

DESALINATION BY FORWARD OSMOSIS

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Summary

Forward osmosis (FO) offers the opportunity to engineer new applications based on the ubiquitous osmotic process utilized by every living organism. Unpressurized FO can desalinate brackish water and seawater using less energy and at potentially lower costs than reverse osmosis (RO). For production of electric power, pressurized FO converts osmotic pressure to hydroelectricity.

Because the successful development of every FO application relies on the development of new ultra-thin FO membranes, our goal is to develop ultra-thin FO membranes for use in the emerging FO industry. FO requires ultra-thin membranes in order to minimize concentration polarization on both sides of its salt-rejecting water-purification membrane.

For use in the emerging FO industry, this project has the objective of developing new, ultra-thin, cellulose ester hollow-fiber FO membranes with the following properties:

1. Thin (40- μm , 1.6-mil) wall to minimize concentration polarization
2. Strength for handling and operation (and 17 bar (250 lb/in²) for osmotic power)
3. High water transport coefficient ($A > 1 \times 10^{-5}$ cm/s/bar)
4. Low salt transport coefficient ($B < 0.2 \times 10^{-5}$ cm/s)
5. High value for the combination A^2/B ($A^2/B > 5.0 \times 10^{-5}$ cm/s/bar²)

During the first six months, the project achieved the following progress regarding the above goals:

1. Created fibers with wall thicknesses less than 40 μm .
2. Membranes with thicknesses of 40 μm and less, however, require improvement in strength.
- 3 & 4. In reverse osmosis tests, achieved target values of transport properties A and B on separate fibers but not on the same fibers.
5. Developed hollow-fiber membranes with values for A^2/B of 2×10^{-5} cm/s/bar², 40-percent of the project goal.

In 2007, the project will include FO performance evaluations. If successful, the project will test FO modules at the [Bureau of Reclamation's \(Reclamation's\) Water Quality Improvement Center \(WQIC\)](#) in Yuma AZ, and if fully successful, supply FO modules for use in the emerging FO industry.

Introduction

Forward Osmosis Phenomenon

The process of osmosis is one of the “magical” consequences of thermodynamics. It is a “colligative” process in the same category as change of freezing and boiling points with change of solute concentrations. All living organisms must cope with osmotic, entropy-maximizing processes as solute concentrations vary, internally or externally. When the concentration of a solute varies in an aqueous solution, diffusion of both the water and the solvent molecules proceeds toward leveling the concentrations, and thus the chemical potential. If a membrane permeable to water but not solute is placed somewhere in the gradient, the water automatically diffuses through, into the compartment with the lower water concentration. This process can be stopped by applying pressure opposite to the flow of water, or reversed, by applying even more pressure. This process of Reverse Osmosis, RO, is absent or

rare in nature because it requires a pressure-bearing, mechanically strong membrane. However, in natural systems, plants, animals, fungi, and bacteria, FO occurs routinely, through various compartmentalizing membranes, while avoiding potentially destructive pressure differences.

Prehistoric Forward Osmosis

Dunaliella algae and sharks represent especially explicit and instructive examples of natural FO systems that have an ancient and successful heritage. The green algae *Dunaliella* species (see **Figure 1**) live in water whose steady salinity can range from brackish to concentrated. The salinity can vary due to evaporation or rain. These algae synthesize glycerol, so that the interior water concentration matches the exterior. The interior is determined by glycerol, the exterior by NaCl and other salts.

