

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.

2. RO Boron Rejection Model

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

Eq. 1 gives the water permeability as water temperature varies while Eq. 2 gives salt permeability as water temperature varies.

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.

$$P_w = A_0 e^{\left(\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right)} \left(\frac{10^{-3}}{24 \times 60 \times 60}\right) \quad (1)$$

$$P_s = B_{st0} e^{\left(\frac{-E_{Bst}}{R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right)} \left(\frac{10^{-3}}{24 \times 60 \times 60}\right) \quad (2)$$

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]. The values for E_A & A_0 as well as B_{st0} & E_{Bst} have to be calculated experimentally for each membrane separately.

Sea Water Density (Hyung and Kim, 2006):

The formula for the calculation of sea water density in relation to the sea water salinity and temperature is presented below.

$$\rho = 498.4 * (1.0069 - 2.757 * (10^{-4}) * (T - 273.15)) \pm \sqrt{248400 * (((1.0069 - 2.757 * (10^{-4}) * (T - 273.15)))^2 + 752.4 * (1.0069 - 2.757 * (10^{-4}) * (T - 273.15)) * CSf)} \quad (3)$$

Where: T is temperature in Kelvin. C_{sf} is salt concentration at the feed stream measured in kg per cubic meter.

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

The following expressions Eq. 4 & Eq. 5 give the osmotic pressure at feed and permeate side of the membrane. Eq. 6 gives the net osmotic pressure deference across the membrane.

$$\pi_F = (0.6955 + 0.0025(T - 273.15)) \times 10^8 \times \frac{C_{SF}}{\rho} \quad (4)$$

$$\pi_P = (0.6955 + 0.0025(T - 273.15)) \times 10^8 \times \frac{C_{SP}}{\rho} \quad (5)$$

$$\Delta\pi = \pi_F - \pi_P \quad (6)$$

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/m³].

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

$$J_W = P_W (\Delta P - \Delta\pi) \quad (7)$$

where J_W is water flux [Kg H₂O/cm²]. ΔP is hydraulic pressure deference across the membrane [Pa].

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

According to Taniguchi et al., 2001 the salt mass transfer coefficient can be described by following equation developed based on the osmotic pressure method.

$$K_S = 1.63 \times 10^{-3} Q_F^{0.4053} \quad (8)$$

where K_S is the mass transfer coefficient [m/s]. Q_F is the volumetric flow rate of feed stream [m³/s].

$$J_S = P_S (C_{SM} - C_{SP}) \quad (9)$$

where J_S is the salt flux, C_{SM} is the salt concentration at membranes feed side surface [kg/m³] and C_{SP} Salt concentration at Permeate side (also defined as $C_{SP} = \frac{J_S}{J_W}$).

By substituting the salt flux expression into $C_{SP} = \frac{J_S}{J_W}$, which is a basic equation of solution diffusion model it gives:

$$C_{SP} = \frac{P_S * (C_{SM} - C_{SP})}{J_W} \quad (10)$$

Solving for C_{SP} it gives:

$$C_{SP} = \frac{C_{SM}}{\frac{J_W}{P_S} + 1} \quad (11)$$

Solving for C_{SM} it gives:

$$C_{SM} = C_{SP} * \frac{J_W}{P_S} \quad (12)$$

Concentration Polarization (Taniguchi et al., 2001):

$$\frac{C_{SM} - C_{SP}}{C_{SF} - C_{SP}} = e^{\left(\frac{J_W}{K_S}\right)} \quad (13)$$

Solving Eq. 13 for C_{SP} it gives:

$$C_{Sp} = \frac{C_{sf} * e^{\left(\frac{JW}{K_S}\right)} - C_{Sm}}{e^{\left(\frac{JW}{K_S}\right)} - 1} \quad (14)$$

Substituting Eq. 14 into Eq. 12 and by eliminating C_{Sp} , C_{Sm} is given by the following relationship:

$$C_{Sm} = \frac{C_{sf} * \exp\left(\frac{JW}{K_S}\right) * \left(\frac{JW}{P_S} + 1\right)}{\exp\left(\frac{JW}{K_S}\right) - 1 + \left(\frac{JW}{P_S} + 1\right)} \quad (15)$$

So by first calculating C_{Sm} using Eq. 15, then C_{Sp} can be calculated by making use of Eq. 11.

