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Scaling tendency assessment in reverse osmosis modules

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ABSTRACT

A mathematical model was developed to predict super saturation along reverse osmosis modules (RO) for water desalination. This model is based on conservation principles and chemical equilibrium equations for concentrated solutions. Pitzer's model was used for the activity coefficient calculations. An average rejection rate for each ionic species was also considered. Supersaturations with respect to all calcium carbonate forms and to calcium sulfate are calculated. The model allows assessing when scale is likely to occur along the RO modules. The results for two brackish water qualities and seawater are shown.

Keywords: Desalination; Reverse osmosis; Supersaturation; Fooling; Scaling assessment; Modelling

1. Introduction

Reverse Osmosis (RO) processes have been widely used for separation and concentration of solutes in many fields. Because of the lack of water sources and the more stringent standards for drinking water quality, applications of RO membrane in water reclamation and seawater desalination will continue to grow. One of the major phenomena encountered in the aqueous systems is scale formation due to precipitation of salts present in the water. Many mineral species exist naturally in the water contributing to the formation of several salts such as: $CaCO_3$ and $CaSO_4$.

Scale appearance seems to be a limiting factor in water desalination operations. Scaling limits the economic reliability of the water desalination process by increasing energy consumption and decreasing efficiency. A better model for describing RO process performance is then highly desirable for designing and optimizing the system to further improve its cost-effectiveness. The performance of an RO process is also governed by membrane properties, operating conditions and feed water quality [1].

Therefore, scaling prevention is crucial for applying the desalination technology to produce clean water. For calcium carbonate many indices, such as: Langelier Saturation Index (LSI), Modified Langelier Saturation Index (MLSI), Ryzner Stability Index, Stiff and Davis Stability Index (S&DSI), Puckorius Scaling Index, Larson-Skold Index and Oddo-Tomson Index, have been proposed for scaling assessment [2,3]. All these indices were originally formulated for processes and applications such as cooling and thermal desalination. For brackish waters with Total Dissolved Salts (TDS) $< 10{,}000\,\text{mg/L}$ in the concentrate stream, the LSI is used

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to express the scaling potential for calcium carbonate [4]. For high-salinity brackish waters with TDS > 10,000 mg/L in the concentrate and for seawater, the S&DSI is used to express the scaling potential for calcium carbonate. Data needed to calculate the S&DSI of a concentrate stream are the same as the data needed to calculate the LSI.

The ability to predict scaling is an important tool for RO processes, both at the design stage and for continous monitoring. If the solubility of a salt will be exceeded at a given recovery rate, i.e. the solution is supersaturated, the salt can precipitate. Concentration of ions for the RO concentrate should be used as a measure of scaling potential. The main factors affecting scale formation is salt concentration, operating temperature, fluid velocity, water pH and time [5]. The supersaturation ratio of a solution can be expressed as:

$$\Omega = \mathrm{IAP}/\mathrm{Ksp} \tag{1}$$

where IAP is the ion activity product, Ksp is the ion activity product at equilibrium. Accordingly, $\Omega > 1$ implies a supersaturated solution, whereas $\Omega < 1$ involves an undersaturated solution. Ion activity is very often approximated by concentration. However, this assumption is only valid for dilute solutions which could be considered as an ideal situation. For desalination, solutions are all concentrated, activity needs to be used and its value can be determined using comprehensive models. According to ionic strength of water, the Pitzer ion-specific interactions could be used as a model to calculate ion activity coefficients [6].

Scaling damages membrane surfaces by fouling through obstruction and particulate abrasion. It is very difficult to remove it with a chemical cleaning. Development of calcium sulphate or calcium carbonate scaling in the membrane can be further complicated by the potential for precipitation to occur even before water concentration along the membrane surface. Scaling in RO membrane depends on raw water composition and on the converted rate obtained. Examination of raw waters composition, resulting from the continental guide, shows that they are chloro-calco-sodic-sulphated waters. Consequently, a significant fraction of the scale formed in the modules is ascribable to calcium carbonate and sulphate precipitation.

