

# **Leveraging Nanotechnology for Seawater Reverse Osmosis**

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## **Abstract**

Permeability and fouling resistance are key economic drivers for membrane-based water treatment systems. These performance characteristics translate directly to the energy intensity and capital expenditures of a reverse osmosis (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 reason why desalination remains expensive compared to most freshwater sources.

Originally used to improve the performance of gas separation membranes, mixed matrix membrane technology was applied to polyamide RO membranes and led to the development of thin film nanocomposite (TFN) membranes. These membranes incorporated zeolite nanoparticles in the interfacially formed separating layer and were found to possess increased permeability relative to membranes made without the nanoparticles. In addition, these membranes show promise as having lower fouling surfaces. Rejection was unaffected by the addition. Since the original publication of the TFN concept, further development and optimization of TFN membrane technology for seawater reverse osmosis (SWRO) resulted in an enhanced flux of more than double that of a 22.7 m<sup>3</sup>/d (6,000 gpd) commercial baseline, with salt rejection at industry standards.

TFN development for SWRO hinged on identification of several failure points hampering synthesis of effective nanocomposites. In particular, aggregation of nanoparticles impacts not only the effectiveness of the permeability increase, but can also lead to increased salt passage, if used incorrectly. Electron microscopy is an effective means of identifying such problems.

Findings from TFN membrane optimization for SWRO illustrate the physical basis of key challenges of nanocomposite membrane synthesis. TFN membrane performance compared against commercial products illustrates opportunities for more efficient desalination. Finally, chemical stability data demonstrate TFN membrane tolerance to environments that may be experienced during cleaning cycles.

## I. INTRODUCTION

### 1.1 Economics of SWRO Desalination with Improved Membranes

Although numerous breakdowns of SWRO cost have been performed, because of individual differences in design, water chemistry, water temperature, energy cost, and financial models, no single breakdown can be considered representative. To establish the economic benefits of SWRO using improved membranes, a model was used to establish the effect of various membrane improvements on 10MGD RO systems using various water types and in both retrofit and newly built plant scenarios. The model used membrane properties to predict system performance, and included a cost model with both operational and debt service contributions.

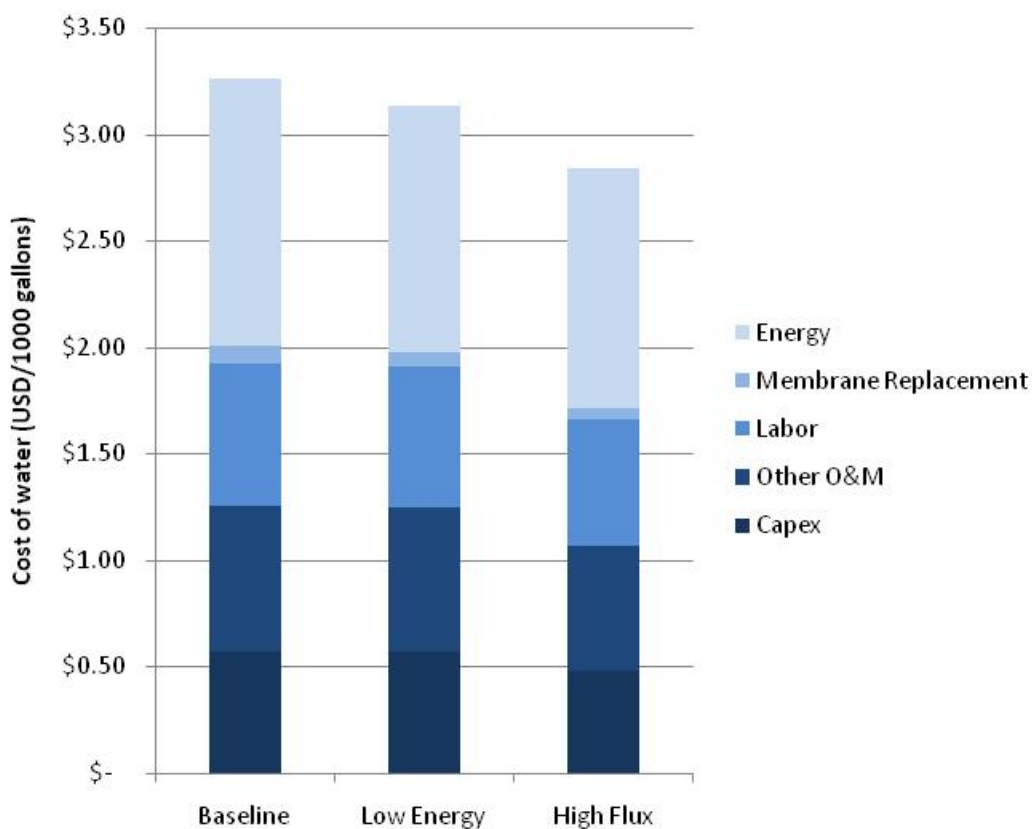
A RO computer projection program was employed to predict the membrane performance. The program, which was similar to the type typically used by membrane manufacturers, was modified to encompass not only conventional but also a SWRO membrane having twice the permeability of existing membranes, and also incorporated a modified fouling factor equation developed to describe TFN membranes. Conditions used in the economic analysis are provided in Table 1.

