ANALYZING THREE YEARS OF SWRO PLANT OPERATION AT ELEVATED FEED pH TO SAVE ENERGY AND IMPROVE BORON REJECTION

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Abstract

The 140,000 m³/day Valdelentisco Seawater Reverse Osmosis Plant, located on the southern coast of Spain, provides an opportunity to evaluate the technical and economic viability of operating a single pass seawater reverse osmosis (SWRO) system at elevated feed pH to increase boron rejection and reduce energy consumption by through the use of lower pressure membranes. Valdelentisco has been in operation for more than three years while intermittently injecting caustic soda (sodium hydroxide) during the high temperature summer seasons to improve boron rejection and achieve the warranted boron concentration of 1 mg/l in the permeate. During periods of caustic injection, antiscalant is dosed as well. Ambient seawater pH of 8.0 is elevated to as high as 8.6 when seawater temperatures climb to a max of 27 C.

Though small scale and short term studies have been done [1,2], there is little data on the long therm operation of a full scale SWRO plant at elevated pH conditions. There is also little economic data on elevated pH operation that is based on actual plant performance. Operating at elevated feed pH to improve boron rejection affects the design and operation of the SWRO plant by reducing capital cost, operating cost, and by providing greater operational flexibility. This paper will evaluate the three years of Valdelentisco performance data to demonstrate the economics of running at elevated seawater feed pH. The data will be used as a reference to compare with other methods of boron reduction, including the use of tighter, higher rejecting membranes and the use of a second pass brackish RO.

I. INTRODUCTION

1.1 Boron

Boron is naturally found in seawater feeds at concentrations between 4 mg/l and 6 mg/l. Specifications for the concentration of boron in SWRO permeate vary between 0.3 mg/l and 1.0 mg/L depending on permeate use. Boron can adversely affect both humans and agriculture. Reduction of boron using reverse osmosis process represents a design challenge due to poor rejection of boron species by RO membranes at neutral and low feed pH. The low rejection of boron is due to small size and the boric molecule's lack of charge. At elevated pH, the ionization rate of the boric species increases, which improves rejection.

Boric acid is a very weak acid in water solution. Its ionization equilibrium may be represented as:

$$B(OH)3\ (aq)\ +H2O = H+(aq) + B(OH)4-\ (aq) \qquad (1)$$

The acidity constant is:

$$K = [H]\ [B(OH)4]/[B(OH)3] \qquad (2)$$

The value of equilibrium constant; K depends on temperature and ionic strength, which a function of water salinity. The value of –log(K) of boric acid equilibrium constant, designated as pK, is in the range of 8.4 to 9.5 depending on ionic strength of the solution and temperature [3]. The equilibrium between boric acid and borate ion shifts to lower values with increasing ionic strength of solution. The practical importance of this relationship is that at given feed pH, higher fraction of boric acid will be dissociated (**Figure 1**) in solution of a higher ionic strength. Due to small size and lack of electric charges at low and neutral pH, the boric species are poorly rejected by the RO membranes. At high pH , with an increased ionization rate of boric acid, the rejection rate increases.

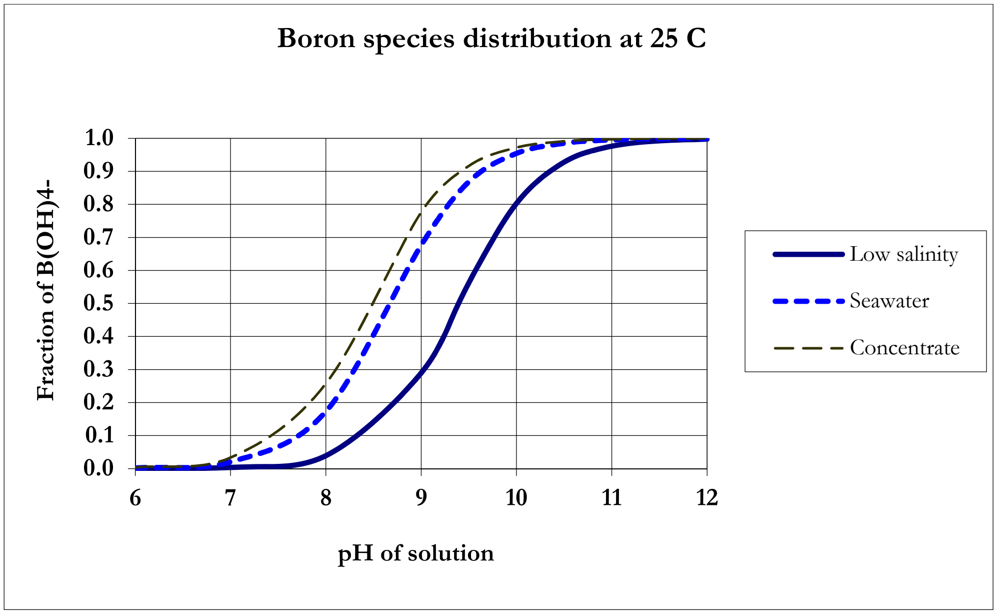


Figure 1 Boron species distribution as a function of pH

Reduction of boron concentration using reverse osmosis process represents a design challenge due to poor rejection of boron species by RO membranes at neutral and low feed pH. The low rejection of boron is due to small size and the boric molecule's lack of charge. At elevated pH, the ionization rate of the boric species increases, which improves rejection.

