

CAPITALIZING ON THE LATEST ADVANCEMENTS IN REVERSE OSMOSIS MEMBRANE TECHNOLOGY

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Introduction

The Southwest United States is in the midst of a prolonged drought. Over the past five years, water supplies in California have been stressed to unprecedented levels. Traditional means of supplying water such as local and imported surface water and groundwater are become less sustainable as supplies continue to diminish. Water purveyors in Southern California are having to consider alternative water supplies to meet both current and future demands. One consideration that has increasingly become part of the water supply equation is planned potable reuse, where municipal wastewater is recycled to augment the water supply. Within this framework, two types of planned potable reuse exist – indirect potable reuse (IPR) and direct potable reuse (DPR). IPR includes introducing treated wastewater into an environmental buffer such as a lake, reservoir or other body of water before entering the water supply. Conversely, DPR is the introduction of treated wastewater directly into the water supply infrastructure. Both scenarios utilize technologies which are coupled together to provide advanced water treatment (AWT). Integral to the AWT process are technologies that remove both dissolved constituents and contaminants of emerging concern. Reverse osmosis (RO) is typically incorporated into AWT designs since it can achieve the necessary removal requirements to satisfy the treatment objectives set forth by the regulatory agencies. At the same time, advances in RO membranes have the potential of delivering a number of operational improvements to the overall AWT process whether configured for IPR or DPR.

Advanced Water Treatment in Southern California

The Orange County Water District (OCWD) first demonstrated the applicability of large-scale RO for treatment of municipal wastewater nearly four decades ago when it commissioned Water Factory 21 (Figure 1). Since that time, other Southern California water agencies such as the Water Replenishment District of Southern California (WRD), utilize RO in similar applications to supply water for the maintenance of seawater intrusion barriers. Given the successful

demonstration of this technology, RO is an option in the treatment portfolio toward developing local and sustainable water management strategies.

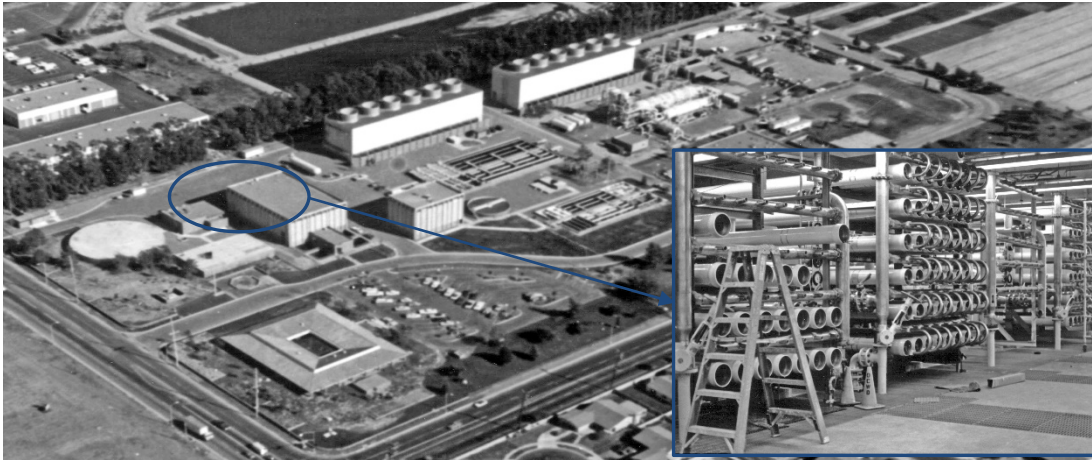


Figure 1. OCWD Water Factory 21.

Since demolishing Water Factory 21 in 2004 and for the past eight years, OCWD has successfully operated the Groundwater Replenishment System (GWRS) - a 100 million gallon per day (mgd) advanced water treatment facility (AWTF) that utilizes RO as the core technology (Figure 2). This facility, located in Fountain Valley, CA, provides purified water for groundwater recharge and maintenance of a seawater intrusion barrier. Source water to the GWRS is secondary municipal wastewater provided by the Orange County Sanitation District. The facility consists of three major treatment processes, including microfiltration (MF), RO and advanced oxidation (ultraviolet disinfection with hydrogen peroxide). Widely considered the benchmark IPR facility, the GWRS proved the viability of AWT using RO and paved the way for other large-scale projects in Southern California, including the 150mgd AWTF currently being proposed by the Metropolitan Water District of Southern California and the Sanitation Districts of Los Angeles County, to be located at the Sanitation Districts' Joint Water Pollution Control Plant in Carson, CA.