For crystallization to occur, solution has to be supersaturated. A given salt may have different crystal structures of which some might be more stable or more readily formed. Calcium carbonate has dealt with anhydrous crystalline polymorphs: calcite, aragonite and vaterite, respectively. The most unstable phase is vaterite followed by aragonite and calcite. Dissolvability is also in accordance with this sequence. An unstable phase could be transformed into a stable phase spontaneously [7]. The hydrate forms among these three crystalline polymorphs are:

- Amorphous calcium carbonate (ACC) which is the most instable form and can be transformed into vaterite and calcite at low temperatures and into aragonite and calcite at high temperatures
- Monohydrate calcium carbonate (MCC) whose synthesis requires the presence of magnesium and some of other ions,
- Hexahydrate calcium carbonate (HCC) which may rapidly decomposes into anhydrous forms at warmer temperatures.

Table 1 presents equilibrium solubility products of polymorphic carbonate of calcium in solubility decreasing order at 25˚C. According to the experimental conditions of precipitation (supersaturation, temperature, pH, presence of additives), one can obtain one of these polymorphic forms or a mixture.

The three major forms of calcium sulphate (hemihydrate, dihydrate and anhydrate) have different solubility isotherms. However, while precipitation of calcium carbonate can often be minimized by reducing pH of feed water, calcium sulphate solubility is independent of this parameter (pH).

Many models have been developed to LSI, pH and ions concentration as a function of the conversion rate. As explained in our previous work, these models lack precision and did not rigorously account for the complex behaviour of the calco-carbonate solutions [3].

The aim of this study is to develop a prediction model of the most scale-forming salts such as all forms of calcium carbonate and calcium sulphate. The adopted approach is based on a numerical technique to calculate supersaturation for a wide range of conversion rates. Activity coefficients will be estimated for each ion using Gibbs free energy of reaction and

Table 1
Equilibrium solubility product KS at 25˚C [8]

Calcium carbonate forms	−logKs
ACC	6.40
HCC	6.62
MCC	7.15
Vaterite	7.91
Aragonite	8.32
Calcite	8.48

incorporating the Pitzer equation which takes into account ion interaction forces.

2. Scaling assessment along RO modules

The concentrations of carbonated species (HCO_3^-, CO_3^{2-}, H_2CO_3) along with hydronium and hydroxide ions in the brine play an important role in alkaline scale formation. Permeability of the membrane to gases particularly to CO_2 plays a significant role in scaling process and the prediction of scale formation. A model has been developed to calculate the concentrations of HCO_3^-, CO_3^{2-}, H_2CO_3, H^+ and OH^- along the RO modules for any given conversion rate. Along the RO modules, the flow is assumed to be a pseudo plug flow.

These concentrations are determined by applying mass and charge conservation equations and an average rejection rate for each ionic species. At all locations, different chemical equilibriums in water are achieved and the following equations are holding:

$$K_1 = \frac{[H_3O^+]\gamma_{H_3O^+}[HCO_3^-]\gamma_{HCO_3^-}}{[H_2CO_3]\gamma_{H_2CO_3}} \tag{2}$$

$$K_2 = \frac{[H_3O^+]\gamma_{H_3O^+}[CO_3^{2-}]\gamma_{CO_3^{2-}}}{[HCO_3^-]\gamma_{HCO_3^-}} \tag{3}$$

$$K_e = [H_3O^+]\gamma H_3O^+[OH^-]\gamma_{OH^-} \tag{4}$$

$$\sum m_i[M_i^{m_i+}] = \sum a_i[A_i^{a_i-}] \tag{5}$$

where: K_1 is the first dissociation constant of carbonic acid; K_2 is the second dissociation constant of carbonic acid; K_e is the water dissociation constant; γ_I is the activity coefficient of species I; and $[I]$ is the concentration of species I. M_i is a cation of a charge $+m_i$ and A_i is a anion of a charge $-a_i$.

