Desalination and Water Treatment
www.deswater.com

15 (2010) 129–133
March

doi: 10.5004/dwt.2010.1676

Understanding boron rejection by reverse osmosis membranes

June-Seok Choi[a], Jae-Seok Cho[a], Sangho Lee[a*], Tae-Mun Hwang[a], Hyunje Oh[a], Dae Ryook Yang[b], Joon Ha Kim[c]

[a]*Korea Institute of Construction Technology, 2311 Daehwa-Dong, Ilsan-gu, Kyonggi-do, Korea*
Tel. +82 (31) 910-0320; Fax +82 (31) 910-0295; email: s-lee@kict.re.kr
[b]*Department of Chemical & Biological Engineering, Korea University, Seoul, 136-701, Korea*
[c]*Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST) Gwangju, 500-712, Korea*

Received 12 November 2009; Accepted in revised form 24 December 2009

ABSTRACT

Reverse osmosis (RO) membranes have high rejection for most of solutes in seawater except for boron. Therefore, boron rejection should be considered in the design and operation of the RO process for seawater desalination. In this paper, we investigated boron rejection and its relation to salt rejection using an irreversible thermodynamic model. Permeability constants for commercially-available RO membranes were obtained using theoretical model and the simulation data from membrane performance test program provided by membrane manufacturers. The effect of pH and concentration of the feed water on the boron rejection was also theoretically investigated under various operating conditions. The model calculations revealed that the rejection of boron follows a different mechanism from those of other ionic solutes and could not be readily correlated with ion rejections. To overcome the limit of mechanistic models, we explored an alternative approach for predicting boron permeability from membrane properties and ion permeability. It appears that this alternative approach can aid to achieve a better understanding of boron rejection by seawater RO membranes.

Keywords: Seawater desalination; Reverse osmosis; Boron; Rejection; Modeling

1. Introduction

RO seawater desalination is spreading as a regular technology to produce fresh water from seawater due to various advantages such as energy saving and small footprint. However, rejection of boron by RO membranes is an important issue [1]. Boron naturally occurs in seawater at an average concentration of 4–6 mg/L, and the WHO requires boron concentration in drinking water to be below 0.5 mg/l [2]. This requirement has affected seawater reverse osmosis (SWRO) process design because of the difficulty of SWRO membranes in achieving such low boron concentration [3].

Boron is present in seawater as boric acid (H_3BO_3) and borate ion ($H_2BO_3^-$), with their respective concentrations depending on pH. Borate ion is rejected by RO membranes at relatively high levels (90–99%) due to charge-repulsion, but boric acid, which does not have a negative charge, is not rejected well (30–90%). Since the pKa1 of the equilibrium $H_3BO_3 \rightarrow H_2BO_3^- + H^+$ at a typical ionic strength of seawater is approximately 8.7, boric acid is the major species in natural seawater (pH of ~8),

* Corresponding author.

Presented at SeaHERO Academic Workshop on Development and Optimization of SWRO Desalination Systems Korea University, Seoul, Korea, November 13–14, 2009

resulting in a relatively low overall boron rejection by SWRO membranes [4].

Potential solutions to this problem include double-pass configurations, multi-stage treatment, and the addition of boron specific ion-exchange resin [5]. For any design option, pH control is critical in determining overall boron removal. Selection of RO membranes is also important because the characteristics of boron rejection by different RO membranes are various. For RO membranes with very high salt rejection, boron rejection can be up to 91–93%. However, it can be lower than 80% even for RO membranes with relatively high salt rejection.

The objective of this study was to investigate boron rejection of RO membranes in connection with their salt rejection. Using projection programs from membrane manufactures, commercially available RO membranes were theoretically examined to obtain apparent transport parameters for water, salt, and boron. The relations among these parameters were evaluated to provide insight into further understanding of boron rejection phenomena.

