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Abstract

For many years, reverse osmosis (RO) elements have been used in the treatment of produced water, including at several sites in California. The RO reduces salts and organics in the produced water to a level that allows for disposal or reuse. The RO elements used to treat produced water are similar in chemistry and construction to the conventional seawater RO membrane. But compared to seawater, the characteristics of produce water are unique and varied. The conventional seawater membrane comes with pressure and temperature limitations that restrict its ability to treat a wide range of produced waters. Specifically, conventional membranes have a temperature limit and a pressure limit. Only a portion of the produce waters needing treatment fall within the membrane's temperature and pressure limitations. Many produced waters, including produce waters associated with SAGD, require membranes that can accommodate higher temperatures up to 60 C. Other produced waters may allow for treatment at ambient temperatures but their higher salinities above 60,000 mg/l TDS require RO membrane to overcome high osmotic pressures and operate at feed pressures up to 1800 psi.

In recent years, membrane manufacturers have enhanced their exiting RO elements to address the challenges associated with the treatment of unique industrial streams such as produced water. Specifically, new, more robust element construction allow designers to push beyond the normal limits of temperature and pressure. One such element allows for operation at temperatures up to 90 C while a second, ultra high-pressure RO (UHPRO), can concentrate the total dissolved salts (TDS) up to 120,000 ppm (12%) while operating at pressures up to 1,800 psi (124 bar).

These unique elements can be used to increase the overall efficiency of the treatment facility by reducing the cost of brine disposal and maximizing water recovery. This paper will show how these new elements perform when operated beyond conventional pressure and temperature limits - including how individual ion passage and water permeability are affected at extreme conditions. This paper will share element performance data from laboratory and pilot studies. The data will be used as a basis for new designs at the extreme conditions associated with produced water treatment.

Introduction

Produced water is that water which is brought to the surface as part of the oil and gas extraction process. The produced water contains a high level of dissolved salts and other organic and inorganic contaminants. Produced water composition varies as a function of geological formation, injection water, and the hydrocarbon properties in various reservoirs. For steam flooding in a sandstone reservoir, as commonly seen in California, produced water possesses unique challenges for treatment such as high silica, high hardness, and high boron. Beneficial reuse involves stringent local regulations on essential toxicity and key water parameters impacting the environment such as TDS, ammonia, and boron. The California Regional Water Quality Control Board regulates the surface water discharge limit on TDS to be less than 500 mg/L and on boron to be less than 0.5 mg/L. Not only does the poor quality and strict regulations make produced water a challenge to dispose of or treat, but the large quantities make handling difficult as well. The volume of produced water can be as much as ten times the volume of the oil extracted.

Historically, the primary method for dealing with produced water is reinjection. A portion of the produced water is injected into the oil producing zones to improve oil recovery through water or steam flooding. Another portion of the produced water is disposed of through deep well injection. Deep well injection is limited by the capacity of the injection wells which in turn limits the oil field productivity. As far back as the 1990s, processes for reclaiming and reusing the produced water were researched and piloted (Bartels, 1990). These processes were shown to be effective but were not initially applied due to their high-cost relative to the low cost of oil. However, as oil prices and oil scarcity began to increase during the first decade of the 21st Century, there was a renewed interest in processes to reclaim and reuse the produced water and increase oil production. During the same period, technologies were also improved to make treating produced water more economically attractive. Several treatment technologies, including membranes, are used to treat produced water for environmental and agricultural reuse. Among these technologies is desalination by reverse osmosis. Specifically, reverse osmosis membranes are used as one of the final treatment steps after oil, grease, solids and hardness removal and pH elevation. The RO step is designed to remove the remaining dissolved salts and organics, including sodium, silica and boron.

Produced water characteristics

The specific characteristics of produced water vary depending on the age and geology of the formation, but most produced waters contain contaminants that pose a challenge to the successful long-term operation of the RO. These contaminants include suspended silt and clay, suspended oil droplets, dissolved organics such as acetic acid and acetone, dissolved gases such as hydrogen sulfide, heavy metals, and sparingly soluble salts. The temperature of the produced water can also pose a challenge to the RO system. The practice of steam injection can increase water temperatures to as high as 80 C while the standard RO membrane is limited to 45 C. **Table 1** below compares the produced water characteristics from two different sites in North America (Nagghappan,2006).

Table 1. Example of produced waters.

	Site 1 (New Mexico)	Site 2 (California)
pH	7.0-7.5	7.5
Temperature (C)	80	85
Calcium	620	80
Magnesium	110	10
Sodium	5,088	2,300
Potassium	95	39.1
Strontium	15	1.0
Bicarbonate	561	670
Carbonate	0.6	-
Sulfate	2,150	133
Chloride	7,800	3,400
Silica	100	240
Boron	3.5	26
Total Dissolved Solids (TDS)	16,000	7,000
Total Suspended Solids (TSS)	55.0	10
Soluble Organics	30	80
Methyl Ethyl Ketone	1.0	-
Acetone	5.0	-
Oil and Grease	10-50	20 ~ 30

RO System Design

Extensive pretreatment of the produced water is required for stable operation of the RO. A number of water treatment technologies are used to reduce oil and grease, hardness, metals, temperature, and suspended solid before going to the RO. At an oil production facility in Central California, pretreatment before the RO is used to address the following (Franks, 2009):

- **Free Oil.** Free Oil concentrations as high as 100 ppm are reduced using induced gas floatation (IGF) , and walnut shell filters to levels less than 1.0 ppm.

