UTILIZING NANOTECHNOLOGY TO ENHANCE RO MEMBRANE PERFORMANCE FOR SEAWATER DESALINATION

Mr. Christopher J. Kurth, NanoH₂O, Inc., El Segundo, CA
Dr. Robert Burk, NanoH₂O, Inc., El Segundo, CA
Mr. Jeff Green, NanoH₂O, Inc., El Segundo, CA
Mr. Lee Portillo, NanoH₂O, Inc., El Segundo, CA

Introduction

Over the past decade, reverse osmosis (RO) has become the dominant method of desalinating seawater to address water scarcity in arid regions. Widespread adoption of seawater reverse osmosis (SWRO) technology has been limited by the cost of desalination relative to other, oftentimes more environmentally damaging, methods of obtaining potable water. Decreasing water cost has become a primary focus for the desalination industry through innovations in energy recovery, module design and pretreatment [1]. However, the SWRO membrane is still based on the same material platform developed 30 years ago.

In 2007, a team at the University of California, Los Angeles (UCLA) reported development of thin-film nanocomposite (TFN) membranes that incorporated nanoparticles into an interfacially-formed polyamide thin film [2]. This new membrane material, initially tested in brackish water, doubled membrane permeability while maintaining salt rejection at industry standards. Changes potentially enabling a reduction in desalinated water cost by decreasing energy consumption, increasing plant output, or a combination of both.

Optimized for use in seawater desalination, nanocomposite membranes currently have more than twice the permeability of some established pure polymer membranes [3]. A manufacturing facility has been built to commercialize this nanocomposite material in an industry standard 8040 SWRO module.

This paper will present system performance and operational data from a retrofit installation in the United States which has demonstrated the ability to increase the output of a small 22,300 gpd (84.5 m³/d) plant to 26,900 gpd (102 m³/d), while simultaneously dropping the operating pressure from greater than approximately 805 psi (55.5 bars) to approximately 732 psi (50.5 bars).

Methods

4 in. (10 cm) Element Production

Prior to fabrication of a coater optimized for TFN manufacturing, trials of several TFN formulations were made on an older 40 in. (1 m) wide flatsheet coating machine. Performance

improvements versus a control formulation were evident in flatsheet testing, although mechanical limitations of the machine prevented typical hand-cast performance from being obtained.

The membranes were rolled into 4040 style elements. The fiberglass coated elements utilized a five-leaf construction with approximately 70 ft^2 (6.5 m^2) of active area. A propylene diamond-shaped feed spacer was used within the element.

8 in. (20 cm) Element Production

NanoH$_2$O prepared 8 in. (20 cm) element modules at their El Segundo, California, manufacturing facility. Support casting, RO membrane coating, element rolling and final QC testing were all performed using a previously optimized process in NanoH2O's facility. The resulting elements contained 365 ft^2 (34 m^2) of active membrane area. A propylene diamond-shaped feed spacer was used within the element.

4 in. (10 cm) Element Production

Feedwater at the U.S. Navy Seawater Desalination Test Facility (SDTF) at Port Hueneme, California, USA facility enters through a screen-fed open ocean intake and passes to a facility-wide intermediate tank. This tank feeds one of two pretreatment systems. The first is a single stage media filter containing anthracite, garnet, and fine and coarse gravel followed by a single-stage 5-micron cartridge filter. The second is a Zenon ultrafiltration (UF) pretreatment system.

4 in. (10 cm) Module Testing

The pilot system pictured in Figure 1 consisted of five, two-element vessels plumbed in series. For all data contained here, only three of the five vessels were employed resulting in six-elements in series, single-pass array configuration. Each end cap of the vessels was equipped with a permeate port. Because plugged interconnectors were used between each element, independent permeate flow and rejection were quantified for each element in the system. The permeate solutions were then sent to a common manifold and blended into a totalized permeate stream, thus allowing system performance to be monitored.

