Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986 © 2009 Desalination Publications. All rights reserved.

10 (2009) 60–63

Boron removal from dual-staged seawater nanofiltration permeate by electrodialysis

Marian Turek*, Piotr Dydo, Barbara Bandura-Zalska

Silesian University of Technology, Faculty of Chemistry, ul. B. Krzywoustego 6, 44–100 Gliwice, Poland
Tel. +48 (32) 2372735; Fax +48 (32) 2372277; email: Marian.Turek@polsl.pl

Received 30 September 2008; accepted in revised form 10 July 2009

ABSTRACT

The dual-staged nanofiltration to desalinate seawater is being proposed. The promising energy consumption, much lower than for RO seawater desalination, is reported. However, further reduction in boron is needed. In the authors' opinion, since the salinity of the second stage NF permeate is rather low, the easiest way to remove boron is to transfer it through an ion-exchange membrane (electrodialysis, ED). The relatively deep demineralization necessity is a shortcoming in the boron removal electrodialysis process, but ED seems to be privileged, since under these conditions boron (most likely borate) with its low mobility has to compete with small Cl^- content only. In order to determine the applicability of the electrodialysis for boron removal from dual-staged nanofiltration the set of laboratory measurements was conducted. The simulated dual-staged nanofiltration permeate composition was as follows (mg/L): Mg^{2+} — 0.2; Ca^{2+} — 0.1; Na^+ — 92; Cl^- — 117; SO_4^{2-} — 0.2; B — 2.4. An ED unit, equipped with AMX and CMX Neosepta (Tokuyama Co.) membranes and 0.4 mm membrane-to-membrane distance, was applied. It was found that boron transport might be enhanced by high ED concentrate pH value, probably due to hydroxide ion back diffusion. Thus, despite the relatively low mean ED diluate pH, hydroxide ion content in the layer adjacent to the membrane is high enough to ensure ionization of boron species. The ED process was carried out to decrease the B content down to 0.4 mg/L. At the same time, the diluate was almost completely deionized to ca. 1 mg/L level of Cl^-. The boron current efficiency reached 30% and boron flux across membrane 40 μg/cm²·h. The energy consumption found was as low as 0.25 kWh/m³, at the promising unit cost equal to \$0.098/m³.

Keywords: Dual-staged seawater NF permeate; Boron removal; Electrodialysis

1. Introduction

Proposed by Long Beach Water Department method of seawater desalination, known as the "Long Beach Method" is the two-stage nanofiltration process which promising feature is 20–30% less energy consumption than in reverse osmosis, described in detail by Vuong [1]. In this process high performance nanofiltration membranes are used. Sufficient pressure of the seawater feed to produce the first stage permeate is between 400 and 600 psi and the second one 200–300 psi and in comparison with traditional RO desalination (1,000 psi) indicates the possibility of significant desalination cost decrease.

Moreover, the dual-stage seawater NF system can produce better quality water than a conventional single stage SWRO. Typical water quality parameters are given in Table 1 [2].

---

* Corresponding author.

Presented at EuroMed 2008, Desalination for Clean Water and Energy Cooperation among Mediterranean Countries of Europe and the MENA Region, 9–13 November 2008, King Hussein Bin Talal Convention Center, Dead Sea, Jordan.

Table 1
Typical water quality [2]

Component	Concentration, mg/L			
	Raw seawater	Stage 1 permeate	**Stage 2 permeate**	LBWD tap
Mg^{2+}	1532	28	**0.2**	13
Ca^{2+}	546	10.1	**0.1**	39
SO_4^{2-}	2888	33	**0.2**	100
Na^+	11912	1280	**92**	75
Cl^-	19737	1806	**117**	59
TDS	37480	3247	**218**	390
Hardness (as $CaCO_3$)	7755	140	**1.26**	151

When the seawater is used as an alternative source of drinking water, the minor contaminants start to appear in the final product. Among these is boron. Traditional single-pass SWRO achieves 43–78% rejection of boron, while the two-stage seawater NF process only 48%. Boron concentration after the first nanofiltration stage is 3.7 mg B/L, and after the second nanofiltration stage — 2.4 mg B/L. Boron rejection into a membrane desalination system can be improved by increasing feedwater pH, as proposed in [3]. To avoid membrane scaling caused by calcium ions in the feedwater, alkaline environment of pH limited to 9.8 was applied after the first nanofiltration stage. Under these conditions permeate boron concentration decreased to the value recommended by WHO (0.5 mg B/L) [4].

