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Simulation of Boron Rejection by Seawater Reverse Osmosis Desalination

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Boron is a vital element for growth of creations, but excessive exposure can cause detrimental effects to plants, animals, and possibly humans. Reverse Osmosis (RO) technique is widely used for seawater desalination as well as for waste water treatment. The aim of this study is to identify how different operating parameters such as pH, temperature and pressure can affect boron concentrations at the end of RO processes. For this purpose, a mathematical model for boron rejection is developed based on solution-diffusion model which can describe solvent and solute transport mechanism through the membranes. After a wide and thorough research, empirical correlations developed in the past are filtered, adopted and calibrated in order to faction with reliability as part of the solution-diffusion model of this work. The model is validated against a number of experimental results from the literature and is used in further simulations to get a deeper insight of the RO process. The general findings of the boron rejection model are supporting the case that with increasing pH and operating pressure of the feed water, the boron rejection increases and with increasing feed water temperature the boron rejection decreases.

1. Introduction

Boron naturally exists in water as boric acid and borate ions. Boron concentrations have an important role in human health and plants prosperity. Mane et al. (2009) reported that the consumption of water with high boron concentrations is responsible of toxicological effects on human's health. Huertas et al. (2008) explained that boron is considered to be among the most important micro-nutrients for plants, playing a key role to plants development, however when irrigated with water containing more than 1mg/l of boron, the plants are badly affected (leaf damage, reduced yields, etc.)..

The demand of freshwater is growing exponentially with nonlinear growth in population and improved standards of living. This puts a serious strain on the quantity of naturally available freshwater. No doubt that the production of freshwater via seawater desalination is the only technological solution for the future. The desalination processes are classified broadly into thermal processes and membrane processes. Although the thermal processes are in existence over 60 years, the use of membrane based RO desalination process, due to advancement in membrane technology, is growing. Salt rejection together with boron rejection using RO process has been gathering momentum steadily.

This work focuses on the study of boron rejection in RO processes using model based technique. A number of different boron rejection models have been developed in the past to study effective rejection of boron using RO processes. The features of these models are summarised in Table 1 (Sassi, 2012). In this work, a mathematical model is developed based on solution-diffusion model. The model incorporates a number of recently developed correlations for effective boron rejection. The model is validated using experimental data from the literature and is then used further to generate boron rejection scenarios under different operating conditions. The model is able to predict the influence of feed water temperature, pH, and pressure on boron rejection.

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2. RO Boron Rejection Model

Water and Salt Permeability (Hung et al., 2009):

Table 1: Boron rejection models from literature

Author (year)	Model used	Parameters studied	Comments
Taniguchi (2001)	Solution–diffusion	Not included	The permeability factors of salt and boron are measured experimentally and the relationship between them are established.
Sagiv and Semiat (2004)	Kedem-Katchalsky	pH, Pressure Temperature,	A numerical model is developed in order to study the effect of parameters on boron rejection
Hyung and Kim (2006)	Spiegler-Kedem	pH, Temperature	Bench-scale cross-flow filtration experiments were used to estimate the rejection of boron by six commercial RO membranes and model parameters updated.
Hung et al., (2009)	Solution–diffusion	pH, Temperature	The permeability of boron through seawater RO membranes was estimated using a lab-scale RO system and then a computer program was developed to estimate the boron rejection at different operating conditions
Mane et al., (2009)	Spiegler-Kedem	pH, Temperature, Pressure	A mechanistic model was developed to simulate boron rejection by pilot- and full-scale RO processes under varying operating conditions.

$$P_W = A_0 e^{\left(-\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right)}\left(\frac{10^{-3}}{24\times60\times60}\right) \tag{1}$$

$$P_S = B_{st0} e^{\left(-\frac{E_{Bst}}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right)}\left(\frac{10^{-3}}{24\times60\times60}\right) \tag{2}$$

where P_W is the water permeability measured in m/Pa sec. A_0 is water permeability coefficient measured at 298.15 K [m/(kPa day)]. E_A is the activation energy for transport of water molecule through the membrane [J/mol K]. P_S is the salt permeability [m/s]. B_{st0} is the salt permeability coefficient, E_{Bst} is the activation energy for the transport of salt through the membrane [J/mol K]. R is the ideal gas constant [J/mol K]. T is the temperature [K].

