Reverse osmosis (RO) is the leading process for brackish and seawater desalination and freshwater purification. Membrane performance characteristics translate directly to the energy intensity and capital expenditures of an RO system and, therefore, to the economics of desalination. This article examines nanocomposite RO membranes and compares their performance to other commercially available products.

Improving Seawater Desalination With Nanocomposite Membranes

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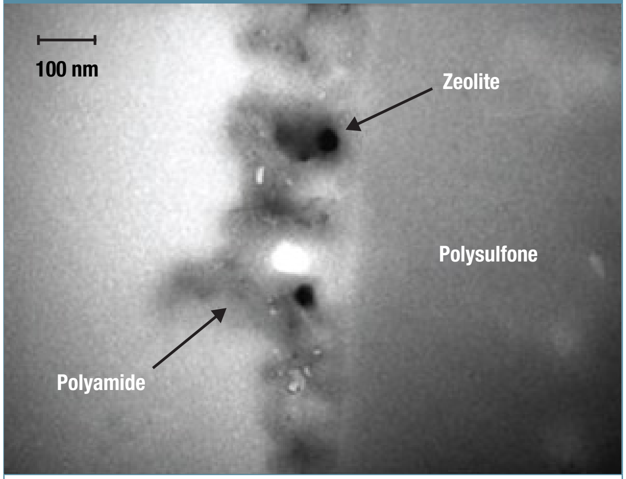
According to the US Desalination and Water Purification Roadmap (US Bureau of Reclamation, 2003), membrane permeability and fouling resistance are key economic drivers for membrane-based water treatment systems. Accounting for 70–80 percent of the total expense of reverse osmosis (RO) desalinated water (USBR, 2003), energy consumption and capital expenditures are the primary reasons desalination remains expensive compared with other treatment options.

Use of thin-film nanocomposite (TFN) membranes for water purification was first described for brackish water RO (BWRO) membranes in 2007 (Jeong et al, 2007). In that work, zeolite nanoparticles were dispersed in the organic solution of an interfacial polymerization. Because polymerization proceeds in the organic solution, nanoparticles present near the aqueous-organic interface became incorporated within the polyamide layer (Figure 1). Incorporation of such nanoparticles into a BWRO membrane formulation increased permeability, altered surface properties potentially related to fouling, and maintained salt rejection.

Figure 1. Cross-sectional transmission electron microscope image of TFN membrane



Source: Jeong et al, 2007

Since publication of the original TFN concept, further efforts have optimized TFN membrane technology for seawater RO (SWRO) (Kurth et al, 2009). Membrane performance data demonstrate a doubling of TFN membrane permeability relative to conventional RO membranes with equivalent rejection. For example, TFN technology transforms an industry-standard 17-gfd membrane into a 56-LMH (33-gfd) membrane. Current performance of TFN membranes leads to elements having an enhanced flux of more than double that of a 24.6 m^3/d (6,500 gpd) commercial baseline with industry-standard salt rejection.

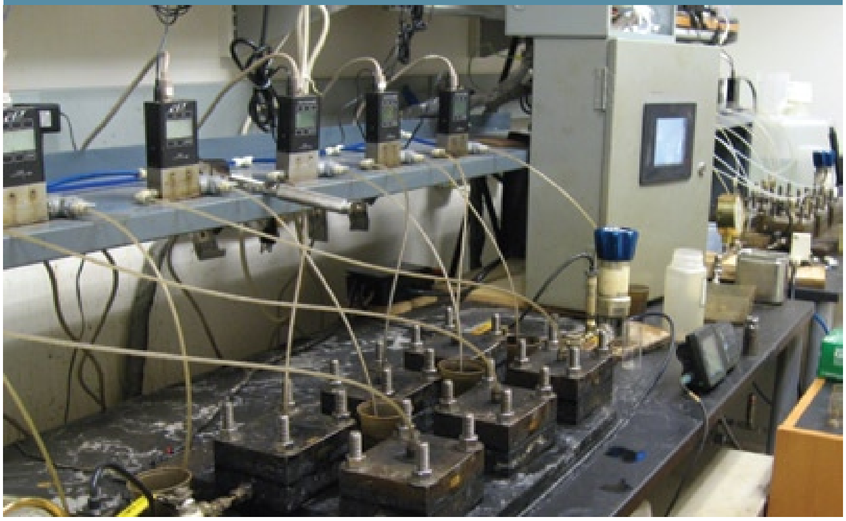
Membrane performance data, using industry-standard cross-flow test equipment, were measured as a function of pressure and salinity after extended exposure to high- and low-pH conditions, as well as after multiple cleaning cycles. These tests allowed development of predictive relationships on performance as a function of operating conditions and demonstrated excellent stability against cleaning solutions and operating conditions used in SWRO installations. Characterizing performance vs. model foulants common in seawater installations helped to determine preferred operating conditions for pilot studies.