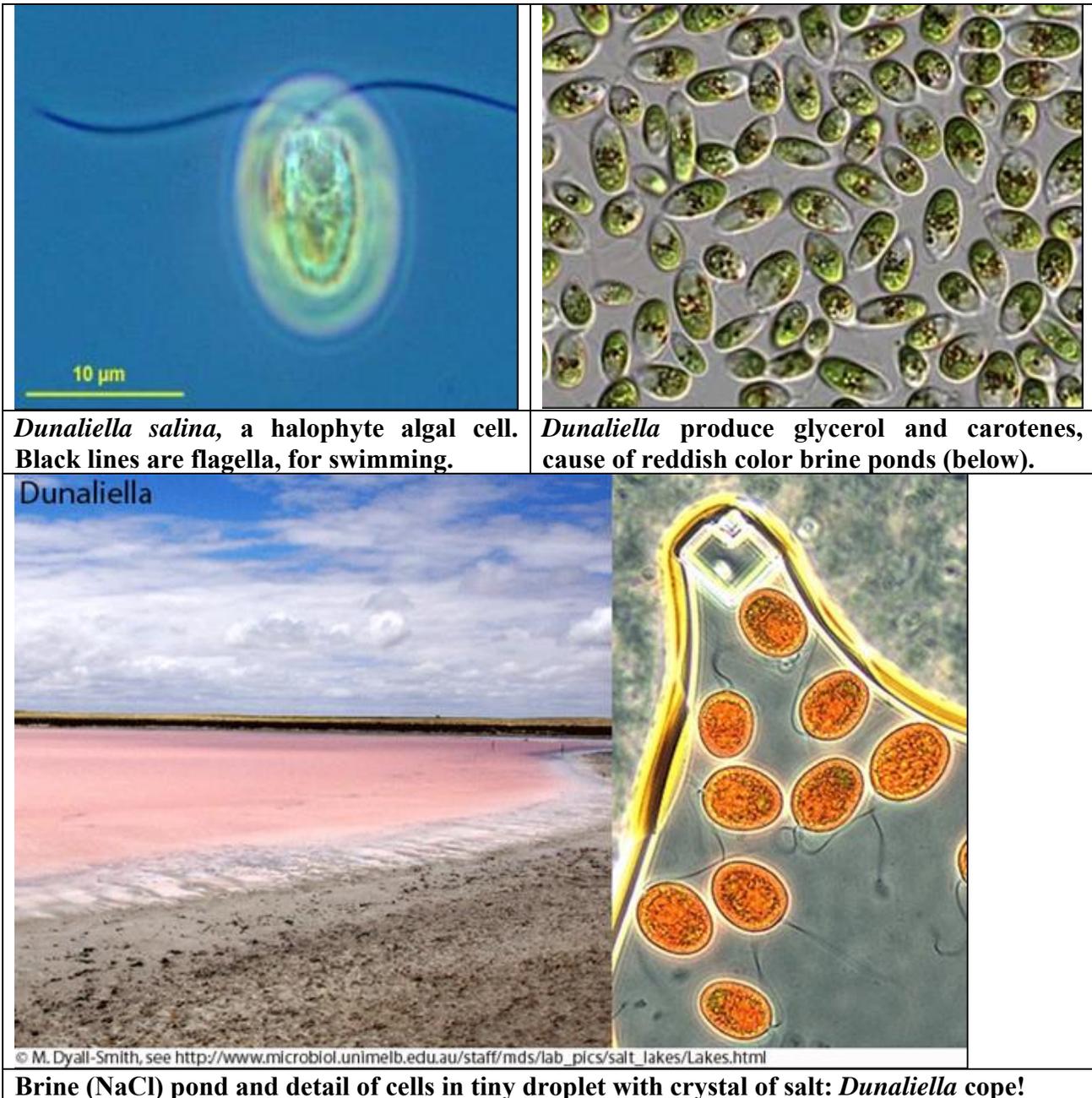


Figure 1.— *Dunaliella* algae osmoregulate with glyderol

When the external salinity changes rapidly, when it rains, for example, water diffuses from saline exterior into the algal cell. This is FO, “driven” by glycerol. To reach equilibrium before the cell pops, the cell discharges or metabolizes excess glycerol. When the pond water evaporates, increasing the salt concentration, the alga synthesizes more glycerol and thereby avoids dehydration and shriveling. Thus, given reasonable rates of change, these algal cells neither pop nor shrivel. This algal species has a pliable semipermeable cell membrane but no cell wall.

Proceeding from a ten-micrometer-size system to one which is ten foot long, sharks “drink” fresh water. Sharks (see **Figure 2**) manage that trick by employing a semi-permeable (water only) membrane in their mouths or gills and by synthesizing urea plus trimethylamine oxide, another solute. This combination drives the FO that extracts fresh water from seawater and moves it into the sharks’ interior. Excess urea is eventually discharged.