Figure 2. OCWD Groundwater Replenishment System.

More immediately, WRD has developed a comprehensive program toward achieving water sustainability in its 420 square mile service area in Southern California. As an integral component of the Water Independence Now initiative, the Groundwater Reliability Improvement Project (GRIP) AWTF is currently under construction in the city of Pico Rivera, CA (Figure 3). Once completed in 2018, GRIP will produce 10,000 acre-feet per year of highly purified water for groundwater replenishment via surface spreading and injection into the local groundwater aquifer. This IPR project will use full advanced treated (FAT) technologies including ultrafiltration (UF), RO and advanced oxidation. Source water to the GRIP project will consist of tertiary effluent provided by the Sanitation Districts of Los Angeles County San Jose Creek Water Reclamation Plant.



Figure 3. WRD Groundwater Reliability Improvement Project.

Similar to designing the GWRS over ten years ago, current AWTF projects such as GRIP will utilize the latest, proven membrane technologies to produce a safe, reliable and cost-effective supply of water for its ratepayers. The capital cost of constructing an AWTF is not insignificant. For example, the initial 70mgd GWRS project and the 30mgd expansion project in 2015 cost a combined total of nearly \$624 million. The challenge faced by water agencies is that given the enormous capital investment, will the technologies selected ultimately meet the overall treatment goals and objectives today and for the next 25 to 30 years. For AWTF treatment trains that utilize low-pressure MF or UF membrane technologies, lack of industry standardization creates challenges when selecting a particular system, since it must adequately and competitively operate both now and into the future. In light of the lack of standardization, the ideal goal would be to select a system capable of modification with minimal infrastructure changes and without significant capital investment.

RO is a more mature technology that has been largely standardized over the years. In recent years, however, the industry has seen new configurations that have addressed the inefficiencies of traditional RO system design to maximize productivity. Such examples include the GRIP RO system, which will essentially consist of decoupled traditional, three-stage RO units, each into two separate units: a primary (two-stage) unit and a secondary (single-stage) unit to increase

overall system performance and recovery. While RO system configurations are changing, the membrane element remains the common denominator. At the same time, advances in RO membrane chemistry and element construction cannot be discounted. Incremental improvements made to the membrane can ultimately lead to reduced CAPEX and OPEX through increasing permeability, reducing fouling and extending membrane life.

Membrane Evaluations

As part of an ongoing effort to evaluate new RO membrane technologies and optimize operations of the GWRS, a comprehensive procurement program is maintained to ensure that the District has viable options when selecting membranes for replacement. Recognizing the potential benefits of operating a new generation of RO element, pilot testing was conducted at the GWRS facility using full-scale, RO test vessels.

Membranes. The spiral wound element was developed in the 1970s to package RO membrane material into a compact, efficient and functional unit. The elements used in the GWRS and most AWWTFs are identical in size with an 8-inch diameter and 40-inches in length. As Figure 4 illustrates, the spiral element consists of different components, including multiple (a) membrane leaves, each sandwiched between a (b) permeate carrier on the low salinity side of the membrane and a (c) brine spacer on the high salinity side of the membrane. Permeate is directed to, and collected in a permeate tube. Multiple elements are coupled together in a pressure vessel by means of connecting individual element permeate tubes.