Feed and Permeate Osmotic Pressure (Hyung and Kim, 2006):

$$\pi_F = \left(0.6955 + 0.0025(T-273.15)\right)\times10^8\times\frac{C_{SF}}{\rho} \tag{3}$$

$$\pi_P = \left(0.6955 + 0.0025(T-273.15)\right)\times10^8\times\frac{C_{SP}}{\rho} \tag{4}$$

$$\Delta\pi = \pi_F - \pi_P \tag{5}$$

where π_F and π_P are the osmotic pressures at the feed side and permeate side of the membrane respectively [Pa]. $\Delta\pi$ is the osmotic pressure deference across the membrane. ρ is the sea water density. C_{SF} is the feed salt concentration [kg/m^3].

Water Flux (Nath, 2008): The water flux across the membrane is given by:

$$J_W = P_W(\Delta P - \Delta\pi) \tag{6}$$

where J_W is water flux [Kg H_2O/cm^2]. ΔP is hydraulic pressure deference across the membrane [Pa].

Salt Mass Transfer Coefficient (Taniguchi et al., 2001) and Salt Flux (Nath, 2008):

$$K_S = 1.63\times10^{-3}Q_F^{0.4053} \tag{7}$$

where K_S is the mass transfer coefficient [m/s]. Q_F is the volumetric flow rate of feed stream [m^3/s].

$$J_S = P_S(C_{SM} - C_{SP}) \tag{8}$$

where J_S is the salt flux, C_{SM} is the salt concentration at membranes feed side surface [kg/m^3] and C_{SP} Salt concentration at Permeate side (also defined as $C_{SP} = \frac{J_S}{J_W}$).

Concentration Polarization (Taniguchi et al., 2001):

$$\frac{C_{SM} - C_{SP}}{C_{SF} - C_{SP}} = e^{\left(\frac{J_W}{K_S}\right)} \tag{9}$$

Boric and Borate Concentrations at Different p^H. Note, boron exists in seawater as boric acid (H_3BO_3) and borate ions (H_2BO_3), and their respective concentration depends on the pH value (Hyung and Kim, 2006). The borate ions are rejected by RO more easily than boric acid as they are negatively charged (charge repulsion between the borate ions and the negatively charged surface of the membrane). The relation between pH and boric and borate concentrations are given in the following (Hung et al., 2009; Mane et al., 2009):

$$pH = pK_a + \log\frac{C_{Bborate}}{C_{Bboric}}; \qquad C_{BF} = C_{Bborate} + C_{Bboric} \tag{10}$$

$$pK_a = \frac{2291.9}{T} + 0.01756 - 3.385 - 3.904\times C_{SM}^{\frac{1}{3}} \tag{11}$$

$$C_{Bboric} = \frac{C_{BF}}{1+10^{(pH-pK_a)}} \tag{12}$$

where, pK_a is the first acid dissociation constant, C_{Bboric} and $C_{Bborate}$ are the boric acid and borate ion concentration of the feed stream [kg/m^3].

