Boron removal in seawater RO desalination.

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Abstract

In the seawater desalination field, WHO requires the boron concentration in drinking water to be below 0.5 mg/l, and this requirement has affected SWRO process design, because of the difficulty to achieve such low boron concentration. In order to overcome this problem, a new SWRO membrane element, which had higher boron rejecting performance, was developed. This new SWRO membrane element exhibits excellent boron rejection performance of 94-96% with high TDS rejection and high water productivity. This new membrane element could reduce the post-treatment loading, and it could be expected the lower drinking water production cost. In order to evaluate the economical impact of the new membrane, the production cost of various SWRO systems with post-treatment processes, the BWRO at high pH condition and the boron adsorbent resin, were estimated. As a result, the cost reduction of the new SWRO membrane was estimated to up to 20 % compared to the conventional SWRO membranes, and the three-stage system, which consists of the SWRO followed by the BWRO at high pH and the boron adsorbent resin for the BWRO concentrate, showed the most cost effective system.

Keywords

SWRO; Boron rejection; Boron adsorptive resin; BWRO; Post-treatment

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1. Introduction

RO seawater desalination processes have been focused and spreading as regular technologies to produce fresh water from the seawater, due to various advantages in the point of energy saving and less installation space. Especially, the recent improvement of the performance of SWRO membranes has enabled to obtain more fresh water at lower cost [1, 2].

In this seawater desalination field, WHO requires the boron concentration in drinking water to be below 0.5 mg/l [3], and this requirement has affected SWRO process design, because of the difficulty for SWRO to achieve such low boron concentration [4].

In these years, the water quality produced by SWRO processes has been improved by the development of the membrane elements with higher TDS rejection [5]. The SWRO membrane element, designated TM820H-370, has exhibited excellent salt rejection performance, average of 99.8%, and the boron rejection of from 91 to 93 %, which are the highest levels of commercialized SWRO membranes [6, 7, 8]. This high performance SWRO membrane element series has been installed to a large number of SWRO plants shown in Table 1. However, even by such good SWRO membranes, it is still difficult to meet the WHO requirement for boron concentration, which is below 0.5 mg/l. Therefore, the mixture of other water from river or post-treatment has been required to meet the water quality requirement. These days, two post-treatment processes for boron removal have been provided to assist SWRO for boron removal. The first process is BWRO (brackish water reverse osmosis), which can reduce boron in the permeate, but BWRO does not have so high boron rejection at neutral pH condition, and the alkaline should be usually dosed to raise the boron rejection by enhancing the dissociation of boron. This system is good from the economical point of view, but it sometimes fails to qualify the boron regulation due to the limit of pH, which should be less than 10 or 11 for the durability of RO membranes. In order to overcome this limit, an integrated system was proposed for Ashkelon by IDE Technologies [9], in which three stages BWRO processes with pH swings, for example. The second process is the boron adsorbent, which is the resin with n-methyl glucamine as the functional group, and is provided by several chemical companies. The performance is very high but the regeneration cost is expensive, and SWRO followed by the adsorbent is cost effective system only if the loading to the adsorbent is small. Therefore, parallel process of BWRO and adsorbent was proposed, which should be the intermediate cost but more flexible for boron reduction [7]. On the other hands, the high boron removal performance has been desired on the SWRO membranes, and our recent progress has achieved to develop new high boron rejecting SWRO membrane, which could reduce the boron concentration in the product water and satisfy above water quality requirement with lower plant cost and lower operation cost. In this study, the cost reduction effect was evaluated considering the advanced seawater desalination system using newly developed highly boron rejecting SWRO membrane.

2. Development of SWRO membrane with high boron rejection

As shown in Table 2, Toray has commercialized four types of SWRO membrane elements, which are for the different pressure conditions due to the TDS concentration and temperature of the seawater. Especially, SU-820BCM is for the brine conversion two stages (BCS) process developed by Toray, which is recognized as an economically effective process [10], and a lot of BCS plants are on stage [11]. However, all listed membranes do not have enough boron rejection performance, even they have the highest performance level in the world.

As known, boric acid has 9.14 ~ 9.25 of pKa, and is not ionized in the natural seawater of pH 7.0-8.0 and dissociates at over pH 9 [12]. Therefore, the electric repulsive force between boric acid and the membrane, both of which are negatively charged at high pH, cannot be expected for the boron rejection.

The new membrane elements were developed based on the two points of view, which were

- Reduction of affinity with boron, and reinforcement of affinity with water.

, and

- Tighter molecular structure (smaller pores) of membrane layer for the size exclusion of boric acid molecule.

The potential level of new SWRO membrane composition is indicated in Fig. 1. In this figure, “conventional” means the variety of membranes made by the conventional methods and compositions, including SU-820, TM820H, SU-820BCM. The new SWRO membrane group shows the higher potential (higher flux and higher boron rejection trend) compared to “conventional” membranes. Next, the elements were manufactured using the selected one of the new membranes, which is designated TM820A-370. The specification and typical performance is shown in Table 3, and actually measured boron removal performances are shown in Fig. 2. The boron passage, which is 100-rejection (%), was decreased to approximately two thirds of conventional SWRO membranes.

3. System evaluation for boron removal

3.1. Three-stage systems

In this study, (1) three-stage system was proposed and evaluated comparing with (2) SWRO system, (3) SWRO + adsorbent system, (4) SWRO + alkali-BWRO (BWRO with alkaline dosing) system, and (5) SWRO + adsorbent and alkali-BWRO (parallel) system. The flow diagrams are shown in Fig. 3, respectively. This new three-stage system consists of SWRO with the post-treatment of alkali-BWRO and the adsorbent for the concentrate recovery, which can perform high boron adsorbing capacity and efficiency due to the high boron concentration of feed water.