Before starting calculations, water chemical analysis is slightly corrected in accordance with the experimental error in determining each chemical species concentration to account for charge neutrality. For any conversion rate, τ, concentrations of all chemical species were calculated with a simple mass balance applied to the reserve osmosis module's corresponding volume. If we consider the chemical entity B, a material conservation equation gives:

$$F_f = F_p + F_c \tag{6}$$

$$\tau = \frac{F_p}{F_f} \tag{7}$$

$$R_B = \frac{[B]_f - [B]_p}{[B]_f} \tag{8}$$

$$[B]_f F_f = [B]_p F_p + F_c[B]_c \tag{9}$$

where: F is the flow rate; the indices f, p, and c are relative to feed, permeate and concentrate respectively. τ is the conversion rate and R_B is the rejection rate of the species B. An average rejection rate was considered for all chemical species.

After a rearrangement, the concentration in the concentrate can be expressed in terms of conversion rate, membrane retention and feed concentration determined numerically as:

$$[B]_c = \frac{[B]_f}{1-\tau}(1 - \tau(1 - R)) \tag{10}$$

The described procedure has been applied for species other then H_2CO_3, HCO_3^-, CO_3^{2-}, H_3O^+ and OH^-. For the later chemical entities an iterative calculation procedure, based on the resolution of the set of equations given by Eqs. (2–5) and considering an average rejection rate for total inorganic carbon, is used.

Activity coefficients were calculated using Pitzer's model, which takes into account interactions between ions. This model is accurate for non-ideal solutions at higher ionic strengths and elevated temperatures. The Pitzer ion interaction approach accounts for various combinations of ion-ion interactions in the solution [6].

Pitzer ion interaction database is the most comprehensive database available to account for non-ideal behaviour 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 parameter data from several other sources [9].

In reality, concentration polarization should be taken into account to get more accurate scaling potential. The polarization concentration depends on the bulk stream turbulence in the RO element and varies from 1.13 to 1.2, meaning that the concentration of salts at the membrane surface is 13–20% greater than in the bulk stream [10]. For a perfectly selective membrane, the polarization factor (P_f) was defined as the ratio of the limiting concentration of the aqueous solution in the polarization layer and that average bulk of

Table 2
Inlet water chemical compositions

Water quality	$[Ca^{2+}]$ (mg/L)	$[Mg^{2+}]$ (mg/L)	$[Na^{+}]$ (mg/L)	$[K^{+}]$ (mg/L)	$[Cl^{-}]$ (mg/L)	$[HCO_3^{-}]$ (mg/L)	$[SO_4^{2-}]$ (mg/L)	pH	Ionic strength
Raw ground water	380	83	450	46	797	100	1,100	7.7	0.07
Acidulated ground water	380	83	450	46	813	91	1,100	7.1	0.07
Seawater	488	1,373	13,300	481	23,567	164.2	3,623	8.0	0.87

solution concentration. The concentration at the surface membrane for the element B is then given by the following equation:

$$[B]_{\mathrm{lim}} = P_{\mathrm{f}}[B]_{\mathrm{c}} \tag{11}$$

After calculating the concentrations along the RO modules, supersaturation of the scaling salts is checked by calculating the corresponding IAP and scaling indexes.

3. Case studies

A proper pretreatment scheme for feed water will depend on feed water source, feed water composition and RO operating conditions. The most frequent scaling problems come from calcium carbonate ($CaCO_3$) because it precipitates fast, once concentrated beyond its solubility limit and also most natural waters are almost saturated with respect to $CaCO_3$. $CaCO_3$ scaling including $SrCO_3$ and $BaCO_3$ can be prevented by acid and/or scale inhibitor adding as well as softening of the feed water, preventive cleaning and low system recovery. Solubility of $CaCO_3$ depends on the pH as shown in the following chemical equation:

$$CaCO_3 + H_3O^+ \rightleftharpoons Ca^{2+} + HCO_3^- + H_2O$$

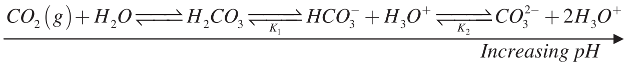
The equilibrium can be shifted to the right side to convert $CaCO_3$ to soluble $Ca(HCO_3)_2$ by adding an acid to lower the pH. If a high-quality scale inhibitor is used, it will reduce or eliminate acid consumption, and also could decrease the potential for corrosion due to the acid. In this study, two qualities of brackish water were considered, row water and acidulated water. Local seawater was considered as well. Data reported in Table 2 give the relevant chemical composition of these three feed water qualities.