The capital costs for major equipment items were based on recent vendor bids for seawater RO systems of similar size. Other component costs, including piping, valves and instrumentation were taken from published EPA data. The capital cost estimates developed for the desalination plants included typical seawater RO pre- and post-treatment systems but did not include feed water intake and wastewater outfall structures. Consumables and labor costs were taken to be current industry standard.

A detailed spreadsheet was developed that calculated the capital and operating costs for the different scenarios and design options. Figure 1 shows one such analysis, the retrofit of an existing plant using standard membrane (baseline) with high flux, low fouling SWRO membranes (low energy and high flux). Two operational modes are shown for the TFN membrane, one involving a low pressure operation to leverage energy savings, the second involving operation at a higher flux and system recovery to produce more water from the plant.

**Table 1: Conditions for Economic Analysis**

Water Salinity	36,000 ppm
Recovery	40%
Temperature	30° C
Energy Cost	\$0.10 per kWh



**Figure 1: Cost of Water Analysis - Retrofit Scenario**

Changes to salinity, water temperature, and energy cost will affect both the absolute and relative cost savings of the different methods. The results showed that a doubling of membrane flux with constant rejection could be used in several operating modes to decrease energy cost, or increase system output. For moderate to low energy costs (shown above) the largest payback was observed for plants leveraging an increased system output, resulting in a 13% reduction in cost of water. For typical water tariffs this can translate into a doubling of the plant's cash flow.

## 1.2 Development of High Permeability SWRO Membranes

Several approaches have been used to improve the permeability of thin film composite (TFC) RO membranes. Simple variations in process conditions are capable of generating membranes with a range of performance typically varying from high rejection and low flux to lower rejection and higher flux [1,2]. In order to improve the permeability of brackish water membranes, producers have also looked at incorporating additives into the production process; for example, Koch has described polar solvents[3], Nitto Denko has mentioned alcohols[4], Toray refers to the use of aliphatic acids and esters[5], and Dow Filmtec teaches phosphorous-based complexing agents[6].

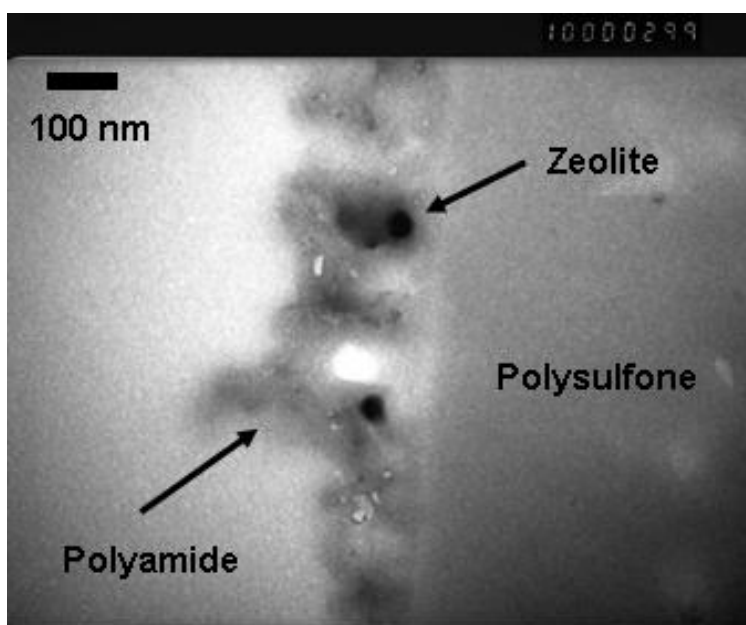
As these additives were discovered and commercialized into low energy brackish water reverse osmosis (BWRO) products, SWRO element permeability from the same producers remained at a relatively constant level. More recently, new SWRO products with improved permeability have appeared. The lack of new patent activity may indicate that some of these products use simple variations in processing

conditions to improve flux at the expense of rejection. Improved rejection for these high flux SWRO products along with increased fouling resistance would increase their market acceptance.

