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Scaling predictions in seawater reverse osmosis desalination

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Abstract. Simulations were conducted to predict supersaturation along Reverse Osmosis (RO) modules for seawater desalination. The modeling approach is based on the use of conservation principles and chemical equilibria equations along RO modules. Full Pitzer ion interactive forces model for concentrated solutions was implement to calculate activity coefficients. An average rejection rate for all ionic species was considered. Supersaturation has been used to assess scaling. Supersaturations with respect to all calcium carbonate forms and calcium sulfate were calculated up to 50% recovery rate in seawater RO desalination. The results for four different seawater qualities are shown. The predictions were in a good agreement with the experimental results.

Keywords: seawater; desalination; reverse osmosis modules; supersaturation; scaling assessment

1. Introduction

Natural fresh water sources can no longer meet the ever increasing water demand from our rising population. Distillation has been traditionally used to get pure water from saline or brackish water sources. Other processes such as ion exchange and electrodialysis have been employed for water purification as well. Lately, Reverse Osmosis (RO) has been established to be the most economical technology for the desalination of brackish and sea waters. RO membranes are capable of rejecting most ions and even monovalent ions such as Na^+ and Cl^- present in seawater with 99% rejection rate. In Seawater Reverse Osmosis (SWRO), it is compulsory to pretreat feed water to limit fouling and avoid scaling. The nature of fouling is strongly dependent on feed water source. Seawater is characterized by high total dissolved solids (TDS), typically ranging from 18 to 45 g/L, as well as particulate and colloidal matter. Fouling and scaling can lead to significant reduction in membrane performance. Poor feed water quality leads to short RO membrane lifetime, short operation period, and high maintenance cost. Consequently, a main factor for successful SWRO operation is maintaining a stable high feed water quality (Valavala *et al.* 2011, Lau *et al.* 2014). Inorganic fouling or scaling is the formation of hard mineral deposits on the membrane surface as

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the feed water salt contents increase along RO modules. The term scale refers to adherent inorganic deposits due to supersaturation. Depending on the operating recovery and rejection efficiencies, RO reject flux has typically salt contents 2 to 3 times higher than feed water.

Scaling remains a major impediment to successful implementation of high recovery water desalination. In RO scale deposition cannot be tolerated because of its highly destructive effects on production capacity and specific energy consumption. As permeate recovery is increased, retentate stream is concentrated, particularly near and at the membrane surface. In desalination calcium carbonate and calcium sulfate dihydrate are the main salts involved in scaling (Hannachi et al. 2009). These mineral salts may crystallize in the bulk and onto the membrane surface, leading to mineral scale formation and thus permeate flux decline, and eventually the shortening of membrane life (Rahardianto *et al*. 2006).

The principal factor determining the intensity of scaling is supersaturation level of deposit-forming species. Supersaturations are achieved when a solution is concentrated beyond the solubility limits of one or more of its constituents by separation of pure water as for RO. In scaling due to calcium carbonate, scale formation depends primarily on the level of calcium hardness and bicarbonate alkalinity of the feed water (Antony *et al*. 2011). Although calcium carbonate is reported to exist in six different forms, in SWRO and because of the operating conditions, the most likely form that can cause scaling is calcite (Elfil and Roques 2006). The reaction involved is

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3 \tag{1}$$

Thermodynamically, scaling occurs when the water is supersaturated with respect to $CaCO_3$. Supersaturation is defined by the ratio of Ion Activity Product (IAP) and the equilibrium constant

$$\Omega = \frac{IAP}{Ksp} \tag{2}$$

Where, K_{sp} is the ion activity product at equilibrium. Accordingly, Ω higher than one implies a supersaturated solution where scaling can occur, whereas Ω lower than one involves an under saturated solution. Because of the chemistry of the calcocarbonic system several equilibrium equations have to be considered. These are related to speciation of carbonate forms depending on the solution pH level. That is why supersaturation can be expressed as a difference between solution pH and a pH of an equivalent saturated solution. Several saturation indexes, in terms of pH difference, were put forward to assess scaling likelihood. Langelier Saturation Index (LSI) and Monohydrated Langelier Index (MLSI) are used for brackish waters and the Stiff & Davis Saturation Index (S&DSI) for sea waters. A positive S&DSI and LSI indicate the tendency to form calcium carbonate scale, while a negative value indicates no tendency for scale formation (Hannachi *et al*. 2007).

Very few experimental investigations to study scaling likelihood within RO modules were reported (Brusilovsky *et al*. 1992, Hasson *et al*. 1998, Drak *et al*. 2000, Pahiadaki *et al*. 2005). The aim of these studies was mostly focusing on determining antiscalant dosage to prevent scaling. Perhaps the most ambitious work that aimed to determine the recovery rate for which scaling could be observed through membrane permeability decline was that of Drak *et al*. (2000). However because of the complexity of the phenomena involved in scaling and the inherent experimental limitations, the reported predictions can only relate to a probable scaling recovery rate interval. That is why simulation is the only technique that could predict for which exact recovery rate supersaturation within RO modules occurs, i.e., a net positive driving force for scaling.