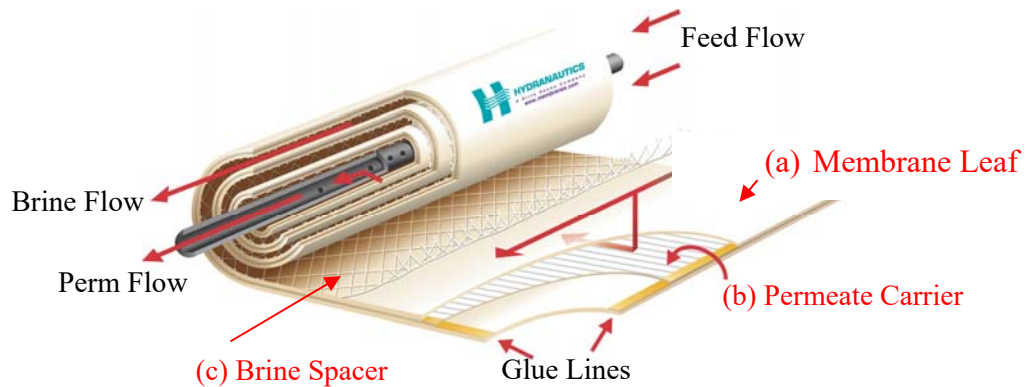


Figure 4. Standard spiral RO element and components.

Each of these three layers has its own thickness and therefore consumes its own proportion of the volume available in the spiral. The thickness of each layer and their percentage of total volume within the spiral is presented in Table 1.

Table 1. Spiral RO element components.

Element Layer	Thickness (mil)	Volume within Element (%)
Membrane Leaf	6	12
Permeate Carrier	10	20
Brine Spacer	34	68

The standard RO element used in AWTs such as the GWRS typically contains 400ft² of active membrane area. Membrane manufacturers are continually seeking new ways to increase the membrane area within the standard size configuration. To do so, however, requires reducing the thickness of one of the other two layers. Manufacturers offer higher, 440ft² elements, but generally require that the brine spacer thickness be reduced to 26 mils since it consumes a majority of the element volume. Reducing the thickness of the brine spacer has the disadvantage of increasing differential pressure losses and increasing fouling rates – all leading to increasing OPEX. The thinner spacer can also be more difficult to clean when fouled. For these reasons, most RO system designers choose to sacrifice the additional membrane area in order to avoid the fouling challenges associated with the thinner spacer. At the same time, selecting a product with a larger active surface area could reduce the quantity of membranes required and lower the CAPEX expenditure.

Recent innovations in membrane materials and construction have resulted in the development of a new RO membrane that contains a higher 440ft² surface area without sacrificing the thicker brine spacer. Specifications of this new membrane are presented in Table 2. For comparison, the specifications for the standard 400ft² element installed in the GWRS are presented. Given the efficiencies that could be realized through operating with this new generation of RO element, testing was conducted at the GWRS RO facility to ascertain the potential benefits of operating a membrane with a larger active area.

Table 2. RO element specifications.

Manufacturer	Product	Classification	Active Membrane Area (ft ²)*	Salt Rejection (%)*	Permeability (GPD)*	Spacer Thickness (mil)*
Hydranautics	ESPA2-LD MAX	Brackish	440	99.6 (99.5 min)	12,000	34
Hydranautics	ESPA2-LD	Brackish	400	99.6 (99.5 min)	10,000	34

* Information obtained from manufacturer specification sheets.

The RO test element represents a new generation of elements with materials of construction that provide a higher active area while keeping the 34 mil spacer. This was done by reducing the thickness of the membrane layer. But modifying the RO membrane is challenging. The RO membrane sheet is composed of three layers:

1. Polyester support layer (150 micron thickness)

2. Polysulfone layer (50 micron thickness)
3. Polyamide layer (0.15 micron thickness)

Considering the differences in layer thickness alone, it is evident that reducing the thickness of the polyamide separation layer would have little effect. The bulk of the membrane sheet is taken up by the polyester support layer. This layer is designed to provide support to a thin polysulfone layer which, in turn, provides support to the polyamide layer. By reducing the thickness of the polyester support, the overall thickness of the membrane sheet can be reduced, thus allowing for additional membrane area to be packaged into the standard 8-inch X 40-inch spiral element. This is done by adding more membrane leaves, or increasing the length of the existing leaves, or a combination of both.