### 1.3 TFN Membrane Technology

As a way of overcoming material limitations for membranes used in gas separations, researchers have utilized composite materials comprising inorganic separating materials within a polymeric film [7,8,9]. This mixed matrix membrane approach allowed the improved selectivity of inorganic materials to be combined with the improved cost, handling, and manufacturability of polymeric materials. This approach has since been extended to pervaporation, ion exchange, and fuel cell membranes [10,11].

In 2007, the use of TFN membranes for water purification was first described for BWRO membranes [12]. These mixed matrix membranes used zeolite nanoparticles dispersed within a traditional polyamide thin film. 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 2: Cross-sectional Transmission Electron Microscope (TEM) Image of TFN membrane [12]**

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 development and optimization of TFN membrane technology for SWRO has resulted in an enhanced flux of more than double that of a 22.7 m<sup>3</sup>/d (6,000 gpd) commercial baseline with salt rejection at industry standards. In addition to discussing performance properties, this paper serves to discuss technical challenges related to the application of mixed matrix membrane technology to SWRO.

## II. MATERIALS AND METHODS

### 2.1 Flat-sheet Membrane Equipment

Testing of flat-sheet membranes was performed on stainless steel cells obtained from Naltex. Cells were used without a feed spacer (unless noted) and had an active area of 3 in<sup>2</sup>. Test benches, shown in Figure 3, 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.



Figure 3: Flat-sheet Cell Testing Bench

### 2.2 Membrane Fabrication

**2.2.1 Hand-cast membranes** – Membranes were prepared by a process widely described in the literature[2,12,13]. After preparation, membranes were refrigerated until testing. In all cases hand-cast membranes were tested within four days of synthesis.

### 2.3 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 degree 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 [14].

## 2.4 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).

## 2.5 TEM Analysis

Distribution of nanoparticles within the thin polymer layer was measured by firmly placing the wet membrane of interest on a TEM grid in a petri dish. Methylene chloride was then poured on the membrane until covered. The solvent dissolved the polysulfone membrane causing the polyester fabric to float to the surface. The wet membrane remained firmly attached to the glass bottom and TEM grid. After 15 minutes, the solvent was removed and a second volume of fresh methylene chloride was applied. After a second 15 minutes, the solvent was removed and the membrane dried at 40° C for 10 minutes. The TEM grid with the film attached was then removed and analyzed for nanoparticle distribution.

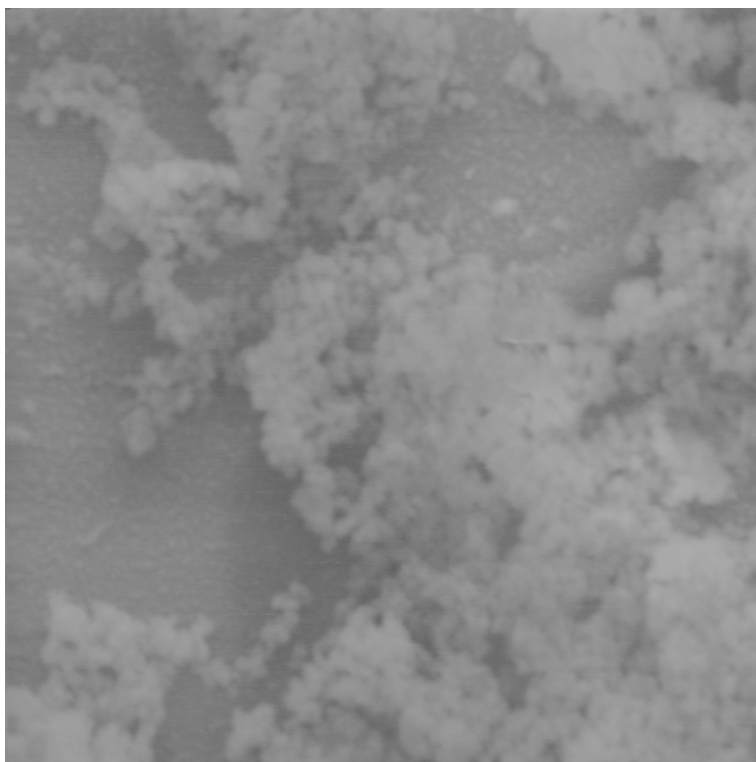
## 2.6 Acid, Base, Chlorine Stability Testing

Membrane samples were placed in jars containing one of the following solutions, NaOCl (10 ppm and 100 ppm), maleic acid buffer (pH 2), or phosphate buffer (pH 13) for the desired time period. During exposure, solution conditions were measured and adjusted as needed to maintain appropriate concentrations. After the exposure, membrane samples were rinsed and performance measured. Performance changes were used as a metric for membrane degradation. pH 2 soaks were conducted with a contact time of 1 week, pH 13 soaks were conducted with a contact time of 24 hours, and chlorine soaks were conducted with a variety of residence times at both concentrations. At each time point 6 membrane coupons were tested.

