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Removal of boron in a multistage SWRO system with pre-crystallization

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ABSTRACT

Recently, the desalination facilities use the membrane method that it is more effective and economical than the thermal method. And, the most recent a multistage seawater reverse osmosis (SWRO) system has been applied to increase the recovery rate. A multistage SWRO system has some more economical advantages for desalination than a single-stage SWRO system, such as high recovery rate, reuse of the brine pressure, and decreased brine quantity. However, there is still a problem related to the boron concentration exceeding drinking water quality standard. Therefore, the purpose of this study was to discuss the removal of boron using a multistage SWRO system with pre-crystallization for the removal of scale-causing substances and to change the form of boron. As a result, the boron concentration in permeate of the second stage-SWRO membrane in the pre-crystallization process (permeate (2)) was 0.48 mg/L, and that via the conventional process was 2.87 mg/L. And, the recovery rate of the experiment that applied pre-crystallization process was observed to be higher than that of the conventional process at the same operating pressure. The pH of the permeate (2) was weakly basic, at 8.53; therefore, it was concluded that the pH control process could be omitted from the post-treatment.

Keywords: Desalination; Pre-crystallization; Boron; Scale

1. Introduction

Due to the shortage of usable freshwater, the numbers and the capacities of desalination facilities have recently increased. Desalination facilities have historically used MED (Multi-Effect Distillate) and MSF (Multi Stage Flash Distillate) using the thermal or vacuum method, but the most recent facilities use the membrane method, mainly due to the drop in membrane prices and improved membrane development. The membrane method is also more effective and economical than the thermal method.

Seawater contains over 70 elemental species with major components including Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+}, Cl^-, SO_4^{2-}, and Br^-, etc., which are removed to about more than 99.5% using a seawater reverse osmosis (SWRO) membrane. In addition, the removal of organic matter and bacteria is quite sufficient. The permeate water quality produced by the SWRO

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membrane has been reported to satisfy the Korean drinking water quality standards [1,2].

Facilities using a reverse osmosis desalination system consist of five main stages in the process. The first step is a seawater intake pumping station; the second, a pre-treatment process, which consists of coagulation, flocculation, micro filtration, and booster pumps; the third is a RO membrane process, which removes dissolved salts; the fourth involves post-treatment, where the water hardness and pH are adjusted; and finally, the storage of water prior to its delivery to the consumers. The main historical issue with the SWRO membrane was the increase in the recovery rate of the permeate in the desalination of seawater with recoveries between 35 and 40% of the influent during one cycle of a single-stage SWRO system [3]. Therefore, a multistage SWRO system has recently been applied to increase the recovery rate. A schematic diagram of a multistage RO system for the desalination of seawater is shown in Fig. 1.

A multistage SWRO system has economical advantages for desalination, such as high recovery rate, reuse of pressure on the brine, and decreased brine quantity. However, there is still persists a problem related to boron concentration exceeding the Korean drinking water quality standard of 1.0 mg/L. Methods for the removal of boron include *solvent extraction*, adsorption membrane, ion exchange, reverse osmosis membrane, and so on [4]. The most effective method is ion exchange, but it is difficult to apply to large seawater desalination systems due to the associated economics [5].

Boron exists at levels from 4 to 5.5 mg/L in seawater. Generally, boric acid (H_3BO_3), borate (H_3BO^{2-}), and complexes with metal ions ($NaBO_2$, $Na_2B_4O_7{\cdot}10H_2O$) are present at 76, 13, and 11% in seawater at 25℃, a salinity of 34.8% and pH 8.2 [1]. Boron is a chemical element with the atomic number 5, and is a trivalent metalloid element. It is a glossy-black semiconductor similar to a pure crystal, has high electrical conductivity at high temperatures, and is almost an insulator at low temperatures. It is an important micronutrient for plants, animals, and humans, but the amount is limited, and its excessive presence is known to cause various diseases. When feed or the water containing boron was administered to rats, mice, and dogs in a short-term animal experiment, testicle obstructions were observed. The long-term intake of boron in humans is known to cause obstruction of the digestive organs and the neuron system of the human body [1]. The drinking water quality standards for Boron set by the WHO, EU, Japan, United Kingdom, Australia, Canada, Germany, and France are 0.5, 1.0, 1.0, 2.0, 4.0, 5.0, 1.0, and 1.0 mg/L, respectively [4]. Korea revised its own standard for boron from 0.3 to 1.0 mg/L in December 2007 because the ability to remove boron in a domestic island area seawater desalination facility is poor. Boron cannot be removed from aqueous solution by the conventional treatment using the flocculation, sedimentation, filtration, or water treatment methods; therefore, requires a separate treatment device, such as a reverse osmosis membrane, which can remove 40–80% of the boron. The removal of boron is affected by various driving conditions, such as the temperature, flux, and ionic strength of the feed, and is highly influenced by the pH. The ionization balance equation for boron in seawater is as follows:

$$\mathrm{B(OH)_3(aq) + H_2O \leftrightarrow H^+(aq) + B(OH)_4^-(aq),}$$
$$\mathrm{pK_a} = 9.14 \text{ at } 25^\circ\mathrm{C}$$

With the application of the reverse osmosis method for the removal of boron, a low removal efficiency has been observed as the boron exists in the boric acid ($B(OH)_3$) form at pH lower than 8. However, the removal efficiency of boron increases at high pH, as it exists as borate ions ($B(OH)_4^-$) that have a negative charge and increased molecular size [6]. However, with the SWRO system, it is not possible to increase the operating pH as scale is formed due to the high concentration of other ions, such as Fe^{2+}, Mn^{2+}, Si^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, and so on.

