



Nanotechnology-based Membranes for Desalination



Eric M.V. Hoek
Assistant Professor

*Civil & Environmental Engineering Department
Water Technology Research Center
California NanoSystems Institute
UCLA*

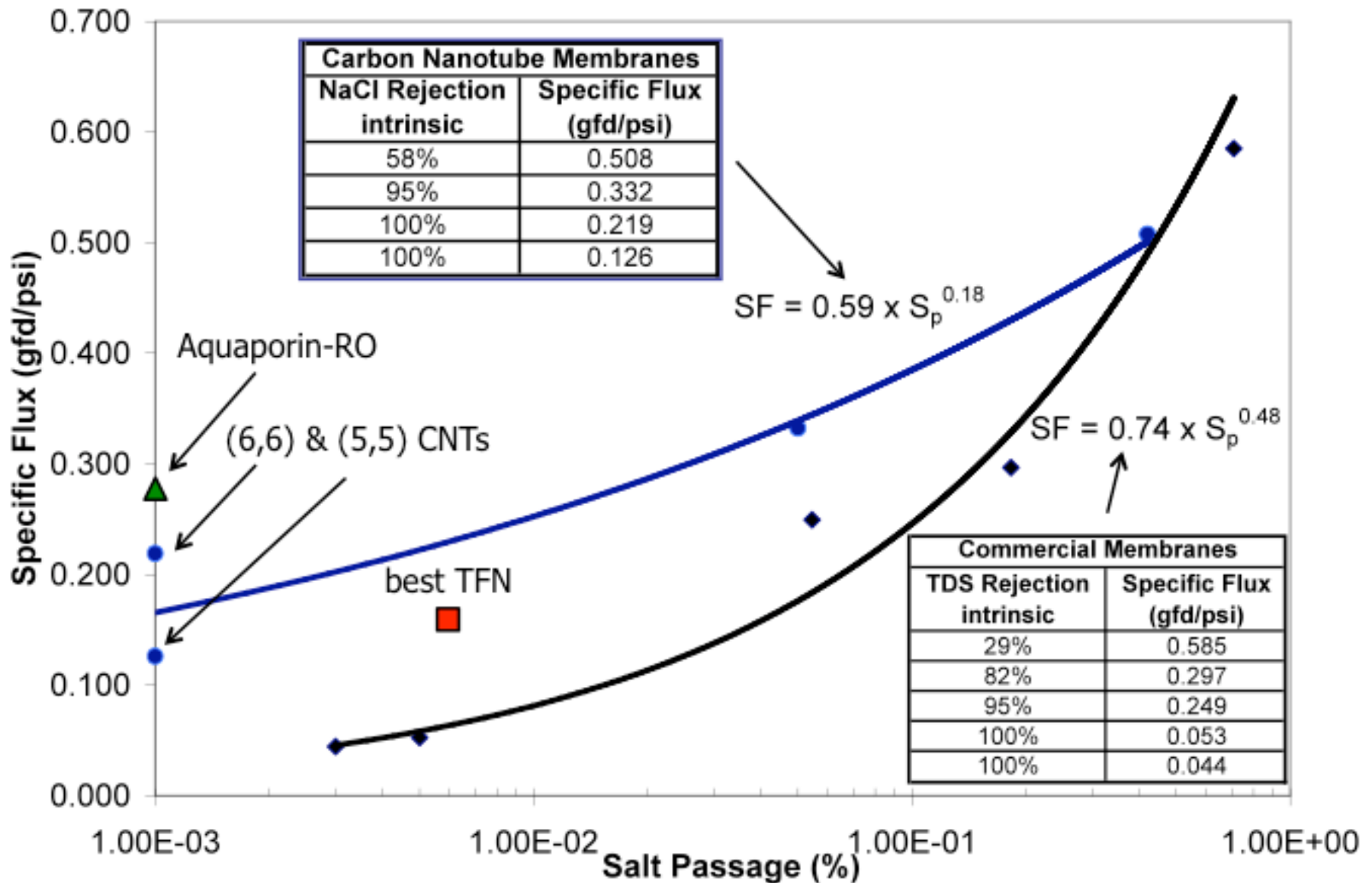


Outline

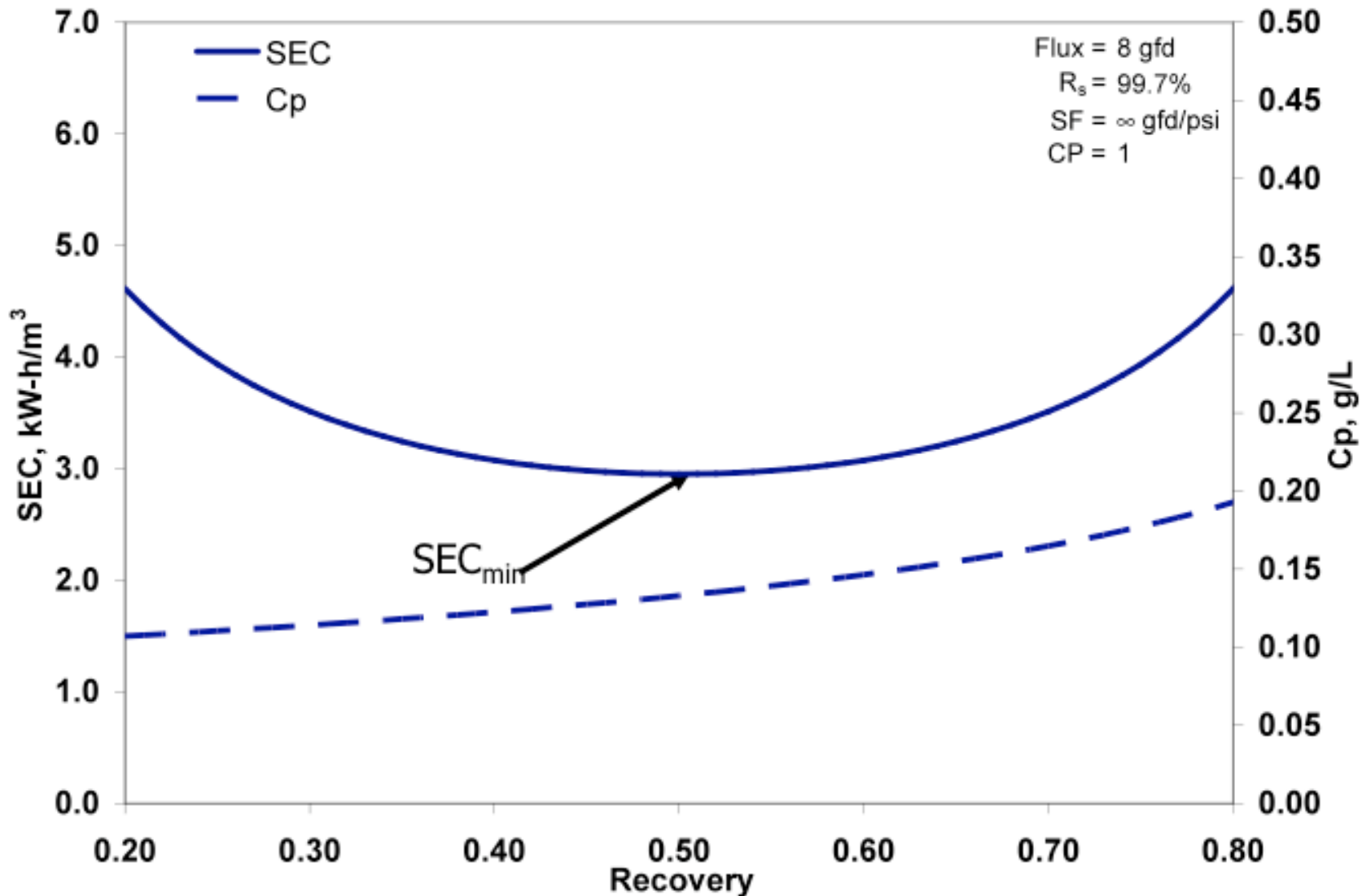


- Conclusions
 - Can nanotechnology fundamentally change energy consumption in desalination?
 - **Maybe, but we probably need to change the way we do desalination to best leverage the benefits...**
- How did I arrive at this conclusion?
 - Concepts and pitfalls associated with:
 - Inorganic-organic nanocomposite membranes
 - Hybrid protein-polymer biomimetic membranes
 - Aligned carbon nanotube membranes
- How might nanotechnology best be leveraged to improve water treatment membrane technology?

