HIGH FLUX, FOULING RESISTANT MEMBRANES FOR RO PRETREATMENT

Final Report - May 31, 2012

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High Flux, Fouling Resistant Membranes for RO Pretreatment, contract number N00014-10-C-0224. The purpose of the contract is to develop pretreatment membranes that improve the desalination process onboard ships. In the case of pretreatment, this means extending the life of the RO membranes and improving the reliability (uptime) of the desalination process. The scope of the contract as proposed by PoroGen and Clean Membranes is to develop a fouling resistant, hollow-fiber, ultrafiltration membrane. Hollow fiber membrane module based on PAN-g-PEO technology was successfully developed in the course of this program. Superior anti-fouling operational characteristics were demonstrated.

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Abstract

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The PoroGen team included Messrs. Jim Macheras and Dean Gates who provided fiber and module development support, and Ms. Joyce Nelson and Dr. Yong Ding who conducted composite membrane development.

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Project Objective

Current Navy desalination technology utilizes the Navy Standard Reverse Osmosis unit (NSRO) where cartridge filters are the pretreatment prior to single pass reverse osmosis. The NSRO system was designed in the 1980's for mainly open ocean use and expected RO membrane life of 3-5 years. Now that the ship deployments are closer to shore and the pollutants are moving further out to sea, actual membrane life is reduced to as little as 4-8 weeks when in turbid waters. This affects current operations by requiring frequent and costly membrane replacement, leads to reduced reliability, increases maintenance and the space requirements to store replacement modules.

Pretreatment prior to the reverse osmosis membranes is a standard practice in industrial applications to extend the reliability and life of the RO. However, current commercial ultrafiltration (UF) and microfiltration (MF) membranes used for RO pre-treatment are inadequate and subject to fouling by particulates, organics and other dissolved components. The filters are irreversibly fouled, resulting in a dramatic decline in flux requiring frequent cleaning, maintenance, and down time. The build-up and deposit of dissolved and suspended solutes near and onto the membrane surface, termed concentration polarization, is another serious limitation that also aggravates fouling.

Contract number N00014-10-C-0224 is a joint project between Clean Membranes and PoroGen. The project objective is to develop low-maintenance, high-flux, low-fouling water filtration modules for reverse osmosis (RO) pre-treatment in order to improve the desalination process onboard ships. Membrane modules developed in this project promise to exhibit improved flux and fouling resistance. This in turn will lead to more compact and efficient filtration systems that reduce maintenance and downtime, costs and energy requirements.

The project brought together the unique capabilities of PoroGen and Clean Membranes. PoroGen provides state-of-the-art hollow fiber membrane and module development expertise that will be combined with Clean Membranes' high flux, fouling resistant membrane technology developed at MIT.

Clean Membranes technology employs combination of PAN and PAN-g-PEO co-polymer. The hydrophobic backbone of PAN and the hydrophilic nature of the PAN-g-PEO co-polymer provide a strong porous membrane that resists fouling by repelling the pollutants and preventing adsorption of foulants. During the course of this project we will scale-up the technology and manufacture a hollow-fiber module that may be used for pretreatment to the reverse osmosis unit in the Navy desalination system.

Project Approach

PAN-g-PEO synthesis

To produce the PAN-g-PEO copolymer all reagents were purchased from Aldrich and used without further purification. Polyacrylonitrile-graft-poly(ethylene oxide) (PAN-g-PEO) was synthesized by free radical polymerization. PEO content of the copolymer was determined by 1H nuclear magnetic resonance (NMR) spectroscopy in deuterated DMSO. The molecular weight distribution of the polymer was determined by gel permeation chromatography in DMF.

Flat Sheet Membrane Casting and Testing

As a model system to characterize starting materials, flat sheets were prepared prior to hollow fiber spinning. Flat sheet membranes were cast following the procedure described in Asatekin *et al., Journal of Membrane Science*, 298 (2007) 136-146. Flat sheet membrane performance is evaluated by measuring flux and rejection as described in the previous report.

The use of surrogate soluble polymers is an industry wide standard procedure for membrane performance evaluation. The polymer marker selection is carried out to provide good representation of foulants encountered in actual sea water. Basic performance criteria used during development included water flux and retention of bovine serum albumin (BSA) as a benchmark of pore size, and resistance to protein fouling by BSA filtration.

Hollow Fiber Development and Testing

Hollow fibers were produced by a generally accepted hollow fiber membrane manufacturing process – a dry-wet spinning process. Initial development was performed on a pilot-scale spinning system; during the course of the project, the system was augmented to allow for higher fiber production volume required to supply high-fiber-count modules.

Working from initial flat sheet results, a hollow fiber formulation was developed and production procedures were optimized to satisfy the requirements of hollow fiber production processes. Design parameters included solvent selection, polymer content and ratios, non-solvent additives including pore forming agents, surfactants, and rheological modifiers; fiber spinning procedures were also optimized through adjustments including spin dope rate and temperature, bore fluid selection and rates, spinneret dimensions, and coagulation bath temperature and composition.

The resulting hollow fibers were primarily tested using a ‘dead-end’ testing methodology described by the following: Three to four fibers are cut to 45 cm length and potted in polyethylene tubing using low temperature adhesive (3M 3972LM). Potted fibers were soaked in water to remove residual preservatives. Fiber modules were attached to the test rig and water was then applied at the specified pressure, and allowed to equilibrate for 20 minutes. During each test, filtrate was collected for a specified time and the mass of the filtrate was measured. Two or more replicate segments were tested from each membrane sample. From these results, promising fiber samples were then down-selected, with fibers assembled into tangential-flow modules for further characterization. A bench-scale tangential-flow test system was acquired and is described in further detail in the following section.

Module Design, Construction, and Testing

Module design was initially targeted for a demonstration module for evaluation at Port Hueneme under condition of 5-10 gpm flows. As the project commenced, the project team learned that the US Bureau of Reclamation would be able to provide testing on an existing system capable of 1 gpm flow. Prototype modules were developed and constructed with primary consideration given to reliable and robust functional results. Modules were then tested under tangential flow conditions with a variety of feed streams and operating conditions to characterize performance.

Additional Work

An additional configuration was explored to learn if the PAN-g-PEO material could be applied as a coating to form a composite membrane upon a porous PEEK substrate. While the application of material was successful, the resultant fiber flux was insufficient to meet commercial requirements. Based on these results, the integral fiber approach was down-selected.

Work Completed

Task 1: Material Preparation and Scale Up of PAN-g-PEO Co-polymer

Synthesis and use of the underlying chemistry is suitable for industrially relevant polymerization processes. Materials were produced and shown to have suitable characteristics and performance for making PAN-g-PEO based membranes. Results from the scale-up process were consistent with research-based laboratory results. It was demonstrated that the PAN-g-PEO polymer can be produced on commercial scale.

Task 2: Hollow Fiber Membrane Development

Throughout this task of the project, efforts were focused on optimizing hollow fiber preparation procedures and performance. Satisfactory results were obtained for a hollow fiber for use in the prototype module construction. The polymer system includes solvent and non-solvent additives that have produced a fiber of acceptable performance, durability, and fouling resistance. Several commercial PAN polymer grades were evaluated for compatibility with PAN-g-PEO, for acceptable mechanical characteristics, and flux, retention, and fouling-resistance. A final PAN grade was down-selected.

A spinning line was constructed consisting of polymer solution and bore fluid delivery systems including pumps, filters and metering control equipment, spinneret, coagulation tank and related take up equipment.

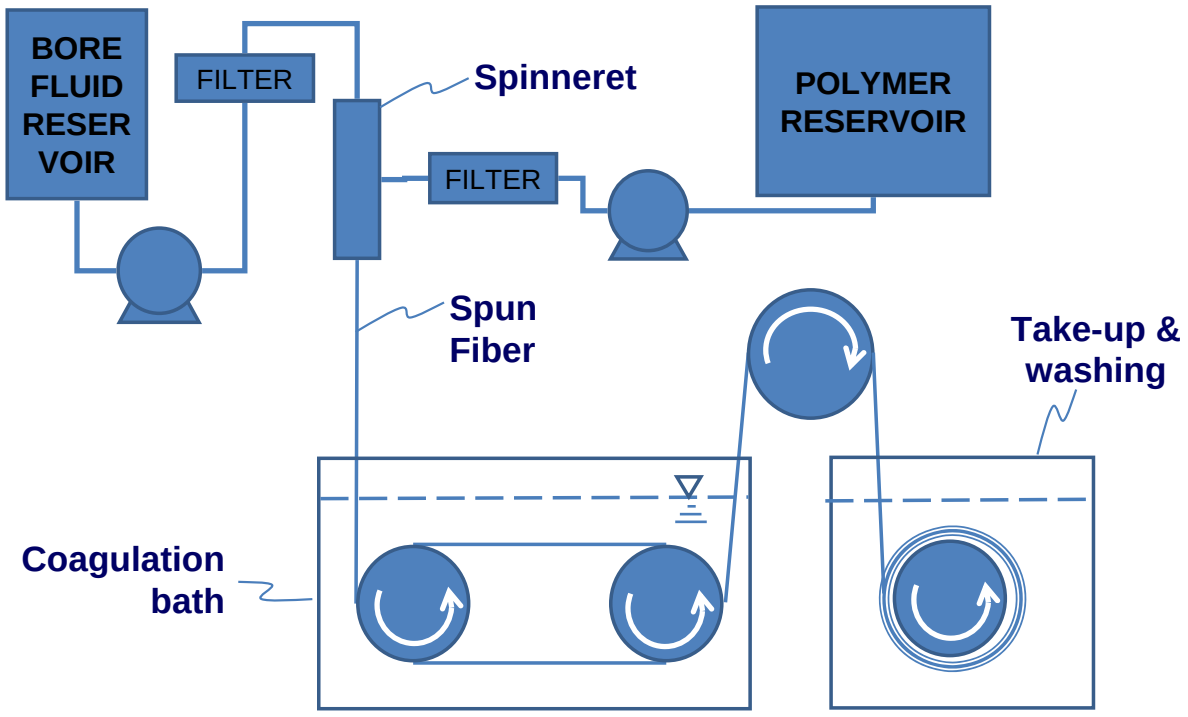

Figure 1. Schematic of dry-wet spinning equipment

The dry-wet spinning line was progressively reconfigured for spinning of PAN-g-PEO/PAN blends. Modifications were required to adjust for spin dope viscosity, coagulation profile, spinning solution and

coagulation bath temperatures. Several iterations in hardware design were required as the spinning dope formulations were progressively modified.