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):

$$pH = pK_a + \log \frac{C_{Bborate}}{C_{Bboric}}; \quad C_{BF} = C_{Bborate} + C_{Bboric} \quad (16)$$

$$pK_a = \frac{2291.9}{T} + 0.01756 - 3.385 - 3.904 \times C_{SM}^{\frac{1}{3}} \quad (17)$$

$$C_{Bboric} = \frac{C_{BF}}{1 + 10^{(pH - pK_a)}} \quad (18)$$

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:

$$\alpha_0 = \frac{C_{Bboric}}{C_{BF}}; \quad \alpha_1 = \frac{C_{Bborate}}{C_{BF}}; \quad \alpha_0 + \alpha_1 = 1 \quad (19)$$

Boron Flux, Mass Transfer Coefficient and Permeability:

Boron flux equation is similar to Eq. 9 but instead of salt concentration, boron concentration is to be used. Also, the boron concentration polarization equation is similar to Eq. 13 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):

$$P_B = \alpha_0 P_{Bboric} e^{(0.067(T-298.15))} + \alpha_1 P_{Bborate} e^{(0.049(T-298.15))} \quad (20)$$

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

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 %. During the Mane et al. (2009) experiments performed using RE4040-SR the feed water salinity was 34,000 mg/l, the temperature was kept constant at 25°C. Also three simulation scenarios which were performed as part of Mane et al. (2009), research (by their model which was based on the Irreversible Thermodynamic Model) were also executed by the model developed during the current research in order to be able to explore and validate the models behaviour at a wider spectrum. All three simulation scenarios were executed by making use of the Macro developer (Programming Facility) within the Excel. Also at all three simulations, the feed water TDS was set at 32,000 mg/l. During the first scenario the pH range varied from 6 to 12, using 0.25 pH increments in-between, while also the pressure was varied from 600 to 1000 psi using 20 psi increments in-between. The temperature during this simulation was held constant at 25°C. During the second simulation the pressure varied from 600 to 1000 psi using 20 psi increments in-between while also the temperature varied from 15 to 45 degrees Celsius using 1.25 °C increments. The pH during this simulation was held constant at the value of 8. During the third simulation the pH level varied from 6 to 12 using 1.25 increments in-between, while also the temperature varied from 15°C to 45°C using 1.25 °C increments in-between. The pressure during this simulation was held constant at the value of 800 psi.

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. Figure 1 presents the graphical representation produced by running the model developed during the current study for the same range of variables and same constants as Mane et al. (2009) model. 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). As can be seen the accuracy of the model is fluctuating from a minimum error of 0.04% to a maximum error of 1.74% with an average error of 0.78%. These results are compared very favourably with the results of the mathematical model developed during the Mane et al. (2009) research. Their mathematical model's predictions had a maximum relative error of 2% which is higher than the relative error of the model developed during the current research, which does not overcome the maximum value of 1.74%. So the reliability of the model developed during the current research is deemed to be relatively high. Finally 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