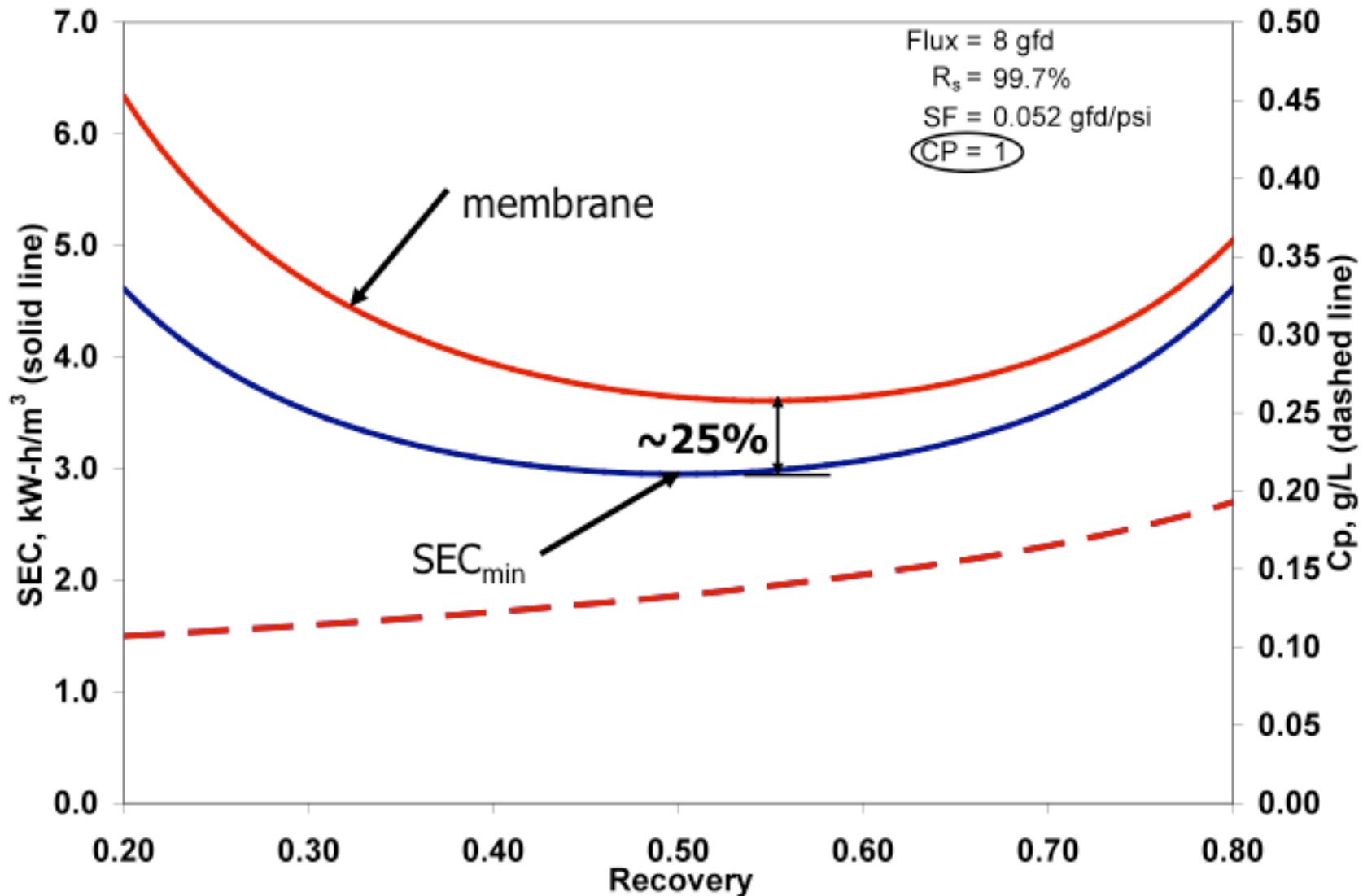
Permeability Trade-Off Curve