3.2. Processes and materials

Seawater

Two seawater conditions (Asia and the Middle East) were evaluated, and the highest temperatures were considered for the severest seawater condition for boron removal. The seawater condition for Asia was considered as 35,000 ppm-TDS, 5.0 mg/l-boron, and the temperature was 32 °C, and that of the Middle East was 45,000 ppm-TDS, 6.5 mg/l-boron, and the temperature was 38 °C. The other temperature conditions were also evaluated but the projected trends were not shown in this paper.

Pretreatment

The coagulation filter using $FeCl_3$ followed by the polishing filter with continuous chlorine and sodium bisulfate dosing were considered.

Desalination (SWRO)

The two different SWRO membranes were considered for the SWRO processes and the 6 membrane elements were connected in series. One was TM820H-370 and the other was TM820A-370, which was newly developed for high boron removal as shown at the previous section. The highest recovery ratio was limited to 50 % for Asia and 45 % for Middle East. In order to clean the SWRO membrane, it was premised to dose MT-901, the disinfection chemical developed by Toray, for one hour per day.

Post treatment

For the BWRO post-treatment process, ultra low-pressure RO membrane elements for brackish water treatment (TMG20-430, Toray, Tokyo) were used, and 6 elements were connected in series. As the boron adsorbent, chelate type ion exchange resin (Diaion UCB02, Mitsubishi Chemicals, Tokyo) was adopted to use, and the performance characteristics were measured in the pilot scale plant at Ehime Factory of Toray.

3.3. Theory for RO performance projection

RO performance projection in this study was carried out based on the concentration polarization theory with considering mass balance and pressure drop through the flow direction of membrane element [13, 14] as follows.

Mass transfer equations are

$$J_V = L_P\left[\Delta P - \sigma \cdot \{\pi(C_M) - \pi(C_P)\}\right] \quad (1)$$

, and

$$J_S = P(C_M - C_P) + (1-\sigma)\overline{C}_S \cdot J_V \quad (2)$$

Concentration polarization equation is

$$\frac{C_M - C_P}{C_B - C_P} = \exp\left(\frac{J_V}{k}\right) \quad (3)$$

where k is a mass transfer coefficient, and $C_P = \frac{J_S}{J_V}$.

A membrane element is divided into N sections along the feed flow direction. Mass balance equations at each section (Δ L=L/N) are given as

$$Q_{PO} = \sum_{i=1}^{N} \Delta Q_{Pi} = \sum_{i=1}^{N} J_{Vi} \cdot \Delta L \cdot W_i \quad (4)$$

$$C_{PO} = \frac{\sum_{i=1}^{N} C_{Pi} \cdot \Delta Q_{Pi}}{Q_{PO}} \quad (5)$$

Using these equations, numerical integration calculation for SWRO and BWRO performance simulation was conducted.

3.4. Results and discussions

The following results were based on the specific conditions for two areas of seawaters, but the qualitative results were the same. (The figures were not shown.)

Asia

The calculated result for Asia, using TM820H-370 as conventional SWRO, is shown in Fig. 4. Changing the recovery ratio could vary the product water quality and its cost. Namely, boron concentration can be reduced with the decrease of recovery ratio, and the production cost increases on the other hand. However, there is limit for the boron concentration, which is approximately 0.7 mg/l at the minimum recovery for System (2), SWRO, and 0.35 mg/l for System (4), SWRO + Alkali-BWRO. System (3) whose post-treatment by the adsorbent can reach the lowest boron concentration but it is not cost effective at less than 0.7 mg/l. Then, the post-treatment cost of System (4) is almost same as Systems (1) and (5), in which only BWRO was operated as the post treatment and the adsorbent was not used. As for System (5), the efficiency of adsorbent is lower than that of System (1) due to the difference of boron concentration, and it makes necessary to have larger adsorbent unit. As a conclusion, in Asia, single SWRO can be adopted at higher than 0.9 mg/l of required boron concentration, System (3) is suitable only in the range of 0.7 to 0.9 mg/l and at nearly 0 mg/l, and System (1) is the best choice to produce the water with less than 0.7 mg/l of boron.

The next result using a new SWRO membrane element, TM820A-370, is shown in Fig. 5 System (3) cannot have advantages to other systems at almost all boron concentration ranges. In this situation, the options are, single SWRO system (2) for higher than 0.4 mg/l and System (1) or (4) for less than 0.4 mg/l. Then Figs. 4 and 5 also indicate that the production cost is to be reduced by the new SWRO membrane, TM820A. For example US$0.51 can be reduces to US$0.48 in case the required boron concentration is 0.5 mg/l in the projected assumption.

The Middle East

The results for both SWRO membranes are shown in Figs. 6 and 7, and the qualitative conclusion is not different as Asia. The quantitative difference of the calculated lines are shifted to the higher boron concentration, which means single SWRO system can be adopted at over 1.0 mg/l using TM820A-370. It also indicates that the post-treatment process is essential in the

Middle East.

4. Conclusions

A new RO membrane element with high boron removal performance was developed based on the concept of affinity control between the membrane surface and boron and tight function layer to enhance the size exclusion performance. This new SWRO membrane was named TM820A and has provided 94 ~ 96 % of boron removal from seawater. Then, new boron removal process, which consists of SWRO followed by the post-treatment of alkali-BWRO and boron adsorbent for BWRO concentrate, was proposed to reduce production cost with high boron removal, and the cost reduction effect was evaluated with other conventional SWRO processes using conventional, TM820H and the new SWRO element, TM820A-370, as the SWRO.

