

BORON REMOVAL IN SEA WATER DESALINATION

Authors: Markus Busch, William E. Mickols, Steve Jons, Jorge Redondo, Jean De Witte

Presenter: Markus Busch

Abstract

This paper starts with an introduction to the boron problem and its relevance in sea water desalination. The chemistry of boron in water is studied in detail from a sea water desalination point of view. Detailed results of boron rejection with various membrane types are presented. The impact of ionic strength, temperature, average permeate flux and harsh cleaning conditions is investigated. Some typical boron results from 4 plants in the field are presented. The use of boron-selective resins in sea water desalination is also covered, studying both the general properties of such a type of product and indicating how it can be applied in sea water desalination.

LENNTECH

info@lennotech.com Tel. +31-152-610-900

www.lennotech.com Fax. +31-152-616-289

I. INTRODUCTION TO THE BORON PROBLEM

Due to increasing demand for water, both for potable use and for irrigation, coupled with a decrease in suitable water sources, suppliers have to turn to alternatives. Sea water desalination or treatment of high saline, eventually contaminated surface waters have become standard. By using those alternative sources more trace contaminants start to appear in the final product. Among these is boron.

Boron in drinking water from brackish surface waters or ground water can be traced back to either residuals from waste water treatment plants (mainly borate from detergent formulations) or to leachables from subsurface strata. In the case of a sea water source the typical boron concentration in the raw water is 4.5 mg/L [1]. Depending on location and seasonal effects, the boron concentration can reach up to 7 mg/L, e.g. in the Arabian Gulf.

There are two predominant reasons for limiting boron in water:

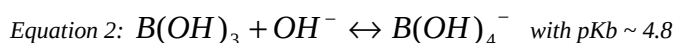
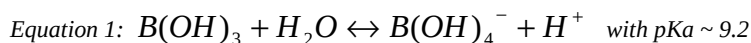
- For humans boron can represent reproductive dangers and has suspected teratogenic properties. The WHO has set a preliminary limit of 0.5 mg/L for drinking water [2]. The EU is suggesting a guideline of 1.0 mg/L.
- A major limiting factor is the possible damage to plants and crops. Although boron is vital as a trace element for plant growth and is supplied in fertilizer it can be detrimental at higher concentrations. Amongst the more sensitive crops are citrus trees, which show massive leaf damage at boron levels of more than 0.3 mg/L in the irrigation water [3]. Excess boron also reduces fruit yield and induces premature ripening on other species such as kiwi.

As a consequence we have seen the appearance of boron limits in the tender documents for medium and large membrane desalination plants with values between 0.3 and 1.0 mg/L.

II. BORON CHEMISTRY

Boron is usually present in waters as boric acid, which has a slightly complicated chemistry: at higher concentrations and temperatures polymers are formed [4]. This behavior is very important in the water cycles in pressurized water reactors. Because of this, the equilibrium constants have been investigated at the extremes of temperature, pressure, and ionic strength and the rates of formation of some of the species have been measured.

In the case of sea water the total boron concentration (in all its forms) is low. The natural seawater concentrations vary but have a maximum near 7 mg/L in the feed. If we assume a maximum recovery from a sea water plant of 60%, the maximum total boron concentration could amount up to about 15 mg/L. For this case the concentration of the higher adducts do not need to be taken into account. Also for these concentrations we don't need to include the pressure dependence of the pK. This means that for most sea water plants, we only need to consider the equilibrium given below.

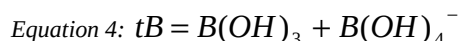


There are several things to note about this equilibrium. It shows that boric acid is a Lewis acid because it abstracts a hydroxide (OH⁻) ion from water releasing a hydrogen (H⁺) ion. In the opposite direction of

borate to boric acid it releases an OH^- ion which recombines with an H^+ ion to form water. Hence, the trivial form of equation 2 can be rewritten to the following

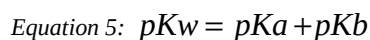


The total boron concentration is simply the sum of the two:



Equation 1 and Equation 2 lead us to two different representations for the equilibrium. These are the acid dissociation constant pK_a for Equation 1 to be used with pH , and the base dissociation constant pK_b for Equation 2 and which goes with pOH .

The earliest determination of the temperature dependence of the equilibrium constants used the newly developed relations for a weak simple acid [5]. These authors showed that the pK_a changed from 9.079 to 9.38 as the solution changed from a temperature of 10 to 50 °C. Later Mesmer [4] used the representation in Equation 2 and did find a different temperature dependence. The differences are simple: The dissociation constant of water pK_w is equal the pK_a plus the pK_b (Equation 5). The constant amounts to 14.35 at 15 °C (59 °F), 14.00 at 25 °C (77 °F) and 13.55 at 20 °C (68 °F). It is important to note that a pH at 30 °C (86 °F) or 15 °C (59 °F) is not the same hydroxide ion activity and hence for boron dissociation as at 25 °C (77 °F) due to the change in the pK of water (pK_w).



Mesmer *et al.* [4] reported the pK_b as a function of temperature and ionic strength using KCl as the method of adjusting ionic strength. Figure 1 shows how the pK_b changes over the range of temperatures of 5 to 50 °C (41 to 122 °F) and ionic strengths that vary from 0.1 (0.5% NaCl) to 1.2 (7.3%). The high end (7.3%) represents a 50% recovery system with a feed of 3.65% NaCl.

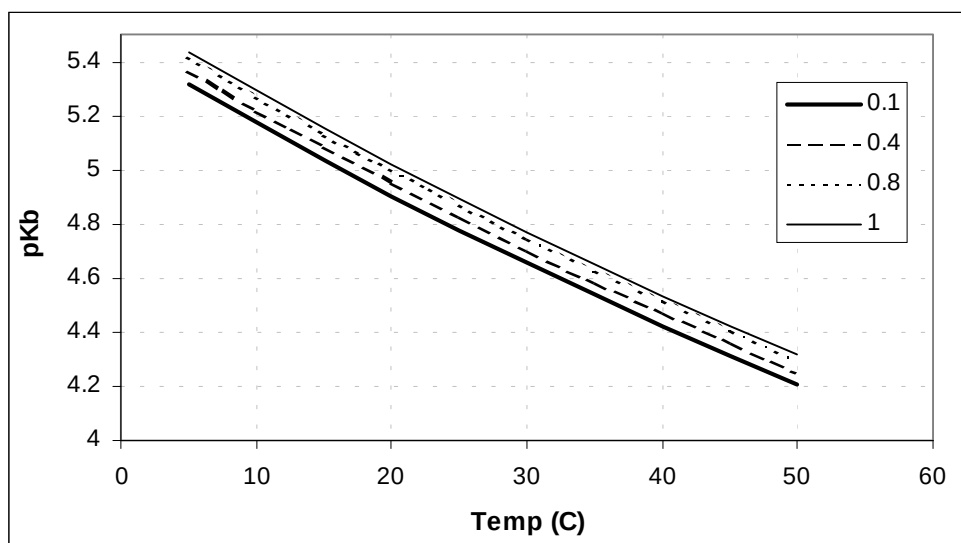


Figure 1: Borate pK_b vs. temperature at different ionic strengths

In the range between 10 to 45 °C (50 and 110 °F), the pK_b ranges from 5.2 to 4.4 (equivalent to a pK_a variation of 8.7 to 9.7). This means that, if the total boron separation was only governed by the pK of the equilibrium, a low temperature water can have a significantly higher amount of the $\text{B}(\text{OH})_4^-$ species and