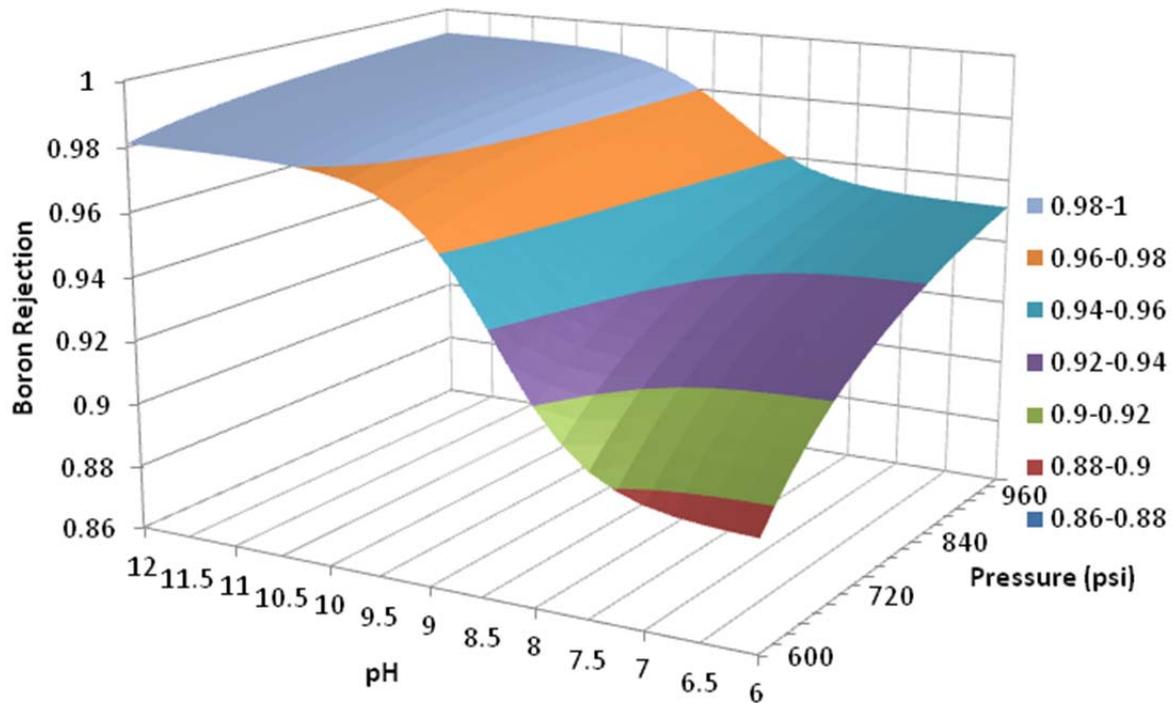


Figure 1: Effect of pH and pressure on boron rejection

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

At this second simulation the behaviour of the model was examined, during Temperature & Pressure Variation at the pH level of 8. Figure 2 presents the graphical representation of the results generated by the simulation described above. The maximum boron rejection percentage of 97.82% was achieved at 15°C and 1000 psi, while the lowest 70.06% was achieved at 45°C and 600 psi. Note, that the results produced by the two models differ by almost 6.5 % especially at the lowest predicted values. For this reason a method was developed in order to calibrate the temperature depended behaviour of the model. It was decided that the most efficient way to do this calibration was through the modification of Boron permeability expression, i.e. Eq.20 which is reproduced below.

$$P_B = \alpha_0 P_{Bboric} e^{(0.051(T-298.15))} + \alpha_1 P_{Bborate} e^{(0.033(T-298.15))} \quad (20a)$$