Finally, the new SWRO membrane, TM820A was to be reduced the production cost, and it was concluded that the single boron adsorbent process was not suitable for the post-treatment of SWRO for boron removal but the combination with alkali-BWRO showed the good production cost at the ranges where SWRO could not achieve the enough boron removal.

Acknowledgement

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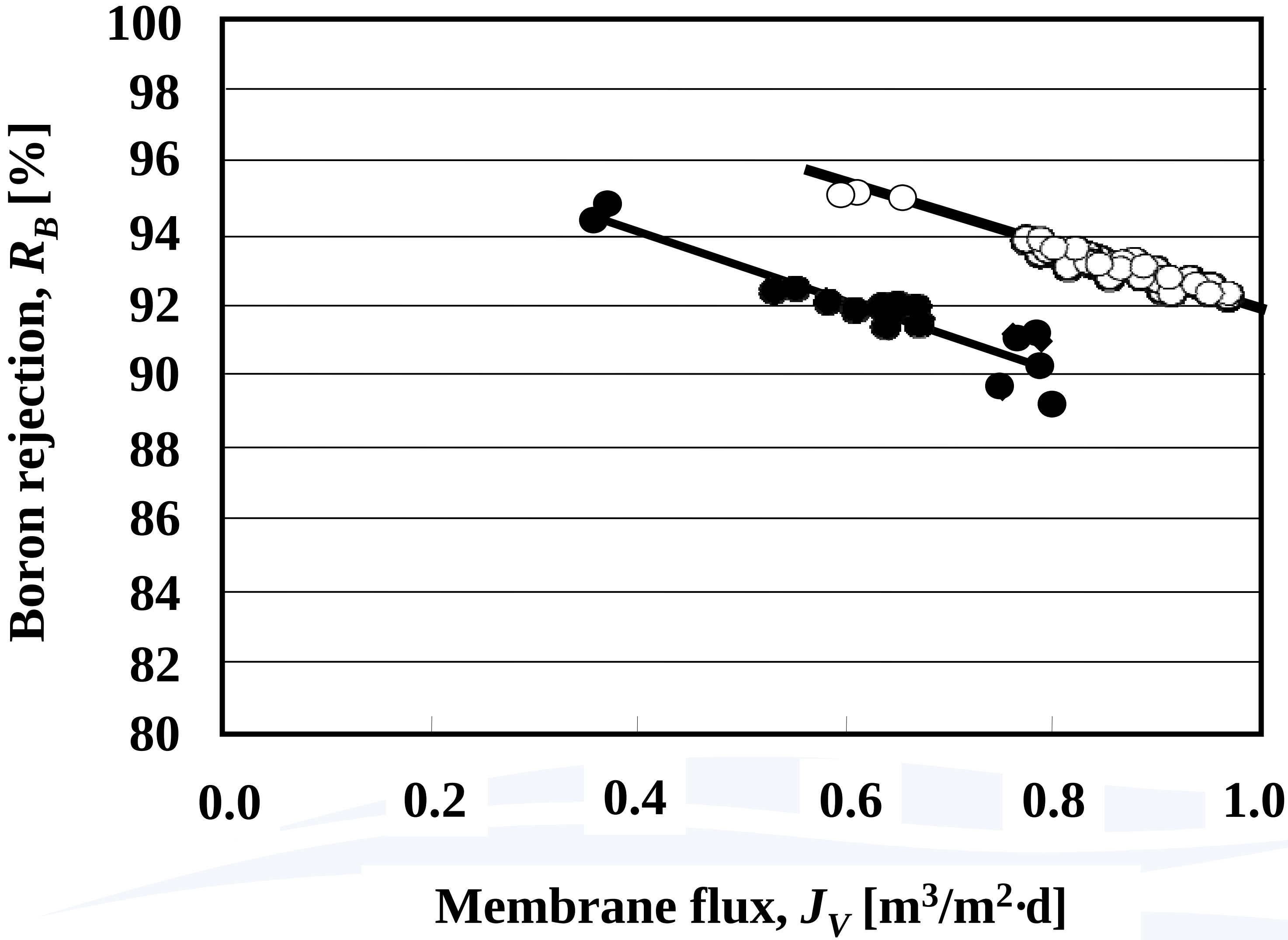
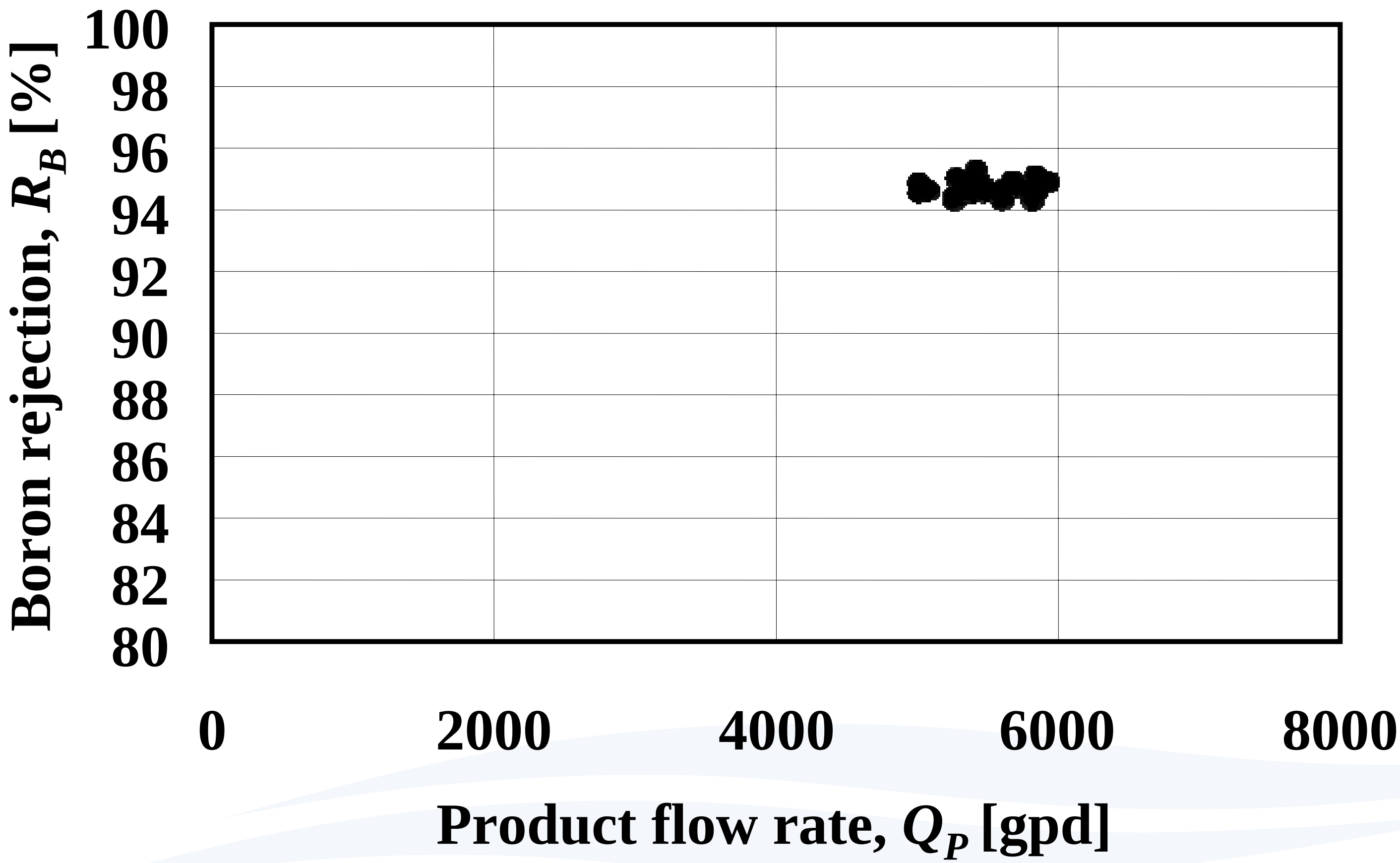

