Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22127

106 (2018) 1–10
February

High recovery MSF desalination process

David Hasson*, Marina Shmulevsky-Lisitsin, Raphael Semiat, Hilla Shemer

Rabin Desalination Laboratory, Wolfson Faculty of Chemical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel, Tel.+97248292936, Fax+97248295672, email: hasson@technion.ac.il (D. Hasson)

Received 28 November 2017; Accepted 15 February 2018

ABSTRACT

Calcium sulfate scale deposition in the widely used multistage flash (MSF) seawater desalination process is prevented by restricting the top heating temperature of the recycling brine to less than 120°C and the fractional water recovery to less than 50% so as not to exceed a concentration factor above 1.8–2.0. Removal of calcium ions from seawater extends the solubility limits of the $CaSO_4$ polymorphs. This should enable MSF operation at higher fractional water recoveries and higher brine temperatures thereby providing significant economic benefits, notably a marked reduction in heating steam requirement. The objective of this study was to evaluate the maximum CF and top brine temperature (TBT) levels at which an MSF process can be operated with seawater depleted from 80% of the calcium ions by a hybrid electrolytic Ca removal-MSF process. A single stage MSF evaporator was constructed enabling long duration desalination experiments. The most significant result of this study was in demonstrating operation of the experimental unit for several days without any scale deposition at a CF of 4 and a heating temperature of 140°C. Comparison of a typical MSF unit of conventional design with the hybrid MSF unit operating at CF of 4 and TBT of 140°C indicates a potential for substantial cost reduction by the proposed concept.

Keywords: Thermal desalination; Concentration factor; Seawater; Calcium sulfate; Scaling

---

1. Introduction

Thermal seawater (SW) desalination processes and in particular multi stage flash desalination are widely practiced in Persian Gulf countries with over 80% desalination units consisting of MSF plants. Though SW desalination by reverse osmosis (RO) has the clear advantage of requiring lower energy consumption [1], the MSF process has the advantage over RO in being a more robust system able to cope much better with contaminated saline feeds.

Currently, there is renewed interest in the MSF system due to its capability to process produced water (PW). Produced water is the high-volume waste stream generated during oil and gas production. It consists of saline water contaminated by hydrocarbons [2,3]. Environmental restrictions and water scarcity are driving increasing interest in treatment and reuse of PW. Beneficial application of the MSF process in PW treatment requires improvement of the fractional water recovery level. The present study is a necessary initial stage of examining a hybrid process enabling high fractional water recovery and reduced energy consumption recovery in the simpler system of MSF seawater desalination.

Currently, fractional water recoveries in seawater desalination by MSF processes are limited to $M_D/M_F < 50\%$ where M_D and M_F represent mass flow rates of distillate and feed respectively. Considerable economic benefits can be realized by overcoming current water recovery limits. The limitation in fractional water recovery is dictated by the solubility limits of calcium sulfate salts. Typical SW contains 400 mg/L Ca^{2+} and 2600 mg/L SO_4^{2-} [4]. The brine concentration effect accompanying the evaporation of distillate can lead to precipitation of sparingly soluble calcium sulfate salts, as discussed in Section 1.3. Since scale deposition in desalination processes cannot be tolerated, calcium sulfate precipitation is prevented as shown below, by restricting the TBT of the recycling brine to less than 120°C and the fractional water recovery to $M_D/M_F < 50\%$.

---

*Corresponding author.

1944-3994 / 1944-3986

The basic concept examined in this study is elevation of the fractional water recovery level and the TBT by widening the solubility levels of calcium sulfate polymorphs in SW concentrates. This is accomplished by removal of a major portion of the calcium ions in SW by the hybrid Electrolysis-Crystallization system (EC) developed in our laboratory [5,6]. The removal of the calcium is undertaken by electrochemical precipitation in the form of calcium carbonate. Because SW contains only 140 mg/L of HCO_3^-, additional carbonate is supplied by injecting CO_2 to the electrochemical cell:

$$Ca^{2+} + CO_{2(aq)} + 2OH^{-} \rightarrow CaCO_{3(s)} + H_2O \tag{1}$$

A possible source of the CO_2 could be from flue gases. The envisaged process flow sheet is outlined in Fig. 1.

The viability of electrolytic removal of calcium ions from SW is demonstrated by data measured in the electrolytic system described elsewhere [5,6]. The effect of CO_2 concentration on $CaCO_3$ precipitation was studied at a constant feed flow rate of 100 mL/min, current density of 200 A/m^2 and voltage of 3.5–4.0 V. More than 80% of the calcium in SW was achieved with an energy demand of about 4 kWh per Kg $CaCO_3$ (Table 1). As discussed in Section 3.1, this is an affordable energy demand. Data presented in the Supplementary Material demonstrate that hydrocarbon contaminants in PW do not hamper electrolytic removal of calcium ions from saline solutions.

This study examines the feasibility of the proposed process by operating an experimental single stage MSF system with an 80% calcium depleted simulated SW feed at elevated temperatures and concentration factors (CF). Economic benefits resulting from the hybrid process are described.

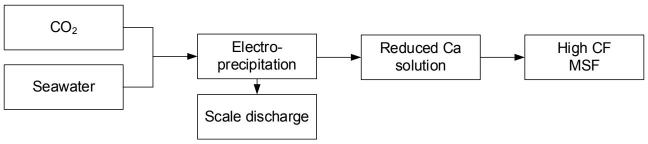

Fig. 1. Flow sheet of the envisaged hybrid process.