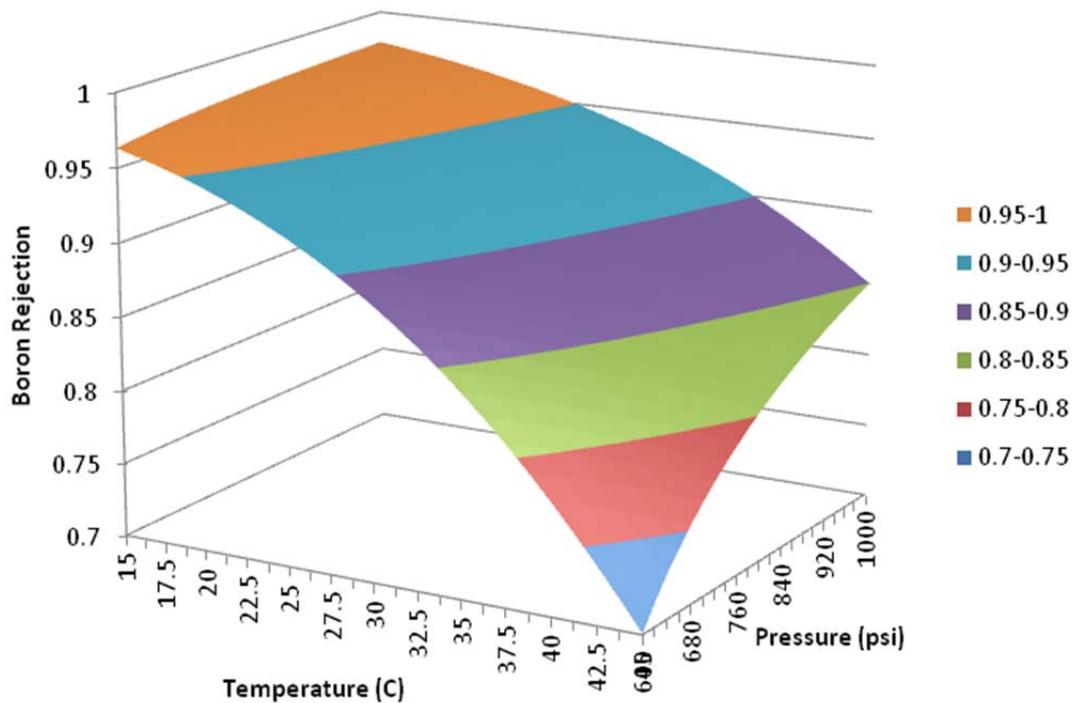


Figure 2: Effect of temperature and pressure on boron rejection

The idea which was employed was that if the boric and borate permeability dependence on temperature variation was made smaller, this would cause a subsequent increase of the models boron rejection. By observing Eq. 20 it can be seen that the boric and borate permeability dependence on temperature, is caused by the two exponential terms that are multiplied with each boron permeability. These two exponential terms are designed to just act as multipliers of the boric and borate permeability, adjusting with this way the temperature dependence of the overall boron permeability. The attention during this attempt of calibration was focused at the two constant terms within the two exponential terms. The idea that was employed, was that by subsequently decreasing the values of the two constant terms, and by calculating the relative average error produced between the maximum and the minimum values produced each time by the model compared with the results produced by the Mane et al. (2009), a reduced combination of those two terms should ultimately give the smallest relative error. Ultimately the two terms had to be reduced both by 0.016 units in order to give the smallest average relative error between the maximum and minimum values predicted by the current model's simulation results, and Mane et al. (2009) model's results. A problem arises from the fact that within the Mane et al. (2009) paper there is no information about any experimental results (except at 25°C), obtained for a variety of temperatures, that could be used in order to actually see if the simulated results much well with the experimental results. The solution to this problem came from the experiments performed by Hyung and Kim (2006) using the same RO membrane (RE4040-SR) used by this projects simulation model. Hyung and Kim (2006), tested the boron rejection performance of the membrane using as feed water a solution containing 14,000 TDS at 9.5 pH. They tested the membrane at a temperature of 35°C, and at 5 deferent pressure levels 600, 700, 800, 900, 1000 psi. Table 4 presents results obtained during the Hyung and Hong (2006) experiments and, also the results obtained by this studies model simulation. The model developed as part of this study, predicted well the experimental results, having a maximum relative error of 1.15% and minimum relative error of 0.66 %.

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.