Test System. A series of full-size pressure vessels are attached to the 1st-stage feed of six, full-scale RO units within the GWRs. Each pressure vessel contains seven, 8-inch X 40-inch elements identical to the 1st-stage vessels within the plant. These vessels were all designed to allow sampling and isolation of permeate and concentrate flows for data collection and chemical cleanings. The vessels are typically operated at a flux rate of 14.8 gallons per square foot per day (gfd) and a recovery of 55% to replicate 1st-stage operating conditions of a 5mgd RO unit. Since the Hydranautics test element contains 10% more active surface area for filtration (Table 2), options include operating at a fixed flux rate and increasing production by 10% or lowering the flux by 10% (14.8gfd to 13.3gfd) and maintaining equivalent production. Water quality, flows and pressures were recorded on a daily basis. A schematic of the test vessel configuration is illustrated in Figure 5. The test vessel mounted on a 5mgd RO unit is shown in Figure 6.

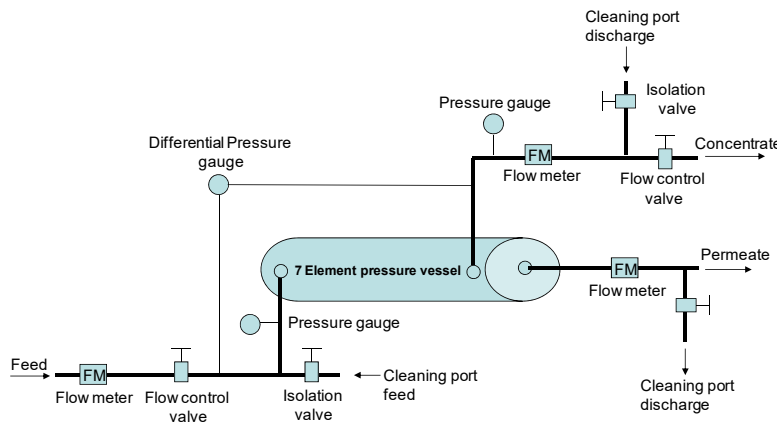


Figure 5. RO test vessel schematic.



Figure 6. Test vessel mounted atop of a GWRS 5mgd RO unit.

Results

Operational Summary. Trialing began in March 2016 and continues today for a total of 225 days (5,400 hours). During this period, the Hydranautics product was evaluated under two sets of conditions: 1. Operations at the typical GWRS 1st-stage flux (producing 10% additional permeate) and 2. Reducing flux by 10% (to match the existing 1st-stage production). Particular attention was placed on the transition from the higher to lower flux rates to note changes attributed to operating a 440ft² element (Table 3). In addition, the product was chemically cleaned after 70 days of operation to evaluate membrane durability and to assess its ability to restore permeability. Has the product exhibited signs of irreversible damage through significant and prolonged increases in salt passage without returning to pre-cleaned conditions? Is permeability reasonably returned to its initial, stabilized value exhibited during startup?

Table 3. RO test element operating conditions.

Duration (days)	Operating Flux (gfd)	Recovery (%)	Test Vessel Flows (gpm)	
			Product	Concentrate
50	14.8	55	31.7	25.9
51 – present	13.3	55	29.0	23.5

Operational Performance. Membrane permeability is expressed as the normalized specific flux - the amount of water produced per area per unit pressure (referenced to a standard temperature of 25⁰C) and measured in units of gallons per square foot of membrane per day per psi (gfd/psi).

Monitoring changes in normalized specific flux provides an assessment of a membrane’s fouling propensity, as well as the pressure (i.e., energy) required to produce an equivalent amount of water. For membranes evaluated at OCWD, historical performance has dictated that a stabilized specific flux of 0.085gfd/psi be maintained throughout the duration of the trial. Membranes are generally evaluated in excess of 5,000 hours to provide a more accurate assessment of performance.

Specific flux data for the Hydranautics product is presented in Figure 7a. Over the duration of the trial, the specific flux remained above the minimum requirement of 0.085gfd/psi, averaging 0.144gfd/psi after the first week of stabilization. The normalized differential pressure data is presented in Figure 7b. For a period of one week prior to making the flux change on Day 50, the differential pressure averaged 21.8psi. Upon making the change and up to one week afterwards, the differential pressure averaged 17.4psi – a reduction of 20%, which can be attributed to reduced feed flow to the vessel. Feed pressure also decreased as a result of operating at a lower flux by approximately 8.9% when compared to operating at the elevated flux rate of 14.8gfd (Figure 7c). Calculated membrane rejection averaged 99.3% over the duration of the evaluations. For the week immediately prior to, and after changing flux on Day 50, rejection remained largely unchanged at 99.4% (Figure 7d).