Figure 1. 4 in. (10 cm) element test system at Port Hueneme

Data was typically collected manually once each day, although more frequent tests were often performed after element changes or cleanings. Feedwater quality was measured between two to five times per week by a single water quality set-up. The metrics monitored were raw water turbidity and RO feed turbidity, Silt Density Index (SDI) and particle count.

8 in. (20 cm) Module Testing

The pilot system pictured in Figure 2 consisted of five, two-element vessels plumbed in series. For all data contained here, only three of the five vessels were employed resulting in seven-elements in series, single-pass array configuration. Each end cap of the vessels was equipped with a permeate port. Because plugged interconnectors were used between each element, independent permeate flow and rejection were quantified for each element in the system. The permeate solutions were then sent to a common manifold and blended into a totalized permeate stream allowing system performance to be monitored. An ERI energy recovery device and variable frequency drive controlled positive displacement Danfoss axial plunger pumps were used to allow efficient operation over a range of operating conditions. For commercial baseline testing, seven new 8 in. by 40 in. (20 cm by 100 cm) modules were used. These modules had a stated productivity of 6,000 gpd (23 m^3/d) and 99.7% salt rejection with an active area of 375 ft^2 (35 m^2).

Figure 2. 8 in. (20 cm) pilot skid

Element Cleaning Procedure

The elements were first recirculated with a solution of 2% ethylenediaminetetraacetic acid (EDTA) at pH 11.8 (with NaOH) in RO permeate at 75 psi (5.2 bars) and 82.4°F (28°C) for one hour. This was then neutralized, drained, and the system was fed with a 1.4% solution of citric acid in water (pH 2.3). This solution was recirculated for two hours at 75 psi (5.2 bars) and 85.5°F (29.7°C). The system was then shut down and the elements were allowed to soak in this solution overnight. The following morning, the solution was neutralized and drained. A third high pH clean was then used for the CIP at ~1,000 hours. A 3% solution of General Electric (GE) RO membrane cleaner at a pH of 11.1 was recirculated for two hours at 87 psi (6 bars) and 86°F (30°C).

The second cleaning that was performed replaced the initial EDTA cleaner with the GE RO cleaning solution and was followed by the citric acid cleaning. No third cleaning step was performed for the second CIP.

Results and Discussions

4 in. (10 cm) Element Production

Figure 3 shows the normalized operating flux and rejection as a function of run time for a single 4 in. (10 cm) element that was allowed to run for a period of 10 months. For the first 4,700 hours, media filtration was used, followed by the Zenon UF for the remainder of the test.
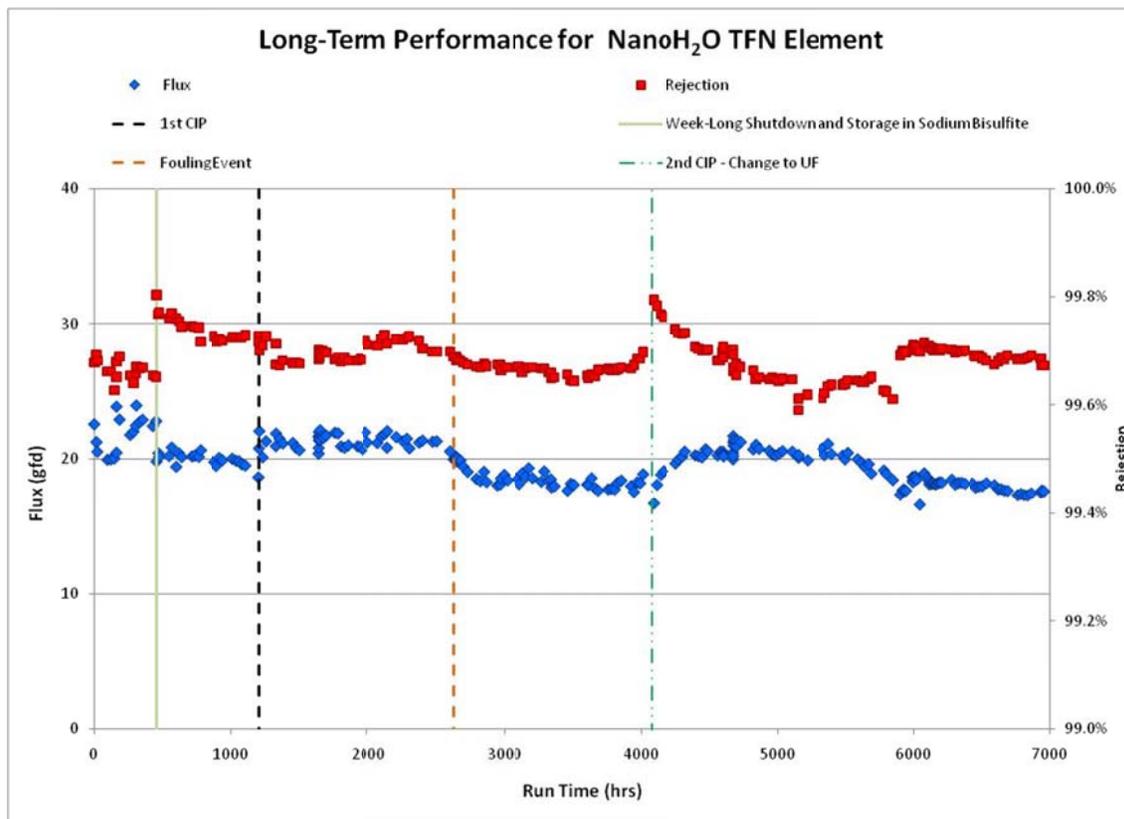
Figure 3. Long-Term Element Test