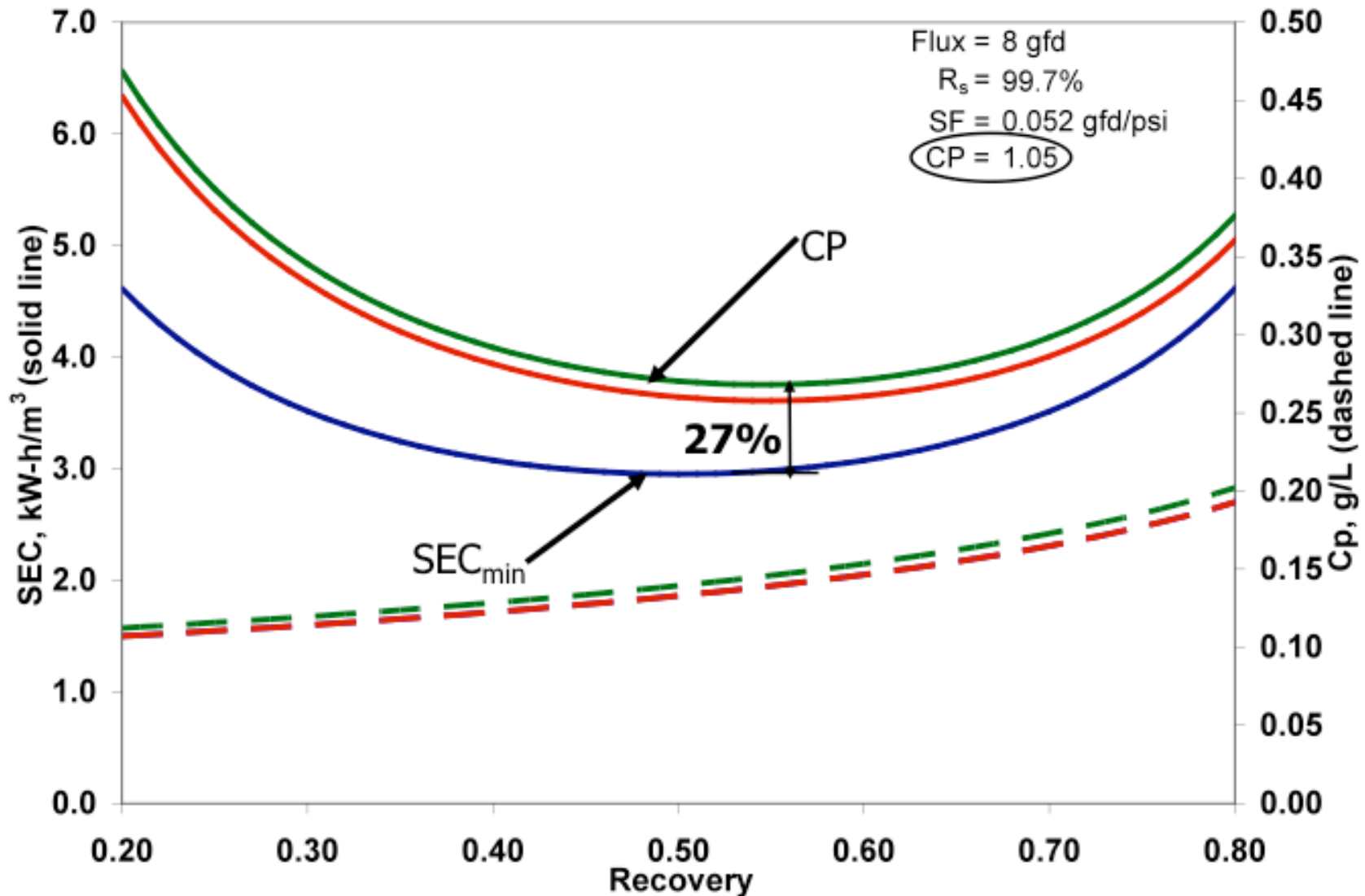
What is the theoretical minimum energy consumption?



