IMPROVED BORON REJECTION USING THIN FILM NANOCOMPOSITE (TFN) MEMBRANES IN SEAWATER DESALINATION

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Abstract

The effect of boron toxicity on humans is comparable to that of table salt which is considered non-toxic. In agriculture, it is a micronutrient that is essential for the growth of plant; however, its concentration must remain below 1 mg/l before it becomes toxic to some plants.

In 2009, the World Health Organization (WHO) revised its guideline level of boron in drinking water to 2.4 mg/l. Seawater RO (SWRO) membrane manufacturers claim a boron rejection varying from 88% to 95% at standard SWRO test conditions, while NaCl is rejected at rate greater than 99.5%. Relatively large concentrations of boron can still be present in the permeate despite its typically low feed concentration of 4 to 6 mg/l in seawater applications.

Recent developments in thin-film nanocomposite (TFN) membranes have resulted in higher salt rejection (99.85%) and greater production capacity. These improvements are leveraged to enhance the product quality, to increase the plant production capacity, to lower plant footprint, or to reduce the plant's energy consumption. Along the high salt rejection, TFN membranes also demonstrate a relatively high Boron rejection.

A field pilot study conducted at San Pedro del Pinatar demonstrated that the TFN membrane consistently performed at a normalized boron rejection of 94%. The pilot system delivered a maximum of 1 ppm of permeate boron content at a maximum temperature of 26 ºC without any pH adjustment.

I. INTRODUCTION

The effect of boron toxicity on humans and animals is comparable to that of table salt which is considered non-toxic. In agriculture, it is a micronutrient that is essential for the growth of plant; however, its concentration must remain below 1 ppm before it becomes toxic [1] to some plants.

In 2009, the World Health Organization (WHO) raised its guideline level of boron in drinking water to 2.4 mg/l. Seawater RO (SWRO) membrane manufacturers claim a boron rejection varying from 88% to 95%, while NaCl is rejected at rate greater than 99.5%.

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However, boron still remains as the main limiting factor in the design of SWRO systems and in the selection of SWRO membrane models in regions where produced water is used for agricultural purposes with stringent boron limits (less 1 ppm). This paper details the findings of the field pilot study that was conducted to evaluate the boron rejection of the TFN membrane.

Boric Acid vs Borate

Boron is present in water as two distinct species: boric acid, $B(OH)_3$ and borate ion, $B(OH)^-_4$.
Boron is soluble in water as boric acid which can ionize into borate ions following the simplified dissociation equation:

$$B(OH)_3\,(aq) + H_2O \rightleftharpoons B(OH)^-_4 + H^+$$

The dissociation constant for boric acid is then defined as:

$$K_a = [H^+].[B(OH)^-_4] / [B(OH)_3]$$

The Ka is a function of temperature and the solution salinity. According to experimental results from Dickson [2], the pKa can vary from 8.3 to 9.2 at solution salinities varying from 5 to 45 g/l. When the pH of the solution is above the pKa value, the dominant species is the borate ion while at lower pH, boric acid prevails.

The presence of boric acid in its aqueous form within the solution is the cause for the overall low boron rejection of the RO membrane. RO separation is based on the ion diffusive mechanism through a semi-permeable membrane and the pressure-driven pore flow transport of the aqueous phase (water). Thus, while the borate ions are rejected in a similar manner as NaCl, the uncharged boric acid is poorly rejected as it passes through the RO membrane.

Common methods to improve the boron rejection of the SWRO system include the alkalization of the feed solution up to 8.6 pH or the post-treatment of the permeate in a BWRO second pass.

II. SAN PEDRO DEL PINATAR PILOT PLANT

San Pedro del Pinatar 2 SWRO desalination plant located in Murcia, in the south east of Spain, has nine trains producing a total capacity of 65 MLD. It was commissioned at the end of 2006 to provide additional potable water to Mancomunidad de los Canales del Taibilla which is the local governmental water authority. The source of the raw water is an open seawater intake.
Adjacent to the main plant is a stand-alone pilot unit.