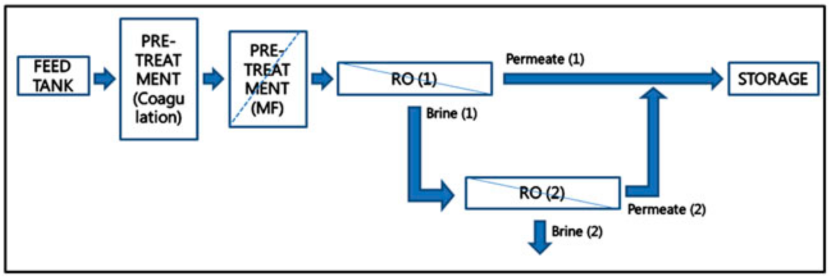

Fig. 1. Schematic diagram of the multistage RO system for the desalination of seawater.

Scale is produced on the surface of the membrane from the combined precipitate of Ca^{2+}, Mg^{2+}, HCO_3^-, and CO_3^{2-}, etc., which is dominated to >90% wt/wt by $CaCO_3$, $MgSO_4$, $MgCO_3$, $MgSiO_3$, SiO_2, and $CaPO_4$ in seawater [7,8]. The removals of $CaCO_3$ and SiO_2 are possible by chemical cleaning, but $CaSO_4$, $BaSO_4$, and $SrSO_4$ are difficult to remove once generated. The scale of calcium carbonate ($CaCO_3$) or magnesium carbonate ($MgCO_3$) is especially formed in the reverse osmosis membrane module because Ca^{2+} and Mg^{2+} exist at markedly higher concentrations than the other dissolved components in seawater. To prevent scaling, acidification pre-treatment (pH 5–6.5) [9] or an anti-scalant, such as SHMP (Sodium hexametaphosphate) have been used historically. The nanofiltration technique was recently introduced to remove hardness from the seawater of the Red Sea, as a pre-treatment step prior to RO membrane desalination [7,10].

Crystallization is the phenomenon in which the solid of a fluid or an amorphous state forms crystals. This is known to selectively occur due to the elements within a liquid and can produce both monocrystalline and polycrystalline structures. The study by Balarew showed that the crystallization was due to dissolved ions, such as Na^+, K^+, Mg^{2+}, Cl^-, Ca^{2+}, and SO_4^{2-}, as major components of seawater [11,12]. Also, according to Drioli, during the progressive concentration of seawater, the first salts to precipitate are calcium carbonate and a certain amount of magnesium carbonate (8–10 mol%) [13].

The purpose of this study was to investigate the removal of boron using a multistage SWRO system with pre-crystallization for the removal of scale-causing substances and to change the form of boron.

2. Experiment

The multistage SWRO system with pre-crystallization consists of a high pressure pump, a nano bubbling unit, and a SWRO membrane. The output capacity of the high pressure pump has a maximum pressure of 100 bar. The nano bubbling unit produces nano-sized bubbles using CO_2 gas. The spiral element of the SWRO membrane was SW21-4040 (Vontron, China). The characteristics of the membrane are shown in Table 1.

Generally, in order to remove boron, the two-pass system is applied using a BWRO membrane. However, this study applied a pre-crystallization process before the second stage SWRO membrane. In this study, the influences of the applied pre-crystallization process, boron removal according to the operating pH and pH adjusting agent, scale according to the CO_2 injection method and crystal seeding, boron removal according to the operating temperature and pressure at high pH, and optimum operating parameters of each applied process were investigated.

Table 1
Characteristics of the RO membrane used in the second stage SWRO system with pre-crystallization

	R/O SW21-4040
Usage	Sea water
Type	Spiral
Material	Polyamide
Size (element)	∅3.9 inch × L40 inch
Active membrane area (m^2)	7.4
Stable rejection rate (%)	99.5
Minimum rejection rate (%)	99.2
Max. working pressure (bar)	70
Max. feedwater flow (m^3/h)	3.6
Max. feedwater temperature (°C)	45
Max. feedwater SDI	5

2.1. Outline of second stage SWRO system

Fig. 2 shows a schematic diagram of the multistage SWRO system with pre-crystallization, for the removal of boron contained in brine of the first stage SWRO. The brine from the first stage SWRO membrane initially flowed to the pre-crystallization process and the supernatant is then subjected to the MF (microfiltration) process, using 10, 5, and 0.45 μm filters (Memtrex MP, GE), and finally flowed to the second stage SWRO membrane for the removal of boron.