- **Hardness and heavy metals.** Softening and metal removal is achieved through chemical softening and settling and ion exchange softening. Hardness levels are reduced below 0.1 ppm as $CaCO_3$.

- **Temperature.** It is necessary to reduce temperatures using a heat exchanger. Temperatures as high as 80 C are reduced below 40 C before sending to the RO system using conventional elements. However, new element construction discussed in this paper would reduce the need for temperature reduction.

- **Suspended solids.** Suspended solid concentration in the raw water to the RO system can exceed 50 ppm. With multi-media filters, the suspended solids concentration is reduced below 0.5 ppm. The Silt Density Index, a measurement of colloidal and particulate fouling potential, is less than 4.0 for stable RO performance.

Despite extensive pretreatment, the presence of dissolved organics means the average RO system flux treating produced water is similar to a RO treating municipal wastewater at 10 gfd to 12 gfd. The conservative flux reduces fouling and cleaning frequencies but does nothing to achieve higher recoveries.

System recoveries can range from 65% to 90% depending on the TDS and the scaling potential of the feedwater. This limitation can be problematic when reinjection capacity of the brine stream is limited by the injection well capacity. The TDS (and associated osmotic pressure) increases with increasing recovery. In the final element, the net driving pressure (NDP) should be sufficient to overcome the osmotic pressure of the concentrated water and produced a permeate flow. Going to a higher recovery results in the absence of permeate flow from the last element unless a higher feed pressure can be applied to the front of the RO system. But the max feed pressure is limited by the construction of the RO element to less than 1200 psi. Newly designed elements discussed below, allow for the use of greater feed pressures up to 1800 psi.

The ability to design for higher recoveries is also limited by the scaling potential of the feedwater. The removal of hardness by one of the pretreatment steps, reduces the potential for CaCO3 scaling. The hardness removal also allows for an increase in pH, which reduces the potential for SiO2 scaling.

Enhanced RO membranes for higher salinity and higher recovery.

As stated above, the pressure limitation on a standard RO element effects the amount of permeate that can be recovered from an RO system treating produced water by limiting the amount of osmotic pressure that can be overcome in the last element. Standard RO elements are limited to a maximum feed pressure of 1200 psi. The maximum pressure limitation is temperature dependent so that the max pressure decreases from 1200 psi as temperature increases above 25 C. (**Figure 1**). Depending on the materials of construction, this pressure vs temperature limitation is governed by either the potential for sudden mechanical failure or a gradual flux loss due to compaction of the membrane and its support layers. Regardless, some membrane manufacturers now offer ultra-high pressure RO (UHPRO) elements which overcome the restrictions of standard elements and allow feed pressure up to 1800 psi. The new UHPRO elements use more robust materials to prevent mechanical failure and reduce flux loss associated with compaction. As with standard elements, the maximum pressure limitation decreases with increasing temperature to mitigate the effects of compaction at higher temperatures (Figure XX). The maximum pressure limit of the UHPRO remains higher than conventional RO up to the maximum temperature of 45 C.