Table 1
Electrochemical calcium removal from standard SW

CO_2 (mM)	Calcium removal (%)	Precipitation rate (g $CaCO_3$/h m^2)	Energy consumption (kWh/kg $CaCO_3$)
9.0	44.6	71.7	4.1
10.9	53.2	86.8	3.4
11.2	55.8	89.8	3.3
10.9	59.4	83.9	3.3
13.1	77.6	86.6	4.5
13.6	82.4	92.8	3.6

1.1. MSF working principles

Brief recapitulation of the working principles of the most frequently used MSF brine circulation process will facilitate assessment of the results of the study. As seen in Fig. 2, a brine circulation MSF unit consists of three sections: a heat supply section, a heat recovery section containing n-j flashing chambers and a heat rejection section containing j flashing chambers [7].

Seawater is preheated by condensing product distillate and then heated by hot condensing steam to a final saturation TBT and corresponding saturation pressure. The hot water enters the first flash chamber through an orifice passage which reduces the water pressure to a lower level and a corresponding lower saturation temperature. The temperature reduction is carried out by partial flash evaporation of the water which produces the desired distillate product. The pressure reduction is performed in successive flash chambers. The temperature profile of the brine flashing in successive chambers is described in Fig. 3.

Important economic parameters are the fractional water recovery M_D/M_F, the energy consumption given by performance ratio $R = M_D/M_S$ (mass flow rate ratio of distillate to heating steam), and the specific area requirement A/M_D (m^2/m^3 h product) where A is the total heat transfer area of the condensing tubes and the steam heater.

1.2. Calcium sulfate solubility limitations in SW desalination

Evaporated SW solutions reaching supersaturated conditions with respect to calcium and sulfate ions can precipitate calcium sulfate in three different forms: gypsum ($CaSO_4{\cdot}2H_2O$), anhydrite ($CaSO_4$) and hemihydrate ($CaSO_4{\cdot}½H_2O$). The most useful way for presenting the solubility limits of the calcium sulfate polymorphs in SW evaporation is by a concentration factor-temperature diagram. The concentration factor CF is defined as the ratio of the total dissolved salts concentration after evaporated water withdrawal to the total dissolved salts concentration in the feed.

Fig. 4 presents the thermodynamic solubility limits of the calcium sulfate polymorphs in standard SW [8] and the optimal temperature-concentration path for preventing calcium sulfate precipitation [9]. The optimal path, based on field experience of operating MSF desalination plants, specifies that scale prevention can be prevented by maintaining a TBT below 120°C and a CF below 2.

Thermodynamics stipulates that the most stable polymorph is that of lowest solubility. However according to the "Ostwald's step rule"in general it is not the most stable but the least stable polymorph that crystallizes first before converting to the most stable polymorph. Fortunately, this condition applies to the MSF process [10–12]. As shown in Fig. 4, the process path is under anhydrite supersaturation conditions with no scale precipitation due to the very slow kinetics of anhydrite crystals at moderate temperatures.

Currently, conditions at which anhydrite does not precipitate under supersaturation conditions are not well understood. Fabuss and Lu [10,11] demonstrated a profound influence of the mode of heat transfer on the nucleating species. In SW made supersaturated by pool boiling at constant temperature, the concentration at which initial precipitation occurred coincided with the true solubil-

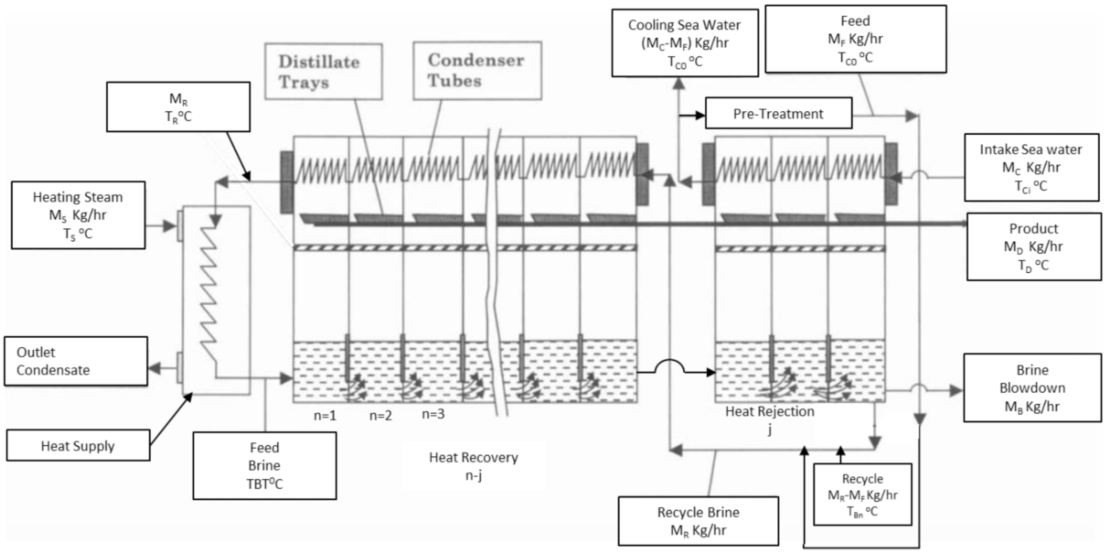

Fig. 2. MSF process flowsheet (adapted from [7]).

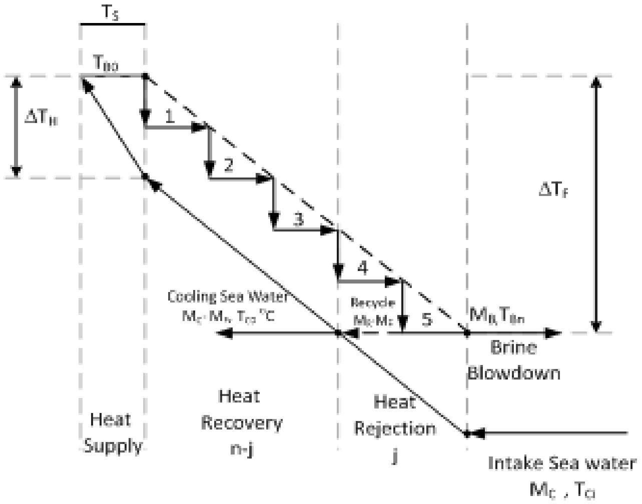

Fig. 3. Temperature profile of the brine flashing in successive chambers in MSF process.