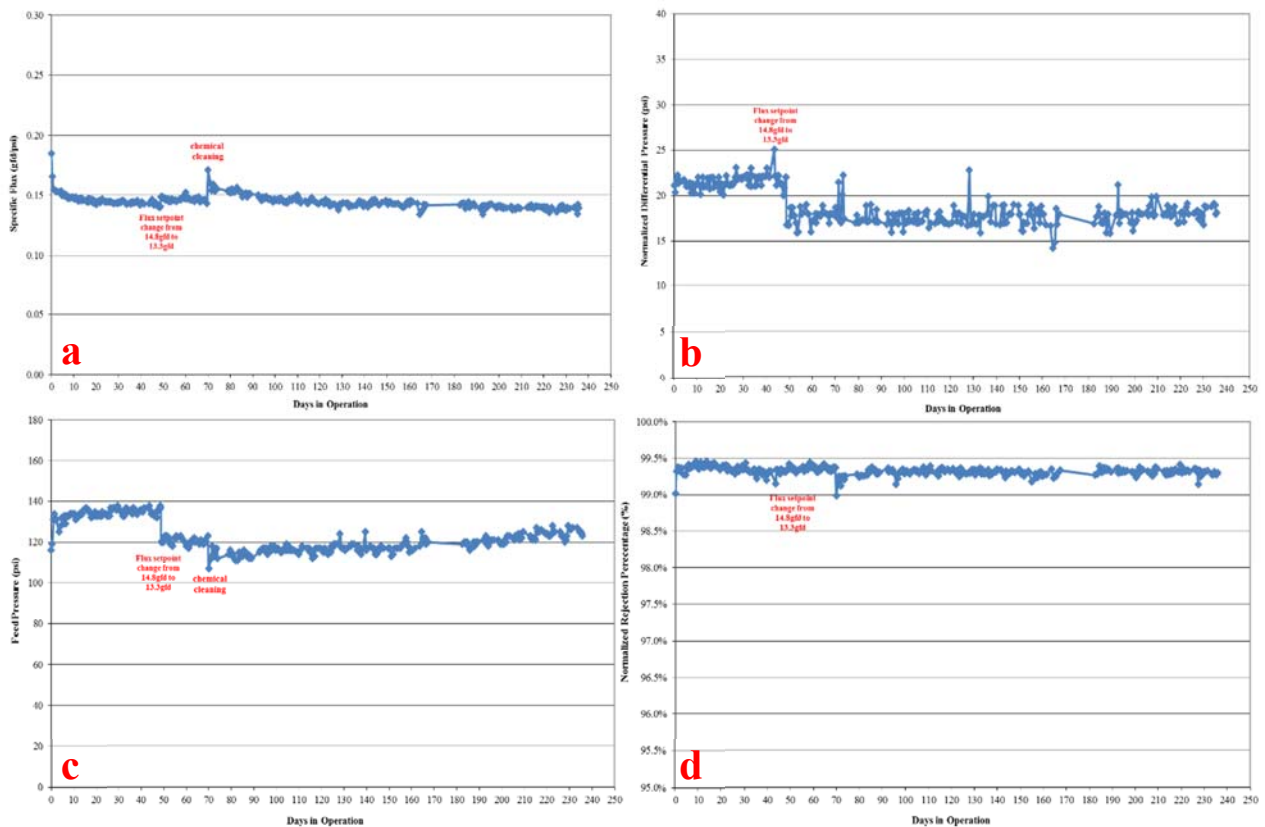


Figure 7. Operating performance data, including a. specific flux; b. normalized differential pressure; c. feed pressure and d. normalized rejection.

In addition to monitoring permeate conductivity, in-line total organic carbon (TOC) analyses was temporarily employed to measure permeate TOC, especially during the transition in operating flux on Day 50. Over a period from Day 47 to Day 52, the concentration of TOC in the permeate ranged from 42ppb to 70ppb, with an average of 52.1ppb (Figure 8). There was no observable change in permeate TOC concentration associated with changing flux. Further, the concentration remained well below the AWTF limit of 500ppb.

