HYDRANAUTICS
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## Boron Removal by Hydranautics RO Membranes

The desalination of seawater by reverse osmosis is increasingly being utilized to obtain water for industrial, agricultural and potable uses. Hydranautics seawater membranes are producing over one million cubic meters of fresh water every day throughout the world. The level of total disolved solids (TDS) in seawater can range from 30,000 mg/L in the Gulf of Mexico to 45,000 mg/L in the Persian Gulf. Seawater's high level of TDS is composed primarily of sodium (Na), chloride (Cl), and other monovalent and divalent ions which are well rejected by the reverse osmosis membrane. But seawater also contains approximately 5 mg/L of boron (B) which, due to its size and charge, is not well rejected by reverse osmosis. Boron has increasingly become a concern in recent years due to its adverse effects on agriculture at concentrations as low as 1 mg/L. Additionally, because the human health effects of boron are under investigation and not yet fully understood, the World Health Organiztion (WHO) has recommended a maximum concentration of 0.5 mg/L[1].

## Hydranautics Experience

The typical Boron rejection of Hydranautics seawater membranes at nominal test conditions[2] is 92% - 93% depending on element permeability. This corresponds to about 80% - 86% boron rejection when operated in a typical commercial seawater system at a flux of 8 gfd (14 lmh) . A comparison of the different Hydranautics SWC membrane performance is shown in **Table 1**.

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[1] *Guidelines for drinking-water quality*, 3rd ed., Volume1, World Health Organization, 2004

[2] Feed TDS = 32,000 mg/L, Feed B = 5 mg/L, Feed Pressure = 800 psi, T = 25C, Rec = 10%, pH = 7

| Membrane | Flow gpd | NaCl Rej % | B Rej % |
|---|---|---|---|
| SWC4+ | 6500 | 99.8 | **93** |
| SWC3+ | 7000 | 99.83 | **92** |
| SWC5 | 9000 | 99.83 | **92** |

**Table 1. Hydranautics SWC element performance at Standard Test Conditions[2]**

Hydranautics routinely performs comparison testing of its elements with those of its competitors to demonstrate and maintain its technological advantage. A test of six different types of randomly selected seawater RO elements from the three leading manufactures confirmed Hydranautics advantage in boron rejection as well as membrane permeability. **Figure 1** below shows the results of this test where each data point represents the average of all the elements tested for that particular element type. The data point for the SW30HR-LE corresponds to a single element while the other data points correspond to an average of multiple elements as follows: TM820-400=6, SW30HR=4, SWC4+=153, SWC3+=18, SWC5=19.

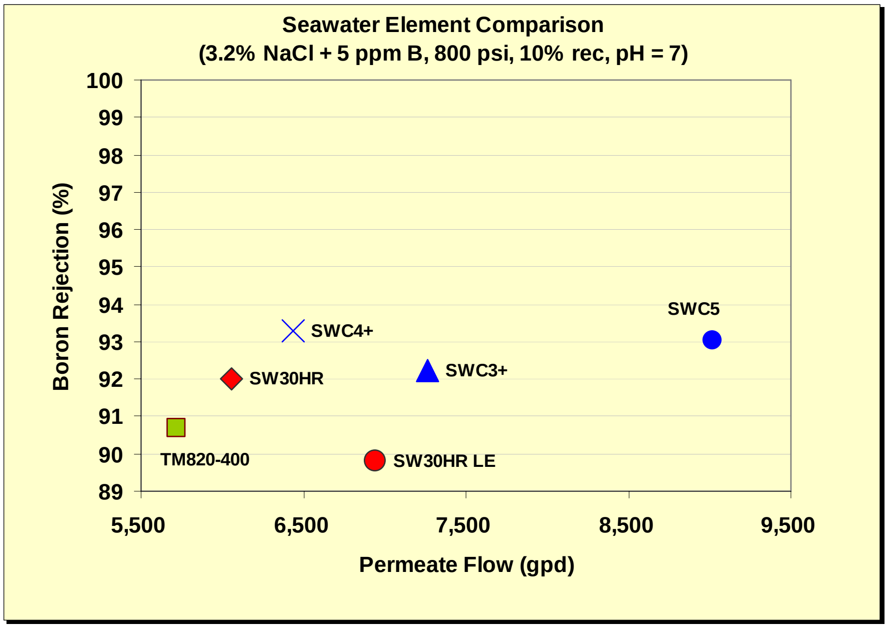

**Figure 1. Boron rejection and permeability of Hydranautics seawater membranes and competitors based on randomly selected elements at a standard test condition of: TDS = 32,000 mg/L, B = 5 mg/L, Pressure = 800 psi, T = 25C, Rec = 10%, pH = 7.**