2. Theoretical approach

A simple model was developed to calculate transport characteristics of RO membranes from simulation or experimental results. The following assumptions were used for the model derivation:

- The solution–diffusion model is valid for the transport of water and solute through the membrane. This can be justified by the fact that the reflection coefficients of salt and boron for seawater RO membranes are close to 1.
- Diffusion coefficient is independent of solute concentration.
- The brine concentration varies linearly along an RO element.
- The thin film theory is applicable for calculating concentration polarization effect.
- Pressure drop in permeate side is neglected.
- Mass transfer coefficient is constant for a given fluid condition.

Based on these assumptions, the solvent and solute transports are given by [6]:

$$J = L_p\left(P_f - \Delta\pi - P_d\right) \tag{1}$$

$$J_{s,i} = Jc_{p,i} = L_{s,i}\left(\frac{c_{m1,i} + c_{m2,i}}{2} - c_{p,i}\right) \tag{2}$$

$$c_{m1,i} = \left(c_{b,i} - c_{p,i}\right)e^{\frac{J}{k_i}} + c_{p,i} \tag{3}$$

$$c_{m2,i} = \left(c_{c,i} - c_{p,i}\right)e^{\frac{J}{k_i}} + c_{p,i} \tag{4}$$

$$Q_f c_{b,i} = Q_c c_{c,i} + Q_p c_{p,i} \tag{5}$$

$$Q_f = Q_c + Q_p \tag{6}$$

where L_p is the solvent transport parameter, $L_{s,i}$ is the solute transport parameter for the ith solute, J is the solvent flux [m/s], $J_{s,i}$ is the solute flux [mol/m^2-s], $c_{m1,i}$ is the wall concentration at the inlet of element [mol/m^3], $c_{m2,i}$ is the wall concentration at the outlet of element [mol/m^3], $c_{p,i}$ is the solute concentration at permeate side [mol/m^3], $c_{b,i}$ is the feed concentration at brine side [mol/m^3], $c_{c,i}$ is the concentrate concentration at brine side [mol/m^3], P_f is the feed pressure, $\Delta\pi$ is the osmotic pressure difference [Pa], P_d is the pressure drop along a RO system [Pa], Q_f is the feed flow rate [m^3/s], Q_c is the concentrate flow rate [m^3/s], and Q_p is the permeate flow rate [m^3/s]. Using this simple model approach, L_v and $L_{s,i}$ were calculated from P_f, P_d, and $c_{p,i}$.

Total 15 RO membranes were selected for this work. Projection programs including ROSA, IMSDesign, and TorayRO were used to simulate rejections of salt and boron as well as water permeability. Two standard conditions were applied as listed in Table 1. The simulation was carried out at a constant flow condition (Q_f = 200 m^3/d).

Boron was assumed to be present in boric acid form at pH 7 and in borate form at pH 12 [4]. Furthermore, the temperature dependence of transport parameters was ignored here because the simulation was performed at constant temperature.

3. Results and discussion

RO simulation was performed using the projection programs to study transport characteristics for salt and boron based on our simple model. Table 2 summarizes these simulation results and transport parameters. The salt rejection of the RO membranes ranges from 0.945 to 0.997. Except for brackish RO membranes, the rejections are over 0.99. On the other hand, the boron rejection at pH 7 (or boric acid rejection) is quite different for different membranes. It ranges from 0.34 to 0.892, indicating high passages through most RO membranes. The boron rejection at pH 14 (or borate rejection) is higher than that at pH 7, ranging between 0.82 and 0.99. These results suggest that charge of ionic species is important in RO rejection.

Since water permeability of each RO membrane is different, feed pressures are various to produce the same amount of permeate. Depending on water permeability, the feed pressure of the RO membranes ranges from 34 bar to 53 bar. Under this condition, permeable flux values are between 16.7 L/m^2-h (for an RO membrane with a surface area of 40.9 m^2) and 19.4 L/m^2-h (for an RO

Table 1
Simulation conditions

	Feed	Element	Temperature (°C)	Recovery (%)	pH
Condition 1	NaCl: 35,000 mg/L Boron: 5 mg/L	Single (8 inch)	25	8	7
Condition 2	NaCl: 35,000 mg/L Boron: 5 mg/L	Single (8 inch)	25	8	12