Fouling Event

After four months of operation (2,600 hrs), a red tide algal bloom in the waters around the SDTF intake resulted in a spike in SDI, particle count and NTU of the incoming feedwater at the facility for a period of two weeks (see Figure 4). At the start of this period, the long-term element was located in the lead position and was operating at a flux of 16.5 GFD (28 lmh) with an element recovery of 5.3%. Over the course of the event, the TFN module lost 14.3% of its permeability. After the next scheduled cleaning (two months later), the flux was recovered to within 95% of its pre-fouled state.

Although early lab studies had indicated some improvements in chemical structure and morphology that are thought to be related to fouling propensity (charge, roughness, hydrophilicty), the relatively modest performance loss and subsequent flux recovery upon cleaning through this red tide event was the first larger-scale evidence that improved fouling properties may be present in some nanocomposite materials. Further testing will be needed to evaluate the repeatability and scope of any such improvement in properties.
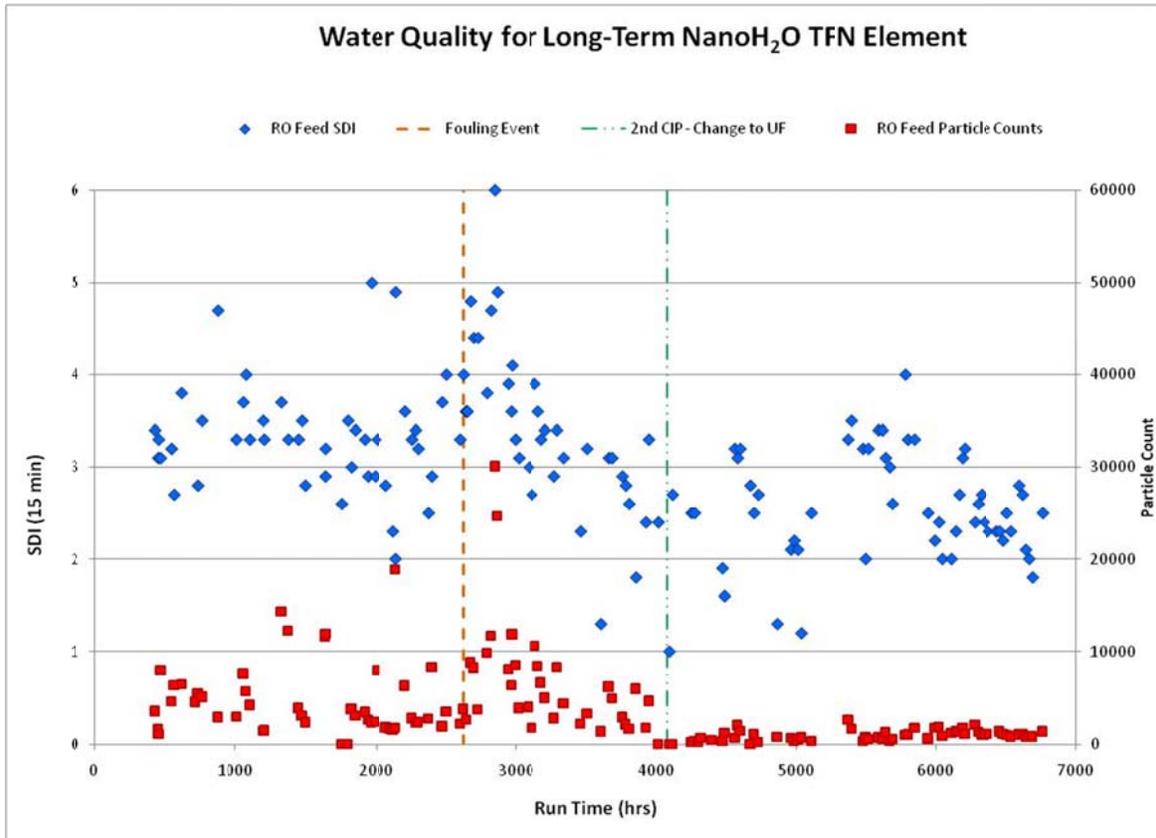
Figure 4. Particle count and SDI