Like other ions, the rejection of boron is influenced by various operating conditions including temperature, flux, and the ionic strength of the feed water. However, boron is unique in how its rejection is influenced by pH. The boron rejections stated above are typical at a pH of 7, when boron is present in the form of boric acid, **B(OH)3**. The ionization equilibrium of boric acid, a very weak acid, is represented as:

**$B(OH)3\ (aq)\ + H2O = H+(aq) + B(OH)4^{-}\ (aq)$** **Equation 1**

The lack of charge and small size of the boric acid molecule results in poor rejection by a reverse osmosis membrane. But at high pH, boron is present as the borate ion, **$B(OH)4^{-}$** ,which is well rejected by the reverse osmosis membrane due to its larger radius and negative charge. **Figure 2** shows estimated nominal boron rejection of the SWC membrane at 24 C and 30 C as a function of feed pH. Further discussion on how the RO system designer can take full advantage of this change in rejection as a function of pH can be found in the next section.

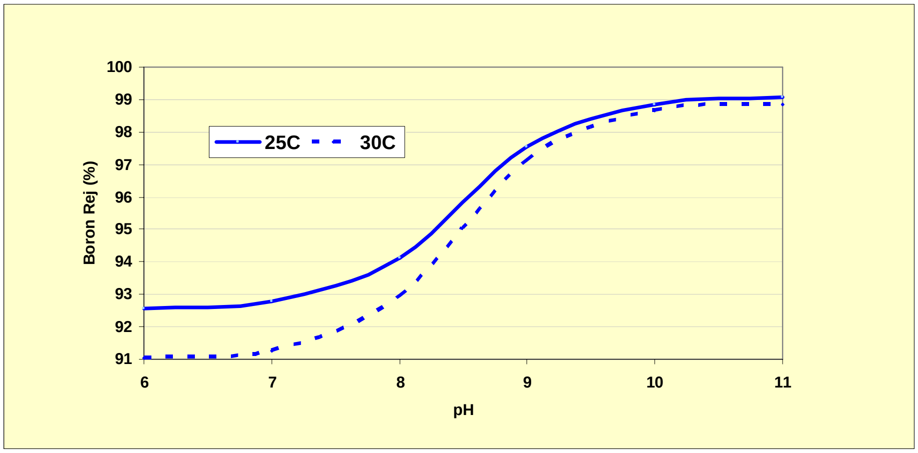

**Figure 2.** **Calculation of boron rejection of SWC membrane at 25 C and 30 C at standard test conditions (based on dissociation ratio of boric acid and the borate ion).**

In addition to extensive testing of the SWC at the Hydranautics facility in Oceanside, CA, the elements have also run at various locations in pilot units and large scale commercial desalination plants. **Table 2** lists actual sites in which the SWC has demonstrated its boron rejection capabilities. One particular site, treating Pacific seawater during a period of high temperature, experimented with dosing sodium hydroxide to elevate feed pH to 8.4 and increase boron rejection. Details of this procedure and other methods for increasing Boron rejection are discussed below.

| Source | Feed<br>pH | Temp<br>C | Recovery<br>% | Flux<br>GFD | B Rej<br>% |
|---|---|---|---|---|---|
| Mediterranean | 6.9 | 24 | 49 | 8.1 | **89** |
| Pacific | 7.7 | 22.2 | 50 | 7.8 | **85** |
| Pacific | 8.4 | 31.4 | 50 | 8.0 | **85** |
| Gulf of Mexico | 6.6 | 34.3 | 61 | 8.8 | **78** |
| Mediterranean | 6.6 | 21 | 40 | 7.2 | **90** |

**Table 2. Demonstration Sites Utilizing the Boron Rejection Capabilities of Hydranautics SWC membrane.**

The first major seawater commercial system using spiral wound reverse osmosis membranes to specify a permeate boron limit was the 50,000 m3/day Mediterranean seawater plant in Larnaca, Cyprus. The plant has been successfully operating since March of 2001. Since that time, Hydranautics' SWC membranes have been producing potable water with a boron specification of less than 1 parts per million (ppm). The SWC elements provide optimal performance in Larnaca's cutting edge system (designed by IDE and Hydranautics) which contains a split partial second pass that treats up to 25% of the overall flow from the first pass when the water temperature ranges between 15-30º C (59-86º F) to ensure the required quality standards.