# III. RESULTS AND DISCUSSION

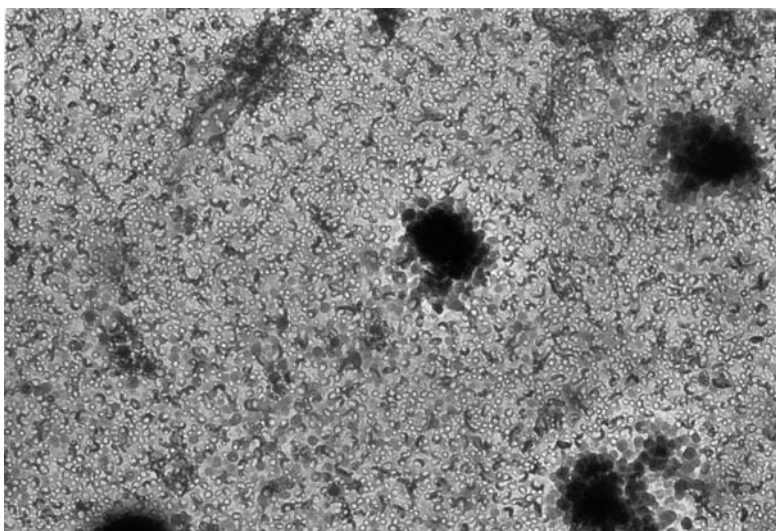
## 3.1 TFN Membrane Evolution

*3.1.1 Nanocomposite Membrane Development.* Development of TFN technology for SWRO involved the identification of several technical failure modes and subsequent method development to prevent and detect the onset of those failure modes. Figure 4 illustrates one such failure mode. Scanning electron microscope (SEM) imaging of this membrane reveals that nanoparticles have aggregated in the organic solution and deposited on the surface of the membrane. In contrast with the nanoparticles shown in Figure 2, this aggregate is not contained within the barrier layer, but rather sits on the surface. Although its appearance is similar to that of a fouling layer, its high porosity leads to minimal resistance to flow. However, the decreased concentration of nanoparticle incorporated within the film minimizes any permeability increase as shown in Table 2.



**Figure 4: SEM Image of Surface-aggregated Nanoparticles in Membrane B**

A second such failure mode illustrates another difficulty related to aggregation, but in this case smaller aggregates are formed that end up incorporated within the film. In Figure 5, a TEM image of the membrane show smaller aggregates contained within a TFN membrane.

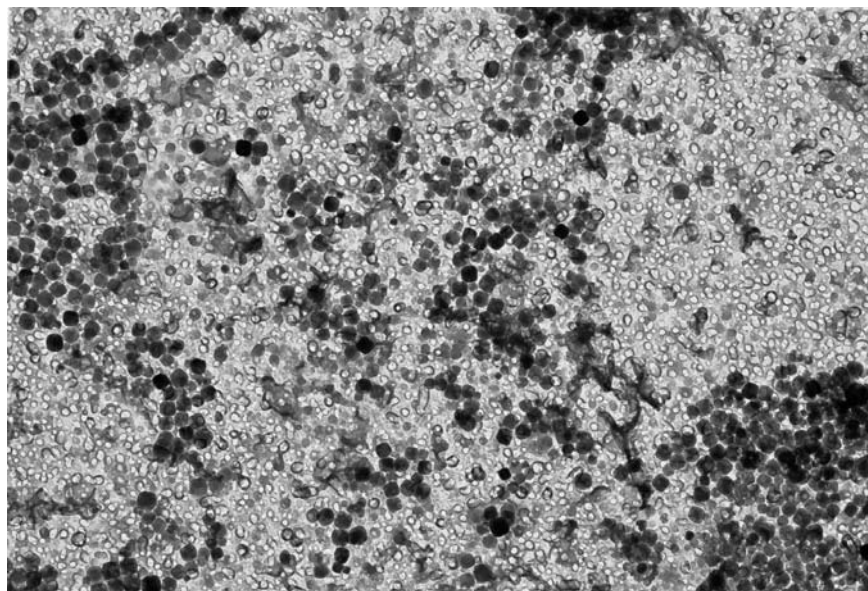


**Figure 5: TEM Image of Nanoparticle Aggregates in Membrane C**

Particle size distribution (from light scattering) reveals that the nanoparticles in the solution used to prepare this membrane were just over 1 micron. This indicates the aggregates were present in solution before being trapped with the forming polymer layer. Defects created by spaces between the

nanoparticles in these aggregates probably contribute to decreased salt rejection for this membrane (Table 2).