100
98
96
94
92
90
88
86
84
82
80
Boron rejection, R_B [%]
0.0
0.2
0.4
0.6
0.8
1.0
Membrane flux, J_V [$m^3/m^2 \cdot d$]

Fig. 1.



Boron rejection, R_B [%]
100
98
96
94
92
90
88
86
84
82
80
0
2000
4000
6000
8000
Product flow rate, Q_P [gpd]

Fig. 2.

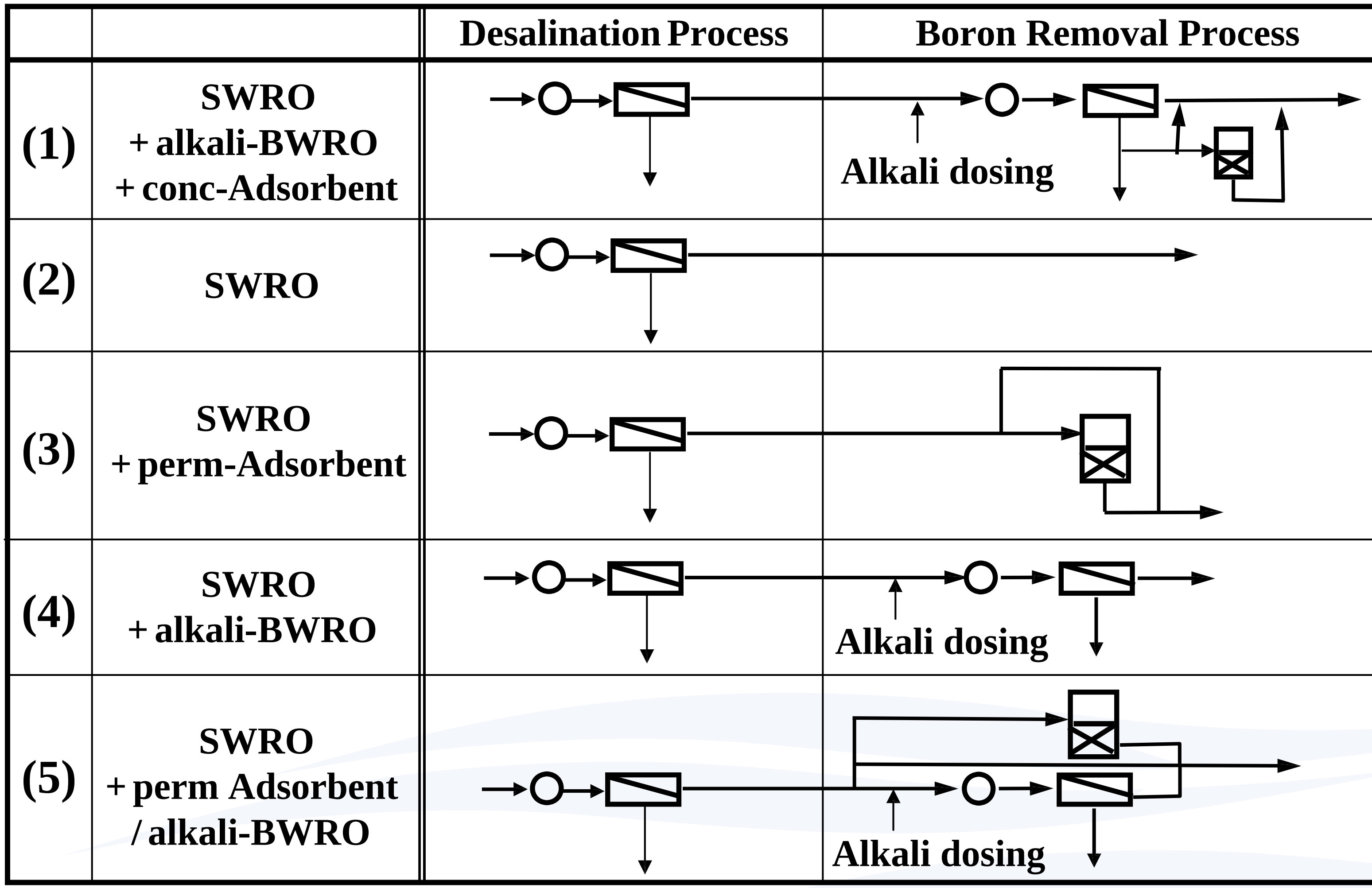