Media vs. Membrane Pretreatment

After the fouling event and subsequent cleaning, the intake water was switched from a media filter to a UF membrane pretreatment. An immediate improvement in treated water particle count was evident and average SDI also improved from 3.4 on the media to 2.6 using the UF membrane. This behavior appeared quite stable over the evaluation period.

At this point, no clear conclusions can be drawn about the relative benefits of either pretreatment technology. Although one could argue that there appears to be a larger drop in flux over time using the membrane pretreatment; the media pretreatment didn't have a sufficiently long operational period to determine a fouling rate.

Clean-in-Place (CIP) Stability

An early question regarding TFN membrane applicability was its stability and performance through cleaning cycles. Certainly, with the earliest published nanoparticles [2],

there was a potential that sufficiently high or low pH could chemically degrade the added nanoparticles, leaving holes in the separating layer and leading to an increase in salt passage.

As a means of determining chemical stability, a CIP was performed on the element early in its operation. After allowing sufficient time for performance to stabilize (~1,000 hrs), a CIP cycle was performed even though no loss of permeability had occurred. This CIP was used not to evaluate effectiveness of the cleaning agents with the membrane, but instead to evaluate the chemical stability of the separating layer. After the CIP, the measured flux and rejection matched initial performance. As nanoparticle degradation and/or deterioration of the nanocomposite matrix would have led to a performance loss, this result indicates a stability of the TFN membrane to the conditions used.

A second CIP was performed later in the module's life after the fouling event previously described. After this cleaning, performance began to improve and eventually reached its baseline performance. Again, the stable flux and rejection suggest no evidence for chemical degradation.

8 in. (20 cm) Element Performance

After the 4 in. (10 cm) testing was completed, a new manufacturing facility was built allowing TFN membranes to be prepared with performance exceeding that demonstrated in the one year trial. This membrane was used to prepare spiral-wound elements containing 365 ft^2 (34 m^2) of active area. To provide a system level performance baseline, commercial modules were also purchased and the system was run in a typical manner. Due to time constraints, the test period of the commercial modules was limited to 500 hrs, and the information below shows a similar 500-hr test period for the nanocomposite Qfx modules. System operating conditions in both stages of the testing are shown below (Table 1). Energy consumption was measured on the RO unit and, as such, only includes power consumed by the RO system itself (excludes pretreatment and intake).