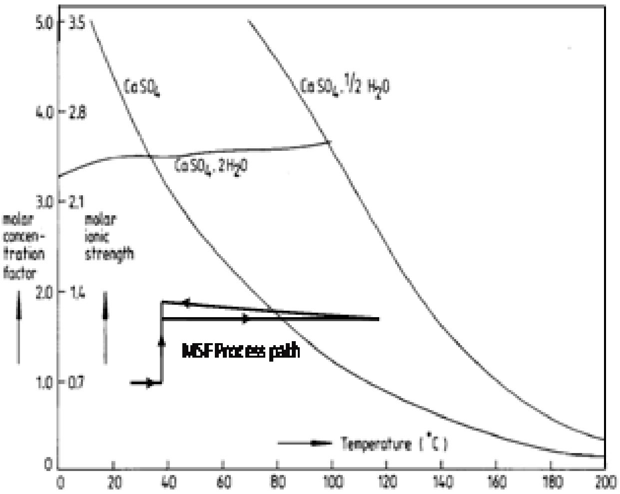

Fig. 4. Solubility of calcium sulfate polymorphs in SW [8] with MSF process path [9].

ity curve of anhydrite. On the other hand, with constant volume heating the temperature at which initial precipitation was detected was nearer to the hemihydrate true solubility curve. Thus, anhydrite nucleation is accelerated under boiling conditions. Water evaporation in the MSF process occurs under non-boiling conditions enabling approach to the hemihydrate solubility at temperatures of about 120°C. As temperature rises, the effective solubility deviates more and more towards the lower anhydrite solubility [9,10] and the propensity for scale precipitation is enhanced.

1.3. Potential benefits of widening calcium sulfate solubility limits

No precise model is known for predicting the solubility limits of different $CaSO_4$ polymorphs in highly saline solutions. Predicted values of the enhanced calcium sulfate solubility limits obtained by depletion of 80% of the calcium ions from standard SW were calculated using the models developed by Fabuss and Lu [10] and Marshall and Slusher [13–15]. The Fabuss and Lu model gave solubility limits lower by about 10% in comparison with the Marshall and Slusher model. The more conservative solubility values of the Fabuss and Lu model were adopted in analysis of the experimental data of this study.

Fig. 5 compares calculated solubility limits of calcium sulfate polymorphs in SW depleted by 80% of the calcium ions with SW solubilities. Assuming that the anhydrite maintains its very slow nucleation so that the precipitation threshold is near the hemihydrate solubility limit, temperatures as high as 140°C and CF nearing 4 would then

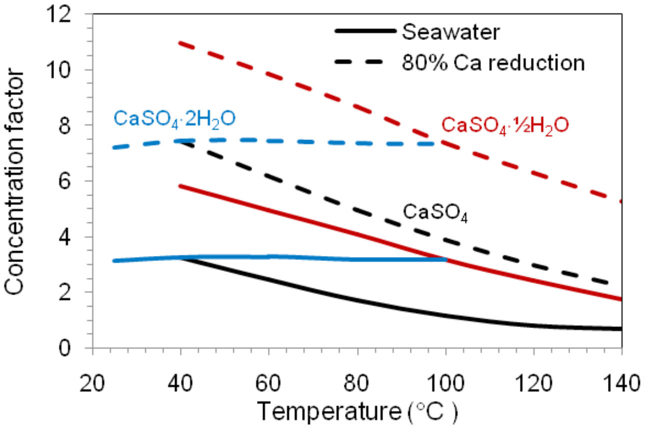

Fig.5. Comparison of $CaSO_4$ solubility limits of SW with solubility limits of SW depleted by 80% Ca^{2+} ions.

be achieved. Such conditions would lead to significant economic benefits.

The main features of the benefits are outlined below using simplified circulation-MSF equations. Plants having the same distillate output (M_D kg/h) are compared.

A. Reduction of the required feed flowrate

The feed flowrate M_F is related to the concentration factor CF by the following mass balance:

$$\frac{M_F}{M_D} = 1 + \frac{1}{CF - 1} \tag{2}$$

Increase of the CF decreases the required feed flow rate. Increase of the current CF of about 2 to 4 enables reduction of M_F by 33%. The economic benefits are in reduction of feed pumping costs and feed pretreatment costs (addition of antiscalants, antifoam compounds and biocides; de-aeration measures).

B. Reduction of the recycle flow stream

A heat balance shows that the ratio of the recycle flow stream M_R to the distillate stream is given by:

$$\frac{M_R}{M_D} = \frac{1}{1 - e^{-\frac{C_P \cdot \Delta T_F}{\lambda}}} \cong \frac{\lambda}{C_p \Delta T_F} \tag{3}$$

where the design flashing range ΔT_F is the temperature difference between the top brine temperature and the brine exit temperature from the last flash chamber:

$$\Delta T_F = T_{Bo} - T_{Bn} \tag{4}$$

and λ and C_P are average values of the latent heat of steam and of the brine specific heat respectively. Increase of the flash range by increase of the TBT is seen to reduce also the recycle stream flow rate and to contribute further to the reduction in pumping costs.

