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Co-precipitation in multiple-effect distillers at nonconventional temperatures

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ABSTRACT

A model has been developed to predict alkaline scale formation in seawater multiple-effect distillers (MED) at high top brine temperature (TBT). The effects of changes in solution composition due to CO_2 release on the formation of crystalline scales in seawater evaporators are studied. Supersaturations of scaling salts are calculated by applying mass and charge conservation equations while considering chemical reactions involved in the process. Pitzer model was used for the activity coefficient calculations. Simulations allowed predicting co-precipitation of alkaline scale: magnesium hydroxide and calcium carbonate. These salts are responsible for scale build-up. Simulation results matched well with the reported experimental data for high TBT in MED.

Keywords: Seawater; MED; High TBT; Calcium carbonate; Brucite; Co-precipitation; Simulation

1. Introduction

Increasing demand for fresh water and the limited available natural water resources drive the request for desalination. Desalination of seawater or brackish water is the most viable solution to provide pure water. Seawater is available in abundance; however, its conversion to fresh water is limited and restricted due to high conversion cost. Seawater contains dissolved salts having a concentration of about 35 g/kg which is too high for use for human consumption and industrial uses. Various desalination processes are being developed to obtain desalinated water from seawater. The most popular process currently used are distillation, reverse osmosis (RO), and electro-dialysis.

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The selection of the right process is the resultant of many considerations among which are inlet water quality, production capacity, and cost.

RO processes are often the most economical for desalting seawater and low salinity waters. Thermal processes readily accommodate highly saline feed waters. Thermal desalination covers a wide range of century proven processes. The majority of thermal desalination plants in operation are multistage flash desalination systems (MSF). Multiple-effect distillers (MED) are commonly designed for low temperature operation with top brine temperatures (TBTs) limited to 65° C. High TBT in MED processes has recently acquired a potential interest. With respect to increasing brine temperature, new generation of MED has been conceived [1,2]. Increasing TBT leads to high

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production yields, enhanced heat transfer coefficients, and better thermal efficiencies with lower number of effects. However, the scaling potential can be increased as the brine gets more concentrated. Scale formation has negative impacts on heat transfer. It hinders heat transfer, increases specific energy consumption and operating costs with frequent shut downs for cleaning.

Temperature is the one of main factors affecting scale formation. In distillation, two kinds of scale are prevailing: alkaline scale (CaCO₃ and Mg(OH)₂) and non-alkaline scale related to gypsum. Of the alkaline scales, mainly CaCO₃ is observed for TBT up to 80°C, but for higher temperatures, Mg(OH)₂ is dominant [3]. Scaling need to be controlled during thermal desalination operation processes, especially for elevated temperature conditions.

Increasing TBT in MED was a challenge for many researches. Experimental pilot tests were carried out to investigate scale formation for evaporators at TBT ranging from 70 to 80°C in a single effect [4,5]. Artificial seawater with various salinities up to 65 g/kg was used for the experiments. In a similar pilot distiller, Doosan has conducted several tests in order to investigate scale formation and antiscalant performances for high TBT distillers [2].

Scale control in every desalination plant is essential to prevent efficiency decline. Several models have been developed to predict scale formation in MED [6], but these models do not hold for high temperatures. Indeed, these theoretical approaches were based on the assumption that only CaCO₃ precipitates. However, experimental pilot tests have shown that at high TBT, multiple compound scales can be formed [4,5]. Moreover, scale formation was not accounted for when calculating scaling species concentrations. Little attention has been paid to investigate interactive effects of co-precipitating salts on scale formation predictions.

The aim of this study is to develop a model for scaling prediction in MED taking into consideration co-precipitation of MgOH₂ and CaCO₃ at high TBT. Unlike previous simulation works, we intend to account for scale formation when calculating scaling species concentrations. The model is based on the conservation principles of chemical carbonated species (HCO₃⁻, CO₃²⁻, H₂CO₃, H⁺, and OH⁻). Pitzer model was used for calculation of activity coefficients. The approach is similar to the one applied to predict the transfer of carbonated species in RO [7,8]. Simulations were conducted to assess scaling for 45 g/kg salinity seawater for which experimental results are available for comparison.

