Improved Nanocomposite Seawater Desalination Membranes

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Abstract

Reverse osmosis (RO) 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, energy consumption and capital expenditures are the primary reasons why desalination remains expensive compared to most freshwater sources.

Thin film nanocomposite (TFN) membranes for water purification, initially described for brackish water reverse osmosis (BWRO) membranes, have been advanced by NanoH_2O, Inc. and optimized for seawater reverse osmosis (SWRO). Demonstrating a doubling of TFN membrane permeability relative to conventional RO membranes with equivalent rejection, NanoH_2O TFN technology transforms an industry standard 29 lmh [17 gallons per square foot per day (GFD)] membrane into a 56 lmh (33 GFD) membrane. Current performance of TFN membranes leads to elements with a flux of approximately 49 m^3/d (13,000 GPD) and industry-standard salt rejection.

Introduction

Reverse osmosis 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 (USBR, 2003), 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 an RO system and therefore to the economics of desalination. Accounting for 70-80% of the total expense of RO desalinated water (USBR, 2003), energy consumption and capital expenditures are the primary reasons 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 (Jeong, 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. Incorporation of such nanoparticles into a BWRO membrane formulation increased permeability and altered surface properties potentially related to fouling, while maintaining salt rejection.

Since the original publication of the TFN concept, further efforts have developed and optimized TFN membrane technology for SWRO (Kurth, 2009). 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 29 lmh (17GFD) 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 m^3/d [6,500 gallons per day (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 1 m (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 [10 cm (4-inch) by 1 m (40-inch)] tested at the U.S. Navy Seawater Desalination Test Facility (SDTF) at Port Hueneme, California USA 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. A similar system deployed at the SDTF for 20 cm (8-inch) pilot testing solely uses ultrafiltration (UF) pretreatment. 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 using 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 were configured with 6 cells (two parallel sets of 3 cells in series). 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 and Testing

Membranes were prepared by a process widely described in the literature (Jeong, 2007; Ghosh, 2008; Cadotte, 1981). After preparation, membranes were refrigerated until testing. In all cases, hand-cast membranes were tested within four days of synthesis. 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 55 bars (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 salinity based on known equations (Dow, 2005).

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: 1) Feed water was changed to a mixed salt solution more closely matching that of seawater (Instant Ocean™) in DI water, and, 2) 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 4,700 hours of testing a single stage media filter[1] was used; the remainder of the test incorporated a Zenon UF pretreatment system.

The pilot system consisted of five two-element vessels plumbed in series. For all of the long-term 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 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. Long-term data on the 10 cm (4-inch) skid were 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. A similar system deployed at the SDTF for 20 cm (8-inch) pilot testing uses data loggers on the 20 cm (8-inch) skid to transmit data to the NanoH_2O office. These data are backed up with manual field data collection.

Element Cleaning Procedure

The elements were first recirculated with a solution of 2% EDTA at pH 11.8 (with NaOH) in RO permeate at 5.2 bar (75 psi) and 28° C for one hour. After neutralization and draining, 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 5.2 bars (75 psi) and 29.7° C. After system shutdown the elements were allowed to soak in this solution overnight. The following morning the solution was neutralized and drained. A third high-pH cleaning was 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 6 bar (87 psi) and 30° C. The second cleaning performed replaced the initial EDTA cleaning with the GE RO cleaning solution followed by the citric acid cleaning. No third cleaning 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 34 m^3/day (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 turbidity on the bench (no prefiltration was used, turbidity ~1NTU) led to fouling of both membranes (Figure 1). 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 less 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 resumed with a similar flux loss 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.

[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.

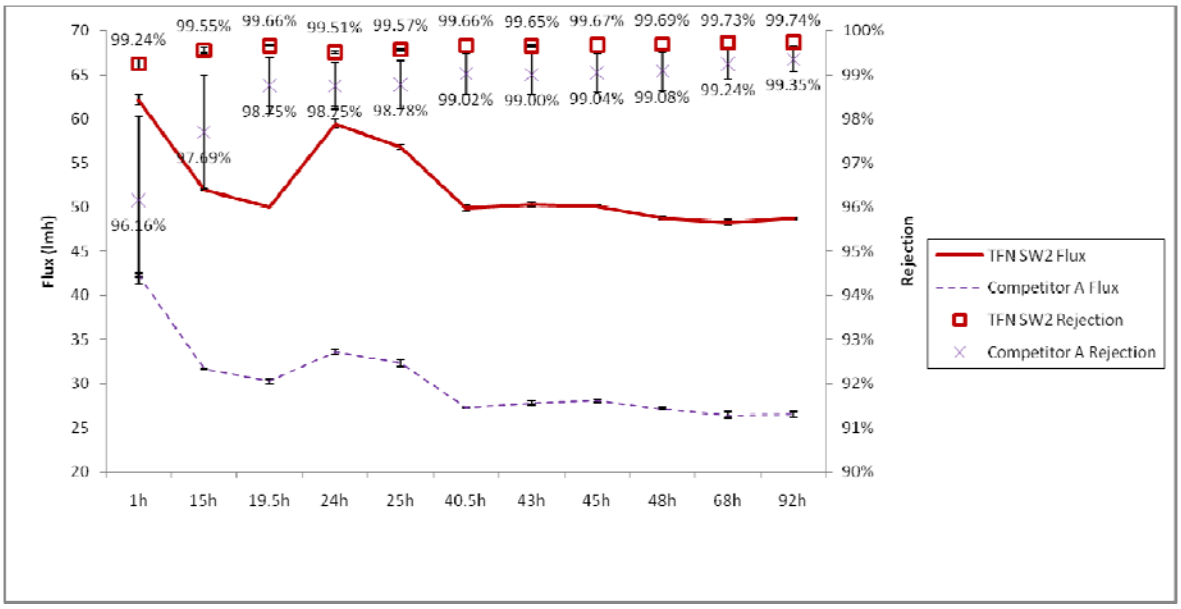

Figure 1: TFN Membrane Performance vs. Competitor A

Element Performance

During 2008, prior to fabrication of a coater optimized for TFN manufacturing, trials of several TFN formulations were made on an older 1 m (40-inch) 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 limitations 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 6.5 m^2 (70 sf) of active area. A 34 mil propylene diamond feed spacer was used within the element. One of the earlier elements made, 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 2 shows the normalized operating flux and rejection as a function of run time.

