New Specialty Membrane Products for Challenging Industrial Wastewaters

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Abstract

Over the past 30-40 years, water reclamation from municipal wastewater has become a common practice and has greatly supplemented water supplies in water-stressed areas, such as southern California, Singapore, and the Middle East. Plants such as the 378 MLD Orange County Reclamation Facility have implemented ultrafiltration (UF), reverse osmosis (RO), and ultraviolet (UV) technologies to reclaim 80-85% of the water, having very high quality for industrial or indirect potable reuse. Reclamation of industrial wastewater has also been employed during this period, but has been limited to smaller systems, much more varied processes and treating very complex wastewaters. In addition, regional issues have forced some industries to fully reclaim their wastewater to achieve zero liquid discharge (ZLD). Recent issues regarding the disposal challenges for industrial wastewaters have put significant stress on these industries to find more economical treatment processes to comply with ZLD requirements.

Industrial wastes are often characterized as having high organic content that can come from solvents, oils, fats, greases, and other materials used or derived in industrial processing. These wastes can also have a variety of dissolved salts and metals, which make treatment difficult due to issues with scaling and osmotic pressure. Typical treatment processes utilize particle filtration technology, softening, RO, evaporation and crystallization to achieve ZLD; however, this can be a very complex treatment process and the evaporation and crystallization processes are very expensive. Also, the resulting solid waste will have a mixture of salts and may not be easily disposed in a landfill.

Through recent developments in fouling resistant membranes, these high organic content wastewaters can be treated with better stability. Another key development has been salt-selective nanofiltration membranes which can separate the salts into chloride rich and sulfate rich streams so that the resulting brine can be potentially reused. Finally, new ultra-high-pressure membranes have been developed which allow economical brine volume reductions and minimize the use of expensive evaporation processes. This paper will report on three case studies where newly developed membranes have been demonstrated in these processes. The results show that the low fouling membrane reduces flux decline by as much as 20%, compared to conventional polyamide membranes. The second case study shows how extra-selective NF membranes are used to concentrate sodium sulfate for reuse in a tannery waste, and finally, new extreme-pressure RO membranes are demonstrated in textile waste treatment to reach TDS values as high as 146,000 mg/l.

Introduction

In areas such as China and India, the rapid growth of industry has put an enormous stress on the water supplies, which is a key resource for virtually all industries. One example of this is in China where there has been significant growth in the number of power plants, especially those that are coal-based. These plants, called Flue Gas Desulfurization (FGD) plants, treat the air emissions to remove SO_x and NO_x. The resulting wastewater is high in organics, salts and metals, making it difficult to treat. The wastewater is primarily composed of blowdown from cooling towers. One report[1] has stated that in 2014, the power and heat generation sectors spent at least RMB3.2 billion (US$ 465 million) on wastewater treatment, which was number 6 out of 42 sectors listed by the Chinese government. Similarly, wastewater from the growing coal to chemical industry is equally challenging to treat. These waters are typically high in sulfates, hardness and metals. A typical wastewater for a coal to chemical plant is shown in Table 1[2].

Parameter	Typical Concentration (mg/l)
TDS	45,000 – 55,000
TSS	<100
COD	100 – 300
Sodium, Na	10,000 – 15,000
Magnesium, Mg	1,000 – 5,500
Calcium, Ca	2,000 – 3,000
Carbonates HCO_3, CO_3	5,000 – 10,000
Sulfates, SO_4	12,000 – 18,000
Chloride, Cl	10,000 – 15,000
Nitrates	700 – 1,000

Table 1: Raw water characteristics for Coal to Chemical wastewater dfsdfsdfsdfdsfsdfd

In India, they have a similar issue with high strength industrial wastewaters, but from different types of industries. Some of the key wastewater generating industries in India include Textile, Tannery, Sugar, Distilleries, and Refineries. According to one source[3] it had been estimated that 501 MLD of industrial effluent wastewater is being discharged and ultimately enters the Ganga River. This has led to a 2015 policy introduced by the Indian Government which stated that all textile plants generating more than 25 m^3/day of wastewater should implement ZLD technology to treat their wastewater[4]. This has greatly impacted many plants, while others were already adopting some form of ZLD technology. A common approach in this region is to send waste from the smaller industrial plants to a Common Effluent Treatment Plant (CETP). One study[3] indicated that a CETP operating with ZLD would have a cost of Rs. 12-15 Crores per MLD, compared to a cost of Rs. 3-4 Crores per MLD for CETP which does not have ZLD. Accordingly, it has been estimated that the ZLD market in India was on the order of USD$ 39 million in 2012 and growing at a rate of 7% per year. Thus, ZLD technology is needed and will rapidly evolve as it continues to be applied and adopted by chemical waste-producing industries.

ZLD Treatment Processes

The basic features of the ZLD are shown in Figure 1. The process would take a combined wastewater, which if containing oils and greases, would be treated by oil separator, such as an API separator, gas flotation separator, or walnut shell filter. This is to ensure that there are no free oils in the water to the treatment system. This is most common for treatment systems in the oil, refinery and chemical industries.

Oil removal is followed by a filtration system to remove the suspended particulate matter in the water. Common filtration systems include multimedia filters (MMF) based on sand and anthracite media, and ultra or micro-filtration membrane units. The latter two achieve much more efficient removal of fine and colloidal particles and may come as polymeric or ceramic membranes. For high temperature or for high strength chemical wastewaters, ceramic membranes have become most common. These processes should reduce turbidity to less than 0.5 NTU, and more preferably to 0.1 NTU to ensure low fouling rates in the RO membranes.

Prior to RO treatment, there may need to be a chemical softening step to remove hardness, which would otherwise lead to scaling in the RO system. The common process to remove hardness is lime softening. This involves the careful addition of chemicals to induce precipitation of the hardness. If not operated properly, there can be floc carry over from this process which can lead to heavy fouling of downstream RO. A new development by a company called Saltworks[5], is a carefully controlled chemical precipitation process that carries this process out in line and avoids the use of big tanks and difficult to control addition processes. The process called BrineRefine has been demonstrated at

