Boron reduction performance of reverse osmosis seawater desalination process

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Abstract

In recent years, seawater desalination systems using reverse osmosis (RO) membranes have been constructed to settle the lack of drinking water. RO desalination membranes have high rejection for most of solutes in seawater. Japanese drinking water standards for the water quality of the permeate can be achieved except for boron. Therefore, the boron rejection needs to be considered in the design of the RO process and during the operation of the plant. Luckily, there is a simple and easy method to estimate boron concentration.

In this paper, we report measured boron permeabilities and their relation to salt permeabilities using cross-linked polyamide membranes. Chemical degradation of the membranes affected these permeabilities to different degrees. Boron concentrations in the permeate were then calculated using a computer program that was based on the boron permeabilities calculated from the measured salt permeabilities. Results obtained were compared with actual data taken at a RO plant of Toray Industries, Inc., Ehime. The model data fitted the experimental result, well. It was also found that a relationship existed in the permeate between salt and boron concentrations and that the boron concentration can be obtained from measurement of the salt concentration.

1. Introduction

In reverse osmosis (RO) seawater desalination plants for drinking water, product water quality must pass the drinking water standards. According to the WHO guidelines, the boron concentration should be lower than 0.2 mg/l. This value is too low for conventional reverse osmosis desalination plants using commercially available membranes, and this problem has been avoided by diluting the permeate with water from other sources, which contain very low boron concentrations, such as those from a distillation plant. Although a two-stage process was studied to reduce boron, it was still difficult to reduce the boron level below 0.2 mg/l [3].

Recently, Japanese drinking water standards have been revised, and the limit of boron concentration in the permeate was raised to 1 mg/l. This value, however, is still low for the standard RO plants, and it is important to determine how to pass this standard. For RO process, the membranes are sometimes degraded by chemical, biological and mechanical stress. Chlorine used for the sterilization of this process is one

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of the main causes. Hence, it is important to estimate the permeate concentration of boron under the various experimental conditions.

In this paper, we first measured the permeabilities of salt (total dissolved salt in seawater) and boron under various operating conditions, and obtained a proportional relationship between the salt and boron permeability. Second, we inserted this relationship into a previously developed and verified computer program [1,2]. Using this program, we estimated the boron concentration from the salt concentration in the permeate. This data was also measured in actual plant. As a result, the estimated value agreed well with the measured value. Finally, simple relationship between salt concentration and boron concentration in the permeate was constructed, using the relationship between salt and boron permeabilities. A reasonable comparison was obtained between this equation and measured data.

2. Theory

2.1. Basic equations

The concentration of salt (total dissolved solids) and boron at a membrane surface, $C_{SM}$ and $C_{BM}$ are given by the concentration polarization model [4].

$$\frac{Q_{PO}}{C_{SM} - C_{SP}} = \exp \left( \frac{J_V}{k_S} \right),$$

(1)
\[ \frac{C_{BM} - C_{BP}}{C_{BB} - C_{BP}} = \exp \left( \frac{J_V}{k_B} \right). \]  
(2)

where \( k_S \) and \( k_B \) are the mass transfer coefficients of salt and boron, respectively. The transport equations of the volume flux and the salt flux through the membranes, whose rejection is very high,

\[ J_V = L_P[\Delta p - \{\pi(C_{SM}) - \pi(C_{SP})\}] \]  
(3)

\[ J_S = P_S(C_{SM} - C_{SP}) \]  
(4)

As for boron flux, boron rejection is not so high as salt, and it is necessary to use following equation and to obtain the value of \( \sigma_B \) by experiment.

\[ J_B = P_B(C_{BM} - C_{BP}) + (1 - \sigma_B)C_B J_V. \]  
(5)

Eq. (5) were transformed by Spiegler and Kedem [5] to eliminate the average concentrations, \( C_B \), and to give the boron rejection \( R_B \), as follows.

\[ R_B \equiv \frac{C_{BM} - C_{BP}}{C_{BM}} = \frac{\sigma_B(1 - F_B)}{1 - \sigma_B F_B} \]  
(6)

\[ F_B = \exp \left[ -\frac{J_V(1 - \sigma_B)}{P_B} \right]. \]  
(7)