C. Reduced heating steam requirement

An enthalpy balance shows that the performance ratio is given by:

$$R = \frac{M_D}{M_S} = \frac{\Delta T_F}{\Delta T_H} \cdot \left\{ \frac{1 - e^{-\frac{C_P \Delta T_F}{\lambda}}}{\frac{C_P \Delta T_F}{\lambda}} \right\} \cong \frac{\Delta T_F}{\Delta T_H} \tag{5}$$

where the design heating range ΔT_H is the temperature increase of the recycle stream M_R in the steam heater:

$$\Delta T_H = T_{Bo} - T_R \tag{6}$$

Eq. (5) shows that increase of the flashing range reduces also the heating steam consumption. Accomplishment of the above benefits is possible only if the scaling thresholds of high CF and high temperature seawater concentrates are within the hemihydrate solubility limits. The main objective of this study was to measure scaling threshold data at high CF and TBT levels.

2. Materials and methods

2.1. Experimental system

Scaling threshold data at high CF and TBT levels were determined in the experimental single stage flash system shown in Fig. 6. Synthetic SW is pumped from feed tank B to a heated pressure vessel at a flowrate of 1 L/min through flowmeter FI-1. The pressure vessel serves to hold the heated feed solution at a desired controlled pressure and a desired controlled solution temperature. The heated pressure vessel is held inside a jacketed sleeve containing a heat transfer oil and four electrical heating elements, each rated at 2 kW. The maximum permissible temperature of the heat transfer oil (Synterm 32) is 320°C. Prior to entering the pressure vessel the feed solution is pre-heated to a temperature around 90–95°C by heat exchange in the titanium plate heat exchanger HE with the hot exit concentrate stream at about 100°C. Since the solution in the heated pressure vessel is maintained at a controlled constant temperature, scale deposition on the walls of the heated pressure vessel increases the temperature of the heat transfer oil. The overall heat transfer coefficient U characterizing heat transfer from the heating oil was calculated from:

$$U = \frac{q}{A \cdot \Delta T_{lm}} \tag{7}$$

where q is power input of the electrical elements immersed in the heating oil, A is the internal surface of the heated pressure vessel (0.1 m^2) and ΔT_{lm} is the log mean of the temperature difference between the heating oil and the solution entering and leaving the heated pressure vessel.

Heating the solution flowing through the heated pressure vessel continuously releases dissolved air. Prevention of air accumulation in the vessel is essential so as to prevent pressure increase and to ensure that the solution fills the entire volume of the vessel. This is accomplished by needle valve bleeding from the top vapor space of the pressure vessel a minute air-vapor stream corresponding

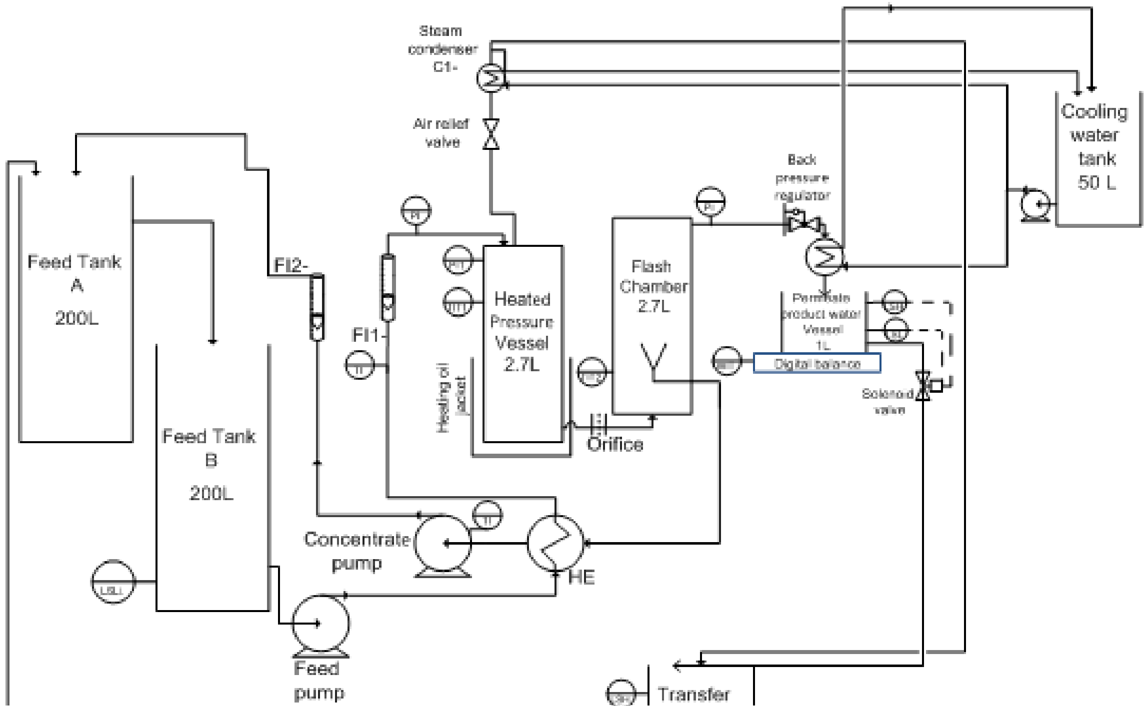

Fig. 6. Schematic diagram of the single stage flash distillation system.

to about 2–4 mL/min of liquid water. The vapor bled by the air release system is recycled to feed tank A through the transfer vessel after condensing in steam condenser C1.

The feed solution flows from the heated pressure vessel to the flash vessel through an orifice passage of 1.5 mm diameter. To minimize heat losses and reduce the heat load of the electrical elements, both vessels as well as connecting pipes are insulated. Flow of the feed solution through the narrow orifice passage generates a frictional pressure drop which induces a pressure decrease of the solution entering the flash vessel. Flash vessel pressure is maintained by a back pressure regulator. The orifice diameter is designed such that pressure reduction induces flash evaporation causing a temperature drop of 3 to 5°C. The flash vapor is condensed by cooling water flowing in condenser C2.