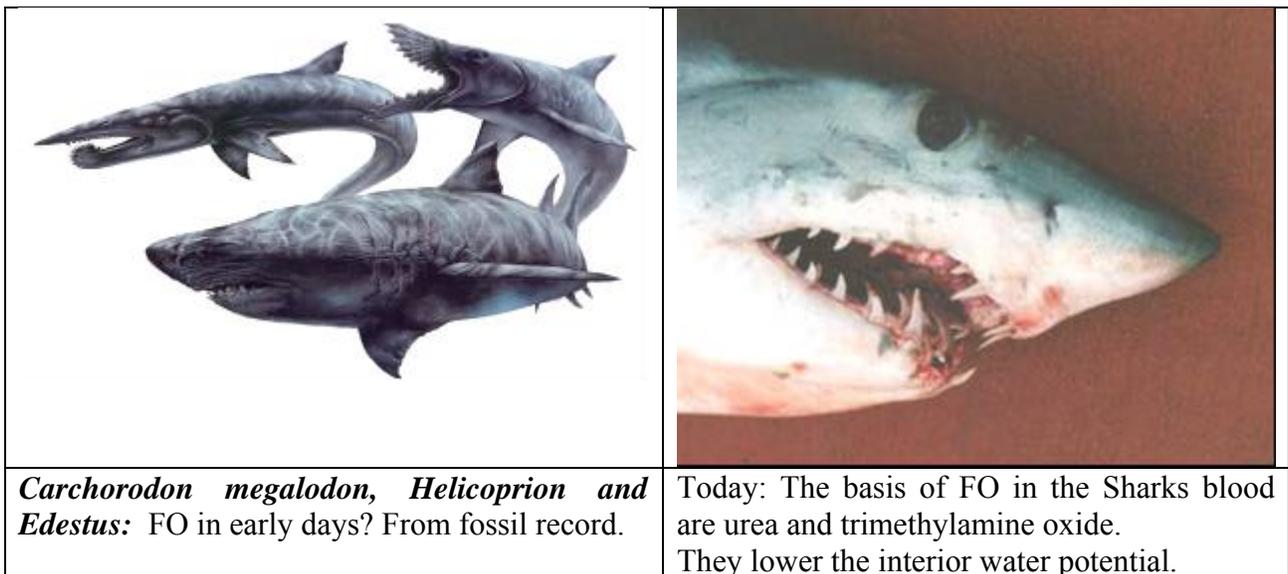


Figure 2.— Sharks osmoregulate with urea and trimethylamine oxide

Learning from nature: The next step Reverse Osmosis

Water desalination using synthetic semipermeable membranes was an obvious development, once such membranes became available. RO has the advantage that it delivers “pure” water. It has the obvious disadvantage that the membranes require intrinsic strength, or a strong support. It also requires power consumption for generating high pressures and for pumping. The osmotic pressure of seawater is of order thirty atmospheres (400 lb/in²)! Nevertheless, RO has become a major desalination technique.

Forward Osmosis

Purification using the natural thermodynamic diffusive process of FO can use thin, mechanically “weak” membranes that at least in principle would generate less concentration polarization than RO. The flow per difference in osmolarity would then be limited by permeability and mixing efficiencies. FO delivers not pure water, but a solution that is at least slightly more concentrated than the source. One possibility for coping with this fact employs a driving solute that, together with the purified water, is a useful end product. Using soluble fertilizer, for agricultural applications, e.g. re-use of brackish effluent from irrigation, is one possibility that we originally investigated (1, 2, 3). Another possibility is the use of dextrose, fructose, and amino acids for producing a potable solution such as infant formula or a sports drink from a source of polluted water or seawater (4). Another FO method uses a driving solution that

can be recycled easily, safely, and economically (5, 6, 7). The present progress report considers the development of membranes for use in these applications. They must be efficient, thin, have excellent rejection of solute, and be highly water permeable.