Table 2
Salt and boron rejection from RO simulations

Membrane	J	TMP	C_f(NaCl)	C_p (NaCl)	C_f (boron)	C_p (boron)	pH	L_p	L_s (NaCl)	L_s (boron)
M1	19.4	38.1	35000	636	5	3.1	7	1.78E+00	8.70E-08	1.25E-05
M1	19.4	38.1	35000	637	5	0.6	12	1.78E+00	8.71E-08	1.24E-06
M2	19.4	52.6	35000	142.8	5	0.6	7	7.75E-01	1.93E-08	1.71E-06
M2	19.4	52.6	35000	224.8	5	0.1	12	7.73E-01	3.04E-08	2.60E-07
M3	19.4	50.9	35000	152.5	5	0.6	7	8.31E-01	2.06E-08	1.66E-06
M3	19.4	52.6	35000	240	5	0.2	12	7.73E-01	3.25E-08	5.29E-07
M4	17.94	45.9	35000	179.6	5	0.9	7	9.77E-01	2.25E-08	2.38E-06
M4	17.94	45.9	35000	282	5	0.2	12	9.73E-01	3.53E-08	4.62E-07
M5	17.94	43.2	35000	246	5	1.2	7	1.14E+00	3.08E-08	3.19E-06
M5	17.94	43.2	35000	386.3	5	0.4	12	1.13E+00	4.85E-08	9.02E-07
M6	16.69	33.8	35000	1918	5	2.7	7	2.18E+00	2.33E-07	8.39E-06
M6	16.69	33.8	35000	1926	5	0.6	12	2.18E+00	2.34E-07	1.10E-06
M7	17.94	38.9	35000	660	5	3.1	7	1.53E+00	8.35E-08	1.28E-05
M7	17.94	38.9	35000	662.3	5	0.6	12	1.53E+00	8.38E-08	1.27E-06
M8	17.94	35.3	35000	1185	5	3.3	7	2.10E+00	1.52E-07	1.34E-05
M8	17.94	35.3	35000	1189	5	0.9	12	2.10E+00	1.53E-07	1.83E-06
M9	17.9	40.5	35000	210.3	5	1.31	7	1.38E+00	2.63E-08	3.34E-06
M9	17.9	40.5	35000	210.9	5	0.07	12	1.38E+00	2.63E-08	1.39E-07
M10	17.9	43.9	35000	140.2	5	0.88	7	1.10E+00	1.75E-08	2.22E-06
M10	17.9	43.9	35000	140.5	5	0.05	12	1.10E+00	1.75E-08	1.08E-07
M11	17.9	43.9	35000	140.5	5	0.88	7	1.10E+00	1.75E-08	2.22E-06
M11	17.9	43.9	35000	140.5	5	0.05	12	1.10E+00	1.75E-08	1.08E-07
M12	17.9	48.5	35000	107.1	5	0.54	7	8.56E-01	1.33E-08	1.40E-06
M12	17.9	48.5	35000	107.1	5	0.04	12	8.56E-01	1.33E-08	9.49E-08
M13	17.9	52.87	35000	149.2	5	0.66	7	7.07E-01	1.86E-08	1.92E-06
M13	17.9	52.87	35000	159.82	5	0.04	12	7.07E-01	1.99E-08	1.03E-07
M14	17.9	42.14	35000	511.17	5	3.1	7	1.20E+00	6.43E-08	1.39E-05
M14	17.9	42.14	35000	159.82	5	0.08	12	1.23E+00	1.99E-08	1.66E-07
M15	17.9	40.58	35000	511.23	5	3.1	7	1.35E+00	6.43E-08	1.33E-05
M15	17.9	40.97	35000	159.82	5	0.08	12	1.33E+00	1.99E-08	1.61E-07

membrane with a surface area of 35.3 m^2). The concentration polarization ratio was estimated to be less than 1.1, which was calculated using the programs provided by membrane manufactures.