Boric acid (α_0) and borate ion (α_1) fractions, expressed as a percentage of total Boron in the feed stream can be calculated by:

$$\alpha_0 = \frac{C_{Bboric}}{C_{BF}}; \qquad \alpha_1 = \frac{C_{Bborate}}{C_{BF}}; \qquad \alpha_0 + \alpha_1 = 1 \tag{13}$$

Boron Flux, Mass Transfer Coefficient and Permeability:

Boron flux equation is similar to Eq. 8 but instead of salt concentration, boron concentration is to be used. Also, the boron concentration polarization equation is similar to Eq. 9 when S is replaced by B (for boron) with $K_S = 0.97K_B$ (Taniguchi et al., 2001). A temperature dependent boron mass transfer co-efficient will be $K_{BT} = K_{B0}e^{(0.04(T-298.15))}$, where K_{B0} is the mass transfer co-efficient at T=298.15 K. The temperature dependent boron permeability P_B is given by (Hyung and Kim, 2006):

$$P_B = \alpha_0 P_{Bboric}e^{(0.067(T-298.15))} + \alpha_1 P_{Bborate}e^{(0.049(T-298.15))} \tag{14}$$

where, P_{Bboric} and $P_{Bborate}$ are the boric acid and borate ion permeability constants at T=298.15K.

Finally, overall boron rejection (BR) then can be calculated by: $BR = 1-\frac{C_{BP}}{C_{BF}}$, where, C_{BP} is boron concentration of the permeate stream.

3. Model Validation

The model presented in section 2 is validated by comparing the model predictions with the actual experimental results for specific RO membranes, and also against predictions by other mathematical models from literature. The experimental results of Mane et al. (2009) using RE4040-SR membrane are used in order to validate the model. The input data (as calculated experimentally by Mane et al., 2009) are presented in Table 2. The experimental and the simulation results using the model are shown in Table 3.

Our simulated results compare very well with the experimental results (maximum value of error is just 1.74 %). Note, Mane et al. (2009) also developed a model based on the Irreversible Thermodynamic Model and validated their model against the experimental results (Table 3) but resulting in a maximum error value of 2 %.

4. Simulation

In this work, we carried out similar simulations to those considered by Mane et al. (2009).

4.1 Simulation 1

In this simulation, the pH is varied from 6 to 12 and the pressure is varied from 600 to 1000 psi at constant temperature of 25 °C. The boron rejections at different conditions are captured in Figure 1. The maximum boron rejection (99.18 %) is obtained at 1000 psi and pH 12 and the lowest boron rejection (89.34 %) is obtained at 600 psi and pH 6 which are closed to that obtained by Mane et al. (2009) (99 % and 88 % respectively). It is clear that pH level of the seawater plays a very important role in the overall boron rejection performance.

Table 2: Inputs of the model

Water Activation Energy, E_A	2.37×10^{5}	Boric Acid Permeability, P_{boric}	5.47454×10^{-7}
Water Permeability coefficient at 298.15 K, A_0	2.37×10^{-4}	Salt concentration at feed stream, C_{SF}	34,000
Salt Permeability coefficient at 298.15 K, B_{st0}	1.5×10^{-3}	Boron concentration at feed stream, C_{BF}	5
Salt Activation Energy, B_{Bst}	3.85×10^{5}	Feed flow rate, Q_F (m^3/s)	5.821×10^{-4}
Borate Ion Permeability, $P_{Bborate}$	8.7963×10^{-8}	Ideal Gas constant, R	8.3145

Table 3: Experimental results (Mane et al.) & model predictions (Membrane RE4040-SR), T = 298.15K

			pH 7.5		
Pressure (psi)	**600**	**650**	**700**	**750**	**800**
Boron Rejection % (Experimental)	87.60	89.50	91.30	92.80	93.50
Boron Rejection % (This work)	89.20	90.76	91.89	92.76	93.43
Error %	1.60	1.26	0.59	0.04	0.07
			pH 8.5		
Boron Rejection % (Experimental)	92.40	93.70	95.50	95.90	96.80
Boron Rejection % (This work)	92.65	93.56	94.20	94.69	95.06
Error %	0.25	0.14	1.3	1.21	1.74
			pH 9.5		
Boron Rejection % (Experimental)	97.40	98.10	98.10	98.50	98.90
Boron Rejection % (This work)	96.88	97.29	97.60	97.76	97.90
Error %	0.52	0.81	0.50	0.74	1.0