hence a much better boron rejection. Figure 2 shows the amount of uncharged $B(OH)_3$ as a function of temperature and ionic strength. The larger shift is found in the temperature and there is a significant shift in the distribution of charged to uncharged species as a function of temperature. Literature data contradicts itself and more detailed studies at high and low temperatures at a pOH of 4-6 (nominal pH of 8-10) will need to be done to resolve this issue.

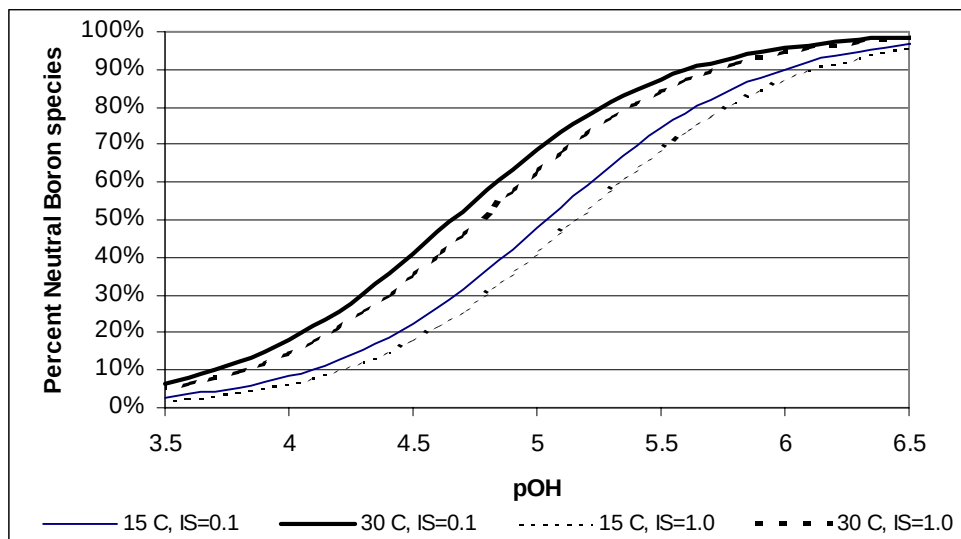


Figure 2: Percent of total boron in the neutral form as a function of pH and ionic strength

Millero [6] used a more complicated simulation of sea water to estimate the extent of dissociation of borate in a complex mixture. The borate passage is commonly assumed to be only governed by the pK of boric acid. Several researchers have reported unexpected rejection vs. pH curves. Rodriguez [7] reported an inflection point of rejection in a brackish water separation of 9.1 which agrees with their quoted pKa. Prats *et al* [8] determined the pH dependence of 3 commercial element types operated on the same feed, at the same recovery, and run at the same time. Under these conditions and with similar NaCl rejection the inflection points should roughly correspond to the pKa of equilibrium (quoted as 9.3). In their paper they reported two element types (with different borate rejections) had the same inflection point. The third element type had a very different inflection point. This shows that membrane parameters affect the separation.

As expected the recovery of the system also affect the apparent borate rejection [6], [7], [8]. At an elevated borate concentration of 35 mg/l [9] the rejection can be improved substantially. This is unusual and has not been explained up to the present, but for the more natural range of boron concentration this is not relevant. The dielectric change that the borate sees when diffusing through the membrane should favor the transport of the neutral species and should shift the apparent pK to a higher pH than expected. A heterogeneous membrane would increase the pH dependence. So the inflection point will depend strongly on the temperature and more weakly on the concentration, ionic strength and the heterogeneity of the membrane structure.

III. FACTORS INFLUENCING BORON REJECTION

The literature study on the chemistry of boron in the above paragraphs indicates the influence of feed water properties such as pH, total dissolved solids (TDS) and temperature on the boron rejection. It is also generally known that membrane type and operational conditions have a strong influence on the

boron rejection of a sea water reverse osmosis system. This extends the list of possible factors to the following:

- Feed water: pH, temperature, TDS
- Membrane element: membrane chemistry, element efficiency
- System design and operation: average permeate flux (APF), system recovery, concentration polarization, cleanings

The interactions of the various factors are shown in more depth below. First, the strongest parameters, pH and membrane type are studied in context. Then the impact of temperature is studied in more detail, since only sparing work has been done to date on this subject. Finally, operational factors analyzed. A special emphasis is put on average permeate flux and the impact of cleanings.

3.1 Boron Rejection As A Function Of pH And Membrane Type

At the natural pH of 7 to 8 of most waters used in desalination the predominant species is boric acid in molecular form. At these pH values, the percentage of the non-dissociated boron species $B(OH)_3$ is between 99.3 (pH 7) and 93.2% (pH 8) of total boron. The rejection of that species is in the range of 82-92% for most sea water RO membrane products in the market, and the rejection for brackish water products ranges between 30 and 80%. Typical boron rejections for the FILMTEC™ products SW30HR-380, SW30HR-320, SW30-380, BW30-400 and BW30LE-440 under FilmTec standard test conditions, based on tests with 300 elements, are shown in Table 1. In the standard test condition at pH 8, 93.2% of molecular boron are present as neutral $B(OH)_3$ and 6.8% as $B(OH)_4^-$. Therefore this condition reflects mainly the rejection of the neutral species.