## Design Considerations

Plants designed with a permeate boron limit usually set that limit at or below the World Health Organization's 0.5 mg/L. Despite its high boron rejection, a single pass system equipped with SWC elements alone may not be sufficient to achieve such low levels when treating typical sea waters, especially at high temperatures. For this reason, Hydranautics recommends a number of design solutions to further reduce the permeate boron level. These solutions include:

1. Partial or full second pass RO processing of first pass permeate with pH increase in the second pass.
2. Using high boron rejecting brackish membranes (ESPAB) in the second pass.
3. Additional permeate polishing with boron selective ion exchange resin
4. First pass pH increase.
5. Elimination of second pass recirculation to the first pass feed.

## Two pass system.

In a two pass configuration, all or a portion of the permeate from the first pass is pH adjusted then processed by brackish membranes in a second pass unit (**Figure 3**). As with the SWC membrane, the pH increase in the second pass stream results in an increased ionization rate of boric acid and subsequently leads to higher boron rejection by the brackish membranes. Due to the risk of scaling at higher pH, the practical pH limit to the second pass is about 10.5, which corresponds to brackish membranes boron rejection rate of approximately 95%.

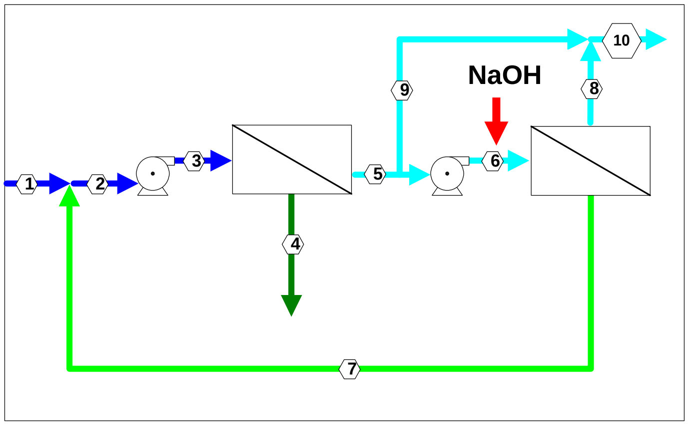

**Figure 3. Two pass partial seawater desalination for increased boron rejection.**

Depending on boron level requirements and operating conditions, the second pass may be either a full or partial second pass design. If partial second pass is sufficient to produce the required boron level in the combined permeate, then application of a split partial configuration (**Figure 4**) can improve process economics. When compared to a conventional two pass design, the split partial configuration can reduce the number of elements required by 6% to 10%, with a similar reduction in power consumption. As shown in greater detail in **Figure 5**, the first pass permeate is collected from both ends of the first pass pressure vessels. The low salinity (and low boron concentration) fraction obtained from the feed end is used for blending. The high salinity fraction obtained from the concentrate end is processed with the second pass unit after pH adjustment. Due to high feed pH, special attention should be paid to calcium and magnesium concentrations in the concentrate to avoid scaling.

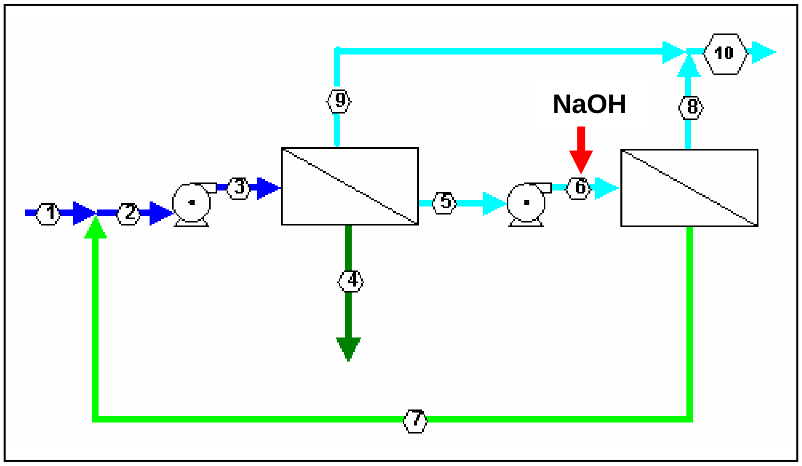

Figure 4. Two pass split partial seawater desalination for increased boron rejection.