The development of effective RO membranes in the 1960's and 1970's stimulated investigations into its sister process: forward osmosis (FO). References 1 to 13 contain major innovative contributions representing FO's "beginnings" in the twentieth century. The U. S. Department of the Interior's Office of Water Research & Technology sponsored many of these contributions to the development of forward osmosis. FO offers many promising application areas including hydration, dehydration, and power production.

Hydration

In hydration mode, FO produces desalted and purified water by employing driving solutes in sufficient concentration to maintain an osmotic pressure higher than that of the salty or contaminated water supply. If the driving solutes consist of plant or human nutrients, then the FO product solution may be used to supply part or all of the required water needs. To produce solute-free water, FO requires a second step to remove and recycle the FO driving solute.

For hydrating human nutrients packaged in semipermeable hydration bags, companies that offer FO hydration bags include Cellopore (14) and Hydration Technologies (15). Because of the low flow afforded by existing RO-type membranes, all existing FO hydration bags require several hours to hydrate, making them impractical for use with low-salinity water and nonfunctional for use with seawater. We are presently developing improved FO membranes for use in Instant Water kits.

To produce solute-free water, FO requires a second step to remove and recycle the FO driving solute. In this case, the driving solute is judiciously selected based on its ease of removal and recycle, high-rejection by FO membranes, and low toxicity and low cost because small amounts may leak through the membrane and some may also remain in the final purified product. **Figure 3** shows a schematic of a Forward Osmosis Desalination Plant (FODP).

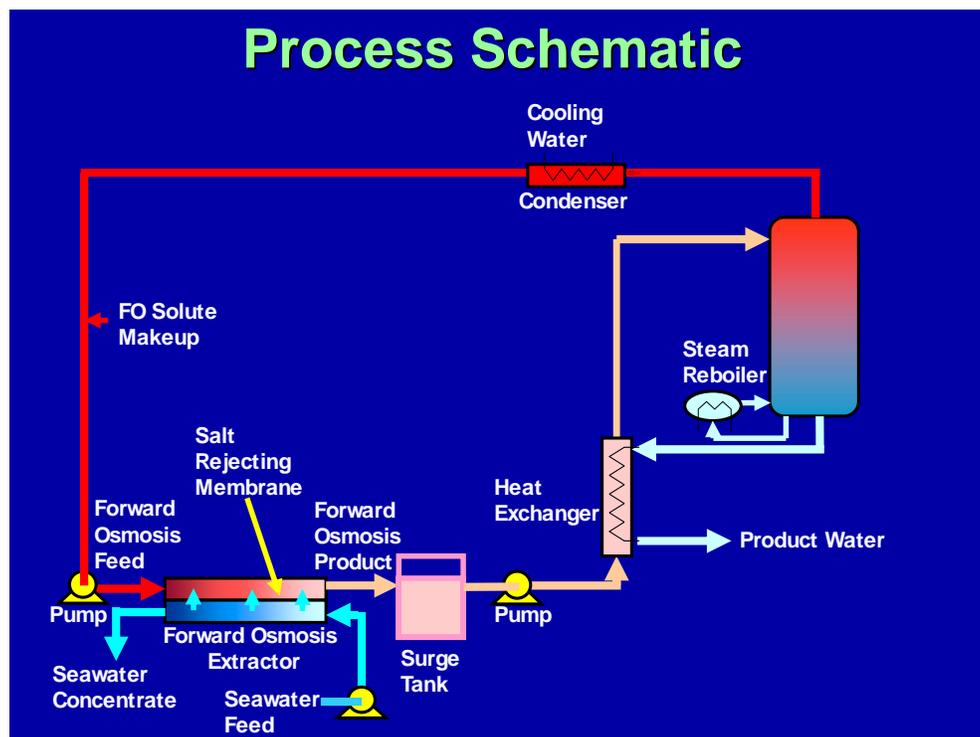


Figure 3.— Forward Osmosis Desalination Plant (FODP) process schematic

The FO extractor operates at atmospheric pressure with a semipermeable FO membrane separating seawater, containing 35,000-mg/L total dissolved solids (TDS), from the driving solution in countercurrent flow. The FO product may contain about 5-percent (50,000-mg/L) driving solute. The bottoms product from the distillation column may contain about 10-mg/L driving solute. The distillate recycle may contain about 14-percent driving solute, which is recycled to the FO extractor.