Table 1: Typical boron rejection with FILMTEC sea water (SW) and brackish water (BW) membranes at standard test conditions

Product	Specification	Boron rejection at natural pH (pH 8)	Boron rejection at high pH (pH 9.5)	Boron rejection at very high pH (pH 11)
FILMTEC SW30HR-380	0.95 m ³ /h (6000 gpd) flow, 99.70% salt rejection	90% (88-92%)	97%	99.5%
FILMTEC SW30HR-320	0.79 m ³ /h (5000 gpd) flow, 99.70% salt rejection	90% (88-92%)	97%	99.5%
FILMTEC SW30-380	1.43 m ³ /h (9000 gpd) flow, 99.40% salt rejection	88% (85-90%)	96%	99%
FILMTEC BW30-400	1.67 m ³ /h (10500 gpd) flow, 99.50% salt rejection	65% (55-75%)	88%	99%
FILMTEC BW30LE-440	1.81 m ³ /h (11500 gpd) flow, 99.0% salt rejection	55% (45-65%)	84%	98%

FilmTec standard test conditions:

- 32000 mg/L NaCl, p=55 bar (800 psi), T=25 °C (77 °F), pH=8, Recovery Y=8% for SW30HR and Y=10% for SW30
- 2000 mg/L NaCl, p=16 bar (225 psi), T=25 °C (77 °F), pH=8, Recovery Y=15% for BW30-400
- 2000 mg/L NaCl, p=10.7 bar (150 psi), T=25 °C (77 °F), pH=8, Recovery Y=15% for BW30LE-440

There are considerable differences between the individual products: the difference between sea water (SW) and brackish water (BW) membranes varies from 90% rejection for the SW30HR-380 to 65% for the tighter brackish water product BW30-400. A further difference can be seen with the lower energy membrane, which uses a more permeable membrane, and has a standard boron rejection of 54%. FilmTec in-house tests have confirmed a very low standard deviation for the boron rejection of standard production: e.g. 96% of all delivered FILMTEC SW30HR-380 product is between 88 and 92%. Boron rejection forms part of a routine audit program for membrane quality at FilmTec. Results from the last

half year are presented in Figure 3. Boron rejection according to the chemical principles described in this chapter 0 and the data in Table 1 has been included in the new version 5.3 of the design program ROSA (Reverse Osmosis System Analysis).

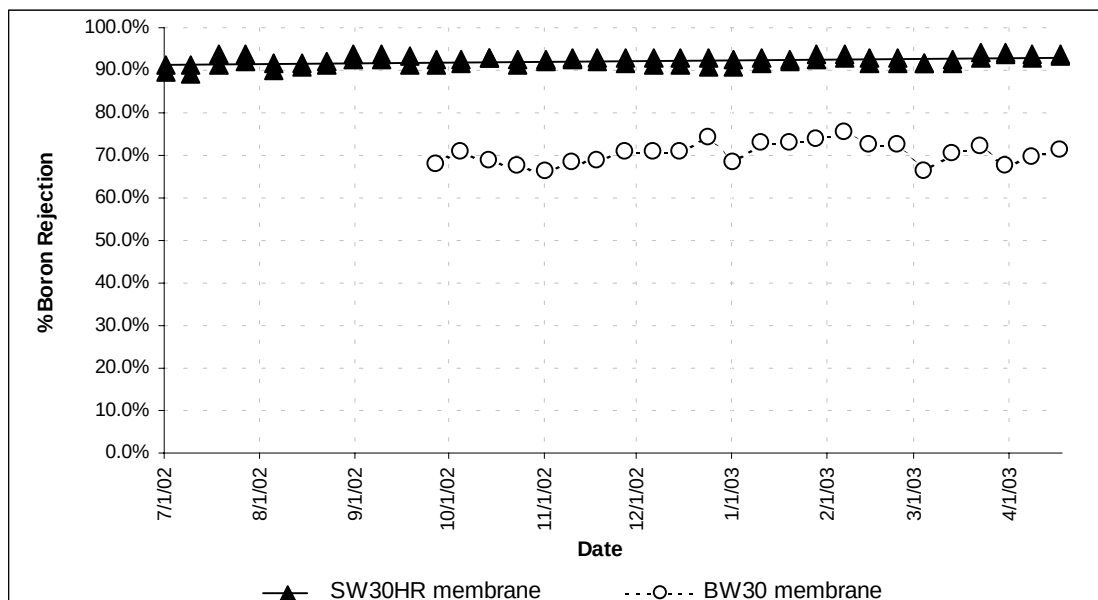


Figure 3: Boron rejection audit program

At higher pH values, rejections are significantly improved, which is due to the shift to the better rejected $B(OH)_4^-$ species. However, even at very high pH values, a small portion of uncharged $B(OH)_3$ is present which has a significant impact on the passage of total boron (tB). This results in the typical dependence of rejection from pH displayed in Figure 4.

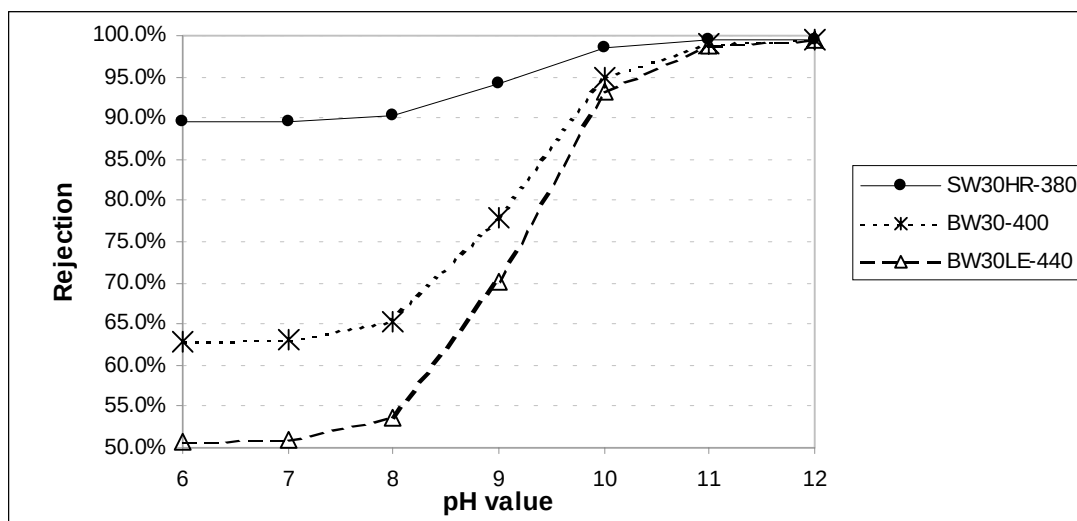


Figure 4: Boron rejection with FILMTEC membrane elements as a function of pH

Figure 4 confirms what can be expected from the distribution of the boron species: in the region around the pH value for the dissociation of boric acid, there is substantial improvement with every unit of pH

shift. A shift to pH 10 brings the total boron rejection to 93 - 99% depending on the membrane chemistry. At a pH of 11, the total boron rejection is 99.0 - 99.5%.

It should be noted that operation in this pH region with FILMTEC membrane elements is safe, provided the appropriate anti-scalants are used. The necessity of scaling prevention will depend upon the composition of the feed water and in many situations the use of anti-scalants is not required. Based on above observations, it is obvious that high pH operation is advantageous for boron rejection.