2. Modeling approach

2.1. Effect of CO_2 in chemical equilibrium

In MED, CO_2 is released from the evaporating brine. Concentrations of HCO_3^- , CO_3^{2-} , CO_2 , H_3O^+ , and OH^- ions in the brine are considerably influenced by CO_2 release which consequently plays an important role in alkaline scale formation [6]. When seawater is introduced into the evaporator, CO_2 partial pressure in the gas phase changes, involving a shifting of the equilibrium between gas and aqueous phases. CO_2 transfer between phases results in a shifting of pH and species concentrations until a new equilibrium between the phases is established. These phenomena are due to a set of chemical reactions, involving carbonated species, when CO_2 is transferred or scale is formed. These reactions will be described in the next section.

2.2. Chemical reaction in carbonate system

Seawater is an aqueous mixed electrolyte attains its equilibrium state through a variety of chemical reactions. The carbonate system involves weak acidbase pairs which exist in seawater as dissolved CO_2 , carbonic acid, bicarbonate, and carbonate ions. Any change in CO_2 partial pressure in the gas phase induces displacement of the equilibrium between gas and aqueous phases. This causes a change in concentrations of species until the reestablishment of equilibrium. When CO_2 comes into contact with an aqueous solution, according to the water pH, one of the following mechanisms prevails:

Acidic mechanism

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$
 (R.1)

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$$
(R.2)

Alkaline mechanism:

$$HCO_3^- \leftrightarrow CO_2 + OH^-$$
 (R.3)

$$\mathrm{CO}_3^{2-} + \mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{HCO}_3^- + \mathrm{OH}^-$$
 (R.4)

The overall reaction which occurs when CO_2 is desorbed from an aqueous bicarbonate–carbonate solution is:

$$2\text{HCO}_{3}^{-} \leftrightarrow \text{CO}_{2} + \text{CO}_{3}^{2-} + \text{H}_{2}\text{O} \tag{R.5}$$

According to Langelier [9], the carbonate ions are formed directly from bicarbonates that thermally decompose at moderate temperatures. This leads to $CaCO_3$ precipitation as its solubility limit is exceeded. For alkaline solutions, as in MED, the alkaline mechanisms predominate, particularly at high temperatures. Carbonate ions hydrolyze to produce hydroxyl groups and CO_2 according to the following reaction:

$$CO_3^{2-} + H_2O \leftrightarrow CO_2 + 2OH^- \tag{R.6}$$

Water dissociates to form H₃O⁺ and OH⁻ ions:

$$2H_2O \leftrightarrow H_3O^+ + OH^- \tag{R.7}$$

The presence of ions in seawater, mainly Ca²⁺ and Mg²⁺, leads to the precipitation of calcium carbonate and magnesium hydroxide according to the following reactions:

$$\operatorname{Ca}^{2+} + \operatorname{CO}_3^{2-} \leftrightarrow \operatorname{CaCO}_3(s)$$
 (R.8)

$$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_2(s)$$
 (R.9)

Equilibrium constant is derived from solubility data. The solubility of a solute is defined as its maximum concentration which can exist in solution under concentration and temperature, is said to be supersaturated. To predict scaling potential, solubility data of scaling species and their actual concentrations in the brine are need. $CaCO_3$ solubility decreases with temperature and increases with salt concentration and CO_2 partial pressure [10]. Equilibrium constants of calcite and aragonite in seawater are given by using the following equations [11]:

$$log(K_{SP}^{calcite}) = -171.9065 - 0.077993T + \frac{2,839.319}{T} + 71.595 \log(T)$$
(1)

$$log(K_{SP}^{aragonite}) = -171.9773 - 0.077993T + \frac{2,903.293}{T} + 71.595log(T)$$
(2)

where *T* is the absolute temperature in K.

Brucite solubility values reported in the literature are limited and conflicting [4,12]. In this work, the equilibrium constant for brucite was taken as $K_{\text{sp,Brc}} = 5 \times 10^{-11} \text{ mol}^3/\text{kg}^3$.