Murray in 1968 (8) and McCutcheon et al, in 2005 (16) have proposed ammonium bicarbonate as a driving solute. We plan to evaluate this and other FO driving solutes at Reclamation's WQIC.

Compared to distillation processes, the FO solute removal and recycle step has much lower energy requirements because it vaporizes much less material - only the driving solute with some of the water. Compared to the RO-based Expeditionary Unit Water Purification (EUWP) (17), a FODP can be lighter because of its low-pressure plastic components and quieter because it operates primarily on thermal power and does not require high-pressure RO pumps or large electrical generators.

Dehydration

In dehydration mode, the high osmotic pressure of high concentrations of FO driving solutes can dehydrate and thereby minimize the volume of concentrated food or waste solutions. For example, Holloway (18) proposes the use of FO for concentrating anaerobic digester concentrate.

For wastewater purification and desalting, the dehydration capability of FO offers very high water recovery, an advantage compared to RO when recovery is limited by operating pressure. Very high recovery means both highest conversion of the source water to low-salinity product water and minimization of the volume of reject concentrate to be disposed.

Hydroelectric Power Production (Osmotic Power)

With osmotic power, FO power plants use the osmotic pressure difference between freshwater and saltwater to produce hydroelectric energy (19). Professor Sid Loeb, co-inventor of the salt-rejecting cellulose acetate membrane that launched the RO desalting industry, originated the "pressure-retarded osmosis" concept (11, 12, 13). The Norwegian power company Statkraft has been developing osmotic power as a "green" energy source (20).

FO Membrane Development

At the University of Arizona, in cooperation with Bob Riley, in 1975 - 1977, John Kessler and Chuck Moody published their initial works on FO.

In 1998 - 2002, sponsored by the Defense Advanced Research Projects Agency (DARPA), SST evaluated RO membranes for FO use and fabricated 2.5-inch diameter by 40-inch long FO modules.

In 2003 - 2005, sponsored by the U.S. Army TACOM - TARDEC, SST developed chemistries and fabrications of semipermeable membranes designed specifically for FO applications.

Figure 4 contains a scanning electron microscope (SEM) image of a flat sheet reverse osmosis membrane. In addition to the thin, active semipermeable membrane skin, it consists of a (1.6-mil, 40- μm) membrane substructure and a (2.7-mil, 70- μm) woven fabric backing. RO water flow creates minor concentration polarization on the exposed skin.

Equation 1 describes the concentration profile based on the one-dimensional flow assumption used in the unstirred film theory:

$$C_{sw} = C_{s\infty} \exp (q\delta_s/D_s) \quad (1)$$

where: q = Membrane water flux, m/s
 C = Concentration
 δ = Unstirred film thickness, m
 D = Diffusion coefficient of solute in water, m²/s
 Subscript s = Source solution side of the membrane

Subscript w = Property at membrane surface (wall)
 Subscript ∞ = Property of the bulk solution