For a better scaling assessment it is very important to have accurate estimates of pH, ionic species' concentrations and activity coefficients at any stage of the RO operation for all water fluxes. This can be obtained by deriving mass conservation equations while considering chemical equilibriums and charge conservation equations along RO modules. Rejection of CO_2 through the membrane, affect the equilibrium of carbonate ions and change the pH in concentrate and permeate. The best estimates of the activity coefficients can be derived from Pitzer model as the former takes into account the ionic specific interaction (Krumgalz 2001). Indeed, for seawater Pitzer model predicts activity coefficients more accurately than Davis or extended Debye Huckel models.

This approach has been successfully applied to conduct scaling assessment with respect to calcium carbonate and calcium sulfate in brackish water (Hchaichi *et al*. 2012). The aim of this study is to extend this approach for seawater where the composition and carbonated species' interactions with RO membrane are much different. Particularly adequate CO_2 rejection rate should be applied. The case of four different seawaters will be considered.

2. Model development

For scaling assessment along RO modules there is a need to describe the change of scaling and non-scaling ions concentration along the RO modules. Concentrations of carbonate species in water are related to dissolved CO_2 concentration. Permeability of the membrane to gases particularly to CO_2 plays a significant role in scaling and the prediction of scale formation. A model has been developed to calculate concentrations of different carbonate species along RO modules for different recovery rates. For $CaCO_3$ scale it is important to track, along RO modules, the concentration of the following species: H_2CO_3, HCO_3^-, CO_3^{2-}, H_3O^+, OH^- and Ca^{2+} ions. All chemical reactions involving these species have to be considered. These are given in Fig. 1.

Concentration of carbonate species along RO modules are related by chemical equilibrium equations given by

$$K_1 = \frac{[H_3O^+]\gamma_{H_3O} + [HCO_3^-]\gamma_{HCO_3^-}}{[H_2CO_3]\gamma_{H_2CO_3}} \tag{3}$$

$$K_2 = \frac{[H_3O^+]\gamma_{H_3O} + [CO_3^{2-}]\gamma_{CO_3^{2-}}}{[HCO_3^-]\gamma_{HCO_3^-}} \tag{4}$$

$$CO_{2(g)} + 3H_2O \Leftrightarrow H_2CO_3 + 2H_2O \Leftrightarrow HCO_3^- + H_3O^+ + H_2O \Leftrightarrow CO_3^{2-} + 2H_3O^+$$

$$\xrightarrow{\hspace{12cm}}$$

Increasing pH

Fig. 1

This is also true for water dissociation which yields

$$K_w = [\mathrm{H_3O^+}]\gamma_{\mathrm{H_3O}} + [\mathrm{OH^-}]\gamma_{\mathrm{OH^-}} \tag{5}$$

Where: K_1 and K_2 are the first and the second carbonic acid dissociation constants; K_w is the water dissociation constant; γ_i and $[i]$ are activity coefficient and concentration of species i respectively. In addition to these equations one has to consider transport equations for all species as the recovery rate increases.

Fig. 2 gives the various water fluxes through finite volumes for both the retentate and the permeate compartments for an elementary increase of the recovery rate ($d\tau$). When a steady state pseudo plug flow is assumed, the concentration of the ion i in the elementary permeate flux, within a finite volume of an RO module yielding a recovery rate of $d\tau$, is related to the bulk concentration on the retentate side by the following equation

$$\frac{d\left(F_c[i]_c\right)}{d\tau} = -\frac{d\left(F_p[i]_p\right)}{d\tau} \tag{6}$$

Where: F is the flow rate; the indices p and c are relative to permeate and concentrate respectively. τ is the recovery rate.

The permeate concentration at any recovery rate can be derived from applying conservation equation yielding

$$[i]_p = [i]_f(1 - R_i) \tag{7}$$

Where: R_i is the rejection rate of the ionic species.

Integration of the transport equation, Eq. (6), between the feed and at given recovery rate τ yields

$$[i]_c = \frac{[i]_f}{1-\tau}\left(1 - \tau(1 - R_i)\right) \tag{8}$$

Concentrations in retentate and permeate of species not involved in chemical reactions such as (Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-} ...) are determined by applying mass and charge conservation equations with an average rejection rate for each ionic species. The retentate can be expressed in terms of recovery rate, membrane retention and feed concentration.