In this work, transport parameters were used to compare the characteristics of RO membranes rather than fluxes. This is because the simulations were carried out under constant pressure conditions. In this case, the driving force is almost constant and the flux can be directly correlated with transport parameters. In practical application of SWRO systems, the permeate flux generally lies between 10–15 L/m^2-h. Thus, it is likely that the effect of the driving force on boron rejection is not important in practical RO systems.

The results in Table 2 seem to show that there is no clear correlation among L_v, L_s (NaCl), and L_s (boron).

Membranes with high salt rejection may have high boron rejection but boron rejection is not proportional to salt rejection. In addition, boric acid rejection and borate rejection do not have clear dependency. Similarly, membranes with low water permeability do not necessarily have high boron rejection. This is probably because the rejection mechanisms of boron and salt are quite different.

To further analyze the rejection characteristics of various RO membranes, a series of plots were attempted using the data in Table 2. Fig. 1 compares the L_s (NaCl) with L_p values. It is likely that these two parameters have clear dependency. Membranes with smaller water permeability generally have tight structures leading to a high salt rejection. A third order polynomial regression results in a reasonable fitting to the data as indicated as a curve in Fig. 1.

Nevertheless, L_s (boric acid) is not dependent on L_p as shown in Fig. 2. For RO membranes with low L_p values, it is likely that L_s (boric acid) slightly increases with increasing L_p. For other membranes, there seems to be no dependency at all. Again, this result suggests that the rejection mechanisms of boric acid and salt are different.

Fig. 3 illustrates the relationship between L_s (borate) and L_p. Compared with L_s (boric acid), L_s (borate) is more dependent on L_p. Nevertheless, it has a poor correlation. A close look at the data in Fig. 3 reveals that there are two groups of RO membranes which have different dependency of L_s (borate) on L_p. Membranes that have L_s (borate) higher than 2×10^{-7} m/s have a linear relationship between L_s (borate) and L_p while those having L_s (borate) lower than 2×10^{-7} m/s have almost constant L_s (borate) regardless of L_p.

L_s (boric acid) and L_s (NaCl) are compared in Fig. 4. It is likely that there is a linear relationship between two values for RO membranes with low L_s (NaCl) (i.e. L_s (NaCl) lower than 1×10^{-7} m/s). For those membranes, L_s (boric acid) values are more than 100 times higher than L_s (NaCl) values, implying that the boric acid passage is much larger than salt passage.

Fig. 5 compares L_s (borate) with L_s (NaCl). Here, the correlation between two values is better than that between L_s (boric acid) with L_s (NaCl). This suggests that the rejection mechanisms of borate and NaCl are similar.

Based on these results, it is likely that there are certain types of RO membranes which have different rejection characteristics for salt, boric acid, and borates. To further analyze this, the ratio of L_s (boric acid) to L_s (borate) was illustrated as a function of L_s (NaCl) in Fig. 6. The boron rejection by the RO membranes with a high value of this ratio can be significantly improved by increasing solution pH. The results indicate that there are two types of RO membranes:

- Type 1: RO membranes with high rejection of salt and high ratio of L_s (boric acid) to L_s (borate).
- Type 2: RO membranes with low rejection of salt and low ratio of L_s (boric acid) to L_s (borate).

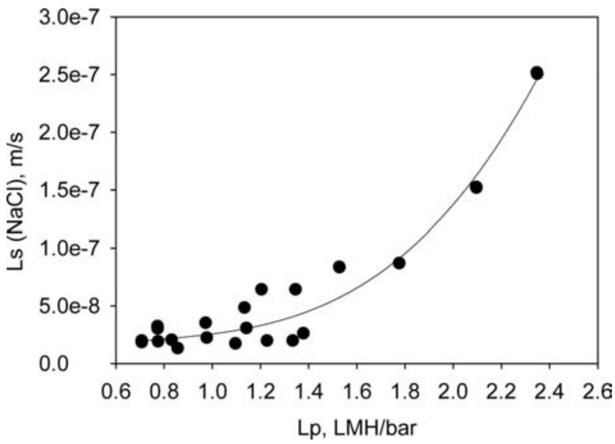

Fig. 1. Correlation between L_p and L_s (NaCl).

