

IMPROVED SEAWATER DESALINATION WITH NANOCOMPOSITE MEMBRANES

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Introduction

Reverse osmosis (RO) is the leading process for brackish and seawater desalination and freshwater purification. Sufficient pressure applied to a saline solution forces freshwater through a semi-permeable membrane that rejects salt and other contaminants. According to the U.S. Desalination and Water Purification Roadmap [1], membrane permeability and fouling resistance are key economic drivers for membrane-based water treatment systems. Membrane performance characteristics translate directly to the energy intensity and capital expenditures of a RO system and therefore to the economics of desalination. Accounting for 70-80% of the total expense of RO desalinated water [1], energy consumption and capital expenditures are the primary reason why desalination remains expensive compared to most freshwater sources.

In 2007, the use of TFN membranes for water purification was first described for BWRO membranes [2]. 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 and altered surface properties potentially related to fouling, while maintaining salt rejection.

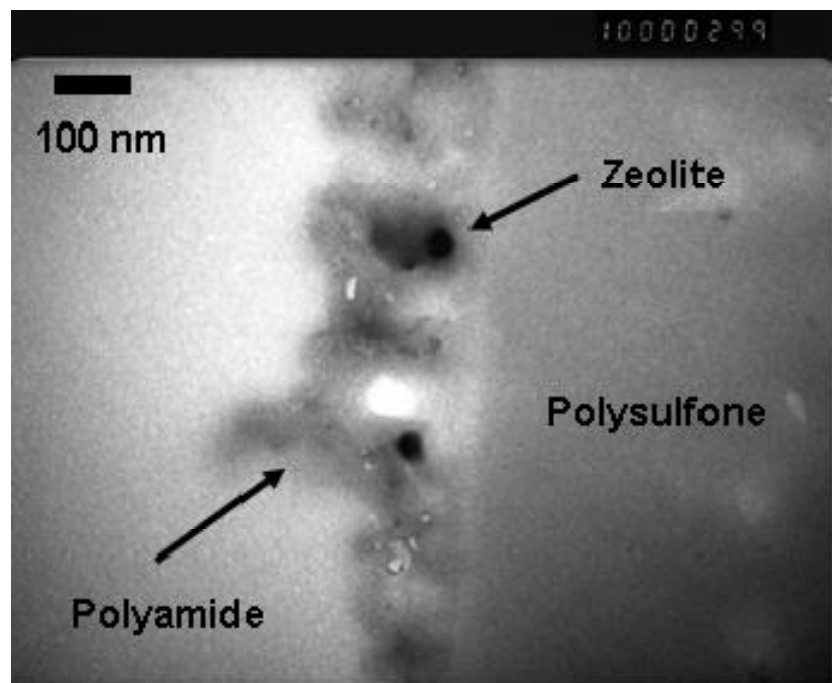


Figure 1: Cross-sectional Transmission Electron Microscope (TEM) Image of TFN membrane [2]

Since the original publication of the TFN concept, further efforts have developed and optimized TFN membrane technology for SWRO [3]. Membrane performance data, using industry-standard cross-flow testing, demonstrates a doubling of TFN membrane permeability relative to conventional RO membranes with equivalent rejection. For example, TFN technology transforms an industry standard 17 gfd (gallons per square foot per day) membrane into a 56 lmh (33 gfd) membrane. Current performance of TFN membranes leads to elements possessing an enhanced flux of more than double that of a $24.6\text{m}^3/\text{d}$ (6,500 gpd) commercial baseline with salt rejection at industry standards.

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, and 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. Performance characterization against model foulants common in seawater installations allowed determination of preferred operating conditions for pilot studies.