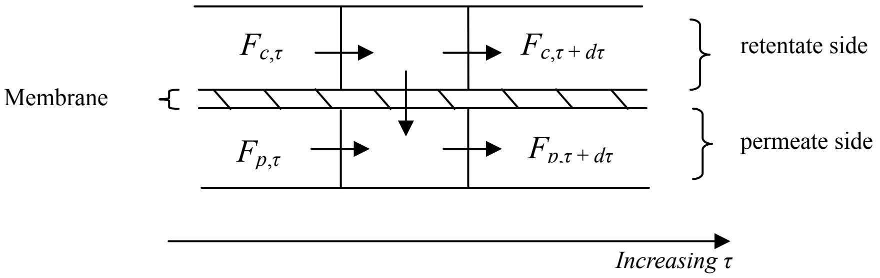

Fig. 2 Water fluxes through finite volume of an RO module

For the species involved in chemical equilibriums (H_3O^+, OH^-, CO_3^{2-}, HCO_3^- and CO_3^{2-}), retentate and permeate concentrations for a given recovery rate are obtained by solving the set of Eqs. (3)-(6) along with charge conservation equation given by

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

Where: M_i is a cation of a charge ($+m_i$) and A_i is an anion of a charge ($-a_i$). Note that in this approach, Eq. (7) is applied for total carbonated species, i.e., carbonates, bicarbonates and aqueous CO_2 are considered as single species. A set of non linear equation is obtained and need to be solved by an adequate iterative procedure taking into consideration an average rejection rate for total inorganic carbon. Since equilibrium equations involve activity coefficients at each recovery rate step that must be evaluated, the Pitzer model, being able to adequately express the thermodynamic properties of the concentrated solution over a wide range of concentrations and temperatures (Krumgalz 2001), was used to calculate activity coefficients as a function of solution ionic strength. In the Pitzer model, interactions of all ions present in the solution are accounted for using concentration dependent interaction coefficients. Values of these interaction coefficients have been determined for many ions and were tabulated in the literature over a large range of temperatures (0-140°C). The database was founded on the original variable-temperature Pitzer parameters supplemented by parameter data from several other sources (Maureen *et al.* 2005).

Feed water chemical analysis was corrected according the error intervals for each chemical species concentration to account for charge neutrality. Concentration polarization is an inevitable effect of the increased salt concentration in the boundary layer, close to the membrane surface. Salt molecules are accumulated in the boundary layer, after being transported by the permeate flow, which crosses the membrane. Most of these salts will be rejected by the membrane itself. For this reason concentration polarization should be taken into account to get more precise scaling potential. Polarization concentration depends on the bulk stream mixing intensity in RO elements and varies from 1.13 to 1.2. Thus, salt concentration at membrane surface is 13-20% greater than in the bulk stream (Hchaichi *et al.* 2012). For a selective membrane, the polarization factor (P_f) is defined as the ratio of the limiting concentration of the aqueous solution in the polarization layer and that of average bulk solution. The concentration at the surface membrane for the species i is then given by the following equation

$$[i]_{\lim} = P_f [i]_c \tag{10}$$

After calculating the concentrations along the RO modules, supersaturation of the scaling salts is checked by calculating the corresponding IAP and scaling indexes at a given recovery rate. The computational strategy follows the algorithm given in Fig. 3.

3. Case studies

Scaling assessment in SWRO following the modeling approach detailed in section two will be conducted for four different seawaters. Natural seawater contains over 70 elements. But, only six of them represent over 99% by weight of all the dissolved solids in seawater. Table 1 gives typical chemical contents of the considered seawaters. Salinity of feed water to RO process varies from location to location and may vary with time at a given location as well. Inlet seawaters have a