Improved solution preparation, for instance by increased sonication time and power (obtainable with a sonic probe), can be used to break up these aggregates. After appropriate preparation, the solution used to prepare the membrane in Figure 6 had a mean size measured by light scattering of ~100 nm, the diameter of the nanoparticles as synthesized.



**Figure 6: SEM of well-dispersed nanoparticles in membrane D**

The membrane in Figure 6 shows a much improved distribution of nanoparticles with high areal incorporation, few aggregates, and little surface coverage. Membrane E in Table 2 lists the performance.

Once protocols were established preventing such problems for occurring, proper selection of nanoparticle type was found to allow the production of TFN membranes having good performance (membrane E in table 2).

**Table 2: Membrane Performance**

<b>Membrane</b>	<b>Flux</b>	<b>Rejection</b>
A. Control- No nanoparticles	18.9 ( $\pm 4.1$ )	99.66% ( $\pm 0.11\%$ )
B. Surface aggregated nanoparticles	19.5 ( $\pm 0.42$ )	99.22 ( $\pm 0.23\%$ )
C. Smaller incorporated aggregates	25.6 ( $\pm 1.3$ )	98.37 ( $\pm 0.02\%$ )
D. Well-dispersed nanoparticles	27.5 ( $\pm 0.34$ )	99.37 ( $\pm 0.01\%$ )
E. Optimized nanoparticle selection	34.2 ( $\pm 2.7$ )	99.65 ( $\pm 0.01\%$ )
F. Shifting process parameters	39.7 ( $\pm 0.64$ )	99.51 ( $\pm 0.01\%$ )

As is found with traditional SWRO production, processing conditions (such as concentrations, temperatures, solvents) are capable of shifting performance of the TFN membranes. The final data point illustrates this; the same nanoparticle was used for the last two membranes (E and F), but increased flux



achieved at the expense of a small rejection penalty was achieved through the modification of processing conditions.

### 3.2 TFN Membrane Performance

**3.2.1 Competitive Performance.** To determine the relative performance of TFN membranes longer-term flat-sheet tests were performed against commercial products. These tests were performed with the TFN membranes and a competitive high flux seawater membrane (equivalent to that used in 9000 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) lead 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.