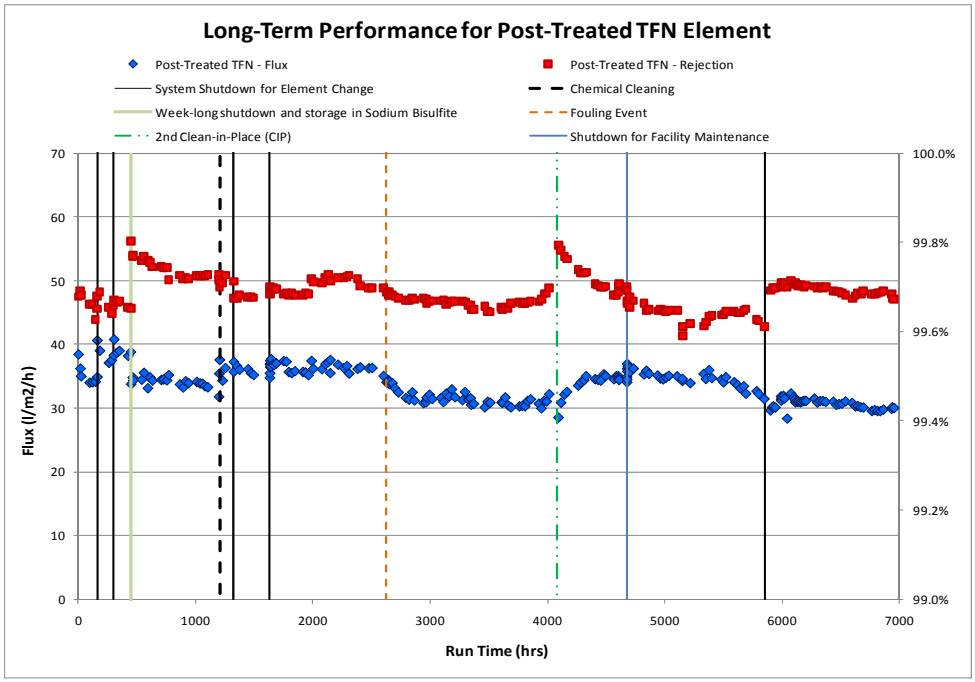

Figure 2: Long-Term Element Test

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 (Figure 2). At the start of this period, the element was operating at a flux of 28 lmh (16.5GFD) and the element recovery was 5.3%. Over the course of the event, the 10 cm (4-inch) TFN module lost 14.3% of its permeability. When the membrane was next cleaned (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, and 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. Further testing will evaluate the repeatability and scope of any such improvement in properties.

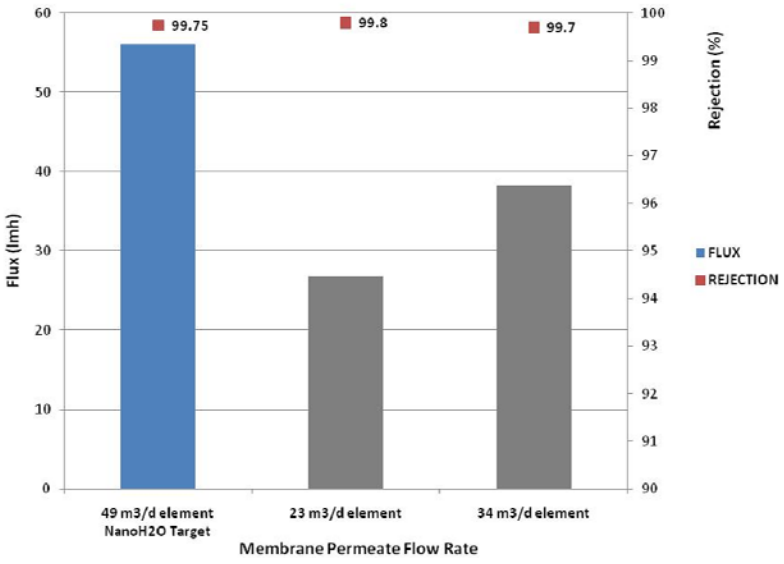

Figure 3: NanoH₂O target performance in comparison with other commercial elements

Although long-term test data are not yet available, initial testing using the 20 cm (8-inch) skid installed at Port Hueneme indicate that NanoH₂O has achieved flux values at approximately 49 m^3/day and greater than 99.7% salt rejection. These values are comparable to NanoH$_2$O target values shown in Figure 3 and compare favorably with other elements commonly in use for SWRO. Optimization of element hydraulics is continuing and 3-month-long test data are expected to be available by the end of 2010.

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 beginning initial commercial production and longer-term pilot testing.

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. Because of 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 led to 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, as well as through mechanical stresses applied during repeated start-ups and shutdowns. 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.

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