1.2 Methods to Remove Boron

The varied boron specifications along with poor rejection of boron by SWRO membranes have driven the development of several innovative design and process configurations to meet the specific permeate boron limits. These innovations include…

1.2.1 Elevating second pass feed pH - Applications requiring a low concentration of boron of less than 0.5 ppm usually involve a two pass system configuration. In such designs, permeate produced in the seawater system operating at low or neutral feed pH is reprocess through a second pass brackish RO unit operating at elevated feed pH up to 10.5. Because the first pass removes more than 99% of the hardness, there is little risk of scaling the second pass at such high pH. Depending on the specific permeate requirements and variation in feed temperature, the second pass design has the flexibility of treating a full or partial portion of the first pass permeate or adjusting caustic injection into the second pass. Though the most popular option for reducing boron, the two pass configuration with caustic injection has the disadvantage of lowering the overall recovery rate and increasing the plant's capital cost, chemical consumption, and energy cost.

1.2.2 Improved, High Boron Rejecting Membranes - New SWRO membranes have been developed to specifically target boron. These membranes achieve 95% boron rejection at standard conditions and pH of 7.5 while still achieving the very high salt rejection of a seawater RO. Typical SWRO membranes achieve only 85% to 90% boron rejection at pH. The down side of these high boron rejecting membranes is the higher feed pressure requirement. These membranes give 30% lower permeability which could result in as much as 6 bar higher feed pressure in a plant such as Valdelentisco.

1.2.3 Elevating seawater feed pH - The patented method of increasing seawater feed pH to increase boron rejection has been technically demonstrated in the laboratory and on pilot units [4]. Several full scale SWRO plants have successfully implemented the process in recent years. Operating at elevated feed pH to improve boron rejection affects the design and operation of the SWRO plant in several ways:

- **Reduced capital cost.** Using the elevated pH process to improve boron rejection reduces capital cost by reducing or even eliminating the need for a second pass. In the case of Valdelentisco, no second pass was required to achieve less than 1 mg/L of boron in the permeate.

- **Reduced operating cost**. The highest operating cost for a SWRO plant is associated with energy consumption. Studies have shown that 34% of the operating cost for a SWRO plant is from the high pressure pumps required to force seawater through the RO membrane (ref). Using caustic to improve boron rejection allows for the use of lower pressure, energy saving SWRO membranes with 40% greater permeability. The process can also lower operating cost by reducing or eliminating the need for tighter, high boron rejecting membranes.

- **Greater flexibility.** Caustic injection can be adjusted and optimized. The caustic injection process can be adjusted depending on the passage of boron as affected by such variables as membrane age, feed boron concentration, and temperature. For example, as will be shown in the Valdelentisco operating data below, the use of caustic may only be required for three months out of the year when temperatures are highest. During colder temperatures, when the RO membranes tighten up and boron rejection is naturally improved, the caustic injection in not required.

One concern associated with elevated pH operation is the increased potential for scaling. Typical seawaters can have 6000 mg/l $CaCO_3$ of hardness which is concentrated to more than 12,000 mg/l $CaCO_3$ in the brine stream. Despite these high concentrations, laboratory and pilot studies have demonstrated the absence of scale on the SWRO membrane after operating at elevated feed pH. The high ionic strength and the use of antiscalant prevents such scale formation up to pH of 8.6. As shown below, operating data from Valdelentisco indicates no sign of scaling. Additionally, as discussed below, tail elements from Valdelentisco analyzed after a period of high pH operation confirm the absence of scale.

II. VALDELENTISCO DESIGN

2.1 Source Water

Since commissioning the newest trains in 2010, Valdelentisco, located on the Southern Coast of Spain (**Figure 2**), has been treating 39,000 mg/l Mediterranean Seawater to produce 140,000 m3/day of permeate with a TDS less than 400 mg/l and a boron concentration less than 1.0 mg/L [5]. See **Table 1** for a full ion analysis of the feed water. Feed water temperatures range from a high of 27 C in the summer months to a low of 14 C in the winter months. Raw water pH is 8.0.

Figure 2. Location of Valdelentisco SWRO plant

Table 1. Full ion analysis of Valdelentisco feed.