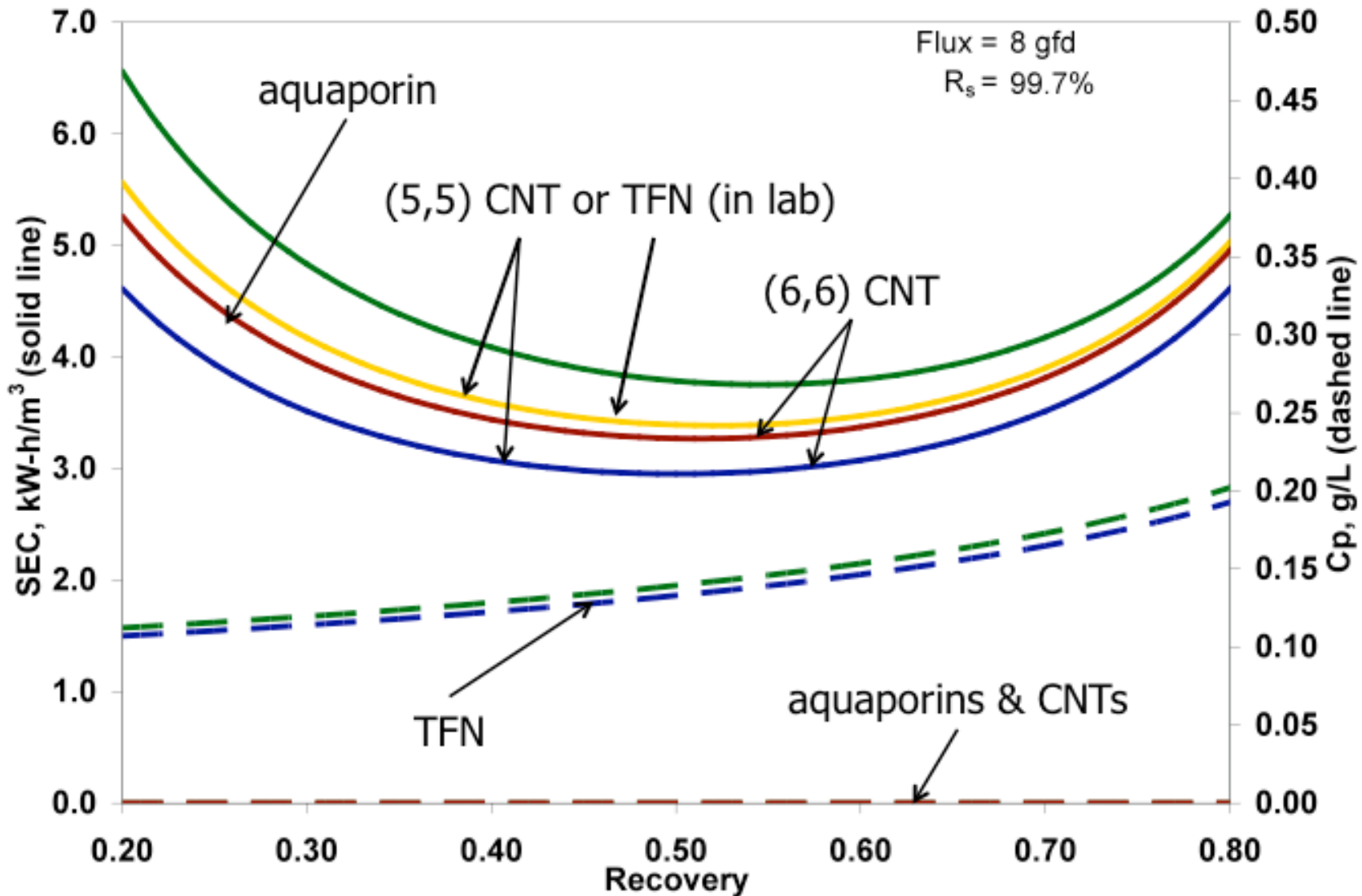
What is the impact of the membrane on energy consumption?