The feed concentrated in the first stage SWRO membrane process was from the K desalination plant in Sokcho-shi. And, the experimental conditions were that the CO_2 gas was injected at 7.5 L/min into the pre-crystallization process, with the water flux passing through the MF and SWRO adjusted to 10 L/min.

The samples for analyses were taken at the feed (the brine of first stage SWRO membrane), pre-crystallized supernatant, after 0.45 μm filtration, the permeate of the second stage SWRO (permeate (2)) membrane, and the brine of the second stage SWRO membrane (brine (2)).

Table 2 shows the experimental conditions for the multistage SWRO system with pre-crystallization.

2.2. Materials and methods

For each sample, boron, sodium, calcium, potassium, and magnesium were analyzed by inductively-coupled plasma (ICPE-9000, Shimadzu, Japan), with chloride and sulfate using ion chromatography

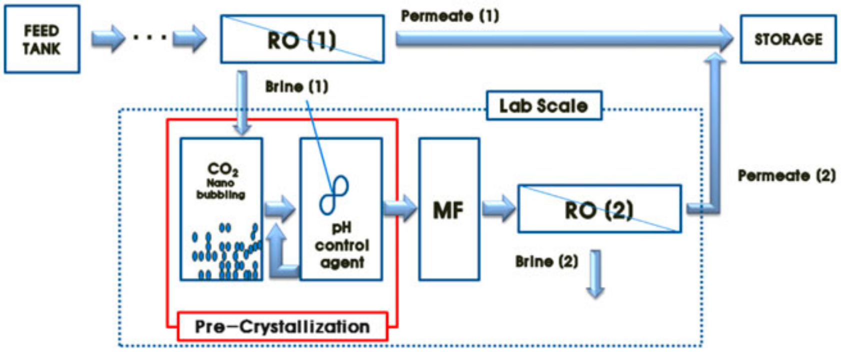

Fig. 2. Schematic diagram of the multistage SWRO system with pre-crystallization.

Table 2
Experimental conditions for the multistage SWRO system with pre-crystallization

Experimental items	Range
Temperature (℃)	20, 25, 30, 35, 40
Operating pressure (bar)	40, 50, 60, 70
pH	9.5–10.5
CO_2 (L/min)	7.5
pH adjustment	NaOH, $Ca(OH)_2$, Na_2CO_3

Table 3
Materials and methods

Item	Method
Cation	ICPE-9000, Shimadzu
Anion	ICS-900, Dionex
pH	ECOMET P25, Istek
Salinity	YSI Model 30, YSI
Specific conductivity	YSI Model 30, YSI

(ICS-900, Dionex, America). Other parameters, such as pH, salinity, and specific conductivity were measured using potable meters: Ecomet P25 (Istek, Korea) and YSI Model 30 (YSI, America), respectively. Table 3 shows the materials and analytical methods.

2.3. Formulae for calculating the boron rejection and recovery ratios

The rejection and recovery rates of the two-stage SWRO system with pre-crystallization were determined by using the following formulae:

$$\text{Recovery rate }(\%) = \frac{\text{Permeate flow rate (permeate (2))}}{\text{Brine water flow rate (brine (1))}} \times 100$$

$$\text{Boron rejection rate }(\%) = \left(1 - \frac{\text{Permeate boron concentration (permeate (2))}}{\text{Brine boron concentration (brine (1))}}\right) \times 100$$

3. Results and discussion

3.1. Influence of pre-crystallization process on boron removal

The results of the boron removal are shown in Fig. 3 with comparisons between the process with pre-crystallization and the conventional process. The experimental parameters for the process with pre-crystallization process were a boron concentration in the feed of 6.98 mg/L, 21.1℃, operating pressure of 65 bar, and pH 9.60, and those for the conventional process were the same with the exception of the pH 6.30. Boron concentration in the permeate of the second stage SWRO membrane with the pre-crystallization process was 0.48 mg/L, and the rejection by the pre-crystallization and SWRO membrane was 93.1%. Boron concentration in the permeate of the conventional process was 2.87 mg/L, and the rejection by the SWRO membrane was 58.9%. When supplied with the same operating pressure, the recovery rate of the experiment with pre-crystallization process was observed to be 18.8% and that of the conventional process was observed to be 4.4%.

From the above, the high boron removal in the process with pre-crystallization was considered to be due to crystal formation when boron ions captured into crystals, or their adsorption by other salts. It was

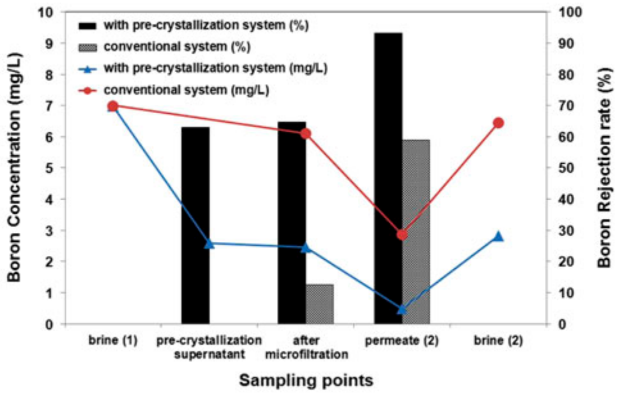

Fig. 3. Boron rejection rate and boron concentration depending on the sampling points (•with pre-crystallization process: operating pressure 65 bar, pH 9.6, temperature 21.1˚C, recovery ratio 18.8%; •conventional process: operating pressure 65 bar, pH 6.3, temperature 21.1˚C, recovery ratio 4.4%).

also considered that the borate ions could have increased due to the high pH; therefore, boron would be satisfactorily rejected by the SWRO membrane due to the production of the negatively-charged ions and increased molecular size.