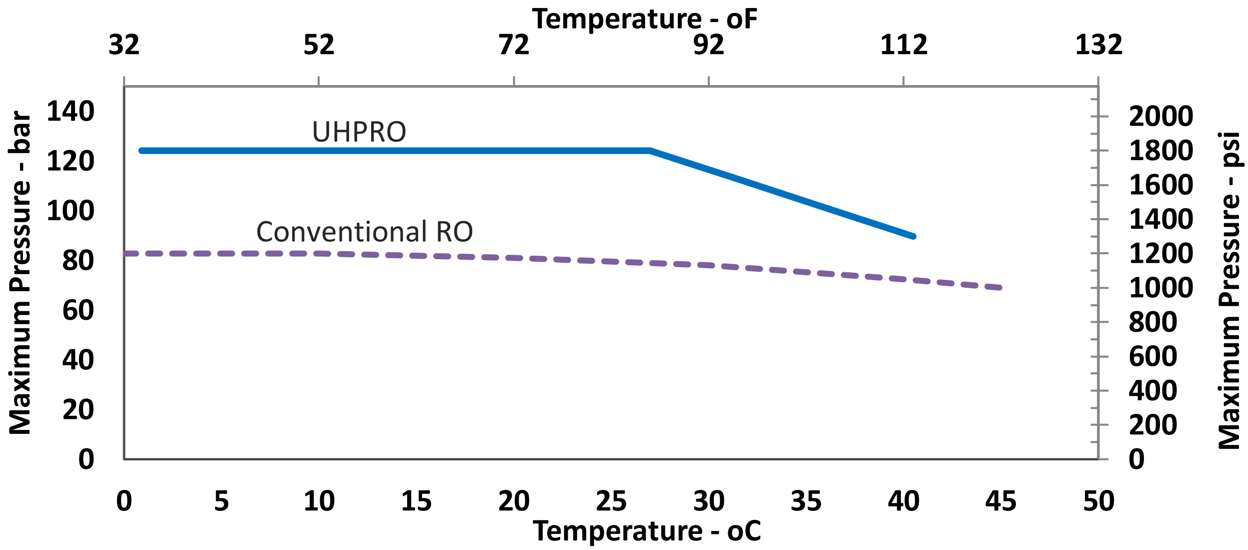

Figure 1. Maximum Pressure vs Temperature limit for UHPRO and Conventional RO

Most of the flux loss in a conventional RO system is caused by fouling with only a very small contribution from compaction. A majority of the flux loss caused by fouling is reversible through cleaning. However, when operating UHPRO at the extreme pressure limits, compaction contributes more to flux loss. The portion of the flux loss caused by compaction is irreversible. This flux loss is a function of both the maximum operating pressure and maximum operating temperature. In other words, the higher the pressure and the higher the temperature, the greater the compaction. The rate of flux loss is greatest during initial compaction period which occurs instantaneously and then stabilizes within the first 24 to 48 hours of operation.

In a controlled laboratory setting, with a pure, non-fouling, sodium chloride feed of 8.5%, the membrane produces an average flux of 10 GFD when pressurized to 1740 psi. Apparent flux loss over a 48-hour period is minimal. However, when the element retested at standard test pressures of 800 psi, the element's permeability is reduced by 50% relative to before the 1740 psi exposure test. When operating in a full scales system, such a flux loss impacts the flux distribution between the lead element and tail element within a pressure vessel and ultimately determines the maximum achievable brine concentration and, therefore, the maximum achievable recovery. Depending on the ionic composition of the feedwater, the brine concentration may reach beyond 120,000 mg/l before the osmotic pressure approaches the pressure limit of 1800 psi and the resulting net driving pressure is insufficient to produce any flux out of the tail element.

Further testing done in a laboratory setting demonstrates ability of the UHPRO to concentrate the salts beyond that of the conventional RO element (Gisclair, 2021). Using a pure sodium chloride feed to eliminate the potential for any fouling, a single element was run at 1740 psi and 25 C while the permeate was sent to drain and the concentrate was recycled. The results shown in **Figure 2** replicate the increasing feed salinity along the length of a pressure vessel from the lead element to the tail element. At the beginning of the test, when replicating the lead position, the element produced the highest flux of 25 LMH (14.7 gfd) and the best permeate quality of less than 500 us/cm. By the end of the test, as the reject stream approached 126,000 mg/l of sodium chloride to simulate the osmotic pressure at the tail position, the permeate flux decreased to 2 LMH (1.2 gfd) while the permeate quality increased to 5500 us/cm.

Lead Position Tail Position

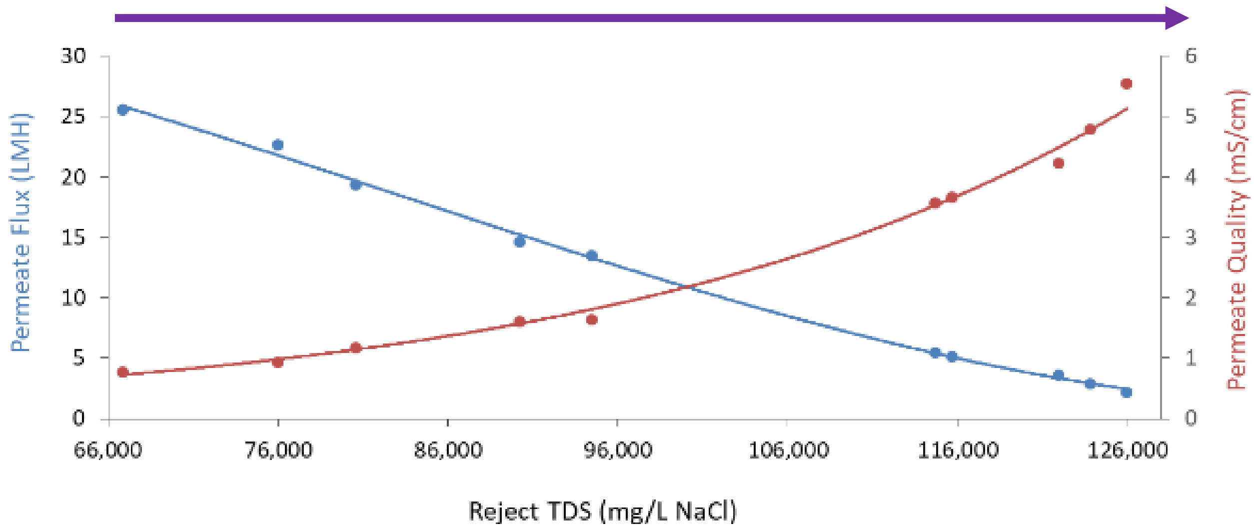

Figure 2. Single UHPRO laboratory test at 1740 psi (120 bar) and 25 C when concentrating a 65,000 mg/l NaCl solution. (Gisclair, 2021).