3.2 Temperature

It had been shown above that temperature had a strong influence on the pKa and pKb value of boron. This is of relevance since sea water feeds between about 10 to 45 °C (50 and 110 °F) are being used for desalination around the world. It was observed that in this temperature range, pKa varies from 8.7 to 9.7, which results in a stronger presence of the $B(OH)_4^-$ and therefore a better boron rejection. In the first pass of a sea water system, the borate passage would be reduced by several percentage for every reduction of 10 °C (18°F) in temperature solely due to the temperature-pK effect. In the second pass, where usually caustic is added to increase pH, caustic savings corresponding to 0.5 to 1 pH units are possible. This could reduce caustic consumption by factors of up to 10.

In addition, the effect of the pK shift is reinforced by the general effect of increased salt passage through membranes in direction of high temperatures. This is due to the fact that membrane permeability, both for solvent (water) and solutes (salts, boron) is a function of temperature. Due to the temperature-pK effect, a stronger temperature dependence on rejection as for other salts is observed for boron. Figure 5 considers this effect with projections of permeate boron and TDS as a function of temperature, using ROSA 5.3 design program, which includes the above mentioned effects. The example is one pressure vessel of seven 8" elements with an average permeate flux of 16 L/h/m² (9.4 gfd), a feed with a TDS content of 39,000 mg/L, a feed boron concentration of 5 mg/L and a feed pH of 7.6.

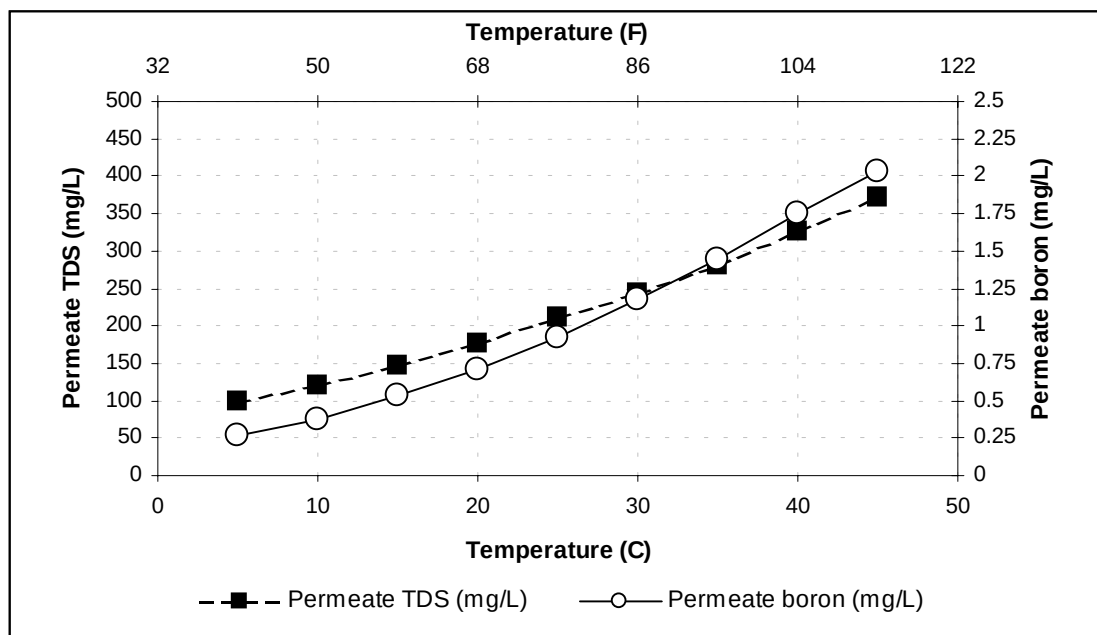


Figure 5: Temperature dependence of permeate TDS and Boron rejection

Expected permeate TDS and boron concentrations are displayed versus temperature. For a temperature below 25°C (77 °F), the boron concentration is below the limit of 1.0 mg/L (EU recommendation) and for a temperature below 15 °C (59 °F) the boron concentration is below 0.5 mg/L (WHO recommendation). It can be seen that indeed the slope of the boron curve is stronger than the slope of the TDS permeate prediction curve. The boron passage increases by 5.5% per °C (2.9% per °F) while the TDS passage only increases by 3.6% per °C (2.0% per °F).

On a practical scale, the stronger temperature dependence has various implications:

- In some cases the lower temperature waters are heated before processing. In the Middle East some plants use thermal-membrane hybrid configurations. In the boron removal case this should be examined more closely from the economics of the improved rejection and favorable pK at lower temperatures.
- Sometimes the designer of a system has the choice between beach well feed and an open intake. Sea water feeds are subjected to seasonal temperature variations of +/- 3 to 6 °C (about +/- 5 to 11 °F). These are reduced by soil filtration to +/- 1.5 to 3 °C (about +/- 3 to 5 °F). In cases where the beach well option is feasible and boron is of high importance, it can be beneficial to select the beach well option, since the high temperature peaks, which will challenge boron passage most, will be reduced.

3.3 Average Permeate Flux

According to the equations of the solution-diffusion model, water transport is a function of the net driving force and membrane water permeability, salt transport is a function of the concentration differential and the membrane salt permeability. Salt flux divided by water flux equates to the permeate concentration. Operation of a membrane system at higher fluxes results in lower concentrations.

Recent progresses in membrane chemistry, such as higher flow products as well as high pressure capability, enable higher system productivity. Advanced pre-treatment, such as ultrafiltration systems, and enhanced operation knowledge, e.g. use of DBNPA treatment [10], enable operating systems at increasing average permeate fluxes.

Therefore the impact of operation of a system at a higher average permeate flux (APF) was assessed in the standard example considered above for the cleaning case. Fluxes between 10 and 20 L/h/m² (6 to 12 gfd) are considered here for a temperature range of 15 to 35 °C (70 to 95 °F). The results are shown in Figure 6.