2.3. Chemical equilibrium constants in seawater

Millero has reported carbonic acid dissociation constants in seawater K_1 and K_2 for temperatures up to 45 °C and for salinities up to 50 g/kg [13]. In this work, correlations suggested by Millero were used:

$$\log K_1^{SW} = 2.18867 - \frac{2,275.0360}{T} - 1.468591 \log(T) + \left(-0.138681 - \frac{9.33291}{T}\right) S^{0.5} + 0.0726483S - 0.00574938S^{1.5}$$
(3)

$$\log K_2^{SW} = -0.84226 - \frac{3,741.1288}{T} - 1.437139\log(T) + \left(-0.128417 - \frac{24.41239}{T}\right)S^{0.5} + 0.1195308S - 0.00912840S^{1.5}$$
(4)

a given set of solution conditions of temperature, pressure, pH, and other species concentrations. A solution that contains less solute than required for saturation is called an unsaturated solution. A solution whose concentration is higher than that of a saturated solution due to any reason, such as change in solvent where K_1 and K_2 are in mol/kg seawater, T is in K, and S is in g/kg.

Water equilibrium constant in seawater, K_w , was reported for temperatures up to 35°C and salinities up to 44 g/kg [13]. In this work, K_w is calculated by the following formula: 3280

$$\log K_w = 148.9802 - \frac{13,847.26}{T} - 23.6521\log(T) + \left(-5.977 + \frac{118.67}{T} + 1.0495\log(T)\right)S^{0.5} - 0.01615.S$$
(5)

where K_w is on the basis mol/kg seawater and *T* is in K and *S* is in g/kg.

2.4. Scaling assessment in MED

CO₂ plays an important role in alkaline scale formation. The concentrations of the carbonic species can be determined applying mass and charge conservation equations in the brine when CO₂ is allowed to desorb. CO₂ desorption is related to water evaporation rate which in turn is proportional to seawater vapor pressure. The later was calculated using the expression based on Raoult's law for a temperature and salinity ranges of 0 < T < 200°C and 0 < S < 240 g/kg, respectively [14]. All reactions are assumed to be controlled by species transport, i.e. instantaneous chemical equilibriums in water are achieved and the following equations hold:

$$K_1 = \frac{[\mathrm{H}_3\mathrm{O}^+]\gamma_{\mathrm{H}_3\mathrm{O}^+}[\mathrm{H}\mathrm{CO}_3^-]\gamma_{\mathrm{H}\mathrm{CO}_3^-}}{[\mathrm{H}_2\mathrm{CO}_3]\gamma_{\mathrm{H}_2\mathrm{CO}_3}} \tag{6}$$

$$K_{2} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}]\gamma_{\mathrm{H}_{3}\mathrm{O}^{+}}[\mathrm{CO}_{3}^{2-}]\gamma_{\mathrm{CO}_{3}^{2-}}}{[\mathrm{HCO}_{3}^{-}]\gamma_{\mathrm{HCO}_{3}^{-}}}$$
(7)

$$K_w = \left[\mathbf{H}_3 \mathbf{O}^+ \right] \gamma_{\mathbf{H}_3 \mathbf{O}^+} [\mathbf{O} \mathbf{H}^-] \gamma_{\mathbf{O} \mathbf{H}^-} \tag{8}$$

where K_1 is the first dissociation constant of carbonic acid, K_2 is the second dissociation constant of carbonic acid, K_w is the water dissociation constant, γ_I is the activity coefficient of species *I*, and *[I]* is the concentration of species *I*.

Charge conservation equation holds:

$$\sum m_i \left[M_i^{m_i+} \right] = \sum a_i \left[A_i^{a_i-} \right] \tag{9}$$

 M_i is a cation of a charge $(+m_i)$ and A_i is an anion of a charge $(-a_i)$.

Several models have been developed to calculate activity coefficients. These models are mainly based on thermodynamic equilibrium calculations using

Debye-Hückel model for the activity coefficient calculation. But, the number of components and the high concentrations of ions may result in inconsistencies in the prediction of scale formation in seawater. For this reason, in our modeling approach, activity coefficients were calculated using Pitzer model which takes into account interactions between ions. This model is more accurate for nonideal solutions at higher ionic strengths and elevated temperatures. The Pitzer ion interaction approach accounts for various combinations of ion-ion interactions in the solution [15]. Pitzer ion interaction database accounts for nonideal behavior of highly concentrated electrolytes over a wide range of temperature (0-140°C). The database was founded on the original variable-temperature Pitzer parameters supplemented by a parameter data from several sources [16].

Before calculation starts, the water chemical content is slightly corrected to account for charge neutrality. Concentrations of ions, not involved in carbonate systems, are calculated by performing material balances on the evaporator to account for species conservation:

Accumulation rate = Inlet flux
$$-$$
 Outlet flux
 $-$ Precipitation rate (10)

All carbonated species, along with OH^- and H_3O^+ , are calculated simultaneously using material conservation and charge neutrality when accounting for equilibrium reactions and CO_2 desorption.