Ion	mg/l		Ion	mg/l
Ca	465		CO3	15.5
Mg	1460		HCO3	154
Na	12100		SO4	2663
K	485		Cl	22120
Sr	0.5		B	5.03
			TDS	39,500

2.2 Pretreatment

Raw seawater is taken from an open intake 25m below sea level and 1250 m from the shore line. The water is transferred to an intake tank at an elevation of 38 m by submersible pumps. The feed tank is continuously dosed with 0.3-0.5 mg/l of iron coagulant. From the intake tank, the seawater is pumped to 42 DMF filters operating in a single stage. The DMF uses sand followed by anthracite, and operates at a maximum filtration velocity of 7 m/h. After DMF, the feed passes through 5 µm cartridge filters before supplying the SWRO trains.

2.3 Seawater RO Design

Each of the 11 SWRO trains operates at 50% recovery and an average system flux of 13.8 lmh. The trains are designed as a single pass with two stages. The two stage array is 78 vessels followed by 52 vessels. Each vessel is loaded with seven spiral elements. A high pressure feed pump supplies the first stage followed by a booster pump for the second stage. The first stage uses tighter, higher boron rejecting SWRO membranes while the second stage contains looser, lower pressure membranes. A comparison of the two membrane types at their standard test condition is shown in **Table 2**.

Table 2. Performance of Valdelentisco SWRO membranes at standard test conditions of 800 psi treating 32,000 mg/L of sodium chloride and 5 mg/L boron.

Element	SW4 MAX[1]	SW5 MAX[2]
Stage	1st	2nd
Feed Spacer	26 mil	26 mil
Surface Area	440 sq ft	440 sq ft
Flow at 800 psi	7,200 gpd	9,900 gpd
Rejection of sodium chloride	99.8	99.8
Rejection of boron at pH = 7	93%	92%

Using a hybrid design with energy saving membranes in the second stage results in lower overall feed pressure and lower booster pressure. The design has the added advantage of improving the flux balance between the two stages and therefore reducing the fouling tendency in the first stage. **Figure 3** illustrates the flux and pressure advantage associated with a hybrid design. Using a hybrid design means that less permeate is produced by the first stage elements which leads to lower pressures in the first stage. Subsequently, more permeate is produced form the energy saving membranes in the second stage resulting in an overall reduction in the system's energy consumption.

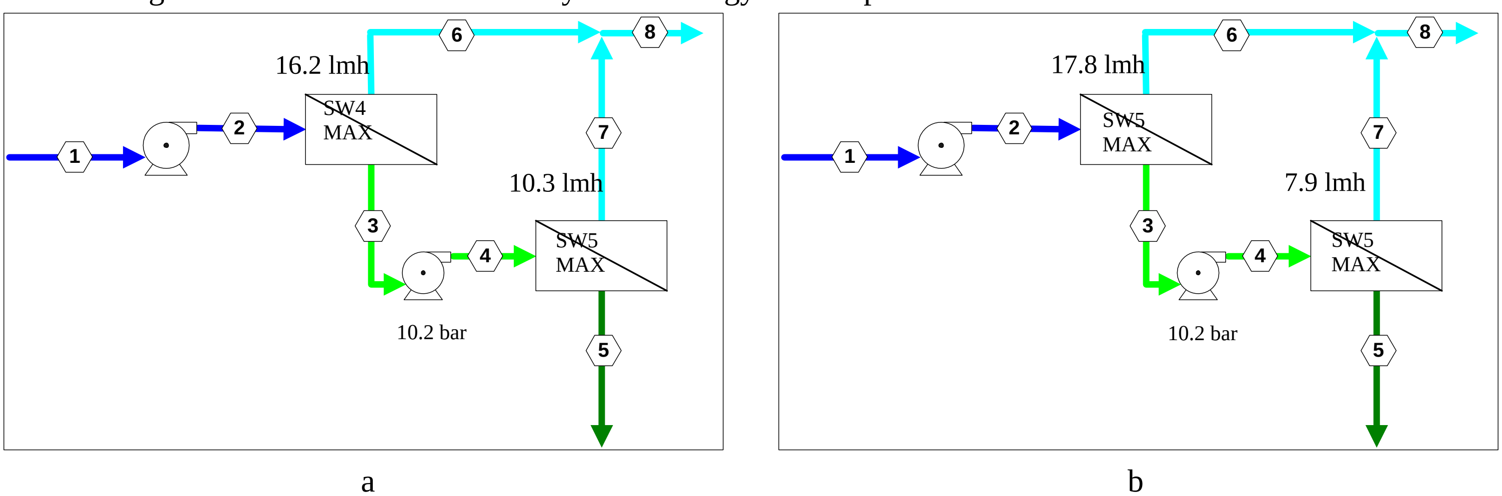


Figure 3. Valdelentisco flux distribution at 27 C when using a) hybrid design with high rejecting membranes in stage1 and energy saving membranes in stage 2 compared to b) standard design using energy saving membranes in both stages.