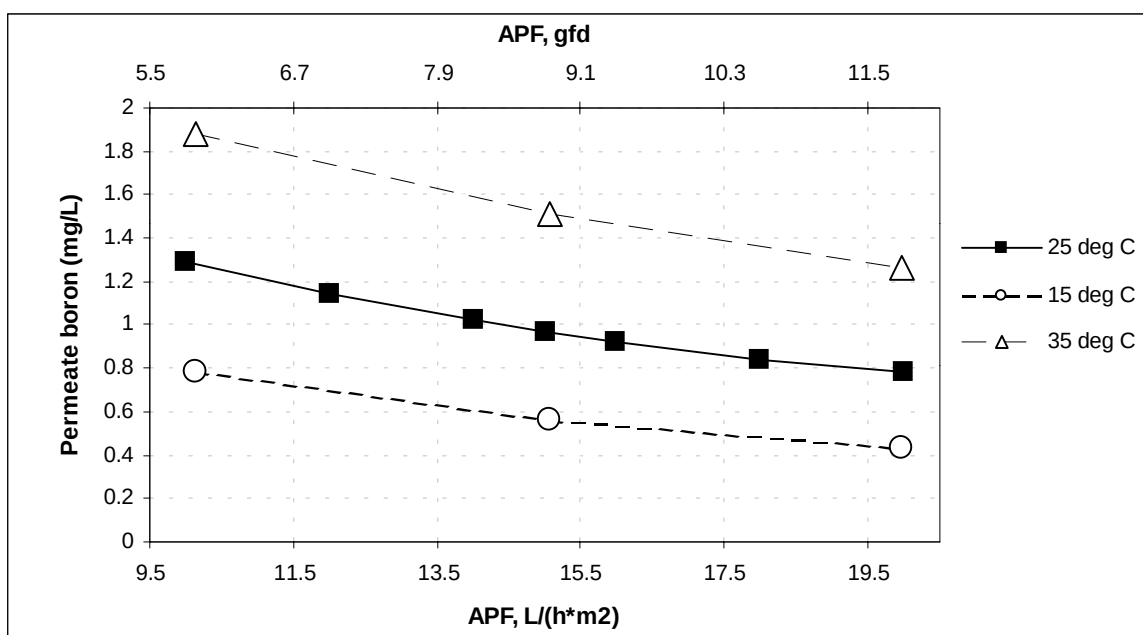


Figure 6: Impact of APF on boron permeate concentration

For a temperature of 25 °C (77 °F), the APF has to be > 15 L/h/m² (8.8 gfd) to produce water with <1.0 mg/L. For a temperature of 15 °C (70 °F), an APF of 17.5 L/h/m² (10.3 gfd) enables producing water with <0.5 mg/L.

3.4 Impact of Cleanings

Since the boron rejection of conventional RO membranes at neutral pH values is lower than the rejection of chlorides, factors that affect chloride rejection might affect boron rejection even more strongly. Hence, long-term membrane stability with regards to chemical exposures remains a crucial question.

Apart from accidental exposures to destructive chemicals, harsh cleaning conditions, especially the high pH conditions, are of interest. Scaling can be well controlled with today's anti-scalants and most scales (carbonates, hydroxides, sulfides) can be removed by relatively mild pH, but fouling control remains difficult and for its removal high pH cleaning conditions have proven extremely useful.

Therefore the impact of cleanings on the boron rejection of sea water membranes was assessed. Three commercially available high rejection sea water elements were used in the study:

- “Brand A”: FILMTEC SW30HR-380, 35 m² (380 ft²) active area, 0.95 m³/h (6000 gpd) flow, 99.70% rejection
- “Brand B”: 34 m² (370 ft²) nominal area, 0.93 m³/h (5900 gpd) flow, 99.70% NaCl rejection
- “Brand C”: 34 m² (370 ft²) nominal area, 0.95 m³/h (6000 gpd) flow, 99.75% NaCl rejection

For each model, five membrane coupons were representatively sampled from 5 different locations of different membrane leaves from three autopsied 8” elements per brand. These coupons were tested after 1 hour of stabilization, then subjected to a 16 hours soak at pH 12 and a temperature of 25 °C (77 °F), then retested after 1 hour of stabilization. The tests were performed in flat cell equipment with 32000 mg/L NaCl feed, 25 °C (77 °F), pressure of 55 bar (800 psi), pH=8, Recovery Y=8%. The results are shown in Table 2.

Table 2: Influence of high pH condition on boron rejection

Parameter	Flux, L/h/m ² (gfd)		R(NaCl), %		R(B), %	
	<i>Before</i>	<i>after</i>	<i>before</i>	<i>after</i>	<i>before</i>	<i>after</i>
Brand A	27.9 (16.4)	33.8 (19.9)	99.89	99.87	92.9	91.5
Brand B	38.4 (22.6)	45.3 (26.7)	99.85	99.81	90.3	86.7
Brand C	42.1 (24.8)	43.1 (25.4)	99.90	99.84	93.6	91.1

The data obtained was somewhat surprising. Even though the corresponding elements of brands A to C have very similar flow specifications (0.93 to 0.95 m³/h or 5900 to 6000 gpd), the fluxes (relative to the active coupon area) were statistically different. This required an explanation and a root-cause analysis was performed. The different flux results were finally explained by a series of 3 membrane autopsies per brand, which indicated that for brands B and C, there was a difference between the “nominal area” of 34 m² (370 ft²) and the “active membrane area”, which was usually in the range of 29 to 30 m² (310 to 320 ft²). Based on these results it seems that higher flux membrane is used to compensate for lower active area. Since most design requests for desalination plants call for operation at a specified flux, the results from Table 2 were normalized to a comparable flux of 25 L/h/m² (15 gfd). These results are shown in Table 3.

Table 3: Influence of high pH condition on boron rejection (normalized to constant flux)

Parameter	R(NaCl), %		R(B), %	
	<i>before</i>	<i>after</i>	<i>before</i>	<i>after</i>
Brand A	99.88	99.82	92.1	88.5
Brand B	99.77	99.66	85.1	75.9
Brand C	99.83	99.72	89.2	84.7

Boron rejection in fact decreases after the high pH exposure, in all three cases. Brand A starts at the highest boron rejection and loses 3.6%-points boron rejection after the high pH treatment. It has a markedly higher boron rejection even after the high pH exposure. Brand B starts at low boron rejection and loses an additional 9.2%-points during the treatment. The boron rejection after the high pH treatment is remarkably low and is in the range of brackish water membranes. Brand C starts at a lower initial rejection of 89.4% and loses 5.1%-points. For all membrane types, NaCl rejection decay follows the lines of the boron rejection during this treatment.

In conclusion, the data indicates that harsh cleaning over a longer term will affect boron rejection. The conditions tested here are aggressive but not unusual in systems with severe fouling problems. For milder cleaning conditions, the effect will have a lower magnitude, but it should be expected that different membrane types will react differently to the challenge. For plants where feed water quality and pretreatment indicate potential fouling problems, it will be beneficial to test the membranes to be used for boron rejection stability after cleaning steps.