Desalination Process
Boron Removal Process
(1)
SWRO
+ alkali-BWRO
+ conc-Adsorbent
Alkali dosing
(2)
SWRO
(3)
SWRO
+ perm-Adsorbent
(4)
SWRO
+ alkali-BWRO
Alkali dosing
(5)
SWRO
+ perm Adsorbent
/ alkali-BWRO
Alkali dosing

Fig. 3.

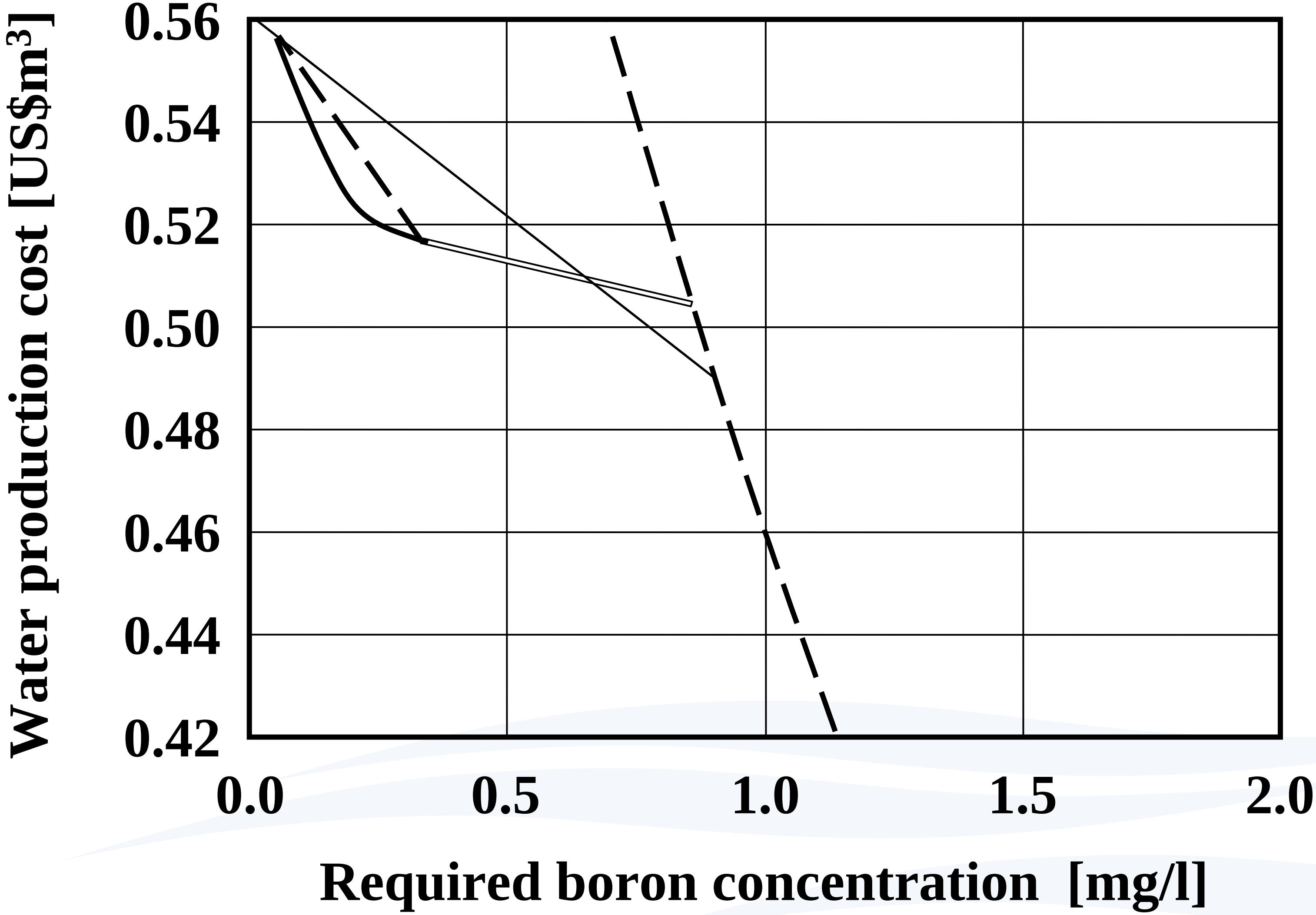
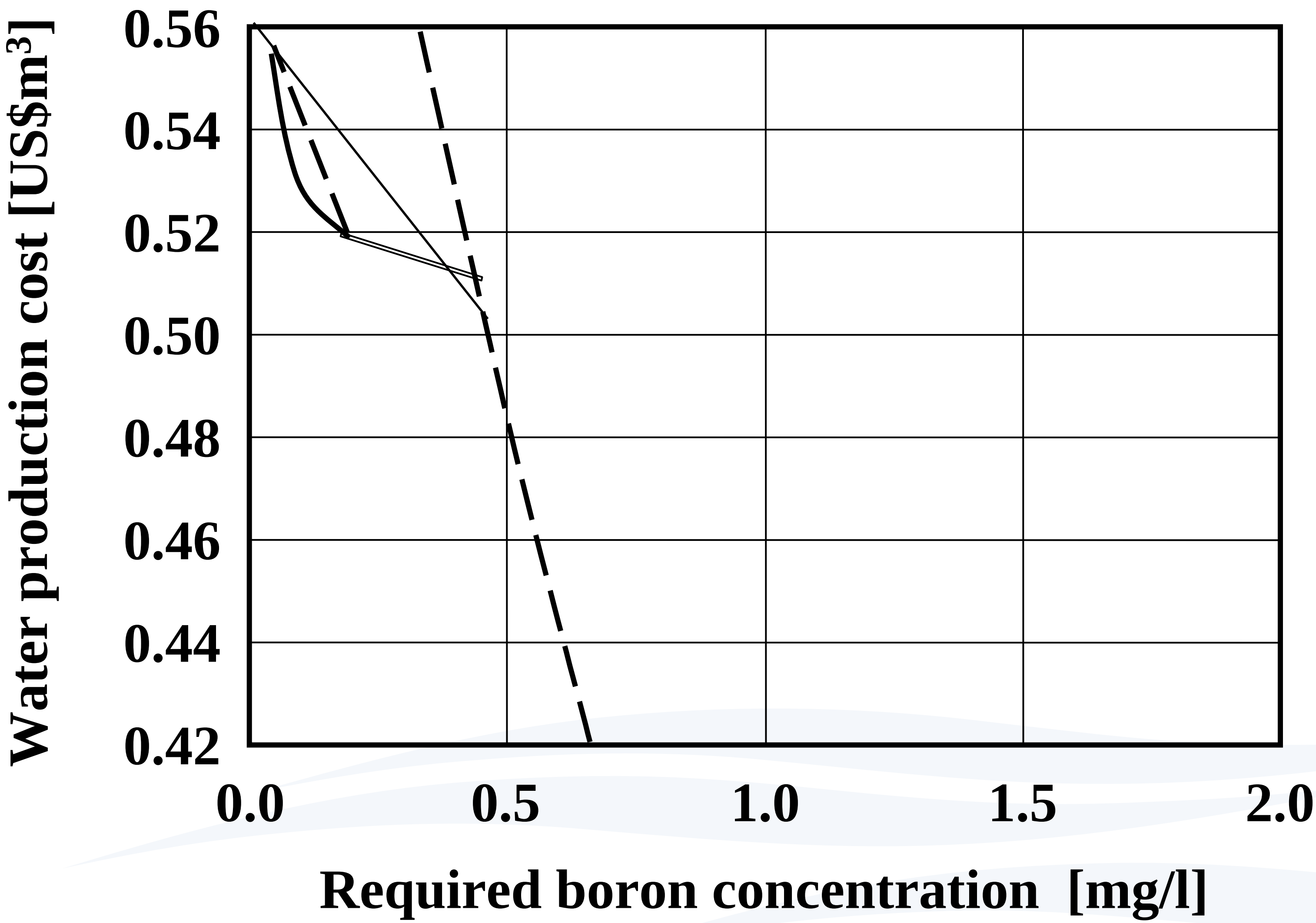