When \( \sigma_B \) are close to 1, the boron flux is also given by

\[ J_B = P_B(C_{BM} - C_{BP}), \]  
(8)

where \( C_{SP} \) and \( C_{BP} \) are also expressed as

\[ C_{SP} = \frac{J_S}{J_V} \]  
(9)

\[ C_{BP} = \frac{J_B}{J_V} \]  
(10)

2.2. Estimation of membrane transport parameters

The mass transfer coefficients of salt and boron are determined by mass transfer equation expressed at Section 4.1. Once they are obtained, the membrane transport parameters of RO element can be calculated from the flux and the salt rejection data, using the computer program previously developed [2].

2.3. Estimation of boron concentration in permeate

A membrane element is divided into \( N \) sections along the feed flow direction. Mass balance equations of salt is same as previous paper [2] and that of boron is given as

\[ C_{BPO} = \frac{\sum_{i=1}^{N} C_{BPi} \Delta Q_{Pi}}{Q_{PO}} \]  
(11)

\[ = \sum_{i=1}^{N} \left( \frac{P_B C_{BMi}}{J_{Vi} + P_B} \right) J_{Vi} \Delta hW. \]  
(12)

When the mass transfer coefficient and membrane transport parameters, \( L_P, P_S \) and \( P_B \), are given, one can estimate \( Q_{PO}, C_{SPO} \) and \( C_{BPO} \) for the RO unit under various operating conditions.

The properties of the seawater were calculated in the same way as our previous paper [1,2].

3. Experimental

3.1. Membranes and test cell

We conducted this experiment to obtain a relationship between the salt and boron permeabilities. In this experiment, we first made four types of membranes, using the cross-linked fully aromatic polyamide membranes, UTC-80, manufactured by Toray Industries, Inc., Ehime, Japan. As a result of dipping in the various concentration of NaClO solutions (Table 1), the membranes which have different permeabilities were obtained from chemical degradation. In this process, the RO membrane is sometimes degraded by chemical, biological and mechanical stress. Chlorine used for the sterilization is one cause

<table>
<thead>
<tr>
<th>No.</th>
<th>Membrane</th>
<th>Concentration of NaClO a (mg/l)</th>
<th>Dip time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>UTC-80</td>
<td>Not</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>40</td>
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</tr>
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</table>

a Solvent: 3.5 wt.% seawater, pH = 7.0, 25°C.
of degradation. Hence, it is reasonable to use this method to simulate the actual membrane property changes in seawater desalination, because this type of degradation is one of the main cause of flux changes.

The test cell used in this experiment is shown in Fig. 1. In this cell, the diameter of the effective membrane is 63 mm (membrane area: 31.2 cm²), and the thickness of feed channel is 3 mm. The measurement of the flux and the rejection is under the conditions, shown in Table 2. By using measured flux and rejection, the permeabilities of the salt and boron were calculated.

For boron, reflection coefficient, \( \sigma_B \), was found to be very close to 1, as shown in Fig. 2, where \( R_B \) is plotted against \( 1/J_V \), and the lines were obtained by curve fitting \([6]\) based on Eqs. (6) and (7). \( R_B \) is equal to \( \sigma_B \) at \( y \) intercept. Hence, the permeability can be calculated by using Eqs. (1)–(4) and (8).

### Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>( \Delta \rho ) (Mpa)</th>
<th>( J_V ) ( \times 10^{-6} ) m/s</th>
<th>( C_{SP} ) (mg/l)</th>
<th>( C_{BP} ) (mg/l)</th>
<th>( L_P ) ( \times 10^{-12} ) m³ Pa s</th>
<th>( P_S ) ( \times 10^{-9} ) m/s</th>
<th>( P_B ) ( \times 10^{-9} ) m/s</th>
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<td>8.34</td>
<td>32.0</td>
<td>1887</td>
</tr>
</tbody>
</table>

\( ^a \) Measured condition \( Q_F = 5.8 \times 10^{-5} \) m³/s; \( C_{SB} = 35,000 \) mg/l; \( C_{BB} = 4.0 \) mg/l; \( \text{pH} = 7.0, 25^\circ \text{C} \).
permeabilities of the salt and boron increase as the concentration of NaClO. It is said that the polyamide membrane is not so durable to chlorine and is degraded because of the cleavage of the amide-bond and Orton transition [7]. The mechanism is shown in Fig. 3.