3.2. Influence of the operating pH and the pH adjusting agent on boron removal

Fig. 4 shows the influence of the operating pH and pH adjusting agent on boron removal. The operating pH was set between 9.50–10.30 with NaOH, $Ca(OH)_2$, NaOH + Na_2CO_3 used as the pH adjusting agent. The initial experimental condition was boron-feeding concentration of 6.98 mg/L, temperature of 24.2˚C, operating pressure of 60 bar, and inflow rate of 10L/min with the operating pH set at 9.50 and 10.30 using NaOH to observe the influence on the removal of boron.

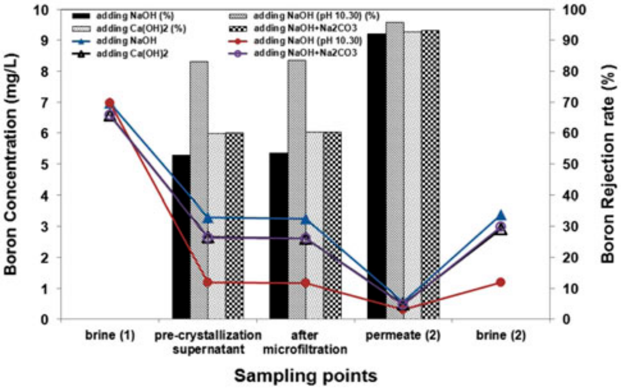

Fig. 4. Boron rejection rate and boron concentration depending on the operating pH and pH control agent (•initial boron concentration 6.98 mg/L: operating pressure 60 bar, temperature 24.2˚C, •initial boron concentration 6.58 mg/L: operating pressure 60 bar, temperature 26.5˚C).

As a result of an operating pH 9.50, the boron concentration in permeate of the second stage SWRO membrane was 0.548 mg/L and with the operating pH 10.30, it was 0.304 mg/L. The reported data from past studies [14,15] showed that the boron removal using a SWRO membrane greatly depended on the operating pH. Crystallization was also observed to occur when the operation pH was high.

Another experimental condition was a boron-feeding concentration of 6.58 mg/L at 26.5˚C, operating pressure of 60 bar, and inflow rate of 10L/min with the operating pH set at 10.01 using $Ca(OH)_2$ as the pH adjusting agent. As a result of adjusting the solution with $Ca(OH)_2$, the boron concentration in the permeate of the second stage SWRO membrane was 0.48 mg/L with a rejection rate of 92.7%.

Use of $Ca(OH)_2$ increased the pH more compared with when the same quantity of NaOH is used, but it also increased the concentration of calcium ions, which are scale inducers. Thus, the use of $Ca(OH)_2$ in the operation could be considered to be disadvantageous because of the formation of scale on the SWRO membrane.

Thirdly, the experimental condition was a boron-feeding concentration of 6.58 mg/L at 26.5˚C, operating pressure of 60 bar, and inflow rate of 10L/min with an operating pH set at 9.72 using NaOH + Na_2CO_3 as the pH adjusting agents. A large amount of Na_2CO_3 was required for pH adjustment of seawater because it is a weakly basic substance. And it was economically unfeasible because of its high price compared with the other pH adjusting agents used. However, with the use of Na_2CO_3, a high removal of the scale-generating material was observed due to the supply of CO_3^{2-} ions required for the production of $CaCO_3$ and $MgCO_3$. So it adjusted with Na_2CO_3 till a pH 8 and NaOH was used after that. The result of the boron concentration in the permeate of the second stage SWRO membrane was 0.458 mg/L with a rejection rate of 93.0%. The use of NaOH + Na_2CO_3 showed better removal efficiency of the scale-generating material compared with the other pH adjusting agents. And, by reducing the amount of NaOH + Na_2CO_3 used, the next experiment was performed using crystal seeding and the CO_2 injection method.

3.3. Influence of CO_2 injection method and crystal seeding on scale formation

In the pre-crystallization process, nano-size CO_2 gas was injected to supply CO_3^{2-} ions, but this caused pH decrease. This meant that the amount of the pH adjusting agent had to be increased. Therefore, experiments were carried out to find the optimum parameters for the CO_2 injection method and crystal seeding. The experiments were classified into four methods which analyzed and compared the pre-crystallization supernatant samples.