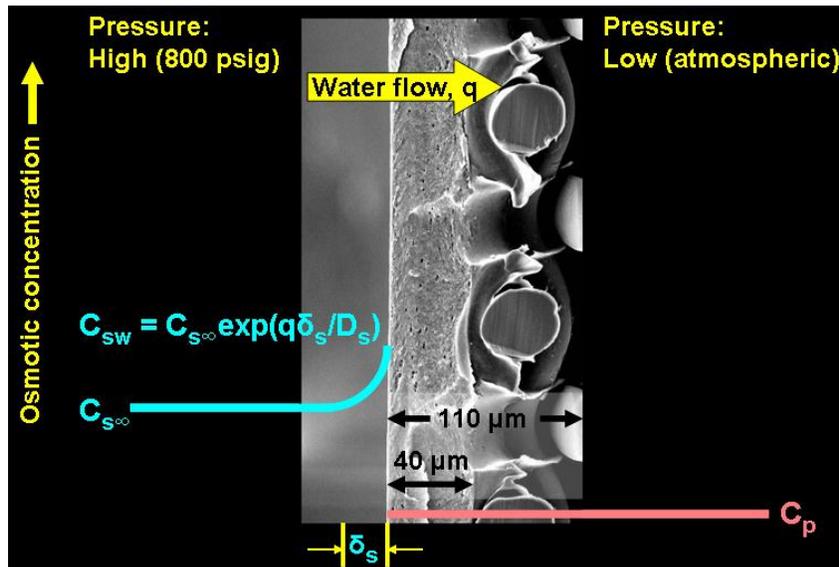


Figure 4.— Schematic of RO concentration polarization illustrating how water flow causes the source solute (salt) concentration to increase near the membrane surface.

FO creates concentration polarization on both sides of the membrane (see Figure 5). With existing RO membranes, the substructure and fabric create significant concentration polarization that greatly reduces the effective osmotic pressure difference and “osmotic efficiency” of the process.

Equation 2 describes the concentration profile on the driving side of the membrane.

$$C_{dw} = C_{d∞} \exp(-qt\delta_d/(\theta_d D_d)) \quad (2)$$

where: Subscript d = Driving solution side of the membrane
 θ = Porosity of unstirred film; $\theta = 1.0$ on smooth asymmetric active side of membrane; $0 < \theta < 1.0$ on porous backing side of membrane
 t = Tortuosity of porous backing; $t > 1.0$

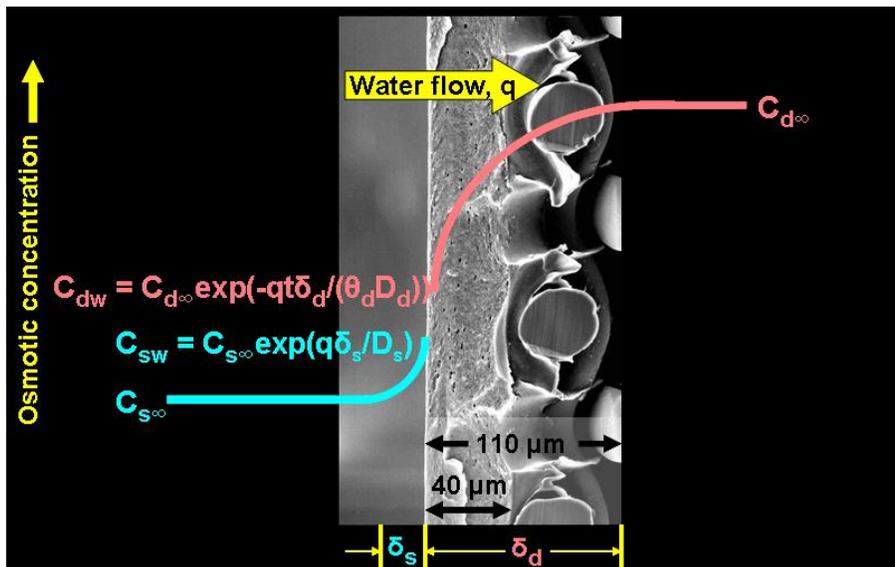


Figure 5.— Schematic of FO concentration polarization.

For use in the emerging FO industry, this project has the objective of developing new, ultra-thin, cellulose ester hollow-fiber FO membranes with the following properties:

1. Thin (40- μm , 1.6-mil) wall to minimize concentration polarization
2. Strength for handling and operation (and 17 bar (250 lb/in²) for osmotic power)
3. High water transport coefficient ($A > 1 \times 10^{-5}$ cm/s/bar)
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5. High value for the combination A^2/B ($A^2/B > 5.0 \times 10^{-5}$ cm/s/bar²)

This paper presents development results for membrane properties 1, 3, and 4 for the first 6 months of funding from the Office of Naval Research (ONR).

Hollow-Fiber Membranes

To achieve the thinnest possible membrane substrates and high packing densities, this project develops hollow-fiber FO membranes. Hollow-fiber FO membranes have several advantages compared to flat sheet membranes. These advantages include high membrane packing density, ruggedness, and reduced concentration polarization.