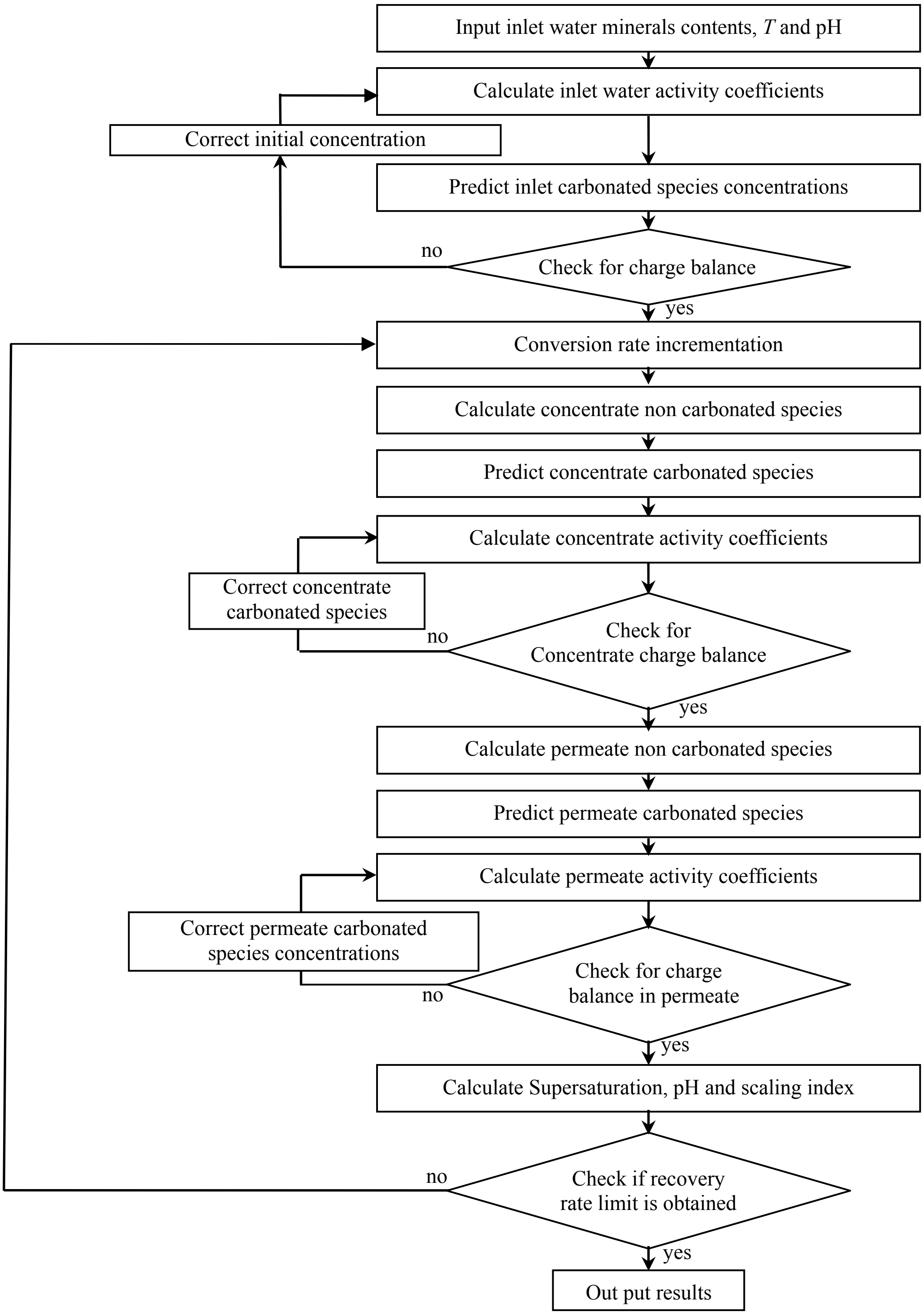

Fig. 3 Computational algorithm

Table 1 Inlet water chemical contents at 22°C

Seawaters	$[Ca^{2+}]$ (mg/L)	$[Mg^{2+}]$ (mg/L)	$[Na^{+}]$ (mg/L)	$[K^{+}]$ (mg/L)	$[Cl^{-}]$ (mg/L)	$[SO^{2-}_4]$ (mg/L)	$[HCO_3^-]$ (mg/L)	pH	TDS (mg/L)
Arabian Gulf *	500	1665	12500	300	23100	3100	155.3	7.8	41119
Gulf of Gabes	488	1373	13300	481	23567	3621	164.0	8.0	42994
Curacao *	466	1406	11741	460	20695	2952	115.6	8.2	37654
Pacific Ocean **	395	1360	11175	398	18875	2533	114.0	8.1	34750

* (Suresh Patel 2009), ** (Anonymous 2005)

relatively small scaling tendency with respect to $CaCO_3$. This is demonstrated with the relatively low S&DSI ranging between -0.1 and 0.2.

4. Results and discussion

Simulations were conducted to assess the scaling potential for four different seawaters. The carbon dioxide gas was supposed to freely pass through RO membranes. In this study, an average rejection rate was assumed for all ionic species at all recovery rates. pH variations in the permeate and concentrate compartments, as predicted by the calculation procedure, are presented in Figs. 4 and 5.