IV. FIELD EXPERIENCE WITH FILMTEC MEMBRANES

Field data with boron rejection from 4 installations is presented in below Table 4. These examples include two high recovery plants, one at 50% recovery and another one at a recovery of 55%. All plants use acidified feeds with pH 7.0-7.3. Results are compared to boron predictions with the new ROSA 5.3 program

Table 4: Boron rejection was tracked in various installations with FILMTEC products

Installation	Operating conditions	Normalized flow	Normalized NaCl rejection	Normalized boron rejection
<u>Case 1</u> 155 m ³ /h (1.0 MGD), FILMTEC SW30HR-380, 1 train 44 PVs* 6 els	TDS of 16560 mg/L, temperature 12.8 °C (55 °F), 50% recovery, Boron feed 2.55 mg/L, feed pH 7.3	Pressure projected 42.0 bar (609 psi), observed 39.3-39.8 bar (574 psi), normalized element flow 1.03 m ³ /h (6500 gpd)	Permeate TDS projected 73 mg/L, observed 43 - 47 mg/L, normalized rejection 99.80 - 99.83%	Boron permeate projected 0.23 mg/L, observed 0.21 mg/L; normalized rejection 91%
<u>Case 2</u> 4 * 295 = 1200 m ³ /h (7.6 MGD), FILMTEC SW30HR-380 4 trains each 52 PVs * 7 els (1 st stage) + 38 PVs * 7 els (2 nd stage)	TDS of 37830 mg/L, temp. 22.3 °C (72 °F), 55% recovery, Feed boron concentration to 1 st stage 4.98 to 5.21 mg/L, feed boron to 2 nd stage 7.4 to 7.6 mg/L, pH 7.3	Pressure projected 67.5 bar (979 psi), observed 65 - 66 bar (950 psi), boost of 10 bar (145 psi), normalized element flow 0.98 to 1.03 m ³ /h (6200 to 6500 gpd)	Permeate TDS projected 256 mg/L, observed 150 to 170 mg/L, corresponding to 99.77 to 99.81% normalized NaCl rejection	Permeate boron projected 0.89 to 0.97 mg/L, observed 0.79 to 0.86 mg/L (0.60 to 0.70 mg/L in 1 st stage and 1.20 to 1.30 in 2 nd stage), corresponding to 90.0 to 90.6% normalized boron rejection
<u>Case 3</u> 67 m ³ /h (0.4 MGD), FILMTEC SW30HR-380, 2 trains each 9 PVs * 6 els	TDS of 37500 mg/L, temp. 29 °C (84 °F), 39% recovery, boron feed concentration 5.5 to 5.6 mg/L, pH 7.1	Pressure projected 59.6 bar (864 psi), observed 57.4 bar (832 psi), normalized element flow 1.06 m ³ /h (6700 gpd)	Permeate TDS projected 220 mg/L, observed 205 mg/L, corresponding to 99.72% normalized rejection	Permeate boron projected 1.3 mg/L, observed 1.2 mg/L, corresponding to 90.8% normalized boron rejection
<u>Case 4</u> 4 * 255 = 1200 m ³ /h (6.5 MGD), FILMTEC SW30HR-380, 4 trains each 61 PVs * 6 els	TDS of 38500 mg/L, temp. 22 °C (72 °F), 36% recovery, feed boron 5.6 mg/L, pH 7.0	Pressure projected 70.4 bar (1021 psi), observed 63.5 bar (921 psi), normalized element flow 1.19 m ³ /h (7400 gpd)	Permeate TDS projected 140 mg/L, observed 100-110 mg/L, corresponding to 99.78% normalized rejection	Permeate boron projected 0.67 mg/L, observed 0.52 mg/L, corresponding to 91.5% normalized boron rejection

Case 1 is for a plant using North Sea water as a feed. Due to the low temperature and low boron feed concentration, achieving a limit of <0.3 mg/L isn't a problem. The observed permeate boron concentration (0.21 mg/L) matches close with the projected boron concentration (0.23 mg/L). This result confirms the strong temperature dependence of the pK in Equation 1. Case 2 is for a plant with 2 recovery stages. The feed is a 37,830 mg/L Atlantic Ocean beach well. The first stage recovery is 35-40%, the second stage powered by a 10 bar (145 psi) boost recovers another 30% of the feed resulting in an overall recovery of 55%. The observed boron concentrations in the permeate (0.79 - 0.86 mg/L) are slightly lower than predicted (0.89 to 0.97 mg/L) using a membrane rejection of 90% that is usually assumed with FILMTEC SW30HR-380. These concentrations correlate to a normalized boron rejection of 90.0 to 90.6%.

Case 3 is for a smaller plant with a relatively high temperature (29 °C, 84 °F) operated in the Caribbean, at a recovery of 39%. The permeate boron concentration of 1.2 mg/L is slightly below the predicted concentration in this case (1.3 mg/L). Case 4 is a plant with a 38,500 mg/L, 5.6 mg/L feed boron, beach

well feed and a good pretreatment. Due to the good feed water quality this plant can be operated at a flux of 22 L/h/m² (12.9 gfd). The permeate boron content of 0.52 mg/L is very close to the WHO limit.

In most cases, except the higher temperature case 3, the permeate boron concentration is below the EU limit of 1.0 mg/L. This indicates that in medium temperature situations, it should be expected that the EU limit can be achieved in a single pass with acidified feed. In cases 1 and 4, the permeate boron concentration is close to or below the WHO limit of 0.5 mg/L. This indicates that in some situations (e.g. low temperature, low boron feed, high flux operation), the WHO limit can even be achieved in a single pass at neutral pH. For situations where the permeate boron concentration is only slightly higher than the EU or WHO limit, operation at higher flux, or slightly higher pH would be an option to achieve the boron concentration target. It can also be seen that the current projections with the FilmTec design program predict boron concentrations slightly on the safe side, within +/- 0.5 to 1.0 %points of the expected boron rejection.

V. BORON REMOVAL WITH BORON-SELECTIVE ION EXCHANGE RESINS

In recent times, some of the design proposals for sea water desalination also have included so-called boron-selective resins. Historically these type of products were typically developed for the removal of boron and other weak acids in high purity applications, such as the semiconductor industry. These types of resins have been adapted for boron removal in sea water desalination applications for both agricultural and drinking water use.

5.1 Dow Boron Selective Ion Exchange Resin XUS 43594

A boron-selective resin is available from Dow, with the denomination DOW Developmental Resin XUS 43594. This resin is a macroporous weak base resin with an n-methyl glucamine functional group (please refer to Figure 7). This resin is a 550 µm uniform particle size resin, which means that its uniformity coefficient (ratio of 60% quantile radius to 10% quantile radius, d_{60}/d_{10}) is <1.1.