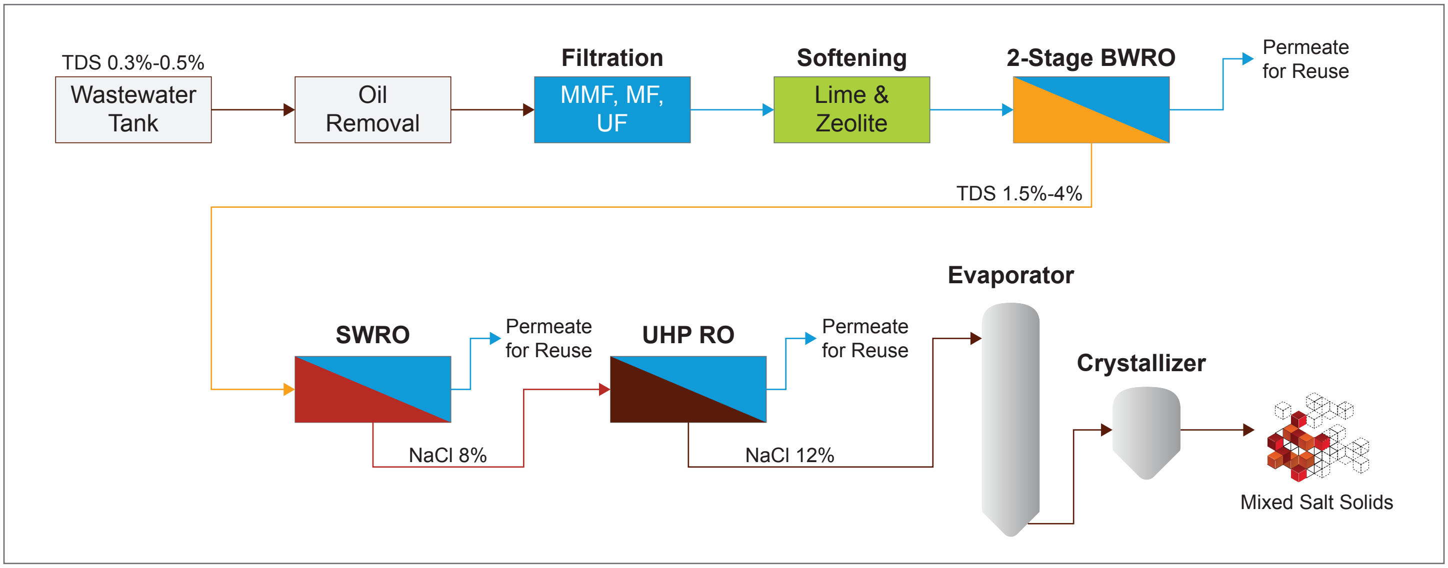

Figure 1: Process flow schematic for ZLD System

a number of sites and is much more compact and simpler than conventional lime softening processes. In addition to this type of hardness removal, some plants may also institute zeolite softeners and weak acid softeners. These are needed to achieve very low values of hardness which may be required in processes where the RO is operated at very high pH. Two such processes have been patented and used commercially, one is called HERO and the other is OPUS. Both typically raise the RO feedwater to pH greater than 10. Operation at high pH has the advantage of keeping silica dissolved at higher concentrations, improving borate rejection and solubilizing some organic acids which would otherwise foul the RO membrane. If none of these issues are present in the wastewater, the ion exchange softeners would not be needed.

After these steps, the wastewater is purified from the dissolved contaminants with RO membranes. For textile plants in India, the TDS of the wastewater may be in the range of 0.2-0.5% TDS. Brackish water RO (BWRO) membranes would be used to concentrate the salts by 4 times, or 75% recovery of water in a two-stage process. Most plants incorporate low fouling BWRO membranes, such as the LFC3 RO membranes from Hydranautics. These membranes are coated with a special hydrophilic top layer, which protects the polyamide membrane from hydrophobic fouling by organics. The concentrate from this 2-stage BWRO system may have a salinity of 1-2%. The COD entering the RO system can be 100-200 ppm and thus close to 1,000 ppm exiting the BWRO. It is critical that the organics are soluble at the concentrations in the RO brine otherwise they will phase separate and cause high fouling rates on the RO membranes. Most ZLD processes will implement a brine recovery RO unit after the 2-stage BWRO. This unit would utilize SWRO membranes in a one stage design, which would operate at much higher pressure and recover another 50% of the water. In the past, the SWRO concentrate would then be dewatered by evaporation and crystallization. However, these are very expensive processes and thus, there has been a growing application of ultra-high pressure RO (UHP RO) which can operate above the 83 bar (1200 psi) limit of conventional SWRO membranes. These membranes may operate up to pressures as high as 120 bar (1750 psi), but the market segment is still in its infancy, as exemplified by the fact that there is no ASME code for RO pressure vessels at this upper pressure limit.

The final two steps are evaporation and crystallization, which are very mature treatment technologies. However, as mentioned above, they are very expensive in terms of capital and operating costs. Table 2 shows typical costs associated with the various water removal technologies. It can be seen that mechanical vapor recompression systems (evaporators) operate at nearly ten times higher energy consumption compared to RO technologies. A slightly different variation of an evaporator is offered by Saltworks. Their Saltmakers utilize evaporation of water from a mist instead of a falling film over a heat exchanger surface. This simplifies the evaporator system making it smaller and requiring less downtime for maintenance.[6]

Technology	Typical Salinity Treatment Range (mg/l TDS)	Typical Specific Energy Consumption ($kWhr_e/m^3$)	Typical Water Treatment costs (US$/$m^3$)
BWRO	500 – 20,000	1.5 – 2.5	0.5 – 2
SWRO	15,000 – 70,000	2 – 6	2 – 5
MVR (evaporators)	80,000 – 250,000	20 – 25	18 – 35
Crystallizers	300,000 and up	52 – 66	25 – 50

Table 2: General Water Treatment Costs for ZLD Technologies[3,4]

Another variation which is often used on Textile wastewater includes nanofiltration (NF) to separate the salts into a chloride-rich stream and a sulfate-rich stream. The latter is a valuable feedstock reused at the plant. This process scheme is shown in Figure 2.

This paper will focus on the development of new improved membranes for the related processes shown in the figures above. These PRO products are shown in Figure 2, with the corresponding roles they play in a ZLD process. Also, some examples of testing these new products will be provided.

