PROGRESS REPORT 7

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Recipient: The University of Texas at Austin

2. Project Title: Novel Fouling-Reducing Coatings for Ultrafiltration,

Nanofiltration, and Reverse Osmosis Membranes

Principal Investigator: Dr. Benny Freeman

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Period Covered: 1 September 2007 – 29 February 2008

4. Executive Summary

Polymeric membranes could potentially be the most flexible and viable long-term strategy for treatment of produced water from oil and gas production, including removal of salts, emulsified oil, other organics and particulates. Depending on the impurities present and the level of purification required, reverse osmosis (RO), nanofiltration (NF), or ultrafiltration (UF) membranes can be used. An inherent drawback of all membranes, including RO, NF, and UF, is that they experience fouling by impurities present in the water. The problem is exacerbated when these membranes are exposed to a mixture of impurities such as salt, emulsified oil droplets, and other particulate matter, and their lifetime decreases dramatically due to largely irreversible membrane fouling.

Two types of fouling may occur, surface and internal. Surface fouling occurs when particles deposited on the membrane surface precipitate, reducing flow through the membrane. This type of fouling is also strongly dependent on interactions between contaminants and the membrane surface. RO and NF membranes have very rough surfaces and a high chemical affinity for oil and other organic components of produced water, characteristics causing their extreme susceptibility to surface fouling by organics. Internal fouling is caused by penetration of particulates into the membrane interior, where they block pores and reduce water flux. Internal fouling is essentially irreversible because the particles accumulate inside the pores and are then resistant to even aggressive chemical and hydrodynamic cleaning procedures. UF membranes are porous and therefore subject to internal fouling by particulates, organics, and other components of wastewater. Thus, fouling is a barrier to more widespread application of membranes for produced water purification.

One approach to improve fouling resistance of commercial RO, NF, and UF membranes is to apply a very thin (on the order of 0.5 microns), nonporous,

hydrophilic coating to the surface. The coating is very water-permeable and simultaneously resists both internal and surface fouling. Due to the nonporous nature of the coating, particles are not able to reach the underlying membrane structure, reducing pore blockage and internal fouling. Additionally, surface fouling is diminished because the coating itself resists adhesion of emulsified oil droplets. Another approach to reduce membrane fouling is to graft molecules to the membrane surface to alter the surface characteristics. These molecules may either be hydrophilic for a direct enhancement of surface hydrophilicity, or may provide double bonds on the membrane surface which permit surface polymerization with a hydrophilic monomer.

During this project period, characterization of the commercial RO membranes (LE and XLE from Dow FilmTec and AG from GE) was performed to determine the effects of feed pH and prefiltration on measured performance values (water flux and NaCl rejection). Although all three membranes have nominally the same polyamide structure, their performance is very different for a given set of operating conditions, highlighting the need to use the optimal conditions for each membrane. Feed pH has an especially interesting effect on the salt rejection properties of all three membranes. Rejection increases with increasing pH, corresponding to the change of the membrane surface charge from positive at low pH to negative at high pH.

Structure-property relationships of PEG-based hydrogels were thoroughly evaluated during previous project periods. Therefore, the preparation of dense coatings composed of PEG-based hydrogels was the main focus during this project period. Efforts were made to further understand the effects of several coating variables on the resulting coating thickness. Future work will continue the current progress of forming composite membranes and testing their fouling behavior.

Future work will focus on optimizing treatment conditions to maximize the flux of XLE membranes grafted with PEG diepoxide. Dip coating and spin coating will be explored as two alternate grafting methods, and other variables including reaction time, temperature, and PEG chain length and concentration will also be explored to determine their ability to tailor the transport properties of the resulting modified membranes. Modified membranes will also be subjected to oil-water emulsions consisting of DTAB or sodium dodecyl sulfate (SLS, an anionic surfactant) and decane. The fouling performance of modified XLE membranes will be compared to that of control LE membranes.

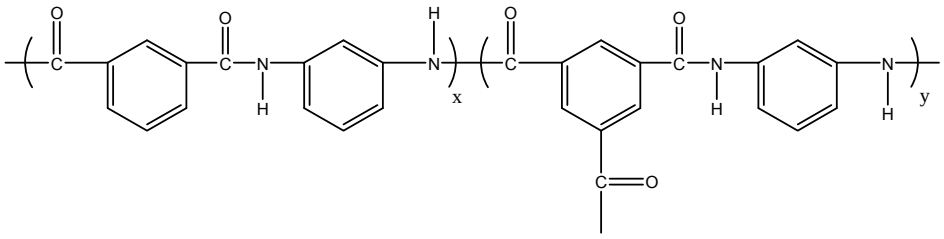
5. Results of Work During Reporting Period

Experimental Approach:

Emulsion Selection, Preparation, and Characterization. Sodium dodecyl sulfate (SLS), an anionic surfactant, and dodecyltrimethylammonium bromide (DTAB), a cationic surfactant, have been used in making emulsions. Decane or

dodecane were used as the oil phase. Emulsion preparation consisted of mixing the oil, surfactant, 2000 mg/L NaCl, and deionized (DI) water (Millipore MilliQ water, 18 MΩ, 1.2 ppb) in a Waring blender on high speed for 3 minutes.

Commercial Membrane Supports. Flat-sheet AG RO membranes manufactured by GE Infrastructure Water Process and Technologies were used for characterization and modification studies. The AG membrane is a commercial brackish water desalination RO membrane (50 LMH at 225 psig, 98-99% NaCl rejection) and is a polyamide thin film composite membrane representative of the vast majority of commercial RO and NF membranes available today. The generic structure of the polyamide layer, which provides salt rejection in this membrane, is:



Flat-sheet membranes from Dow FilmTec were also obtained for use in characterization and modification studies. They include the LE (low energy, 49 LMH flux at 150 psi, 99.0-99.3% NaCl rejection) and XLE (extra low energy, 67 LMH at 150 psi, 98.0-99.0% NaCl rejection) reverse osmosis membranes. These membranes all share the same general chemical structure shown above. The XLE membrane will be used for modification studies, while the LE will be used as a control for comparison with the modified XLE membranes. Surface modification decreases water flux, so comparing a control membrane with a pure water flux similar to that of the modified XLE membrane will provide a better gauge of the fouling resistance of the modified membranes.