A view of a portion of the spinning process where the polymer dope is cast into the coagulation bath is shown in Figure 2.

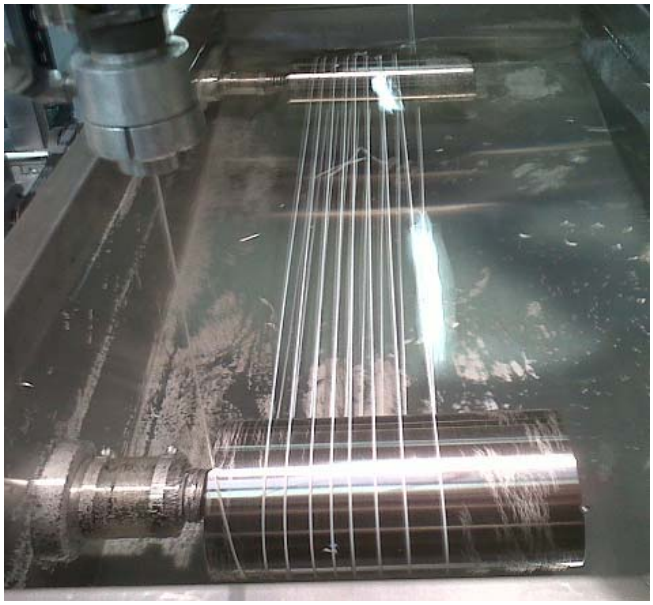

Figure 2. Coagulation Bath

Multiple hollow fiber runs were conducted to optimize fiber morphology and performance. Initial optimization was focused on spin line process parameters. Hollow fibers were produced utilizing a matrix of spinning experiments that included spinning temperature, air gap and draw ratio. Following these optimization steps, a series of water permeable PAN hollow-fiber membranes were produced. These membranes had sufficient mechanical strength to be shaped into test modules.

Membranes were then produced from PAN/PAN-g-PEO co-polymer blends. Polymer solutions solids content was formulated to obtain a high viscosity spinning dope for processing while producing the desired porosity and flux. Further optimization of spinning dope formulations included addition of non-solvents to spin dope composition. Solvents systems that generated compatible blends at high polymer concentrations were down-selected. Solvents screened included DMF (dimethyl formamide), NMP (*N*-methyl-2-pyrrolidone), and DMSO (dimethyl sulfoxide). NMP based formulations were ultimately down-selected as they were shown to produce the most reliable overall performance.

Task 3: Hollow Fiber Membrane Performance Testing

Lab space was allocated and lab test systems constructed to conduct membrane performance evaluation in support of membrane development. The lab equipment was designed to accommodate flat sheet membranes as well as hollow fibers.

The equipment used for initial screening and characterization of fiber samples consists of three elements as shown in Figure 3. The feed assembly is used in all tests, whereas two modules, one for flat sheet membrane testing and the other for hollow fibers, can be exchanged easily with quick release connections. The feed assembly included an air compressor equipped with a pressure regulator to pressurize feed liquid (i.e. water or model foulant solutions) contained in a dispensing reservoir. A feed pressure of 10 psig was used throughout the evaluation testing of UF membranes. The system was equipped to handle industrially relevant feed pressures.

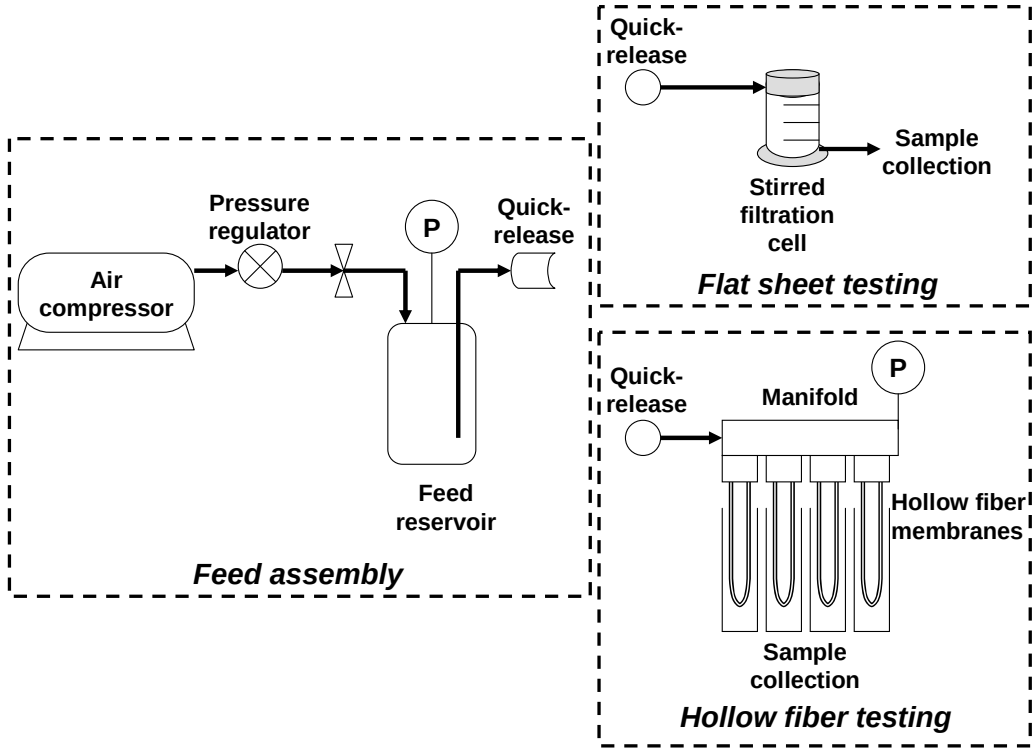

Figure 3. Schematic of 'dead-end' membrane test equipment

Flat sheet testing was utilized initially in membrane development because the PAN/PAN-g-PEO blends for UF membrane preparation were well characterized in the flat sheet format. Previous peer reviewed publications have documented performance of these membranes as well as the influence of some casting parameters (blend composition, copolymer composition) on membrane performance. Hence, preliminary testing of flat sheets was an important benchmark in evaluating specific casting parameters, variations in materials such as the grade/purity/manufacturer of PAN, PAN-g-PEO, solvents and other additives. Flat sheet testing was done using a dead-end stirred cell, manufactured by Millipore (Amicon model 8010) attached to this feed assembly. Hollow fiber module testing was performed on a four-position manifold.

The flat sheet tests were aimed to confirm that materials synthesized on commercial scale met the desired high flux and protein fouling resistance, indicative of proper membrane morphology and brush structure as shown in previous studies on flat sheet membranes (Asatekin 2007, Kang 2007). Protein fouling experiments

were also indicative of fouling resistance to other feeds, such as bacteria suspensions (Adout 2010) and oily wastewater (Asatekin 2009).

Flat sheet membranes were cast from blends of commercial grade PAN and PAN-g-PEO synthesized in commercial sized batches following the procedure described in Asatekin *et al.*, *Journal of Membrane Science*, 298 (2007) 136-146. The resultant membranes appeared physically very similar to membranes cast from research grade PAN and small-batch PAN-g-PEO.

A major milestone achieved: the industrial grade raw materials generated membranes with performance comparable to membranes produced from laboratory grade materials used in MIT lab studies. This result is crucial for high volume manufacture, as high purity, high cost research grade ingredients would be cost-prohibitive. Key performance metrics of this study were the high membrane flux (up to 1500 L/m2.h.MPa) (Asatekin 2007) and complete resistance to irreversible protein fouling, as evidenced by complete flux recovery following a water rinse.

The results verified *the superior performance of PAN/ PAN-g-PEO blend membranes when manufactured with commercial grade raw materials.* The data also confirms that commercial production of PAN-g-PEO was successful. The kg-scale batch manufactured satisfies not only the preliminary parameters of composition, molecular weight and purity, but also produces high-performance, fouling resistant membranes.