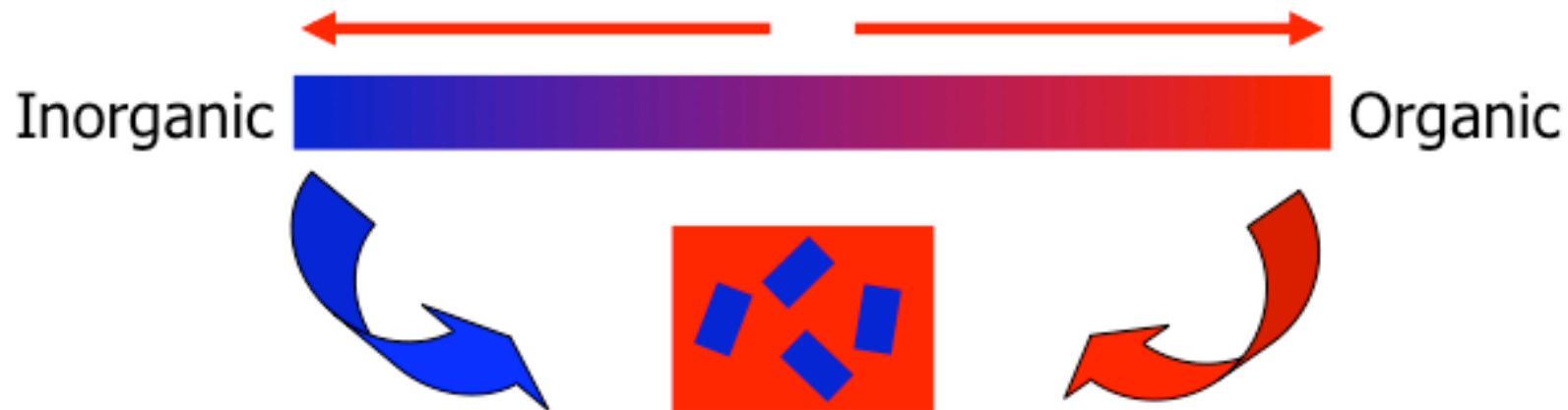
What is the impact of concentration polarization on energy consumption?



How close to the theoretical minimum can nanotechnology get?



Inorganic-organic nanocomposites



Inorganic/Ceramic

Advantages

- tunable selectivity
- excellent stability
- easy to clean

Disadvantages

- poor processing
- inflexible, brittle
- low packing density

Nanocomposite

Advantages

- improved selectivity
- improved stability
- easy to process
- high flexibility
- high packing density

