{p}K_{\mathrm{sp}} + \mathrm{p}[\mathrm{Ca}^{2+}] + \mathrm{p}[\mathrm{TA}] \tag{6}$$

where the concentrations designated by the letter p can be calculated from the logarithmic values (–log10).

The range of Ryznar index and its relation to the scaling potential of seawater is summarized in Table 3.

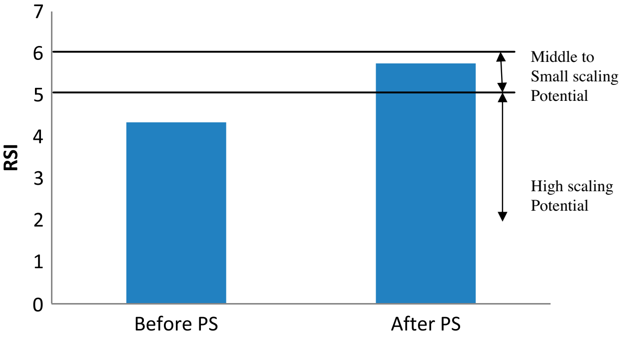

Fig. 3. Ryznar stability index (RSI) of seawater before and after Pellet Softening (PS) at 70°C.

The influence of PS pretreatment on the Ryznar stability index (RSI) at 70°C is presented in Fig. 3. The results presented in Fig. 3 represent that the seawater after treatment with PS process is transferred from the high scaling potential status to the condition of medium to small scaling potential.

The Langelier index for seawater is a useful parameter to characterize the supersaturation of calcium carbonate. A positive value indicates that scaling will occur whereas negative values mean that the scaling process will not occur since it is not yet saturated with calcium carbonate. The Langelier index is defined as the difference between the really measured pH value of the seawater (pH) and the pH value of water in the state of equilibrium with $CaCO_3$ ($\mathrm{pH_S}$). It can be expressed in the following equation:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pHs} \tag{7}$$

The indications for the scaling potential of seawater and its relation to the LSI are based on the following values:

The calculated LSI values at 70°C before and after PS process are 1.95 and 0.81, respectively. This indicates that the seawater LSI is reduced by 58.5% from its initial value after PS process and the scaling sever-

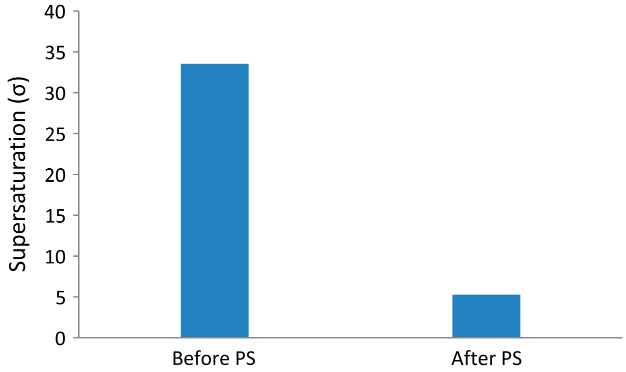

Fig. 4. Supersaturation of seawater with respect to calcium carbonate before and after pellet softening (PS) at 70°C.

Table 4
The scaling potential of seawater related to the Langelier Stability Index

LSI	Properties of seawater
LSI < 0	Water is undersaturated with respect to calcium carbonate
LSI = 0	Water is considered to be neutral
LSI > 0	Water is supersaturated with respect to calcium carbonate ($CaCO_3$) and scale forming may occur

ity becomes not as much as before. Although the seawater is still supersaturated with calcium carbonate, the level of supersaturation is extraordinarily reduced.

Reducing the supersaturation of seawater with respect to calcium carbonate results from the reduction of calcium carbonate scaling parameters, such as calcium ion concentration and total alkalinity. The influence of PS pretreatment at 70°C on the degree of supersaturation with respect of calcium carbonate as calcite is depicted in Fig. 4.

The results presented in Fig. 4 demonstrate that the level of supersaturation with respect to calcium carbonate is reduced dramatically after treatment with PS process. The reduction of supersaturation value means that the deposition of calcium carbonate on heat transfer surfaces can be mitigated, thus the life and the cost of desalination will be reduced. The reduction in calcium ion concentration using the PS processes is moderately positive but there is still a scaling risk due to the remaining supersaturation. This can certainly be improved by for e.g. increasing pH and temperature for removing more Ca, or in a more efficient reactor design. These reactions are usually carried out in a countercurrent continuous flow reactor (e.g. crystalactor).

4. Conclusions

The scaling potential and the supersaturation of seawater with respect calcium carbonate could be reduced noteworthy by subjecting seawater to PS technique. This technique can contribute significantly in scale control/prevention and can be integrated with thermal and membrane desalination systems as a promising pretreatment stage for the control of the scaling potential in seawater. However, it is recommended that PS units should be designed with short retention times and higher efficiency. The large retention time is one of the drawbacks which need further studies to augment the growth of the particles.

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Symbols

$[Ca^{+2}]$ — calcium ion concentration, mol/kg
$[H^{+}]$ — hydrogen ion concentration, mol/kg
K_2 — the equilibrium constant for the dissociation of bicarbonate ions to carbonate ions in seawater (Eq. (3)), mol/kg
$K_{SP,calcite}$ — solubility product constant of calcium carbonate in seawater (eq. 4), mol^2/kg^2
LSI — Langelier saturation index
N — the normality of the titrate, N
pH — the really measured pH-value of the seawater, –
pH_s — the pH value of water in the state of equilibrium with $CaCO_3$, –
RSI — Ryznar Stability Index, –
TA — total alkalinity as calcium carbonate, mol/kg
V_P — the volume of probe, mL
V_T — the volume of titrate, mL

Greek letters

σ — supersaturation of calcium carbonate in seawater, –

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