High Membrane Packing Density

Hollow-fibers have a much higher area-to-volume ratio than flat sheets so that more membrane area can be packaged into a small volume. For example, with 0.3-mm-diameter hollow fibers, a 1.5-inch-diameter by 6-inch-long cylindrical module with a void percentage of 50 percent can hold four thousand 12-inch-long (looped to fit in the 6-inch-long module) fibers with a total area of 12 ft². The 1.5-inch-diameter by 6-inch-long hollow-fiber module contains about the same area but is much more compact than a 2.5-ft by 2.5-ft FO hydration bag or a 2.5-inch-diameter by 20-inch-long (2520) spiral-wound RO element (containing a flat sheet membrane envelope measuring 1.7-ft wide by 3.3-ft long).

Ruggedness

For thin membranes without a fabric backing, fibers are self-supporting and less susceptible to damage by tearing during routine handling and manufacturing.

Reduced Concentration Polarization

Because of their rugged self-supporting geometry, hollow-fiber membranes can be made with thinner substrates and no fabric backing. Eliminating the backing used in flat sheet reduces concentration polarization, which obstructs membrane surface renewal rates. Because of the hollow fiber's high area-to-volume ratio, a small unit with high membrane area can afford to operate at lower membrane water fluxes, thereby decreasing concentration polarization which varies exponentially with water flux rate.

Membrane Development Procedure

To develop and improve the membrane properties, we have implemented an organized, efficient hollow-fiber membrane development procedure consisting of sequential "trials" with the following experimental design steps:

1. Select process variables from **Table 1** for testing.
2. Select two levels of each process variable.
3. Use two-level fractional factorial designs (21) to prescribe process conditions.

4. Measure response variables (see **Table 2**).
5. Evaluate effects of the selected process variables and process variable interactions on response variables by statistical analysis.
6. Review and discuss results in preparation for the next trial.

Table 1. Process variables

Polymer Five-component composition Flow dynamics	Spinneret Type and design Dimensions	Aqueous gelation bath Temperature
Bore Composition Flow dynamics	Convection chamber Gas composition Residence time	Post-treatment Anneal temperature Chemical surface treatment Drying procedure
Fiber extrusion speed	Temperature Humidity	Other process variables

Table 2. Response Variables

Response variable	Target values	Measurement method
Wall thickness	40 μm	Scanning electron micrograph
Water transport coefficient (A) ¹	1.0×10^{-5} cm/s/bar (1.0×10^{-12} m/s/Pa)	8 to 16 hours of operation at 25 to 30 lb/in ² (2 bar) pressure with 1,000 mg/L sodium chloride.
Salt transport coefficient (B) ²	0.2×10^{-5} cm/s (0.2×10^{-7} m/s)	
Combination of water and salt transport coefficients A ² /B	5.0×10^{-5} cm/s/bar ²	
Salt rejection at 30-lb/in ² net pressure	91 percent	

¹ The water transport coefficient (A) represents the proportionality coefficient between product water flux (q [cm/s]) and hydrostatic and osmotic pressure difference (ΔP [bar] and $\Delta \pi$ [bar]) across the membrane in the equation: $q = A (\Delta P - \Delta \pi)$

² The salt transport coefficient (B_i [m/s]) represents the proportionality coefficient between solute flux (j_i [g/m²/s]) and concentration difference (ΔC_i [g/m³ = mg/L]) across the membrane in the equation: $j_i = B_i \Delta C_i$

Figure 6 contains scanning electron micrographs from four combinations of two process variables in an October 2006 trial. The micrographs and values of response variables show the effects of the two process variables on hollow-fiber membrane properties. Properties with underline meet the project goals. The fiber walls on the right side have larger radial pores than the fiber walls on the left side. These may offer the advantages of low tortuosity and high porosity, but may offer the disadvantage of lower strength.