Disadvantages

- I/O compatibility
- NP loading limits

Organic/Polymer

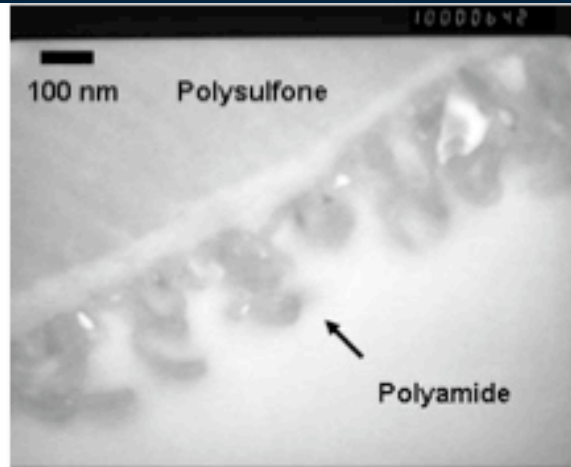
Advantages

- easy to process
- high flexibility
- high packing density

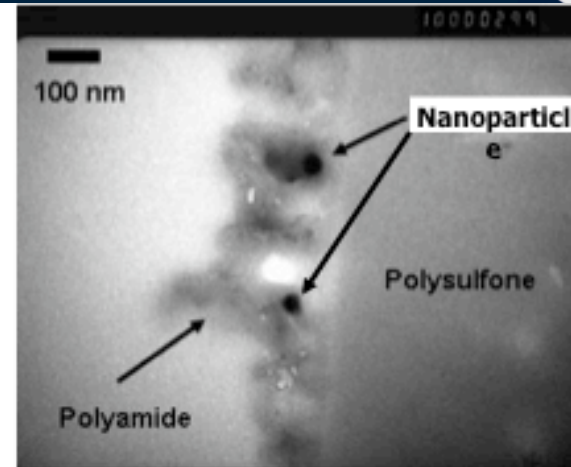
Disadvantages

- fixed selectivity
- poor stability
- difficult to clean

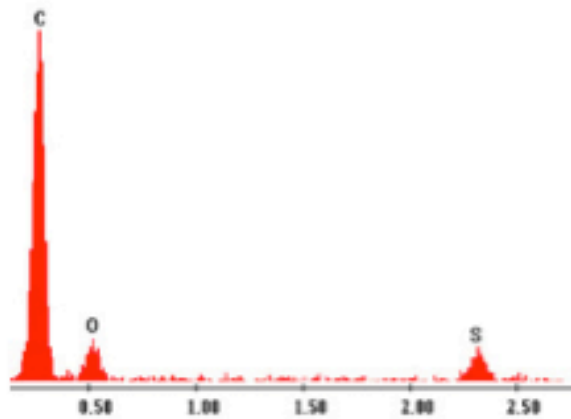
Thin film nanocomposites



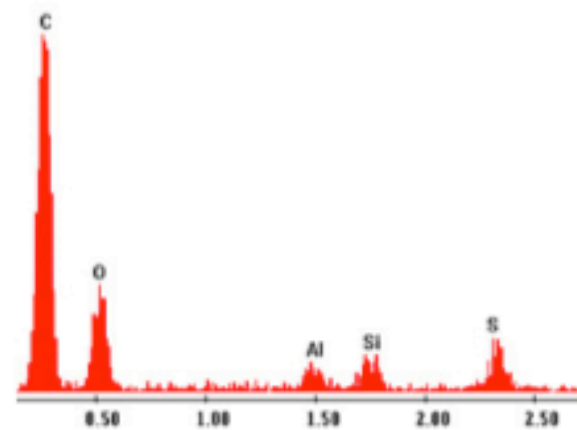
(a) TFC membrane, 100kX



(b) TFN membrane, 100kX