Consistent results from bench-scale membrane tests prompted scale-up of TFN technology using a pilot 1-m-wide (40-in.-wide) continuous coating process for manufacturing SWRO TFN membranes. In addition to TFN membranes, thin-film composite (TFC) membranes were made

Test results in the lab and field indicate suitability of TFN technology for SWRO installation and demonstrate significant flux enhancement while maintaining industry-standard salt rejection.

in the production facility and used as controls so the effect of the TFN technology could be isolated. TFC or TFN membranes in 4040-style modules—10 cm (4 in.) x 1 m (40-in.)—tested at the US Navy Seawater Desalination Test Facility (SDTF) at Port Hueneme, Calif., used an open intake Pacific Ocean seawater feed. The test skid used dual media filtration followed by cartridge filtration, producing water with an average silt density index (SDI_{15}) of 3.3 and turbidity of 0.051 ntu. During a 10-month testing period, performance was measured at various operating flux rates and system recoveries. Test results in the lab and field indicate suitability of TFN technology for SWRO installation and demonstrate significant flux enhancement while maintaining industry-standard salt rejection.

Figure 2. Flat-sheet cell testing bench



NANOH$_2$O

Materials and Methods

Flat-Sheet Membrane Equipment. Flat-sheet membranes were tested on stainless steel cells[1] without a feed spacer (unless noted) and had an active area of 19.4 cm^2 (3 $in.^2$). Test benches, Figure 2, were configured with six cells—two parallel sets of three cells in series.

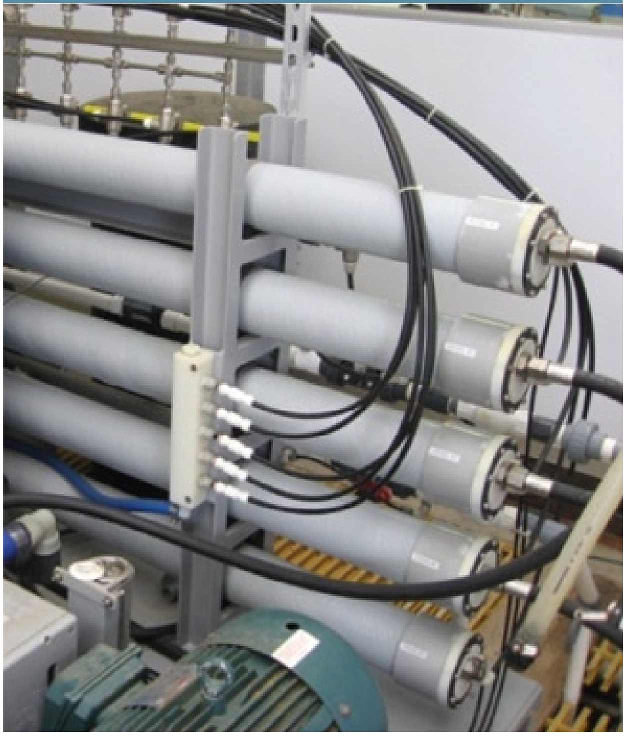
Individual permeate flow meters were equipped for real-time measurement of permeate flow rates with programmable logic controller data logging. Each bench was equipped with a 5-gal feed reservoir, a chiller to maintain temperature, and a 1-μ polypropylene depth filter. A salinity meter[2] calibrated at two concentrations daily was used.

Membrane Fabrication. Membranes were prepared by a process widely described in the literature (Jeong et al, 2007; Ghosh et al, 2008; Cadotte, 1979) and refrigerated until testing was conducted. In all cases, hand-cast membranes were tested within four days of synthesis.