It can be observed that feedwater pH of 9.8 is too high since magnesium ion content in the second stage permeate is significant, and could cause scaling because of magnesium hydroxide or its basic salts precipitation, especially at a high recovery level. To mitigate the boron rejection shortage we propose the use of electrodialytic boron removal from dual-stage nanofiltration product instead of the second stage alkaline treatment. This would help to avoid magnesium hydroxide scaling. Efficient electrodialytic boron removal by borate transport through an anion exchange membrane was already proved [5,6]. In this paper the influence of the ED concentrate pH on the boron transport was examined in detail. Concentrate pH was kept high to assure reliable boron transport since back-diffusing hydroxyl ions are suspected to increase borate content near the diluate boundary layer [6]. Efficient ED boron removal under alkaline conditions was also examined in the case of SWRO permeate [7]. Till now an additional RO stage at elevated pH or ion exchange has been applied for boron removal from SWRO permeate to meet the aforementioned WHO requirements. Nadav in his paper [8] described the cost of boron removal from SWRO permeate utilizing the Amberlite IRA 743 resin. In the case of IX the total boron removal cost consists of the resin, chemicals and operating costs. According to the author's opinion, energy consumption could be negligible. This process needs chemicals, e.g NaOH and HCl, to regenerate the column, so it produces additional harmful wastes of high boron concentration. Jacob (Rohm & Haas) [9] calculated the power consumption, chemicals usage and cost of combine two stages RO and ion exchange processes. The power consumption for only IX is equal to 0.06 kWh/m3. The author gives the total cost of boron removal from SWRO permeate containing 1.6 mg/L, using IX process, calculated for 20 years lifetime with no performance loss, as 0.03 $\$/m^3$. Glueckstern et al. [10] describe the boron removal process from SWRO permeate containing 0.62 mg B/L. The treatment cost of IX system with the capacity 20,000 m^3/d is 0.096 $\$/m^3$.

2. Experimental

The electrodialytic treatment of the permeate after dual-stage nanofiltration, containing 2.4 mg/L of boron and other components (mg/L): Mg^{2+} — 0.2; Ca^{2+} — 0.1; Na^+ — 92; Cl– — 117; SO_4^{2-} — 0.2, was examined in a laboratory ED stand, equipped with four pairs of AMX and CMX Neosepta (Tokuyama Co.) ion-exchange membranes. According to the Tokuyama Co. data, 5% caustic soda solution (which corresponds to 1.32 M) only slightly attacks the AMX anion-exchange membrane. In our investigation pH of the concentrate solution is equal to 12, which mean that the concentration of sodium hydroxide is equal ca. 0.01 M and should not influence the stability of this membrane. The lifetime of the membranes at such a high pH was not examined, but we worked a couple of months on the same sheet of membrane, and we did not notice deterioration of it.

Diluate and concentrate spacer applied was of 0.4 mm thickness and the active membrane area was 18 cm^2. The linear flow velocity for each (diluate, concentrate and electrode) compartment was equal to 7.5 cm/s. To avoid water split and its resulting pH change into the desalination compartment, the voltage drop was limited to 1.2 V per membrane pair.

Boron content was measured fluorometrically, applying chromotropic acid in alkaline environment at 350 nm excitation and 384 emission radiation wavelengths. The composition of the solution is tabulated in Table 1 (Stage 2 permeate). Deionized water of pH corrected by the addition of small volume of 0.1 or 1 M NaOH constituted the concentrate. Applied pH values were as follows 11, 11.5 and 12. For each test 70 mL volume of both diluate and concentrate was used.

3. Results discussion

For each selected concentrate pH level, the boron electric current efficiency, boron flux, pH and the most important diluate boron content vs. charge per unit volume were investigated (Figs. 1 and 2).