0.56
0.54
0.52
0.50
0.48
0.46
0.44
0.42
Water production cost [US$m3]
0.0
0.5
1.0
1.5
2.0
Required boron concentration [mg/l]

Fig. 4.



Water production cost [US$m3]
0.56
0.54
0.52
0.50
0.48
0.46
0.44
0.42
0.0
0.5
1.0
1.5
2.0
Required boron concentration [mg/l]

Fig. 5.

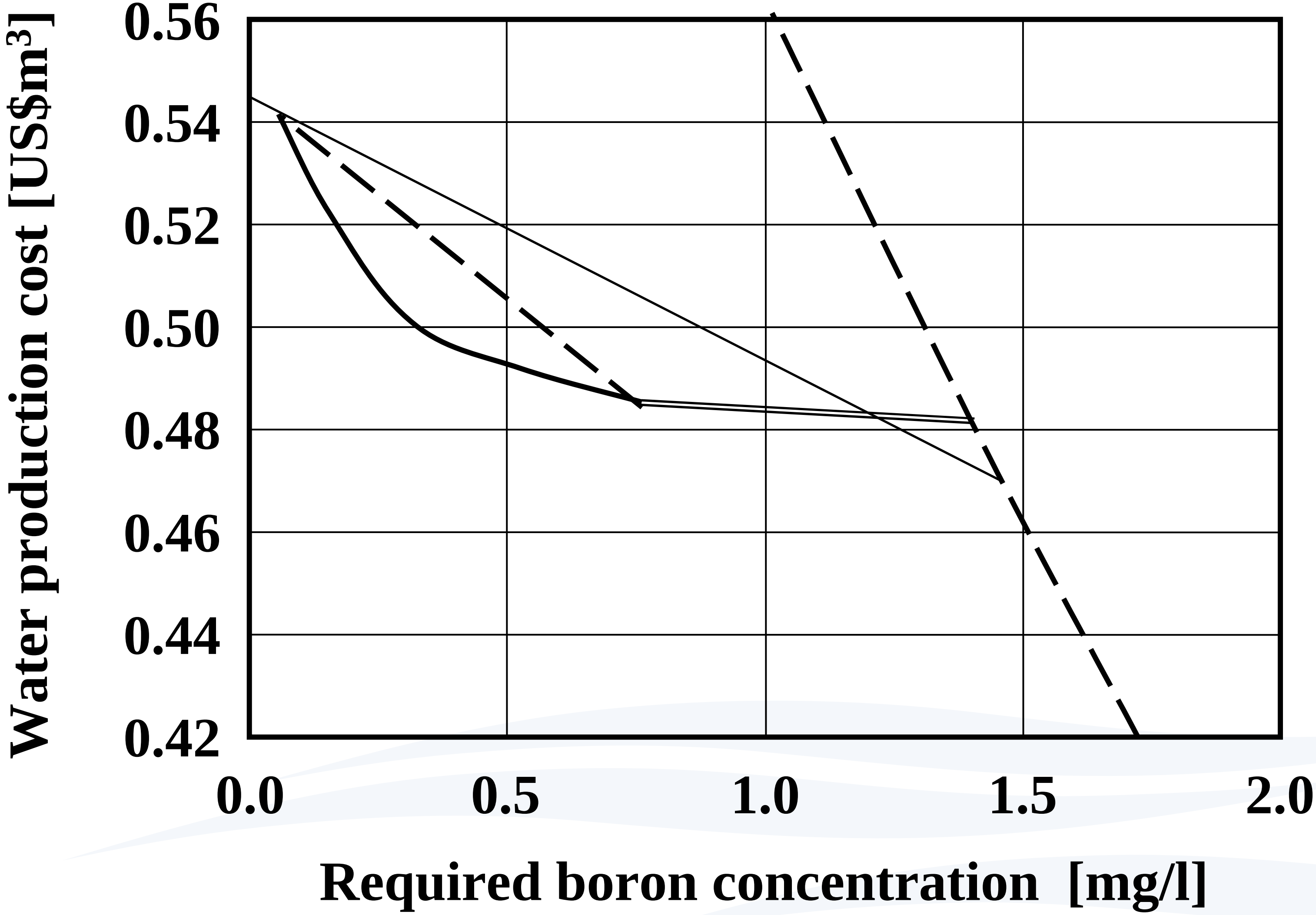