Short-Term Testing. Membrane performance was usually measured after 1 hour of operation. For clean water, which consisted of NaCl in tap water with an in-line filter, performance was found to accurately indicate longer-term performance. Feed temperature was maintained within 1°C of 25°C, and feed salinity was maintained within 500 ppm of 32,000 ppm. After a 1-hour stabilization period at 800 psi, flux was determined by measuring permeate volume collected at a fixed time interval and salt passage measured by conductivity measurements on the feed and obtained sample. Individual flux and rejection measurements were normalized for pressure and temperature to 25°C and 32,000 ppm based on known equations (Dow Chemical).

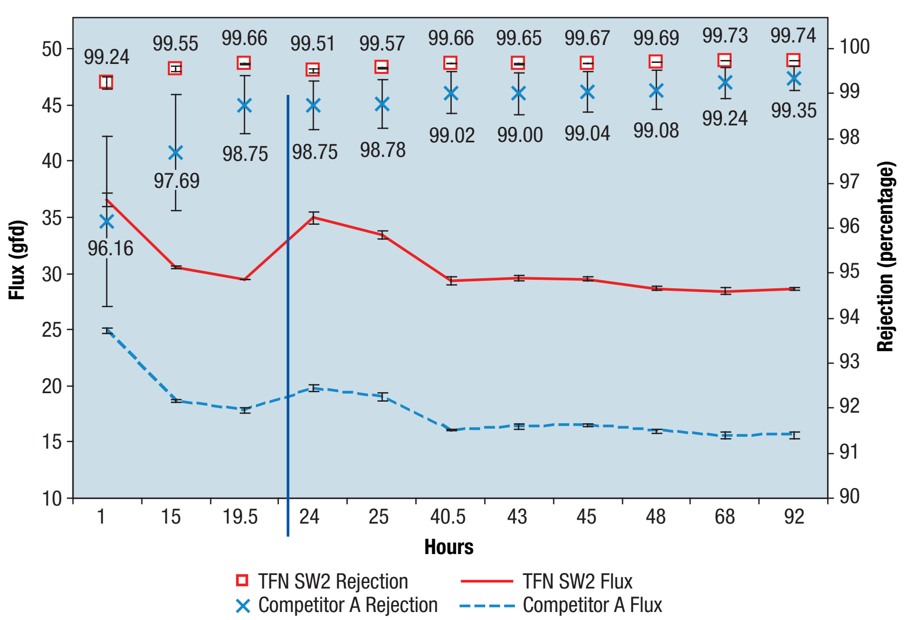
Long-Term Testing. For tests requiring more than 1 hour, performance was determined in a manner similar to that used in the short-term tests, except the feedwater was a mixed salt solution more closely matching seawater[3] in deionized water. No in-line filter was used, allowing

Figure 3. Element test system at Port Hueneme, Calif.



NANOH$_2$O

Figure 4. TFN membrane performance vs. competitor A



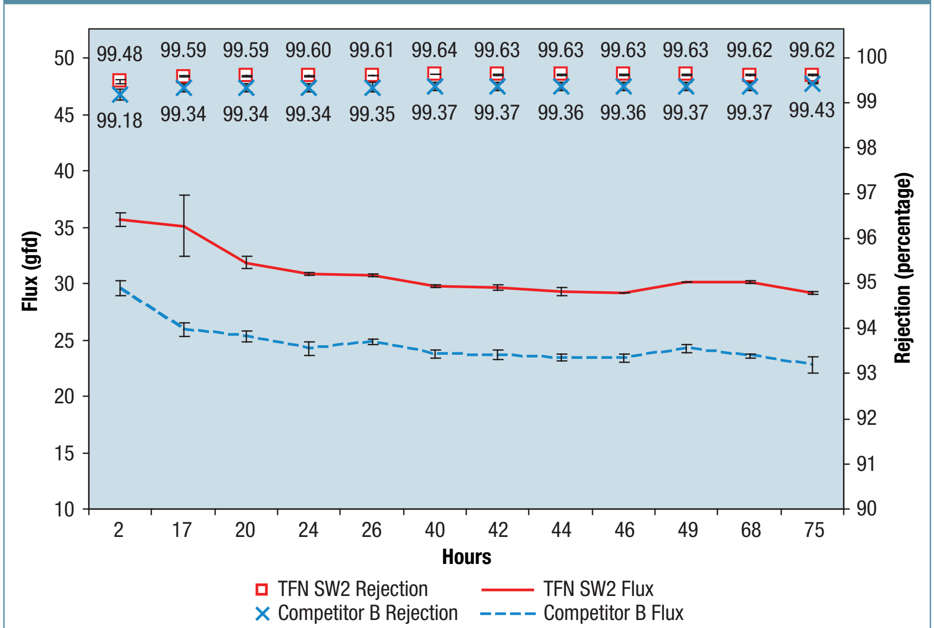
Note: The test was conducted with both membranes run in parallel on a NaCl feed (32,000 ppm) at 800 psi at 25°C.

measurable turbidity to accumulate during the test (typically 1 ntu).