As a screening tool, static fouling experiments were employed. The modules were prepared in a dead-end flow configuration. In the first step, pure water flux through the membrane was measured; in the second step, membranes were challenged with a protein solution; and finally the water flux was measured again after a brief water rinse. Fibers were also characterized for handling characteristics and mechanical durability. In-process samples were initially used to evaluate the hollow-fiber spinning setup, but ultimately to demonstrate the efficacy of the casting process and proper fiber morphology and UF performance. To evaluate fiber morphology and porosity, hollow fibers were freeze-fractured in liquid nitrogen, and imaged by SEM. Hollow fiber morphology of an experimental fiber is shown in Figure 4.

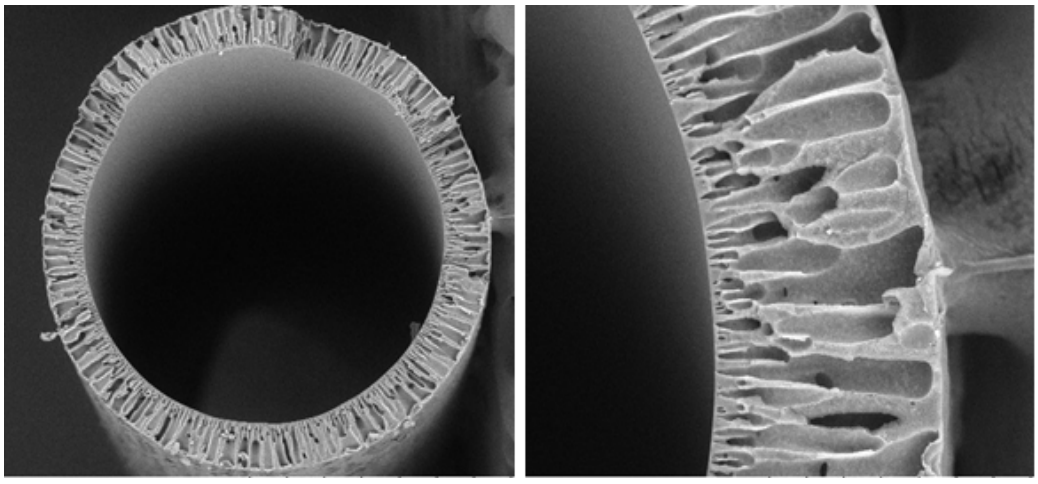

Figure 4. Hollow Fiber Cross Section

Membrane performance was further characterized in a bench-scale tangential-flow filtration system, as shown in Figure 5. The tests supported optimum module development, as well as development of operational protocol. Prototype modules were evaluated utilizing this tangential flow system with feed flow rates up to 2 liters per minute corresponding to shear rates on the order of 4000 sec^{-1}.

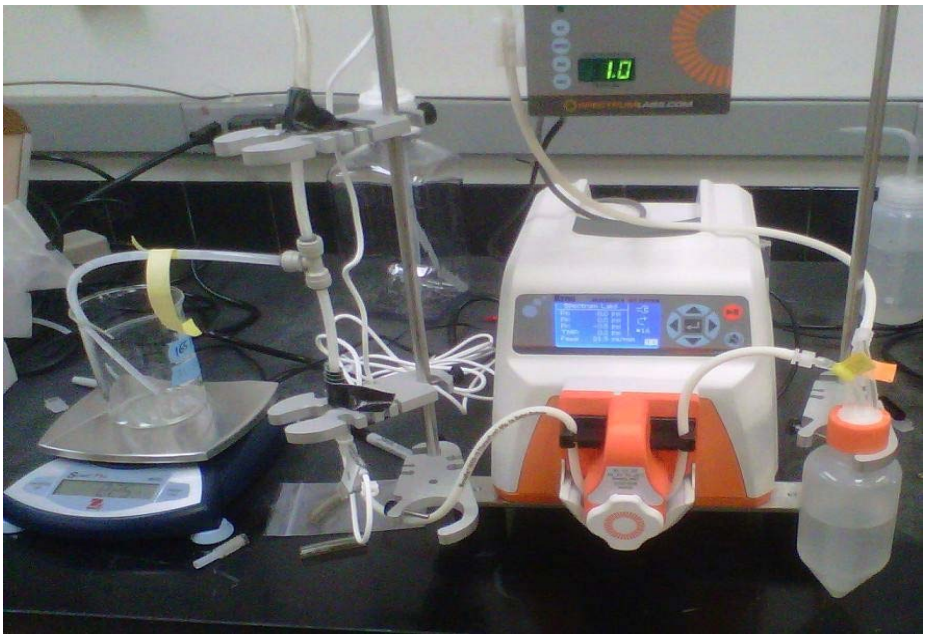

Figure 5. Bench-scale tangential flow test system

Final tests of the evaluation modules were conducted under conditions that approximated the target application's flows, pressures, and temperatures.

Task 4: Composite Membrane Development

Composite membranes based on PAN-g-PEO separation layer and porous PEEK hollow fiber substrate were prepared. The casting line for composite membrane preparation available at PoroGen was reconfigured to accommodate PAN-g-PEO solvent system characteristics.

Strong composite PAN-g-PEO hollow fibers were produced utilizing porous PEEK hollow fiber as a substrate. However, the composite PAN-g-PEO membrane flux was low and did not meet program objectives. Although the performance could be improved by further optimization and development efforts, this task was discontinued and fabrication of membranes by integral dry-wet spinning process was down-selected.

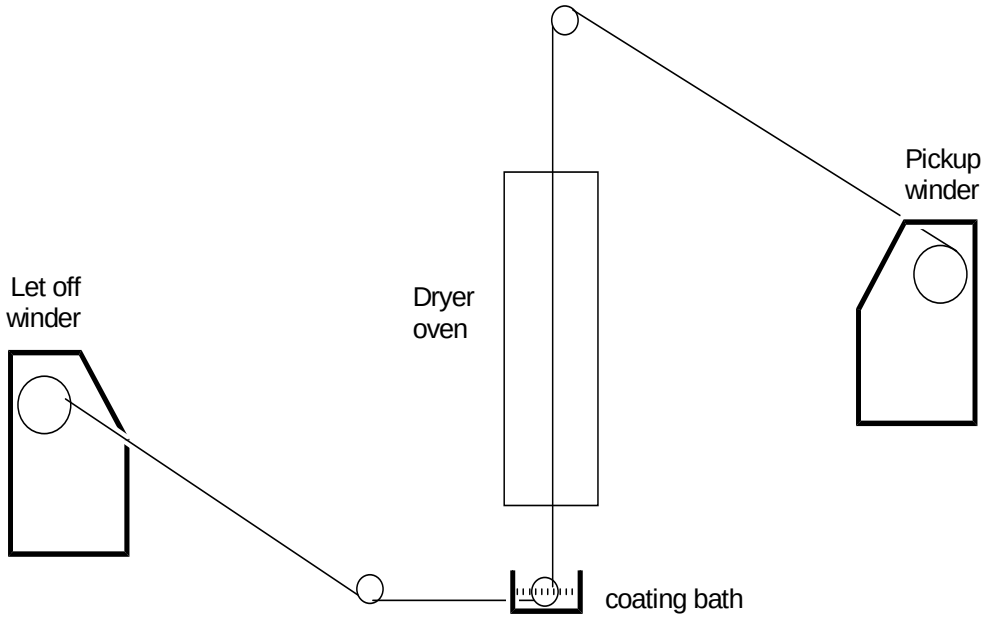

Figure 6. Coating line assembly for preparation of composite hollow fiber

Tasks 5 and 6: Module Design and Prototype Construction

During the course of the project, the team learned that the test platform for the evaluation phase of the project would be provided by the Bureau of Reclamation in Denver, Colorado. The module size was chosen for compatibility with the Bureau of Reclamation system's flow capability. Several modules, with 1.25" nominal diameter and 20" effective length, were prepared and integrity tested. Test runs with several challenge feed solutions were conducted to characterize module performance, as well to develop a valid operational protocol. A representative module is shown in Figure 7, below.

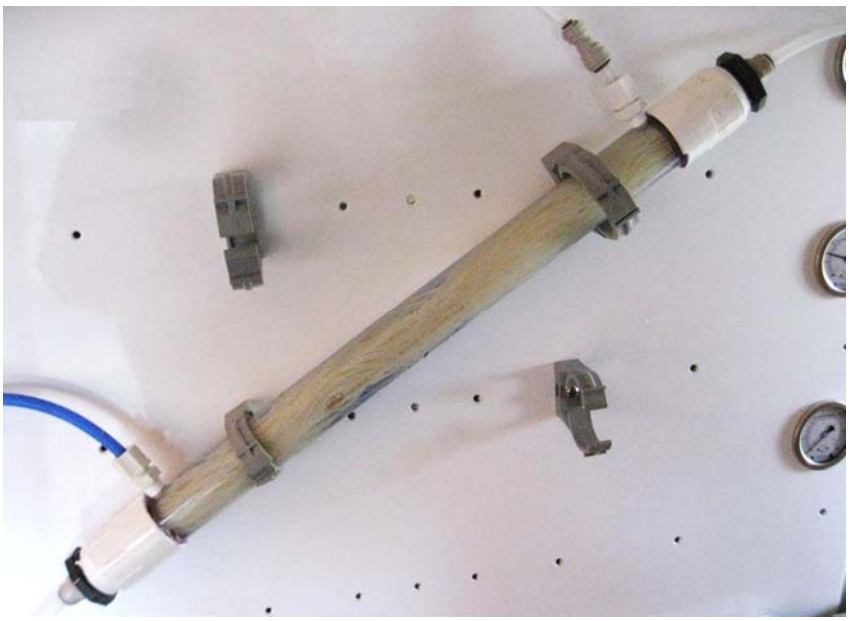

Figure 7. Module to accommodate 1 gallon/minute USBR test platform

Results

Synthesis of PAN-g-PEO at kg-scale quantities

The first task of this project was scale-up of PAN-g-PEO synthesis at quantities relevant to industrial production. Until the start of this project, PAN-g-PEO was synthesized in lab scale, at quantities ranging between 5-200 g. This synthesis involved several lab practices that are not easily applied when reactions are performed in commercial scale. The large scale synthesis of PAN-g-PEO was performed successfully as part of this project, with alterations to the synthesis process (e.g. adjusted initiator concentration, reactor configuration). Two 1-kg batches of PAN-g-PEO were synthesized. Key polymer properties of these two batches are given in Table 1.