Consistent results from bench-scale membrane tests prompted scale-up of TFN technology using a pilot 1m (40-inch) wide continuous coating process for manufacturing SWRO TFN membranes. In addition to TFN membranes, thin film composite (TFC) membranes were also made in the production facility to serve as controls so the effect of the TFN technology could be isolated. TFC or TFN membranes in 4040-style modules [10cm (4-inch) by 1m (40-inch)] tested at the U.S. Navy Seawater Desalination Test Facility (SDTF) at Port Hueneme used an open intake Pacific Ocean seawater feed. The test skid used dual media filtration followed by cartridge filtration and produced water with an average SDI_{15} of 3.3 and turbidity of 0.051 NTU. Testing was conducted over the course of 10 months, and performance measured at various operating flux rates and system recoveries. Test results in both the lab and the field indicate the suitability of TFN technology for SWRO installation and demonstration of significant flux enhancement while maintaining industry standard salt rejection.

Materials and Methods

Flat-sheet Membrane Equipment

Testing of flat-sheet membranes was performed on stainless steel cells obtained from Delstar Technologies. Cells were used without a feed spacer (unless noted) and had an active area of 19.4 cm^2 (3 in^2). Test benches, shown in Figure 2, were configured with 6 cells, (two parallel sets of 3 cells in series).



Figure 2: Flat-sheet Cell Testing Bench

Individual permeate flow meters were equipped to allow real time measurement of permeate flow rates with programmable logic controller (PLC) data logging. Each bench was equipped with a 5-gallon feed reservoir, a chiller to maintain temperature and a 1 micron polypropylene depth filter. Salinities were measured with a Hach Sension 5 Conductivity/TDS/Salinity meter calibrated at two concentrations daily.

Membrane Fabrication

Membranes were prepared by a process widely described in the literature [2,4,5]. After preparation, membranes were refrigerated until testing. In all cases, hand-cast membranes were tested within four days of synthesis.

Short-term Testing Procedure

Membrane performance was typically measured after 1 hour of operation. For clean waters (NaCl in tap water with an in-line filter), this performance was found to accurately indicate longer-term performance. Feed temperature was maintained at 25° C to within 1° C; feed salinity was maintained at 32,000 ppm to within 500 ppm. After a 1 hour stabilization period at 800 psi, flux was determined by measuring permeate volume collected in a fixed time interval and salt passage measured by conductivity measurements on the feed and the obtained sample. Individual flux and rejection measurements were normalized for pressure and temperature to 25° C and 32,000 ppm based on known equations [6].

Long-term Testing Procedure

For long-term tests (longer than 1 hour), performance was determined in a manner similar to that of the short-term tests with the following differences; Feed water was changed to a mixed salt solution more closely matching that of seawater (Instant Ocean™) in DI water. No in-line filter was used allowing measurable turbidity to accumulate during the test (typically 1 NTU).

Element Field Testing Procedure

Feed water at the SDTF facility enters through a screen fed open ocean intake and passes to a facility wide intermediate tank. This tank then feeds one of two pretreatment systems. For the first 4700 hours of testing a single stage media filter¹ was used, for the remainder of the test a Zenon UF pretreatment system was used.

The pilot system pictured in Figure 3 consisted of five, two-element vessels plumbed in series. For all data contained here only three of the five vessels were employed resulting in a six-element 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 was 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.

¹ The media filter contained anthracite, garnet, and fine and coarse gravel. Water then passes through a single stage 5 micron cartridge filter and fed to the pilot system.



Figure 3: Element test system at Port Hueneme

Data was typically collected manually once daily, although more frequent testing was often performed after element changes or cleanings. Feed water quality was measured between two to five times a week by a single water quality setup. The metrics monitored were raw water turbidity and RO feed turbidity, SDI and particle count.

Element Cleaning Procedure

The elements were first recirculated with a solution of 2% EDTA at pH 11.8 (with NaOH) in RO permeate at 75 psi and 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 2 hours at 75 psi and 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 ~1000 hours. A 3% solution of GE RO membrane cleaner at a pH of 11.1 was recirculated for 2 hours at 87psi and 30° C.

The second cleaning that was performed replaced the initial EDTA clean 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 Discussion

TFN Membrane Performance

To determine the performance of TFN membranes relative to commercial products, longer-term flat-sheet tests were performed. These 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 feed water). Over the first 20 hours both membranes lost flow because of the presence of turbidity on the bench (no prefiltration was used, turbidity ~1NTU) led to fouling of both membranes (Figure 7). At 20 hours the membranes were cleaned with a pH 11 NaOH solution containing 50 ppm of EDTA for 30 minutes. After the bench cleaning, the flux of the TFN membrane recovered to its initial value, while relatively little of the commercial membrane's flux was restored. This difference in flux recovery after cleaning is ascribed 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 up period rejection of the TFN membrane was above 99.7% for the duration of the test.

