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Boron removal from seawater by combined system of seawater reverse osmosis membranes and ion exchange process: a pilot-scale study

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ABSTRACT

One of the problems of seawater reverse osmosis desalination plants is high boron concentration in product water. Accordingly, several post treatment methods have been researched for boron removal. One objective of this study is to evaluate the effect of key operating parameters such as pH, temperature, pressure and feed concentration on boron rejection and in pilot-scale SWRO-IX system. The performance of boron-selective ion exchange resin Amberlite IRA 743 was also evaluated by two resin columns treating SWRO permeate. The experimental results at various operating conditions would help optimize the process operation.

Keywords: Desalination; Seawater; Reverse osmosis (RO); Boron removal, Boron selective resin

1. Introduction

Seawater desalination technology using reverse osmosis (RO) membranes has been considered as the most attractive and environmentally friendly way among many desalination processes. With development of seawater reverse osmosis (SWRO) desalination technology, presently, majority of the commercialized RO membranes are able to remove above 99% of salt in seawater. However, due to the ability to diffuse through the membranes in a non-ionic way and very small molecule of boron [1,8,11], an RO membrane is not very effective for boron removal to meet the drinking water quality requirements [2]; The limit of boron concentration of the World Health Organization(WHO) in SWRO desalination plant permeate is 0.5 mg/L [3]. In this study using WOONGJIN (RE4040-SHN), FILTEC (SW30HRLE-4040) and TORAY (TM810L) membranes, boron rejection was 82–85%, and about 1 mg/L of boron was normally found in permeate as the system was operated with seawater containing 4–5 mg/L boron at operational conditions of pH 8 and 25°C. Therefore, several modifications and post-treatment methods would be necessary in order to improve the efficiency of boron rejection [4–8]. Previous studies suggested that boron rejection by RO membranes would improve as pH is increased, temperature decreased and operating pressure increased [9,11]. Particularly, much higher boron rejection was obtained (98%) at pH of 10.5 than those at the natural pH level of seawater (7.8–8.2) [12,14] as the fraction of negatively-charged borate $B(OH)_4^-$ ion becomes dominant [1,13,15]. However, increasing pH can cause another serious problem, making scale that damages membranes. Hence, boron rejection process under relatively low pH conditions is needed to prevent this problem. Many additional treatment steps for boron removal have been studied such as pH adjustment of feed water, dilution of RO permeate, passing the desalinated

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water through extra RO stages and ion exchange post-treatment of RO permeate [7]. Consequently, as one of the most effective and applicable methods, compounding high rejection RO membranes boron selective resins has been taken into consideration. In this study, a pilot-scale combined system of high rejection RO membranes and boron selective resins was evaluated in terms of boron rejection.

2. Experimental

2.1. Materials and apparatus

Artificial seawater (ASW) was used in the experiments. All chemicals used are pure grade chemicals. Raw sea salt, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, KCl and $MgSO_4$ were provided by DC Chemicals (Korea) and boric acid was provided by Sigma-Aldrich (USA). Concentrations of each material in ASW are summarized in Table 1.

Three commercialized polyamide thin-film composite SWRO membranes — RE4040-SHN, SW30HRLE-4040 and TM810L — manufactured by WOONGJIN Chemical (Korea), Dow Chemical (USA) and TORAY (Japan), respectively, were used in this study. Table 2 is a detailed specification that each company provides. Boron-selective ion exchange resin Amberlite IRA 743 (Rohm & Haas) was utilized to remove boric acid and borate from seawater was used for the column test.

2.2. Description of the pilot plant

A 4-inch SWRO pilot was used to evaluate the performance of a 4-inch SWRO membrane (Fig. 1). It was designed to be able to simultaneously assess the performance of two membranes under the same conditions. A feed tank is able to store 400 L of solution. The feed solution was pre-treated by a safety filter that contained microfiltration polypropylene membranes in cylindrical modules. Feed temperature was controlled by a cooler as designed condition. An industrial pump (Wanner Engineering, USA, model G-35) was used to give high pressure to membranes, and applied pressure could be controlled using valves which are near the concentrate line. Pressure and flow rate of the concentrate and permeate were measured by a pressure gauge (P252 SERIES) and flow meter (Dwyer, USA) in order. The SWRO permeate was treated further with two vertical columns of 1.35 L filled with Amberlite IRA 743 resins whose properties are summarized in Table 3. The column height was 700 mm and its diameter was 50 mm.