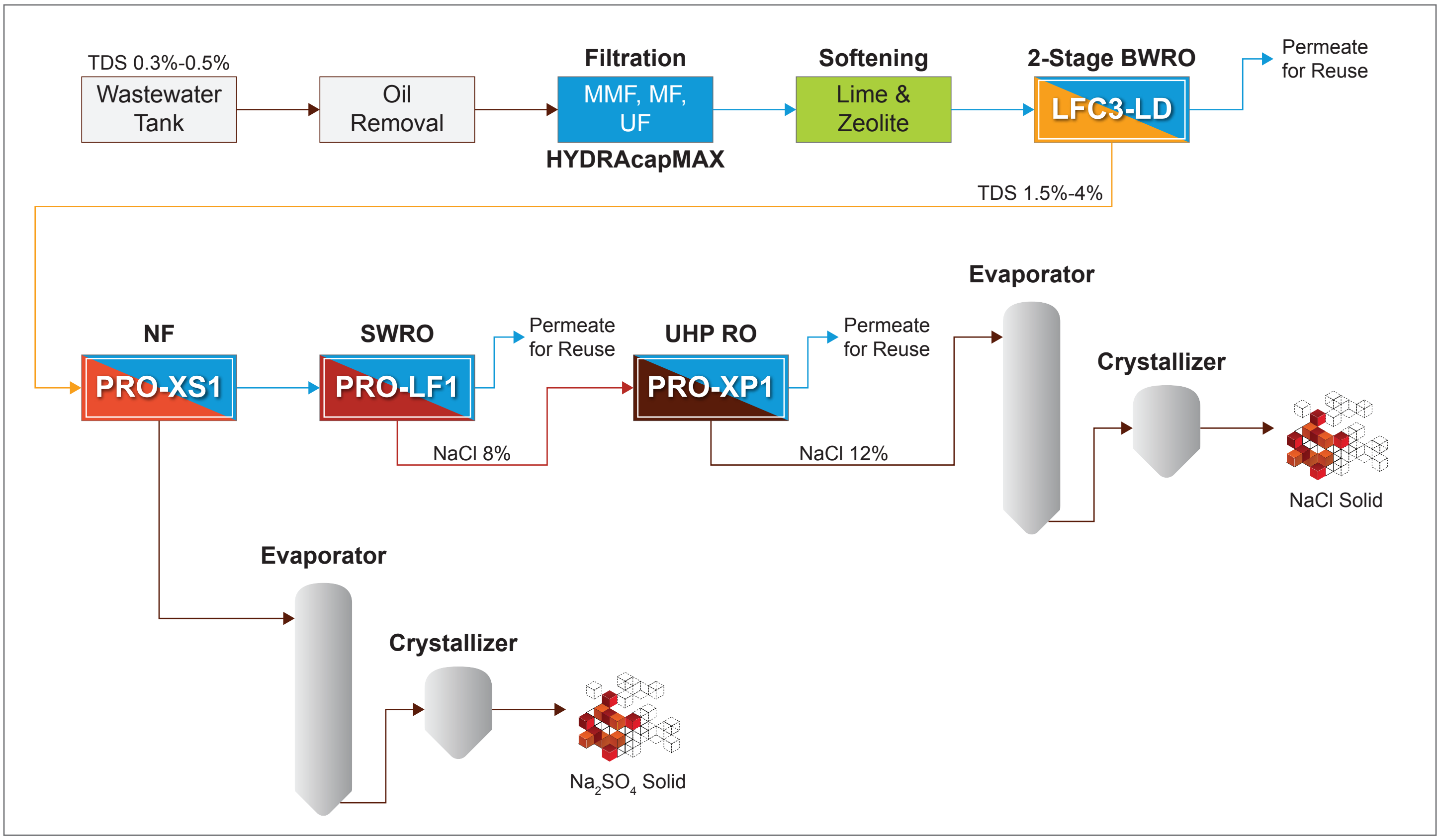

Figure 2: ZLD process for treating Textile wastewater

Low Fouling, High Rejection, High Pressure Membranes

For years, RO industrial wastewater treatment has been done with low fouling membranes. One of the first of these products introduced was the LFC1 membrane[7]. These BWRO membranes have been coated with a neutrally charged, hydrophilic coating which minimizes fouling by certain surfactant compounds. Most recently, Hydranautics has applied similar low fouling coatings to the high rejection, higher pressure seawater-type RO membranes. The lower fouling nature of the novel hydrophilic coated PRO-LF1 is demonstrated in a test where the membrane was exposed to a protein, bovine serum albumin. The attraction force of the BSA to the membrane surface was measured by Atomic Force Microscopy (AFM). The test arrangement and measured absorption forces are shown in Figure 5. It can be seen that the attraction force of the protein to the conventional membrane is between 3 times higher (pH 5) and 20 times higher (pH 7) compared to that of the low fouling PRO-LF1 membrane. Other tests show that the fouling rates of cationic, non-ionic and amphoteric surfactants is less for PRO-LF1 compared to conventional SWRO membranes.

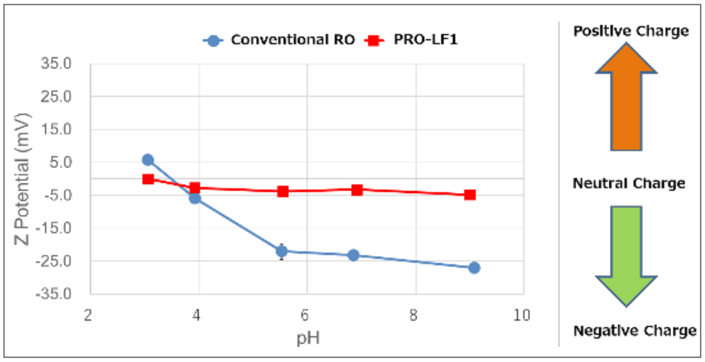

Figure 3: Surface Zeta potential of neutrally charged PRO-LF1 and conventional SWRO membrane.

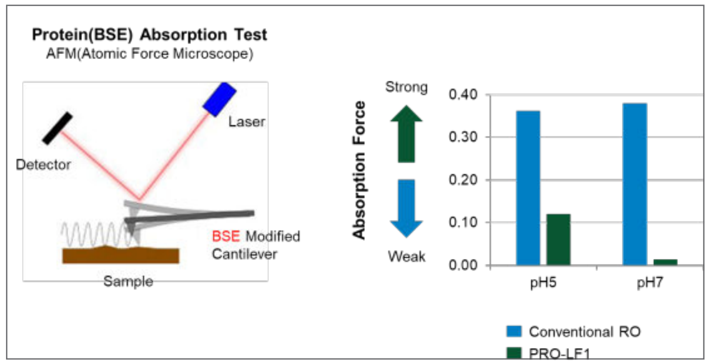

Figure 5: Measurement of the attraction forces between BSA and membrane surfaces.

Figure 3 shows the surface zeta potential of the PRO-LF1 membrane, which ranges from 0 to -5 mV for the pH range shown. In comparison, the conventional SWRO membrane has a surface zeta potential averaging -25 mV in the pH range of 6 – 12, where it is normally used. Not only does the PRO-LF1 membrane have a more neutral charge, but it is also hydrophilic, as shown in Figure 4. The contact angle was measured to be 25 degrees, compared to a 45-degree contact angle for a conventional SWRO membrane.

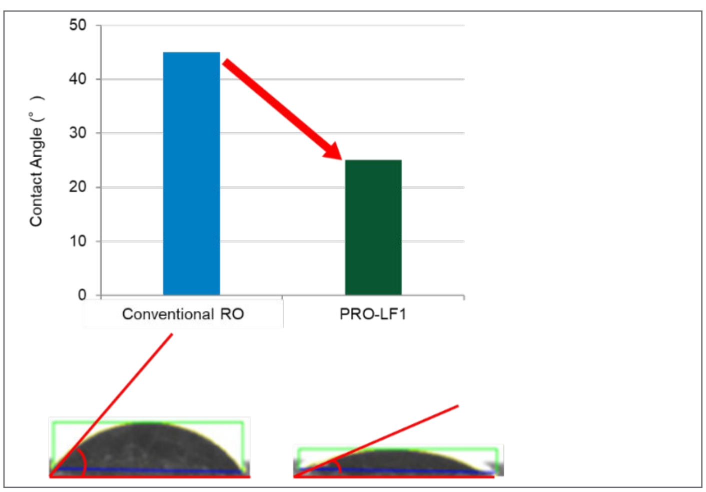

Figure 4: Contact angle measurement for low fouling PRO-LF1 and Conventional SWRO membrane.

To determine the actual benefit of the low fouling, high-pressure membrane, we carried out a test at a Tannery CETP. At this plant the treatment process consisted of a clarifier, aeration basin, secondary clarifier, Dual Media Filter, HYDRAcapMAX 80 UF modules, RO and evaporators. The RO skid is shown in Figure 6. The RO is arranged with 2 pressure vessels (PV) feeding one 2nd stage vessel, which directly feeds a single 3rd stage vessel. The 1st stage of train 3 was fitted with the low fouling PRO-LF1, while the 2nd stage vessel of train 2 was fitted with new conventional SWRO elements.

Tannery CETP (3-Stage RO system)		
Total no. of trains	3	
3 stages per train	2:1:1 (6 elements per vessel)	
Membrane type	1st stage of Train #3	PRO-LF1
	1st stage of Train #2	Conventional RO
Start-up	October 2018	
Feed flow	13.0 m^3/h	
Permeate flow	5.7 m^3/h (1st stage)	
Feed quality to RO	pH	6.0 - 6.5
	Turbidity	< 2 NTU
	SDI	< 5.0
	TDS	15,000 - 16,000 ppm
	Hardness	1,100 ppm
	COD	600 ppm
Total system		
Equalization → Clarifier → Aeration → Secondary clarifier → Tertiary clarifier → DMF 1 and 2 → UF with 12 HYDRAcapMAX 80 → RO Evaporator		

Figure 6: Trial of PRO-LF1 low fouling membrane at a Tannery CETP.