Element Field-Testing. SDTF feedwater enters through a screen-fed open-ocean intake and passes to a facility-wide intermediate tank that feeds one of two pretreatment systems. For the first 4,700 hours of testing, a single-stage media filter containing anthracite, garnet, and fine and coarse gravel was used. Next, water passes through a single-stage 5-µ cartridge filter and fed to the pilot system. For the remainder of the test, a UF pretreatment system[4] was used.

The pilot system shown in Figure 3 consisted of five, two-element vessels plumbed in series. For all data presented here, three of the five vessels were used, resulting in a six-element in series, single-pass array configuration. Each vessel's end cap 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.

Figure 5. TFN membrane performance vs. competitor B



Note: The test was conducted with both membranes run in parallel on a NaCl feed (32,000 ppm) at 800 psi at 25°C.

Data were usually collected manually once each day, although more frequent testing was often performed after element changes or cleanings. Feedwater quality was measured 2–5 times a week by a single water quality setup. Metrics monitored were raw water turbidity, RO feed turbidity, SDI, and particle count.

Element Cleaning. First, the elements were recirculated with a solution of 2 percent ethylenediaminetetraacetic acid (EDTA) at pH 11.8 (with NaOH) in RO permeate at 75 psi and 28°C for one hour. Next, the solution was neutralized, drained, and fed with a 1.4 percent solution of citric acid in water (pH 2.3).

Ongoing work will determine optimal cleaning conditions for TFN membranes after exposure to various fouling agents, as well as to determine compatibility and effectiveness of existing cleaning products.

This solution was recirculated for 2 hours at 75 psi and 29.7°C. The system was then shut down, allowing the elements to soak in the solution overnight. The next morning, the solution was neutralized and drained. A third high-pH clean was then used for the clean-in-place (CIP) procedure at about 1,000 hours. A 3 percent solution of RO membrane cleaner (pH 11.1) was recirculated for 2 hours at 87 psi and 30°C.

The second cleaning replaced the EDTA clean with the RO cleaning solution, followed by citric acid cleaning. A third cleaning was not performed.

Results and Discussion

TFN Membrane Performance. To determine TFN membrane performance relative to commercial products, longer-term flat-sheet tests were performed with the TFN membranes and a competitive high-flux seawater membrane (equivalent to that used in 9,000-gpd elements) in parallel (tested at the same time, pressure, cross-flow conditions, and feedwater). During the first 20 hours, both membranes lost flow because turbidity on the bench (no prefiltration was used, turbidity was about 1 ntu) led to fouling of both membranes (Figure 4).

At 20 hours, the membranes were cleaned with a pH 11 NaOH solution containing 50 ppm of EDTA for 30 minutes. After bench cleaning, TFN membrane flux recovered to its initial value, while relatively little of the commercial membrane's flux was restored. The difference in flux recovery after cleaning is attributed to altered surface properties of the TFN membrane. The test was then resumed with a similar loss of flux over the next 20 hours, after which performance was stable for the remainder of the test. After a rinse period, TFN membrane rejection was more than 99.7 percent for the duration of the test.

Although initial flux of the competitive product met listed flux specification, fouling during the first 20 hours decreased flux to a level that cleaning did not restore.

Similar testing (Figure 5) was performed against a second manufacturer's high flux seawater RO membrane (also equivalent to that used in a 9,000-gpd element). In this case, the competitive product began at a higher initial flux than the first test. After 40 hours flux, it stabilized at about 23 gfd, in specification for the manufacturer's product. The TFN membrane in this test performed similarly to the earlier test (Figure 4), stabilizing at approximately 30 gfd with good rejection. No cleaning cycle was performed for this test, so a relative comparison is not possible.

Element Performance. During 2008, prior to fabrication of a coater optimized for TFN manufacturing, trials of several TFN formulations were made on an older 40–in. flat-sheet coating machine. Performance improvement vs. formulation control was evident in flat-sheet testing, although mechanical limitations prevented typical hand-cast performance from being obtained. These specific mechanical limitations have been identified and addressed in recently installed coating equipment designed for the initial commercialization of TFN membrane technology.