III. VALDELENTISCO OPERATION AND PERFORMANCE

3.1 SWRO Operation

Five of the newest trains at Valdelentisco were started in 2010 with the goal of producing 12,360 m³/day from each train and achieving less than 1 mg/l of boron and less than 400 mg/l of TDS in the permeate. Specifically, Train 9 started on March 27, 2010. Feed pressure, differential pressure, and permeate conductivity from both stage 1 and stage 2 were continuously monitored and used to normalize the

[1] SWC4 MAX, Hydranautics, Oceanside, CA, USA
[2] SWC5 MAX, Hydranautics. Oceanside, CA, USA

permeate flow, differential pressure, and salt passage. The normalized performance of train 9 during the first 2.5 years operation can be seen in **Figure 4 and 5**. **Figure 4** shows the normalized salt passage of both stage 1 and stage 2. Naturally, since stage 1 has the tighter membranes, it also has the lower salt passage. But if we consider the rate of change in salt passage, we see that both stages have the same rate of increase in salt passage. Both stages have increased by 13% during the 29 month period for an average annual increase of 5.5%. This is less than the typical 10% per year salt passage increase. But what is most telling is the stability of stage 2 during the times of high temperature when caustic is dosed to reduce boron passage. If caustic dosing were to adversely affect system performance, it would appear as an increase in stage 2 salt passage and a decrease in stage 2 permeate flow. However, stage 2 stability is similar to stage 1 during the periods of high temperature and during the entire 2.5 year period.

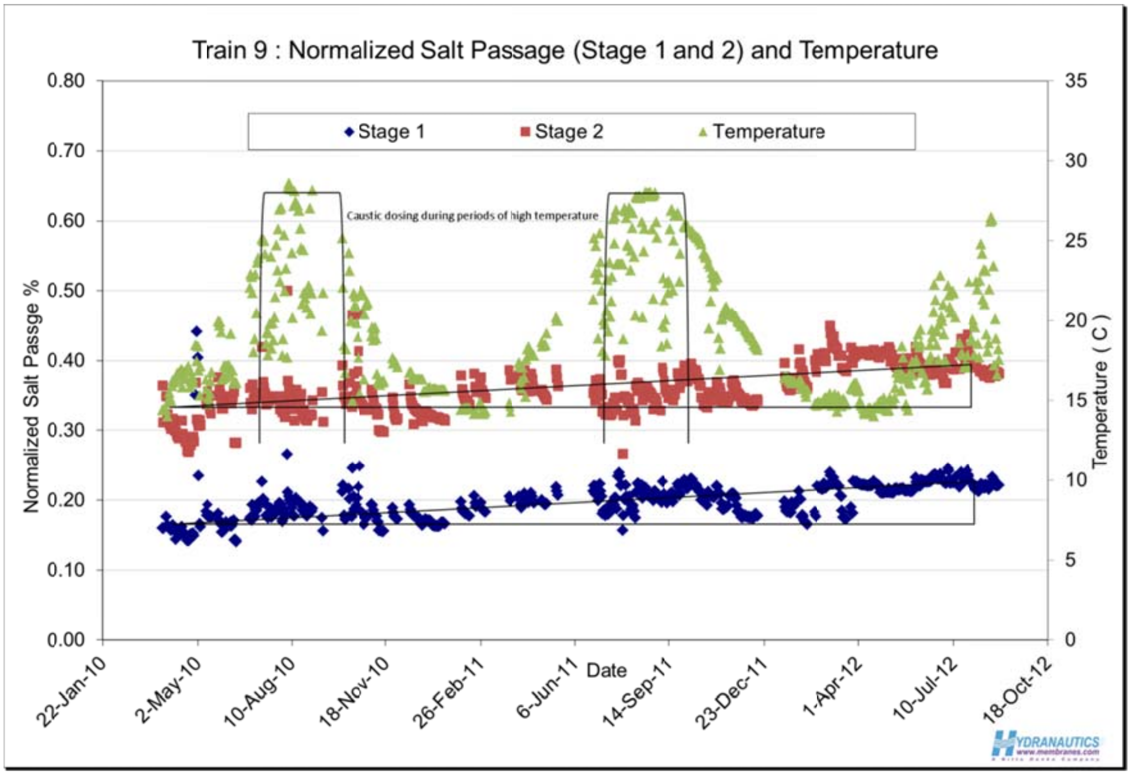


Figure 4. Normalized salt passage of Train 9 during the first 2.5 years of operation.