Discussion

During the first six months, the project achieved the following progress for project goals 1 to 5:

1. Created fibers with wall thicknesses less than 40 μm .
2. Membranes with thicknesses of 40 μm and less, however, require improvement in strength.
- 3 & 4. In reverse osmosis tests, achieved target values of transport properties A and B on separate fibers but not on the same fibers.
5. Developed hollow-fiber membranes with values for A²/B of 2×10^{-5} cm/s/bar², 40-percent of the project target value of 5×10^{-5} cm/s/bar².

In 2007, the project will conduct strength tests and FO performance evaluations. If successful, the project will test FO modules at the [Bureau of Reclamation's Water Quality Improvement Center](#) in Yuma AZ, and if fully successful, supply FO modules for use in the emerging FO industry.

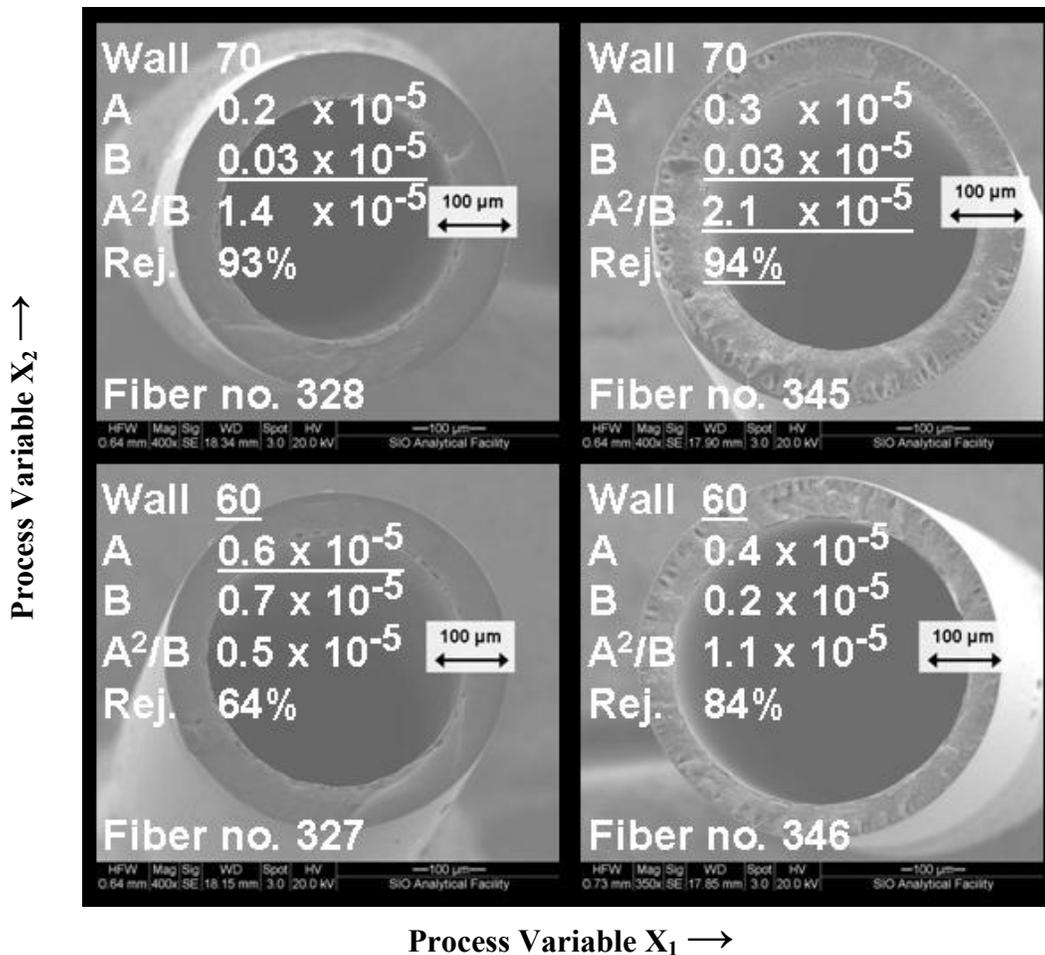


Figure 6.— Results of October 2006 Experimental Trial

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