The controlled laboratory testing characterizes the UHPRO element performance in the absence of any fouling. But based on RO systems currently treating high fouling produced water, it is assumed that a combination of fouling and compaction will lead to greater flux loss in the UHPRO. The flux loss associated with both fouling and compaction was carefully monitored in a pilot study using UHPRO to treat cooling water blowdown (Mandel, 2021). The raw water was softened, treated by ultrafiltration and then concentrated up to 82,429 mg/L TDS by standard seawater RO membranes. This seawater RO concentrate was then sent to the UHPRO and further concentrated up to 119,167 mg/l. **Figure 3** shows the membrane UHPRO flux during the first six days of pilot operation. Flux varies hourly as the pilot operates in recycle mode and the original feed salinity is concentrated up. After an hour in recycle mode, the concentrated feed is discharge and new feed is reintroduced. In the first three hours of operation at 1494 psi (103 bar) and 25 C, the membrane saw its greatest flux loss, decreasing 45% from a max flux of 32 gfd (55 LMH) to 18 gfd (30 LMH). Within the first 24 hours, the membrane stabilized at a max flux of 10.6 gfd (18 LMH) - a 67% reduction. After flux stabilization, the temperature was increased to 30 C and the feed pressure was increased to 1653 psi (114 bar). No further flux decline occurred during the remaining five days of pilot operation.

After completing the pilot study, the element was evaluated and found to have good mechanical integrity. Retesting of the element at its original standard test pressure of 800 psi confirmed the 67% flux loss seen during pilot operation. The element retest also showed rejection improved from 99.80% at original factory test to 99.86%. The improved rejection was caused by organic fouling.

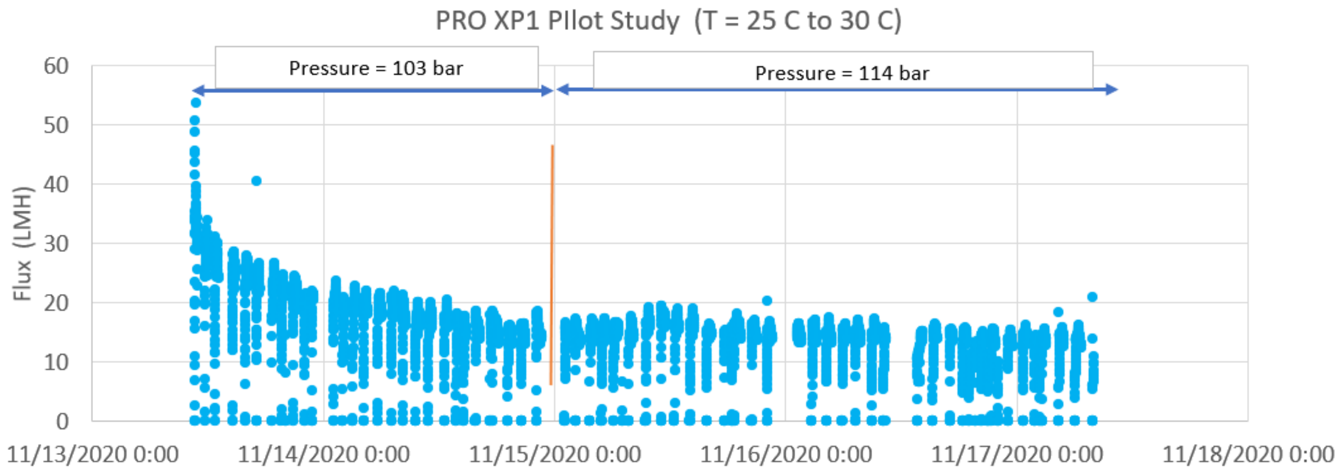

Figure 3. Single UHPRO laboratory test at 1740 psi (120 bar) and 25 C when concentrating a 65,000 mg/l NaCl solution. (Mandel, 2021)

The combination of laboratory testing and pilot testing with the UHPRO sufficiently characterizes the performance of this membrane and allows designers of an UHPRO treating produced water to project the required feed pressure after compaction and fouling occurs. If precipitation of organics and salts can be controlled, the use of UHPRO for treating produced waters allows the already concentrated TDS from the conventional RO to be concentrated further to almost 130,000 mg/l and allows an increase in the overall recovery of the RO system.