Figure 1: San Pedro del Pinatar 2 Desalination Plant

The pilot unit has the following design:

- Raw feed water is treated by the main plant media filters before serving the pilot unit
- Cartridge microfilter
- Piston pump controlled with a variable frequency drive (VFD) serves as the high pressure pump
- One 7-element pressure vessel with RO elements of 8-inches in diameter from one of the main plant racks.

Figure 2: Pilot Test Facility

Figure 3: Pilot Test Pressure Vessel and Instrumentations

Pilot test operators recorded the following measurements three times per day:

1) Raw Feed:
    a. Conductivity [µS/cm]
    b. Temperature [ºC]
    c. pH
    d. SDI
2) RO feed:

a. SDI
b. Pressure

3) Permeate:
   a. Conductivity [µS/cm]
   b. Pressure [bar]
   c. Flow rate [m3/h]
   d. pH
   e. Temperature [ºC]
4) Concentrate:
   a. Conductivity [µS/cm]
   b. Pressure [bar]
   c. Flow rate [m3/h]

In addition, RO feed and permeate samples were collected daily and sent out to their in-house laboratory for the analysis of the boron concentrations.

III. RESULTS AND DISCUSSIONS

1) Test Operating Conditions

Seven LG SW 440 SR elements with TFN membranes were loaded into the pilot system in September 2014 under the following initial operating conditions:

- 45% feed water recovery producing 3 m^3/hr at system flux of 10.4 lmh
- 26 deg C and a feed salinity of 39,080 ppm at pH 6.2