Characterization of Fouling and Separation Performance. Baseline flux and rejection testing of commercial RO membranes was conducted in crossflow filtration using an industry-standard 2000 ppm NaCl feed, prepared using deionized water from the Millipore system, and the optimum pressure and flowrate for each material, as specified by the manufacturer. Membranes were supplied on a roll, and several rotations of material were discarded before taking samples for testing. Feed pH was adjusted by addition of $NaHCO_3$. The feed was prefiltered, using an activated carbon + particle filter, or unprefiltered depending on the test conditions of the manufacturer.

Concentration polarization was accounted for in all characterization experiments by measuring pure water flux at the beginning of each experiment, so that subsequent observed rejection data (taken after addition of 2000 ppm NaCl) could be adjusted for the increased salt concentration at the membrane surface. This allowed determination of the actual salt rejection inherent to the membrane.

The osmotic pressure model used (Sutzkover, Hasson and Semiat, *Desalination* 131 (2000) 117-127) relies on the fact that the membrane permeance, A, is a constant material property. For a pure water feed, the general solution-diffusion model equation ($J = A(\Delta p - \Delta\pi)$) is simplified to give the pure water flux, $J_{w(pw)}$:

$$J_{w(pw)} = A \times \Delta p \tag{1}$$

Water flux in a feed containing NaCl, $J_{w(NaCl)}$, is given by:

$$J_{w(NaCl)} = A\left[\Delta p - \left(\pi_{so(m)} - \pi_{s\ell}\right)\right] \tag{2}$$

where $\pi_{so(m)}$ and $\pi_{s\ell}$ are the osmotic pressure ($\pi \approx cRT$) at the membrane surface and in the permeate, respectively.

Equations (1) and (2) can be combined to give the osmotic pressure at the membrane surface, a quantity that cannot be measured experimentally, as:

$$\pi_{so(m)} = \pi_{s\ell} + \Delta p \times \left(1 - \frac{J_{w(NaCl)}}{J_{w(pw)}}\right) \tag{3}$$

Equation (3) can then be used to find the actual salt rejection of the membrane:

$$R_{actual} = \left(1 - \frac{\pi_{s\ell}}{\pi_{so(m)}}\right) \times 100\% \tag{4}$$

The concentration polarization modulus, M, is given by:

$$M = \frac{\pi_{so(m)} - \pi_{s\ell}}{\pi_{so} - \pi_{s\ell}} = \frac{\Delta p}{\pi_{so} - \pi_{s\ell}} \times \left(1 - \frac{J_{w(NaCl)}}{J_{w(pw)}}\right) \tag{5}$$

where π_{so} is the osmotic pressure of the bulk feed.

Fouling studies were also conducted in crossflow filtration mode as described above. Model foulants and emulsions, described above, were used, and rejection of organic carbon was measured using a Shimadzu TOC 5050A Total Organic Carbon Analyzer.

Synthesis of Fouling-Resistant Materials. The crosslinking agent, poly(ethylene glycol) diacrylate (PEGDA), was obtained from Sigma-Aldrich (Milwaukee, WI) and used as received. Poly(ethylene glycol) acrylate (PEGA), 2-

hydroxyethyl acrylate (HEA), and acrylic acid (AA) (see Figure 1), all from Sigma-Aldrich, were used without further purification to synthesize copolymers. The photoinitiator was 1-hydroxycyclohexyl phenyl ketone (HPK), also available from Sigma-Aldrich.

Pre-polymerization mixtures were prepared using the above-mentioned materials, deionized (DI) water, and 1.0 wt% (based on solids content) photoinitiator. Copolymers were prepared on a molar basis with each sample denoted as XX, where XX is mole percent comonomer. Water content in the prepolymerization mixture was based on total mixture weight. For example, a 60PEGA film contains 60 mole percent PEGA and 40 mole percent PEGDA, with 60wt% of the final prepolymerization mixture being H_2O.

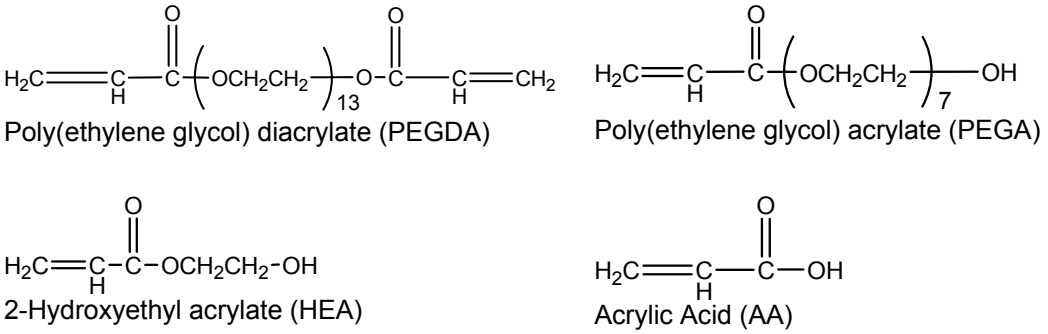


Figure 1. Chemical structures of materials used.

Preparation of Coated and Surface-Modified Membranes. Spin coating was used to apply PEG hydrogel prepolymerization mixtures to RO membrane substrates. Membranes were soaked in DI water to remove glycerin before spinning. Then, membranes were blotted dry and taped to a silicon wafer, ensuring the membrane was completely flat. Three mL of prepolymerization mixture were added to the membrane. Samples were spun at a given speed for a specified time after a 5 s acceleration period. The films were crosslinked in a nitrogen-purged chamber using UV light at 312 nm, 3000 $\mu W/cm^2$, for 90 s.

Surface modification was performed on commercial Dow FilmTec XLE RO membranes. Before modifications were made, membrane samples were soaked in 25%(v) isopropanol for twenty minutes, then rinsed in deionized water, to remove glycerin from the membrane pores. Poly(ethylene glycol) diglycidyl ether, commonly referred to as PEG diepoxide, was the main focus of chemical modification studies. Membranes were dip coated in aqueous solutions of PEG diepoxide, where several PEG diepoxide chain lengths (n values in Figure 2, n = 5, 9, 14 and 23), and concentrations (0-0.2%(mol)) were used.