Distillate flow rate, pressure and temperature in the heated pressure vessel and the flash vessel temperature were recorded by a data logger every 2 min. The system was operated in full recycle. Distillate, concentrate and bleeding stream were all recycled to feed tank A. To ensure safe unattended continuous long operation the system is designed with control loops and interlocks.

The heated pressure vessel was fed at a constant flowrate of 1 L/min with solutions of CF varying in the different runs in the range of 1.8 to 5.0. Inlet solution pressure was maintained constant in the range of 1.7–1.9 bar abs. and inlet solution temperatures were varied in the different runs in the range of 123 to 140°C. The duration of each run was 96 h or until scale initiation was detected.

At the end of each run, the heated pressure vessel was opened for visual detection of any scale deposition on the heated surface. Deposited scale was dissolved by recycling through the system a Na_4EDTA solution followed by a citric acid wash. Numerous tests were carried out in commissioning and debugging the system until reliable repeatable tests could be performed.

Table 2
Standard SW serving as basis for preparation of feed solutions

Ion	Concentration	
	(mg/L)	(mol/L)
Calcium	400	0.010
Sodium	10561	0.476
Magnesium	1272	0.054
Chloride	18980	0.555
Sulfate	2649	0.030

2.2. Feed solutions

Experiments were carried out with synthetic solutions based on the composition of standard SW (Table 2) as specified by Fabuss and Korosi [1]. Feed solutions were prepared by dissolving in deionized water analytical grade salts according to the desired CF and calcium concentration. All calcium reduced solutions contained 80% of the concentration in standard SW.

3. Results

Experimental work involved continuous flow of SW solution of a specific concentration factor and calcium content through the single stage flash system at constant solution temperature and pressure in the heated pressure level for 96 h. The occurrence or absence of scale precipitation from the solution flowing through the heated pressure vessel was the major parameter investigated.

Occurrence of scale deposition was evident during the run from several indications: (i) Pressure increase in the heated pressure vessel due to partial blockage of the orifice. (ii) Increase in the heating oil temperature for overcoming the thermal resistance induced by the scale depositing on the heated pressure vessel walls. (iii) Decrease in the heat transfer coefficient characterizing heat transfer from the heating oil to the heated pressure vessel. (iv) Decrease in distillate flowrate. (v) Decrease in the temperature of the solution in the flash vessel.

The main experimental results are summarized in Table 3. Runs 27 and 21 were carried out using standard SW with no calcium depletion at a solution temperature of 123°C and at concentration factors of 1.8 and 2.5 respectively. Fig. 7 displays the location of these operating conditions on a CF-temperature diagram of SW. Scaling was detected in the CF run of 1.8 after a few hours of operation from temperature and pressure measurements shown in Figs. 8 and 9 and from the gradual decline in distillate flow rate. Referring to the Fabuss and Lu scale formation data in SW concentrates [10,11], the run of CF 1.8 and temperature of 123°C is at the diffuse border separating non-scaling from scaling conditions. The detection of scaling in this run after a few hours of operation is not therefore an unexpected result. XRD analysis of the scale deposit shown in Fig. 10 indicates that most of the deposit consisted of anhydrite with minor amounts of gypsum and hemihydrate. Phase transitions are known to occur between the various calcium sulfate polymorphs [12].

Scale formation was detected in the CF run of 2.5 shortly after the beginning of the Run. This result is expected since operating conditions were at the maximum solubility limit of the hemihydrate (Fig. 7).

The possibility of operating at high concentration factors and high temperature with SW solutions depleted of 80% of the calcium ions is demonstrated in runs conducted at a solution temperature of 123°C and CF levels of 2.5 and 3.5 respectively and in runs conducted at a CF of 4 and solution temperature levels of 123, 130 and140°C respectively. These conditions are marked in Fig. 7 as open circles.

Indication of the persistence of non-scaling conditions during the 96 h of each of these tests is illustrated in Figs. 11 and 12. For Run 28 performed at the highest temperature (140°C) and CF 4, it is seen that values of parameters that would decrease if scaling occurred maintained flawlessly constant levels. A test performed at a CF of 5 and a temperature of 130°C (star in Fig. 7) resulted in immediate scaling, indicating that optimal non-scaling conditions at a solution temperature of 130°C are at a maximum CF of about 4.

3.1. Preliminary analysis of the benefits of the improved MSF system

Standard MSF design equations [7] were used to compare the benefits of a hybrid MSF unit operating at CF of 4 and TBT of 140°C from which 80% of the calcium was removed versus a conventional MSF unit fed with standard

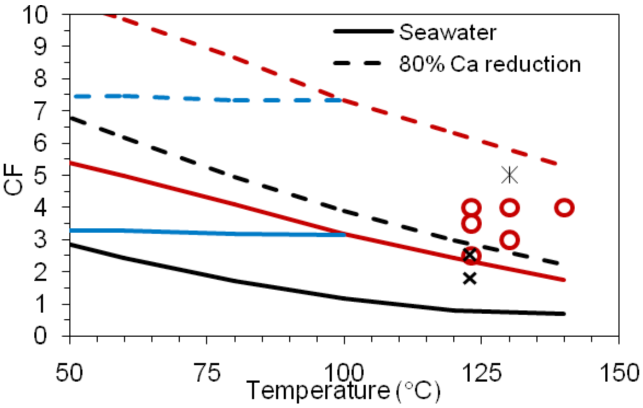

Fig. 7. Experimental conditions on the CF-Temperature curve (✕ - Full SW (runs 21, 27); ○ - 80% Ca depletion w/o scaling (runs 20–23, 25, 26, 28) and ✳ with scaling, run 29).