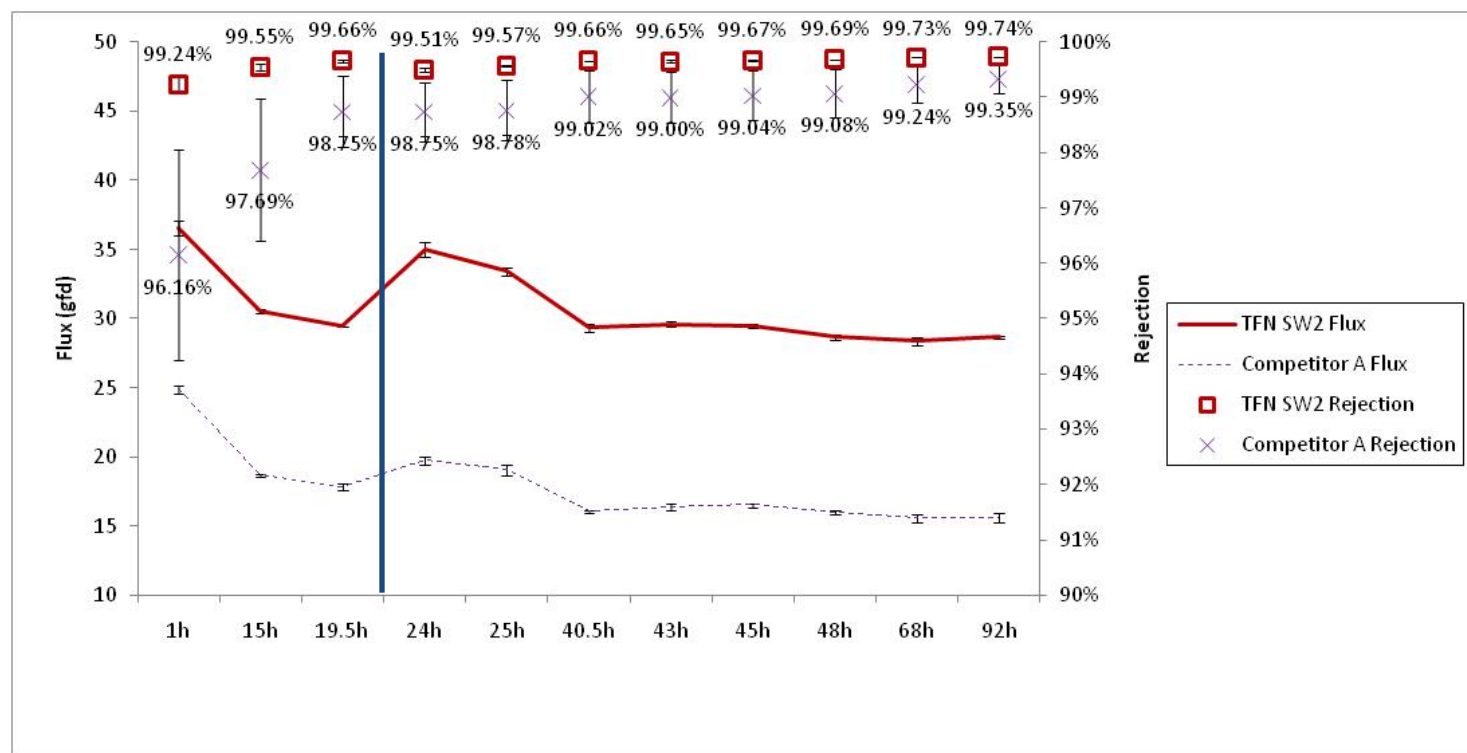


Figure 7: TFN Membrane Performance vs. Competitor A

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.

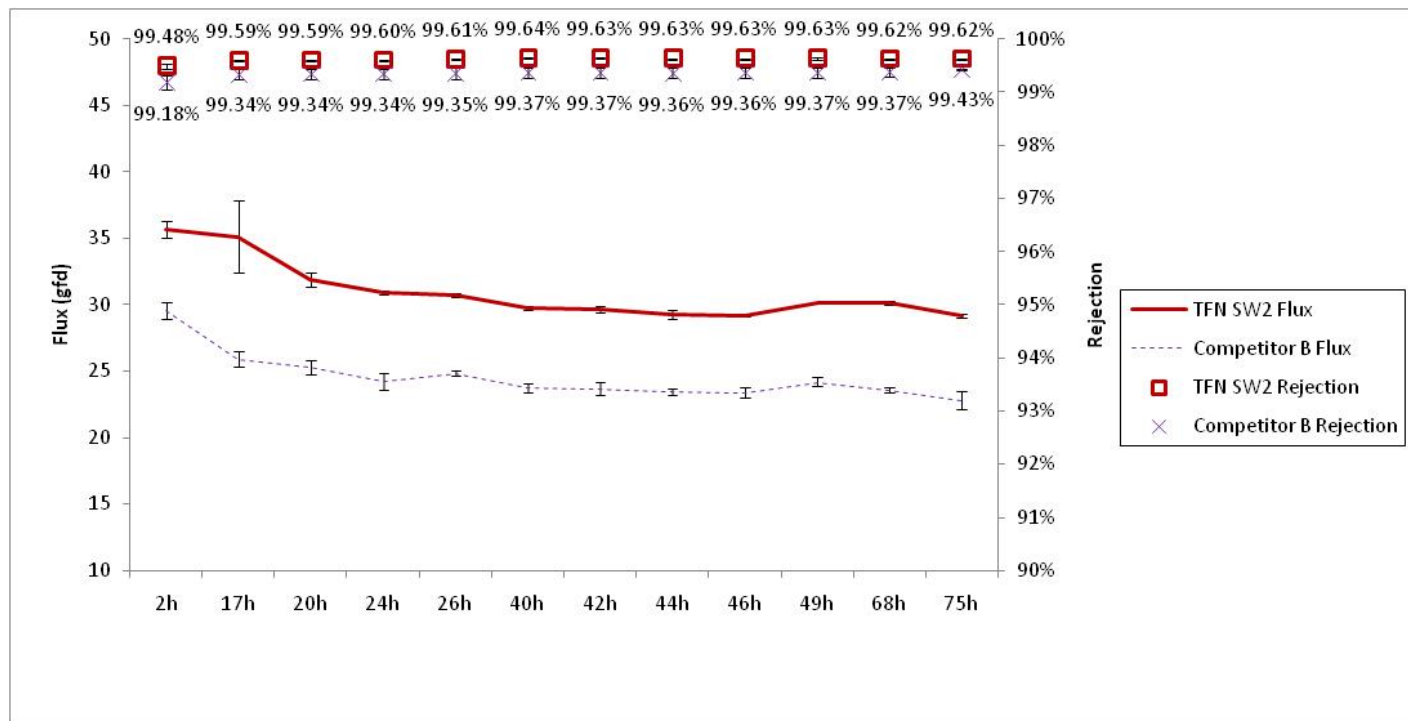
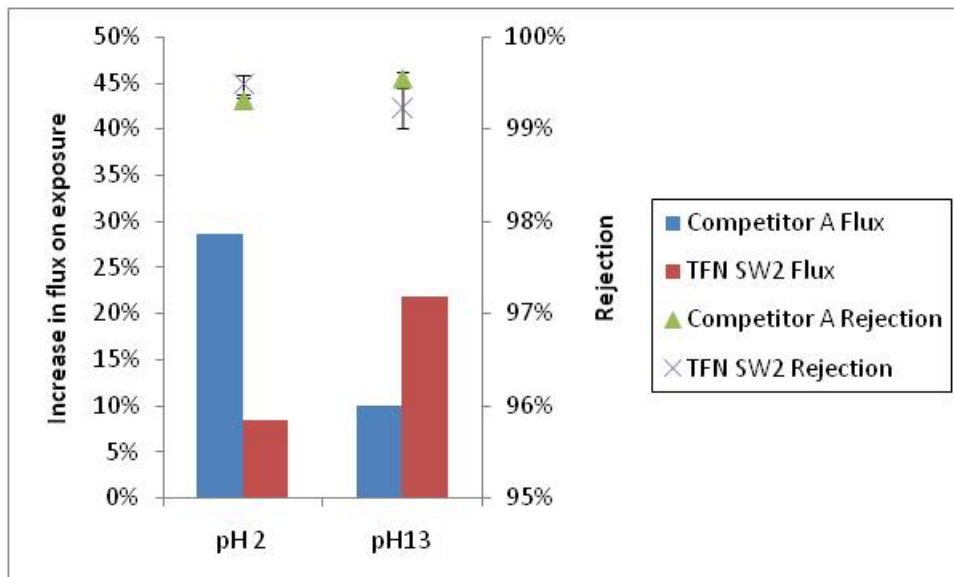