Precipitation, or scale formation, will occur only if brine will be supersaturated with respect to one or more of the sparingly soluble salts. Supersaturation of a given insoluble salt is calculated using:

$$\Omega = IAP/Ksp \tag{11}$$

where IAP is the ion activity product of appropriate salt and *K*sp is the ion activity product at equilibrium. Accordingly, $\Omega > 1$ implies a supersaturated solution, whereas, $\Omega < 1$ involves an under-saturated solution. If the solution is supersaturated, in the expression of

material balance, we take into account the salt deposit rate. Several models have been used to describe the precipitation rate of a given salt. In this work, the following rate expression was used:

$$\frac{dm_{Salt}}{dt} = k_{Salt}(\Omega_{Salt} - 1) \tag{12}$$

 $(\Omega_{Salt} - 1)$ is the driving force for scale formation and k_{Salt} is the rate constant.

3. Simulation results

A computer program was developed and implemented for simulating the scale build-up in MED. The program allows calculating concentrations of all chemical species in the brine and rate of scale deposition.

Few pilot testing for studying scale formation in distillers were reported [2,4,5,17,18]. In this work, experiments reported by Glade et al. were considered [4]. In these tests, the pilot evaporator is composed of six horizontal tubes. Feed water was artificially prepared with a salinity of 45 g/kg. The simulations were performed with the same seawater whose mineral composition is given in Table 1. The operating conditions were brine temperature of 70°C and wetting rate of 0.1 kg/s/m. The TBT is exceeding regular evaporation temperatures in industrial MED by 5°C. Initially, a seawater volume was assumed to be 240 L. As distillation takes place, steam is obtained along with the remaining brine which gets concentrated. The evaporation was assumed to be continued for over than 50 h.

In the experimental work previously mentioned, it was found that the scale deposit on the tubes contains calcium carbonate and magnesium hydroxide. Experimental results suggest an exclusive Mg(OH)₂ scale formation for the first 25 h. This was attributed to a decrease of the CO_3^{2-}/OH^- ratio. For longer periods between 25 and 50 h, brine was characterized by a constant CO_3^{2-}/OH^- ratio favoring CaCO₃-induced scale as predicted by Langelier's theory [9].

Fig. 1 gives the predicted CO_3^{2-}/OH^- ratio for identical operating conditions as in the experimental work. It shows a clear decrease in the ratio. However, the

decrease is much sharper for the first 25 h, where the ratio drops by nearly 88.5%. In the remaining period, the CO_3^{2-}/OH^- ratio does not drop that much.

In distillation processes, chemical monitoring and particularly loss in total alkalinity (TA) are used as a scale indicator. TA decrease is mainly due to CaCO₃ precipitation because of the presence of calcium ions. On the other hand, the involved chemical processes lead to the production of hydroxide ions which can yield the formation of magnesium hydroxide. In Fig. 2, calculated and experimental TA value of the brine are presented. TA decreases over time, which indicates a considerable scale formation.

The pH variations in the brine as function of time are shows in Fig. 3. There is an increase of hydroxyl ions concentration as indicated by the pH growth. This increase is due to CO_2 release from the evaporating brine. The alkaline mechanisms given by reactions (3) and (4) predominate. It is worthy to note that the predicted pH increase is much higher when scaling is not allowed. However, the reported experimental pH value after 50 h, 8.9, is higher than the predicted value when scaling is considered. The difference could be related to cathodic reactions at the metal surface that tend to generate OH⁻ as suggested by Glade et al. [17]. The cathodic reduction reactions were not considered in the simulation.