2.3. Experimental methods

The membrane operating pressure tested was 42.18 kg_f/cm^2 (600 psi), 49.21 kg_f/cm^2 (700 psi), 56.25 kg_f/cm^2 (800 psi), 59.76 kg_f/cm^2 (850 psi). Conductivity and pH were measured by OAKIN conductivity meter (Singapore) and Orion pH meter (USA) respectively. Concentration of boron was analyzed by ICP-OES

Table 1
Feed analysis (mg/L)

Na	10,000
Ca	310
SO_4	320
Boron	5
Mg	2,100
K	620
Cl	19,000
TDS	33,000

Table 3
Properties of IRA743 (mg/L)

Matrix	Macroporous polystyrene
Functional group	N-methylglucamine
Physical form	Beige-coloured beads
Ionic form as shipped	Free base (FB)
Total capacity	0.7 eq/L
Harmonic mean size	0.500–0.700 mm

Table 2
Specification of SWRO membranes used

Product name	Effective membrane area	Permeate flow rate	Stabilized salt rejection (%)	Stabilized boron rejection (%)	Test conditions
RE4040-SHN (WOONGJIN)	74 ft^2 (6.9 m^2)	1,200 GPD (4.5 m^3/d)	99.6	90	32,000 mg/L NaCl, 800 psi (5.5 MPa), 77°F (25°C), 8% recovery, pH 6.5–7.0
SW30HRLE-4040 (FILMTEC)	85 ft^2 (7.9 m^2)	1,600 GPD (6.1 m^3/d)	99.75	91	32,000 mg/L NaCl, 800 psi (5.5 MPa), 77°F (25°C), 8% recovery. pH 8, 5 ppm boron
TM810L (TORAY)	73 ft^2 (6.8 m^2)	1,600 GPD (6.1 m^3/d)	99.75		32,000 mg/L NaCl, 800 psi (5.5 MPa), 77°F (25°C), 8% recovery. pH 7

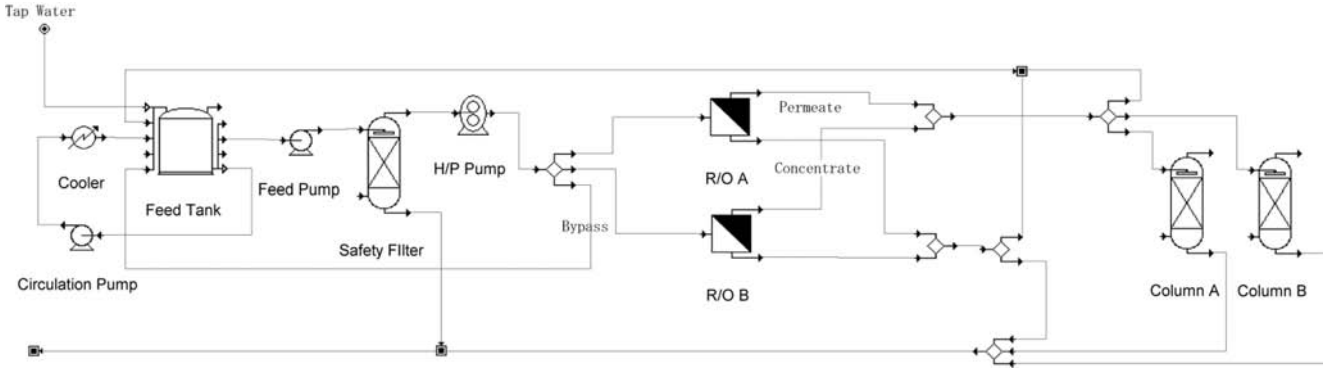

Fig. 1. Schematic of the pilot system.

(inductively coupled plasma–optical emission spectrometer). Permeate from RE4040-SHN, SW30HRLE-4040 and TM810L membranes was passed to a designated column with 270 ml/min flow rate and 5 min retention time in accordance with reference [17].

3. Results and discussion

3.1. Effect of pressure and salinity on boron rejection

Three permeate samples were taken on a hourly basis at each pressure (600, 700, 800, 850 psi) and average data was used with the following conditions: 33,000 ppm NaCl, 5 ppm boron, 77°F (25°C), pH 7.5–8. The impact of pressure on boron rejection is shown in Fig. 2. As expected, as the membrane pressure increased from 600 to 850 psi, the permeate flux also increased for three membrane types. This result suggested that boron rejection increased as the feed pressure increased due to the dilution effect of the permeate water at a higher water flux. In this study, boron rejection of three membranes from 600 psi to 850 psi increased by around 10%.

Fig. 3 demonstrates the experimental data conducted with the variation of salinity. Boron rejection of all RO membranes tested showed a similar tendency to decrease as salinity increased. The permeate flux decreased considerably as the salinity increased due to the increase of osmotic pressure. On the other hand, the boron flux somewhat decreased in comparison with the permeate flux. Accordingly, the decline of water flux made boron concentration in the permeate higher. Since the differences in boron rejection are relatively small compared to pH and temperature effect, the inherent experimental errors in permeate boron measurements should be considered.