Figure 8: TFN Membrane Performance vs. Competitor B

### 3.3 Stability at High and Low pH

A common concern with the introduction of new membrane materials is the stability to chemical agents that may be encountered during operation. To address this concern membrane stability was measured using static soaks.

Testing after a pH 2 soak for 1 week revealed a small change in performance for both membranes. Figure 9 shows that after exposure the TFN membrane had experienced an 8.3% increase in flux and had a final rejection of 99.5%. The competitive product experienced a larger 28.5% increase in flux and had a final rejection of 99.3%. This shows a slightly improved acid tolerance for the TFN membrane.



**Figure 9: Membrane Performance after High and Low pH Soaks**

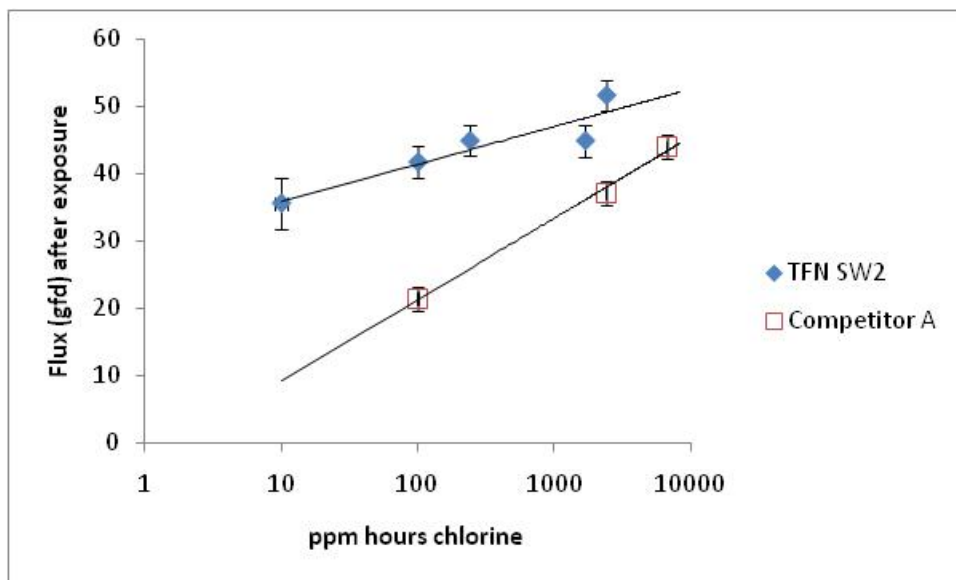
Testing after the pH 13 soak showed the opposite response, with the TFN membrane increasing 21.9% with the competitive product increasing 9.9%. Rejection for the TFN was also lower for the high pH exposure at 99.2%; the competitive product ended the high pH soak at 99.5%.