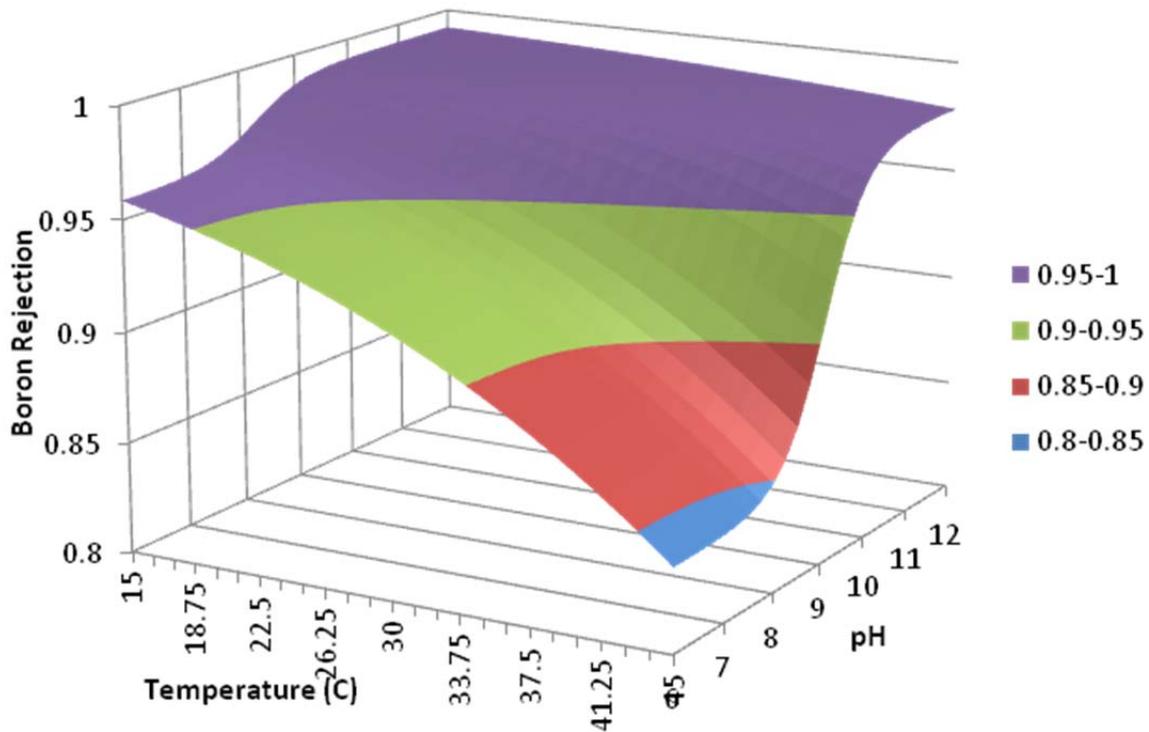


Figure 3: Effect of temperature and pH on boron rejection

5. Results and Discussion

5.1 Operating Pressure Influence on Boron Rejection

During the first and second simulations which were performed during this project, the fact was indicated that boron rejection percentage is generally increased as operating pressure is increasing. This increase is a result of the so called dilution effect that takes place because of the fact that the water flux through membrane is directly proportionally to the operating pressure increase (see Eq.7), while on the other hand the boron flux does not depend at all on the operating pressures variations. The pressure effect is more obvious and more intense at lower pH and higher temperatures.

For example during first simulation, by using a 32 kg/m³ TDS feed water, at 25°C and pH level of 6, at 600psi the model was predicting a boron rejection percentage of 89% while at 1000 psi this percentage was increased at 95%, achieving a 6% increase. For the same conditions but at a pH level of 12 at 600 psi, the boron rejection percentage was 98% and at 1000 psi 99%, causing a 1% increase.

Also the effect of pressure and temperature to the boron rejection, was studied during the second simulation, where again by using a 32 kg/m³ TDS feed water, at 8 pH and 45°C, at 600psi the model was predicting a boron rejection percentage of 76% while at 1000 psi this percentage was increased at 88%, achieving a 12% increase. For the same conditions but at a temperature of 15°C at 600 psi the boron rejection percentage was 95% and at 1000 psi 97%, causing a 2% increase of the boron rejection percentage.

5.2 Operating Temperature Influence on Boron Rejection

During the second and third simulations which were performed during this study, the fact was indicated that boron rejection percentage is generally decreasing as feed water temperature is increasing. This decrease is caused mainly because boron flux is directly proportional to the boron permeability which is directly proportional to temperature variations, while on the other hand the water flux dependence on temperature variations is much smaller. The temperature effect is more obvious and more intense at lower pressures and lower pH levels.

For example by using a 32 kg/m³ TDS feed water, at 8 pH and 600 psi, at 15°C the model was predicting a boron rejection percentage of 95% while at 45°C this percentage was decreased at 76%, causing a 19% decrease. For the same conditions but at a pressure level 1000psi at 15°C, the boron rejection percentage was 97% and at 45°C 88%, causing a 9% decrease of the boron rejection percentage.

Also the effect of temperature and pH level in relation to the boron rejection percentage was studied during the third simulation where again by using a 32 kg/m³ TDS feed water, at 800psi and 6 pH, at 15°C the model was predicting a boron rejection percentage of 96% while at 45°C this percentage was decreased at 83%, achieving a 13% decrease. For the same conditions but at a pH level of 12 at 15°C the boron rejection percentage was 99% and at 1000 psi 97%, causing a 2% decrease of the boron rejection percentage.

5.3 Operating pH Level Influence on Boron Rejection

During the first and third simulations which were performed during this study, the fact was indicated that boron rejection percentage is generally increasing as feed water pH level is increasing. This increase is caused because the increase of the pH level is causing the better rejected borate ion (H₂BO₃) to become the dominant species, decreasing with this way the boron permeability and i.e. decreasing the boron flux. The pH effect was more obvious at lower pressures and higher temperatures and more intense while the pH level was increasing from 8 to 9.

For example during first simulation, by using a 32 kg/m³ TDS feed water, at 25°C and 600psi, at the pH level of 6 the model was predicting a boron rejection percentage of 89% while at the pH level of 12 this percentage was increased at 99%, achieving a 10% increase. For the same conditions but at 1000 psi, the boron rejection percentage at 6pH was 95% and at 12pH was 99%, causing a 4% increase of the boron rejection percentage.

Also the effects of pH and temperature in relation to the boron rejection, was studied during the third simulation where again by using a 32 kg/m³ TDS feed water, at 800psi and 45°C, at 6 pH the model was predicting a boron rejection percentage of 84% while at 12 pH this percentage was increased at 98%, achieving a 14% increase. For the same conditions but at a temperature level of 15°C, at 6 pH the boron rejection percentage was 96% and at 12 pH 99%, causing a 3% increase of the boron rejection percentage.

6. 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 different 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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