Feed ground water has a relatively high tendency to generate calcium carbonate scale. This is demonstrated with the relatively high LSI (0.62). The LSI of the feed water added with acid is near to zero. The inlet seawater has a relatively small scaling tendency with respect to $CaCO_3$.

4. Results and discussion

An RO membrane will reject ionic species; however, the carbon dioxide gas will freely pass through the membrane. The dissolved CO_2 gas that passes through the membrane will again be ionized and carbonate ions are formed. Equations below describe the reactions that govern the chemistry of carbon dioxide in water. At low pH, the equilibrium is shifted to carbon dioxide gas, when the pH is high the equilibrium shifts to the ionic species. The equations reported in Fig. 1, describe the reactions that govern the chemistry of carbon dioxide in water.

In this study, an average ion and organic carbon rejection is assumed for all conversion rates. Scaling indices' values along with the pH variations are presented as a function of the conversion rate in Figs. 2 and 3 for raw and acidulated ground waters



$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3 \underset{K_1}{\rightleftharpoons} HCO_3^- + H_3O^+ \underset{K_2}{\rightleftharpoons} CO_3^{2-} + 2H_3O^+$$

Fig. 1. Reaction of carbon dioxide in water.

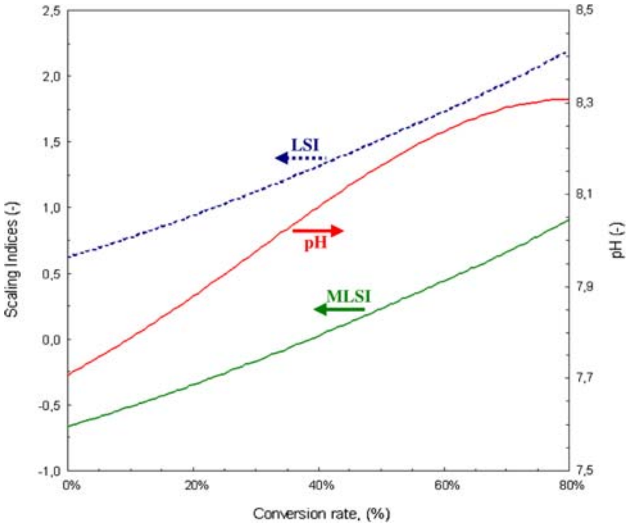


Fig. 2. Variation of LSI, MLSI and pH with the conversion rate for raw ground water.

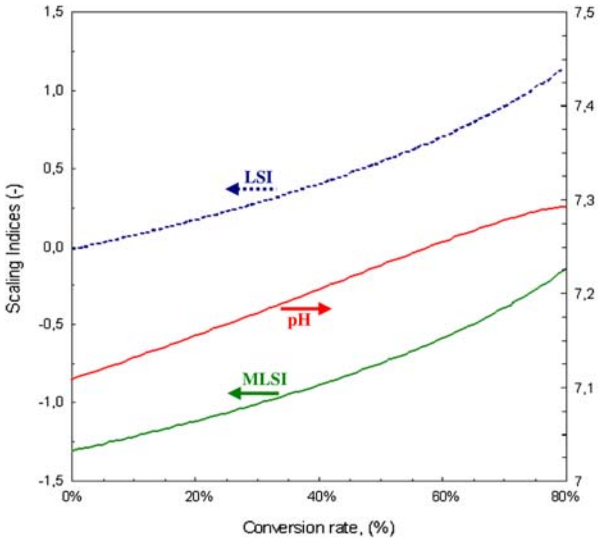


Fig. 3. Variation of LSI, MLSI and pH with the conversion rate for acidulated ground water.