The resulting performance of the two membrane types is shown in Figure 7. The normalized permeate flow of the conventional SWRO membrane drops from 7 m^3/hr to as low as 1.5 m^3/hr, before a 2nd chemical cleaning restores the normalized flow back to the range of 3 – 5 m^3/hr. In contrast, the PRO-LF1 drops from 7 m^3/hr to about 3, before the 2nd chemical cleaning restored the normalized flow to a range of 3 – 6 m^3/hr. Thus, there was roughly 15 – 20% higher normalized flow for the low fouling PRO-LF1 compared to the conventional SWRO.

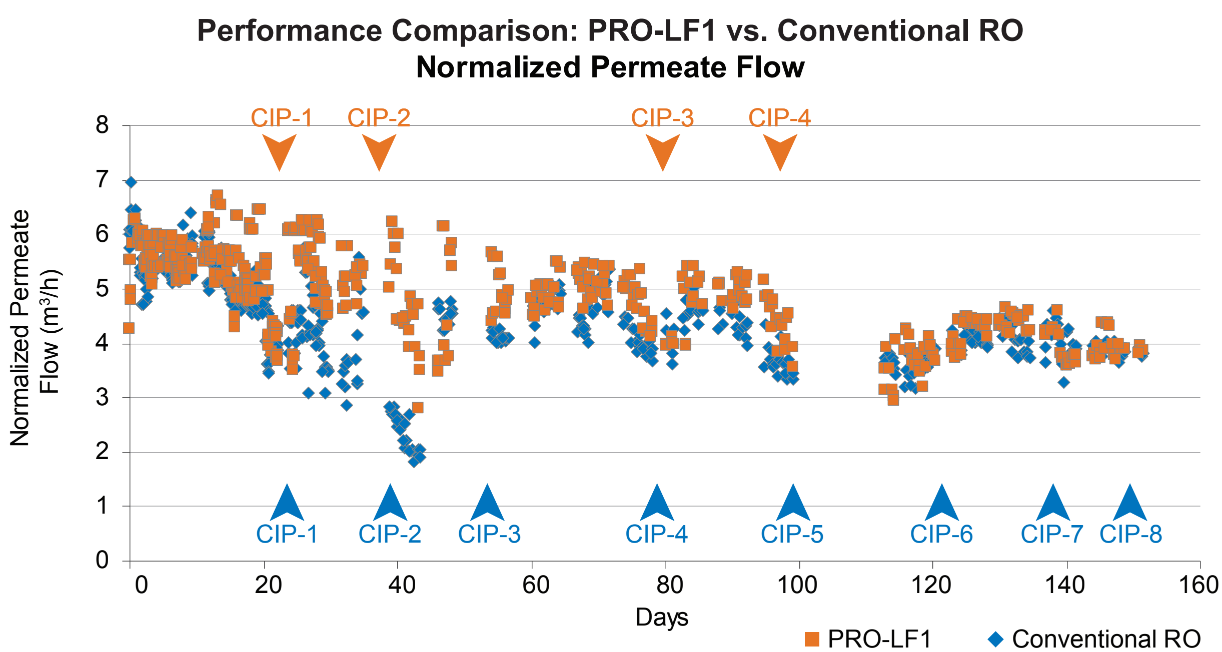

Figure 7: Normalized Flow for two types of high pressure membrane operating at a Tannery CETP in India.

Low Fouling, Highly Selective Nanofiltration Membranes

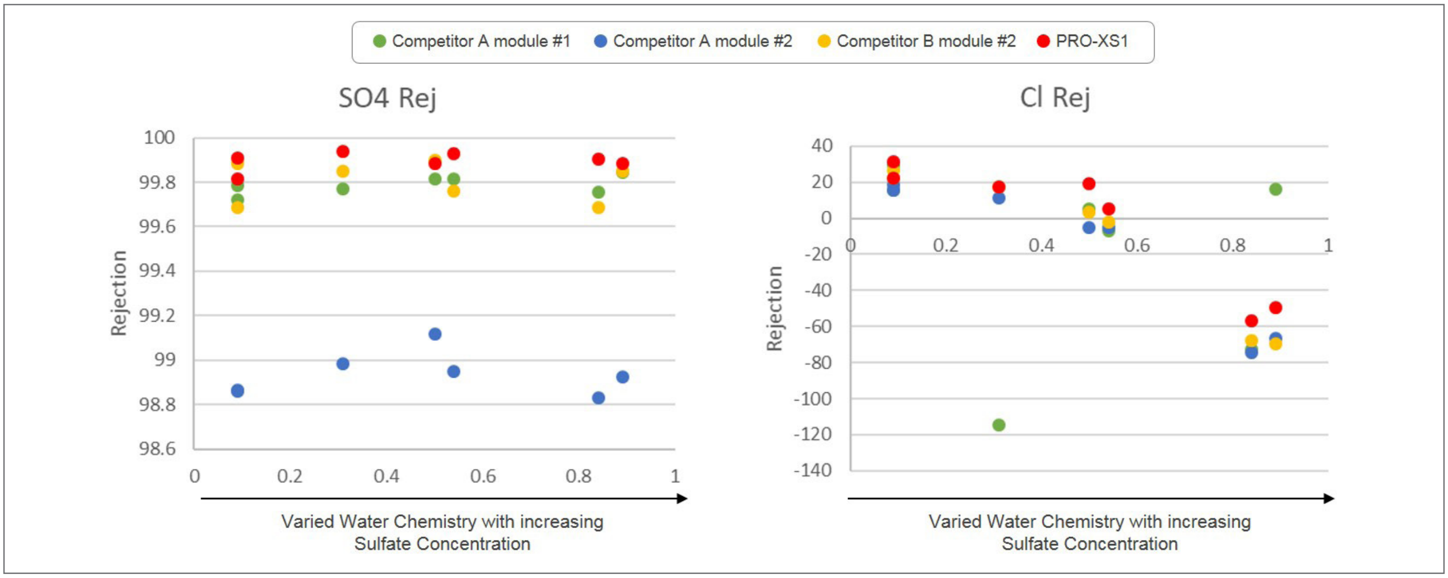

Figure 8: Sulfate and chloride rejection for various NF membranes.

A new type of extra selective nanofiltration membrane, PRO-XS1, has been developed by Nitto/Hydranautics to treat these difficult ZLD membranes. The membrane is a polyamide membrane which has a novel coating to interact with the different charges on mono and divalent ions. When tested on a 2000 mg/l $MgSO_4$ test solution, the rejection is over 99.8%. When testing PRO-XS1 on a mixture of mono and divalent anions, the divalent sulfate ion is highly rejected (>99.9% rejection), while the chloride rejection is as high as 20%, but can drop below 0% and even show selective removal of chloride from the permeate, depending on the overall salinity. The results are shown in Figure 8, where the PRO-XS1 has the highest sulfate rejection of the NF elements tested. In addition, the PRO-XS1 was designed to operate at high pressures (up to 83 bar or 1200 psi) associated with ZLD applications.

A test of the new PRO-XS1 was carried out at a textile plant in India. The plant treats the textile wastewater with 5 stages of RO, where the last RO stage concentrates the salinity to 75,000 mg/l to feed a DTRO system, which achieves 115,000 mg/l salinity. The PRO-XS1 NF membrane was piloted as a potential substitute for the 5th stage RO membranes. The goal of using the novel NF membrane was to recover a sulfate-rich stream for reuse, and also to make a sodium chloride rich stream for further concentration by the DTRO. This test arrangement is shown in Figure 9. As can be seen in Figure 9, the feedwater was high in organics, and the concentrate after 30% recovery, is even darker.