Table 3
Experimental results

Run	CF	Solution	Scale detection	Temp. (°C)			Pressure (bar abs.)		Heat transfer coefficient (W/m^2°C)	
				Pressure vessel	Flash vessel		Pressure vessel			
					Initial	Final	Initial	Final	Initial	Final
27	1.8	SW	Within hours	123	118.6	113.5	1.9	2.7	241	221
21	2.5	SW	Almost immediately	123	116.0	112.0	1.9	4.5	275	312
20	2.5	SW with 80% Ca depletion	No scaling	123	119.0	119.0	1.8	1.8	291	290
23	4.0	SW with 80% Ca depletion	No scaling	123	118.5	118.4	1.8	1.8	340	340
22	3.5	SW with 80% Ca depletion	No scaling	123	117.8	118	1.9	1.9	327	328
25	3.0	SW with 80% Ca depletion	No scaling	130	127.5	127.3	1.8	1.8	281	285
26	4.0	SW with 80% Ca depletion	No scaling	130	127.1	127.4	1.8	1.8	315	314
28	4.0	SW with 80% Ca depletion	No scaling	140	136.0	133.7	2.6	2.6	277	276
29	5.0	SW with 80% Ca depletion	Immediate scaling	130	127.0	NM	1.8	NM	NM	NM

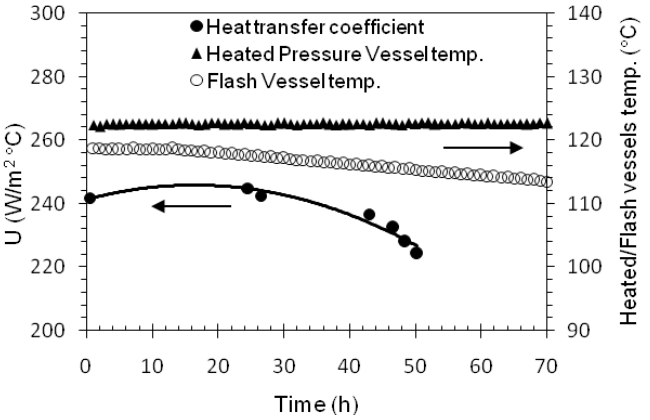

Fig 8. Decline in flash vessel temperature and in overall heat transfer coefficient in Run 27 due to scale formation.

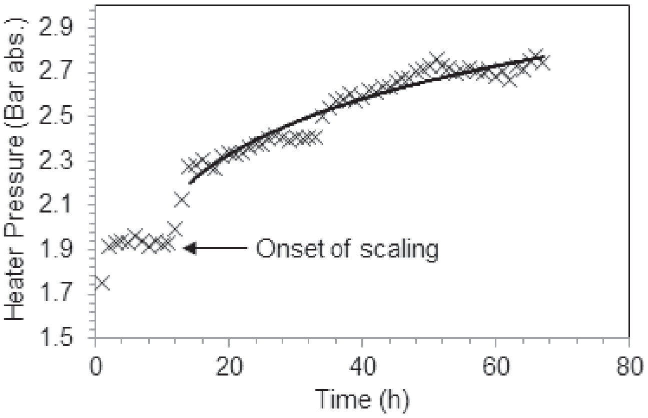

Fig. 9. Pressure increase in the heated pressure vessel in Run 27 due to orifice blockage by scale deposition.

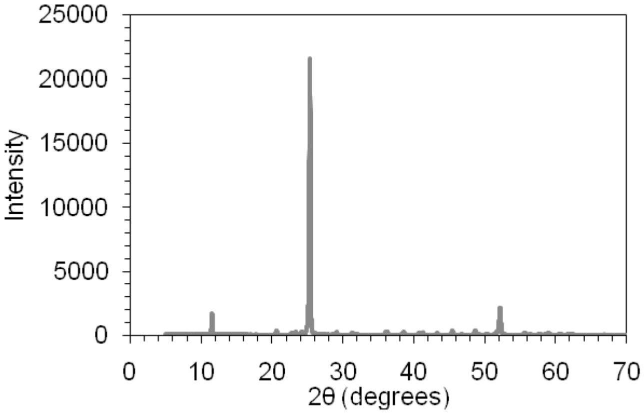

Fig. 10. XRD spectrum of the scale formed on the heated pressure vessel walls (Run 27).

SW. Table 4 presents calculated process characteristics of a conventional MSF operated at CF of 2 and TBT of 110°C and an MSF unit in which 80% of the calcium operated at CF of 4 and TBT of 140°C. Calculations were performed for an output of M_D = 1000 Kg/h distillate in both systems with an identical condenser heat transfer area.

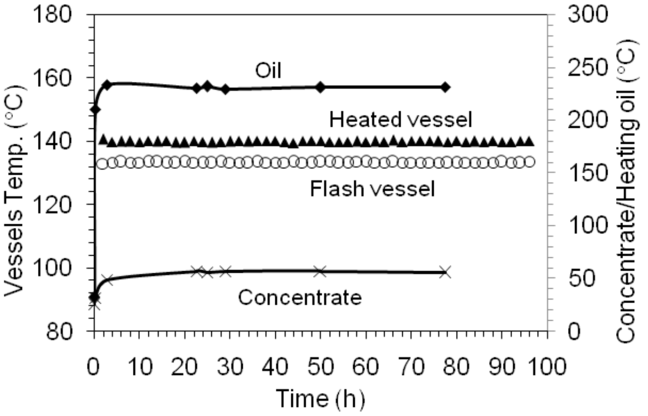

Fig. 11. Temperature measurements performed at CF of 4 (Run 28).