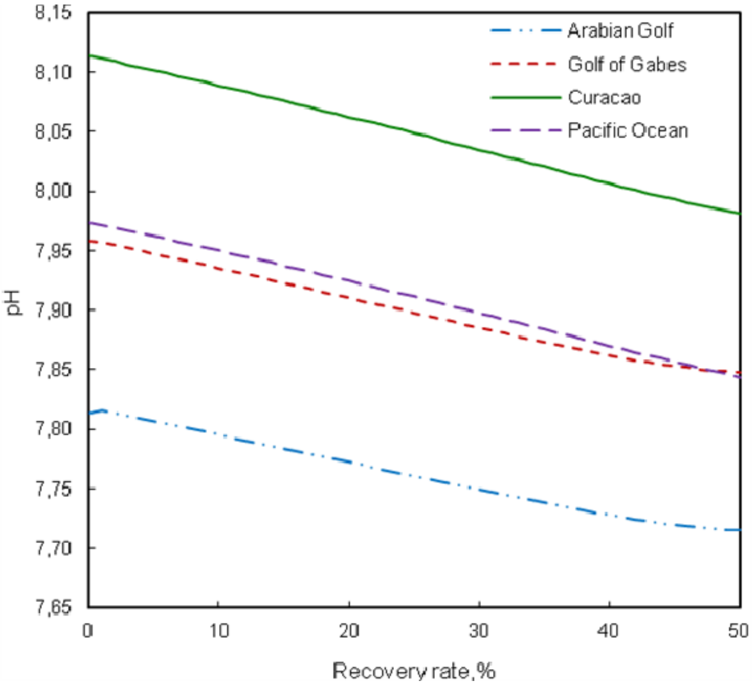

Fig. 4 Concentrate pH vs. recovery rate for different seawaters

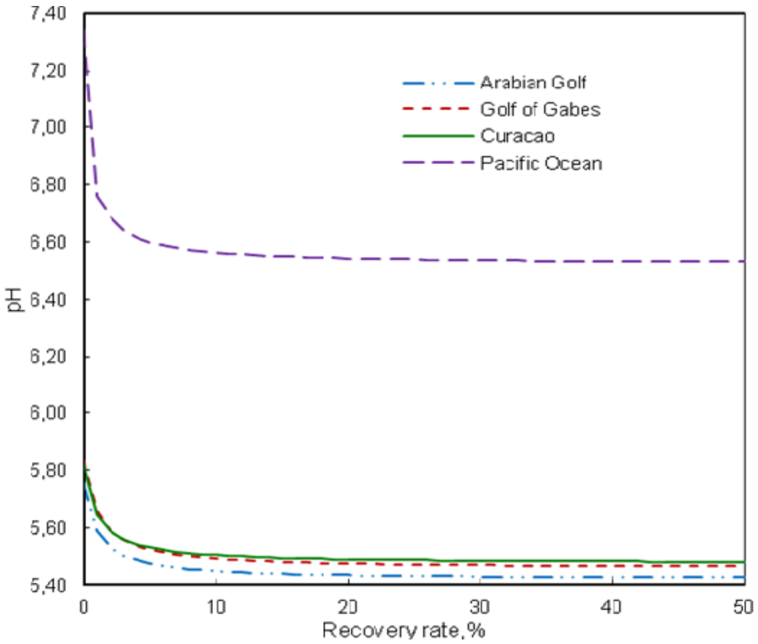

Fig. 5 Permeate pH vs. recovery rate for different seawaters

Table 2 Comparison of calculated pH with experimental pH for Pacific Ocean and Golf of Gabes (T = 22°C)

	Pacific Ocean (at recovery rate 50%)		Golf of Gabes (at recovery rate 38%)	
	Concentrate	Permeate	Concentrate	Permeate
Experimental pH	7.90*	6.50*	7.90	5.40
Calculated pH	7.84	6.53	7.86	5.46
Relative difference	-0.76%	0.46%	-0.51%	1.11%

* Anonymous (2005)

The dissolved CO_2 gas that passes through the membrane allows for an arrangement of carbonate species which causes pH variation in both retentate and permeate compartments. Up to around 45% recovery rate, a slight and steady decrease in the concentrate pH was predicted. The observed retentate average pH decrease rate was 0.024 per unit of recovery rate percentage. This trend can be related to the CO_2 passage through the membrane in accordance with an increase in the concentration of the various carbonate forms. Regardless of the seawater origin, the permeate pH decrease is more important, ranging from 0.3 to 0.8. It is much sharper and occurs basically for low recovery rates. For higher recovery rates, above 10% to 15% depending on the seawater contents, the permeate acidity reaches a pseudo plateau with slight decrease with τ. Unlike the concentrate, it seems that the permeate adjusts its pH value within the first 10% recovery rate.

Referring to Table 2, a comparison of calculated and real values for pH in concentrate and permeate solutions was performed for the experimental results that were available. There is very good matching between experimental and calculated data. The differences did not exceed 0.06 on pH scale for both retentate and permeate regardless of the seawater origin.

S&DSI variation with recovery rate for the considered seawaters is shown in Fig. 6. The scaling indices were calculated at membrane surface using an average polarization concentration of 1.2 for all chemical species. Seawaters entering RO modules have a relatively small scaling tendency as predicted by the low S&DSI, ranging from -0.1 to 0.2, at entrance. As the recovery rate increases the scaling propensity for the considered seawaters increase with slightly different trends because of their slightly different mineral compositions. The scaling index increase has two trends. For recovery rates below around 30%, S&DSI increases steadily. When recovery rates are higher, the scaling character of the retentate increases exponentially. Curacao seawater, which has the highest S&DSI at entrance, will be as scaling as the Golf of Gabes for 45% recovery rate.