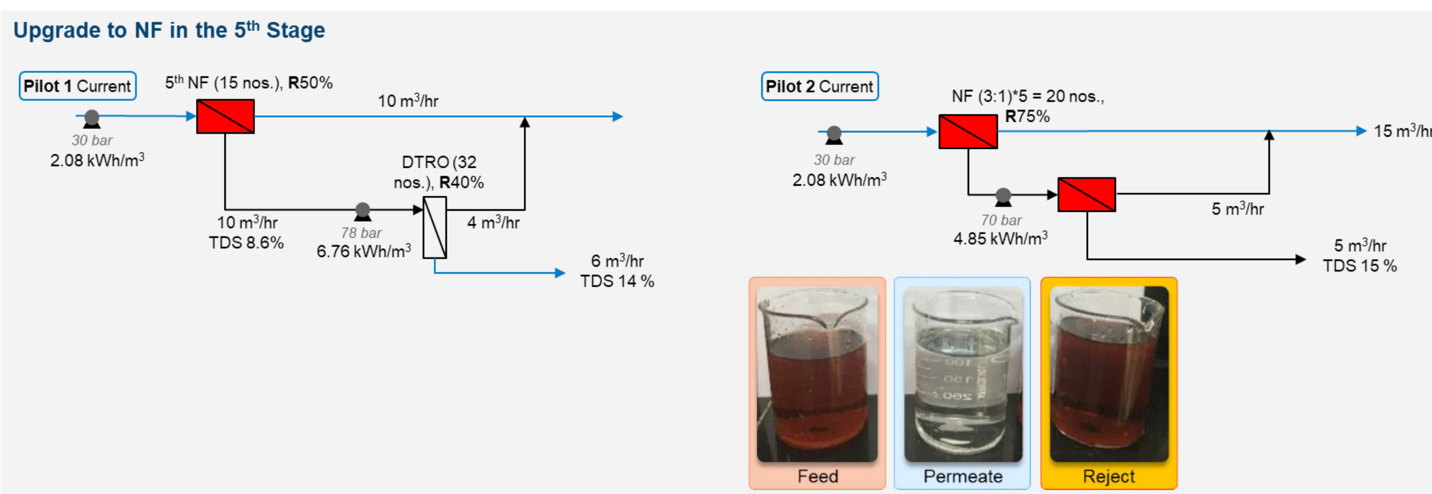

Figure 9: Pilot Operation scheme to test NF membranes in a ZLD process for selective sulfate concentration.

Parameter	Feed Value	Reject Value	Permeate Value	Rejection % (based on feed / brine average)
Feed Press, kg/cm^2	27.1	26.8		
TDS, mg/l	60,050	95,960	20,550	74%
Tot Hardness, mg/l	310	390	12	97%
Chloride (Cl), mg/l	7,705	6,000	9,000	-31%
Sulfate (SO_4), mg/l	28,900	55,370	2,230	95%
Color, CU	1,647	3,210	12	99.5%

Table 3: Results of pilot testing PRO-XS1 nanofiltration membrane on textile wastewater

The NF membranes were tested at three different recoveries, 30, 40 and 50%. The results at the 50% recovery condition and 30°C are shown in Table 3. The system was operated at 27.1 bar of pressure and 22 m^3/hr flow rate. The essential composition of the feed stream, as shown in Table 3, is very high in sulfate. At these conditions, the feed TDS was increased from 60,000 mg/l to 95,900 mg/l and the permeate was 20,550 mg/l TDS, giving 74% rejection. As can be seen in the table, the hardness and sulfate are highly rejected while the color was almost completely rejected. The high rejection of the dyes which cause color is clearly seen in Figure 9 as well. To achieve charge neutrality, the chloride is preferentially drawn into the permeate, resulting in a higher concentration of chloride in the permeate than in the feed/reject stream to give -31% rejection.

As desired, the concentrate has become highly enriched in sulfate, which is desirable for reuse, while the permeate is rich in chlorides, and contains minimal amounts of sulfate. The former can be reused in the textile process scheme and the latter can be further concentrated by the DTRO or UHP RO. Based on the success of this test, the customer will install the PRO-XS1 nanofiltration membrane in their commercial process.

Ultra-High Pressure RO Membranes

Both ZLD and MLD (Minimum Liquid Discharge) result in a high recovery of water at a significant price. As mentioned above and shown in Table 2, the largest contributor to this high cost is the final steps of evaporation and recrystallization. Thus, process engineers have actively pursued the maximum use of RO to dewater their wastewater streams. Typical seawater membranes are rated up to 83 bar (1200 psi) or approximately 83,000 mg/l TDS. Recent material developments have resulted in a class of extreme RO membranes, such as the PRO-XP1, which can operate at much higher pressures up to 120 bar (1750 psi).

The ultra-high-pressure RO has required a quite significant redesign of the standard seawater RO element. More robust materials have been selected for the permeate spacer, glue, product water tube, ATD and the fiberglass/epoxy outer shell. The key contributor to element productivity, though, is the permeate spacer. Normal materials show quite extensive embossing of the membrane into the permeate