Also, the permeabilities of salt and boron do not change with the applied pressure.

Next, a correlation between salt and boron permeabilities is shown in Fig. 4.

\[ P_B = 94.3 P_S. \]  
(14)

For reference, we obtained membranes, which were mechanically degraded by scratching the surface of the membranes, and measured their permeabilities. The results are shown in Fig. 4 as filled circles.

Mechanical degradation causes the feed water to leak to the permeate side. The higher the rejection, the larger the influence to the permeate concentration. The experimental result in Fig. 4 indicates that boron permeability did not change as much as the salt permeability.

The result of Eq. (14) is quite simple, but it is not clear as to the reason this relationship is valid and

Fig. 3. Chlorine degradation mechanism proposed for aromatic polyamide.

Fig. 4. Salt permeability vs. boron permeability obtained by flat sheet membrane. Feed solution is sea water (TDS: 35,000 mg/l and boron: 4.0 mg/l); \( \bigcirc, \bigodot, \blacksquare \) are chemical degraded and operated at the applied pressures of 4.4, 5.5 and 6.9 MPa, respectively; \( \bullet \) is mechanical degraded and operated at 5.5 MPa.
whether the simple relationship should be applicable to different membranes. Generally, rejection for RO membranes depends on the filtration through its pore size and electrical repulsive force. Boron exists in the seawater as boric acid, \( \text{H}_3\text{BO}_3 \). Since it is not dissociated, the rejection of boron is related to its molecular size. On the other hand, salt rejection is related to its size and the electric force of the dissociated ions. To solve this, further study is necessary to determine the mechanism of degradation and rejection, considering the distribution of membrane pores and electrical charges.

4. Estimation of boron concentration in permeate

4.1. Mass transfer coefficient of spiral-type element

For the simulation calculations, the mass transfer coefficients of a spiral-type element, designated SU-820, were used obtained before [2].

4.2. Estimated result

Using all of the results explained above, first, one can calculate the \( L_P \) and \( P_S \) values from daily-measured data on volume flux and salt concentration in the permeate, and thus one can follow their change with time using the computer program developed earlier. Next, \( P_B \) values can be estimated from \( P_S \) using Eq. (14). Finally, the boron concentration in the permeate can be estimated using \( P_B \) and an integrated computer program, used Eq. (14). Actual running data were taken from the 140 m³/day RO test plant at Toray Ind. Factory in Ehime, a flow diagram of which is shown in Fig. 5.

Due to changes in the membrane permeabilities, it is necessary to correct the operating pressure effect, and the permeate temperature effects on \( L_P \) and \( P_S \), which were obtained in previous paper [2].

It is assumed that the same corrections to \( P_S \) can be also applied to \( P_B \), as a first approximation. This assumption will be examined by comparing the calculated and the measured data.

The first result obtained is shown in Fig. 6, where the \( L_P \) and \( P_S \) data taken for one year are shown. A slight decrease in \( L_P \) and a slight increase in \( P_S \) can be observed in Fig. 6. The results for boron concentrations are shown in Fig. 7, where the agreement of calculated values with measured values is seen to be good. This result means that the imposed mechanical degradation had minimal effect, because the Eq. (14) accurately predicted the actual results.

5. Relationship between salt and boron concentration in permeate

A method was successfully established to determine the boron concentration in the permeate using the relationship between the salt permeability and the boron permeability. However, this method is complicated, and it is desirable to determine the boron concentration in the permeate from the salt concentration in the permeate, which is easily obtained from the electric conductivity.

In the course of the above calculations, we found that there is a definite relationship between salt and boron concentrations regardless of various operating conditions. This was confirmed by developing the following equations.

The value of the boron concentration divided by the salt concentration is expressed as follows, using

![Flow diagram of test plant at Ehime factory.](image-url)
Fig. 6. $L_P$ and $P_S$ of test plant vs. time calculated from actual operating data (normalized at 25°C and 5.5 MPa of applied pressure).