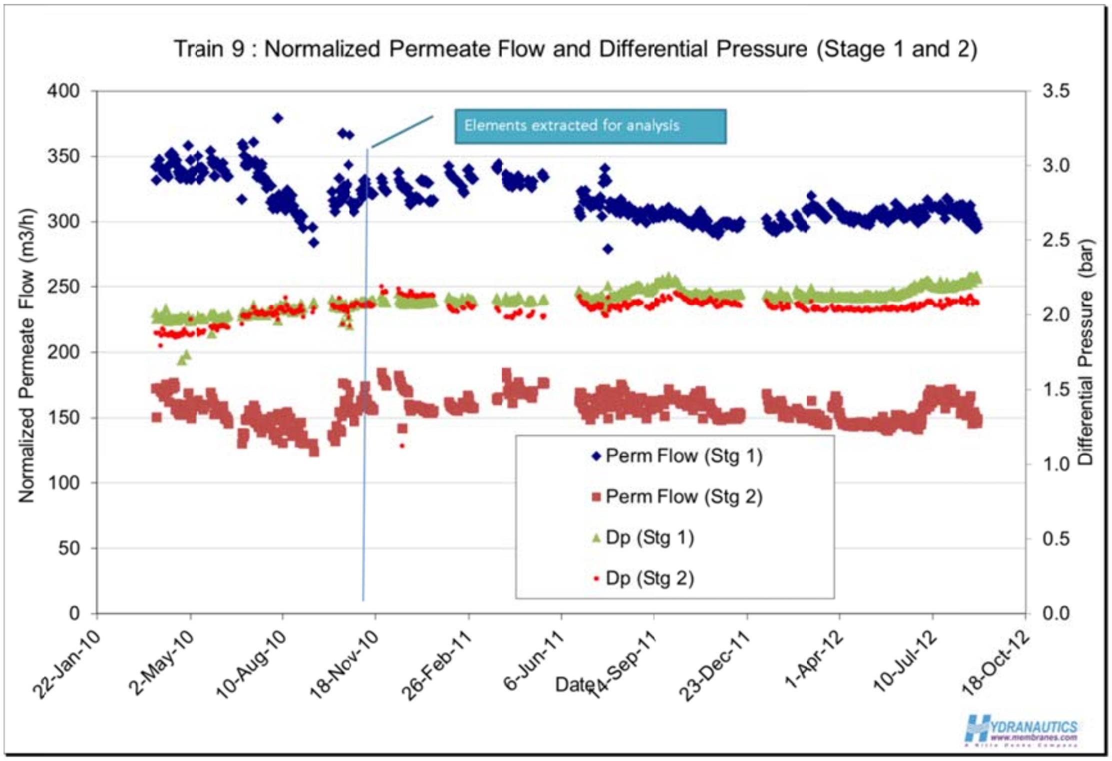


Figure 5. Normalized permeate flow and differential pressure of Train 9 during the first 2.5 years of operation.

The normalized permeate flow of stage 1 and 2 as seen in **Figure 5**, follows a different trend than normalized salt passage. The permeate flow of stage2 shows some initial loss during the first six months of operation. But the overall trend during 2.5 years is stable. In contrast a notable change in performance occurs in stage 1 during the first six months of operation from March to August of 2010. The suspected cause of fouling was related to iron fouling from the intake pipes. Cleanings did serve to recover stage 1 flow, but the overall decrease in permeate flow for stage 1 was 4% per year. This is still better than the typical 7% flow loss per year. The greater loss in normalized flow in stage 1 is also typical of a seawater RO where the lead elements absorb the majority of incoming particulate or colloidal foulants. The more stable normalized permeate flow in stage 2, especially during periods of caustic dosing, also confirms the absence of any scaling. **Figure 5** also shows the trend in differential pressure to be similar in both stages. Only a moderate increase in differential pressure of 6% per year occurs.

Boron concentration in the combined Stage 1 and Stage 2 permeate, along with feed pH and feed temperature, were monitored periodically and plotted in **Figure 6 and 7**. At startup, in March, 2010, the feed boron was at 5.0 mg/l. feed pH was at 8.1, and the water temperature was at 14.5 C. Permeate boron was at 0.65 mg/l, well below the 1.0 mg/l requirement. No caustic injection in the seawater feed was required during the first three months of plant operation. Not until June 2010, when feedwater temperatures began to climb above 20 C, was caustic injected. During the following four summer months, pH was increased from an ambient of 8.0 to as high as 8.6 when water temperature climbed to near 27 C. The exact caustic dosage was adjusted to maintain a permeate boron between 0.90 mg/l and 0.95 mg/l. On only one occasion was boron allowed to exceed 1.0 mg/l up to 1.08 mg/l. During periods of elevated pH operation, 0.9 to 1.3 mg/l of antiscalant is dosed into the seawater feed.