In the first method, $NaOH + Na_2CO_3$ were injected without CO_2, respectively. In the second method, $NaOH + Na_2CO_3$ is injected with the distilled water saturated with CO_2 gas. In the third method, $NaOH + Na_2CO_3$ were injected with direct aeration with nano-sized CO_2 bubbles. In the fourth method, $NaOH + Na_2CO_3$ were injected with direct CO_2 gas aeration and included the crystal obtained from the previous experiment. All experiments were performed at an operating pressure of 55 bar, 27.2℃, and operating pH of 9.75. The results of the experiments are shown in Fig. 5.

For each experiment, the rejection rates of Ca^{2+} were 49.4, 79.0, 79.5, and 77.3%, and those of Mg^{2+} were 12.9, 35.9, 32.4, and 30.1%, respectively. The second method showed the highest removal efficiencies, but it was considered due to the dilution caused in the process by injecting the distilled water saturated CO_2 gas. The third method required the most pH adjusting agent because of the direct aeration of the CO_2 gas. A large dosage of the pH adjusting agent affected Na^+ concentration in the permeate (2) resulting in economic unfeasibility. The fourth method showed that with the injection of crystals obtained from the previous experiment, it was possible to reduce the amount of the pH adjusting agent. It was considered that the injection of crystals arising from the previous experiment would increase the pH and new crystals would be adsorbed onto the surface of the injected crystal seed. As a result, the fourth method showed the high rejection rate, therefore, was determined to have the optimum parameters.

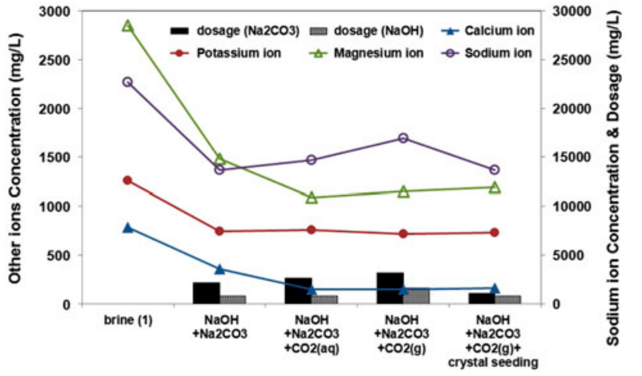

Fig. 5. Cations concentrations in the pre-crystallization supernatant using the CO_2 injection method and crystal seeding (operating pressure 55 bar, temperature 27.2℃, operating pH 9.75).

3.4. *Influence of operating temperature and pressure on cations removal at high pH*

The influence on cations removal was investigated with respect to the operating temperature and pressure at high pH. Experimental methods A–D used operating pressures of 70, 60, 50, and 40 bar, respectively, at an operating temperature of 20℃ and pH of 9.74. Methods E—H used operating temperatures of 25, 30, 35, and 40℃, respectively, at an operating pressure of 70 bar and pH of 9.74. The characteristics of the initial feed are shown in Table 4 and experimental results in Figs. 6 and 7.

The boron concentrations in the permeate (2) were 0.441, 0.529, 0.682, and 0.865 mg/L when operated at 70, 60, 50, and 40 bar, respectively. Therefore, higher

Table 4
Sample characteristics prior to passing through the second stage SWRO membrane

(mg/L)	B^{3+}	Ca^{2+}	K^+	Mg^{2+}	Na^+
Brine (1)	6.58	784	1,256	2,854	22,700
Pre-crystallization supernatant	2.81	77.5	675	1,450	14,500
After microfiltration	2.79	75	634	1,400	14,350

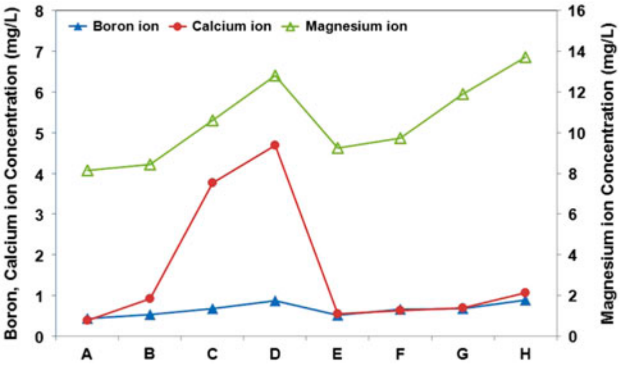

Fig. 6. The dependence of the boron, calcium and magnesium ion concentrations on the operating pressure and temperature (•A: operating temperature 20℃, pH 9.74, operating pressure 70 bar, •B: operating temperature 20℃, pH 9.74, operating pressure 60 bar, •C: operating temperature 20℃, pH 9.74, operating pressure 50 bar, •D: operating temperature 20℃, pH 9.74, operating pressure 40 bar, •E: operating temperature 25℃, pH 9.74, operating pressure 70 bar, •F: operating temperature 30℃, pH 9.74, operating pressure 70 bar, •G: operating temperature 35℃, pH 9.74, operating pressure 70 bar, •H: operating temperature 40℃, pH 9.74, operating pressure 70 bar).