Scaling assessment could be based on supersaturation with respect to precipitating salts. Supersaturation depends on mineral composition of water and its temperature. The solubility of salts is not only the consequence of ions concentrations. It is also dependent on the presence of other ions in solution. The adopted approach was able to account for the effects of concentration level through a good estimate of the activity coefficient along RO membranes.

Supersaturation for calcium carbonate is given by

$$\Omega_{\mathrm{CaCO_3}} = \frac{[\mathrm{Ca}^{2+}]\gamma_{\mathrm{Ca}^{2+}}[\mathrm{CO}_3^{2-}]\gamma_{\mathrm{CO}_3^{2-}}}{Ksp_{\mathrm{CaCO_3}}} \tag{11}$$

Where, Ksp_{CaCO_3} is the solubility product of the appropriate $CaCO_3$ form at a given temperature.

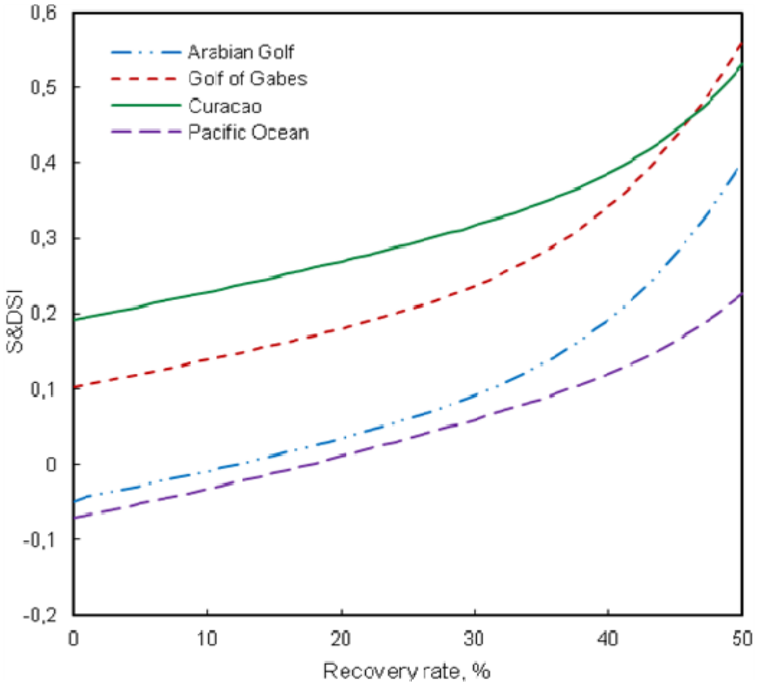

Fig. 6 S&DSI vs. recovery rate for different seawaters

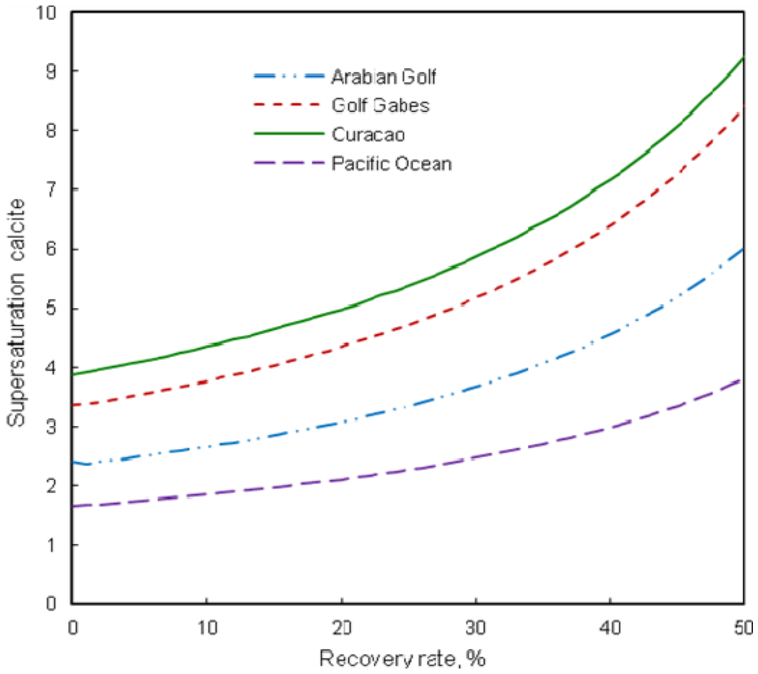

Fig. 7 Retentate supersaturation with respect to Calcite vs. recovery rate for different seawaters