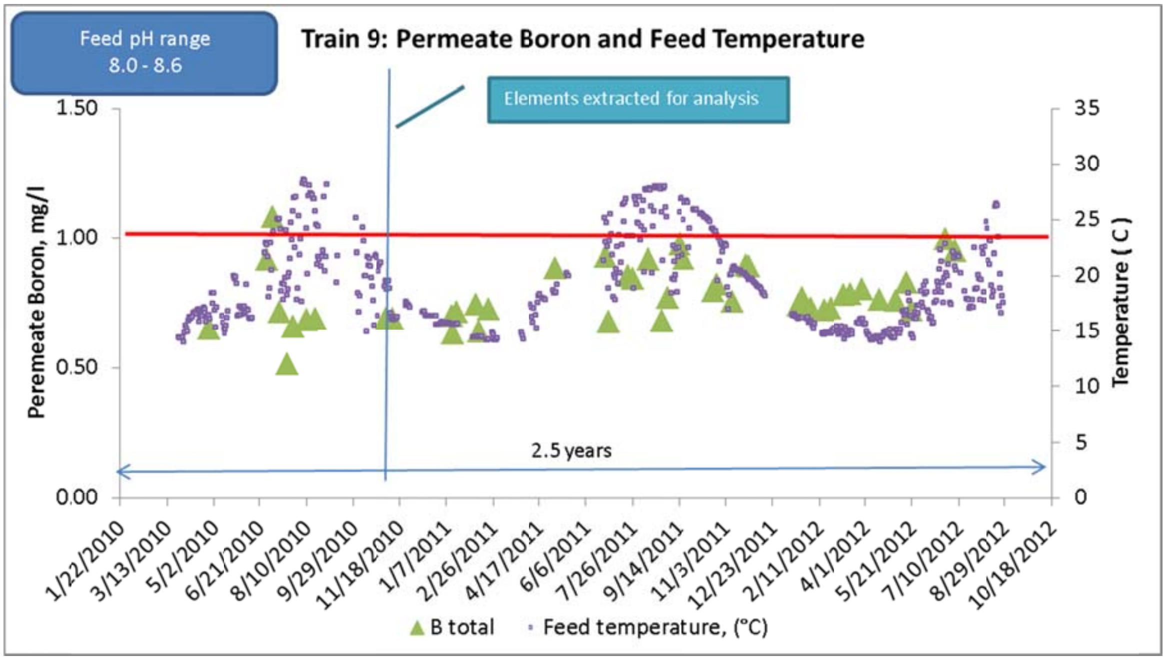


Figure 6. Permeate boron concentration and feed water temperature for Train 9

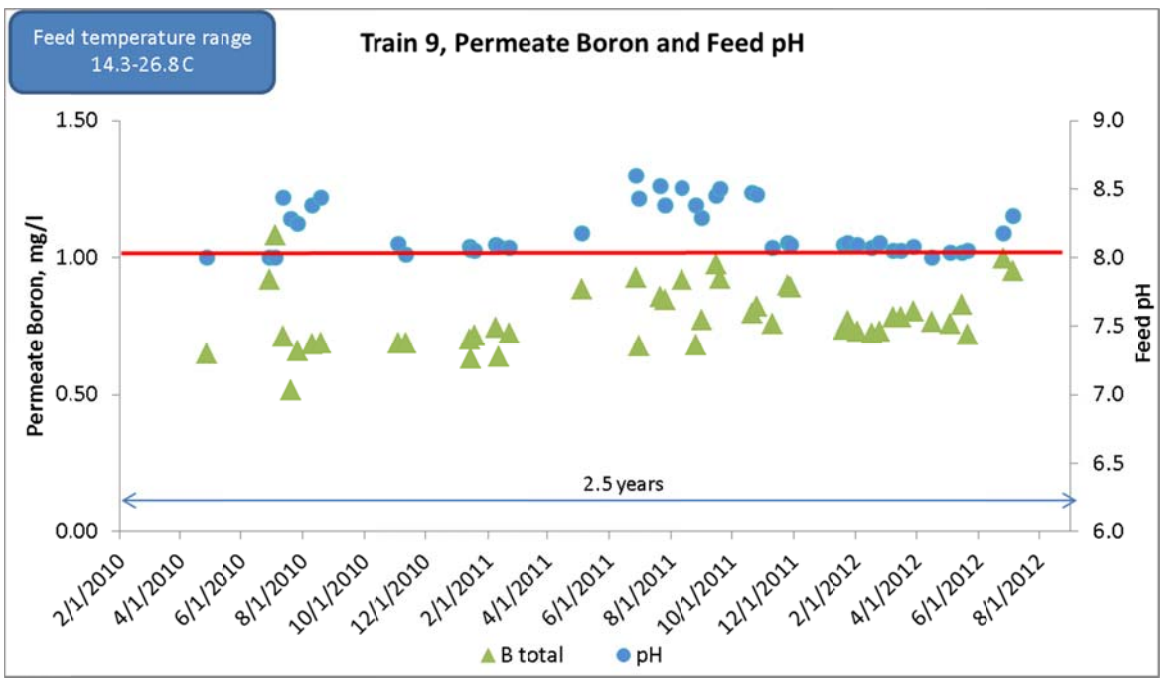


Figure 7. Permeate boron concentration and feed water pH for Train 9

3.2 Element Autopsy

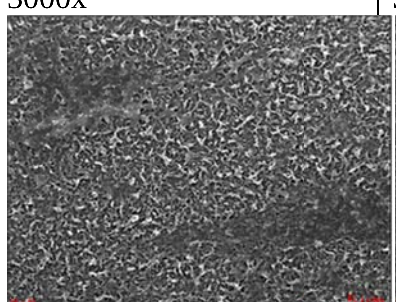
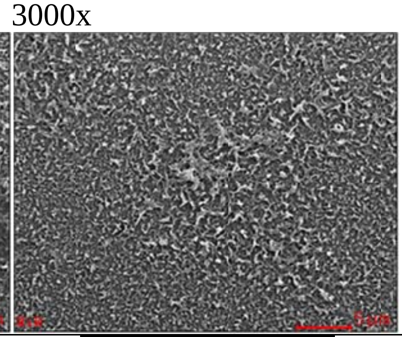
To further investigate the potential for scaling at elevated pH operation, two elements were extracted from Train 9 in the first year of operation. The elements were extracted after the summer season in which the train had run at a pH of 8.3 to 8.4 for one month. The primary element under investigation was extracted from the tail position of the second stage where scaling is most likely to occur. For comparison, a second element was taken from the lead position of the first stage. The details of this individual element analysis are shown in **Table 3**. From this analysis in can be shown that operating at elevated pH did not impact element performance.

The two extracted elements were first weighed and their mass compared to that of a typical new element weight of 34 lbs to determine the mass of any foulant present on the membranes. The lead and tail both weighted 35 lbs, indicating a small accumulation of foulant on both elements. Such accumulation is to be expected of any membrane exposed to a seawater feed. The fact that both element had similar weight suggests that the accumulation of foulant was not greater on the tail element than on the lead element.

The elements were also retested at a standard test condition and compared to their original performance at the same condition before leaving the manufacture's facility. The retesting showed the lead element to have lost 11% of its original flux while the tail element lost 23% of its original flux. This difference in flux loss suggest a greater accumulation of foulant on the tail element.