It was shown that electrodialysis of the permeate in question is efficient enough to remove boron to the desired level, which is commonly set at 0.5 mg/L. As can be seen in Fig. 1, boron concentration decreased rapidly when pH of concentrate was approximately 12. This was probably caused by back-diffusion of the hydroxyl ions into the diluate solution, which may be confirmed by diluate pH increase. Under this condition boric acid is more ionized and could be transported through the anion exchange membrane. The more alkaline solution is applied, the better boron removal rate appears. Approximately 110 C/L charge is needed to remove boron from 2.4 to less than 0.5 mg/L, it complies with 30 min

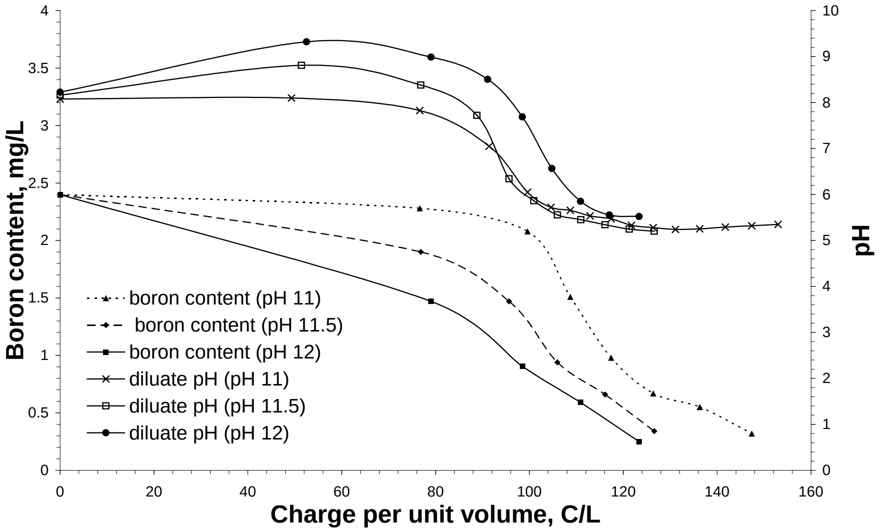

Fig. 1. Diluate boron content and diluate pH vs. electric charge per unit volume; concentrate pH is given in brackets.

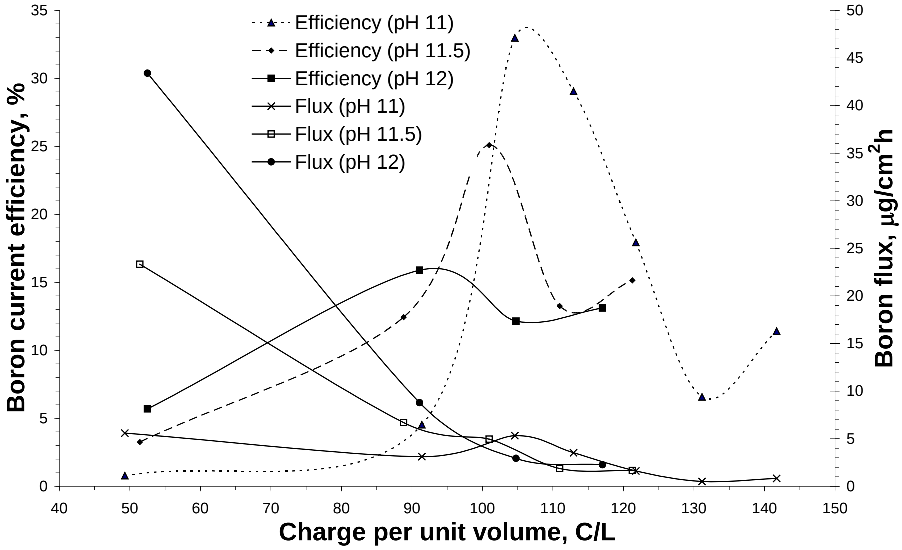

Fig. 2. Boron current efficiency and boron flux through the membrane vs. electric charge per unit volume; concentrate pH is given in brackets.

of electrodialytic boron removal process. In the case of processes with concentrate pH 11.5 and 11,about 45 and 60 min time was needed, respectively.