Table 3
Comparison of LSI and pH calculated values for acidulated brackish water with experimental data (conversion rate: 74%, $T = 30^\circ C$)

	LSI	pH
Experimental data [11]	1.04	7.36
Calculated values	0.98	7.30

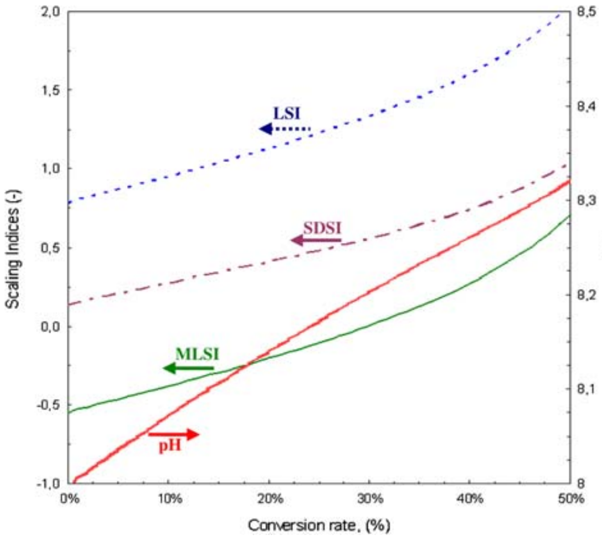


Fig. 4. Variation of LSI, SDSI, MLSI and pH with the conversion rate for seawater.

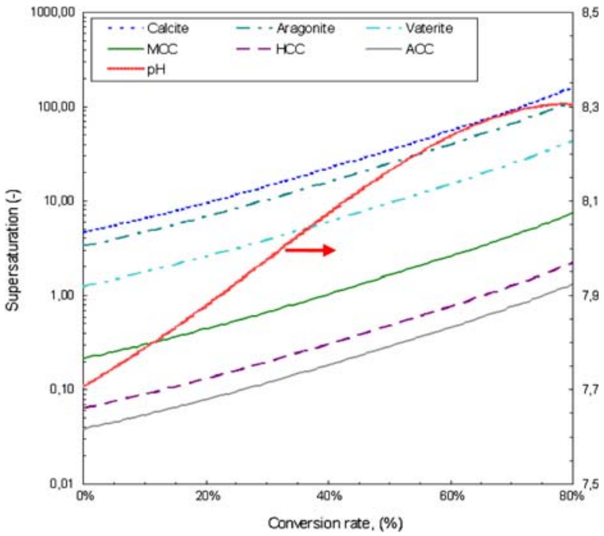


Fig. 5. Supersaturation as function of conversion rate for brackish water.

respectively. LSI and MLSI were calculated at the membrane surface. The increase in the pH value is related to the CO_2 passage through the membrane in accordance with an increase in the concentration of the different forms of carbonate.

The LSI and MLSI of the acid treated feed water are lower than those for the raw water. LSI indicates that water has a scaling tendency with respect to $CaCO_3$ all along the membrane modules for both raw and acidulated brackish water. However, MLSI predicts that the scaling water character is prevented all along the RO modules for the treated ground water. In the case of the raw brackish water the scaling tendency using MLSI is predicted for conversion rates above 40%.

Referring to Table 3, a comparison of calculated and real values for pH and LSI was performed for the experimental results that were available [11]. There is very good matching between experimental and calculated data.

For the considered seawater scaling assessment predictions are shown in Fig. 4. In the case of seawater, calculations were limited to 50% conversion rates. LSI and S&DSI foresee scaling solutions with respect to calcium carbonate all along the RO modules. MLSI predicts that water becomes scaling for conversion rates above 30%.

Ions concentrations at the desired conversion rate were calculated from the Eq. (10) and the set of Eqs. (2–5). To account for concentration polarization the concentration is multiplied by the concentration P_f. These concentrations were then put into Eq. (12). The saturation ratio for different forms of calcium carbonate is given by:

$$\Omega_{CaCO_3} = \frac{[Ca^{2+}]\gamma_{Ca^{2+}}[CO_3^{2-}]\gamma_{CO_3^{2-}}}{Ksp_{CaCO_3}} \tag{12}$$

where, $Ksp_{\mathrm{CaCO_3}}$ is the solubility product of the appropriate $CaCO_3$ form and temperature.

Supersaturations relative to different forms of calcium carbonate were calculated for various conversion rates. Only those which have a supersaturation greater than 1 are shown in Figs. 5 and 6 for ground water and seawater, respectively. The feed water without acid addition is supersaturated with respect to the Calcite form ($\Omega_{\mathrm{calcite}} > 1$), these results are already shown in Figs. 2 and 3.