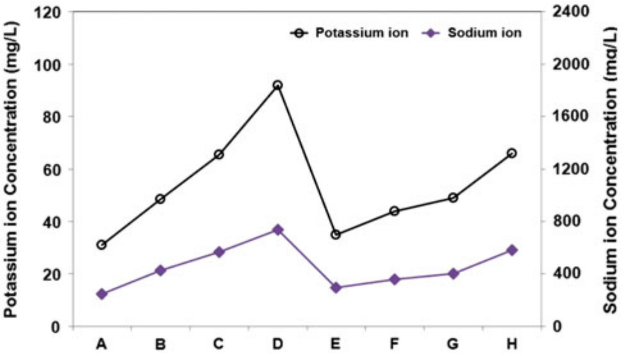

Fig. 7. The dependence of the potassium and sodium ion concentrations on the operating pressure and temperature (•A: operating temperature 20℃, pH 9.74, operating pressure 70 bar, •B: operating temperature 20℃, pH 9.74, operating pressure 60 bar, •C: operating temperature 20℃, pH 9.74, operating pressure 50 bar, •D: operating temperature 20℃, pH 9.74, operating pressure 40 bar, •E: operating temperature 25℃, pH 9.74, operating pressure 70 bar, •F: operating temperature 30℃, pH 9.74, operating pressure 70 bar, •G: operating temperature 35℃, pH 9.74, operating pressure 70 bar, •H: operating temperature 40℃, pH 9.74, operating pressure 70 bar).

rejection rate was observed with increasing operating pressure, with the WHO criterion for boron satisfied at an operating pressure of 70 bar. In this way, the removal efficiency of the boron is high by the increasing operating pressure that the transmission amount of the water molecule is due to increase more than the transmission amount of the boron molecule.

The boron concentrations in the permeate (2) were 0.521, 0.657, 0.685, and 0.887 mg/L when respectively operated at 25, 30, 35, and 40℃, at 70 bar. Therefore, higher removal efficiencies were observed with decreasing operating temperature. In a membrane comprised of polymer, the diffusion of solution is caused by the pressure difference with the hall formed by the thermal kinetics of the molecular chain. If the temperature of the inflow water is high, the motion of the molecular chain becomes more active and the frequency of the hall formation increases, with transmission rate of the boron also considered to be increased.

The optimum operating conditions were found to be an operating pressure of 70 bar at 20℃. The concentrations of the other ions in the permeate (2) were 0.381, 31.1, 8.15, and 245 mg/L for Ca^{2+}, K^+, Mg^{2+}, and Na^+, respectively, with removal efficiencies between 97.8 and 99.9%.

3.5. *Influence of operating parameters on the process*

The optimum operating parameters were determined from the experimental results of the previous steps, and applied to the pre-crystallization process; operating pH of 9.74, 20℃, operating pressure of 70 bar, the use of $NaOH + Na_2CO_3$, and the injection of CO_2 gas and the crystal seeding method to reduce the boron in the permeate (2).

The characteristics of the sample used under the optimal operating parameters are shown in Table 5 and Figs. 8 and 9. pH, specific conductance, and salinity are shown in Table 6 and Fig. 10.

With respect to the cations, 93.3% of the boron ions were removed which satisfied the WHO boron criterion. The calcium ions were removed to about 90.1% with the pre-crystallization process, with a further 9.8% removed by the SWRO membrane. The potassium ions were removed to about 97.5% corresponding to 31.1 mg/L. According to the WHO guidance, the recommended daily dietary requirement for calcium is more than 3000 mg/day, but there are currently no specific guideline values for potassium [16]. The magnesium ions were removed to about 49.2% with the pre-crystallization process, with 50.5% removed by the SWRO membrane. The sodium ions were removed to about 98.9% corresponding to 245 mg/L. There are no health-based guideline values for sodium [16]. In addition, as to anions, the chloride, and sulfate ions were removed to about 44.8 and 42.7% with the pre-crystallization process, with 54.5 and 52.7% removed by the SWRO membrane. In this way, the removals of the other ions as well as the calcium and magnesium ions were observed by pre-crystallization process.

Table 5
Sample characteristics under the optimal operating parameters applied

(mg/L)	B^{3+}	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	SO_4^{2-}
Brine (1)	6.58	784	1,256	2,854	22,700	47,387	6,079
Pre-crystallization supernatant	2.81	77.5	675	1,450	14,500	26,138	3,484
After microfiltration	2.79	75	634	1,400	14,350	25,876	3,389
Permeate (2)	0.44	0.38	31.1	8.15	245	291	3.29
Brine (2)	3.15	89.7	1,014	2,114	18,600	31,225	3,882

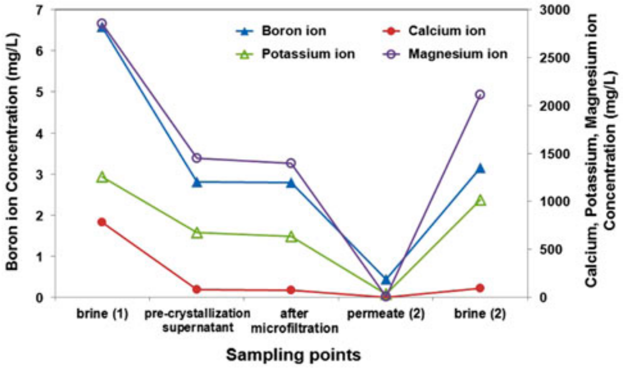

Fig. 8. Boron, calcium, potassium, and magnesium ion concentrations of the sample under the optimal operating parameters (operating temperature 20˚C, pH 9.74, and operating pressure 70 bar).