Several methods are used for predicting scale formation. Some are based on scaling index determination (Langelier saturation index, Riznar saturation index, and Siff and Davis saturation index). Some use supersaturation to assess when scale could be formed. Supersaturation with respect to calcium carbonate forms and magnesium hydroxide is given the following equations respectively:

$$\Omega_{CaCO_{3}} = \frac{[Ca^{2+}]_{\gamma_{Ca^{2+}}}[CO_{3}^{2-}]_{\gamma_{CO_{3}^{2-}}}}{Ksp_{CaCO_{3}}}$$
(13)

$$\Omega_{Mg(OH)_2} = \frac{[Mg^{2+}]\gamma_{Mg^{2+}}[OH^-]^2\gamma_{OH^-}^2}{Ksp_{Mg(OH)_2}}$$
(14)

Table 1		
Inlet seawater	chemical	contents

[Ca ²⁺]	[Mg ²⁺]	[Na ⁺]	[K ⁺]	[Cl ⁻]	[SO ₄ ²⁻]	[HCO ₃ ⁻]	pН	TDS
(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		(mg/L)
964	1,665	13,469	456	25,112	3,484	182	8.1	45,332

8,8

8.7

8,6

8,5

Hd



Fig. 1. Calculated ratio CO_3^{2-}/OH^- vs. time (TBT = 70 °C, S = 45 g/kg, and $\Gamma = 0.1$ kg/s/m).



Fig. 2. Brine TA vs. time (TBT = 70 °C, S = 45 g/kg, and $\Gamma = 0.1$ kg/s/m).

 $^{8,4}_{8,3}$ $^{8,2}_{8,1}$ $^{9,2}_{0}$ 1000 1500 2000 2500 3000 Time,t/min Fig. 3. Brine pH variation vs. time (TBT = 70°C, S = 45 g/kg, and $\Gamma = 0.1$ kg/s/m).

with precipitation of CaCO3 and Mg(OH)2



Fig. 4. Supersaturation with respect to Mg(OH)₂ and CaCO₃ vs. time (TBT = 70 °C, S = 45 g/kg, $\Gamma = 0.1$ kg/s/m).

where Ksp_{CaCO_3} is the solubility product of the appropriate $CaCO_3$ form and temperature. $Ksp_{Mg(OH)_2}$ is the solubility product of brucite.

According to experimental results [4], $Mg(OH)_2$ platelets cover the metallic surface forming a "base layer." Unlike what has been reported in the experimental work, simulations indicate that conditions are favorable for the formation of both calcium carbonate

and magnesium hydroxide all along the distillation period. Indeed, Fig. 4 clearly shows that the brine is supersaturated with respect to $CaCO_3$ and $Mg(OH)_2$ all along the investigated period. It is worthy to note that supersaturation with respect to $Mg(OH)_2$ continues to increase over time, but with respect to $CaCO_3$ itdecreases exponentially. The discrepancies between experimental and simulation results could be related



Fig. 5. Deposited scale specific weight vs. time (TBT = 70 °C, S = 45 g/kg, $\Gamma = 0.1 \text{ kg/s/m}$).

Table 2 Comparison of calculated and experimental scale weights after 50 h

	Experimental	Predict	Relative difference
	(g/m ²)	(g/m ²)	(–)(%)
CaCO ₃	7.80	11.44	31.8
Mg(OH) ₂	0.20	0.21	4.8

to induction periods and local supersaturation which were not accounted for the simulation.

Supersaturations with respect to $Mg(OH)_2$ and CaCO₃ lead to scale deposition on metallic surfaces. Depending on the scaling conditions, calcium carbonate can precipitate in three different anhydrous crystalline forms: vaterite, aragonite, and calcite. Supersaturation alone cannot orient the formation of one of this form, but it is influenced by several other factors such as temperatures and the presence of dissolved cationic and ionic species. It has been shown that the Mg^{2+}/Ca^{2+} ratio is the principal factor defining the predominant CaCO₃ forms. In the explored conditions of the current investigation, CaCO₃ will deposit as aragonite [4]. The calculated deposits as aragonite and brucite weight are presented in Fig. 5. The deposited scale amount per unit of evaporation area for both CaCO₃ and Mg(OH)₂ increases with time. Unlike $Mg(OH)_2$, the CaCO₃ precipitation rate decreases with time. Simulations indicate that 90% of CaCO₃ precipitate is obtained in the first 25 h. However, for Mg (OH)_{2,} only 36% is deposited after 25 h. No induction periods are considered in the simulations.

Referring to Table 2, a comparison of calculated and experimental values for scale weights at the tube surface after 50 h is shown. Good agreement was obtained for Mg(OH)₂. However, the predicted CaCO₃ scale is about 32% higher than experimental value. This is expected, as part of the scale remains in the solution as suspended matter as suggested in the experimental work.