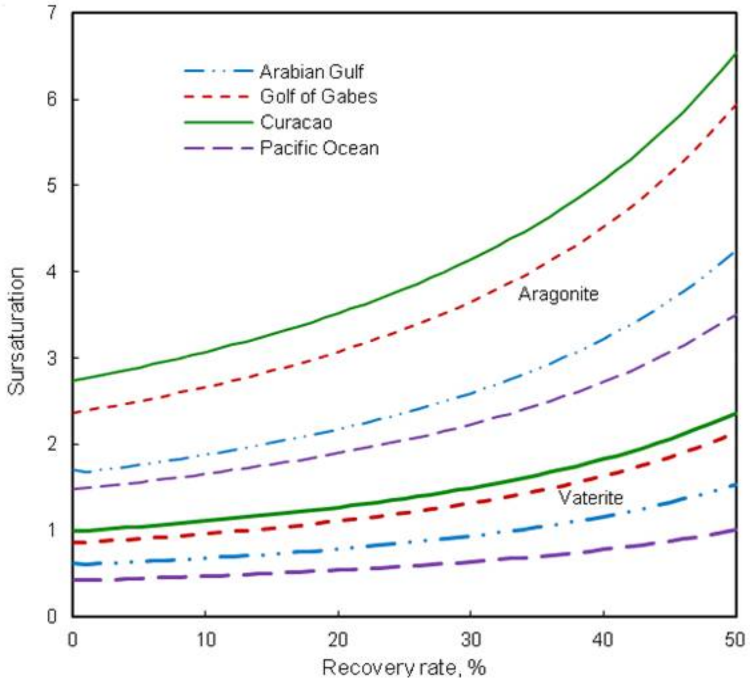

Fig. 8 Retentate supersaturation with respect to Aragonite and Vaterite vs. recovery rate for different seawaters

As for pH and S&DSI, calculations were limited to 50% recovery rates. Supersaturations relative to all calcium carbonate forms were predicted for various recovery rates. Results for calcite which is the most likely form to cause scaling are shown in Fig. 7. Similarly, as for S&DSI, the curves suggest that the driving force for scaling is positive and increases with recovery rates. That is why a thorough pretreatment and short residence time are needed to prevent scaling within RO modules.

Supersaturations of the remaining calcium carbonate forms (aragonite and vaterite) which are exceeding one are shown in Fig. 8. Curacao seawater has the highest supersaturation values with respect to calcite, aragonite and vaterite. Supersaturations with respect to aragonite are above 1, but lower than for calcite, for all recovery rates in all seawater cases. However for vaterite, supersaturation exceeded one only for Curacao and Golf of Gabes seawaters after recovery rates of 5% and 30% respectively.

The degree of supersaturation with respect to gypsum was also predicted for the considered seawaters. The corresponding supersaturation is defined by

$$\Omega_{\mathrm{CaSO_4,2H_2O}} = \frac{[\mathrm{Ca}^{2+}]\gamma_{\mathrm{Ca}^{2+}}[S\mathrm{O}_4^{2-}]\gamma_{\mathrm{SO}_4^{2-}}a_{\mathrm{H_2O}}^{2}}{Ksp_{\mathrm{CaSO_4,2H_2O}}} \qquad (12)$$

Where, $Ksp_{\mathrm{CaCO_3,2H_3O}}$ is the equilibrium solubility product of gypsum and $a_{\mathrm{H_2O}}$ is the water activity.

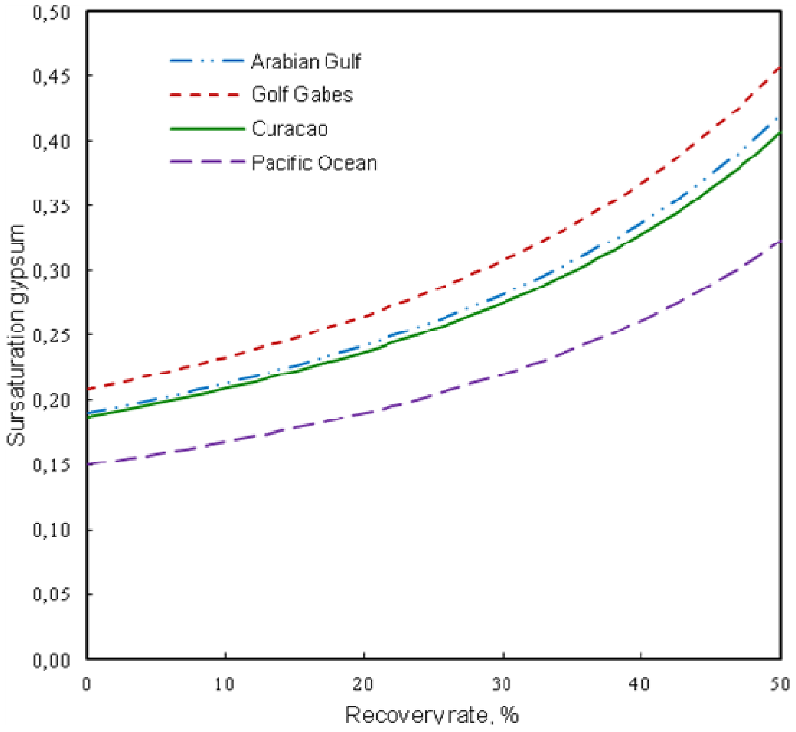

Fig. 9 Supersaturation of gypsum as function of recovery rate

The results are presented in Fig. 9. For all cases supersaturation were below 1 meaning that there is no risk of $CaSO_4$ scaling. Unlike for $CaCO_3$, Golf of Gabes seawater has the highest supersaturation with respect to gypsum.