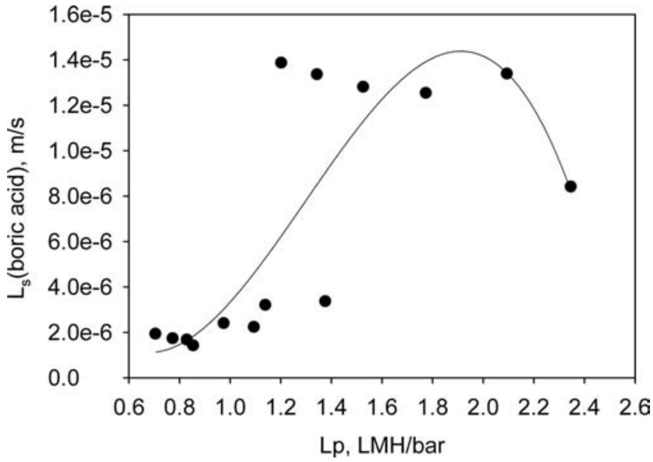

Fig. 2. Correlation between L_p and L_s (boric acid).

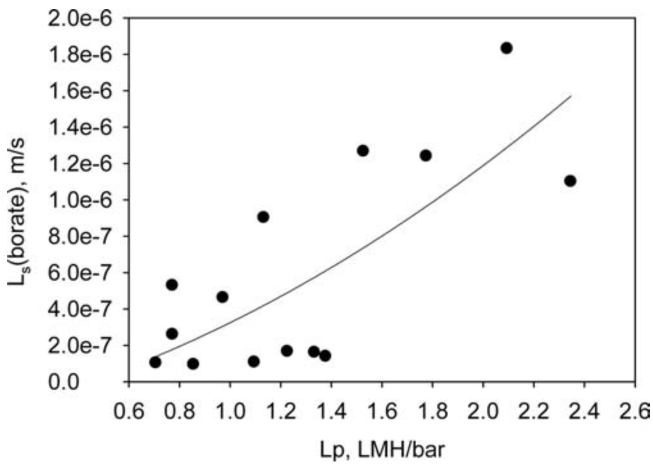

Fig. 3. Correlation between L_p and L_s (borate).

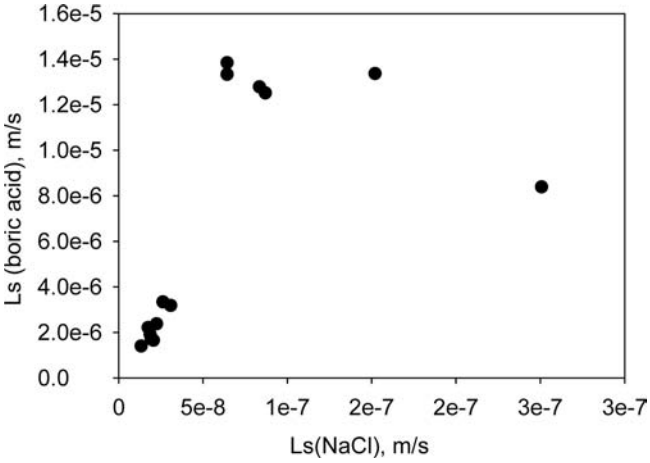

Fig. 4. Correlation between L_s (NaCl) and L_s (boric acid).