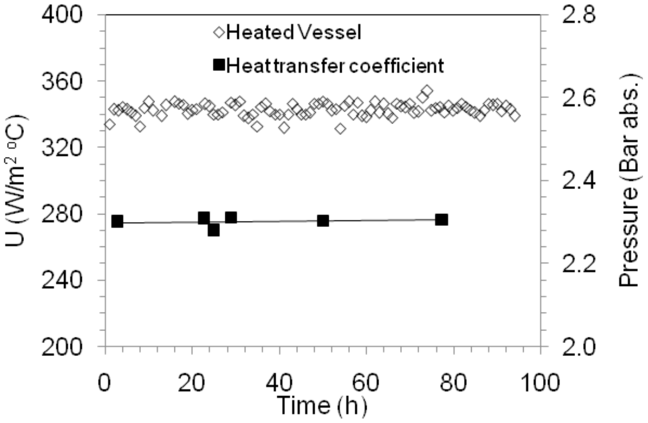

Fig. 12. Pressure and heat transfer coefficient in the heated vessel (Run 28).

The economic benefits are outlined in Table 5. The main cost elements are in the heat energy saved in the hybrid system and the electric energy required for the electrolytic calcium ion removal. The thermal energy in the high CF hybrid system is reduced from about 64 to 46.5 kWh/m^3 distillate. According to the European Environmental Agency, the efficiency of thermal plants is 44 to 48% so that the saving in thermal energy of 17.5 kWh /m^3 is equivalent to a saving of 7.7 to 8.4 kWh /m^3 in terms of electrical energy.

The electrical energy requirement for electro chemical removal of the calcium ions from SW is of the order 4 kWh (electric)/kg $CaCO_3$ precipitated (Table 1). Electrolytic removal of 80% Ca present in standard SW at a concentration of 400 mg/L would consume 4.4 kWh (electric)/m^3 distillate. Thus, there is a net electric energy saving of about 3.5 kWh/m^3 distillate without taking into account the additional energy saving in pumping due to the significant reductions in feed and recycle flow rates.

4. Concluding remarks

The major achievement of this research is in being the first study overcoming the current operating limits of MSF seawater desalination by a hybrid calcium ions electro

Table 4
Calculated process characteristics of a conventional MSF and an MSF process with 80% Ca depletion

Conventional MSF		MSF with 80% Ca depletion	
Input data	Output data	Input data	Output data
Top brine temp.: T_{b0} = 110°C	Number of stages: n = 25	Top brine temp.: T_{b0} = 140°C	Number of stages: n = 31
Blowdown temp.: T_{bN} = 30°C	Recycle flowrate: M_R = 7000 kg/h	Blowdown temp.: T_{bN} = 30°C	Recycle flowrate: M_R = 5090 kg/h
Flashing range: ΔT_F = 80°C	Feed flowrate: M_F = 2000 kg/h	Flashing range: ΔT_F = 110°C	Feed flowrate: M_F = 1333kg/h
Heating range: ΔT_H = 8°C	Blowdown flowrate: M_B = 1000 kg/h	Heating range: ΔT_H = 8°C	Blowdown flowrate: M_B = 250 kg/h
B.P.R = 1.5°C	Distillateflowrate: M_D = 1000 kg/h	B.P.R = 1.5°C	Distillate flowrate: M_D = 1000 kg/h
ΔT_X = 3.6°C	Performance ratio: R = 10	ΔT_X = 3.6°C	Performance ratio R = 13.75
CF = 2	Condensers heat transfer area: 29 m^2	CF = 4	Condensers heat transfer area: 29 m^2

Table 5
Economic benefits derived by high CF MSF process

Parameter	Conventional system	Hybrid system	Benefits of high CF system	Cost of electrolytic Ca removal
Performance ratio (R)	10	13.75	Heating steam requirement reduced by 27%	
Recycle flow rate (kg/h)	7000	5090	Recycle pumping energy cost reduced by 27%	
Feed flowrate (kg/h)	2000	1333	Feed pumping energy cost reduced by 33% Feed pre-treatment cost reduced by 33%	
Electric energy for electrolytic removal of 80% Ca				~3 to 4 kWh/m^3distillate
CO_2 consumption for Ca ions electrolytic removal				~0.4 Kg/m^3 distillate
Equipment cost			Reduced piping and pumps costs	Cost of electrolytic equipment

removal process followed by an MSF Unit. An experimental single stage MSF pilot unit was operated at a concentration factor of 4 and a TBT of 140°C far exceeding the present limits of CF of 1.8 and a TBT of about 120°C. Comparison of a typical MSF system of conventional design with a hybrid system based on electrolytic calcium ions removal indicates significant economic benefits justifying further development of the proposed hybrid MSF process.

Acknowledgment

This research forms part of the Ph.D. thesis of M.S.L. The electrochemical experiments were carried out by O. Gorni-Pinkesfeld. Thanks are due to the Israel Ministry of Science for supporting this work.

References

[1] M.A. Darwish, F.M. Al Awadhi, M.Y. Abdul Raheem, The MSF: enough is enough, Desal. Water Treat. 22 (2010) 193–203.

[2] Colorado School of Mines. Technical Assessment of Produced Water Treatment Technologies RPSEA Project 07122-12. 1st ed., 2009, 158pp.

[3] E.T. Igunnu, G.Z. Chenm Produced water treatment technologies, Inter. J. Low-Carbon Technol., 4 (2012) 1–21.

[4] B.M. Fabuss, A. Korosi, Boiling point elevations of seawater and its concentrates, J. Chem. Eng. Data, 11 (1966) 606–609.

[5] D. Hasson, H. Shemer, R. Semiat, Removal of scale forming ions by a novel cation exchange electrochemical system – a review, Desal. Water Treat., 57 (2016) 23147–23161.

[6] D. Hasson, H. Shemer, R. Semiat, Intensified precipitation of scale-forming ions by a hybrid Electrolysis - Crystallization system - a review. Chapter 4 in Industrial Water Treatment: New Trends, Challenges, and Solutions, Edited by Zahid Amjad and Tao Chen, Publisher NACE International, Houston, Texas 2017.