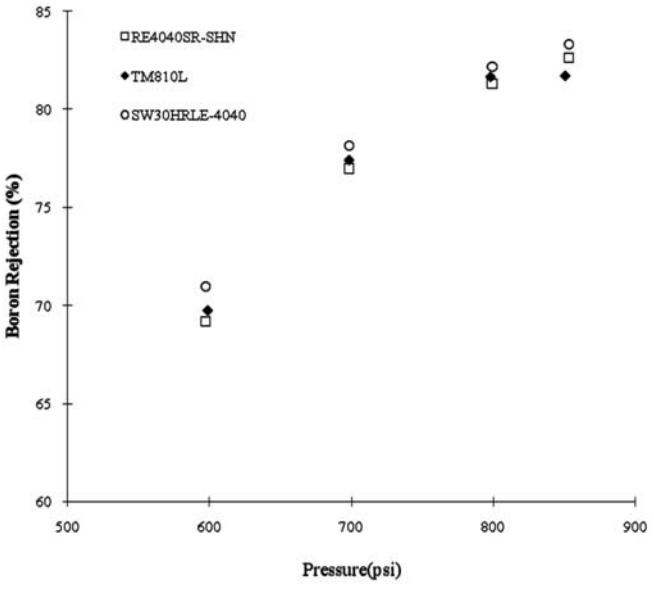

Fig. 2. Impact of pressure on boron rejection.

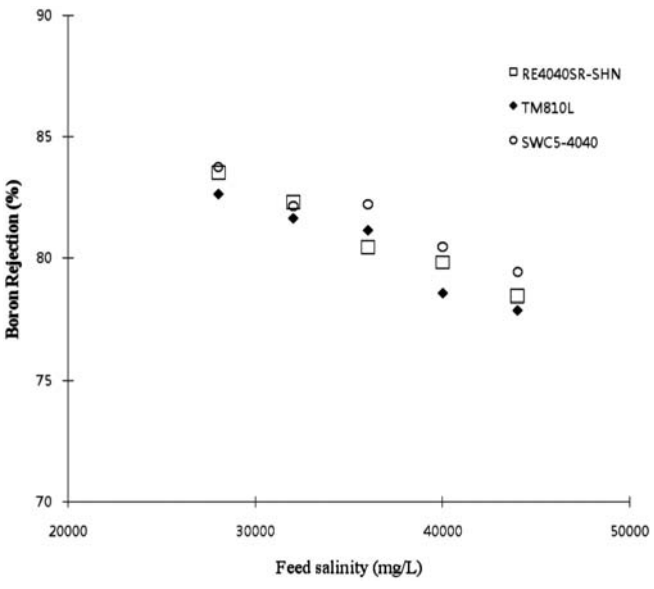

Fig. 3. Impact of salinity on boron rejection.

3.2. Effect of pH and temperature on boron rejection

A circulation mode was applied in the membrane performance test. In the circulation mode, both concentrate and permeate streams were returned to the feed tank. Therefore, concentration of boron and other materials in the feed tank did not increase during the membrane performance test. The performance test of the RO membrane in terms of boron rejection was conducted for 24 h under the conditions of 33,000 mg/L TDS, 5 mg/L boron, operating pressure 800 psi and temperature 25±1°C. The boron rejection of the RO membranes tested at nominal conditions and natural seawater pH was relatively constant between 82 and 85% during the 24 h operation period. About 0.7–0.9 mg/L of boron was normally found in the permeate from artificial seawater. The low boron rejection at low pH is because a majority of boron exists as boric acid $B(OH)_3$ which is very small and uncharged at a natural pH range. The fraction of negatively-charged borate ion $B(OH)_4^-$ becomes a dominant species as pH increases.

$$B(OH)_3 + 2H_2O \Leftrightarrow B(OH)_4^- + H_3O^+,\ pKa = 8.6–9.2$$

It is known that charged species for many ionic compounds are rejected to a greater extent by many RO membranes through electrostatic repulsion. The charge repulsion between negatively charged borate ions and the negatively charged membrane surface at high pH results in decreased diffusive transport of boron through the membrane.

Experimental results obtained at varying temperature conditions from 5 to 35°C are shown in Fig. 4 suggesting that the boron rejection of all membranes tested was largely dependent on temperature variation. Temperature is another significant factor which affects the boron rejection properties of the SWRO membranes. The higher temperature, the higher boron concentration in the permeate water. The effect of temperature on the performance of reverse osmosis process is attributed to the change of diffusion rate [6,11]. Boron transport is principally controlled by diffusion. As temperature increases, the diffusivity of both boron and water permeability would increase. Boron passage rate through the membrane is increased faster than water flux as the temperature increases [17]. As a result, boron rejection would decrease as the temperature increases.