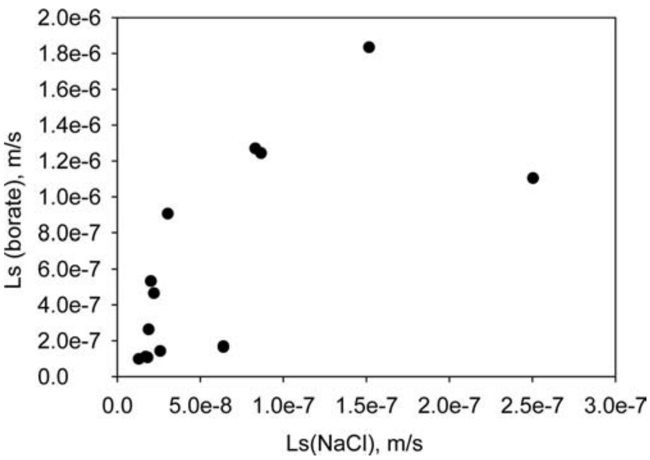

Fig. 5. Correlation between L_s (NaCl) and L_s (boric acid).

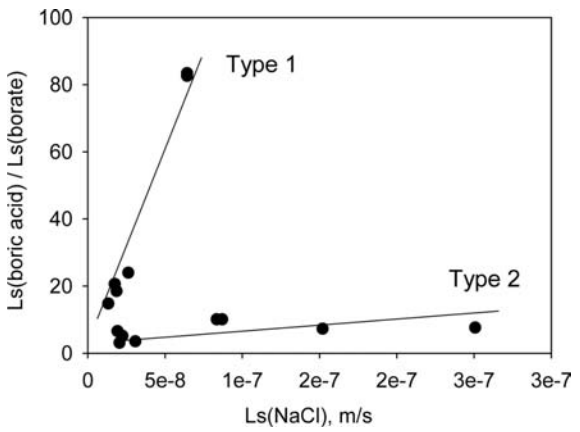

Fig. 6. Correlation between the ratio of L_s (boric acid) to L_s (borate) and L_s (NaCl).

Since the negative charge of solute is important for salt and borate rejections, it is likely that Type 1 membranes have higher charge density than Type 2 membranes. However, further study should be done to correlate the physico-chemical characteristics of RO membranes with these transport properties.

4. Conclusions

In this work, boron rejection by RO membranes was theoretically investigated using the RO simulation results from projection programs of membrane manufactures. A simple model based on the solution–diffusion model and thin film theory was applied to estimate apparent transport parameters for RO membranes. It was found that L_s (NaCl) was proportional to L_p, suggesting that tighter RO membranes have higher salt rejection. However, L_s (boric acid) was not clearly dependent on L_p. L_s (borate) was also proportional to L_p, but its dependency was worse compared with that between L_s (boric acide) and L_p.

Comparison of L_s (boric acid) and L_s (NaCl) indicates that the rejection mechanisms of salts and boric acid are different. It is hypothesized that the physico-chemical characteristics of RO membrane materials are more important for boron rejection than for NaCl rejection. It is evident from the results that there are two types of RO membranes having different boron rejection characteristics. This may be attributed to a different charge densities of RO membranes. Further works should be done to correlate the physico-chemical characteristics of RO membranes with these transport properties.

Acknowledgements

This research was supported by grants 07seaheroB03-02 and 07seaheroB02-01-02 from the Plant Technology Advancement Program funded by the Ministry of Land, Transport and Maritime Affairs of the Korean government.

References

[1] A. Mnif, B. Hamrouni and M. Dhahbi, Boron removal by membrane processes. Desal. Wat. Treat., 5 (2009) 119–123.
[2] E. Borads, Guidelines for Drinking Water Quality. WHO, 2nd ed., 1993.
[3] P.P. Manea, P.-K. Park, H. Hyung, J.C. Brown and J.-H. Kim, Modeling boron rejection in pilot- and full-scale reverse osmosis desalination processes. J. Membr. Sci., 338 (2009) 119–127.
[4] H. Hyung and J.-H. Kim, A mechanistic study on boron rejection by sea water reverse osmosis membranes. J. Membr. Sci., 286 (2006) 269–278.
[5] Y. Magara, A. Tabata, M. Kohki, M. Kawasaki and M. Hirose, Development of boron reduction system for sea water desalination. Desalination, 118 (1998) 25–33.
[6] H.-J. Oh, T.-M. Hwang and S. Lee, A simplified simulation model of RO systems for seawater desalination. Desalination, 238 (2009) 128–139.