The obvious downside to operating with UHPRO is the increased energy consumption. But the high energy can be partially offset by applying existing energy recovery technology in new ways. Specifically, the use of multiple energy recovery devices in a multistage RO means the ultra-high brine energy from the last stage can be proportionally and efficiently distributed between more than one stage. This concept, known as BiTurbo^{TM}, is shown in **Figure 4**. A version of the BiTurbo^{TM} design has been proven on two-stage seawater RO systems and can be applied to RO systems treating produced water (Gisclair, 2021). For a multi-stage RO treating produced water, the initial stage(s) would use conventional RO elements. Depending on when the pressure limit of the conventional RO is reached, the later stage(s) would use UHPRO. Two turbos would be installed to boost two separate stages. Most of the energy would be used by the first turbo (Turbo 1) to boost the final stage. After the Turbo 1, there would still be sufficient energy remaining for Turbo 2 to boost the first stage and therefore reduce the energy consumption of the high-pressure pump (HPP) on the feed stream. To illustrate the multistage turbo design more clearly, **Table 2** lists the projected flows, pressures, and salinities associated with the design in **Figure 4**. The projected results are based on treating a high salinity feed of 46,371 mg/l TDS at 25 and achieving a recovery of 60%. In this design, Turbo 1 transfers the energy from the UHPRO brine (Stream 6) to the feed of the UHPRO (Stream 4) resulting in a boost pressure of 500 psi. The exhaust pressure from Turbo 1 is still at 575 psi and is used in the second Turbo 2 to provide a boost of 160 psi to the feed of the first stage. The use of the turbos provides good flux balance between stages with an average flux in the first stage of 9 gfd and an average flux in the second stage of 6.3 gfd.

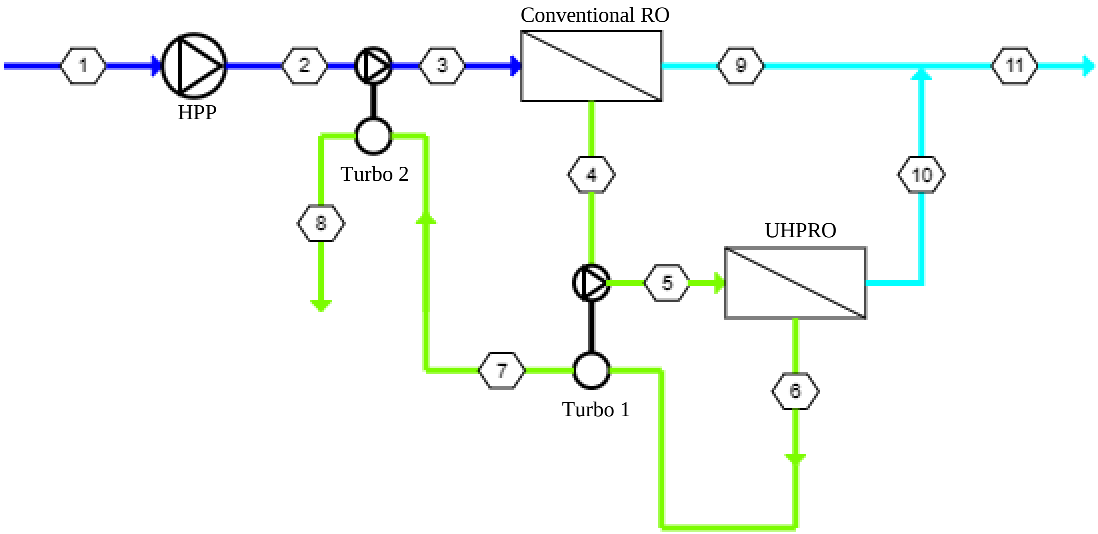

Figure 4. Multistage turbo design with conventional RO membranes in the first stage and UHPRO membranes in the second stage.

Stream No.	Flow (gpm)	Pressure (psi)	TDS (mg/l)
1	1540	0	46372
2	1540	829	46372
3	1540	989	46372
4	838	979	84967
5	838	1479	84967
6	616	1463	115115
7	616	575	115115
8	616	33.9	115115
9	701	0	271
10	222	0	1365
11	924	0	534

Table 2. Projected flow, pressure, and TDS of each stream in the multistage turbo design shown in Figure4.

Enhanced RO membranes for higher temperatures

Produced water coming out of mature steam floods has temperature as high as 90 °C, which requires significant cooling if commercial RO treatment processes are considered. The high silica and petroleum organics in such produced water, on the other hand, would prefer a warmer temperature procedure which reduces the risks on fouling to the heat changer and RO membrane. Conventional RO membranes are limited to a maximum temperature of 45 C. Therefore, high temperature RO membrane attracts special interest in treating produced water.

Boron and silica rejections with high temperature membrane were studied in the lab using synthetic produced water and real produced water collected from the field. Hydranautics PRO-XT2 membrane was used in this study. Salt rejection is above 99.7% when treating a standard test solution of 32,000 mg/L NaCl at 800 psi applied pressure. All the laboratory tests used a single element system layout.

Operating conditions were controlled at fixed design parameter settings. Laboratory synthetic water composition is listed in the **Table 3** below.