4.2 Simulation 2

Here, the pressure and temperature are varied from 600 to 1000 psi and from 15 to 45 °C respectively while the pH is held constant at 8. The boron rejections are captured in Figure 2. The maximum boron rejection (97.82 %) is achieved at 15 °C and 1000 psi, while the lowest 70.06 % is achieved at 45 °C and 600 psi. The corresponding values obtained by Mane et al. (2009) are 98.2 % and 76.5 % respectively. Note, that the results produced by the two models differ by almost 6.5 % especially at the lowest predicted values. This could be due to incorrect estimation of boron permeability using Eq. 14. If the boric and borate permeability dependence on temperatures variation is made smaller, this would cause a subsequent increase of the boron rejection. From Eq. 14, it can be seen that the boric and borate permeability dependence on temperature is caused by the two exponential terms. In this work, the two constants 0.067 and 0.049 in Eq. 14 are adjusted to minimise the error between the predicted boron rejections at 45 °C. The revised Eq. 14 is given below where the constants are now 0.051 and 0.033 respectively:

$$P_B = \alpha_0 P_{Bboric} e^{(0.051(T-298.15))} + \alpha_1 P_{Bborate} e^{(0.033(T-298.15))} \quad (14a)$$

The lowest boron rejection predicted by the revised model at 45 °C and 600 psi is 76.32 %. The maximum boron rejection predicted by the revised model at 15 °C and 1000 psi is now 97.45 %. These values are now very close to those predicted by Mane et al. (2008). The simulation results suggest that boron rejection increases with decreasing temperature and increasing operating pressure.
For the same membrane *RE4040-SR* and for pH 9.5, Hyung and Kim (2006) presented experimental results at a higher temperature (35 °C) using the revised model the system is simulated at their condition. The comparative results are presented in Table 4. The revised predictions compare well with the experimental results, having a maximum relative error of 1.15 % and minimum relative error of 0.66 %.