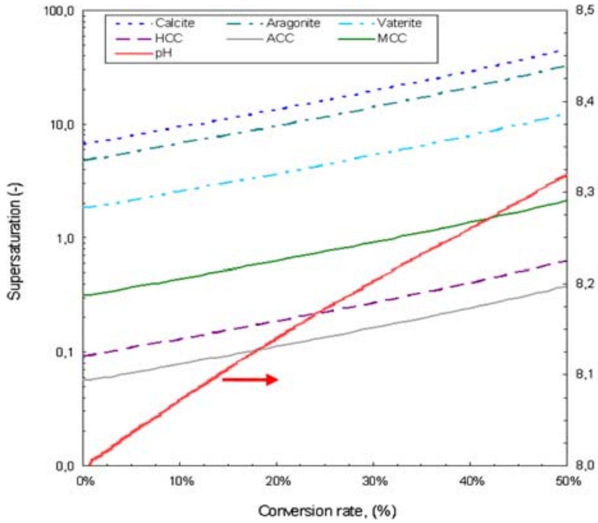


Fig. 6. Supersaturation as function of conversion rate for seawater.

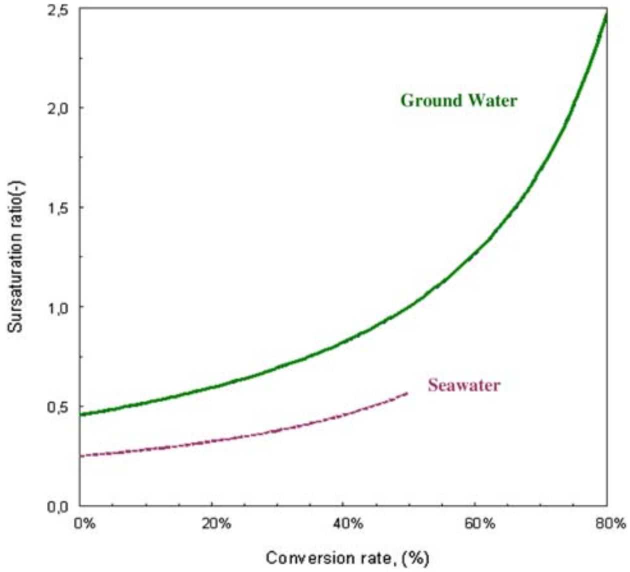


Fig. 7. Supersaturation of gypsum as function of conversion rate.

Calcium sulfate supersaturations were calculated using the following relation:

$$\Omega_{\mathrm{CaSO_4\cdot 2H_2O}} = \frac{[\mathrm{Ca^{2+}}]\gamma_{\mathrm{Ca^{2+}}}[\mathrm{SO_4^{2-}}]\gamma_{\mathrm{SO_4^{2-}}}a^2_{\mathrm{H_2O}}}{Ksp_{\mathrm{CaSO_4\cdot 2H_2O}}} \tag{13}$$

Where, $Ksp_{\mathrm{CaSO_4\cdot 2H_2O}}$ is the equilibrium solubility product of gypsum and a_{H2O} is the water activity.

The supersaturation ratio values for all feed water qualities are given in Figs. 5 and 6. For seawater all supersaturations with respect to $CaSO_4$, up to a 50% conversion rate, are below 0.6 (Fig. 7). In such case, $CaSO_4$ is unlikely to precipitate. As expected, the results are confounded for raw and acidulated ground water. The concentrate is supersaturated with respect to calcium sulfate for conversion rates higher than 50%.

5. Conclusion

A theoretical approach to predict supersaturation for major scaling salts in RO modules has been developed. The mathematical model is based on conservation principles and chemical equilibrium equations for concentrated solutions. An average rejection rate for each ionic species was also considered. Pitzer's model was used for the activity coefficient calculations. In this work simulations were conducted to assess scale occurrence likelihood with respect to calcium carbonate and gypsum along RO modules for ground and sea water desalination. The effect of pH on scaling propensity with respect to calcite and gypsum was investigated and discussed. Simulation results were in accordance with experimental data.

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