Eqs. (1), (2), (4), (8)–(10).

$$\frac{C_{SB} - C_{SP}}{C_{SP}} = \frac{P_B \exp(J_V/k_B)}{P_S \exp(J_V/k_S)} \frac{C_{BB} - C_{BP}}{C_{BP}}.$$  \hspace{1cm} (15)

The next three relationships are reasonable in this RO seawater desalination process

RO membranes used for seawater desalination has a performance of high rejection, and the first approximation is as

$$C_{SB} \gg C_{SP}.$$  \hspace{1cm} (16)

The second, $C_{BM}/C_{BB}$ is less than 1.3 at general operating conditions, and

$$\frac{J_V}{k_B} = \ln \left( \frac{C_{BM} - C_{BP}}{C_{BB} - C_{BP}} \right) < \ln(1.3).$$  \hspace{1cm} (17)

The last relation is obtained by the mass transfer equation, using diffusivity, calculated from Wilke–Chang’s Equation [8],

$$\frac{k_S}{k_B} = \left( \frac{D_S}{D_B} \right)^{0.75} = 0.97.$$  \hspace{1cm} (18)

Fig. 7. Boron concentration in the permeate vs. time; (—) calculated line by computer program; (○) measured data.
and Eq. (19) is reached.

$$\frac{\exp(J_N/k_B)}{\exp(J_N/k_S)} \approx \frac{\exp(J_N/k_B)}{\exp(J_N/0.97k_B)} = \exp\left(\frac{J_N}{k_B}\right)^{0.03} \approx 0.96$$  

(19)

Therefore, Eq. (15) can be simplified to Eq. (20).

$$C_{BP} \approx \frac{C_{BB}C_{SP}}{C_{SB}(P_S/P_B)} + C_{SP}.$$  

(20)

Here, Eq. (20) means that the relationship between $C_{BP}$ and $C_{SP}$ is influenced only by the value of $P_S/P_B$, because $C_{SB}$ and $C_{PB}$ can be treated as constant values in one kind of seawater as follows.

However, the actual operating data may be influenced by changes in flow conditions along the membrane elements. We simulated the relation between the $C_{BP}$ and $C_{SP}$ by a computer program under various operating conditions. The calculation result is shown in Fig. 8, in which the symbol (●) represents the value obtained by the simulation, (○) values were obtained at the actual plant and the solid line is obtained using Eq. (20), confirms that $C_{BP}$ is a function of $C_{SP}$ and can be easily estimated from $C_{SP}$. In addition, it is useful to adopt Eq. (20) to estimate $C_{BP}$ approximately without a computer simulation. Thus, the boron concentration can be determined by measuring only the salt concentration.

6. Conclusions

To cope with the revised Japanese drinking water standards regarding boron, which need to be lower than $1.0 \times 10^{-3}$ kg/m$^3$ (1.0 mg/l), the permeabilities of boron were determined using a RO membrane, UTC-80, made by Toray Industries, Inc., and were reported. In the measurement, four pieces of membrane were used, which were chemically degraded to a different degree by NaClO treatment to clarify the effect of membrane degradation on salt and boron permeabilities. As a result, we found that they can be correlated by a proportional relationship at UTC-80 membrane. Using a computer program, developed previously, $L_P$ and $P_S$ values and their changes with time were first obtained from the daily volume flux and salt concentration in the permeate taken from the RO unit running at Toray Ind., Factory at Ehime, for one year. $P_B$ values were then obtained from $P_S$ using the relation stated above and were used to calculate the boron concentrations, which coincided well with the actual data. This result shows that mechanical degradation hardly affected permeabilities in this RO unit.

Furthermore, we also found that a specific relationship exists between the salt and boron concentrations in the permeate regardless of the various operating conditions, and this was confirmed by solving transport equations. The results in this study enables one to estimate the boron concentration in the permeate from the measurement of salt concentration in the permeate, by using the computer programs or easy calculation. However, it was obtained using our cross-linked polyamide membranes, and further research is necessary to clarify the mechanism which enables to apply to other different membranes.

References