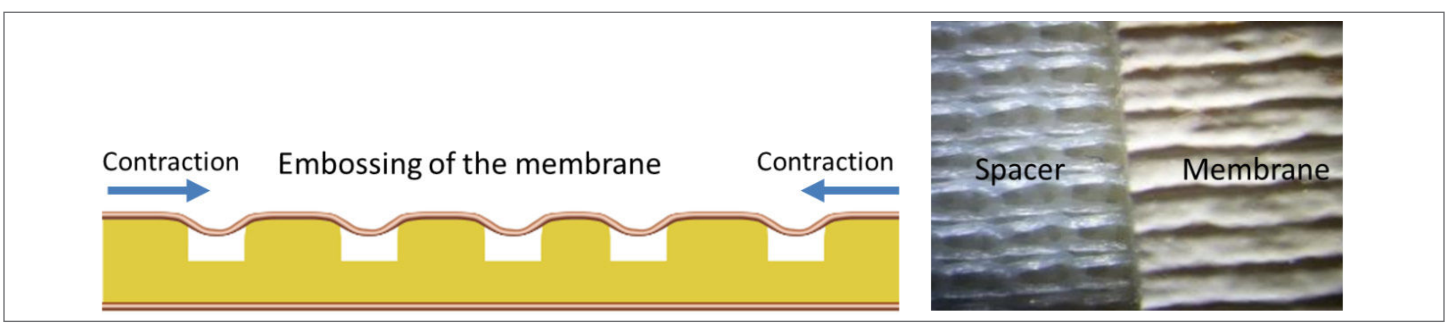

Figure 10: Depiction of membrane embossing into the permeate support

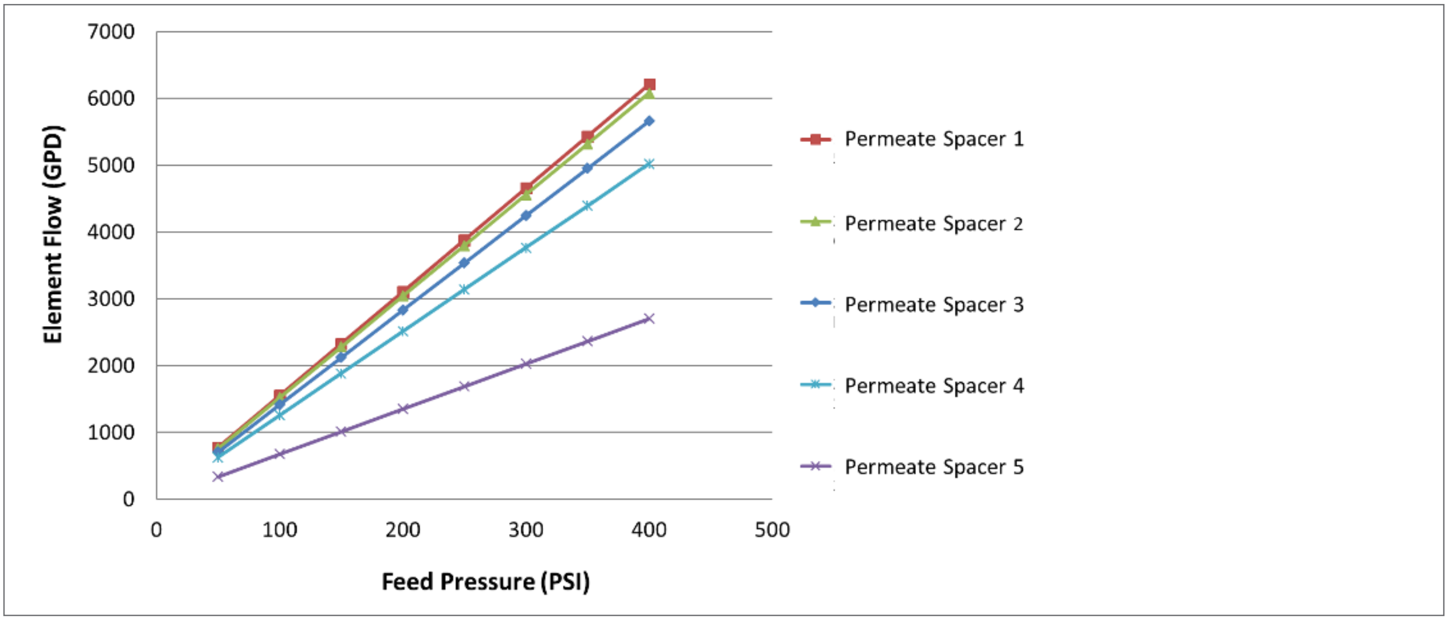

Figure 11: Permeate flow rate from a ultra-high pressure element with various permeate spacers.

spacer at ultra-high pressures, which greatly narrows the channel for the water to pass to the product water tube. This is illustrated in Figure 10.

We have developed new materials which minimize this effect and make the element more robust to resist the ultra-high pressures. A careful consideration of many spacer materials and designs was undertaken to optimize this issue. As always in development, there were trade-off's that were balanced. Using smaller sized channels reduces embossing, but also increases the pressure drop to remove the water from the leaf. Some examples of the impact of various permeate spacer materials and designs are shown in Figure 11.

With these material improvements to the element, we then carried out element testing in the laboratory. The first of these was with a standard sodium chloride feed using our PRO-XP1-4040 element operating at 120 bar. The results in Figure 12A show the variation on flux and permeate quality over a range of reject concentrations from 66,000 mg/l TDS to 126,000 mg/l TDS. The increasing reject salinity results in higher osmotic pressure, which thus reduces the net driving pressure. At these conditions the flux dropped from 25 to 2 lmh. Also, the permeate concentration increased in conductivity from 1 to 5 mS/cm. Again, this is normal and expected as feed/reject TDS rises and permeate flux decreases.

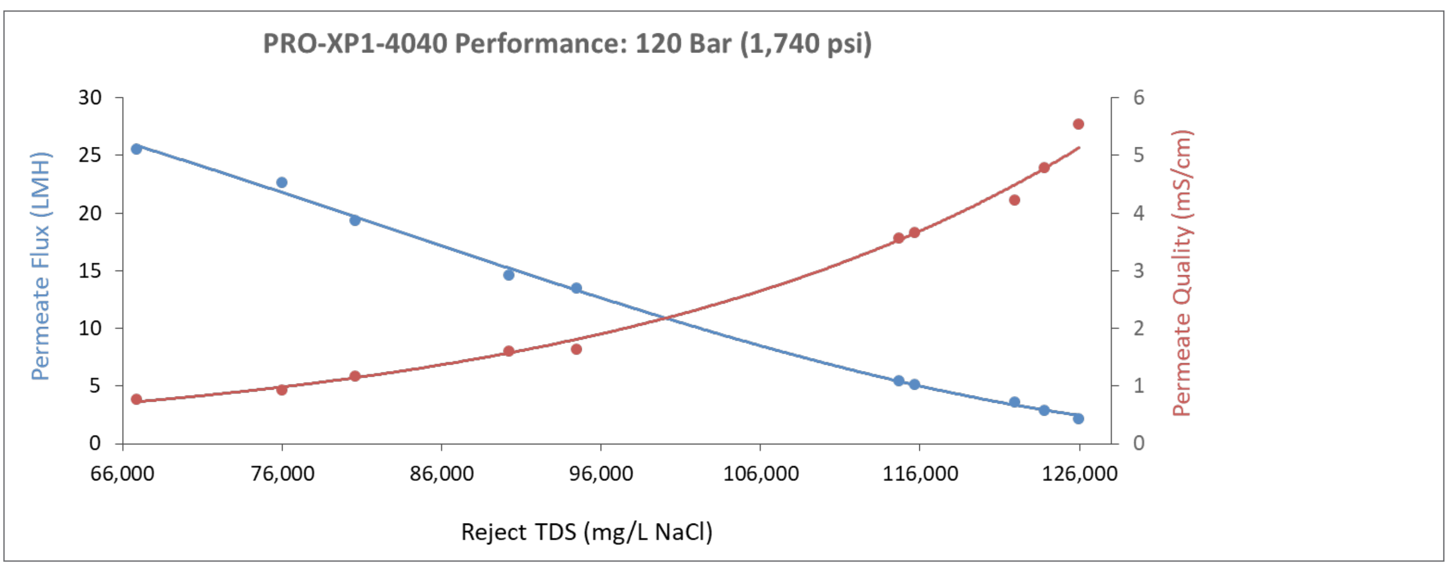

Figure 12A: Flux and permeate TDS values as a function of the increasing feed TDS with sodium chloride feed.