Finally, to determine the specific composition of foulant on the membrane surface, the elements were autopsied and membrane samples were scanned with SEM/EDAX. Based on SEM/EDAX, the lead and the tail both appeared clean relative to the control element that had never been used. The only difference between the lead and tail elements was the presence of trace amounts of iron on the lead element. Most notably, no scale was found on the tail element. This confirms previous studies which show that operating a seawater RO at elevated pH up to 8.6 does not cause scaling of the tail membranes.

Table 3. Comparison of analysis done a lead and tail element extracted from Train 9 after operation at elevated feed pH.

Element	Control	Lead - SW4 MAX	Tail - SW5 MAX
sn		10011587	A1681830
Weight (lbs)	34	35	35
Flux loss		11%	23%
SEM	3000x 	3000x 	3000x 
EDAX	***Element*** / ***Wt%*** ***C*** 71.38 ***N*** 08.60 ***O*** 08.50 ***S*** 11.16 ***Cl*** 00.37	***Element*** / ***Wt%*** ***CK*** 71.31 ***NK*** 07.23 ***OK*** 10.98 ***NaK*** 01.66 ***SK*** 06.68 ***ClK*** 01.32 ***FeK*** 00.83	***Element*** / ***Wt%*** ***CK*** 73.81 ***NK*** 07.69 ***OK*** 09.48 ***NaK*** 01.16 ***SK*** 06.95 ***ClK*** 00.92

VI. RESULTS

4.1 Cost Comparison

The following comparison uses the actual design and operating data from Valdelentisco to compare and contrast with the alternative designs

4.1.1 Valdelentisco – Current Hybrid Membrane Design with Caustic Injection - Three years of data demonstrates that caustic injection in the seawater feed is required only during the year's four winter months. The average dose of 50% NaOH during these four months is 40 mg/l. With 50% caustic at 322 $/1000kg (250 Euros/1000 kg) (1 euro = 1.2911 US dollars) the total annual cost of caustic for all 11 trains at Valdelentisco is **$430,000 ($US).**

The annual cost of caustic can be compared to the energy savings that results from Valdelentisco's Hybrid Design using lower energy seawater membranes in the second stage. Energy consumption at Valdelentisco averages **3.1 kwhr/m3**. At an energy cost of **0.19** $/kwhr,(0.15 Euro/Kwhr.) the annual cost to operate the high pressure feed and booster pumps on all 11 trains is **$58.9 M.** As shown below, this represents a significant savings relative to the cost of operating the plant containing all high boron rejecting membranes.