Table 1. PAN-g-PEO polymer properties

Batch	**1**	**2**
PEO acrylate content (wt%)	49.4	50.3
Number average molecular weight (M_n) (kg/mol)	780	886
Weight average molecular weight (M_w) (kg/mol)	1140	1130
Polydispersity index (PDI)	1.5	1.3

The key polymer properties of both batches were well within specs (defined as PEO acrylate content 50 ± 2 wt%, number averaged molecular weight (M_n) > 40 kg/mol). The similarity in the composition and M_w of the two batches also showed that large scale synthesis of PAN-*g*-PEO can be performed in a reproducible and repeatable manner, which is critical for commercial success of membrane technology.

Membrane development

To identify optimal conditions for the manufacture of PAN/PAN-g-PEO blend hollow fiber membranes, a pilot scale dry-wet spinning system was constructed. Batches of hollow fiber membranes were formulated, spun, and evaluated. Key parameters investigated in the optimization process, included solvent selection, polymer and additive concentrations, spinning parameters, annealing process, and preservation and drying processes.

Seventy-five batches of fiber were spun as part of this project. The resultant hollow fiber membranes were characterized in filtration experiments for pure water permeability, protein retention, and fouling resistance. Physical and mechanical properties were also evaluated. In addition, the membranes were characterized by scanning electron microscopy, and the morphology of the fibers was correlated with spinning process parameters.

The final formulation was down-selected to produce fibers with a combination of high retention, mechanical robustness, high fouling resistance, as well as good flux. The fibers manufactured by down-selected procedures were used for the development of module manufacturing methods and for testing on-site and at the US Bureau of Reclamation.

An SEM micrograph of a representative hollow fiber is shown in Figure 8. The membrane has a well-centered bore, continuous selective layer on its inner surface, with macrovoids (also known as finger-like structures) filling the bulk of the hollow fiber wall. This morphology is an important feature, as it gives the membrane mechanical integrity with low hydraulic resistance, resulting in a high permeability. The membrane also exhibits a thin skin layer on its outer surface, supported by smaller macrovoids. While this can cause a lower permeability, it also provides for improved mechanical properties, crucial for successful manufacture of modules and for a reliable long-term operation.

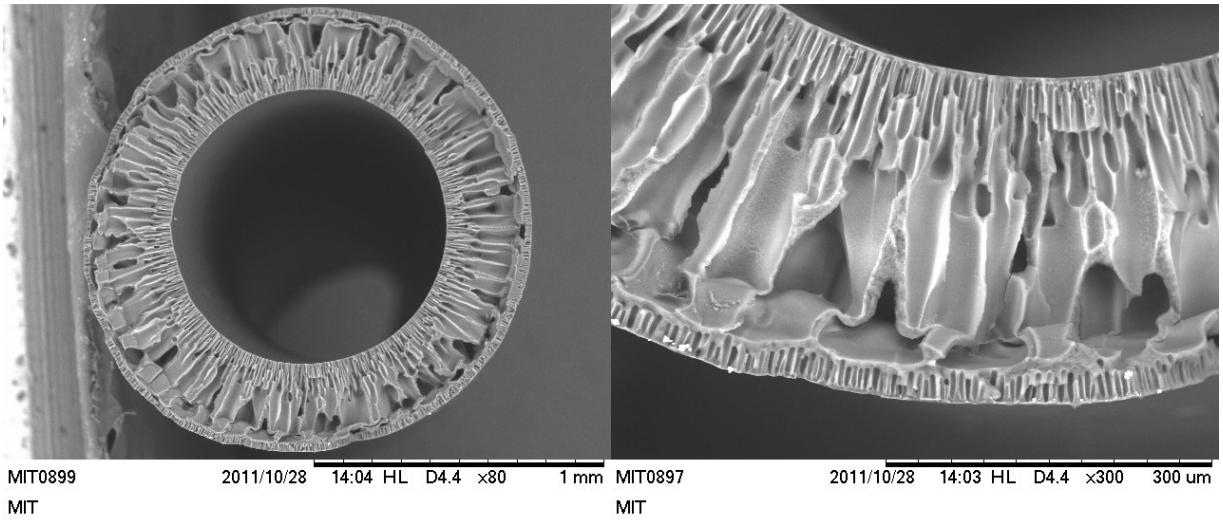

Figure 8. Cross-sectional SEM micrographs of PAN/PAN-g-PEO blend hollow fiber membrane

Performance data for a representative batch of fiber is given in Table *2*.

Table 2. Performance data for final batch of PAN/PAN-g-PEO blend hollow fiber membrane

Pure water permeability (L/m^2 h MPa)	695
Bovine serum albumin (BSA) rejection (%)	95%
Estimated molecular weight cut-off (Da)	~30,000 – 40,000

The hollow fiber membrane molecular weight cut-off (MWCO) of 30,000-40,000 Daltons is sufficient to effectively remove organic foulants in seawater, while maintaining a high flux. Organic foulants commonly found in seawater include humic substances and alginates in a range of molecular weights, from short oligomers to very long chains, depending on source. However, it has been shown that humic substances aggregate to form large clusters of molecules with effective molecular weights well over 1,000,000 Da (Costa, 2006; Asatekin, 2006). Alginates also have a similar tendency to aggregate, especially in the presence of calcium ions, which complex with carboxylic acid groups in alginates and humic acids (Ye 2005). Therefore, the molecular weight cutoff selected for hollow fiber membrane is expected to effectively remove foulants that would affect RO membrane performance and thus would act as an efficient pretreatment process for ship-board desalination units.

Module Development

Module development was originally targeted to a 4" diameter assembly sized for the expected evaluation system to be located in Port Hueneme. As the project commenced, the team learned that the test platform for the evaluation phase of the project would be provided by the Bureau of Reclamation in Denver, Colorado. A module design was chosen that would be compatible with this system's flow capability. The final module design comprised 1.25" diameter by 20" long housing containing circa 100 fibers potted in an epoxy compound tube sheet. A number of modules were assembled per this design and evaluated.

Module Testing

Module performance evaluation included testing at Clean Membranes and at the US Bureau of Reclamation.

Initial tests were performed with a formulation developed at the USBR that simulates seawater. This solution contains 3.2% sea salt, 75 mg/l blue-green algae powder, and 20 mg/l Orchid Pro plant food containing humic and fulvic organics (Chapman 2011).

The recipe contains key components that were identified as foulants in surface and sea water. One significant source of membrane fouling is natural organic matter (NOM), which consist of organic components formed by decomposition of dead organisms (often termed humus) and carried to surface and seawater with rain water drainage. The most important components of NOM are humic and fulvic acids. Another important organic foulant is alginates, which are polysaccharides secreted by microorganisms such as algea and bacteria. Finally, particulates and microorganisms contribute to fouling, especially by forming a cake layer. In this simulated seawater formulation, NOM components are introduced by Orchid Pro, which is a plant food formulation made from humus deposits. Blue-green algae is used as a source of alginates and microrganism cells. Finally, bentonite clay introduces particulates. The formulation also includes sea salt at a concentration similar to seawater. Salinity can have significant effect on fouling, as high ionic strengths can shield membrane surface charge, which can otherwise limit fouling by like-charged foulants. As such, the formulation developed at the USBR provides a composition representative of littoral seawater feeds.

Module Testing at Clean Membranes

The first set of tests on a target module were performed in a cross-flow mode at three different levels of cross flow velocity, with each test run at a constant trans-membrane pressure (TMP) of 12 psi. Membrane permeance and flux are two main parameters that were monitored throughout filtration tests. Flux J [L/m^2.h (LMH) or gal/ft^2.day (gfd)] through a membrane is defined as

$$J = Q/A \qquad \textit{(Eq 1)}$$

where Q is the volumetric flow rate through the membrane [L/h or gal/day], and A is the available surface area of the membrane [m^2 or ft^2]. For clean water, the flux through a membrane is directly proportional to the TMP during operation. Membrane permeance, ρ, is obtained by normalizing the flux with the TMP,

$$\rho = J/\Delta P \qquad \textit{(Eq 2)}$$

where ρ is the permeance [LMH/MPa or gfd/psi] and ΔP is the TMP [MPa or psi].