The dip coating procedure began with heating deionized water to 40°C using a Barnstead Electrothermal heating unit with stirrer. The appropriate amount of PEG diepoxide, allowed to equilibrate to room temperature, was then added to the water. The stirrer was turned off and the membrane was immediately

immersed in the solution, to reduce the possible reaction time of PEG diepoxide and water. The membrane was left in the solution (keeping the temperature constant) for ten minutes. Finally, the membrane was removed from solution, triply rinsed in deionized water to remove unreacted PEG diepoxide, and stored in deionized water until use.

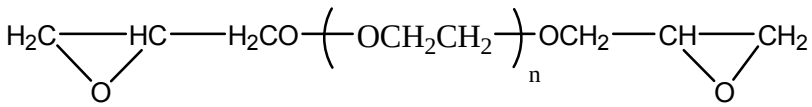


Figure 2. Chemical structure of poly(ethylene glycol) diglycidyl ether (PEG diepoxide) (n ≈ 5, 9, 14, or 23).

Characterization of Fouling-Resistant Materials and Coated Membranes.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used to verify the presence of a crosslinked PEGDA coating on the RO membrane surface. ATR-FTIR was performed using a Thermo Nicolet Nexus 470 FTIR (Madison, WI) with an Avatar Smart MIRacle ATR accessory (Zinc Selenide crystal). Data were collected and analyzed using Omnic software. Spectra were collected using 128 scans at a resolution of 4 cm^{-1} between 600 and 4000 cm^{-1}. Prior to analysis, samples were placed under vacuum overnight at room temperature to remove excess water.

Water flux measurements of spin-coated membranes were done and a flux resistance model were used to evaluate coating thicknesses. Pure water flux measurements were done using either Sterlitech HP4750 stainless steel high pressure dead-end filtration cells or crossflow filtration at 225 psig. A flux resistance model was used to calculate the coating thickness:

$$J_{H_2O} = L_{pT}(\Delta p) \tag{6}$$

where J_{H_2O} is the measured water flux, and Δp is the applied pressure. L_{pT} is given as:

$$L_{pT} = \left[\frac{1}{L_{pRO}} + \frac{\ell}{P_{wPEG}}\right] \tag{7}$$

where L_{pRO} is the RO membrane permeance, ℓ is the coating thickness, and P_{wPEG} is the hydrogel water permeability, previously measured for free-standing films.

Scanning electron microscopy (SEM) was also done on composite membrane cross-sections to evaluate coating thickness. Samples were freeze-fractured in liquid nitrogen and mounted to an SEM stage. The samples were sputter coated for 35 s using an Au target. Images were taken on a LEO 1530 SEM (Carl Zeiss SMT Inc) at 10 kV.

Results and Discussion:

Emulsion Characterization. An optical microscope was used to estimate the droplet size distribution and stability of a 150 ppm SDS and decane emulsion. The emulsion contained 2000 mg/L NaCl, 15 ppm SDS, and 135 ppm decane, a 1:9 ratio of surfactant to oil. The emulsion was examined approximately one hour after blending, and the number average diameter of each droplet, d_N, was 0.94 μm. The polydispersity index (PDI) was 1.25, indicating a narrow droplet diameter distribution. The same emulsion was examined 24 hours after blending and did not show any significant changes in droplet size or distribution. Future work will characterize a DTAB/decane emulsion in the same manner.

Characterization of Fouling and Separation Performance. After demonstrating that the manufacturer-specified water flux and NaCl rejection values could be achieved through careful matching of testing conditions and correction for the effects of concentration polarization, focus turned to demonstrating the effect of prefiltration and feed pH on membrane performance. The differences in water flux and actual (i.e., corrected for polarization) NaCl rejection for membranes tested with and without continuous feed prefiltration through a carbon + 5 μm particle filter are clearly demonstrated in Figure 3.

For all three membranes, water flux was much more stable with time when the feed was continuously prefiltered. The water flux of the LE and XLE membranes increased slightly over the first 3-4 hours and after 24 hours fell back only to the initial value, but the flux of the AG membranes decreased slowly from the start, eventually falling by ~ 4 L/(m^2h) in 24 hours. However, differences in behavior among the three membranes in prefiltered feed were minor in comparison to the stark differences observed for experiments with unprefiltered feed. Twenty-four hours of operation with unprefiltered feed led to flux declines of 10-15 L/(m^2h) for the LE, XLE, and AG membranes.

The actual salt rejection of the LE and XLE membranes only increased by ~ 0.2% over 24 hours using continuously prefiltered feed, far less than the 0.5% increase observed in unprefiltered feed (cf. Figures 3(a) and (b), respectively). The larger increase in actual salt rejection and decline in water flux in the unprefiltered feed experiments (versus the rather stable flux and rejection behavior in the prefiltered feed experiments) for the LE and XLE membranes could be explained as the result of fouling. Although no obvious foulants were added to the system and ultrapure water was used as the feed water, there could be particulate matter in the water, introduced either from the air (the feed tank lid is not entirely air-tight) or from the wetted stainless steel parts of the crossflow system. Running the feed continuously through the carbon/particle filter removes any particulate matter from the feed and also prevents biogrowth in the system. Without continuous prefiltration, the feed may pick up enough contaminants to cause the sensitive reverse osmosis membranes to foul, blocking surface area and resulting in lower water flux and higher NaCl rejection. Over time, additional foulant buildup would cause the flux to decrease and the rejection to increase further. In contrast, the

carbon/particle filter continuously removes any foulants, resulting in more stable flux and rejection values over time, as well as higher flux and lower rejection due to the lack of foulants. These results also give insight into Dow's choice of a run time of 20 minutes before taking flux and rejection measurements, to report performance values before the effects of fouling become significant (since they do not use continuously prefiltered feed).