Analyte	Concentration, mg/L
Calcium	10.1-12.7
Magnesium	0.17-2.6
Sodium	3120-3310
Potassium	103-126
Chloride	4300-4533
Sulfate	192-205
Alkalinity as $CaCO_3$	622-1134
Boron as B	77.7-85.7
pH	10.9-11.3
TDS (Total dissolved solids)	8450 -9219

Table 3: Laboratory synthetic water used to characterize high temperature RO elements.

Boron and TDS rejections were evaluated with synthetic water tests using a single element at temperatures between 25 °C and 60 °C. Test results (**Figure 5**) were compared with projection software simulation results which revealed the accuracy of TDS rejection prediction by the software. The boron rejection was underestimated by the software (**Figure 6**).

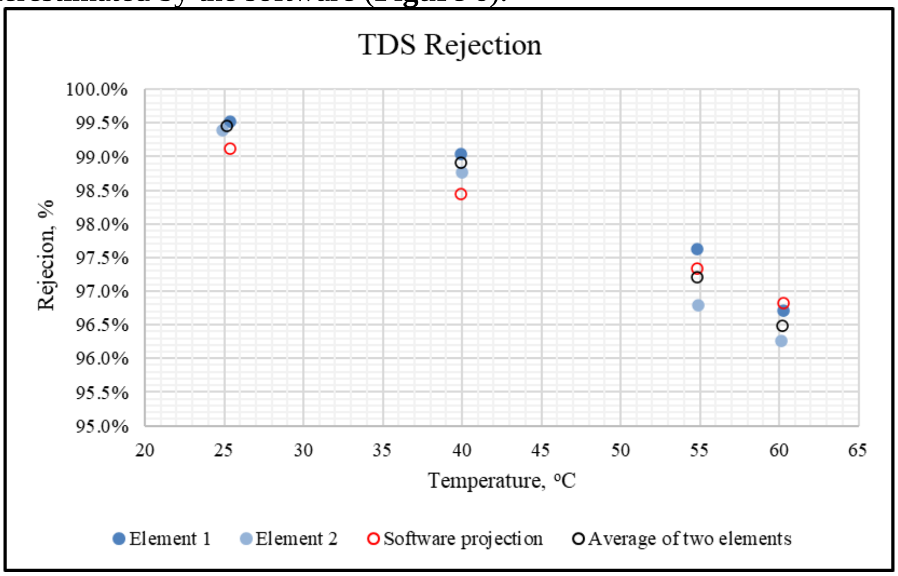

Figure 5 TDS rejection vs temperature for synthetic water, permeate flux was at 10.5 GFD, recovery rate was at 15%.

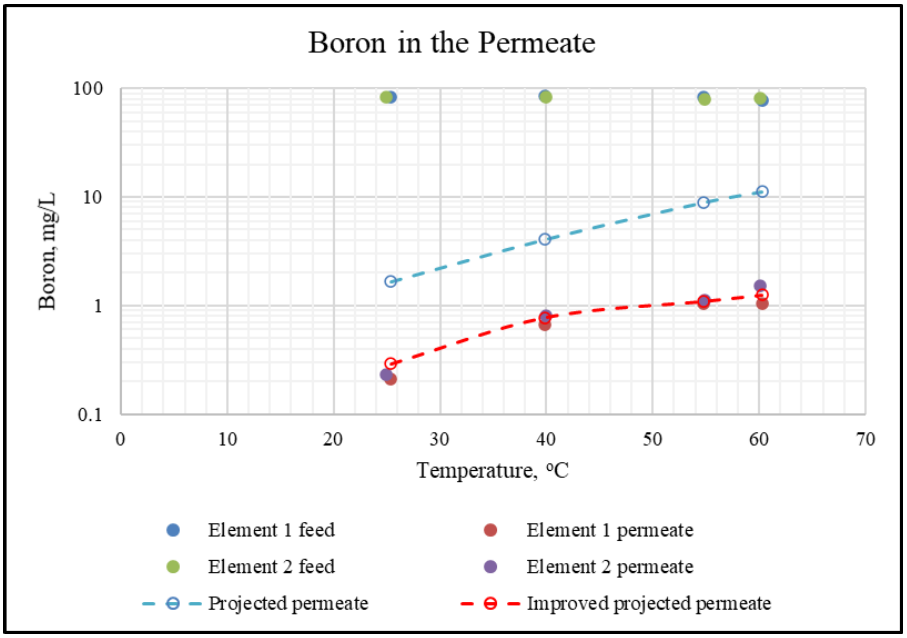

Fig 6. Permeate boron concentration vs temperature for synthetic water, permeate flux was at 10.5 GFD, recovery rate was at 15% at raised pH 11.

Tests with real field produced water (**Figure 7 & 8**) produced similar boron rejection results as from synthetic water. Sodium rejection was observed to be significantly lower than chloride rejection, which is attributed to the "swelling" effect at higher pH that increases hydroxyl ion passage and "pulls" sodium into the permeate. [Franks et al, 2009]. Field produced water test gave lower sodium rejection than synthetic water, which is believed to be due to the influence of petroleum organic compounds in the real field water that can exacerbate the membrane swelling effects [Chen et al, 2021].