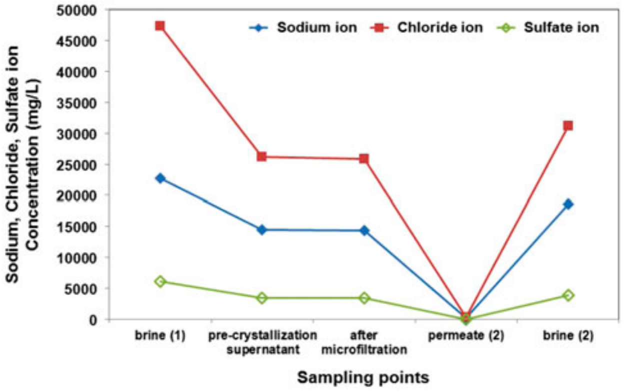

Fig. 9. Sodium, chloride, and sulfate ion concentrations of the sample under the optimal operating parameters (operating temperature 20˚C, pH 9.74, and operating pressure 70 bar).

Table 6
pH, specific conductance, and salinity of the sample under the optimal operating parameters applied

Unit	pH	Specific conductance (ms/cm)	Salinity (‰)
Brine (1)	7.75	96.9	77.8
Pre-crystallization supernatant	9.76	70.5	48.3
After microfiltration	9.74	70.2	48.0
Permeate (2)	8.53	1.4	0.7
Brine (2)	9.41	85.4	56.8

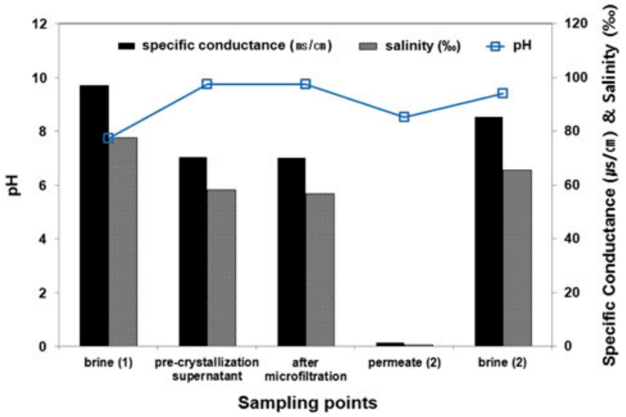

Fig. 10. pH, specific conductance, salinity of sample under the optimal operating parameters (operating temperature 20˚C, pH 9.74, and operating pressure 70 bar).

The initial pH of 7.75 is increased to 9.76 for the pre-crystallization process, and the supernatant was passed through the second SWRO membrane. As a result, the pH of the permeate (2) was weakly basic, at pH 8.53, and the pH also decreased as with that of the permeate from the first SWRO membrane. The pH of the permeate (1) was weakly acidic, with pH 5–6; therefore, a neutral pH range will be formed in the storage tank when the permeates were mixed. It is considered that the pH control process could be omitted from the post-treatment. The specific conductance was reduced to about 27.2% by the pre-crystallization process, with a further 98.0% reduction through the SWRO membrane. The salinity is reduced to about 25.1% by the pre-crystallization process, with a further 98.1% reduction through the SWRO membrane. The specific conductance of the permeate (2) was slightly high, at 1.4 ms/cm, as occlusion and degradation were thought to occur with the SWRO membrane due to the long operation period and frequent membrane clean-in-place (CIP).

4. Conclusions

This study introduced the pre-crystallization process for the removal of the boron within the permeate (2) of a multistage SWRO facility. The following conclusions were reached.

1. The applied pre-crystallization process was compared with the conventional process in the multistage SWRO system. As a result, the boron concentration in the permeate (2) of the second stage SWRO membrane in the pre-crystallization process was 0.48 mg/L, and that via the conventional process was 2.87 mg/L. The recovery rate of the experiment that applied pre-crystallization process was observed to be higher than that of the conventional process with the same pressure. Thus, the pre-crystallization process can be advan-

tageous for the removal of boron by the SWRO membrane.