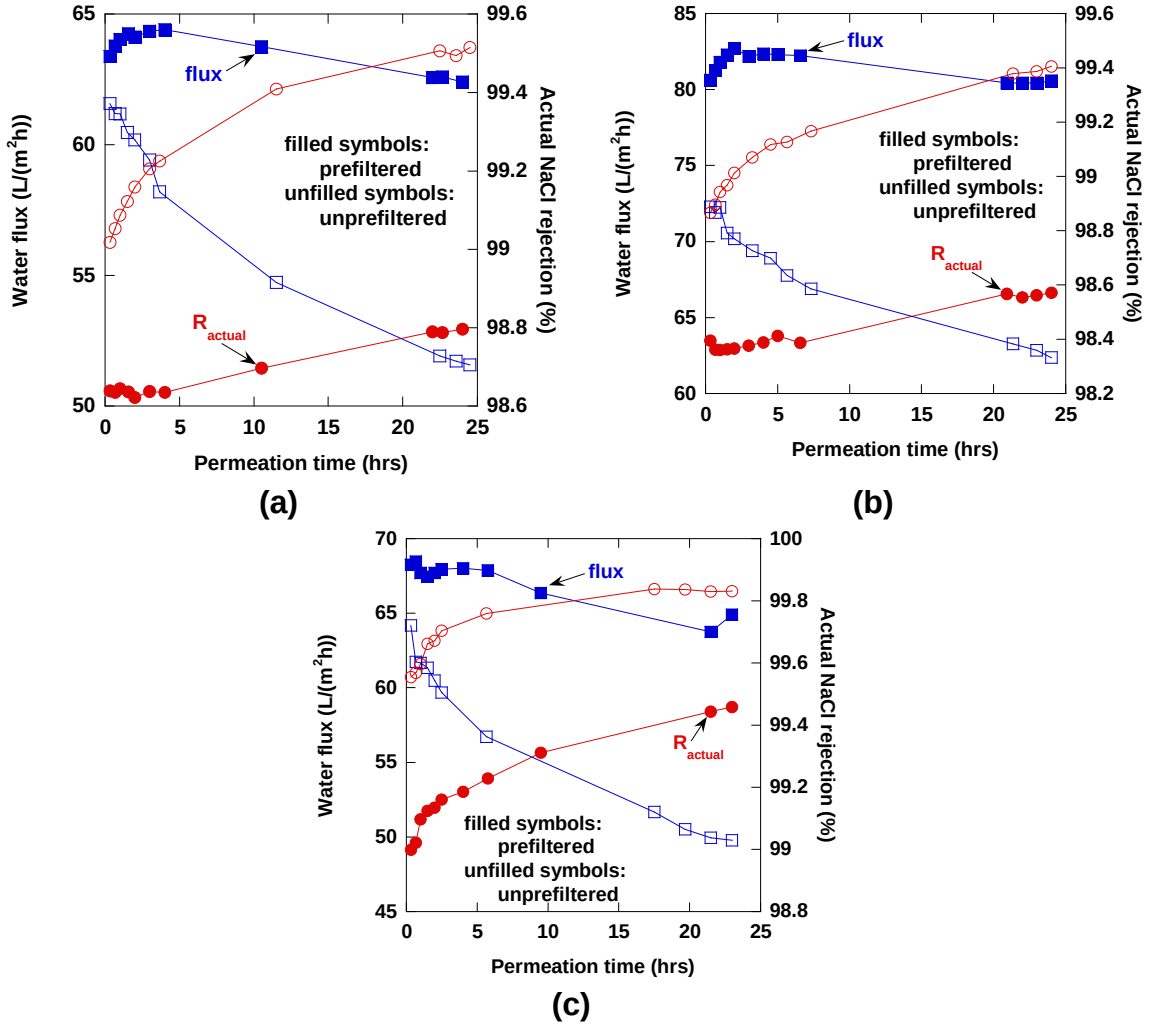


Figure 3. Comparison of average water flux and actual NaCl rejection as a function of time for **(a)** LE (T = 24-25°C, Δp = 150 psig, flowrate = 1.0 gpm, feed pH = 7.8), **(b)** XLE (T = 24-25°C, Δp = 150 psig, flowrate = 1.0 gpm, feed pH = 7.8) and **(c)** AG (T = 24-25°C, Δp = 225 psig, flowrate = 0.5 gpm, feed pH = 7.2) membranes tested in unprefiltered feed (unfilled symbols) and prefiltered feed (filled symbols).

The AG membranes displayed slightly different rejection behavior than the LE and XLE membranes, with actual rejection increasing more over time in prefiltered feed (~ 0.5%) than in unprefiltered feed (~ 0.3%) (cf. Figure 3(c)). The observed rejection for the AG membrane in the unprefiltered feed experiment was so high initially (99.4%) that not much increase was possible over the 24 hour test. The observed rejection started off a full 1% lower (98.4%) in the

prefiltered feed experiment, allowing much more room for increase over 24 hours. As comparison, the difference in initial observed rejection between prefiltered and unprefiltered feeds was much smaller for the LE (98.5% and 98.8%) and XLE (98.1% and 98.5%) membranes. Significantly higher observed rejection in the unprefiltered versus prefiltered feed experiments may explain why the actual rejection increased less in the unprefiltered feed experiment than the prefiltered feed experiment with the AG membranes. Irrespective of the time-dependent trends, water flux was always higher and actual rejection was always lower in continuous prefiltration experiments than unprefiltered feed experiments for all three membranes.

The water flux and actual NaCl rejection as a function of feed pH are given for the LE, XLE, and AG membranes in Figures 4(a)-(c). Although rejection was strongly influenced by feed pH, dropping dramatically at pH values below the pKa of the membrane surface (pH ~ 4-5), water flux was independent of pH. It should be noted that if large amounts of HCl or NaOH were required to reach extreme pH values, water flux was adjusted to account for the larger osmotic pressure. The drop in rejection observed at pH values less than the pKa may be explained by the membrane surface charge. Zeta potential measurements have shown that the polyamide surface is positively charged at low solution pH, uncharged at the isoelectric point, and becomes increasingly negatively charged with further increase in pH. Surface carboxylic acid and primary amine groups that are protonated at low pH (i.e., -COOH and $–NH_3^+$) become deprotonated (i.e., $-COO^-$ and $–NH_2$) as pH is increased beyond the pKa of the membrane surface, giving rise to the ampholytic character detected by the zeta potential. Rejection versus pH curves similar to those seen in Figure 4 for polyamide RO membranes have previously been observed in studies of polyamide nanofiltration membranes with similar surface charge properties. The numbers on Figures 4(a)-(c) indicate the order of the measurements (i.e., the history of the imposed pH changes), emphasizing that the effect of pH on rejection was reversible. That is, all three membranes recovered from periods of exposure to low pH, easily recovering their excellent rejection properties when the pH was increased.