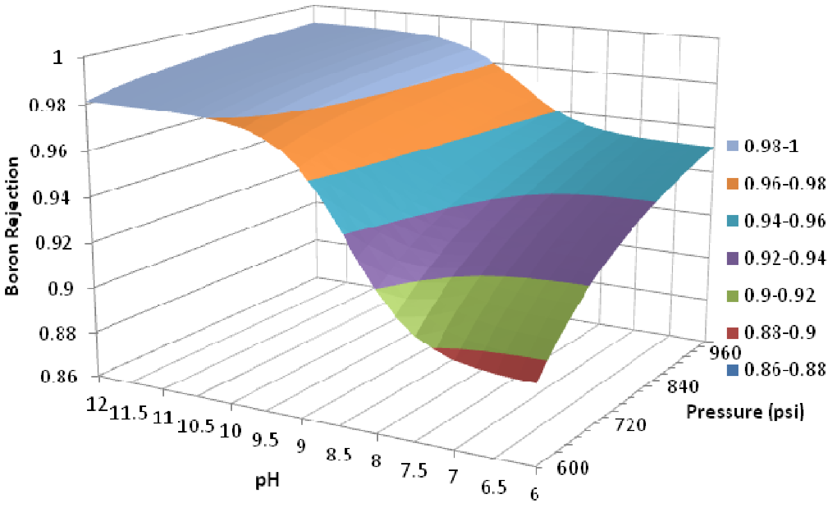

Figure 1: Effect of pH and pressure on boron rejection

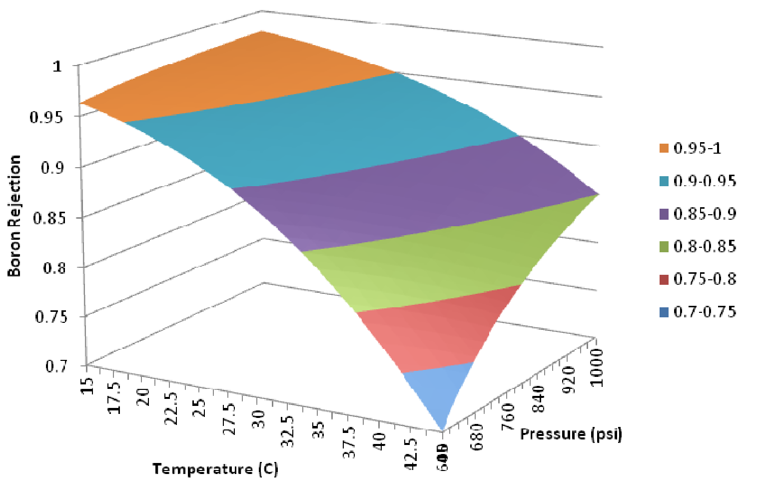

Figure 2: Effect of temperature and pressure on boron rejection

Table 4: Experimental results (Hyung & Kim) & model predictions (Membrane RE4040-SR)

Pressure (psi)	**600**	**700**	**800**	**900**	**1000**
Boron Rejection % (Hyung and Kim, 2006)	92.02	93.68	94.63	94.75	95.21
Boron Rejection % (This work, revised model)	93.17	94.61	95.31	95.68	95.88
Error %	1.15	0.93	0.67	0.92	0.66

4.3 Simulation 3

This simulation is carried out at constant pressure of 800 psi with the pH being varied from 6 to 12 and the temperature from 15 to 45 °C using the revised model. The results are shown in Figure 3. The results are very close to those predicted by Mane et al. (2009). The results show that boron rejection increases with increasing pH but decreases with increasing temperature. The effect of pH is more obvious at higher temperatures and more intense with pH level between 8 to 9. The maximum boron rejection of 99.16 % is obtained at 15 °C and pH 12 and the lowest boron rejection of 83.74 % is obtained at 45 °C and pH 6.

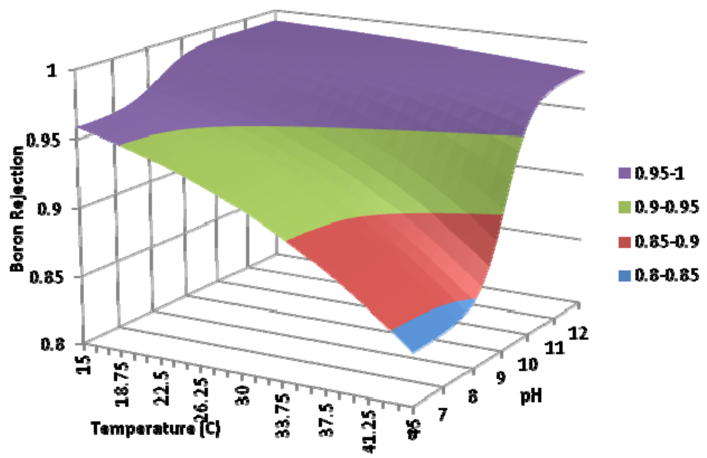

Figure 3: Effect of temperature and pH on boron rejection

5. Conclusions

In this work, a reliable model for RO desalination process is developed based on well known solution-diffusion model incorporating a number of recently developed correlations for effective boron rejection. The initial model has been validated against a set of experimental results operating at constant temperature of 25 °C. At higher temperature (45 °C), discrepancy is noticed between the predictions by this initial model and those by other boron rejection models available in the literature. The initial model is then revised to minimise this discrepancy and the revised model is revalidated against another set of experimental results from literature which was carried out at a higher temperature (35 °C). The revised model is then used for further simulations by varying operating conditions such as pH and temperature. The computational results of other models are found to be comparing well with those obtained by using our revised model. The simulations carried out under three deferent operating conditions (pH, temperature, pressure) provides the opportunity to choose the best combination of these operating conditions that could yield the better end result, concerning the water quality with respect to boron levels.

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