4.1.2 Valdelentisco using High Boron Rejecting Membranes - If the same plant eliminated caustic injection and instead used the higher boron rejecting membranes in both the first and second stages, the resulting feed pressure would be 3 bar higher. That 3 bar increase would result in a 4% increase in pumping power to **3.22 kwhr/m3**. The annual cost to operate the plants feed and booster pumps would then increase from **$58.9 M** to **$61.2 M**, an increase of $2**.3 M**. Comparing this increase in pumping cost with the **$430,000** annual cost of caustic injection results in a savings of **$1.85 M.** The details of the comparison between the current Valdelentisco Hybrid and a Valdelentisco with all high boron rejecting membranes are found in the table below.

Table 4. Comparison between the current Valdelentisco Hybrid and a Valdelentisco with all high boron rejecting membranes

Trains		11
Perm Flow	m3/hr	515
Rec	%	49.60%
Feed Flow	m3/hr	1038
Feed Flow	l/hr	1038306.452
Caustic Dose	mg/l	40
Caustic Consumption	mg/hr	41532258.06
Caustic Consumption	kg/hr	41.53225806
Cost of Caustic	euros/1000 kg	250
Cost of Caustic	$/1000 kg	322.5
Cost of Caustic	$/hr	13.39415323
Cost of Caustic per year per train	$/ 4 summer months	$39,110.93
Cost of Caustic per year - Plant Total	$/ 4 summer months	**$430,220.20**
Energy Hybrid (SW4/SW5)	kwhr/m3	3.1
Cost Hybrid	$/m3	0.589
Cost Hybrid	$/year/train	$5,357,287.50
Cost Hybrid	million $/year/plant	**$58.93**
Energy Conv. (SW4/SW4) (increase of 4.87%)	kwhr/m3	3.22
Cost Conv	$/m3	0.6118
Cost Conv	$/year	$5,564,666.37
Cost Conv	million $/year/plant	**$61.21**
Energy Savings	kwhr/m3	0.12
Energy cost	$/kwhr	0.19
Cost savings (Hyb vs Conv)	$/m3	0.0228
Energy Cost Savings per year	$/year/train	**$207,378.87**
Energy Cost Savings per year	million $/year/plant	**$2.28**
Net Operation Savings	million $/year/plant	**$1.85**

4.1.3 Valdelentisco using Two Pass with Elevated pH in the Second Pass - The same plant could be installed with energy saving seawater membranes in both stages of the first pass. This would reduce the first pass feed pressure by **3.5 bar** relative to the current system. However, more boron would pass to the permeate and increase the boron concentration above the specified 1.0 mg/l. To meet the specification would require the use of a second pass with energy saving brackish RO membranes. About 30% of the first pass permeate would need to be treated by the second pass. To improve boron rejection in the second pass, caustic would be injected into the second pass feed to raise the pH to 10.0. To raise the permeate pH from about 8.0 to 10.0 would require 20 mg/l of caustic. This lower dose, combined with the lower flow to the second pass, results in lower annual chemical consumption cost of **$69,000**. However, the use of second pass feed pump results in slightly higher (<1%) energy consumption. The obvious down side of the two pass system is the higher capital cost associated with installation of the second pass. Capital cost for the second pass at a plant such as Valdelentisco would be as high as **$3.1 Million.**

V. CONCLUSIONS

- Caustic injection in seawater feed to a SWRO is a viable design option for improving boron rejection while allowing the use of lower pressure seawater membranes. Valdelentisco demonstrated three years of stable performance while intermittently running at an elevated feed pH of no more than 8.6 when feed temperatures climbed up to 28 C.

- Large scale SWRO plants such as Valdelentisco can save as much as **$1.85 Million** in operating cost each year by using caustic in the seawater feed to improve boron rejection.

- The use of a hybrid design at Valdelentisco produced permeate salinity and boron concentration below warranty limits during more than three years of operation. To date, no elements have been.

- The use of higher area, 440 sq. ft., SWRO elements reduced the number of elements and pressure vessels required by 10% relative to the older trains that had been operating since 2008 with 400 sq. ft. elements.

- Analysis of a tail element after extended operation at elevated pH shows no signs of scaling. This is long term, full scale confirmation of previous studies which exposed pilot membranes to elevated seawater feed pH for shorter periods.

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