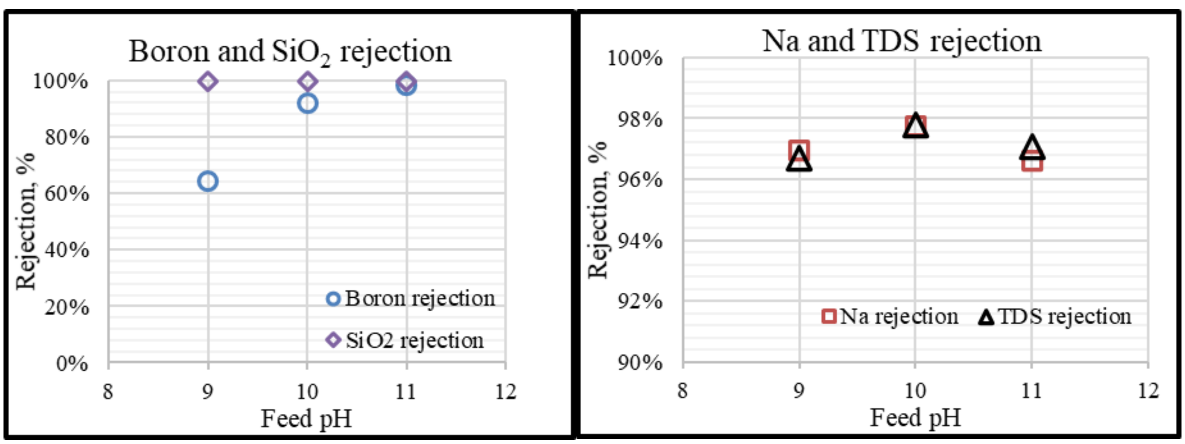

Figure 7. Boron, SiO2, Na and TDS rejection at different pH in the field produced water tests at 55 °C; permeate flux was at 15 GFD, and system recovery rate was at 10%.

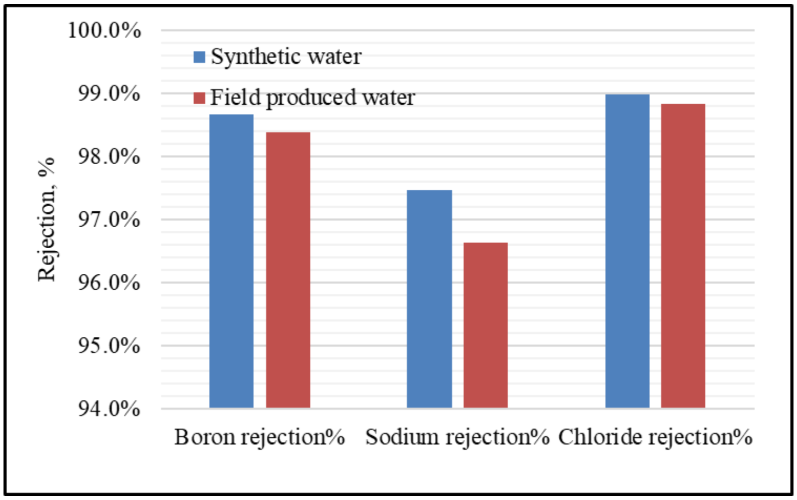

Figure 8. Rejection comparison between synthetic water and field produced water at pH 11, 55 °C.

Membrane projection software was calibrated using synthetic water test results on boron. Full scale system design was carried out using calibrated software. Three recovery scenarios were examined at 40%, 60%, and 75% using lab skid with close-loop batch filtration mode with single element (**Figure 9 & 10**). This assumed a treatment feed flow capacity at 44 m^3/h using a 4inch PRO-XT2 element. Design pH was at 11 and water temperature was set at 55 °C. Lab permeate boron measured at 75% recovery operation condition was 1.24 mg/L. This low boron level allows an easy post treatment options such as a secondary pass RO or polishing IX resin to satisfy the final boron target at 0.5 mg/L.

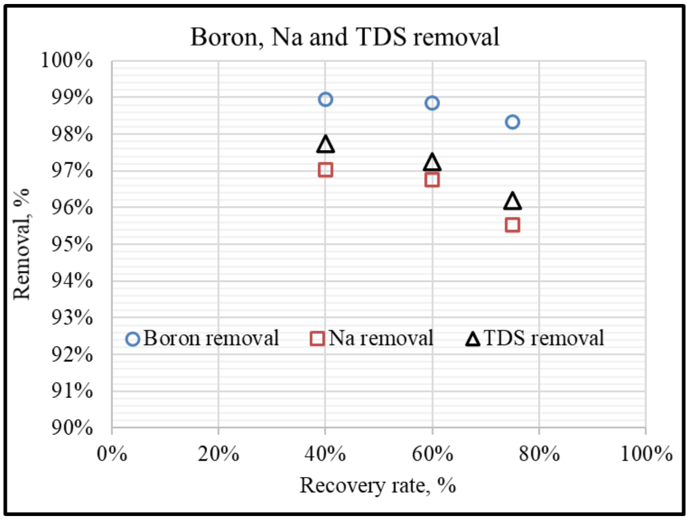

Figure 9. Boron, sodium, and TDS removal rate for high recovery single element tests with field produced water at pH 11, 55 °C.