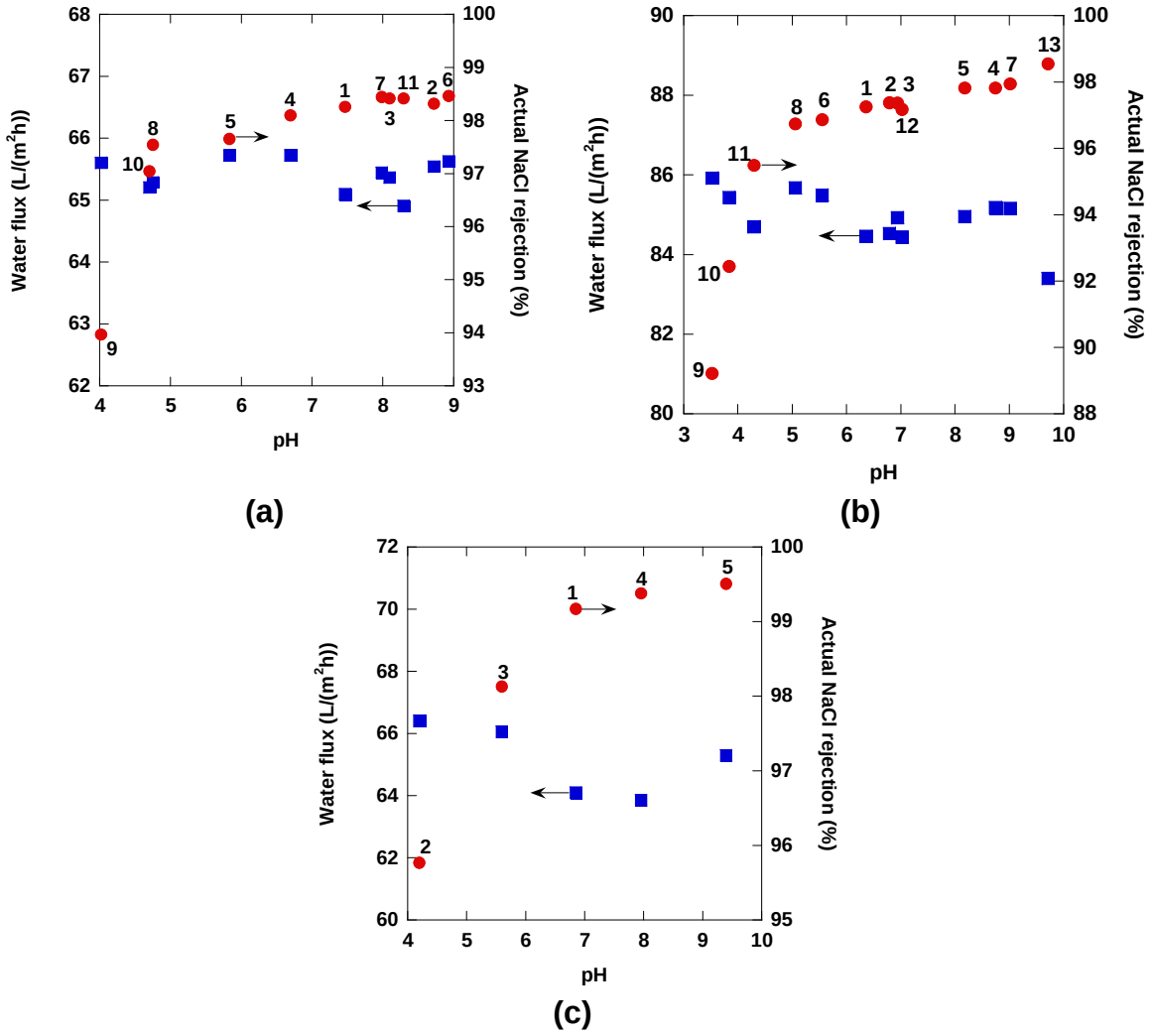
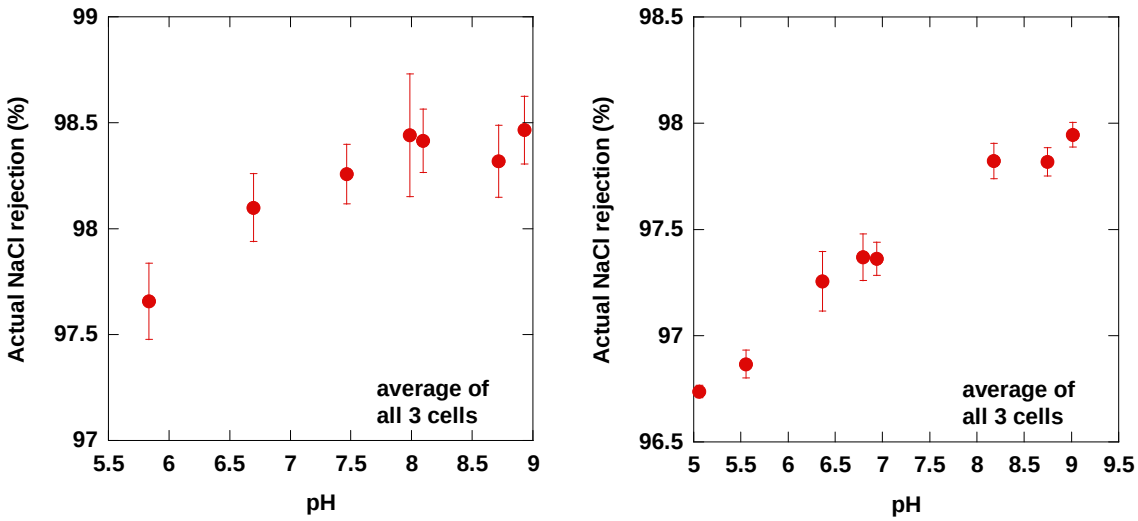


Figure 4. Average water flux and actual NaCl rejection as a function of feed pH for **(a)** LE (Δp = 150 psig, flowrate = 1.0 gpm), **(b)** XLE (Δp = 150 psig, flowrate = 1.0 gpm) and **(c)** AG membranes (Δp = 225 psig, flowrate = 0.5 gpm). For all three membranes tested, temperature was 24-25°C, feed was run continuously through carbon/particle filter, and feed pH was adjusted using 1 M HCl or 5% NaOH. Note: numbers on the figures indicate the order of the measurements, and demonstrate the reversibility of the pH/rejection phenomenon.