Figure 4: RO Feed Water Conditions

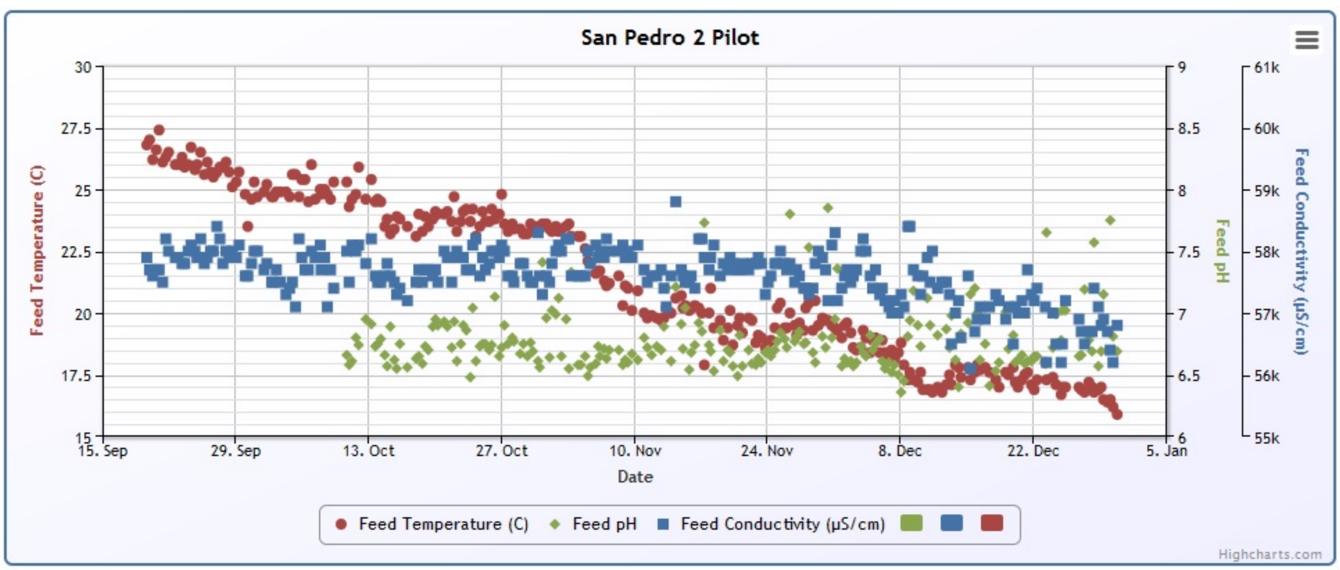
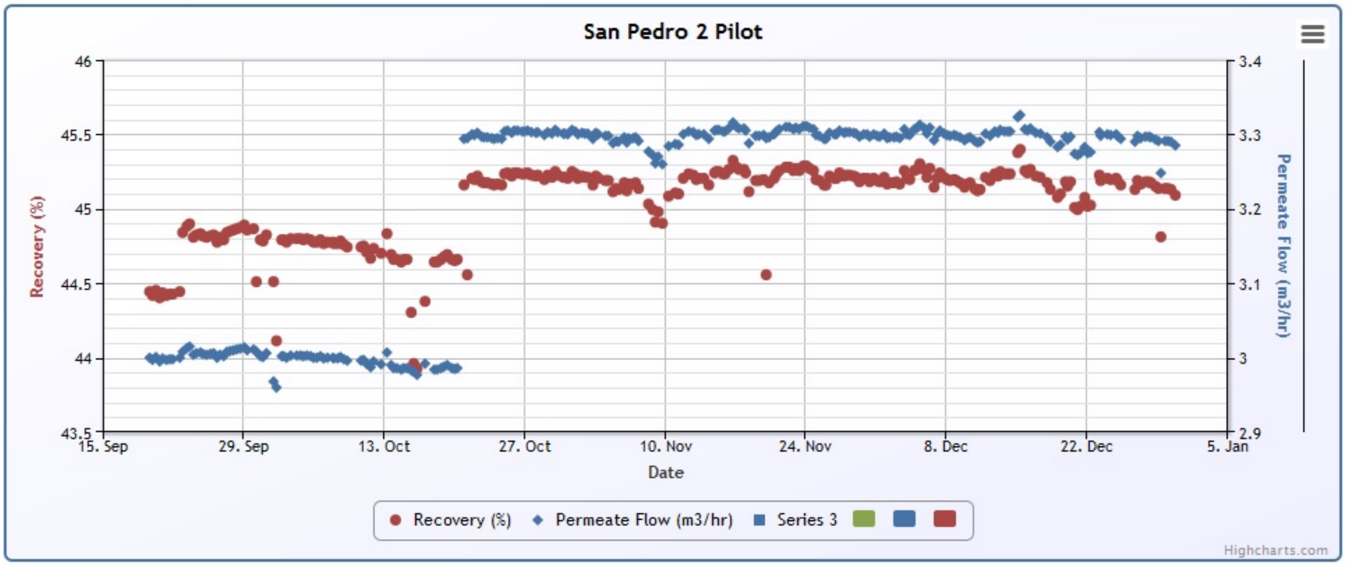


Figure 4 shows the trends of the RO feed water for the duration of the pilot test. The feed conductivity varies within a relatively narrow range of 57,000 and 58,000 µS/cm while the pH averages about 6.7. The temperature gradually declines from 26 ºC (summer) to 15.5 ºC (winter). The RO feed water to the pilot test was not subjected to any pH adjustment/increase to improve the boron rejection performance of the SWRO membranes.

Figure 5: Pilot Test Operating Conditions



The pilot test was conducted under two distinct conditions (Figure 5):