Table 1. Summary of System Operating Conditions

	Qfx	Commercial
Water Production	26,945 gpd (102 m^3/d)	22,322 pgd (84.5 m^3/d)
System Recovery	44.1%	42.4%
Feed Pressure	719 – 741 psi (49.6 – 51.1 bars)	805 – 848 psi (55.5 – 58.5 bars)
Energy Consumption	6.55 kwh/1000g (1.73 kwh/m^3)	7.31 kwh/1000g (1.93 kwh/m^3)
Water Quality	192 – 246 ppm	110 – 165 ppm
Water Temp	55 - 61°F (12.5 – 16.1° C)	53 - 59°F (11.7 – 15.1°C)

Baseline testing with the seven commercial elements was performed at a system recovery of 42.4% and a design flux of 8 GFD (13.5 lmh). Feed flow was 52,570 gpd (199 m^3/d). As can be seen below (Figure 5), operation was fairly constant throughout the test with an average operating pressure of 821 psi (56.6 bars).
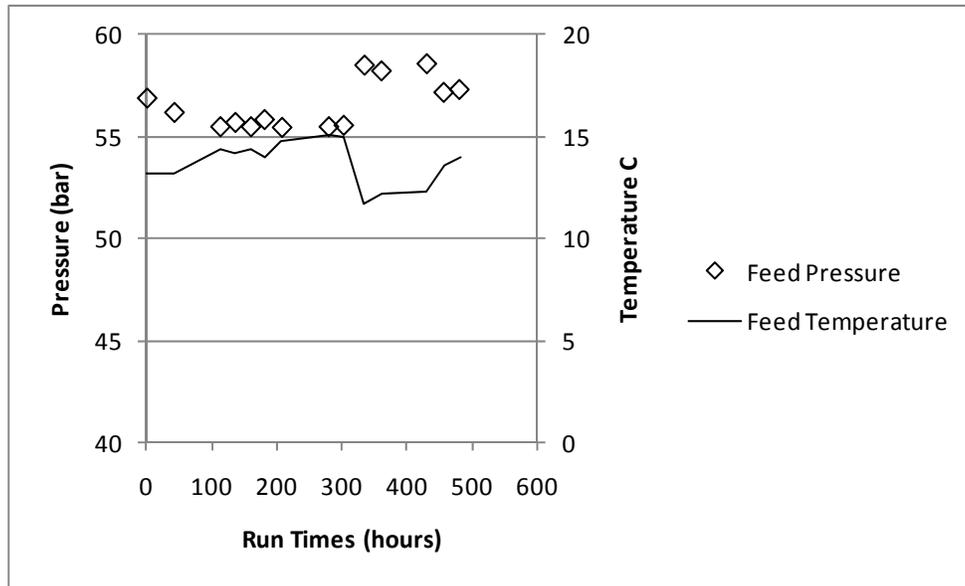
Figure 5. Commercial baseline pressure

After this stage of testing was complete, Qfx modules were installed. Due to the increased membrane permeability, the feed pressure was reduced to 725 psi (50.1 bars) while the average system flux actually increased to 10 GFD (16.9 lmh). To maintain a constant concentrate flow to the ERI device, feed flow rate was increased to 61,024 gpd (231 m^3/d). Similar to the commercial baseline performance, pressures were constant throughout the test period (Figure 6).
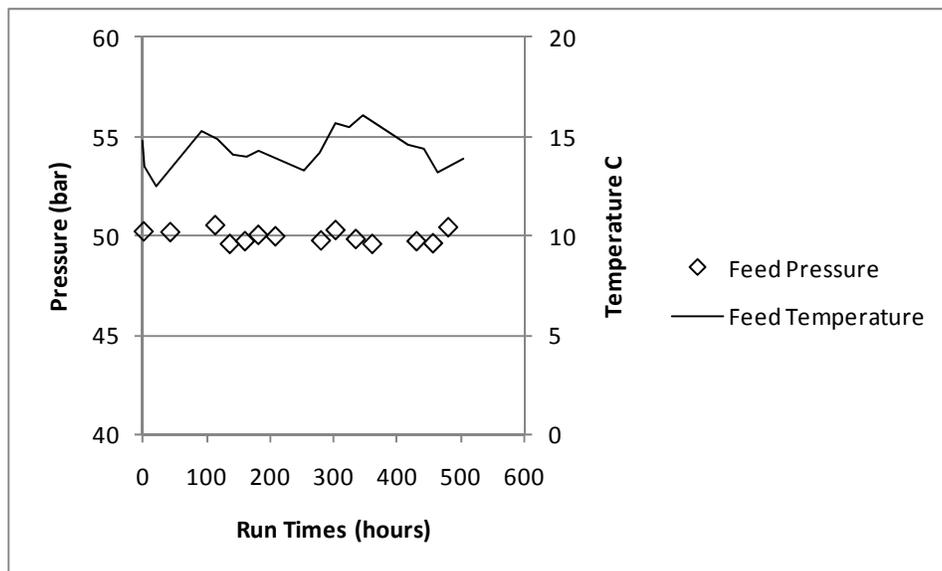
Figure 6. Qfx pressure