Figures 5(a) and (b) show the actual salt rejection of the LE and XLE membranes at pH values greater than 5. It is interesting to note that rejection increased linearly in this range, despite being at pH values above the pKa. One possible explanation is that not all surface COOH groups are deprotonated at the pKa, and as more groups are ionized, the rejection continues to increase. Regardless, the fact that rejection shows a linear dependence on pH in normal solution pH ranges emphasizes the necessity of careful pH control, since a difference of only one pH unit can change actual rejection by nearly 0.5%.



(a) **(b)**

Figure 5. Actual NaCl rejection as a function of feed pH for **(a)** LE and **(b)** XLE membranes (T = 24-25°C, Δp = 150 psig, flowrate = 1.0 gpm, feed run continuously through carbon/particle filter, feed pH adjusted using 1 M HCl or 5% NaOH).

Several experimental data points for the LE, XLE, and AG membranes are compiled in Figure 6 in the form of a permeability/selectivity tradeoff plot. Water flux is given as the indicator of membrane permeability, and salt passage (=100-R_{actual}) is the measure of selectivity. For the same salt passage, the XLE and AG membranes had higher water flux than the LE membranes. The points falling below the general trend lines established for each membrane come from the pH experiments (c.f., Figure 4), where drastic declines in salt rejection (increases in salt passage) were observed with little effect on water flux. For all three membranes, flux and salt passage values obtained in experiments using unprefiltered feed fell further to the upper left corner of the plot than those values obtained in the continuous prefiltration experiments (c.f., Figure 3), possibly due to surface fouling by the unprefiltered feed (resulting in decreased flux and salt passage).

This type of permeability/selectivity tradeoff plot is commonly used to compare gas separation membranes, but is rarely used to depict the reciprocal relationship between water flux and salt rejection observed in liquid separations. As expected, selectivity decreased (salt passage increased) with increasing permeability (increasing water flux), indicating an upper bound of separation ability for reverse osmosis membranes similar to that noted by Robeson for gas separation membranes. It is interesting that the data in Figure 6 seem to fall on two parallel lines, one for the LE membrane and one for the XLE and AG membranes.

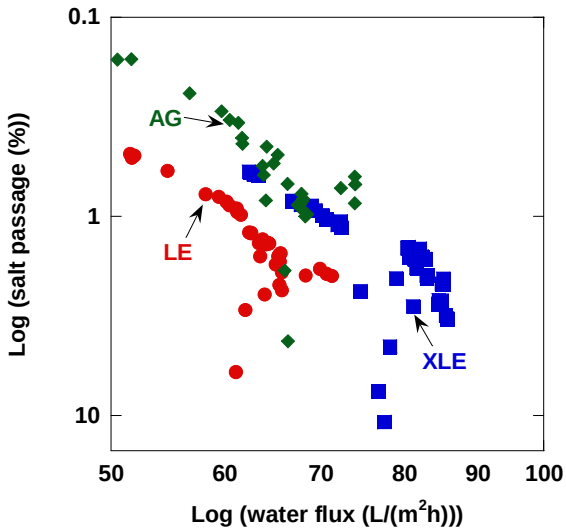


Figure 6. Permeability/selectivity tradeoff plot for LE, XLE, and AG membranes. Note: salt passage (%) = 100 – R_{actual}.

Synthesis and Characterization of Fouling-Resistant Materials. Work on fouling-resistant materials has two main directions: (1) synthesis of new coating materials and (2) direct chemical modification of the RO membrane surface. The synthesis of new coating materials focused on UV-polymerized hydrogels. As previously reported, these hydrogels, based on poly(ethylene glycol) diacrylate (PEGDA), are highly hydrophilic, a key feature for promoting water transport and preventing oil fouling.

Preparation of Coated and Surface-Modified Membranes. Preparation of coated membranes using spin coating was continued during this project period. The focus was to demonstrate the effectiveness of the flux resistance model by applying coatings of different water permeability. Based on previously reported results, spin conditions were 10 s at 2000 rpm with no high molecular weight PEO added. PEGDA and 80PEGA were selected as coating materials because of their different water permeabilities; PEGDA water permeability is 10 (L micron)/(m^2 hr bar) and 80PEGA permeability is 26.1 (L micron)/(m^2 hr bar). 80PEGA is a copolymer containing 80 mole% PEGA and 20 mole% PEGDA. Both the PEGDA and 80PEGA polymerization solutions contained 60 wt% water. Based on the flux resistance model, the water flux for these two composite membranes is expected to be noticeably different. Figure 7 shows model predictions using Eqs. 6 and 7 for water flux as a function of coating thickness for these two composite membranes.

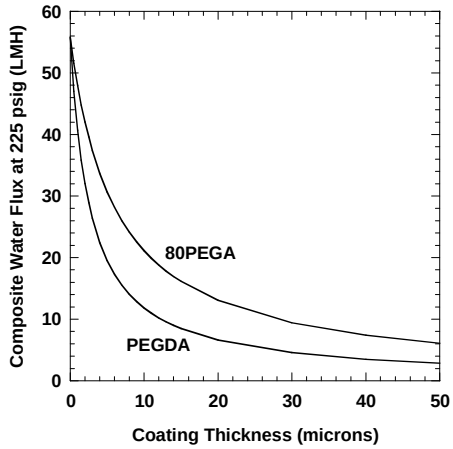


Figure 7. Model predictions for pure water flux of composite membranes.

First, ATR-FTIR was done on a PEGDA-coated membrane to verify the existence of a coating layer. Figure 8 shows spectra of an uncoated membrane, a PEGDA-coated membrane, and a dense PEGDA film. An additional peak is distinctly seen at 1724 cm^{-1} in the PEGDA-coated spectrum. This peak represents the vibrations of the C=O bond in the acrylate group of PEGDA. This peak is not observed in the uncoated membrane spectrum, but is prominent in the free-standing PEGDA spectrum. The presence of this peak confirms the presence of PEGDA on the membrane surface. However, the small intensity of the PEGDA peak relative to the RO membrane peaks suggests that (1) the coating layer is quite thin, and/or (2) the coating layer has defects and is not continuous over the membrane surface.