0.56
0.54
0.52
0.50
0.48
0.46
0.44
0.42
Water production cost [US$m3]
0.0
0.5
1.0
1.5
2.0
Required boron concentration [mg/l]

Fig. 6.

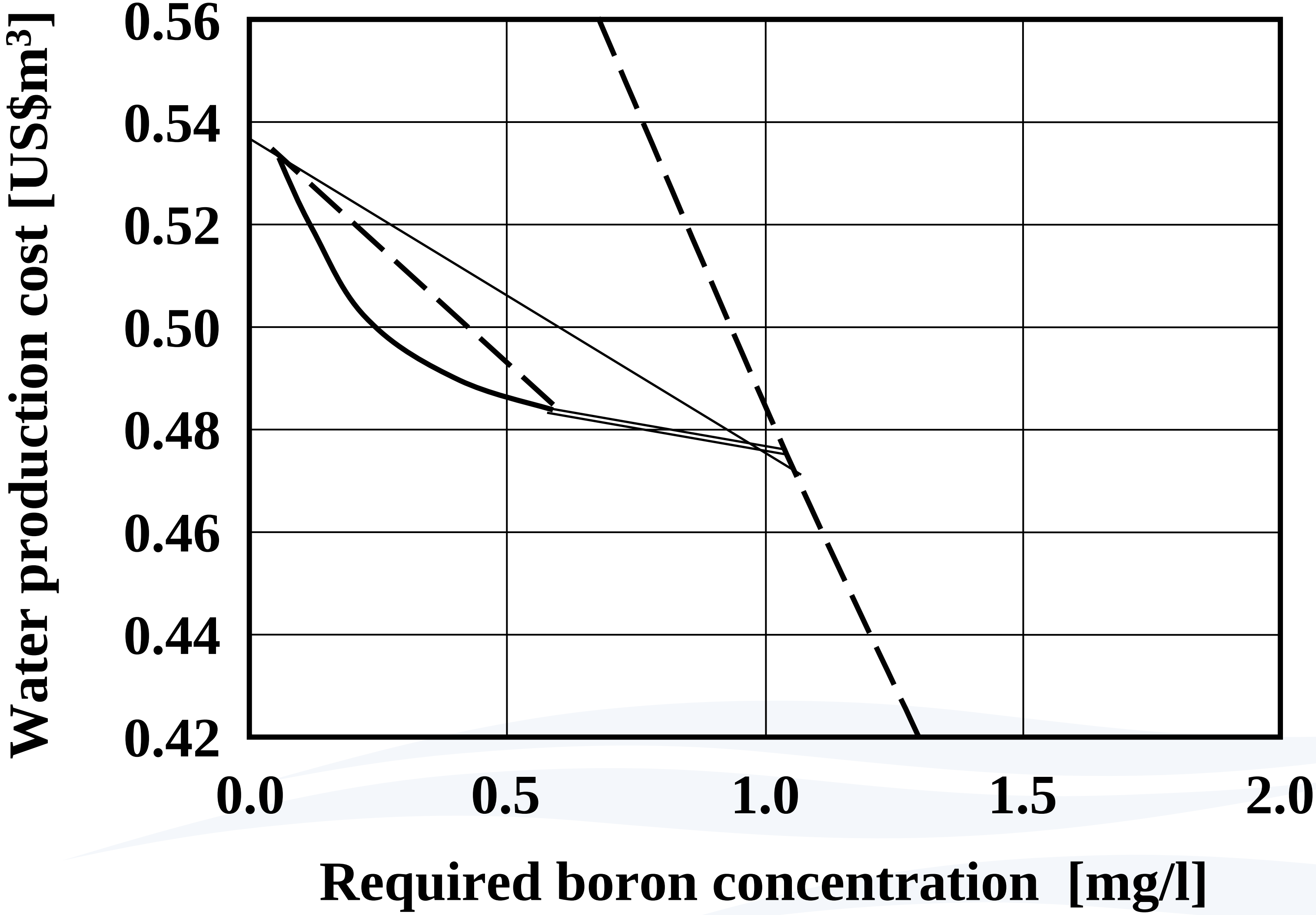

Water production cost [US$m3]
0.56
0.54
0.52
0.50
0.48
0.46
0.44
0.42
0.0
0.5
1.0
1.5
2.0
Required boron concentration [mg/l]

Fig. 7.