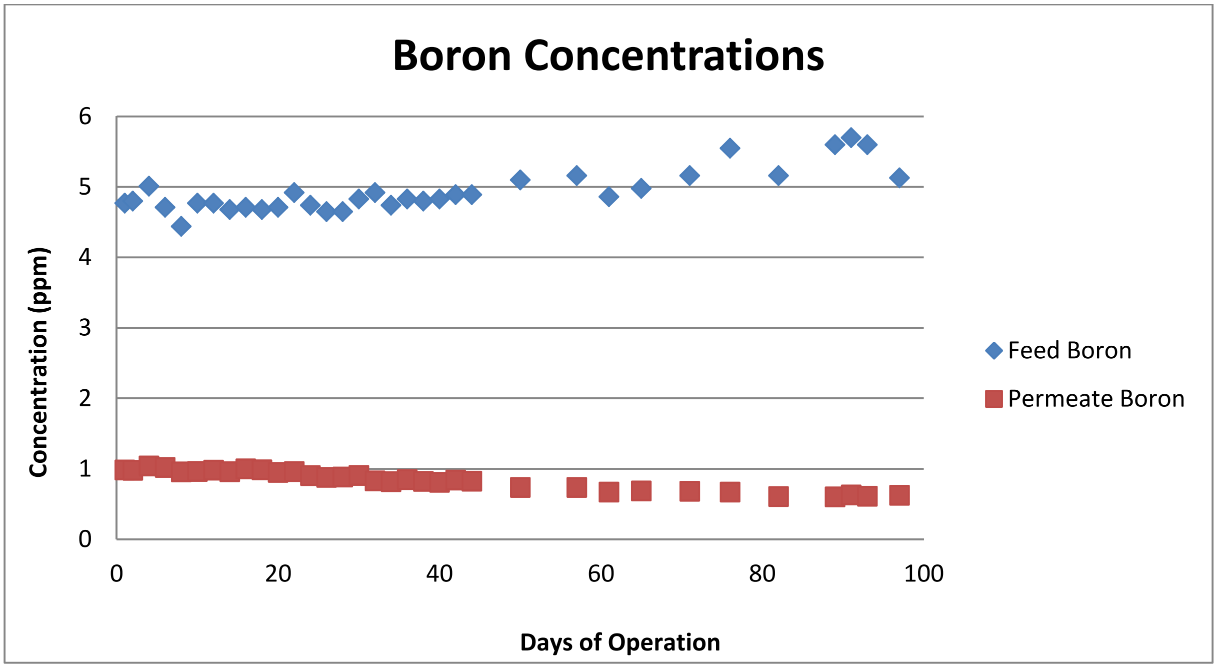
- From startup to October 20th: the system recovery was 44.7% and the production capacity was 3 m^3/hr. The associated system flux was 10.4 lmh
- From October 20th to December 20th: the system ran at a higher system flux of 11.5 as the production capacity was increase to 3.3 m^3/h. The recovery slightly increased to 45.3%

2) Results

Figure 6 graphs the measured boron concentrations in the permeate and RO feed samples. The boron concentration in the feed slowly increased from 4.5 to 5.5 ppm. The permeate boron concentration remained at or below 1 ppm at high temperature conditions and without pH adjustment then slowly decreased to 0.6 ppm as the temperature approached 15 ºC.