Overall, the permeance of the membrane is the best parameter for comparison, as it is an intrinsic property of the membrane itself, independent of operating parameters. Figure 9 shows the change in membrane permeability with time during the filtration of the artificial seawater formulation described above, at three levels of cross-flow velocity.

The shear rate, γ [sec^{-1}] for laminar flow regimes is calculated from the formula

$$\gamma = 8v/d \qquad \textit{(Eq 3)}$$

where v is the cross flow velocity and d is the inner fiber diameter (for inside-out operation).

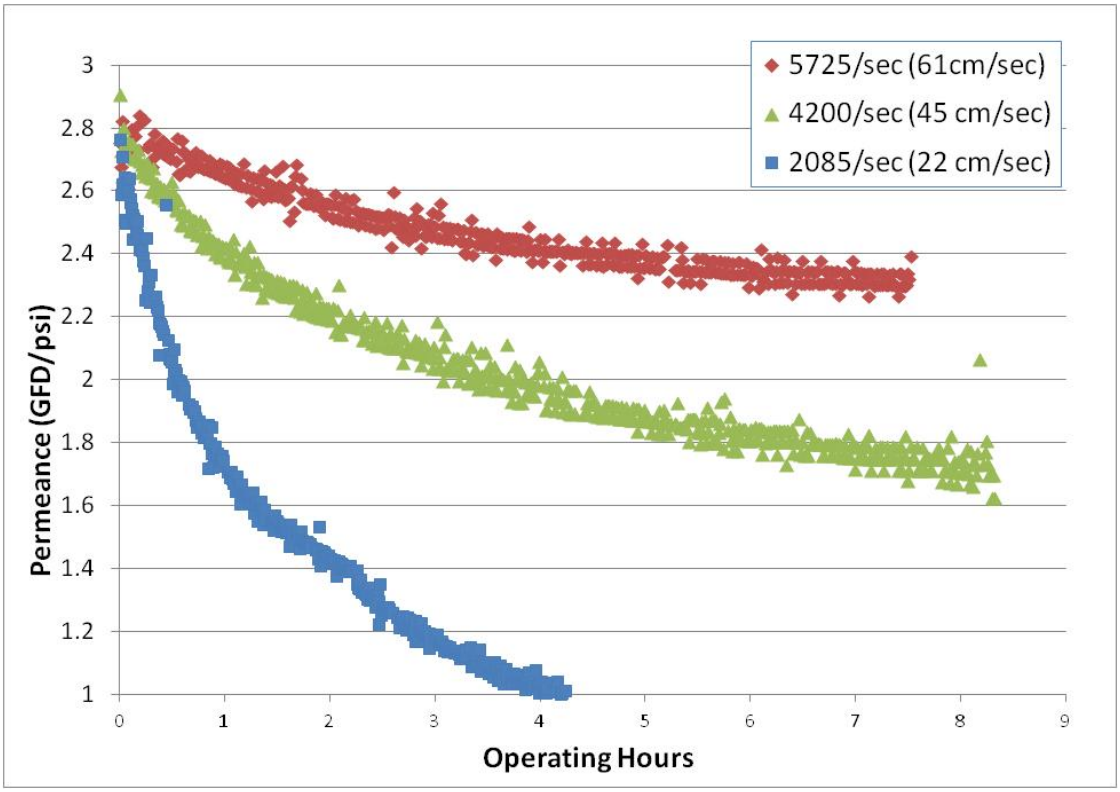

Figure 9. Successive tests of artificial seawater feed at 12 psi trans-membrane pressure and noted levels of cross-flow velocity and shear rate.

As expected, the membrane exhibited a lower degree of flux loss when the shear rate was higher. High shear rates can significantly decrease cake fouling as the tangential flow removes particulates from the surface more effectively. Concentration polarization, another contributor to flux loss, is also reduced upon increase in shear rate.

One notable aspect of these flux curves is that no instantaneous flux loss is observed upon the exposure of the membrane to the fouling solution. This behaviour is reported for most membrane materials, and is associated with adsorptive fouling by organic components such as humic acid, proteins and alginates. Adsorptive fouling occurs at much faster time scales than cake formation, and is typically mostly irreversible by physical methods such as flushing, back-washing, or air scouring. A chemical cleaning is required to

remove these foulants. The fact that the PAN/PAN-g-PEO blend membrane does not exhibit this behavior is further evidence of its resistance to organic fouling.

A subsequent test on the target module was performed in the following test modes: tests were conducted at lower shear rate (1800 sec^{-1}) using an artificial seawater formulation in which the fouling characteristics which were "enhanced" by increasing the concentrations of algae and organics. The intention was to accelerate the rates of fouling and simulate "worst case scenario" situations. This "enhanced" feed contained 3.2% sea salt, 150 mg/l blue-green algae powder, and 200 mg/l Orchid Pro plant food.

These tests were performed at three levels of TMP while keeping the cross-flow velocity and shear rate constant, to observe the effect of pressure and permeation rate on fouling, permeability and rejection. Two physical cleaning methods were employed in this test to ascertain their efficiency in cleaning the membrane. Figure 10 shows the change in permeance versus time throughout the different stages of testing. TMP values, cleaning procedures, and feed and permeate turbidities (in NTU) are shown for each stage. The '8 hour rest' marks an overnight shutdown of the system.

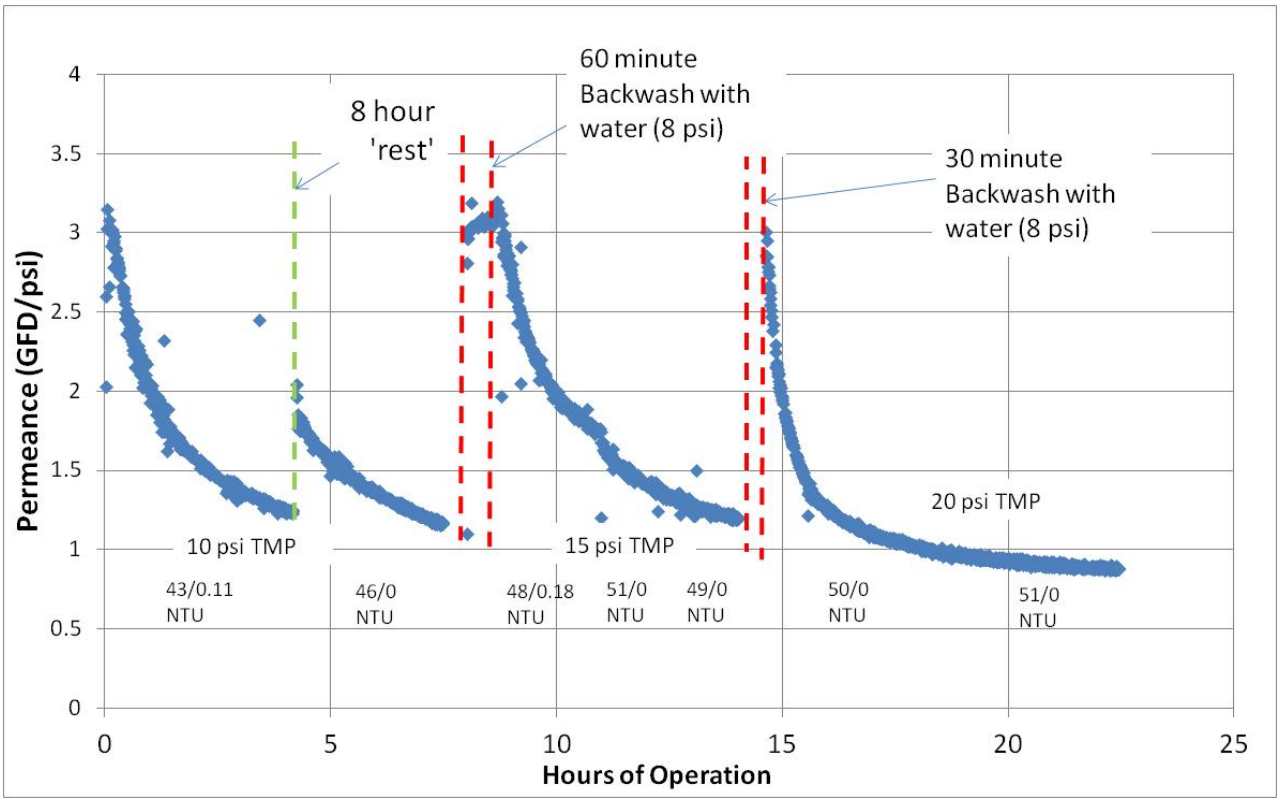

Figure 10. Module operation at three levels of trans-membrane pressure with "fouling enhanced" artificial seawater. Tests performed at nominal 1800 sec^{-1} shear rate, 19 cm/sec crossflow velocity.

No chemical cleaning was needed and the pure water flux was apparently fully recovered upon removal of the cake layer. This confirms that the PAN/PAN-g-PEO blend hollow fiber membranes developed in this project show exceptional organic fouling resistance reported in the MIT studies on lab-scale flat sheet membranes. Like the initial academic results, the hollow fiber membranes developed in this project appears to be easily cleanable with pure water, even under challenging fouling conditions.