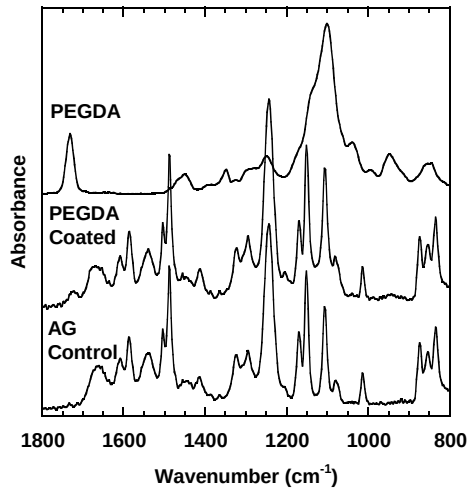


Figure 8. FTIR spectra of an uncoated RO membrane, a PEGDA coated membranes, and a free-standing PEGDA film.

Next, composite membrane samples were tested in crossflow filtration at 225 psig, 0.8 gpm, and 25°C using water with 100 mg/L NaCl (to help stabilize pH) for 4 hours to collect the "pure" water flux. Then 2000 mg/L NaCl was added and the samples were run for another 4 hours to collect salt water flux and rejection data. Membrane flux and rejection values are presented in Table 1. Coating

thicknesses were calculated using the given data and Eqs. 6 and 7.

Table 1. Composite membrane performance.

Sample	Water Flux (LMH)	Salt Water Flux (LMH)	NaCl Rejection (%)	Calculated Thickness (μm)
AG Uncoated	74 ± 1	62 ± 1	99.1 ± 0.1	NA
PEGDA	44 ± 3	42 ± 3	98.1 ± 0.3	1.4 ± 0.2
80PEGA	53 ± 3	49 ± 2	98.4 ± 0.7	2.0 ± 0.4

As expected, the composite membrane made with 80PEGA had higher water flux than the composite membrane made with just PEGDA, because 80PEGA has higher water permeability. This result supports the use of a flux-resistance model to help predict coating layer thickness and also composite water flux. The small differences in calculated coating layer thickness can be attributed to higher swelling by 80PEGA materials.

The composite membranes were also tested using different charged surfactants. Two feed solutions, one with 15 ppm SDS, an anionic surfactant, and one with 15 ppm DTAB, a cationic surfactant, were used. As demonstrated in Figure 9(a) and (b), both feed solutions fouled the membranes, but the fouling behavior was remarkably different for each surfactant. As seen in Figure 9(a), addition of DTAB caused an immediate decline in water flux, followed by a much more gradual decline, especially for the coated membranes. The coated membranes retained more of their initial water flux than the uncoated membrane. Figure 9(b) shows the more gradual fouling by SDS, a stark comparison to the drastic flux decline observed with DTAB. However, once again, the coated membranes retained more of their initial water flux than the uncoated control membrane.

Also, PEGDA-coated membranes retained more of their initial water flux than 80PEGA-coated membranes. This behavior could suggest a possible effect of coating chemistry on fouling behavior. The 80PEGA copolymer has the same PEO content as a pure PEGDA polymer, but has a lower crosslink density and more hydroxyl groups to participate in hydrogen bonding. Future work will carefully probe the effects of coating chemistry on fouling behavior.

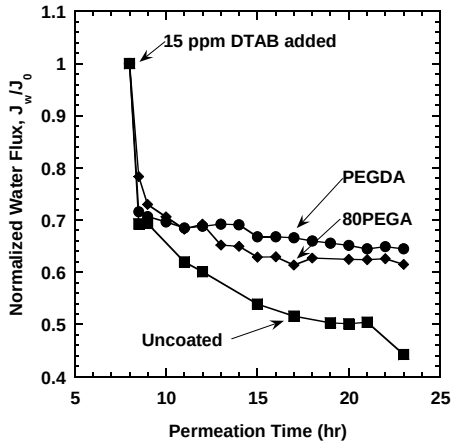


Figure 9(a). Normalized water flux membranes in 15 ppm DTAB solution. J_0 for uncoated, PEGDA, and 80PEGA samples were 61, 39, and 46 LMH respectively.

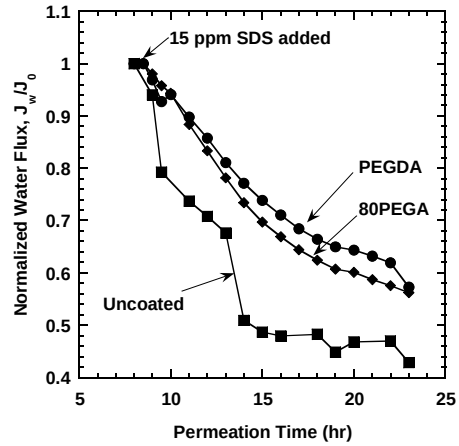


Figure 9(b). Normalized water flux membranes in 15 ppm SDS solution. J_0 for uncoated, PEGDA, and 80PEGA samples were 63, 45, and 51 LMH respectively.

Finally, composite membrane resistance to oil fouling was tested using a 150 ppm SDS/decane emulsion (1 part SDS to 9 parts decane) with 2000 mg/L NaCl. As Figure 10 demonstrates, the uncoated control membrane experiences a drastic decline in water flux, while the two coated membranes maintain their initial water flux for longer, and experience a smaller loss in water flux. After 24 hours, the coated membranes showed higher water flux than the uncoated one, although there was no significant difference seen between the PEGDA and 80PEGA membranes. Here, it appears that coating chemistry has a negligible impact on fouling behavior. However, fouling as a function of coating chemistry will be explored further in future work.