Table 1. Sample element performance

TFN	Flux (gfd)	Rejection (percent)
Element A	21.3	99.69
Element B	22	99.74
Element C	25.1	99.72

The membranes made were rolled into 4040-style elements and installed and tested at SDTF. The fiberglass-coated elements used a five-leaf construction with about 70 ft^2 of active area. A 34-mil propylene diamond-feed spacer was used within the element. Table 1 shows representative element performance from flat-sheet made on this older machine.

One of the earlier elements made, Element A was left in place to evaluate long-term performance. During the course of 10 months, other elements were replaced; the long-term element's position was altered; and various system operating conditions were investigated. Figure 6 shows the normalized operating flux and rejection as a function of run time.

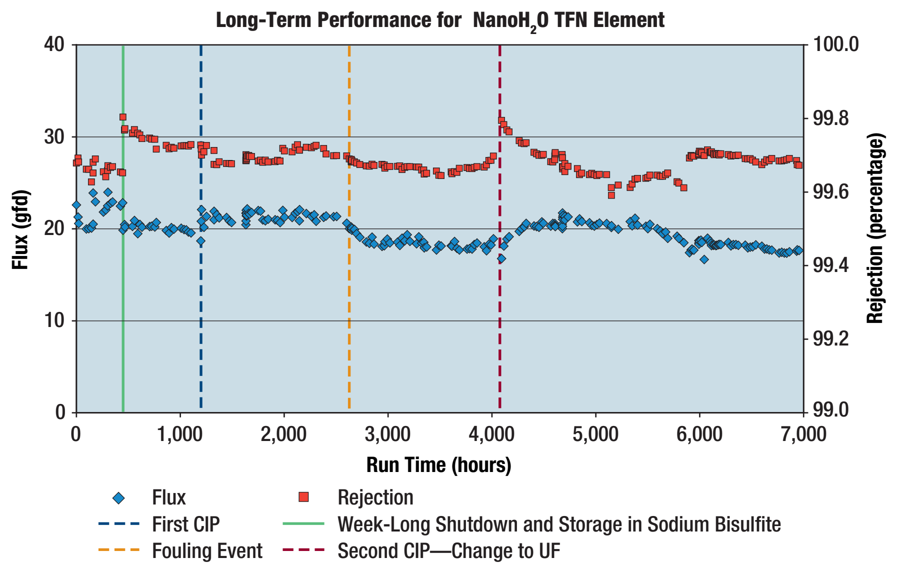
Fouling Event

After 4 months of operation (2,600 hrs), a red tide algal bloom around the SDTF intake resulted in a spike in SDI, particle count, and ntu in incoming feedwater for a period of 2 weeks (Figure 7). At the start of this period, the element was operating at a flux of 16.5 gfd, and the element recovery was 5.3 percent. During the event, the TFN module lost 14.3 percent of its permeability. When the membrane was cleaned two months later, flux had recovered to within 95 percent of its prefouled state.

Although early lab studies indicated some improvement in chemical structure and morphology, which were thought to be related to fouling propensity (charge, roughness, hydrophilicity), a relatively modest performance loss and subsequent flux recovery on cleaning through the red tide event is the first large-scale evidence that improved fouling properties may be present in some nanocomposite materials. Further testing is needed to evaluate repeatability and the scope of improvement in properties.

The long-term element has since been removed and is currently being autopsied to determine membrane performance and identity of species still present on the membrane surface.

Figure 6. Long-term element test



using the membrane pretreatment, the media pretreatment didn't have a sufficiently long operational period to determine a fouling rate.

CIP Stability

An early question regarding TFN membrane applicability was its stability and performance through cleaning cycles. Certainly with the earliest nanoparticles (Jeong et al, 2007), there was a chance that sufficiently high or low pH could chemically degrade the added nanoparticles, leaving holes in the separating layer and leading to increased salt passage.

To determine chemical stability, a CIP was performed on the element early in its operation. After allowing time for performance to stabilize (about 1,000 hours), a CIP cycle was performed even though no loss in permeability had occurred. The CIP was used to evaluate cleaning agent effectiveness, as well as to evaluate the separating layer's chemical stability. After the CIP, measured flux and rejection matched initial performance. Because nanoparticle degradation and/or deterioration of the nanocomposite matrix would have caused performance loss, this result indicates TFN membrane stability under the conditions used.

