

Boron Removal in Radioactive Liquid Waste by Forward Osmosis Membrane

Doo-Seong Hwang*, Hei Min Choi, Kune Woo Lee, Jei-Kwon Moon
KAERI, Daeduck-daero, Youseong-gu, Daejeon 305-353, Korea
*Corresponding author: dshwang@kaeri.re.kr

1. Introduction

Liquid radioactive waste is generated during nuclear reactor operations. The chemical composition and radioactivity level of the liquid waste depend on the reactor type and the performed operation. PWRs have experienced leakages of boric acid into liquid radioactive waste systems. These wastes contain about 0.3-0.8 wt% boric acid and have been concentrated through an evaporation treatment. Boric acid tends to crystallize owing to its solubility, and to plug the evaporator. The volume reduction obtained through evaporation is limited by the amount of boric acid in the waste [1].

As an emerging technology, forward osmosis (FO) has attracted growing interest in wastewater treatment and desalination. FO is a membrane process in which water flows across a semi-permeable membrane from a feed solution of lower osmotic pressure to a draw solution of higher osmotic pressure [2]. However, very few studies on the removal of boron by FO have been performed [3]. The objective of this study is to evaluate the possibility of boron separation in radioactive liquid waste by FO. In this study, the performance of FO was investigated to separate boron in the simulated liquid waste under the factors such as pH, osmotic pressure, ionic strength of the solution, and membrane characteristic.

2. Material and Experimental

Simulated waste solutions containing boric acid were prepared for the test. Draw solutions of various concentrations were prepared using a NaCl. FO membrane was obtained from HTI (Hydration Technology Innovations). Two commercial FO membranes were used and they are CTA (cellulose triacetate)-NW and CTA-ES of HTI.

The concentration of boron was measured through inductively coupled plasma atomic emission spectrometry (OPTIMA 7300 DV). The pH of the working solutions was measured by pH meter (Orion 3 Star Plus).

An FO membrane sheet with an effective membrane area of 5 cm (W) X 10 cm (L) was housed in a cross flow membrane cell. Rectangular-patterned stainless steel spacers were placed on both side of the membrane to allow cross flows of the feed solution as well as the draw solution. The initial volume of the feed and draw solution tank was 250 ml. Two pumps were used to recirculate the feed and draw solutions, and a pressure

gauge and flow meter were installed through a tubing line, respectively. The cross flow velocity of the feed and draw solution was fixed at 25 and 17 cm/s and the pressure was 8.5 and 5.5 psi, respectively. The cross flow velocity is calculated based on the ratio of the cross flow rate to the cross section area, which is 5 cm (W) X 0.2 cm (D), of the flow channel. The feed and draw solution temperature was maintained at 20 °C. The membrane permeate flux such as water and boron flux was determined at a certain time interval by measuring the weight change of the feed solution tank with a digital mass balance connected to a computer data logging system.

3. Results and Discussion

The structure of the CTA-NW with a cellulose triacetate polymer cast on a weldable nonwoven screen is similar to that of a typical thin film composite membrane. The CTA-ES membrane which is supported by an embedded polyester mesh is different from the thin film composite membrane. Most researchers use a CTA-ES type of membrane in their FO studies because of its higher water flux as compared to a CTA-NW [4].

Internal concentration polarization (ICP) is one of the most important phenomena in osmosis membrane processes. It is known that the water flux in FO decreases from ICP. Two types of ICP, namely dilutive ICP (active layer facing feed, ALFF) and concentrative ICP (active layer facing draw, ALFD) can occur within the membrane support layer, as shown in figure 1 [5]. When the draw solution is placed against the membrane support layer, dilutive ICP will occur within the membrane support layer as water permeates across the membrane from the feed solution to the draw solution. In the alternative membrane orientation (i.e. the feed solution facing the membrane support layer), concentrative ICP occurs as the solute in the feed solution accumulates within the membrane support layer [4]. Therefore, both membrane orientations, ALFF and ALFD, were tested in this study.

Figure 2 shows a pure water flux as a theoretical osmotic pressure of the draw solution and the sodium chloride concentration. As expected, the water flux increased with osmotic pressure. The water flux of the CTA-ES is higher compared to the CTA-NW. It is confirmed that the CTA-ES is more permeable compared to the CTA-NW. The water flux of the ALFD membrane orientation is higher than the ALFF orientation. This is due to a drastic loss of the effective osmotic driving force of ALFF (dilutive ICP) compared

to the ALFD (concentrative ICP), as shown in figure 4. The water through the active layer of the membrane dilutes the concentration of the draw solution inside the membrane support layer for the ALFF.