3.3. Elimination of boron from seawater RO permeate by ion exchange resin

The permeate from the membranes was passed through two different columns and then the outlet was returned to the feed tank. Therefore, maximum 10% of boron in the feed tank was able to be decreased as ion exchange resin sorbed boron during the column test. Additional boron was added to maintain boron concentration in the feed solution (5 mg/L). Boron concentration of the permeate of RE4040-SHN, SW30HRLE-4040 and TM810L was between 0.7 and 0.9 mg/L. Fig. 5 shows boron concentration after passing the columns as a fraction of bed volume (BV-volume of packed column) treated. The experiment was conducted up to around 2300 BV of each column so far; and both columns have not been saturated. Selective sorbability of boron onto the N-methylglucamine resin has been recognized to be a consequence of the complexation of boron species with functional groups of the resin [19]. The presence of two vicinal hydroxylic groups allows boric acid and borates to form a stable complex [19]. As shown in Fig. 5, the sorption ability of the ion exchange resin for boric acid and borate was so high that the removal was very efficient with 98% rejection. The main reason for higher complexibility of the N-methylglucamine resin would be electrostatic attraction between borate anions and protonated amino groups [19]. Sorption capacity until

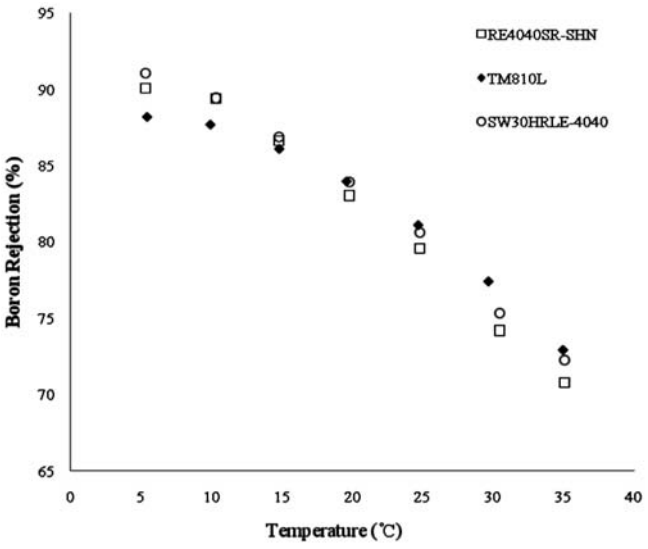

Fig. 4. Impact of temperature on boron rejection.

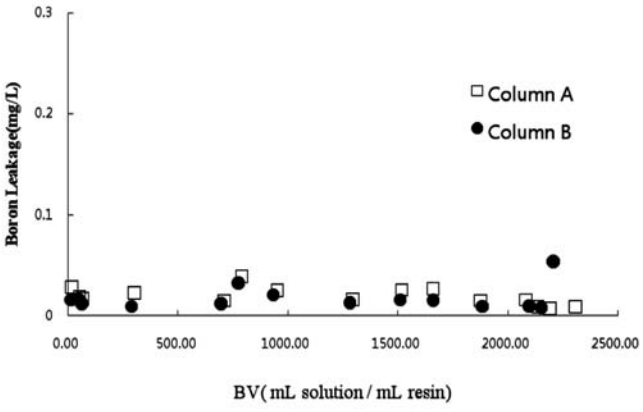

Fig. 5. Boron leakage curve.

this point was about 1.8 mg B/ml resin and it is possibly higher. According to other experiments conducted by Nadav (1999) and Jacob (2007), sorption capacity was 0.95 and 1.43 mg B/ml resin respectively [8,18].

4. Conclusion

Evaluation of boron rejection of three SWRO membranes at pilot scale revealed that boron concentration was always higher than the WHO standard for SWRO permeate. In addition, pilot-scale experiments suggested that boron rejection was largely influenced by pressure, salinity, temperature and pH. The most influential factor on boron rejection by RO membranes among the operating conditions was pH. Moreover, variation of pressure from 600 to 850 psi and temperature from 5 and 35°C affected the performance of the SWRO membrane in terms of boron rejection more than 10% in this study. Salinity was also able to affect boron rejection. Boron selective resin (IRA 743) showed great performance for the elimination of boron from SWRO permeate irrespective of salinity and temperature of the solution. Thus, the combined system of high rejection RO membrane and ion exchange process would be one of the most effective and applicable methods for seawater desalination.

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