At all TMP levels, the PAN/PAN-*g*-PEO blend membrane removed all turbidity from the feed, which once again shows that the MWCO of the UF membrane was selected correctly. The membrane is expected to perform as an effective pretreatment step in Navy shipboard desalination units.

Module Testing at Bureau of Reclamation

A series of tests were conducted at the US Bureau of Reclamation in Denver, Colorado, hosted by Drs. Michelle Chapman and Katherine Guerra. The tests were performed in three sessions between March and May 2012. These tests were of particular utility, as Dr. Guerra's recent work (Guerra 2012) provided a comparative measure of fouling performance to a commercially available modified polyethersulfone (mPES) membrane.

In all tests, the feed challenge was as follows: 10 ppm Klamath blue-green algae, 40 ppm bentonite, and 5 ppm humic and fulvic organic matter (from Orchid Pro plant food). The use of this formulation allowed direct comparison between PAN-g-PEO membranes (subsequently abbreviated as "PgP membrane") and data sets acquired by Dr. Guerra from a commercial hollow fiber modified polyethersulfone membrane module (subsequently abbreviated as "mPES membrane") used in studies at the Bureau of Reclamation. As this feed solution contained a substantial amount of "bentonite" nanoclay, it also should provide a fair representation of the types of feed water Navy ships might encounter during coastal operations.

The test system at the USBR, including the PgP membrane module in operation on this skid, is shown in Figure 11. This system is capable of characterizing the performance of membrane modules under a wide range of conditions (e.g. shear rate, TMP, a range of foulant solutions and cleaning protocols). Tests were performed in a constant-flux operating mode, wherein the TMP was modulated to maintain a constant permeate flow rate. This mode of operation is common in many industrial applications where a constant rate of permeate must be produced independent of membrane module age.

Figure 11. PgP prototype module under test at USBR

The series of tests were performed at varying shear rates in cross-flow mode, as well as in dead-end mode. Table *3* details the operating conditions for the tests performed.

Table 3. Operating Conditions for USBR tests of PgP module

Test #	Test Date	Feed Flow (ml/min)	Crossflow Velocity (cm/s)	Filtrate Flow (ml/min)	Shear Rate (sec^{-1})	Starting Pressure (psi)	Ending Pressure (psi)	Average Temp (deg C)	Peclet Number
1	3/21/2012	1180	33.6	150	3110	18.5	25.8	14.4	4.6
2	3/22/2012	651	15.5	150	1716	24.4	38.1	14.1	5.9
3	3/22/2012	125	-	125	-	15.4	19.7	19.7	(∞)
4	4/19/2012	150	-	150	-	19.1	25.6	17.3	(∞)
5	5/8/2012	481	12.3	210	1268	23.5	37.6	18.0	8.8

Initial runs on the test module were made with clean (tap) water. The pure water permeability of the PgP membrane module was lower than that of the commercial mPES membrane used as a benchmark (Figure 12). Nevertheless, the more important parameter for the performance of the membrane in operation is its permeability during the filtration of the feed of interest. Tests described above and some which are discussed in subsequent pages indicate that PgP membranes can resist fouling better than commercial membrane materials, and retain higher permeability during operation with high fouling feeds.

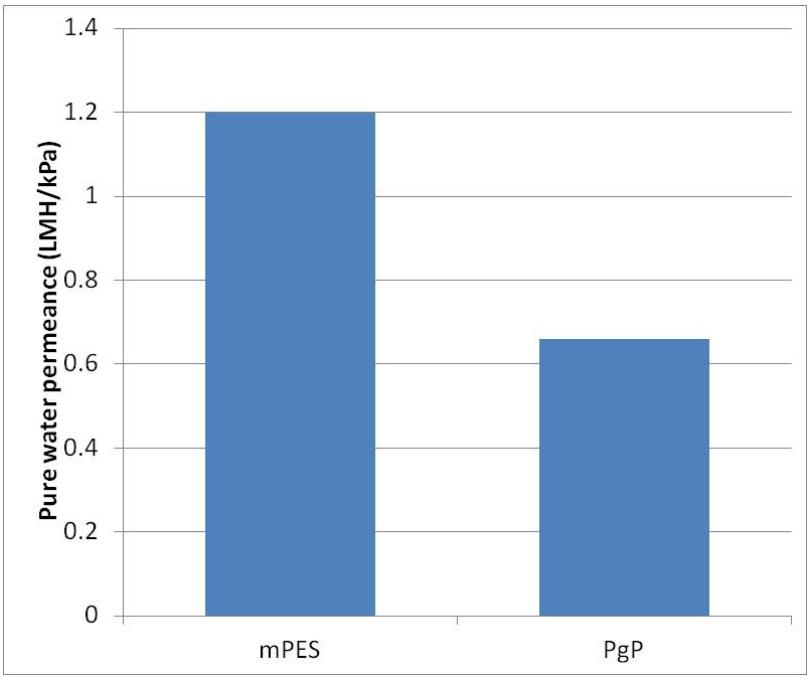

Figure 12. Pure water permeance of the mPES and PgP membranes

Though the pure water permeability was lower in the PgP membrane, the fouling test results can be compared with those from commercial membranes by normalizing the hydrodynamic test conditions. The method described in Dr. Guerra's thesis (Guerra 2012), normalizes fouling potential that arises from the flow

within the channel into a single parameter, the Peclet number. The Peclet (Pe) number describes the ratio of the mass transport of the fouling components in the feed fluid *toward* the membrane surface (advection) to the transport of these materials *away* from the membrane surface (diffusion). In terms specific to this system, the value can be determined by the ratio of flux (J) to mass transfer coefficient (k), as

$$Pe = J/k \qquad \textit{(Eq 4)}$$

A correlation for mass transfer coefficients for flow inside a cylindrical tube has been proposed by Cussler, as

$$\frac{\mathrm{kd}}{\mathrm{D}} = 1.62\left(\frac{\mathrm{d}^2\mathrm{v}}{\mathrm{LD}}\right)^{1/3} \qquad \textit{(Eq 5)}$$

where d is the inside fiber diameter, D is effective diffusivity, v is velocity of fluid within the fiber lumen, and L is the overall fiber length (Cussler 2009).

The effective diffusivity (D) is a proportionality constant between the flux due to molecular diffusion and the gradient in the concentration of the species between the bulk fluid and those accumulating upon the membrane surface. In her prior work, Dr. Guerra estimated the effective diffusivity for the complex mixture in water as 1.6×10^{-6} cm^2/sec. We have assumed the same value for this analysis.

Combining equations 1, 4, and 5, the Peclet number can be found for a hollow fiber with inside-out operating condition as

$$Pe = \frac{Q/A}{1.62\left(\frac{\mathrm{D}^2\mathrm{v}}{\mathrm{dL}}\right)^{1/3}} \qquad \textit{(Eq 6)}$$

This relation allows reporting of comparative fouling results that are specific to the fouling behavior of the membrane and independent of hydrodynamic test conditions.

Higher flux through the membrane is either due to a high permeability or is due to a high TMP, which increases the advective force that carries foulants to the surface, increasing the Peclet number. Higher back-diffusion will result from advantageous channel hydrodynamics (higher cross-flow velocity, larger diameter channel, and shorter channel length). Therefore, the Peclet number bundles all these different factors (channel geometry, TMP, membrane permeability) into one parameter that allows a valid comparison between modules.

As such, the Peclet number can be thought of as an indicator of the hydraulic conditions under which a module is tested. High cross-flow velocities and other process conditions designed to limit concentration polarization and fouling lead to low Pe numbers. High Pe numbers are the norm for systems that operate at high recovery ratios. In dead-end operation, the Pe number approaches infinity.

After the initial pure water test, successive runs were performed at various conditions to characterize the membrane's fouling potential. Figure 13 compiles outcomes for those tests conducted in tangential flow mode, showing the required increase in TMP to sustain the target filtrate volume rate for the PgP membrane.

In these cross-flow tests, it was shown that higher cross-flow velocities (lower Pe numbers) led to slower pressure increase, as expected.