5. Conclusions

A theoretical approach for scaling assessment in reverse osmosis seawater desalination was presented. The mathematical model is based on conservation principles and chemical equilibria equations along RO modules. An average rejection rate for ionic species was considered. Pitzer's model was used for the activity coefficient calculations. The modeling approach can estimate the supersaturation of different salts at different recovery levels for any type of RO desalination modules. Scaling indexes were calculated for four different seawaters. Permeate and concentrate pH were calculated along RO modules. Effects of pH and composition variations on scaling propensity with respect to calcite and gypsum can be investigated and discussed for all seawaters. Experimental results were in accordance with simulation results.

References

Anonymous (2005), "Ocean Water Desalination Pilot Plant Project: Investigation of Microfiltration and Reverse Osmosis Seawater Desalination", *NWRI Final Report*, July.

Antony, A., Low, J.H., Gray, S., Childress, A.E., Le-Clech, P. and Leslie, G. (2011), "Scale formation and control in high pressure membrane water treatment systems: A review", *J. Membr. Sci.*, **383**(1-2), 1-16.

Brusilovsky, M., Borden, J. and Hasson, D. (1992), "Flux decline due to gypsum precipitation on RO membranes", *Desalination*, **86**(2), 187-222.

Drak, A., Glucina, K., Busch, M., Hasson, D., Laime, J. and Semiat, R.I. (2000), "Laboratory technique for predicting the scaling propensity of RO feed waters", *Desalination*, **132**(1-3), 233-242.

Elfil, H. and Roques, H. (2001), "Role of hydrate phase of calcium carbonate on the scaling phenomenon", *Desalination*, **137**(1-3), 177-186.

Hannachi, A., Naimi, I., Zinoubi, R. and Elfil, H. (2007), "A new index scaling assessment", *Proceedings of the IDA World Congress on Desalination and Water Reuse*, Maspalomas, Gran Canaria, Spain, October.

Hannachi, A., Hchaichi, H., Cherni, S. and Elfil, H. (2009), "Operating a RO desalination plant without an inlet water pH adjustment", *Proceedings of the IDA World Congress on Desalination and Water Reuse*, Dubai, UAE, November.

Hasson, D., Semiat, R., Bramson, D., Busch, M. and Limoni-Relis, B. (1998), "Suppression of $CaCO_3$ scale deposition by anti-scalants", *Desalination*, **118**(1-3) 285-296.

Hchaichi, H., Elfil, H., Guichardon, P. and Hannachi, A. (2012), "Scaling tendency assessment in reverse osmosis modules", *Desalination Water Treat.*, **51**(4-6), 892-898.

Krumgalz, B.S. (2001), "Application of the Pitzer ion interaction model to natural hypersaline brines (In memory of the late Prof. Kenneth Pitzer)", *J. Mol. Liq.*, **91**(1), 3-19.

Lau, W.J., Goh, P.S., Ismail, A.F. and Lai, S.O. (2014), "Ultrafiltration as a pretreatment for seawater desalination: A review", *Membr. Water Treat., Int. J.*, **5**(1), 15-29.

Maureen, A., Sutton, M. and Carroll, S. (2005), "Evaporative evolution of a Na–Cl–NO_3–K–Ca–SO_4–Mg–Si brine at 95°C: Experiments and modeling relevant to Yucca Mountain", *Geochem. Transact.*, **6**(2), 31-45.

Pahiadaki, T., Tzotzi, Ch., Andritsos, N., Yiantsios, S.G. and Karabelas, A.J. (2005), "An experimental study of $CaCO_3$ scaling of RO and NF membranes", *Proceedings of the IDA World Congress on Desalination and Water Reuse*, Singapore, September.

Patel, S. and Chomiak, A. (2009), "Antiscalant for first pass seawater reverse osmosis", *Proceedings of the*

IDA World Congress on Desalination and Water Reuse, Dubai, UAE, November.

Rahardianto, A., Shih, W., Lee, R. and Cohen, Y. (2006), “Diagnostic characterization of gypsum scale formation and control in RO membrane desalination of brackish water”, *J. Membr. Sci.*, **279**(1-2), 655-668.

Valavala, R., Sohn, J., Han, J., Her, N. and Yoon, Y. (2011), “Pretreatment in reverse osmosis seawater desalination”, *Environi. Eng. Res.*, **16**(4), 205-212.

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