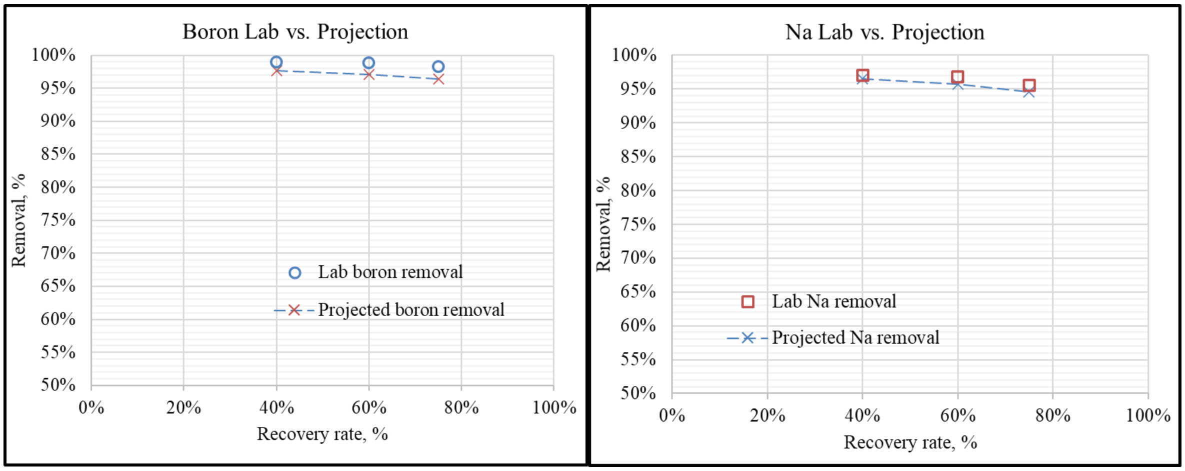

Figure 10. Full scale system boron and sodium rejection prediction vs actual lab results using single element simulation.

Full scale system projection results on boron and sodium rejections were compared with lab single element test results. Good matching was found on lab and simulation results with lab rejections slightly higher than the program. A visual comparison of the water samples collected from the test can be seen in **Figure 11**.

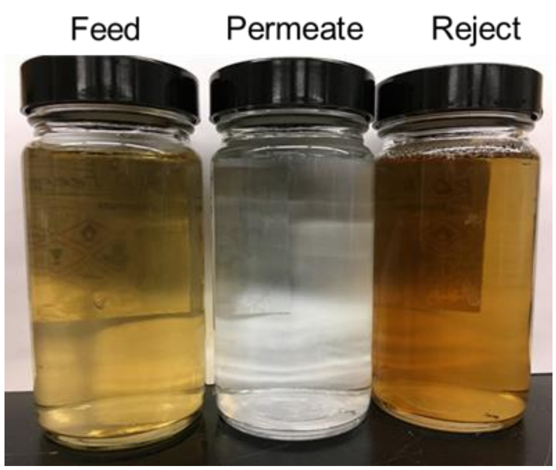

Figure 11. Water samples collected from the feed, permeate, and reject streams at 75% recovery test with field water.

Conclusion

The use of standard RO elements for the treatment of produced water was originally piloted more than 30 years ago. For more than 15 years, RO elements have been used in full scale systems in California to treat produced water. But the pressure and temperature limits of the standard RO element have created limitations on the salinity and temperature of produced water than can be treated. But newly designed RO elements, with new, more robust materials of construction, have been developed to treat a wider range of industrial feedwaters, including produced water. These elements have pushed the temperature limits from 45 C up to 60 C. They have also pushed the pressure limits from 1200 psi up to 1800 psi.

Using the new RO elements for the treatment of produced water requires a clear understanding of how permeability and ion passage are affected when operating at the extreme pressures and temperatures. In the case of permeability, designers should expect a flux loss of more than 50% due to compaction.

Additional flux loss will be caused by the high fouling nature of produced water. Projected feed pressures should account for flux loss from both compaction and fouling.

In the case of ion passage, ultra-high pressure has relatively little impact. But operating at higher temperatures significantly effects ion passage, especially the passage of boron. Projected permeate quality should account for the higher temperatures over a wide pH range. The lab tests and software predictions demonstrated encouraging results on high temperature RO membrane treating produced water. At the examined condition of 55 °C and pH 11, boron rejection was greater than 98% while sodium rejection was lower at 95%.

Acknowledgement
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