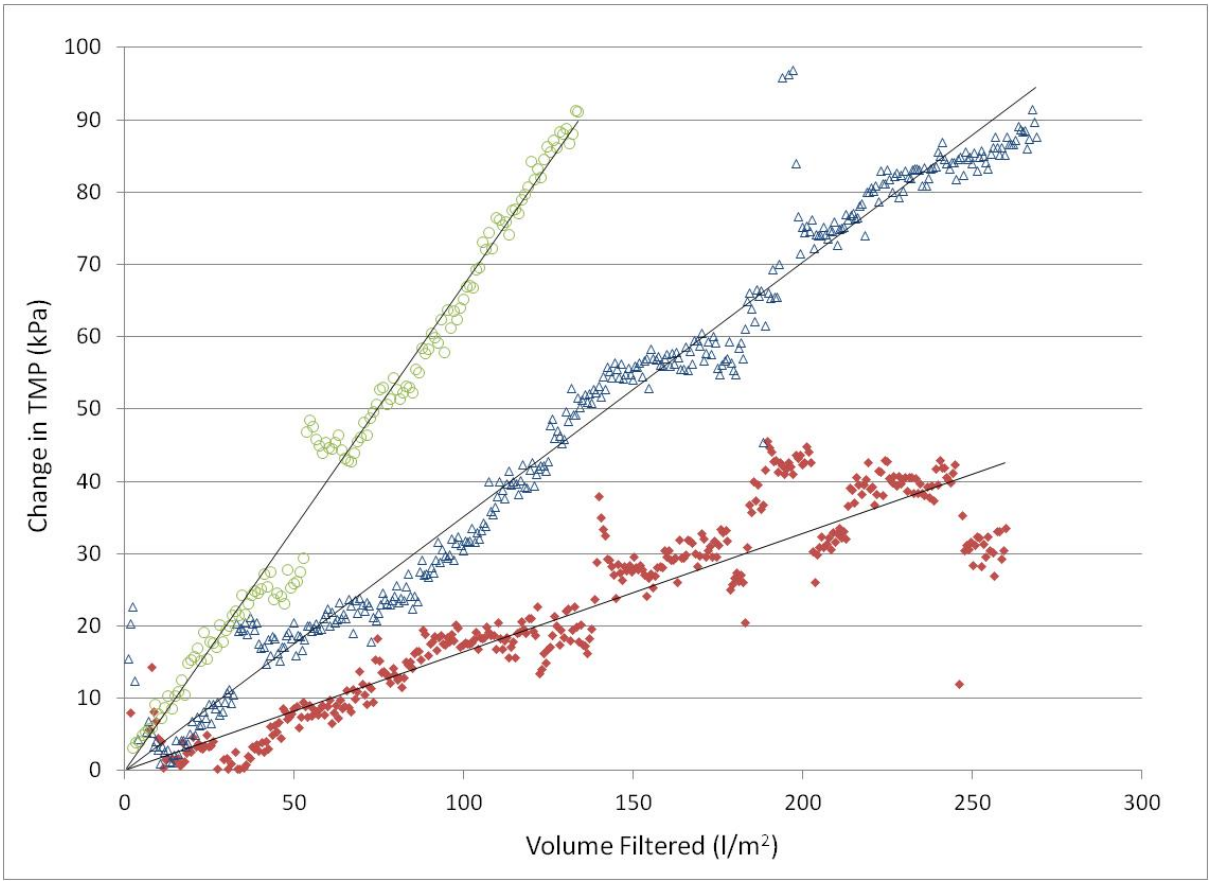

Figure 13. Test results for tangential flow runs at USBR for PgP module. Fouling rates of 0.16, 0.35, and 0.67 kPa m^2/l at 4.6 (◆), 5.9 (△), and 8.8 (○) Peclet numbers, respectively, were observed.

In comparison, at identical Pe values and hence under comparable hydraulic conditions, Figure 14 shows that the PgP membrane fouls at substantially lower rates than the benchmark mPES membrane. At high Pe numbers, the difference is dramatic, with the mPES membrane fouling over 4 times faster than the PgP membrane at similar hydrodynamic conditions. These results further support the exceptional fouling resistance properties of the PAN/PAN-*g*-PEO blend membranes, and document the energy and projected operating savings that can be obtained by their use.

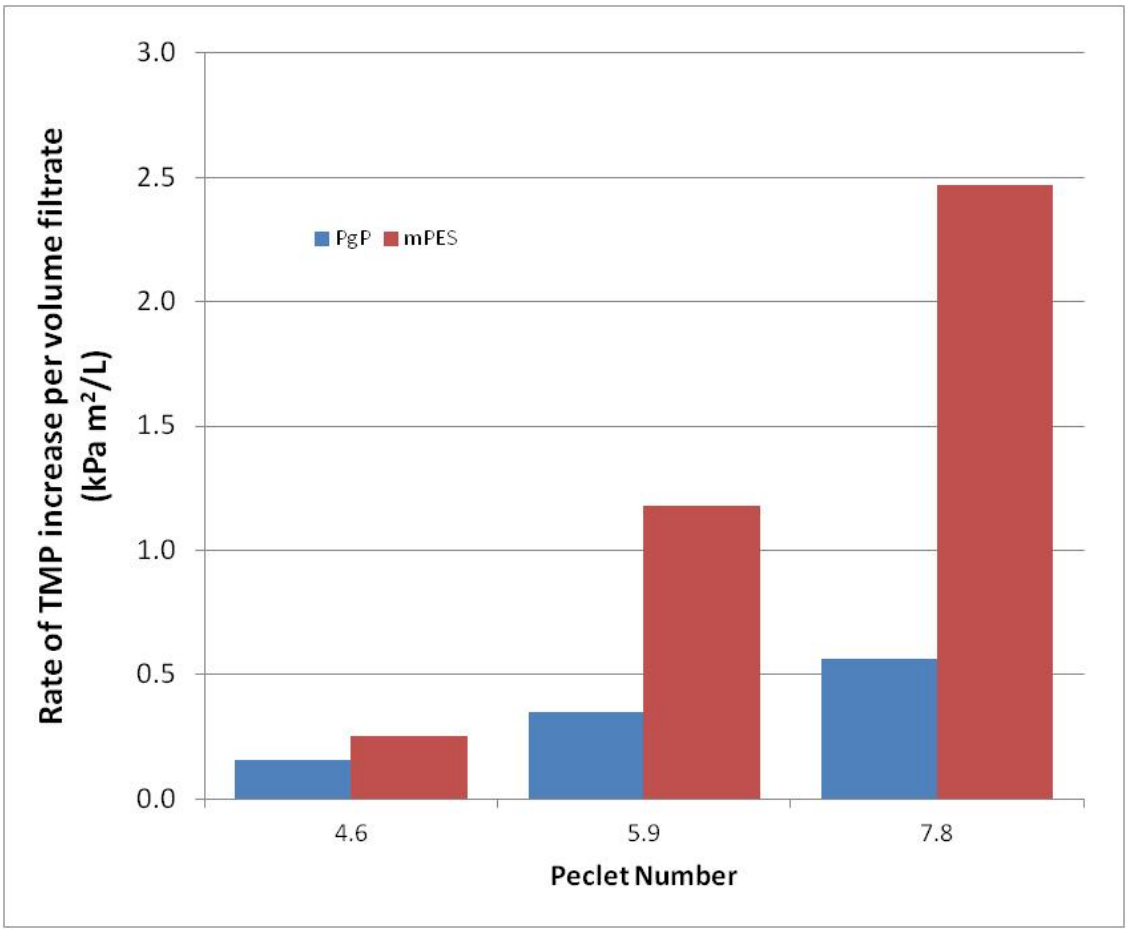

Figure 14. **Fouling tendency of PgP and mPES membranes under various hydrodynamic conditions (as defined by Peclet number).**

Under dead-end operation, the rate of fouling was found to be lower than some values under cross-flow filtration (0.29 kPa m^2/l). This was a surprising result, as typically cross-flow operation leads to less severe fouling. This is believed to be due to the formation of a more porous and permeable cake layer during dead-end filtration. The shear forces in cross-flow operation can impact the effective particle size in the feed and compact the cake layer. In most cases, this effect is not necessarily as visible, since adsorptive fouling typically accounts for a significant part of the flux loss. In the case of PgP membranes, where adsorptive fouling is mitigated, this effect becomes more visible. Dead-end operation of the mPES membrane was also found to be lower than high-velocity operation, with a fouling rate of 0.38 kPa m^2/l.

Pure water permeance measurements at various stages of the evaluation of the PgP membrane are summarized in Table 4. The summary includes the filtration process conditions used, as well as cleaning protocols evaluated. The cleaning protocols tested were water backwash, and air scour, both of which are cleaning protocols that involve no chemicals. Air scour protocol included a clean (tap) water backwash with simultaneous application of airflow through the fiber lumen.

Table 4. **Summary of pure water permeance at various stages of USBR testing of PgP module**

Date	Event	Permeance (LMH/kPa)	Comments
21-Mar	Initial Pure Water Permeance	**0.68**	
21-Mar	Post Run (34 cm/sec lumen vel; Pe = 4.6)	0.60	3.7 hour run
21-Mar	After Water-only Backwash	*0.62*	20 min. backwash at ~10 psi
22-Mar	After overnight soak	0.62	
22-Mar	Post Run (15.5 cm/sec lumen vel; Pe = 5.9)	0.38	3.6 hour run
22-Mar	After Water-only Backwash	*0.63*	20 min. backwash at ~12 psi
22-Mar	Post Dead-End Run (3/22)	0.56	1.5 hour run
22-Mar	After Water-only Backwash	*0.63*	20 min. backwash at ~18 psi
22-Mar	After Water-only Backwash + Air Scour	**0.68**	5 min BW with air scour
19-Apr	Before Dead End run	**0.66**	
19-Apr	After Dead End run	0.42	2 hour run
19-Apr	After Water-only Backwash	*0.62*	
19-Apr	After Water-only Backwash + Air Scour	**0.66**	5 min BW with air scour
8-May	Pre run	**0.66**	
8-May	Post Run (12.3 cm/sec lumen vel; Pe = 8.8)	0.48	1.7 hour run
8-May	After Water-only Backwash + Air Scour	**0.64**	5 min BW with air scour

Results for the commercial mPES dead-end run on May 22 are summarized in Table 5. Note that after a backwash with air scour, the permeance recovered to 60% of the initial value. Only after a 20 minute chemical backwash, alternating acidic and basic treatments, was the flux fully restored.