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

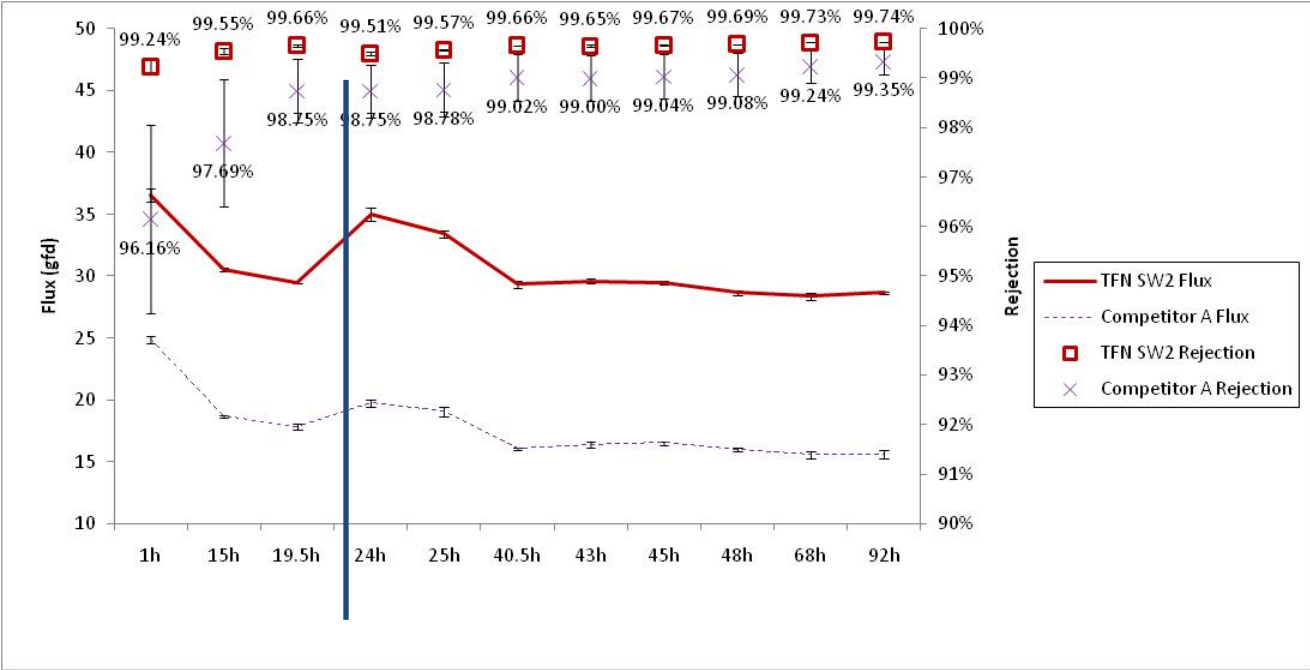


Figure 4: TFN Membrane Performance vs. Competitor A

Similar testing (Figure 8) was performed against a second manufacturer's high flux seawater RO membrane (also equivalent to that used in a 9000 gpd element). In this case the competitive product began at a higher initial flux than the first test. After 40 hours flux it had 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 7) stabilizing at approximately 30 gfd with good rejection. For this test no cleaning cycle was performed so a relative comparison is not possible.