8 in. (20 cm) Performance improvements

While the first phase of testing showed the ability of the first generation Qfx module to reduce energy consumption and increase water production, Table 1 demonstrates a decrease in observed rejection that led to an increase in permeate TDS. As a result, a series of improvements

were made to the membrane and element to yield better water quality. These versions were each installed into the 8 in. (20 cm) test machine and operated for about one month. Figure 7 shows the progression in system performance as these alterations were made.
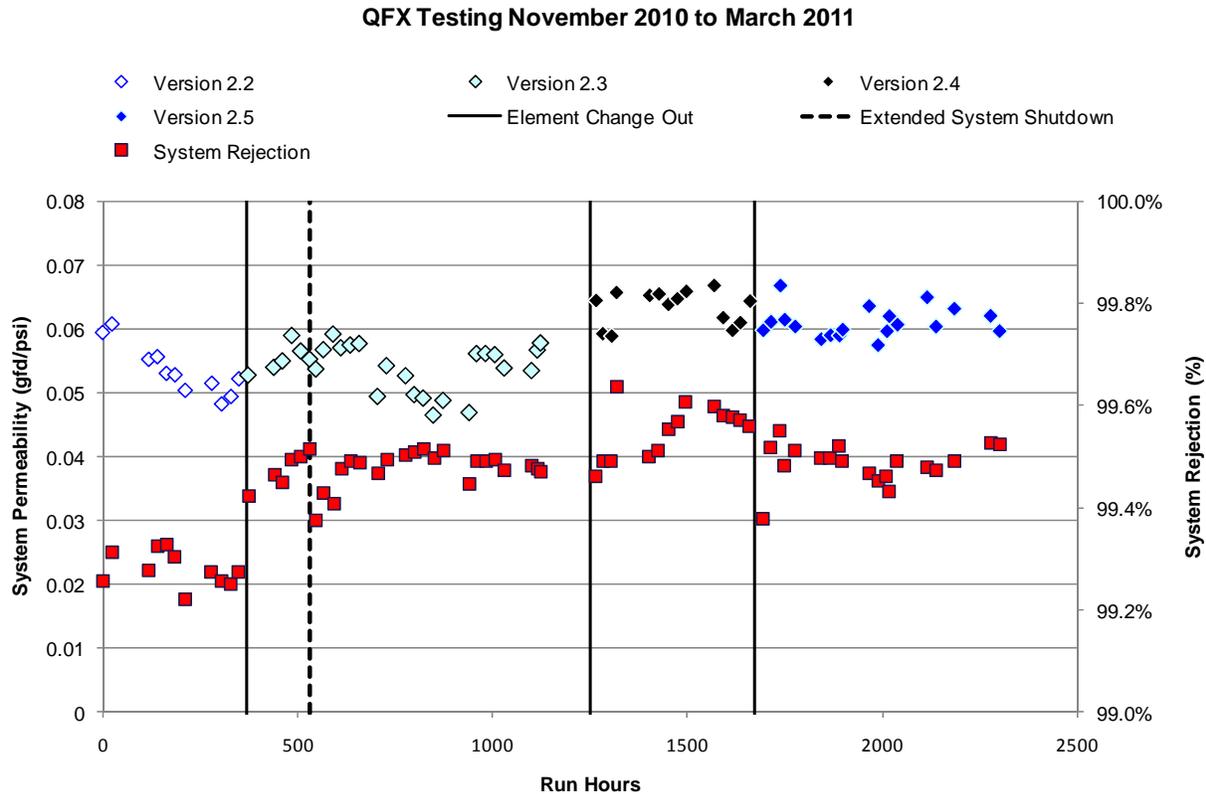
Figure 7. Qfx element improvements