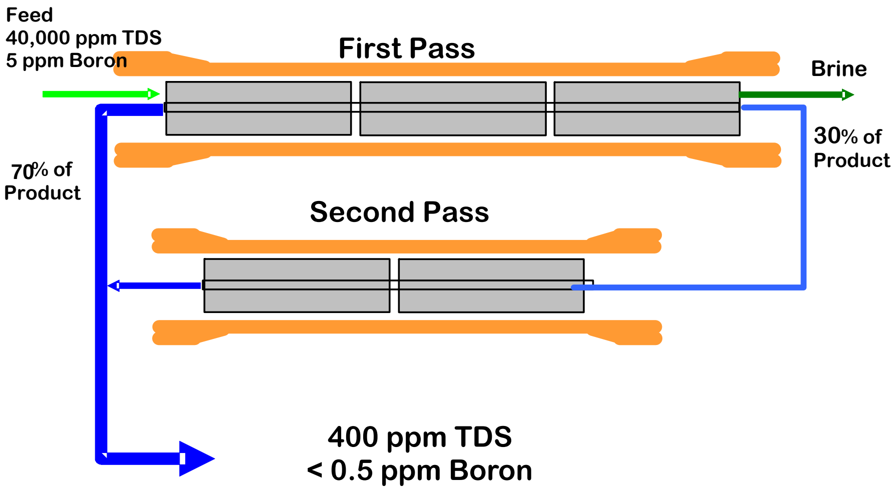

Figure 5 Boron Reduction using Split Partial Two Pass Configuration

## ESPA-B high boron rejecting brackish element.

To further improve the Boron rejection of a two pass RO system, or to remove Boron from a brackish water source, Hydranautics offers the high boron rejecting ESPA-B. Built on Hydranautics proven Energy Saving Polyamide (ESPA) technology, the ESPA-B operates at lower pressures like other low energy brackish elements, but with 33% lower boron passage. At an elevated pH of 10 and standard brackish test conditions, the ESPA-B can achieve a boron rejection of 96%.

## Ion exchange

The ion exchange system for boron reduction utilizes boron selective resin, which is regenerated with acid and caustic. In the past, use of ion exchange for boron reduction was limited mainly to applications in the semiconductor industry. The advantages of ion exchange resin are low concentration of boron in the effluent (< 0.1 ppm), low power consumption, and low water losses (high recovery rate). The disadvantages are the high cost of resin replacement and chemicals for regeneration. Also, because ion exchange process does not result in any reduction of water salinity, the required level of permeate salinity must be produced in the first pass unit. **Figure 6** shows a typical integrated system in which ion exchange is used after the first and second pass RO to further reduce Boron levels.