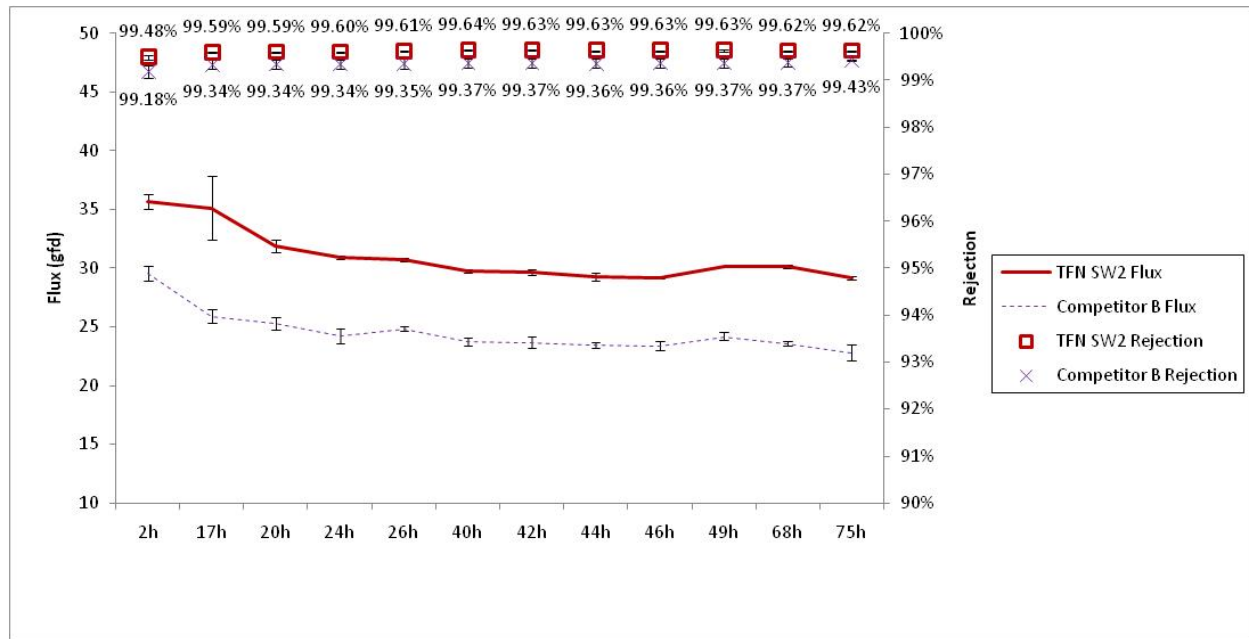


Figure 5: TFN Membrane Performance vs. Competitor B

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" flat-sheet coating machine. Performance improvement versus a control formulation was evident in flat-sheet testing, although mechanical limitations of the machine prevented typical hand-cast performance from being obtained. These specific mechanical limitations have been identified and have been addressed in recently installed coating equipment designed for the initial commercialization of TFN membrane technology.

The membranes made were rolled into 4040 style elements and installed and tested at the SDTF. The fiberglass coated elements utilized a 5 leaf construction with approximately 70 sf of active area. A 34 mil propylene diamond feed spacer was used within the element. Representative element performance from flat-sheet made on this older machine is shown in Table 1.