The most noticeable shift resulted from the improvements in version 2.3 where system salt rejection increased from 99.3% to 99.5%. That shift corresponded to a reduction in permeate TDS to a value between 137 ppm and 175 ppm for the testing range discussed in Table 1. Although changes to versions 2.4 and 2.5 were focused on improving product consistency, an additional 9% increase in permeability was observed in the alterations applied to versions 2.4 and 2.5. Normalized to standard testing conditions (32,000 ppm NaCl, 5 ppm boron, 800 psi, 25°C, pH 8, 8% recovery), these field data indicate the element performance was 13,200 gpd and 99.75%.

Conclusions

Nanocomposite membrane technology has been used to develop a new commercial SWRO module. Operation of this Qfx element over the course of this testing has given some insight as to the expected behavior of this new membrane. The relatively stable flux and rejection has indicated that the performance enhancement of the nanocomposite film is not short-term, but

rather a fundamentally different separation layer. Further, conditions that would have led to a loss of nanoparticles would have also led to an increase in passage; the lack of such a change supports the inherent stability of the nanocomposite film. This includes the high and low pH conditions used during the CIP cycles and the mechanical stresses applied during repeated start-ups and shutdowns. Although further testing is needed to fully validate these findings, the relatively modest flux loss and later flux recovery during a red tide event also suggest the possibility of improved tolerance to some biofouling events and may open up the possibility of increasing system design flux.

Operational experience from this work demonstrates an ability to retrofit existing plants containing conventional 8 in. by 40 in. (20 cm by 100 cm) modules in order to not only increase capacity without additional capital investment in equipment (by 21% in this test), but in some instances actually reduce specific energy consumption as well (10% in this test). Further, multiple pilot installations have now been running these elements and have desalinated more than 13,800,000 gallons of seawater over a combined 28,000 hours.

In the last five years, research into nanocomposite RO membranes has resulted in the development of what is now a commercially-viable mixed matrix membrane material for seawater desalination. In this relatively short period, nanocomposite membranes have shown the potential for performance exceeding that of existing commercial products based on the standardized polymer chemistry used in RO membranes for the last several decades. This technology has now been commercialized and is available for sale on a limited basis.

References

1.   USBR (U.S. Bureau of Reclamation and Sandia National Laboratories). (2003), *Desalination and Water Purification Technology Roadmap*: Springfield, Virginia.

2.   Jeong B.H., Hoek E.M.V., Yan Y., Subramani A., Huang X., Hurwitz G., Ghosh A.K., Jawaor A. (2007), Interfacial polymerization of thing film nanocomposites: A new concept for reverse osmosis membranes. *Journal of Membrane Science,* **294** (1), 1-7.

3.   Kurth CJ, Burk R., Green J. (2009), Leveraging nanotechnology for seawater reverse osmosis. In the IDA World Congress.

4.   Ghosh A.K., Jeong B.H., Huan X., Hoek E.M.V. (2008), "Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties", *Journal of Membrane Science,* Volume **311** (1-2), 34-45.

5.   Cadotte J.E. (1981), Interfacially synthesized reverse osmosis membranes. US4277344.

6.   Dow (2010), System design: system performance projection. Technical manual excerpt, Form No. 609-02057-604.