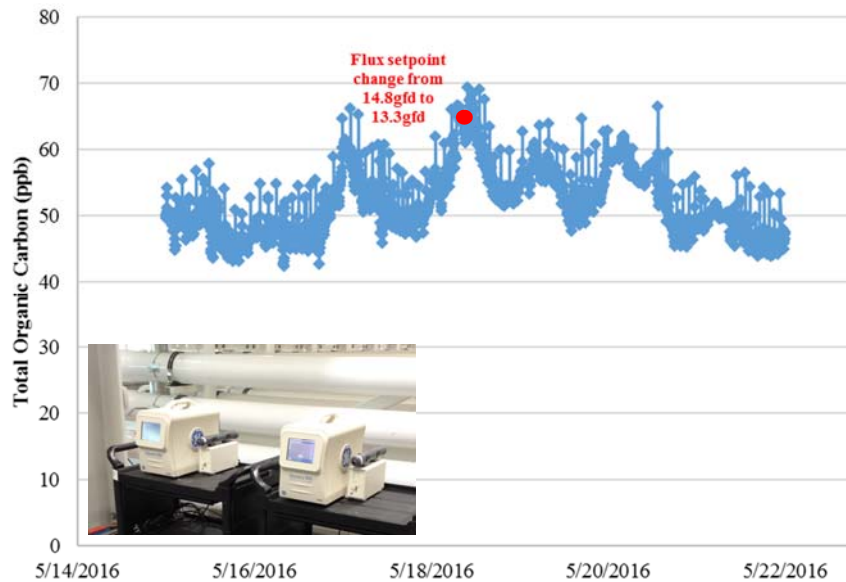


Figure 8. In-line TOC analyzer connected to the RO test vessel permeate sample tap.

Specific Constituent Rejection. To develop a more comprehensive understanding of the test element’s removal capability and potential impact associated with changing flux, water samples were collected from the test vessel when operating at 14.8gfd and after the flux was reduced by 10% to 13.3gfd. Results for both inorganic and organic constituents are presented in Tables 4 and 5, respectively. Similar to the previous findings, rejection of specific constituents remained largely unchanged.

Discussion

Use of larger active surface area elements is common in many RO applications with higher quality feed water. Larger 440ft² elements in AWTFs are not widely accepted due primarily to concerns surrounding the thinner spacer materials which are typically employed. There is also concern about how the change in flow dynamics associated with increased area would affect overall system performance. Since the new, thinner membrane allows for both 440ft² and a 34 mil spacer, there is little change to the flow dynamics or fouling potential when replacing conventional 400ft² membranes with the newer 440ft² variety. When considering the RO train as a whole, flows into and out of the train do not change when switching to the newer RO element. Further, when considering the actual spiral element, flow into and out do not change. To

illustrate the similarities and differences, Table 6 compares performance of two modeled GWRS trains, each installed with the different element types. If the trains were operating at the same permeate flow of 5mgd and a recovery of 85%, the differences in surface area would cause a difference in flux and, therefore, a difference in feed pressure and permeate TDS. The reduction in feed pressure is comparable to the decrease observed when transitioning to a lower operating flux in the test vessel (Figure 7c). Ultimately this could lead to operational efficiencies through a lower energy requirement. At the same time, since both elements have the same spacer thickness, identical flows into and out of the pressure vessels would result in the same differential pressure losses across each train.

Table 4. Specific (inorganic) constituent rejection at varying flux rates.