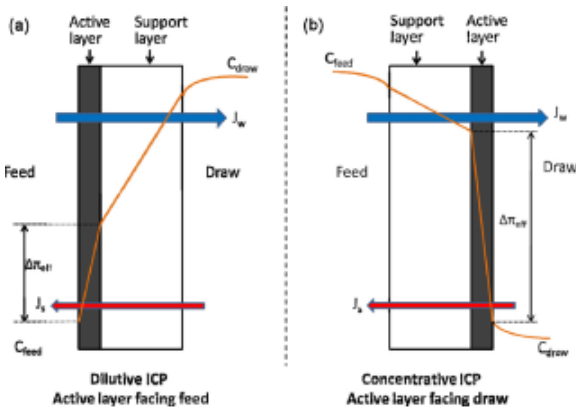


Fig. 1 Schematic of dilutive and concentrative ICPs across an FO membrane.

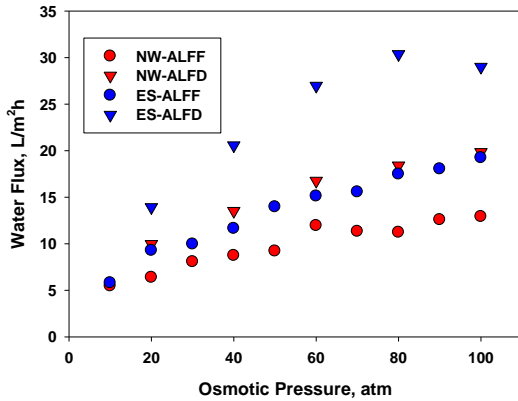


Fig. 2 Pure water flux as a theoretical osmotic pressure of the draw solution.

The measured water and boron flux as a pH through the ALFF and ALFD orientation of the CTA-NW membrane are shown in figures 3 (a) and 3 (c), respectively. The boron concentration in the feed solution was 300 mg/l, and the osmotic pressures of the draw solution were 40 and 80 atm. The water flux is not influenced by the pH of the feed solution, and the behavior of the water flux with osmotic pressure and membrane orientation is similar to the results of figure 5. The boron flux increases with an increase in the osmotic driving force, such as the water flux, but it begins to decline from pH 7 regardless of the osmotic pressure and membrane orientation. The hydrolyzed species of boron in an aqueous solution are a $B(OH)_3$ less than pH 7, $B(OH)_4^-$ more than pH 10 and a slight amount of $B_2(OH)_7^-$ and $B_3(OH)_{10}^{3-}$ in the range of pH 7-10. Boron is present for borates of more than pH 7, and borates do not permeate through the membrane [1]. It was confirmed that boric acid in an aqueous solution of less than pH 7 can permeate through the membrane easier than borates in an alkali aqueous solution. The behavior

of the boron flux with osmotic pressure and membrane orientation is just like the water flux. It is known that the ALFD orientation shows a lower boron flux at a higher salinity feed solution because of the concentrative ICP influence of salt in support layer [3]. However, this influence is thought to not affect the boron permeation because there is no salt in the feed solution. The boron permeation rate as a pH through the ALFF and ALFD orientation of the CTA-NW membrane are shown in Figures 6 (b) and 6 (d), respectively. The permeation rate of boron in the membrane is defined as in the following equation:

$$\text{Permeation} = C_{d,B}/C_{f,B} \quad (C_{d,B} = J_B/J_W) \\ = J_B/(J_W * C_{f,B})$$

where $C_{d,B}$ and $C_{f,B}$ are the boron concentration in the feed and draw solution and J_B and J_W are the boron and water flux, respectively. The boron permeation also begins to decline from pH 7 regardless of the osmotic pressure and membrane orientation. The permeation rate is constant regardless of the osmotic pressure and membrane orientation because permeation is as a function of the boron and water flux.