Later in the module's life, a second CIP was performed 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 of chemical degradation.

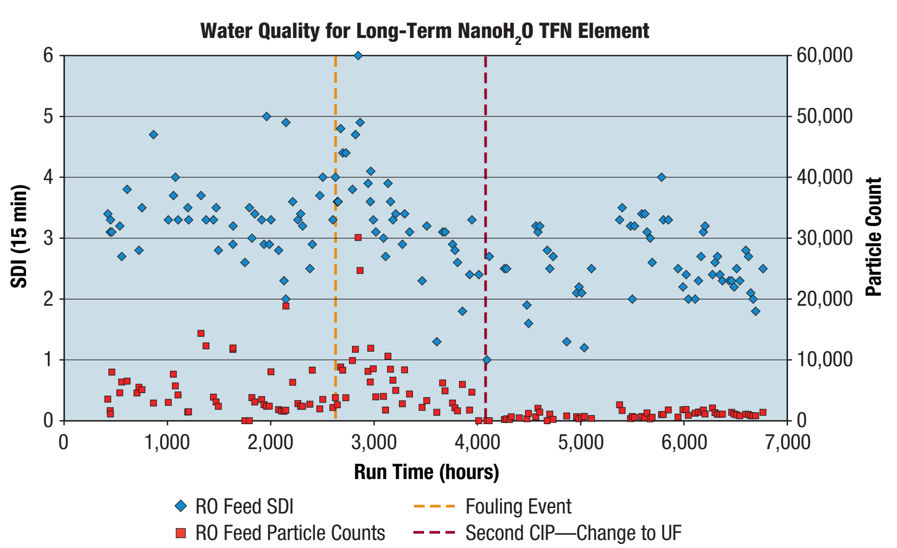
Ongoing work will determine optimal cleaning conditions for TFN membranes after exposure to various fouling agents, as well as to determine compatibility and effectiveness of existing cleaning products.

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 improved from 3.4 on the media to 2.6 using the UF membrane. This behavior appeared stable during the evaluation period.

At this time, no clear conclusions can be drawn about the relative benefits of either pretreatment technology. Although one could argue that there is a larger drop in flux over time

Figure 7. Particle count and SDI



Relatively stable flux and rejection indicate the performance enhancement of nanocomposite film is fundamentally a different separation layer, not a short-term performance enhancement.

Conclusions

During a 30-month evaluation, research into nanocomposite RO membranes has resulted in development of a new mixed matrix membrane material for seawater desalination. In this relatively short period, nanocomposite membranes have illustrated the potential for out-performing existing commercial products based on standardized polymer chemistry used in RO membranes for the last several decades. The technology is currently being commercialized with trials on a specially designed full-scale manufacturing line under way for a 2010 product release.

Optimized TFN membranes were compared with current commercial high-flux SWRO products and found to provide improved flux and rejection. These promising results from hand-cast membrane samples prompted efforts to scale-up to a continuous process enabling 40-in.-wide membranes to be made and elements to be manufactured. The resulting performance appears to validate the contention that—with the appropriate procedures and techniques to prepare and handle nanoparticle dispersions—a conventional coating machine and element fabrication facility can be used for TFN membrane technology scale-up. Due to the relatively low mass of nanocomposite film used, only a minor effect on the total element cost is observed.

Operation of this TFN element technology during pilot testing has provided insight about the expected behavior of this new membrane. Relatively stable flux and rejection indicate the performance enhancement of nanocomposite film is the result of a fundamentally different separation layer and is not a short-term performance enhancement. Further, conditions that would have caused loss of nanoparticles would also have caused increased passage. The lack of such a change supports the inherent stability of the nanocomposite film, including the high- and low-pH conditions used during CIP cycles and mechanical stresses applied during repeated start-ups and shut-downs. Although further testing is needed to fully validate these findings, the relatively modest flux loss and later flux recovery during a red tide event suggests the possibility of improved tolerance to some biofouling events and may open up the possibility of increasing system design flux.

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Footnotes

[1]Delstar Technologies, Middletown, Del.

[2]sensION5 Conductivity Meter, Hach, Loveland, Colo.

[3]Instant Ocean Sea Salt, Instant Ocean, Mentor, Ohio

[4]Zenon ultrafiltration membrane, GE, Trevose, Pa.

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Editor's Note

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