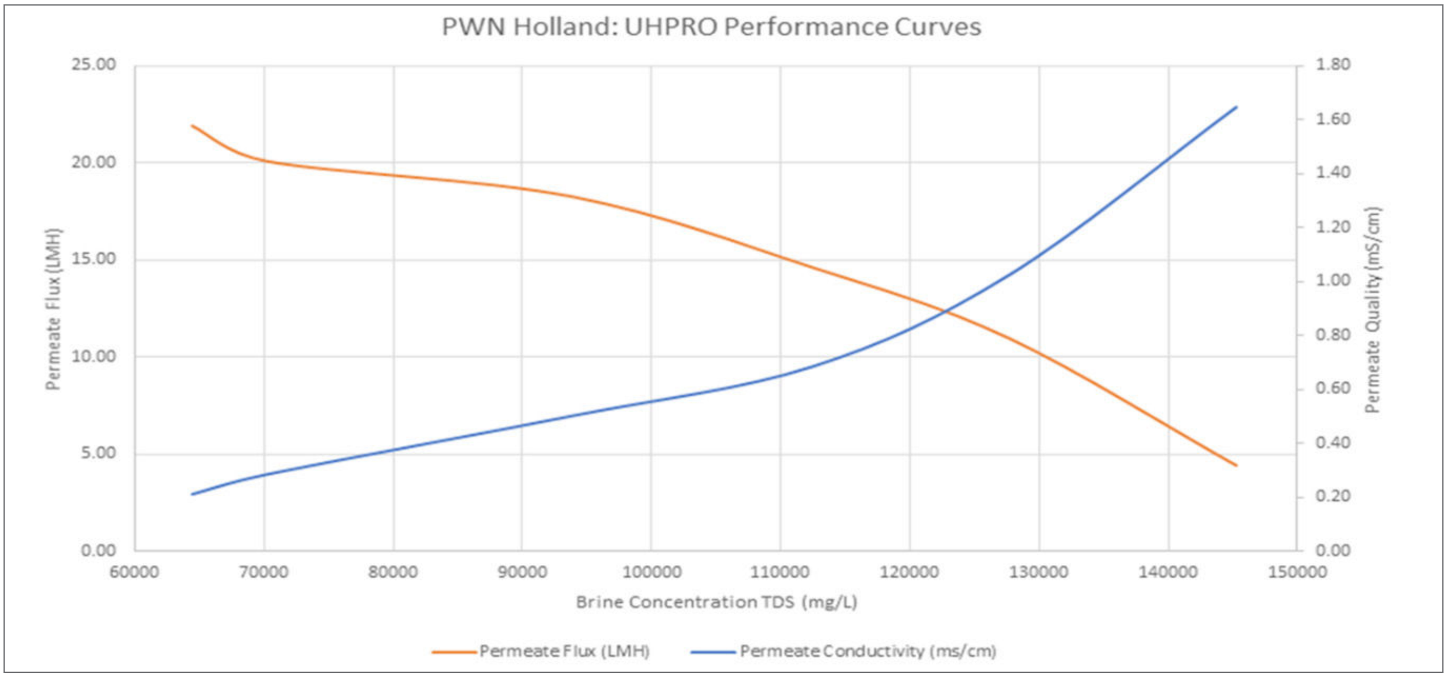

Figure 12B: Flux and permeate TDS values as a function of the increasing feed TDS with softened, mixed TDS feed.

A second study was carried out on a water sample from a site looking to implement ultra-high pressure RO to maximize water recovery and minimize their waste (MLD). This water was primarily composed of sodium, chloride, sulfates and hardness. After softening the water with Saltwork's BrineRefine process, the feedwater to the RO was composed of sodium, chlorides, sulfates and low levels of hardness and a variety of metals. The water was treated in two phases, one phase that concentrated the solution from 30,000 ppm TDS up to 64,000 mg/l TDS. This remaining solution was then treated a second time by the PRO-XP1 ultra-high-pressure RO element at 120 bar. The resulting performance is shown in Figure 12B. The solution was concentrated from 64,000 mg/l TDS up to 148,000 mg/l TDS while the permeate ranged from 0.1 mS/cm at the start of the trial to 1.6 mS/cm at the highest feed concentration. The flux ranged from 25 lmh at the lower concentration and dropped to 5 lmh at the highest feed concentration. Both

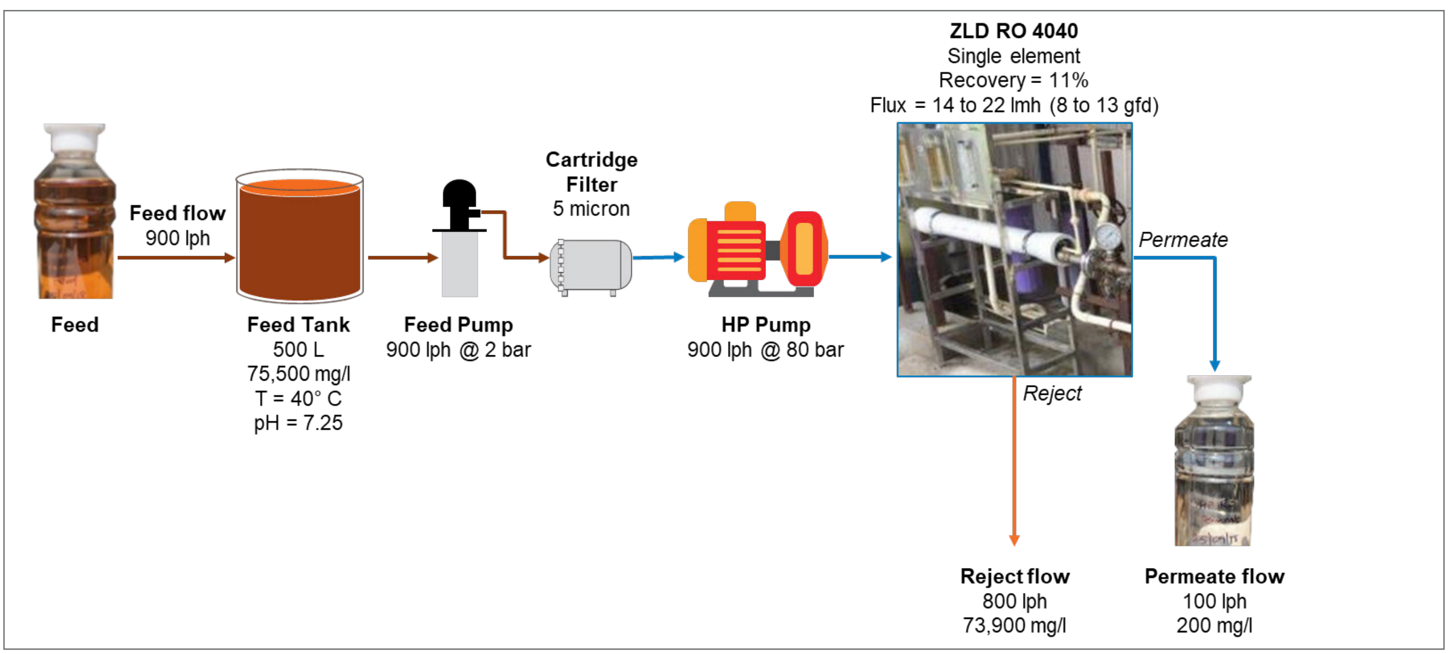

Figure 13: Ultra high pressure RO pilot at a Textile plant CETP in Rayapuram, India.

trials demonstrated that it was possible to achieve brine concentrations well in excess of 120,000 mg/l TDS with PRO-XP1 element.

The PRO-XP1 was then operated at a pilot in India to demonstrate the long-term performance of the product. The plant was a CETP in Rayapuram, India, which is a complex treating textile mill wastewater and producing 5,500 m^3/d of treated water. The treatment at the plant consisted of biological treatment, clarification, hypochlorite treatment to remove color, UF, ion exchange for color removal, and 5 stage RO. The 5-stage RO brine had a TDS of 75,500 mg/l and COD of 1,940 mg/l. Further treatment by costly DTRO, multiple effect evaporators and recrystallizers would be needed to fully dewater this stream. Thus, a pilot with a single PRO-XP1-4040 element was set up to treat the 75,500 mg/l TDS brine to recover 50% of the water for reuse. The pilot system schematic is shown in Figure 13. The RO element was operated at flux ranging from 14-22 lmh (8-13 gfd) at 11% recovery. The feed temperature was 40 °C.