The initial boron flux was also the highest when the pH in the concentrate was approximately 12. The shape of the boron current efficiency vs. charge per unit volume curve indicates that at the highest pH applied, initial boron current efficiency was relatively high, and most of the boron was transferred throughout the membrane. At concentrate pH of 12 the current efficiency is more widely distributed, therefore the maximum is not as high as in the case of concentrate pH of 11 or 11.5, however the total electric current efficiency is the highest of all observed. For the lowest pH applied (11), the initial boron current efficiency is low and increases when the solution becomes ion depleted. The only ionic species that seems to compete with borate is chloride. Since the reported mobilities of chloride are higher than those of borate, it is suspected to be removed preferentially. Once all or most of the chloride has been removed, the boron (borate) removal efficiency is suspected to achieve its maximum. Calcium, magnesium and sulfate ions which could possibly cause scaling are almost completely removed in the dual-staged seawater NF process.

It was then proved that for pH 12 the process is more efficient, less time and energy consuming, and allows for economical boron removal. To confirm this we estimated the boron removal cost.

4. Cost estimation

The costs of the boron removal from dual-staged seawater nanofiltration permeate was estimated in the proposed manner. The removal of boron was considered based on results obtained at ED concentrate pH = 12. Several assumptions concerning ED plant cost components were made: the membrane cost $100/m^2, effective membrane area 70%, membrane durability period of 80000 h (10 years); the contribution of membranes in the total ED capital and maintenance costs is equal to 33%; energy cost of $0.06/kWh of alternate current, AC/DC converter electric efficiency of 95%; pumping efficiency of 85%. Estimated consumption of direct current was equal to 0.164 kWh/m^3, energy for pumping 0.081 kWh/m^3, the cost of energy $0.015/m^3 and finally the capital and maintenance costs $0.083/m^3. Thus the total boron removal cost was estimated at $0.098/m^3.

In our study the boron initial concentration (2.4 mg/L) is higher than in the papers concerning its removal from SWRO permeate [8–10] and the boron removal cost is less than 0.1 $/m^3. We used a rather low resistance membrane in our experiments, but we found that the cost of energy has low portion of total treatment costs. Thus, a low-cost but more resistive membrane may be used to decrease the investment cost and subsequently total cost of boron removal.

5. Conclusions

It was shown that electrodialytic boron removal method could be applied instead of high pH treatment in the "Long Beach Method". ED seems to be economically efficient and allows avoiding magnesium hydroxide nanofiltration membrane scaling in the second nanofiltration stage. By the proposed method, boron could be removed to the desired level (0.5 mg/L), at the initial concentrate pH of 12. The calculated total cost of ED boron removal is low, and in the authors' opinion, could be possibly lower, if only the membrane cost decreases.

Acknowledgement

The electrophoresis system, applied in this work for ionic composition validation was sponsored by PKN Orlen (Poland). Most of this work was financially supported by the Polish Ministry of Science and Higher Education grant No. 3T09B 084 28.

References

[1] D.X. Vuong, Two stage nanofiltration seawater desalination system, US Patent 7144511, 5 December 2006.

[2] S. Adham, R.C. Cheng, D.X. Vuong and K.L. Wattier, Long Beach's dual-stage NF beats single-stage SWRO, Intern. Desalination & Water Reuse Quart., 13(3) (2003) 18–21.

[3] T.J. Tseng, R.C. Cheng, D.X. Vuong and K.L. Wattier, Bench and pilot-scale investigation of boron removal for seawater membrane desalination, presented at AWWA 2004 Annual Conference, 15 June 2004.

[4] K.L. Wattier, Long Beach Water Department's approach to seawater desalination, presented at AWWA 2004 Annual Conference, 15 June 2004.

[5] M. Turek, P. Dydo, J. Trojanowska and B. Bandura, Electrodialytic treatment of boron-containing wastewater, Desalination, 205 (2007) 185–191.

[6] M. Turek, B. Bandura and P. Dydo, The influence of concentrate alkalinity on electrodialytic boron transport, Desalination, 223 (2008) 119–125.

[7] M. Turek, B. Bandura and P. Dydo, Electrodialytic boron removal from SWRO permeate, Desalination, 223 (2008) 17–22.

[8] N. Nadav, Boron removal from seawater reverse osmosis permeate utilizing selective ion exchange resin, Desalination, 124 (1999) 131–135.

[9] C. Jacob, Rohm & Haas Ion Exchange Technology, Seawater desalination: boron removal by ion exchange technology, Desalination, 205 (2007) 47–52.

[10] P. Glueckstern and M. Priel, Boron removal in brackish water desalination systems, Desalination, 205 (2007) 178–184.