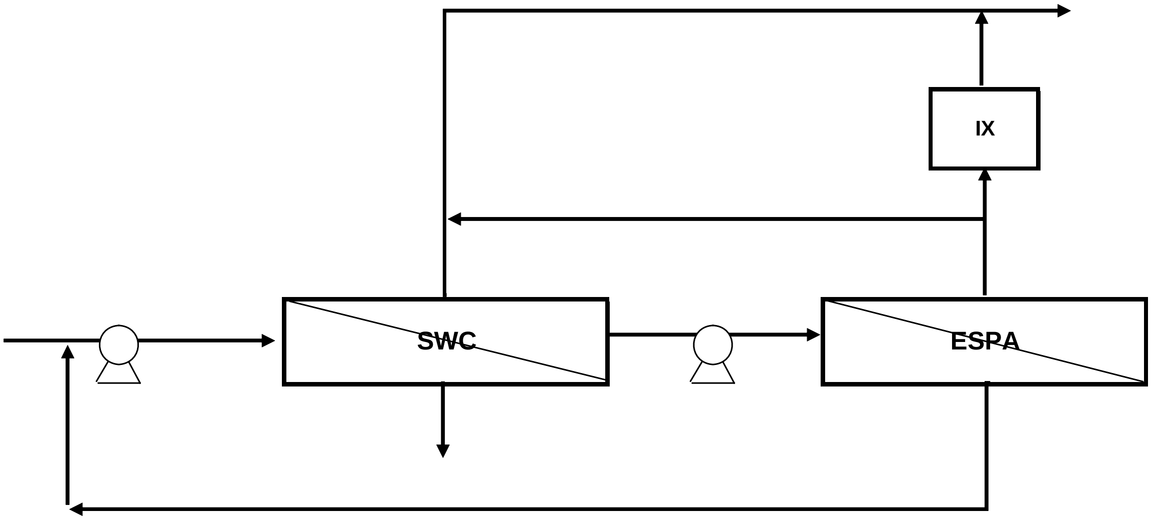

**Figure 6. Boron Reduction Using Split Partial Second Pass and Ion Exchange**

**Increase in first pass pH**

It has been established that operation at elevated feed pH increases boron rejection. This approach has been utilized in the second pass RO units where the relatively low levels of calcium and magnesium allow for operation at higher pH while still avoiding scaling. But what about an increase in pH to the first pass for the purpose of improved Boron reduction? Scaling potential in RO seawater systems is not well defined. Early research postulated operating at a feed pH that would result in negative value of the Stiff and Davis saturation indicator[1], commonly accepted in seawater design for estimation of calcium carbonate scaling potential. For this reason, commercial seawater systems operate at reduced feed pH (through acidification) or at native seawater pH, adding scale inhibitor to prevent potential scaling. Seawater does contain high concentrations of calcium and magnesium. However, due to its high ionic strength, the solubility of calcium carbonate and magnesium hydroxide is higher than in low salinity water. Additionally, in the high ionic strength seawater, ionization of boric acid is shifted to a lower pH. For this reason, the possibility of increasing boron rejection by increasing seawater feed pH was explored.

Tests using Pacific seawater spiked with sodium chloride, calcium chloride and magnesium chloride to simulate concentrate composition were conducted by Hydranautics to evaluate precipitation potential of calcium carbonate and magnesium hydroxide in the pH range of 8.1 to 10.4[2]. The laboratory experiments were followed by test operation of commercial seawater units at high feed pH with good results. The testing demonstrated the technical and economic feasibility of operating a seawater system in the feed pH range of 8.3-8.5. Raising the feed pH to such levels could provide a solution to high boron passage during operating periods of high feed water temperature, high levels of feed boron, or unexpected deterioration of the membranes' boron rejection.

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[1] J. W. Strantz, Predicting CaCO3 scaling in seawater RO systems, Technical Proceedings WSIA 10th Annual Conference and Trade Fair; Water Supply Improvement in the Next Decade, Honolulu, HI, July 25-29, 1982

[2] M. Wilf, EVALUATION OF BORON REDUCTION PROCESSES IN RO SEAWATER SYSTEMS, Hydranautics Internal Technical Report, Oceanside, CA November, 2002.

**Elimination of second pass concentrate recycle.**

In a two pass seawater system, it is desirable to recycle the second pass brine stream back to the first pass feed to reduce overall feed salinity. Unfortunately, in the case of boron, the opposite is true. Because of the already low feed boron level, recycling the brine stream may lead to an increase in boron concentration to the RO. For this reason, elimination of the second pass concentrate recycle, though decreasing the overall efficiency of the system, can further decrease the final permeate boron level.

## Hydranautics IMSdesign Projection Software

In response to the boron requirements of newly proposed seawater systems, Hydranautics offers its popular IMSdesign© Software. This projection program is available for download from www.membranes.com to assist with the design of reverse osmosis systems- including those seawater systems having a stringent permeate boron requirement. The program includes the following features:

1. The ability to design a STANDARD partial or SPLIT partial two pass system.
2. The ability to increase pH to the first AND second pass.
3. A printout which supplies a detailed water analysis (including boron) of the first and second pass streams as well as front and back streams when designing a SPLIT partial system.

## Summary and Conclusions

The typical reverse osmosis membrane's poor rejection of the boron present in seawater poses a challenge to the growing demand for desalinated water for municipal or agricultural uses. Hydranautics meets the boron challenge with its high Boron rejecting seawater and brackish water membranes. At 92-94% boron rejection, the SWC is the highest boron rejecting seawater membrane available. At 96% boron rejection, the ESPA-B is the highest boron rejecting brackish membrane available. The use of SWC and ESPA-B with the various design options presented in this paper provides our customers with a means to achieve their required boron levels. Meeting the boron challenge with the best membranes in the industry, along with technical support, computer software, and research and development, demonstrates Hydranautics continued commitment to leadership and excellence in the field of seawater desalination.

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