4. Conclusion

A model has been developed for predicting concentration of carbonate species in ME distiller at high TBT. The pH as well as concentrations of CO₂, carbonates, and bicarbonates is determined by applying conservation principles when chemical reactions involving scaling species are considered. Predicted supersaturations with respect to magnesium hydroxide and calcium carbonate indicate that conditions are favorable for scale formation by both salts all along the evaporation period. When calculating concentration of species involved in scaling, the model accounts for salt deposition rate. Simulation results compared fairly well with experimental data for TA and deposited magnesium hydroxide scale.

References

- H. El-Dessouky, I. Alatiqi, S. Bingulac, H. Ettouney, Steady-state analysis of the multiple effect evaporation desalination process, Chem. Eng. Technol. 21 (1998) 437–451.
- [2] F. Rezzadeh, S.W. Imh, K. Bourouni, H.S. Choi, M. Yousouf, Doosan advanced MED-TVC design, in: Proceeding of Conference on Desalination and Water Reuse, China, 2010.
- [3] J.C. Cowan, D.J. Weintritt, Water Formed Scale Deposits, Gulf Publishing Co., Houston, TX, 1976, pp. 204– 206.
- [4] H. Glade, C. Wildebrand, S. Will, M. Essig, J. Rieger, K.H. Büchner, G. Brodt, Pilot plant investigations on scale formation and control in multiple-effect distillers, in: Proceedings of the IDA World Congress, Singapore, 2005.
- [5] H. Glade, K. Krömer, S. Will, S. Nied, S.M. Pancera, G. Schürmann, Scale formation of mixed salts in multiple-effect distillers, in: Proceeding of IDA World Congress, Dubai, 2009.
- [6] A.E. Al-Rawajfeh, Modeling of alkaline scale formation in falling film horizontal-tube multiple-effect distillers, Desalination 205 (2007) 124–139.
- [7] H. Hchaichi, H. Elfil, P. Guichardon, A. Hannachi, Scaling tendency assessment in reverse osmosis modules, Desalin. Water Treat. 51 (2013) 892–898.
- [8] H. Hchaichi, S. Saanoun, H. Elfil, A. Hannachi, Scaling prediction in reverse osmosis modules for different sea waters, in: Proceedings of the Conference on

Desalination using Membrane Technology, Sitges, Spain, 2013.

- [9] R. Dooly, J. Glater, Alkaline scale formation in boiling sea water brines, Desalination 11 (1972) 1–16.
- [10] Z. Amjad, The Science and Technology of Industrial Water Treatment, CRC Press & IWA publishing, London, 2010.
- [11] H. Elfil, H. Roques, Role of hydrate phases of calcium carbonate on the scaling phenomenon, Desalination 137 (2001) 177–186.
- [12] F. Risacher, et B. Fritz, Estimation des variations en fonction de la température des produits de solubilité des principaux sels des milieux évaporitiques (Predictions of solubility product variations as function of temperature of major salts in evaporating media), Sci. Géol. Bull. 3 (1984) 229–237.
- [13] F.J. Millero, Thermodynamics of the carbon dioxide system in the oceans, Geochim. Cosmochim. Acta 59 (1995) 661–677.
- [14] M.H. Sharqawy, J.H. Lienhard, S.M. Zubair, Thermophysical properties of seawater: A review of existing

correlations and data, Desalin. Water Treat. 16 (2010) 354–380.

- [15] B.S. Krumgalz, Application of the Pitzer ion interaction model to natural hypersaline brines, J. Mol. Liq. 91 (2001) 3–19.
- [16] A. Maureen, M. Sutton, S. Carroll, Evaporative evolution of a Na–Cl–NO3–K–Ca–SO4–Mg–Si brine at 95°C: Experiments and modeling relevant to Yucca Mountain, Nevada, Geochem. Trans. 6 (2005) 31–46.
- [17] H. Glade, K. Kromer, S. Will, K. Loisel, S. Nied, J. Detering, A. Kempter, Scale formation and mitigation of mixed salts in horizontal tube falling film evaporators for seawater desalination, in: Proceeding of International Conference on heat Exchanger Fouling and Cleaning, Budapest, 2013.
- [18] H. Glade, M. Hermersdorf, J. Ulrich, M. Essig, J. Rieger, G. Brodt, Scaling in Multiple effect distillers: New approach to study mechanism and control, in: Proceeding of International Desalination Association, Bahamas, 2003.