Table 1: Sample Element Performance

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

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

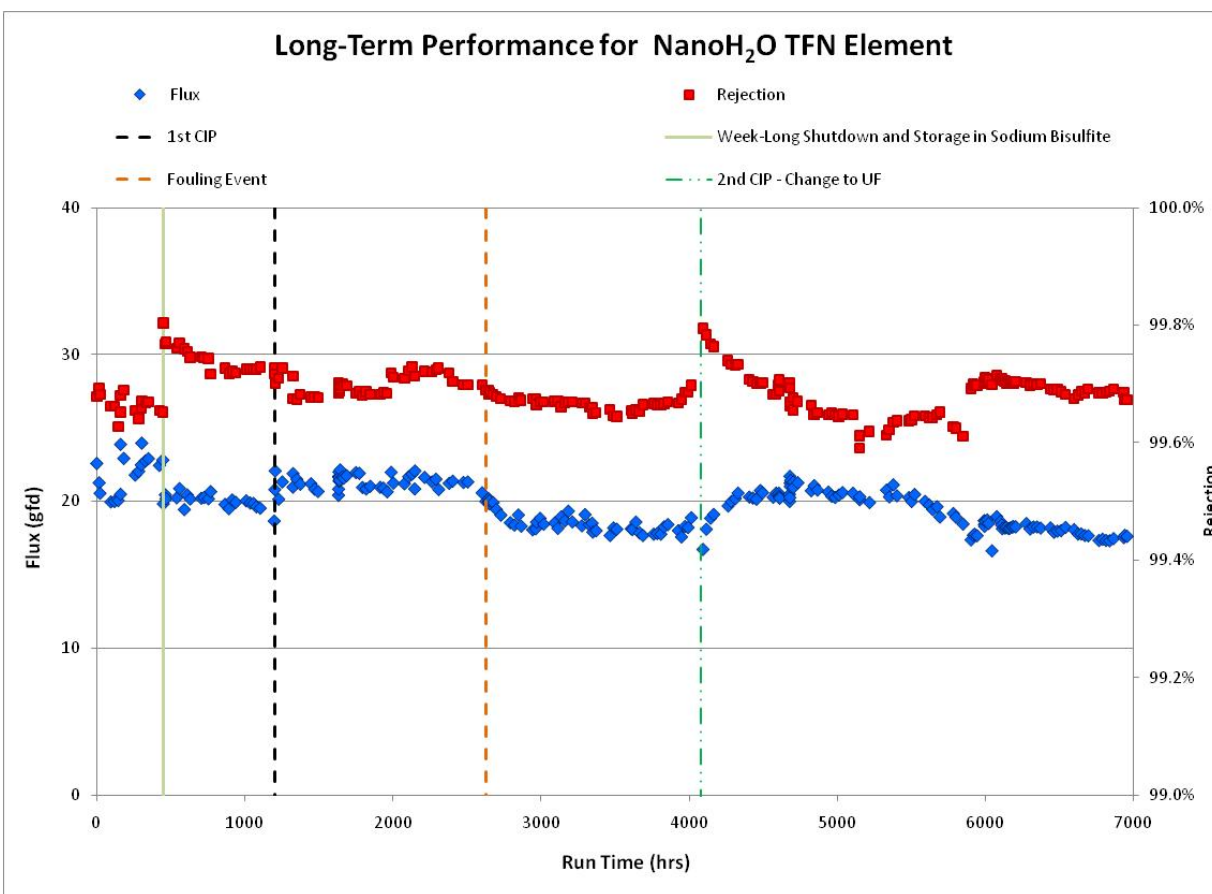


Figure 6: Long-Term Element Test

Fouling Event

After 4 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 feed water at the facility for a period of 2 weeks (see 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%. Over the course of the event the TFN module lost 14.3% of its permeability. When the membrane was next cleaned (two months later²), 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, hydrophilicity), the relatively modest performance loss, and subsequent flux recovery on cleaning through this red tide event is the first large-scale evidence that improved fouling properties may be present in some nanocomposite materials. Of course further testing will be needed to evaluate the repeatability and scope of any such improvement in properties.

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

² As mentioned earlier, multiple experiments ran on this 4" machine while the long-term element was installed. During the fouling test a 3-month long experiment was in process that a CIP would have upset. As a result the cleaning was delayed until the experiment was complete.