2. The operating pH was set between 9.50 and 10.30, with NaOH, $Ca(OH)_2$, NaOH & Na_2CO_3 used as the pH adjusting agents to monitor their influence on the removal of boron. The removal of boron via the SWRO membrane is known to greatly depend on the operating pH. The amounts of NaOH + Na_2CO_3, as pH adjusting agents that would be advantageous to the quality of the permeate (2) were determined.
3. In the pre-crystallization process, experiments were carried out to find the optimum parameters for the pre-crystallization process using the CO_2 injection method to supply CO_3^{2-} ions and crystal seeding to reduce the amount of the pH adjusting agent injected. As a result, the introduction of the direct aeration of nano-sized CO_2 gas, the injection of crystals obtained from the experiment, and NaOH + Na_2CO_3 was deemed advantageous. This method is expected to easily increase pH with new crystals adsorbed onto the surface of the injected crystal seed. Therefore, this was also determined as one of the optimum parameters.
4. The influence on the removal of cations was investigated according to the operating temperature and pressure at high pH. The removal efficiency of boron was increased on increasing the operating pressure due to the increased transmission of the water molecules relative to that of the boron molecules. Higher removal efficiencies were also observed with decreasing operating temperature. In the membrane comprised of polymer, the solution diffusion effect is caused by the pressure difference from the hall formed by the thermal kinetics of the molecular chain. If the temperature of the inflow water is high, the motion of the molecular chain becomes more active and the frequency of the hall formation increases. The transmission rate of boron would also be increased.
5. The optimum operating parameters were determined from the experimental results of the previous steps, and applied to the pre-crystallization process; pH 9.74, 20℃, 70 bar, the use of NaOH + Na_2CO_3, and the introduction of CO_2 gas and the crystal seeding method to reduce the boron in the permeate (2). As a result, the concentration of boron ions in the permeate (2) was 0.44 mg/L, which satisfied the WHO boron criterion. The pH of the permeate (2) was weakly basic with pH 8.53; therefore, it was concluded that the pH control process could be omitted from the post-treatment. The specific conductance and salinity were also reduced indicating a reduction of the ions occurred with the pre-crystallization.

Further study will be required on the reuse of the crystals formed during the pre-crystallization process of this study. By injecting the seeding material into the phosphorus crystallization method [17], it is expected that the cost of the expensive injection material could be reduced that would in turn reduce the treatment cost of a waste from the reuse of a waste.

References

[1] C. Kim, H. Chung, Removal of boron in reverse osmosis process for drinking water production, Journal of Korean Society of Water Quality 15 (1999) 13–22.

[2] Maung Htun Ooab, Say Leong Onga, Boron removal and zeta potential of RO membranes: Impact of pH and salinity, Desalination and Water Treatment 39 (2012) 83–87.

[3] Byeong-Cheol Kima, Vu Phan, Xuan Hunga, Seung-Hyeon Boron removal from seawater by combined system of seawater reverse osmosis membranes and ion exchange process: A pilot-scale study, Desalination and Water Treatment 15 (2010) 178–182.

[4] N. Hilal, G.J. Kim, C. Somerfield, Boron removal from saline water: A comprehensive review, Desalination (2010).

[5] C. Jacob, Seawater desalination: Boron removal by ion exchange technology, Desalination 205 (2007) 47–52.

[6] B. Andrews, B. Dave, P. Lopez-Serrano, S.-P. Tsai, R. Frank, M. Wilf, E. Koutsakos, Effective scale control for seawater RO operating with high feed water pH and temperature, Desalination 220 (2008) 295–304.

[7] S. El-Manharawy, A. Hafez, Technical management of RO system, Desalination 131 (2000) 329–344.

[8] S. El-Manharawy, A. Hafez, Study of seawater alkalization as a promising RO pretreatment method, Desalination 153 (2002) 109–120.

[9] S. El-Manharawy, A. Hafez, Water type and guidelines for RO system design, Desalination 139 (2001) 97–113.

[10] A.M. Hassan, A.M. Farooque, A.T.M. Jamaluddin, A.S. Al-Amoudi, M.A.K. Al-Sofi, A.F. Al-Rubaian, N.M. Kither, I. A.R. Al-Tisan, A Rowaili, A demonstration plant based on the new NF-SWRO process, Desalination 131 (2000) 157–171.

[11] C. Balarew, Solubilities in seawater-type system: Some technical and environmental friendly applications, Pure & Apply Chemistry 65 (2) (1993) 213.

[12] E. Curcio, S. Al Obaidani, F. Macedonio, G. Di Profio, S. Gualtieri, E. Drioli, Advanced membrane systems for seawater desalination. Kinetic of salts crystallization from RO brines promoted by polymeric membranes, Membrane Journal 17 (2007) 93–98.

[13] E. Drioli, E. Curcio, A. Criscuoli, G. Di Profio, Integrated system for recovery of $CaCO_3$, NaCl and $MgSO_4*7H_2O$ from nanofiltration retentate, Journal of Membrane Science 27 (2004) 239.

[14] Y. Magara, A. Tabata, M. Kohki, M. Kawasaki, M. Hirose, Development of boron reduction system for sea water desalination, Desalination 118 (1998) 25–34.

[15] M. Htun Oo, L. Song, Effect of pH and ionic strength on boron removal by RO membranes, Desalination 246 (2009) 605–612.

[16] Public Health and the Environment World Health Organization Geneva 2007, Desalination for Safe Water Supply.

[17] E.-H. Kim, S.-B. Yim, H.-C. Jung, E.-J. Lee, J.-K. Cho, Recovery of high concentrated phosphates using powdered converter slag in completely mixed phosphorus crystallization reactor, Journal of Korean Society on Water Quality 21(1) (2005) 59–65.