Table 1.

	Country	Location	Capacity Mgpd (m^3/d)	Membrane Element	Start-up date
1	Trinidad and Tobago	Point Lisa	36.0 (136,000)	SU-820	2002
2	Saudi Arabia	Al Jubail III	24.0 (91,000)	SU-822H	2000
3	Spain	Alicante	13.2 (50,000)	SU-820FA	2003
4	Spain	Bl Mallorca	11.1 (42,000)	SU-820	1998
5	Japan	Okinawa	10.6 (40,000)	SU-820	1996
6	Spain	Mas Palomas I-V	7.2 (27,360)	SU-820BCM	1997-2000
7	Netherlands	Curacao I-II	3.0 (11,400)	SU-820/SU-820BCM	1999

Table 2.

	Standard SWRO		High pressure SWRO	Ultra high pressure SWRO
Product name	TM820-370	SU-820	TM820H-370	SU-820BCM
Salt rejection [%]	99.75	99.75	99.80	99.83
Product flow rate [gpd]	6,000 (23 m^3/d)	5,100 (19 m^3/d)	6,000 (23 m^3/d)	6,000 (23 m^3/d)
Boron rejection [%]	91-93	91-93	91-93	91-93
Membrane area [m^2]	34	29	34	29
Max. pressure [psi]	1,000 (6.9 MPa)	1,000 (6.9 MPa)	1,200 (8.3 MPa)	1,450 (10.0 MPa)

Table 3.

	High boron rejection SWRO
Product name	TM820A-370
Salt rejection [%]	99.80
Product flow rate [gpd]	5,500 (21 m^3/d)
Boron rejection [%]	94-96
Membrane area [m^2]	34
Max. pressure [psi]	1,200 (8.4 MPa)

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Figures and Tables

Fig. 1. Boron removal potential of newly developed SWRO membranes and conventional SWRO membranes. ({) Developed; (z) Conventional. Solid lines are potential lines. Measured conditions; Feed seawater; 35,000 ppm-TDS with 5 mg/l-boron, pH=6.5, Temperature = 25 °C, pressure = 5.5 MPa (798 psi.)

Fig. 2. Boron rejection performance of newly developed SWRO membrane element, TM820A-370. Tested conditions were applied pressure of 800 psi (5.52 MPa), and recovery ratio of 8 %. Feed solution of 32,000 ppm-NaCl with 5.0 mg/l-boron. pH=8, and a temperature of 25 °C.

Fig. 3. Seawater desalination processes specialized for boron removal.

Fig. 4. Correlation between water production cost and boron concentration requirement for [*the Asian Seawater*] using [*TM820H-370*]. System (1) = thick solid line; System (2) = broken line; System (3) = thin solid line; System (4) = double line; System (5) = dashed line.

Fig. 5. Correlation between water production cost and boron concentration requirement for [*the Asian Seawater*] using [*TM820A-370*]. System (1) = thick solid line; System (2) = broken line; System (3) = thin solid line; System (4) = double line; System (5) = dashed line.

Fig. 6. Correlation between water production cost and boron concentration requirement for [*the Middle East Seawater*] using [*TM820H-370*]. System (1) = thick solid line; System (2) = broken line; System (3) = thin solid line; System (4) = double line; System (5) = dashed line.

Fig. 7. Correlation between water production cost and boron concentration requirement for [*the Middle East Seawater*] using [*TM820A-370*]. System (1) = thick solid line; System (2) = broken line; System (3) = thin solid line; System (4) = double line; System (5) = dashed line.

Table 1. Representative SWRO plant using Toray membranes. Element specifications of SU and TM indicate the element compositions, but same membrane used in case following numbers are same.

Table 2. Standard specifications of TORAY SWRO membrane elements. Tested conditions were applied pressure of 800 psi (5.52 MPa), and recovery ratio of 8 %. Feed solution of 32,000 ppm-NaCl with 5.0 mg/l-boron. pH=8, and a temperature of 25 °C. Element specifications of SU and TM indicate the element compositions, but same membrane used in case following numbers are same.

Table 3. Typical performance of newly developed SWRO membrane element. Tested conditions were applied pressure of 800 psi (5.52 MPa), and recovery ratio of 8 %. Feed solution of 32,000 ppm-NaCl with 5.0 mg/l-boron. pH=8, and a temperature of 25 °C.

Symbols

C_B	= concentration in the bulk	[kg/m^3]
C_M	= concentration at feed side of membrane surface	[kg/m^3]
C_P	= permeate concentration	[kg/m^3]

C_{PO}	= total permeate concentration	[kg/m^3]
J_S	= salt flux	[kg/m^2 • s]
J_V	= volume flux	[m^3/m^2 • s]
k	= mass transfer coefficient	[m/s]
L_P	= solution permeability	[m^3/m^2•Pa•s]
P	= salt permeability	[m/s]
Q_{PO}	= total permeate volume flow rate	[m^3/s]
W	= width of membrane	[m]
ΔP	= applied pressure	[Pa]
π	= osmotic pressure of seawater	[Pa]
σ	= reflection coefficient	[-]