Inorganic Constituent	Detection Limit	Percent Rejection	Percent Rejection
		14.8gfd	13.3gfd
Nitrite Nitrogen	0.002mg/L	>99.2	98.3
Silica	1mg/L	>95.1	>95
Total Organic Carbon (Unfiltered)	0.05mg/L	99.4	99.4
Bromide	0.1mg/L	>61.5	>41.2
Chloride	0.5mg/L	99.4	99.5
Nitrate Nitrogen	0.1mg/L	97.7	97.1
Sulfate	0.5mg/L	>99.7	>99.7
Total Kjeldahl Nitrogen	0.2mg/L	>87.5	88.9
Boron	0.1mg/L	54.5	50
Calcium	0.1mg/L	>99.4	>99.4
Iron	1ug/L	>98.6	>98.7
Potassium	0.1mg/L	>97.1	>97.1
Magnesium	0.1mg/L	>97.8	>97.8
Sodium	0.1mg/L	98.5	98.3
Total Hardness (as CaCO ₃)	1mg/L	>99.6	>99.6
Silver	1ug/L	-	>95.0
Aluminum	1ug/L	>68.7	>70.6
Barium	1ug/L	>96.8	>97.1
Copper	1ug/L	>83.6	>79.2
Gadolinium	10ng/L	>88.9	>78.1
Manganese	1ug/L	>96.6	>97.0
Nickel	1ug/L	>67.7	>84.4
Selenium	1ug/L	-	>23.1
Vanadium	1ug/L	-	>23.1
Zinc	1ug/L	>94.6	77.2
Phosphate Phosphorus (orthophosphate)	0.01mg/L	>95.7	>95.8
Total Dissolved Solids	1mg/L	98.5	98.9
Electrical Conductivity	1uS	98.9	98.8
Total Alkalinity (as CaCO ₃)	1mg/L	97.1	97.3
Bicarbonate (as CaCO ₃)	1mg/L	97.1	97.3
Ammonia Nitrogen	0.1mg/L	84.0	81.8

Table 5. Specific (organic) constituent rejection at varying flux rates.

Organic Constituent	Detection Limit	Percent Rejection 14.8gfd	Percent Rejection 13.3gfd
Acetaminophen	5ng/L	>87.4	>90.5
Atenolol	5ng/L	>98.5	>98.6
Azithromycin	10ng/L	>93.5	>98.4
Caffeine	3ng/L	>99.8	>99.5
Carbamazepine	1ng/L	>99.5	>99.6
Chloroform	0.5ug/L	81.5	59.4
N,N-diethyl-m-toluamide	1ng/L	>99.5	99.7
Diclofenac	5ng/L	>97.6	>97.8
Dilantin	10ng/L	>92.9	>92.3
1,4-Dioxane	1ug/L	>65.5	>44.4
Diuron	0.005ug/L	>88.1	>94.5
Erythromycin	1ng/L	>96.8	>96.9
Fluoxetine	5ng/L	>70.6	>67.7
Gemfibrozil	1ng/L	>99.6	>99.7
para-Chlorobenzene sulfonic acid	200ng/L	-	-
Ibuprofen	1ng/L	>99.6	>99.4
Iohexol	20ng/L	>99.7	99.8
Iopromide	10ng/L	-	>82.3
Meprobamate	5ng/L	>99.1	>98.7
Naproxen	5ng/L	>99.1	>98.8
NDMA	2ng/L	75.2	83.1
NDMA FP	2ng/L	98.8	99.5
Neotam	10ng/L	-	-
Primidone	1ng/L	>94.6	>98.9
Simazine	0.005ug/L	-	-
Sucralose	100ng/L	>99.8	>99.8
Sulfamethoxazole	1ng/L	>99.9	>99.9
Tris-2-chloroethyl phosphate	5ng/L	>98.5	>98.4
Trimethoprim	5ng/L	>98.5	>98.5
Total THM	0.5ug/L	70.0	65.1

Table 6. Comparing performance of identical GWRS trains loaded with two element types. Differences are highlighted in red.

	ESPA2-LD	ESPA2-LD MAX
Surface area (ft ²)	400	440
Spacer thickness (mil)	34	34
System flux (gfd)	11.9	10.8
Permeate flow (mgd)	5	5
Feed flow per vessel (gpm)	52.4	52.4
Concentrate flow per vessel (gpm)	25.4	25.4
Feed pressure (psi)	115.9	106.4
Differential pressure (psi)	43.2	43.2
Perm TDS (mg/L)	39.7	43.7
Recovery (%)	85	85
Array	(78+48+24) x 7M	(78+48+24) x 7M

To understand the difference in flow dynamics between the two element types, one must consider what is occurring in the feed channel where there is a slight decrease in crossflow velocity in the higher 440ft² element. This is because the area within the element is increased by adding more leaves, which increases the feed channel cross sectional area while maintaining the same channel height. With additional channel cross sectional area, flow in each channel is reduced and therefore the crossflow velocity is reduced. Proportionally, the reduction in flow and velocity is very small. The increase in surface area of 10% equates to 10% more channel cross sectional area which results in a 10% reduction in velocity through each channel.