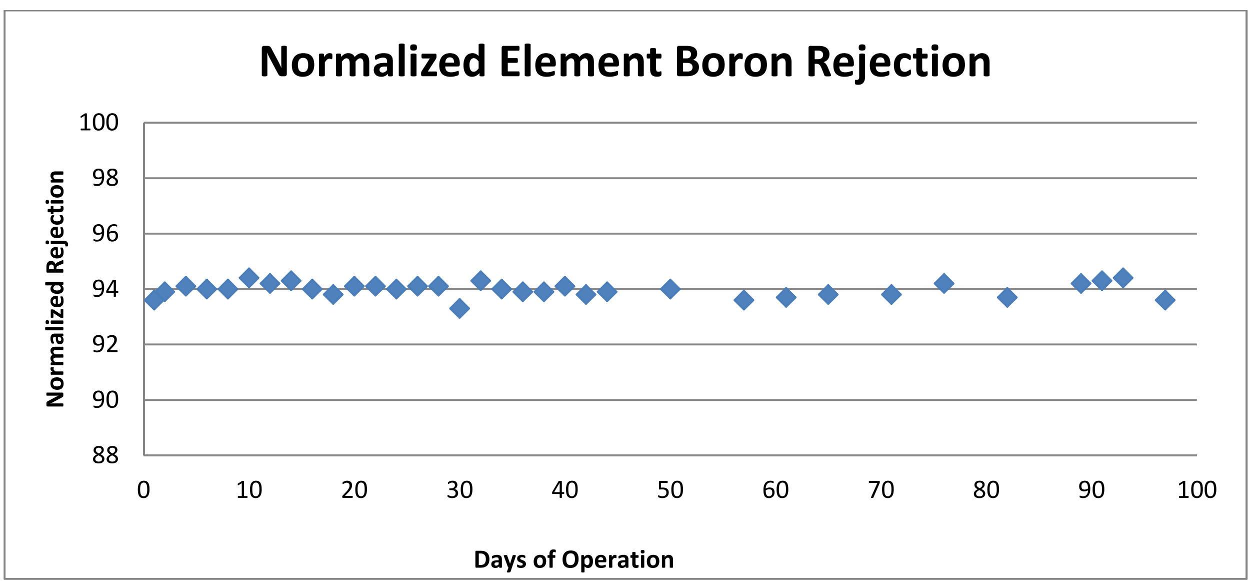
The change in operating conditions with an increase of the system flux from 10.4 to 11.5 lmh resulted in a slight drop in permeate boron concentration from 0.9 to 0.82 ppm.

Figure 6: Boron Concentrations



Based on the pilot test system data, the element boron rejection was normalized to standard SWRO test conditions: 800 psi, 32,000 ppm NaCl, 5 ppm feed boron, 8% recovery, pH : 8 and 25 ºC. The results are shown in Figure 7 below. The TFN membranes used in the pilot test have a constant boron rejection of 94%. This value is 1% greater than the specified value presented in the manufacturer data sheet of 93%.

Figure 7: Boron Concentrations



3) Temperature Correction Factor

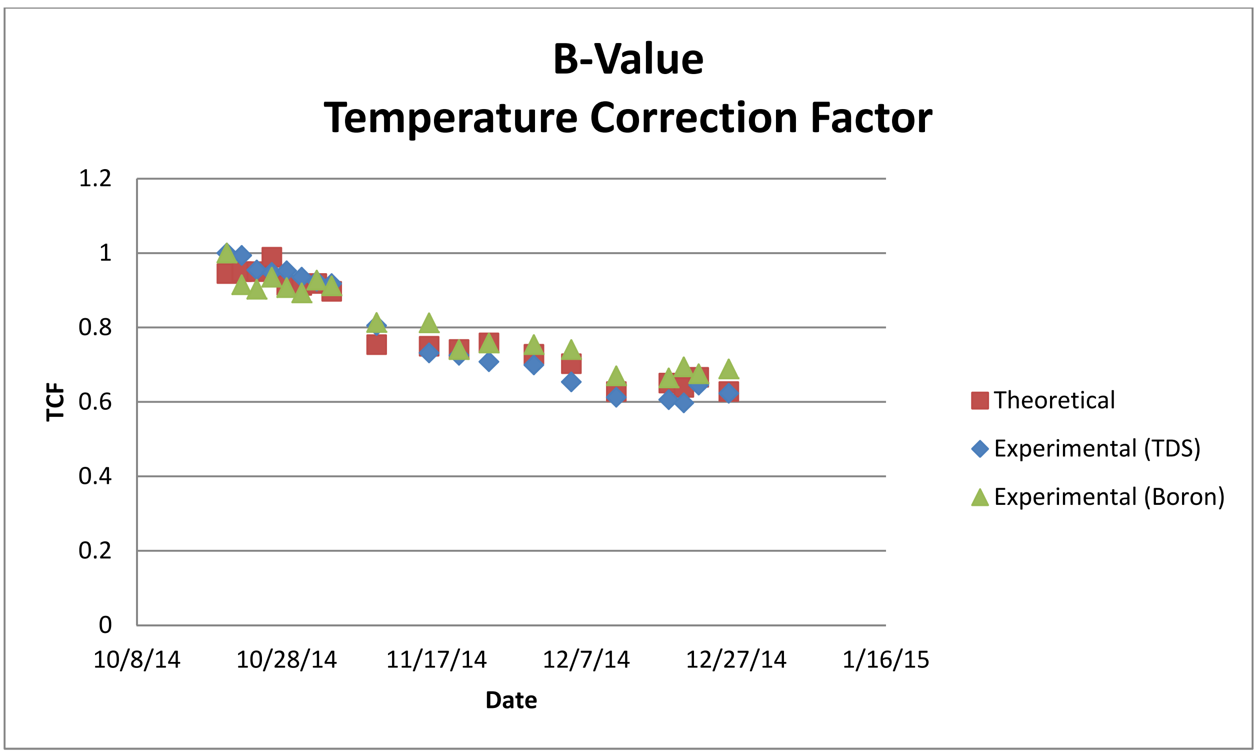
The effect of temperature on the permeate quality (TDS and Boron) was determined and verified. Temperature dependence of the membrane salt diffusion coefficient, B-value, follows the empirical equation [3]:

$$TCF = e^{(K(1/298-1/T))}$$

TCF: Temperature correction factor
T: Feed water temperature (Kelvin)
K: Activation Energy

Figure 8 graphs the theoretical TCF that is used in LG NanoH_2O's Q+ projection software and compares it to the values determined experimentally from TDS and Boron data. The experimental results fit very closely to the theoretical model. Therefore, the model is validated.

Figure 8: B-Value Temperature Correction Factor



IV. ECONOMICS: CASE STUDY

The pilot test results demonstrate that 1-ppm permeate boron can be achieved at the plant maximum temperature of 26 ºC, reached during the test, without any pH adjustment and caustic dosing. The main plant is equipped with a caustic dosing system that can increase the pH of the feed water to improve the boron removal capability of the SWRO elements. Caustic dosing system can be used in the cases when the permeate boron concentration exceeds the limit of 1 ppm.

Premise: Supposing the main plant at San Pedro del Pinatar II uses a standard 440-square foot TFC element performing at 8,250 gpd, 99.80% salt rejection, and 92% boron rejection.

Q+ projections [4], with this standard element, show that a feed pH adjustment of at least 8 is required to achieve a permeate boron level of 1 and below when temperature exceeds 22ºC. According to www.seatemperature.org [5], the average seawater temperature in that region is equal or above 22ºC from the months of June to September (four months out of the year).

Table 1 details the minimum caustic chemical cost for the San Pedro del Pinatar II plant to meet the permeate boron limit if operated with the standard TFC elements.

Table 1: Caustic Cost Analysis

Production Capacity	65 MLD
Recovery	45%
Raw Feed	144 MLD
Caustic Dosing from pH 6.7 to 8.0	25 mg/l
Daily Caustic Consumption	3,600 kg
Caustic Cost	$0.5/kg
Daily Caustic Cost	$1,800
Annual Caustic Cost*	$219,000

*assuming 33% of the time (warm season, temperature < 22ºC)

In this case study, by using TFN elements in lieu of standard TFC, pH adjustment of the raw feed to achieve the permeate boron limit could be eliminated, thereby saving the plant a minimum of $219,000 each year.

V. CONCLUSIONS

The findings of the pilot test at San Pedro del Pinatar on TFN membranes are as follows:

- 1 ppm permeate boron can be achieved at the highest tested temperature without any pH adjustment.
- The TFN membrane consistently performs at a normalized boron rejection of 94%.

- Field data validates the Temperature Correction Factor model for the salt diffusion coefficient used in LG NanoH_2O's Q+ projection software.

VI. REFERENCES

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