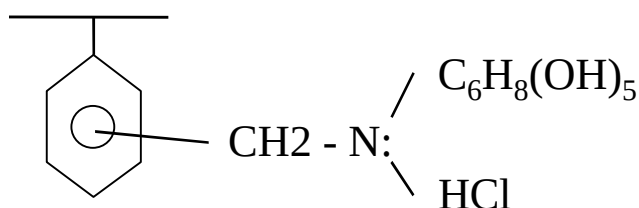


Figure 7: Functional group of boron-selective resin XUS 43594

The two most important parameters for a boron selective resin are the operating capacity and the kinetic capability. The operating capacity will determine the frequency of regeneration and the chemical consumption. The kinetic capability will have a major influence on the flow velocity and hence on the size and the cost of the ion exchange unit. A typical profile for a breakthrough curve with 2 resins operated at 30 bed volumes per hour (BVH) using a boron feed with a 2.5 ppm B is shown in Figure 8.

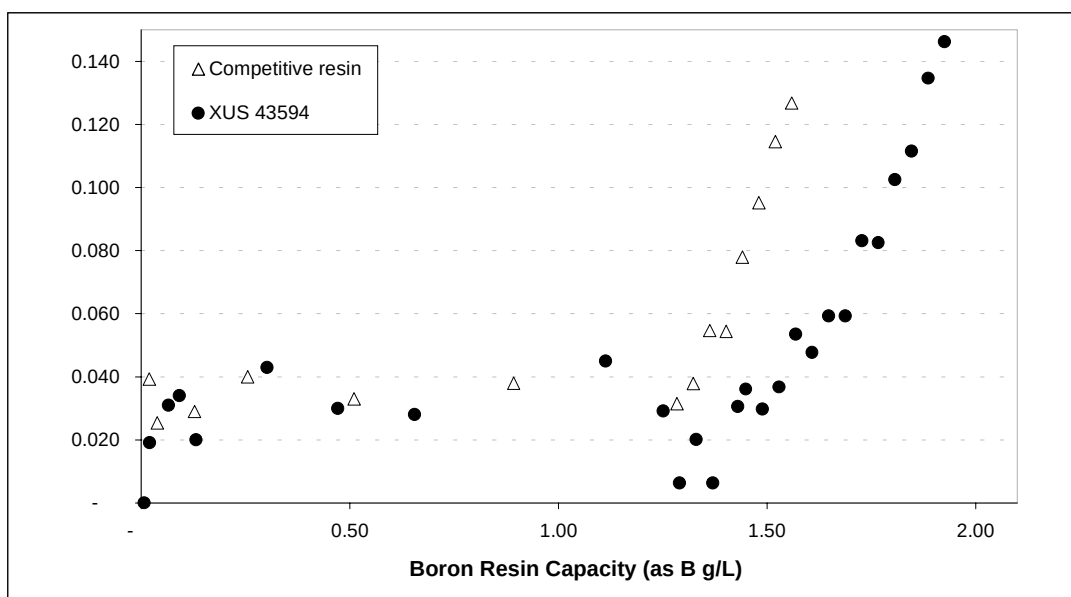


Figure 8: Boron product concentration after ion exchange as function of Boron operating capacity

It can be seen that the outlet boron concentration is initially at a plateau below 0.1 mg/L B, until the region close to the exhaustion point, where leakage starts to occur. The operating capacity for a set point of 0.1 mg/L B is 1.45 g/L B (per volume of resin) with the competitive resin and 1.75 g/L B with XUS 43594. The outstanding performance of XUS 43594 is very likely due to its uniform particle size, which positively impacts both kinetic capability and operating capacity.

Boron-selective resins will typically remove boron to levels of <0.1 mg/L B, far below the required limits. Due to the low levels of boron achieved in the product water of the boron-selective resin, an alternative approach is to treat part of the permeate from a membrane stage with the boron-selective resin and blend with the untreated part. Depending on system design and operation conditions, the price of water will be in the range of 5 to 11 US cents per liter. DOW XUS 43594 has received NSF certification under standard 61 for potable water applications. The capability of Dow to provide both the membrane element and the boron-selective ion exchange resin is a clear benefit for systems with boron removal.

5.2 Integration Of A Boron-Selective Resin To RO Desalination Plants

The boron problem has most frequently been encountered in sea water desalination. Sea water membranes have the highest boron rejection which is however still insufficient to comply with the most stringent requirements (e.g. boron concentration of 0.4 mg/L in the final product). Several design concepts have been developed by original equipment manufacturers (OEMs), engineering companies, process consultants, end users (plant operators), etc. to achieve an efficient and safe boron removal at competitive costs. Among the proposed concepts are the following [11], [12], [13], [14], [15], [16], [17], [18]:

- 1 sea water reverse osmosis (SWRO) pass with natural sea water feed pH as well as lower or higher feed pH
- 2 passes with increased pH, especially in the 2nd pass. Above include options with high and low recovery in the 2nd pass.
- 2 passes with boron-selective ion exchange resins (IER), with options treating a part of the 1st pass permeate, which does not feed the 2nd pass [16], [17]

- 3 passes with low and high pH stages in the 2nd pass [15], [14].

The authors of this paper have presented details on the above concepts for boron removal in a previous publication [19], which we would like to recommend for readers interested in additional information.

The boron removal by IER process is in about the same range of cost as the 2nd pass treatment, i.e. it adds in average 7 to 9 US cents per m³ product water to the part streams undergoing the respective processes.

Depending on the approach of the designer and the feed water conditions, various ways of designing a system with a boron-selective resin can be imagined. The most efficient option is to totally avoid the operation of a second membrane pass. Where removal to levels much lower than 0.4 mg/L is required or when special safety considerations are taken into account, it is possible to use a partial second pass and a partial stream to the ion exchange resin.

The concept of using a first sea water desalination pass followed by a treatment with boron-selective resin is especially attractive in plants that have not been designed for boron removal and want to achieve a more stringent boron limit without a major redesign of the plant. Also, in situations where the observed or projected boron permeate concentration is very close to the target boron concentration, the addition of a small ion exchange system makes sense.

The concept of combining a second membranes pass with a boron selective resin has been proposed for sea waters containing 4.5 to 6.0 mg/L boron and with a request for boron concentration of less than 0.4 mg/L in the final blend of streams from 1st, 2nd pass RO systems and the boron selective ion exchange resin. A typical block diagram of this hybrid RO/IER process is shown in Figure 9.