To illustrate these flow differences, consider a single pressure vessel operating with a feed flow of 52.4 gpm and therefore 52.4 gpm feed flow into the lead element, regardless of which type of element is installed in the vessel. If the lead element is the standard, 400ft² element with a 34 mil spacer, the channel cross section area would be 164 cm² – resulting in an average velocity of 0.202 m/s through the channel. If the lead element were constructed with 440ft² of active area and contained the thicker 34 mil spacer, the channel total cross section area would increase to 180 cm², the velocity into the channel would be 0.183 m/s – a reduction of nearly 10%.

Maintaining optimal hydraulic conditions within a 5mgd RO unit which contains 7M pressure vessels and operates at a recovery of 85% are critical when it comes to minimizing the incidence of fouling, including mineral scaling. How this reduction in velocity affects performance and fouling can be understood by considering the differences in both concentration polarization and Reynolds numbers.

As water flows through the membrane while salts are rejected, a boundary layer is formed near the membrane surface whereby the salt concentration at the surface exceeds the salt

concentration in the bulk solution. This increase of concentration is known as concentration polarization. The effect of concentration polarization is a reduction in permeate flow and salt rejection. The Concentration Polarization Factor (CPF) can be defined as a ratio of salt concentration at the membrane surface (C_s) to bulk concentration (C_b), and is expressed as follows:

$$CPF = C_s/C_b$$

This ratio is directly proportional to the average feed/brine flow and the permeate flow. As stated previously, these flows are identical in the two element types. Only the velocities within the channel and at the membrane surface are different. For this reason, the ratio of the channel velocity and the permeate velocity must be considered. A decrease in velocity through the channel will decrease the mixing and increase the salt concentration layer at the membrane surface. A decrease in permeate velocity through the membrane, however, will have the opposite effect. A decrease in permeate velocity will decrease the delivery rate of ions to the membrane surface and decrease the concentration at the surface. Comparing the ratio of these two velocities within the two elements shows their ratios to be the same (Table 7). If these two ratios are the same, then the concentration polarization factor at the membrane surface is the same.

Table 7. Comparing the water velocity ratios of the two element types.

	ESPA2-LD (400ft ²)	ESPA2-LD MAX (440ft ²)
Channel velocity (m/s)	0.202	0.183
Permeate velocity (m/d)	0.48	0.44
Ratio (channel to permeate)	0.42	0.42

Because the velocity of water within the feed/brine channel is different in the two elements, the difference in Reynolds (Re) number can illustrate the difference in fouling potential.

Considering the standard formula for Reynolds number:

$$Re = \frac{\text{Dynamic Pressure}}{\text{Shearing Stress}} = \frac{\rho v L}{\mu}$$

Where:

ρ = density of water (997 kg/m³)

v = velocity in channel (m/s)

L = characteristic channel length (0.001123 m)

μ = dynamic viscosity of water (0.001002 kg/m/s)

The two velocities in the same channel, with a 34 mil height, would result in a Reynolds number of 225.2 for the standard element vs. 204.8 for the new element. Both Re numbers are well within the laminar flow range. Their difference is negligible relative to a Reynolds number of 10^5 for turbulent flow. This very small difference in Reynolds number would, therefore, make a negligible difference in the rate of fouling for each of the two elements.

Conclusions

RO technology plays a critical role in capturing alternative sources of water which have previously been discounted. Coupled with other technologies, these treatment trains represent the core of many advanced water treatment facilities and provide the means to develop local and sustainable water supplies that are safe, reliable and cost-effective. At the same time, the RO membrane remains the single most integral component responsible for achieving targeted water quality specifications and production goals. The RO spiral wound configuration has remained largely unchanged since it was developed in the 1970s. Advances in membrane materials and design have resulted in incremental, yet tangible improvements in system operations. System designers can now utilize elements with a larger membrane area and spacer thickness without compromising one for the other. Since the RO process is typically the most energy intensive within many facilities such as the GWRS, elements of this design represent an option to expand and optimize AWTF system operations.

Acknowledgments

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