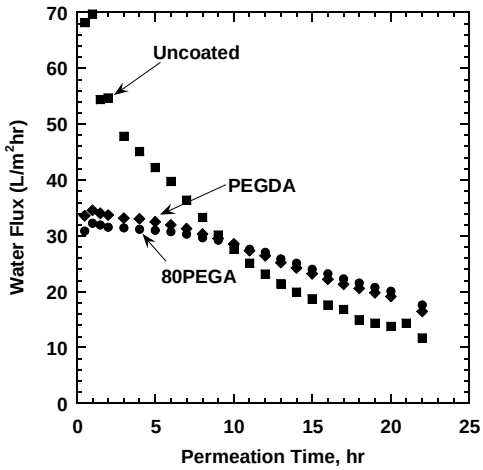


Figure 10. Oil fouling of an uncoated membrane and two coated membranes. Feed solution was a 150 ppm SDS/decane emulsion (9:1 ratio oil to surfactant) with 2000 mg/L NaCl. Operating conditions were 225 psig, 0.8 gpm, 25°C.

In conjunction with the crossflow tests and model calculations to predict coating thickness, the coatings were evaluated using SEM. Previous work had shown good agreement between a calculated thickness and the SEM image. However, further work has shown some inconsistencies. The image in Figure 11(a) shows a coating thickness of approximately 8 microns. The calculated thickness for this sample was 2.4 microns. However, the image also shows the coating delaminating from the membrane layer. Figure 11(b) is an image of a different section of the same sample imaged in Figure 11(a). A thick coating layer is noticeably absent in this image. There are two possibilities to explain this lack of coating layer. One is that the drying of the sample before imaging causes the coating layer to shrink, and therefore the coating layer coverage is reduced. Another explanation is that the coating layer is non-uniform. This would also explain the differences between the coating thickness taken from the SEM image in Figure 11(a) and the calculated coating thickness. An incomplete coating layer would create a higher than expected composite membrane flux.

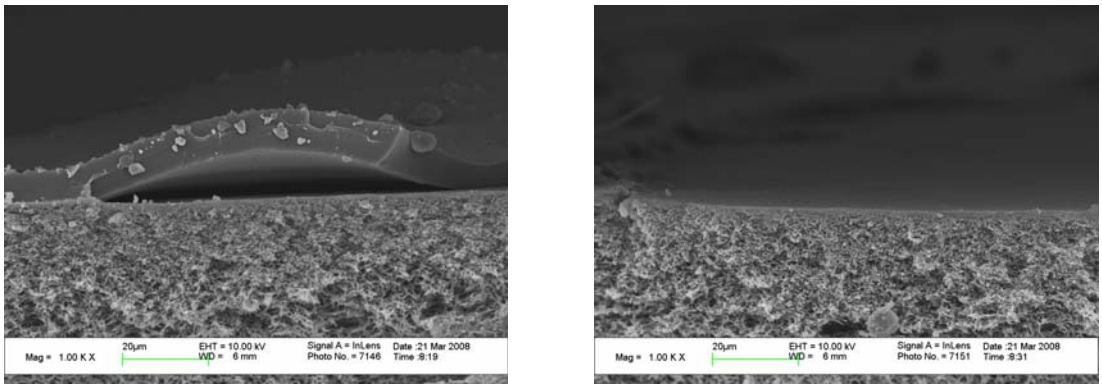


Figure 11(a) and (b). SEM images of different sections of a PEGDA-coated membrane.

Future work will focus on improving reproducibility and uniformity of membrane coatings. Previous work in our laboratories has suggested that increasing solution viscosity by adding high molecular weight PEO can improve the coating quality. Instead of increasing solution viscosity with high molecular weight PEO, which can cause phase separation, glycerol will be added to the prepolymerization solution.

Conclusions:

Commercial RO membranes were carefully characterized, controlling important variables such as feed pH and prefiltration. The effects of these testing conditions on highly selective, charge-sensitive polyamide RO membrane materials cannot be ignored. Well controlled experiments are crucial to obtaining repeatable, reliable performance values in accordance with manufacturer specifications.

Initial work on this project has shown that commercial RO membrane performance for oil in water emulsion filtration falls far below that of pure water filtration, demonstrating the need for fouling-resistant materials. PEG-based hydrogel films were synthesized and characterized and found to be excellent candidates for fouling-resistant materials based on their hydrophilic nature. Initial fouling tests using charged surfactants showed the hydrogel-coated composite membranes to retain more of their initial water flux than the uncoated membranes. Oil fouling results were similar, with the coated membranes experiencing less fouling than the uncoated membranes.

6. Milestones Not Met During the Reporting Period

All milestones for the seventh six months of the project were met.

7. Cost and Schedule Status

Cost Status:

Budget Period: 1 September 2007 – 31 August 2008

Total approved DOE budget during this budget period: $38,246.01

Total applicant cost sharing during this budget period: $32,859

Actual costs incurred during the period 1 September 2007 – 29 February 2008:

DOE cost: $24,578.99 Applicant Cost Share: $21,906

Schedule Status:

Task	Title	Year 1	Year 2	Year 3
1	Emulsion Selection, Preparation, and Characterization	_____	_____	
2	Selection of Commercial Membrane Supports	____		
3	Synthesis of Fouling-Resistant Coating Materials	_____	_____	__
4	Preparation of Coated Membranes		_____	____
5	Characterization of Fouling and Separation Performance	_____	_____	_____
6	Project Management and Reporting	_____	_____	_____

Within Task 1, produced water emulsion selection has been made in cooperation with the U.S. Bureau of Reclamation. The procedure for preparing an oil in water emulsion has been established in our laboratory for some time. Characterization of emulsions consisting of n-decane and SDS was done, and characterization of n-decane and DTAB is planned. Task 2, selection of new commercial membrane supports, is complete. Task 3, synthesis of fouling-resistant materials, began in November 2004 and is near completion. Task 4, preparation of coated membranes, has begun and currently continues. Task 5, characterization of fouling and separation performance, began in October 2004 and will continue throughout the duration of this project. Task 6, project management and reporting, occurs regularly and will continue for the duration of the project.

8. Accomplishments

The most significant developments produced by the current work show that coated and grafted RO membranes are more resistant to fouling than untreated commercial membranes. Also, careful control of testing conditions has proven invaluable for obtaining industry-standard performance values in our laboratory.

9. Actual or Anticipated Problems or Delays

There are no problems, anticipated or actual, to report at this time.

10. Technology Transfer Activities

Both students will travel to Honolulu, Hawaii in July 2008 to present their findings at the International Congress on Membranes (ICOM).