[7] T.H. El-Dessouky, M.H. Ettouney, Multi-stage flash desalination, Chapter 6 in Fundamentals of Salt Water Desalination Elsevier B.V. 2002.

[8] J.A.M. Meijer, G.M. Van Rosmalen, Solubilities and supersaturations of calcium sulfate and its hydrates in seawater, Desalination, 51 (1984) 255–305.

[9] J.W. McCutchan, E.N. Sieder, Scale control in saline water evaporators: A review of current status, U.S. Office Saline Water, Research and development progress report, 411 (1969) pp. 62.

[10] B.M. Fabuss, C. H. Lu, Investigation of calcium sulfate precipitation, U.S. Office Saline Water, Research and development progress report, 258 (1967) pp. 100.

[11] C.H. Lu, B.M Fabuss, Calcium sulfate scaling in saline water distillation, I&EC Process Deign Develop., 7 (1968) 206–212.

[12] J. Glater, K.S. Murdia, R. Dooly, Calcium sulfate hemihydrate scaling threshold enhancement by magnesium ion augmentation, Desalination, 14 (1974) 197–207.

[13] W.L. Marshall, R. Slusher, E.V. Jones, Aqueous systems at high temperature XIV. Solubility and thermodynamic relationships for $CaSO_4$ in NaCl-H_2O solutions from 40 to 200°C, 0 to 4 Molal NaCl, J. Chem. Eng. Data, 9 (1964) 187–191.

[14] W.L. Marshall, R. Slusher, Thermodynamics of calcium sulfate dihydrate in aqueous sodium chloride solutions, 0-110°, J. Phys. Chem., 70 (1966) 4015–4027.

[15] W.L. Marshall, R. Slusher, Aqueous systems at high temperature. Solubility 200°C of calcium sulfate and its hydrates in seawater and saline water concentrates, and temperature-concentration limits, J. Chem. Eng. Data, 13 (1968) 83–93.

Supplementary material

1. Electrochemical removal of calcium ions from produced waters

Produced waters are composed with the same saline species as seawater at different relative abundance but are invariably polluted with hydrocarbon contaminants. An important issue is the question if hydrocarbon contaminants interfere with the effectiveness of the hybrid electrolysis-crystallization system which is proposed in this study for calcium ions removal. This issue was investigated using the electrochemical cation exchange membrane system (EMC) described in previous publications [5,6].

Calcium ions were electrolytically precipitated as $CaCO_3$ from solutions of the standard seawater of Table 4 in the manuscript, polluted with compounds selected from two groups of organic contaminants characteristic of PW: aromatic hydrocarbons and volatile fatty acids. As before, CO_2 gas supplied to the feed solution was the source of the carbonate required for $CaCO_3$ precipitation. Table S1 summarizes the experimental conditions in all runs.

Table S2 compares results of runs performed with seawater contaminated at two phenol concentrations with results of uncontaminated solutions. The presence of phenol had no significant effect on the calcium carbonate removal level, on the precipitation rate and on the energy consumption. The TOC measurements showed that concentration of the organic material remained constant and that the voltage did not change during the electrochemical process. These results indicate that organic material did not foul the membrane.

The effect of the type of aromatic hydrocarbon (Phenol, Benzene, Toluene and Ethyl benzene)and volatile fatty acids (Acetic acid, Propanoic acid and Butyric acid)on calcium carbonate removal was studied at the highest concentrations listed in PW publications. Results summarized in Table S3 show no difference in the calcium removal level or indeed in all other characterizing parameters.

The major conclusion derived from the above work is that the performance of the ECM system in calcium removal by $CaCO_3$ precipitation is virtually unaffected by the presence of organic pollutants in seawater. Precipitation rates of around 100 g $CaCO_3$/h m^2 cathode area were obtained with and without the presence of the organics. The energy consumption of about 3 kWh per kg $CaCO_3$ precipitated was also unaffected by the presence of the organic compounds. These results indicate that the calcium ions removal from organics polluted PW can be dealt with by the electrochemical cation exchange membrane system.

Table S1
Experiments conditions in calcium electro precipitation of contaminated seawater

Feed flow rate	6 L/h
Current	4 A
Current density	200 A/m^2
Voltage	3.8–4.4 V
CO_2 concentration	8.5–9.6 mmol/L
Crystallizer residence time	100 min
Feed pH	4.9–5.2
Steady state crystallizer pH	8.3–9.2
Temperature	22.2–28.9°C

Table S2
System performance with and without the presence of phenol in seawater

TOC (phenol) (mg/L)	CO_2 (mmol/L)	$pH_{(crys.)}$	Calcium feed concentration (mg/L)	Calcium removal (%)	Precipitation rate (g/h/m^2)	Energy consumption (kWh/kg $CaCO_3$)
0	9.1	9.0	526.0	67.3	106.1	2.9
48	9.9	9.2	529.4	68.2	108.4	2.8
112	9.6	8.6	539.8	64.7	104.8	3.3

Table S3
System performance with four aromatic hydrocarbons

Organic ccompound	TOC (mg/L)	$pH_{(crys.)}$	Calcium feed concentration (mg/L)	Calcium removal (%)	Precipitation rate (g/h/m^2)	Energy consumption (kWh/kg)
Phenol	25	8.3	528.7	65.5	103.8	2.9
Benzene	30	8.7	525.6	67.5	106.4	3.0
Toluene	40	9.1	541.0	68.3	110.9	3.0
Ethylbenzene	20	9.0	531.3	68.8	109.7	2.9
Acetic acid	50	9.0	534.4	67.1	107.6	2.9
Propanoic acid	50	8.6	518.9	67.8	105.6	3.0
Butyric acid	50	8.3	518.0	67.4	104.7	2.9