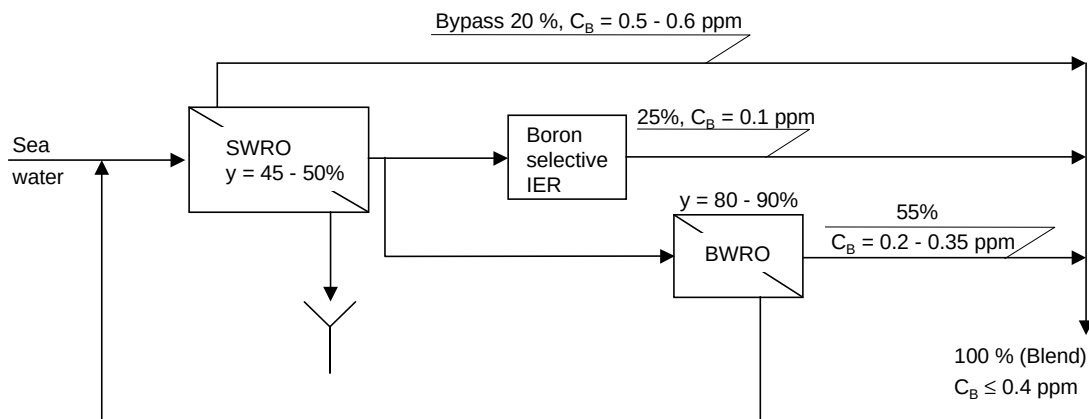


Figure 9: Typical block diagram for a hybrid RO / IER boron removal concept

This combination has been projected and offered for various medium and large plants in the last two years with typical unit costs in the range of 0.50-0.55 US\$ per m³ product water, i.e. close to the figures seen for the previous process. This type of system has been described in more detail by part of the authors of the present paper [19].

VI. SUMMARY AND CONCLUSIONS

There have been significant and proven improvements in the basic flow and salt rejection properties of sea water reverse osmosis (SWRO) membranes and elements. Flow rates in the range of 6000 - 6700 gpd (0.95 - 1.06 m³/h) and TDS rejections of 99.70 - 99.85% have been documented in operational SWRO systems. These developments have also yielded improvements in the rejection of boron at neutral pH values. In combination with innovative process solutions, improved membranes have enabled substantial progress in the economic reduction of boron in SWRO permeates to the stringent levels currently required. It is now feasible to consider SWRO designs with recovery ratios in the range of 40 - 60% whilst operating on feed waters containing up to 48,000 mg/L and boron concentrations in the range of 3.5 to 7.0 mg/L.

There have also been improvements in alternative technologies for boron removal from sea water. The development of boron-selective ion exchange resins enables improving boron removal after an initial sea water treatment by membranes and can be performed at comparable cost.

Typical water production costs for plants with boron removal appear to be in the order of 0.40 to 0.50 US\$/m³ of treated water with product boron contents of 0.6 to 1.0 mg/L and 0.47 to 0.60 US\$/m³ with product boron contents of 0.3 to 0.5 mg/L for drinking and agricultural applications. The reported figures are based upon large and very large plants (10,000 to 300,000 m³/d) at convenient locations and infrastructures. Pumps and energy recovery devices with efficiencies in the range of 85% and up to 95% including isobaric chambers, as well as energy costs in the order of 4 to 7 US cents/kWh and convenient interest rates of 3.5 to 6.5% per year contribute to the overall low cost of production.

The combination of improved membrane products with varied process possibilities for boron removal, the progress in all the ancillary equipment and positive financial climate make possible the use of this technology in very large water purification applications previously not considered viable and holds the potential for further improvements in the near future.

VII. ACKNOWLEDGEMENTS

We want to first thank our customers for the good co-operation in designing and following plants with boron removal. We have learned a lot from this work. Special thanks are due to Miriam Brusilovsky, Boris Lieberman, Manuel Farinas, Jose-Luis Loidi, Miguel Sanz, Yakob Mansdorf, Antonio Sanchez, Juan Bethencourt and Fernando Castro. Thanks are also due to Jim Thorpe, Don Streeter, Duane Jacobson, Kurt Buchanan, David Wintergrass, Deanna Porter, Phu Thrac and John Sundberg for the boron data in the membrane section. Thanks to Steve Wrigley, Sara Fessler, Andre Medete, Dominique Delmond and Vinciane Montier for the ion exchange resin part.

VIII. LITERATURE

1. Moss, S.A., "Ambient Water Quality Guidelines for Boron" in Water quality - Standards - British Columbia - 2. Boron Environmental aspects, Prepared pursuant to Section 2(e) of the *Environment Management Act*, 1981, British Columbia Water Protection Branch
2. World Health Organisation (WHO), Guidelines for drinking-water quality, 2nd ed. Addendum to Vol. 1. Recommendations. Geneva, 1998. pp. 4-6.
3. Environmental Protection Agency (EPA). 1975. Preliminary investigation of effects on the environment of boron, indium, nickel, selenium, tin, vanadium and their compounds. Vol. 1. Boron. US Environmental Protection Agency Rep. 56/2-75-005A.
4. Mesmer, R. E.; Baes, C. F., Jr.; Sweeton, F. H., *Inorganic Chemistry* (1972), 11(3), 537-43
5. Owen, Benton B., *J. Am. Chem. Soc.* (1934), 56, 1695-7
6. Millero, Frank J., *Geochimica et Cosmochimica Acta* (1995), 59(4), 661-77
7. Rodriguez, M., Ferrandiz Ruiz, A., Chillon, M. F., Prats Rico, D., *Desalination* (2001), 140, 145-52
8. Prats, D., Chillon-Arias, M. F., Rodriguez-Pastor, M., *Desalination* (2000), 128, 269-273
9. Magara, Y., Tabata, A., Kohki, M., Kawasaki, M., Hirose, M., *Desalination* (1998), 118, 25-34
10. Sehn, Peter, "Experiences with fouling resistant membranes in combination with intermittent biocide dosage", 9th Aachen Membrane Colloquium, 18-20 Mar-2003, preprints, Druck und Verlag Mainz, ISBN 3-86130-185-7
11. Farinas, M. (2002), personal communication
12. Farinas, M., "Infraestructuras hydraulicas municipales", Expert seminar, Andalucia International University, Jan. 2003
13. Glueckstern, P. & Priel, M., Mekorot Water Co., "Potential cost reduction of sea water desalination", IWW- 5th Conference, Muelheim / Ruhr, Germany Sept. 2002
14. Israel Desalination Engineering (IDE), Extract from Ashkelon Tender Documents 2002
15. Lieberman, B., Lieberman, I. "Method of Boron Removal in Ashkelon Desalination Plant", IWW 5th Conference, Mülheim an der Ruhr, Germany, Sept 22-26, 2002
16. Loidi, J.L. and Gonzalez, L., ACS-Tedagua projections for the two pass SWRO & IER Boron rejection process, July 24th, and Nov.4th, 2002
17. Mansdorf, Y. "Flow sheet draft for 2 pass SWRO & IER, Boron rejection process" Tambour Ecology Graph, May 07, 2002
18. Sanz, M. A., Meeting on Desalination Technology and Costs, Paris, Nov. 2002
19. Redondo, J., Busch, M., De Witte J. P., "Boron removal from sea water using FILMTEC high rejection SWRO membranes", Conference on Desalination and the Environment – Fresh Water for All", 4-8 May 2003, Malta, published in *Desalination* 156 (2003)