The performance of system during the 100 day trial is shown in Figure 14A. During the first phase of testing, the RO element was operated in once-through condition, where the feed and permeate were discarded. The feed pressure ranged from 65-80 bar and the normalized flux was fairly stable. At the conclusion of the 30 day Phase 1 test, the membrane was permeate flushed and the flux returned to within 5% of the original flux. After this, the RO element was run in recirculation mode (Figure 14B), in which the feed was concentrated and only the permeate was discarded. During this phase some batches of water were concentrated to as high as 110,000 mg/l TDS. Rejection was stable during the 70 days of operation, with permeate in the range of 150 mg/l TDS for 60,000 mg/l feed concentration, and 500 mg/l TDS for feed concentration of 110,000 mg/l. The testing demonstrated the capability of the new PRO-XP1 to achieve nearly 50% reduction of the textile wastewater high in dissolved organics and justifies the use of this technology to significantly reduce the size of evaporators.

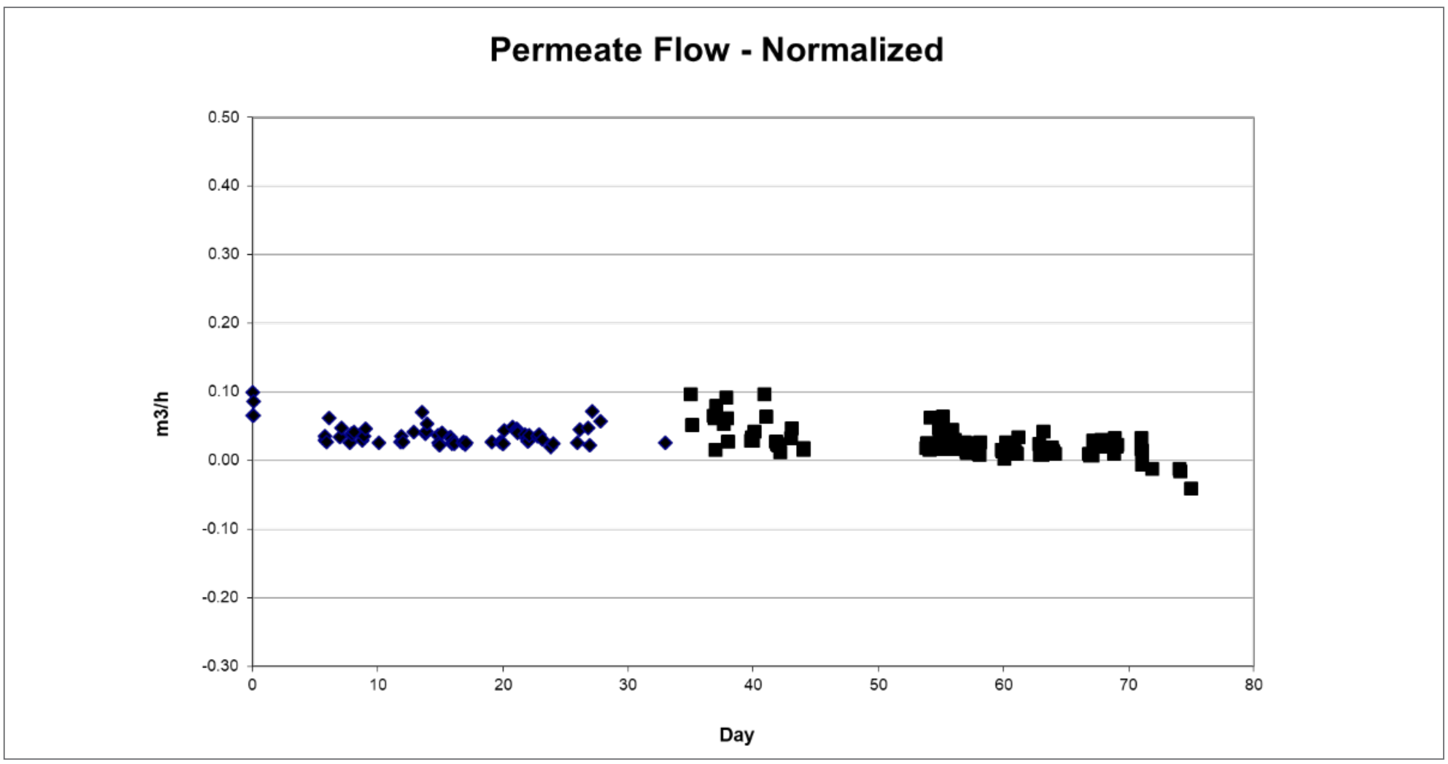

Figure 14A: Performance of the PRO-XP1 ultra high pressure RO element on textile wastewater – operation mode is once-through

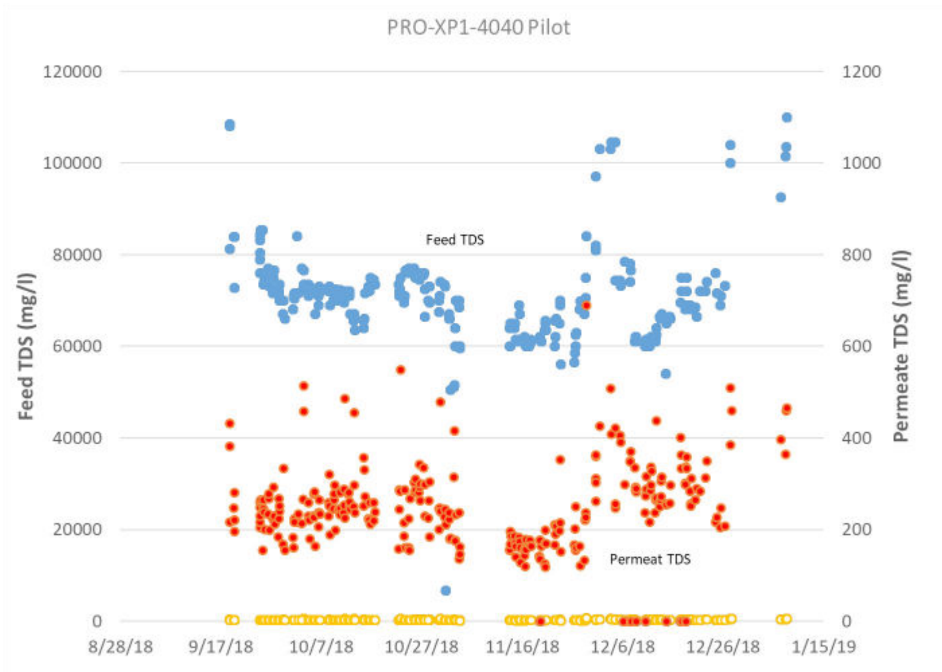

Figure 14B: Performance of the PRO-XP1 ultra high pressure RO element on textile wastewater – operation mode is re-circulation to increase feed concentration significantly

Conclusion

There is a growing need worldwide to treat industrial waters to achieve zero or minimum liquid discharge. In most cases, the treatment is very complicated and has many processes to achieve the desired water recovery. Some of the key issues are high fouling rates on RO elements due to high organic content of the feedwater, high cost of disposing a mixed salt waste, and high energy cost of evaporators and recrystallizers. This paper has shown that three new products have been developed which can significantly reduce the treatment costs of ZLD and MLD systems. Full commercialization of these technologies is demonstrating their value on real industrial wastewaters and showing that long-term performance can be successfully achieved.

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