Slight shifts in acid and base stability are reported among products from various commercial manufacturers; posted operating ranges for cleanings vary from pH 1-2.5 for acidic cleanings and between pH 11-13 for high pH cleaning depending on the specific manufacturer. These differences may result from variations in manufacturing processes.

### 3.4 Chlorine Stability

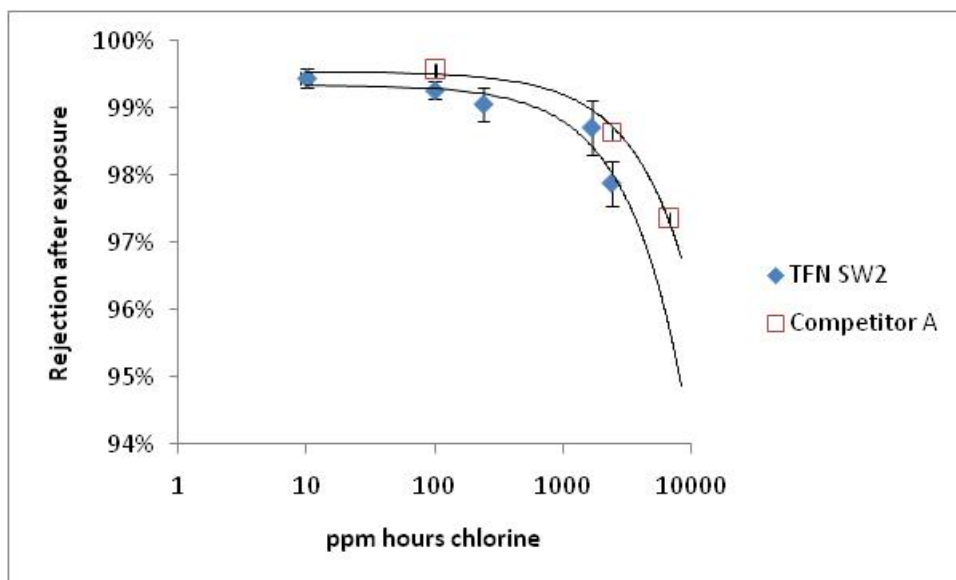
The degradation of polyamide membranes during exposure to chlorine has been well documented; the analysis in this study was performed to determine if introduction of thin film nanocomposite technology would affect such stability. Figures 10 and 11 show membrane performance as a function of chlorine exposure. In both of these figures a data point at 1680 ppm hours was removed for the competitor product. Because of the reasonable performance of the sample at 2400 ppm hours and 6720 ppm hours, it appears to have suffered a premature failure with 46.8 gfd and 96.9% rejection.

Figure 10 shows the trend of flux with exposure time. The increased slope of the flux versus log exposure for the competitive product may indicate a slight improvement in TFN stability, but more data would be required to more fully explore any such difference.



**Figure 10: Membrane Flux after NaOCl Exposure**

Figure 11 shows a similar plot of rejection performance. Despite the differences in flux shown in figure 10 both membranes are clearly sensitive to chlorine and after exposure to ~1000 ppm hours rejection have fallen to levels unacceptable for seawater desalination.



**Figure 11: Membrane Rejection after NaOCl Exposure**

These changes in flux and rejection appear consistent with current polyamide membrane performance and no increased degradation has been observed. TFN membranes are expected to require similar dechlorination, where applicable.

## IV. CONCLUSIONS

Performance and economic modeling were used to show the reduced water cost resulting from SWRO membranes having improved permeability without any increase in salt passage. The water cost reduction can either come from energy savings because of operation at lower pressures or from increased water output from a plant running at increased flux and recovery. Such performance improvement can be achieved through the proper incorporation of nanoparticles within interfacially formed TFN membranes.

TFN membrane performance is sensitive to the production process used and prevention of nanoparticle aggregation is essential to optimal performance. Electron microscopy is well suited to diagnosing aggregation problems that can affect performance. Although surface aggregation appears not to degrade performance, it does little to increase performance as fewer nanoparticles are incorporated in the polymer film itself. Aggregates contained within the film can result in increased passage through the creation of film defects between the nanoparticles making up the aggregates. Nanoparticle selection also has a strong effect on the final membrane performance.

Optimized TFN membranes were compared with current commercial high flux SWRO products and found to have improved flux with slightly improved rejection. Online stability with time appears comparable to commercial products despite operation at high flux, and some early indications of improved cleanability are present.

In the last 20 months, industrial research into nanocomposite RO membranes has resulted in the development of a new mixed matrix membrane material for 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 an early 2010 product release.

## V. ACKNOWLEDGEMENTS

Thanks to Chris Haussman, Tom Wolfe, and Bill Bourcier for economic and performance modeling.

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