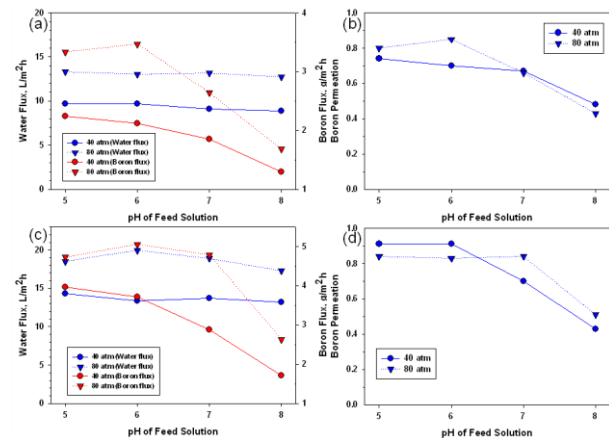


Fig. 3 Water/boron flux and boron permeation behavior as a pH of feed solution through the ALFF (a, b) and ALFD (c, d) orientation of the CTA-NW membrane.

Figure 4 shows the water and boron flux and the boron permeation rate of the CTA-ES under the same condition of the CTA-NW. The results of the CTA-ES are approximately similar to that of the CTA-NW, but there are some differences between the two membranes. The water flux seems to not be influenced by the pH of the feed solution, but the ALFD orientation (c) shows a slightly decreasing trend. The boron flux tends to decrease with an increase in pH, but the decrement is smaller than in the CTA-NW. In addition, the boron flux of the ALFF orientation (a) does not depend nearly on the osmotic pressure. The boron flux of the ALFD orientation (a) is relatively much lower than in the other membrane or orientation. It is thought that the active layer of the CTA-ES membrane would reject the boron somewhat, unlike the CTA-NW membrane.

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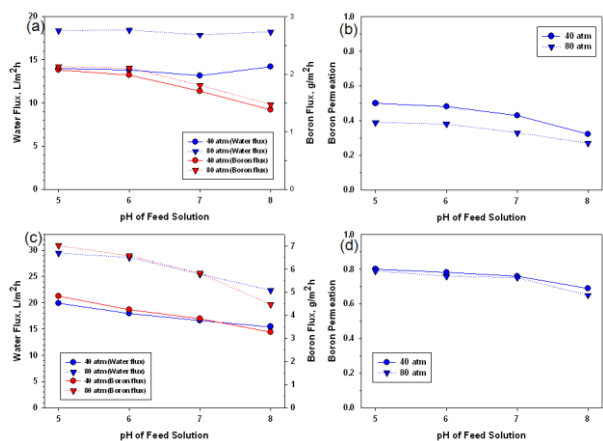


Fig. 4 Water/boron flux and boron permeation behavior with a pH variation of the feed solution through the ALFF (a, b) and the ALFD (c, d) orientations of the CTA-ES membrane.

Figure 5 shows the results of the boron flux and permeation rate at different salt (KCl) concentrations using the ALFF orientation of the CTA-NW membrane. The boron concentration and pH in the feed solution were 300 mg/l and 6, and the osmotic pressure of the draw solution was 80 atm. The boron flux decreases slightly, but it is not heavily influenced by salt. It is known that the boron removal is better at a higher salinity [6], but salt at 1,000 mg/l is thought to not affect the boron permeation.

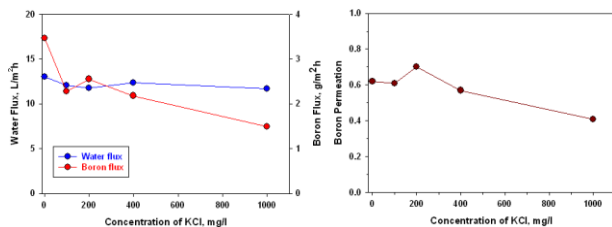


Fig. 5 Effect of KCl concentration on boron flux and permeation rate.

4. Conclusions

The boron separation in radioactive borate liquid waste was investigated with an FO membrane. When the feed solution containing boron is treated by the FO membrane, the boron permeation depends on the type of membrane, membrane orientation, pH of the feed solution, salt and boron concentration in the feed solution, and osmotic pressure of the draw solution. The boron flux begins to decline from pH 7, and increases with an increase in the osmotic driving force. The boron flux of the CTA-ES and ALFD membrane orientation is higher than those of the CTA-NW and ALFF orientation, respectively. The boron permeation rate is constant regardless of the osmotic pressure and membrane orientation. The boron flux decreases slightly with the salt concentration, but it is not heavily influenced at a low salt concentration.