Table 5. **Pure water permeance of mPES membrane during dead-end test**

Date	Event	Permeance (LMH/kPa)	Comments
22-May	Initial Pure Water Perm on **mPES membrane**	**0.96**	
22-May	After Dead End run	0.50	1.5 hour run
22-May	After Water-only Backwash + Air Scour	**0.57**	5 min BW with air scour
22-May	After 20 minute citric acid (ph3) + NaOH (pH10.5) chemical backwash	**0.96**	

Water Quality Results

To measure the capability of the PgP membrane to remove contaminants that lead to RO membrane fouling, two parameters were used. The first was turbidity, which is correlated with the amount of particulates and suspended solids in the water sample. In all cases, the PgP membrane successfully removed >98% of turbidity from the feed (Table 6). The effluent turbidity was reproducibly below 0.30 NTU, well below the 1 NTU specification included in the proposal. This shows that the PgP UF membrane effectively removes particulates and suspended solids, which are significant foulants for RO membranes further along this treatment train, from this simulated water sample.

Another parameter that was monitored was the absorption of UV light (measured at a wavelength of 340 nm). Many organic materials, especially humic and fulvic substances, absorb UV light around this wavelength. High rejections at this wavelength indicate that these foulants are effectively removed. PgP membrane showed a UV-based rejection of 80%. While the feed is a complex feed and it is difficult to interpret the exact components that are removed in this process, this rejection value agrees with what would be expected from the MWCO of the membrane. Humic and fulvic acids, as well as alginates, are biopolymers that have wide molecular weight distributions. This UV-based organic rejection indicates most high molecular weight organics, which have a higher fouling potential, are effectively removed.

***Table 6*. Summary of Average Water Quality Results for USBR test runs**

Test Date	Crossflow Velocity (cm/sec)	Peclet	Feed: UV abs (at 340nm)	Permeate: UV abs (at 340nm)	UV Rejection	Feed Turbidity: (NTU)	Permeate Turbidity: (NTU)	Turbidity Rejection
21-Mar	30.0	4.6	0.147	0.027	82%	19.7	0.07	100%
22-Mar	15.5	5.9	0.149	0.028	81%	18.5	0.10	99%
22-Mar	Dead End	∞	0.153	0.032	79%	19.3	0.08	100%
19-Apr	Dead End	∞	0.153	0.032	79%	18.4	0.28	98%
8-May	12.3	8.8	---- Data not collected ----			---- Data not collected ----		

Overall, the effluent quality from the PgP hollow fiber UF membranes was found to be well within (and significantly better than) specifications discussed in the project proposal. This effluent will pose a much lower fouling potential, leading to a longer membrane life for the RO module on shipboard units.

Backwash and Air Scour

A notable result from our studies at the USBR was the ability of the membrane to achieve full flux recovery when a water-only backwash step is performed *in combination* with a brief and simultaneous air scour inside the fiber.

At the conclusion of each of the first three fouling performance test runs, a 20-minute backwash was conducted on the fouled membrane. Each of these three backwash operations was able to achieve (nearly identical) 92% recovery of initial pure water permeance. At the conclusion of the third test, we also applied a 12 psi air scour to the inner diameter of the fiber with a remarkable result: *the pure water permeance was fully recovered*.

The water-only backwash process was relatively slow, and at the end of the backwash period, the recovered wash water appeared only turbid. When the backwash was combined with an air scour, to mechanically agitate the solution on the bore side of the membrane, a small volume (~200 ml) of very concentrated solution of cake layer was removed and recovered from the membrane within a few minutes of this treatment. Figure 15 displays the dramatic difference in result from these operations.

Figure 15. **Fluid recovered from water-only backwash at 12 psi (left), and water recovered through combination of water backwash with bore-side air scour (right)**

As shown in Table 4, above, complete or nearly complete flux recovery was achieved utilizing bore-side air scour in a much shorter time period (5 minutes as opposed to 20 minutes) with a minimal consumption of backwash water.

In contrast, the commercial mPES membrane (Table 5) showed 60% recovery of flux with water backwash in combination with air scour. Full flux recovery was achieved with a 20 minute acid/base chemical clean.

Therefore, backwash with air scour was identified as the most efficient method of PgP membrane cleaning.

Summary of Project Deliverables

Table 7. Summary of project deliverables

Initial Targets	Results
•Hollow Fiber dimensions: OD 1.1 mm / ID 0.7 mm	For Prototype fiber: OD = 1.52 mm / ID = 0.86 mm
•Water flux: ≥ 50 GFD	For Prototype Module: 3.1 gfd/psi @ 15 psi = 46.5 GFD*
•Membrane separation characteristics MWCO = 100,000	MWCO ≈ 30,000 - 40,000
•15-minute silt density index values (ASTM D4189-07) of less than 3.0	Less than 3.0 with artificial sea water feeds
•Turbidity values less than 1.0 NTU	Less than 1.0 NTU with artificial sea water feeds
•Filtration Mode: Tangential flow that induces Dean Vortex with reverse flow/fast flash capability for back washing, mechanically capable of forward and backward-flow	Tangential flow with backwashing capability; module not helically wound
•Cleaning: We do not expect any chemical cleaning to be necessary. If some cleaning are necessary after extensive continuous operation (>1000 hours), we will provide provisions for backwashing capabilities.	Water-only backflush on ASW appears to have greater than 97% recovery of flux. With air-scour assist, consistently achieved 100% flux recovery. (Did not reach 1000 hours of operation)
•Cartridge size: Final cartridge diameter 8", initial Phase 1 demonstration cartridge diameter 4"; Cartridge length 40"	Sized to meet requirements of USBR test skid. 1.25" diameter x 24" OAL
•Militarized packaging and safety conformance	Not Militarized for USBR tests

*** higher fluxes obtained but not yet implemented in module construction**

Conclusions

Novel hollow fiber membrane module to address UF pretreatment needs of shipboard desalination was developed. The hollow fibers are manufactured from a blend of PAN and PAN-g-PEO polymers. The approach is based on materials technology originally developed at MIT. During the course of the program the technology was scaled up from the original flat sheet laboratory scale to operational hollow fiber modules. The scale up included: PAN-g-PEO material synthesis on commercial scale, PAN-g-PEO/PAN blend hollow fiber preparation, and hollow fiber module construction. UF module tests demonstrated exceptional anti-fouling characteristics that will allow efficient, chemical-free, low maintenance operation.

We expect that all objectives of the ONR program can be met with a compact, fouling-resistant PAN-g-PEO membrane platform.

Tests at Clean Membranes and the USBR have demonstrated that the newly developed membrane exhibited exceptionally low fouling characteristics superior to state-of-the-art commercially available polymeric membranes. Of particular note is the ability of the membrane to recover original flux by implementing a simple air-scouring protocol.

The results demonstrate that the PAN-g-PEO based hollow fiber membrane can address ONR's need for improved pretreatment of RO desalination feed streams; the membrane can treat the most challenging feeds with low rates of fouling; the membrane does not require chemical cleaning and complete flux recovery can be attained with an appropriate backwash/air scour protocol.

Parallel to the development of an integral PAN-g-PEO membrane development of a composite PAN-g-PEO membrane was carried out. The composite membrane was made with PAN-g-PEO separation layer deposited on commercially available PEEK hollow fiber substrate. This composite membrane exhibited low flux and did not offer an apparent advantage to integral PAN-g-PEO membranes made through direct spinning.

It was originally anticipated that module construction using helical hollow fiber winding method may be required to improve anti-fouling characteristics through generation of Dean Vortexes in a tangential flow mode operation. However, excellent anti-fouling properties demonstrated by PAN-g-PEO membranes and Navy preference for high recovery UF operating mode precluded the need for this approach.

Recommendations

PAN-g-PEO membrane technology platform has shown significant advantage as compared to state-of-the-art membrane processes deployed for seawater RO pretreatment. Future efforts will include:

- Further optimization of the membrane manufacturing process to tailor performance towards SWRO pretreatment
- Develop optimum operating protocols appropriate for existing naval infrastructure
- Build fully operational pretreatment system and conduct long-term performance tests
- Work with Port Hueneme team to formulate Phase II program for technology demonstration to bring the technology to Technology Readiness Level 6

Proposed Follow-on Research and Development

CM and PoroGen are committed to PAN-*g*-PEO technology commercialization and plan to provide financial and business resources. CM has secured initial financing and is in process of upgrading technology piloting facilities. Manufacturing will be scaled to support application development with commercial modules in production by latter part of 2013.

Full-scale systems capable of pretreating seawater onboard naval ships for RO desalination should be built to demonstrate technical readiness.

Additional target applications for PAN-*g*-PEO hollow fiber technology include conventional and non-conventional oil & gas market segments and biotech separations.

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List of Symbols, Abbreviations and Acronyms

BSA: Bovine serum albumin
FNC: Future Naval Capabilities
MF: Microfiltration
mPES : modified polyethersulfone
NSRO: Navy Standard Reverse Osmosis technology
ONR: Office of Naval Research
PAN: Polyacrylonitrile
PAN-g-PEO: Polyacrylonitrile-*graft*-polyethylene oxide
Pe: Peclet Number
PgP: PAN-g-PEO
RO: Reverse Osmosis
TMP: trans-membrane pressure
UF: Ultrafiltration
USBR: US Bureau of Reclamation

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