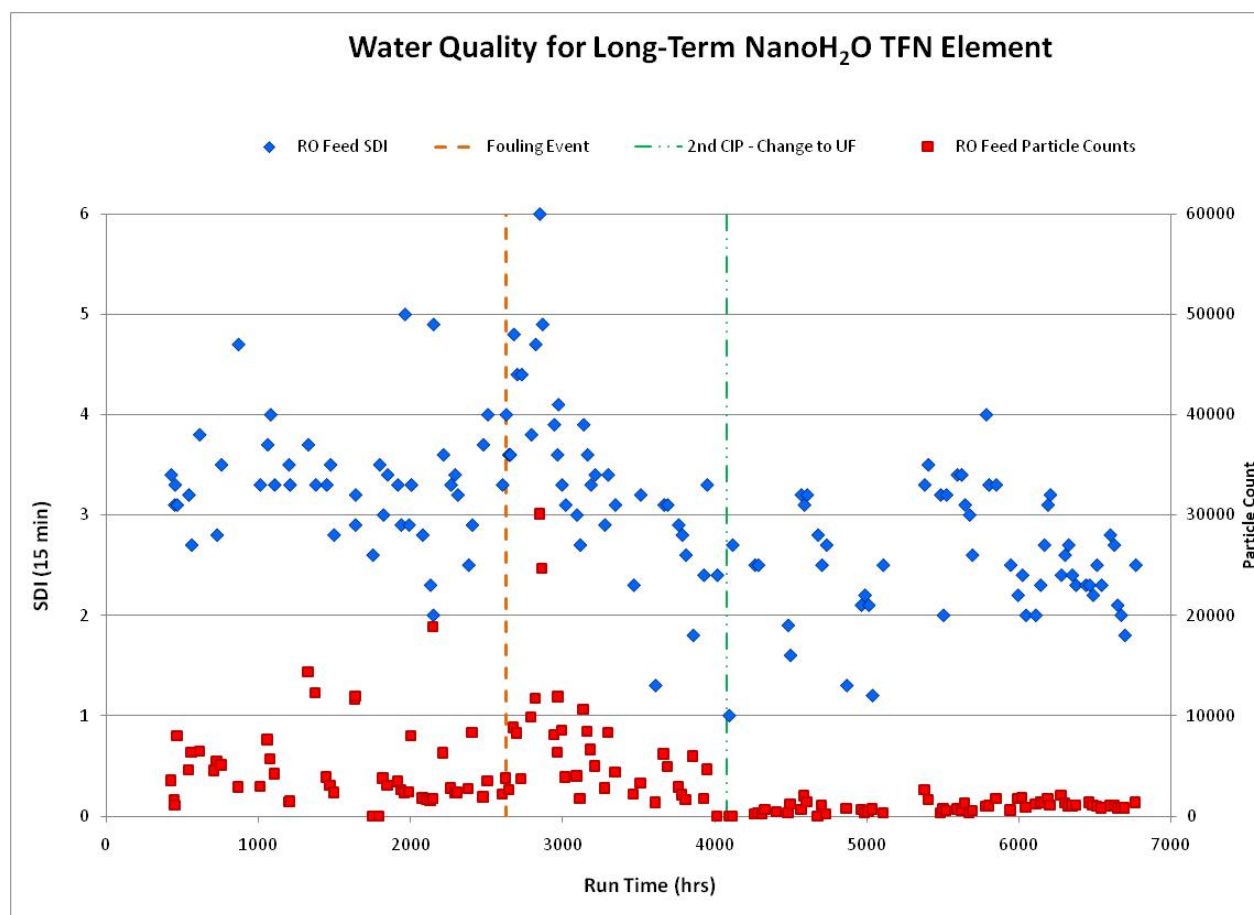


Figure 7: Particle Count and SDI

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 period of time evaluated.

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 with 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 giving time for performance to stabilize (~1000 hrs), a CIP cycle was performed even though no loss in 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 lead 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 modules 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.

Upcoming 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.

Conclusions

In the last 30 months, industrial research into nanocomposite RO membranes has resulted in the development of a new 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 is now in the process of being commercialized with trials on a specially designed full-scale manufacturing line underway for a mid-2010 product release.

Optimized TFN membranes were compared with current commercial high flux SWRO products and found to have improved flux and rejection. These promising results from hand-cast membrane samples prompted efforts to scale-up to a continuous process enabling 40" wide membrane 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 the nanoparticle dispersions, a conventional coating machine and element fabrication facility can be used for scale up of the TFN membrane technology. 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 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 the performance enhancement of the nanocomposite film is not a short-term performance enhancement, but rather a fundamentally different separation layer. Further, conditions that would have lead to loss of nanoparticles would have also lead 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, as well as through mechanical stresses applied during repeated start-ups and shut-downs. Although further testing is needed to fully validate, the relatively modest flux loss and later flux recovery during a red tide event also suggests the possibility of improved tolerance to some biofouling events and may open up the possibility of increasing system design flux.

Acknowledgements

Thanks to Bill Varnava and his team at the US Navy SDTF at Port Hueneme, California for field testing assistance.

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