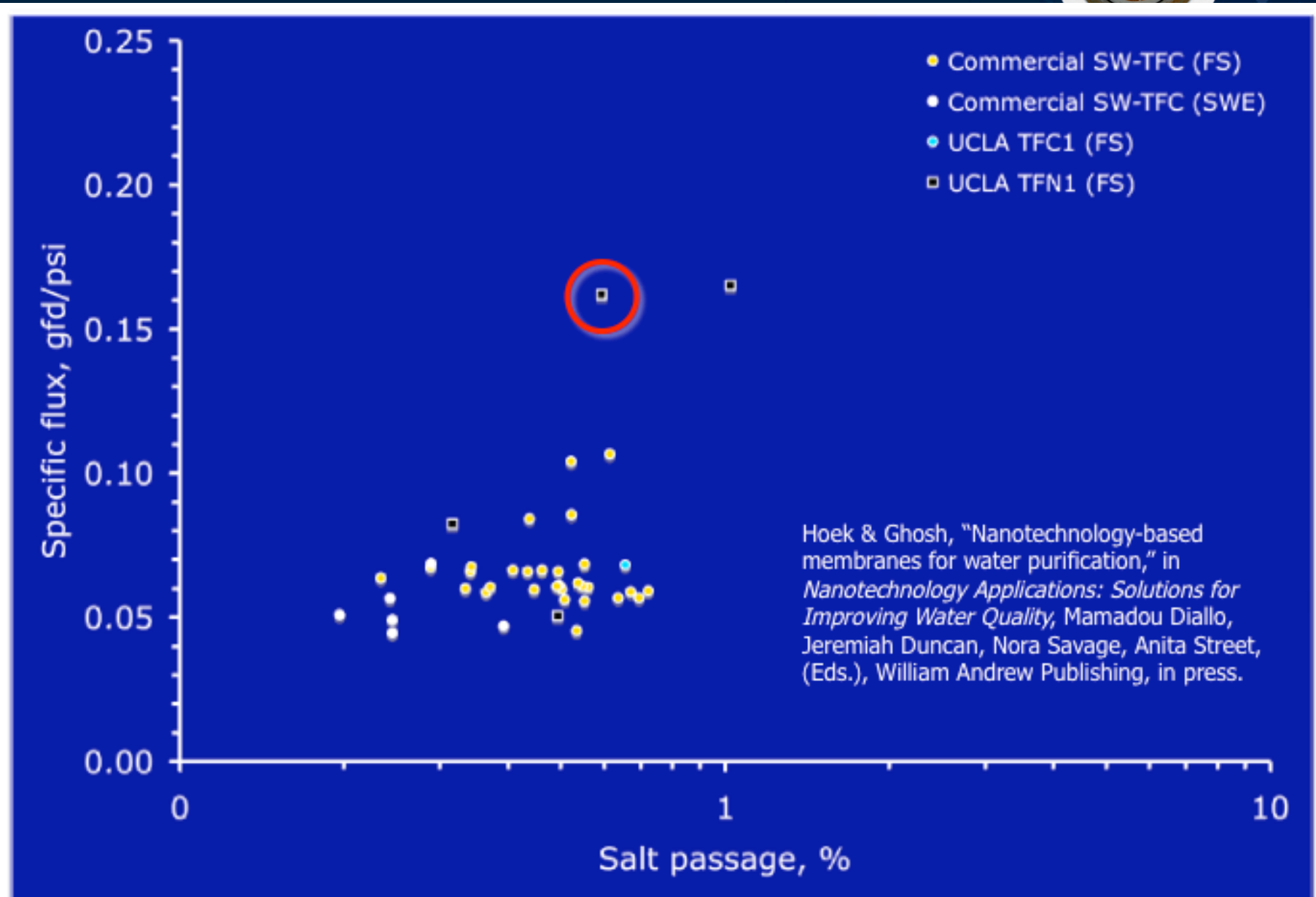


(c) TFC membrane, EDX

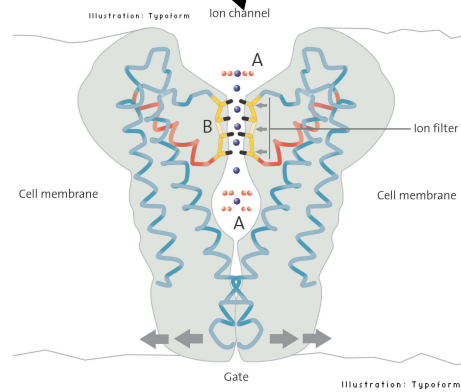
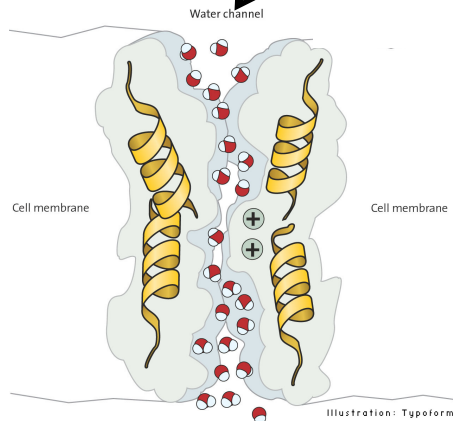
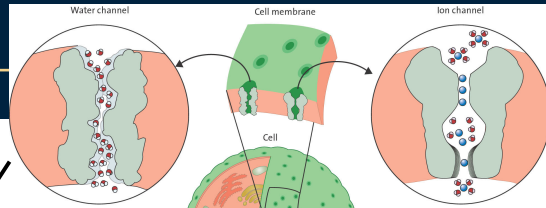


(d) TFN membrane, EDX

TFC and TFN separation performance



Biomimetic membranes



p_f/p_d ratio of 11.9, in good agreement with experimentally measured ratio of 13.2 for AQP1

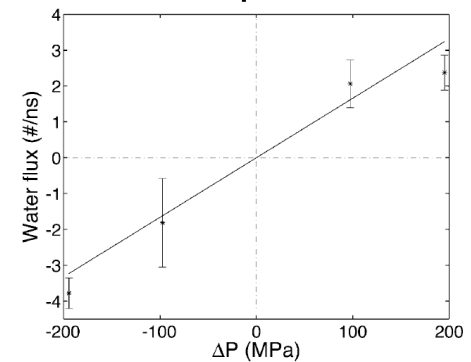
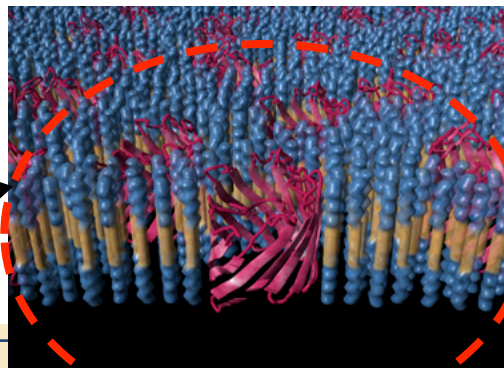
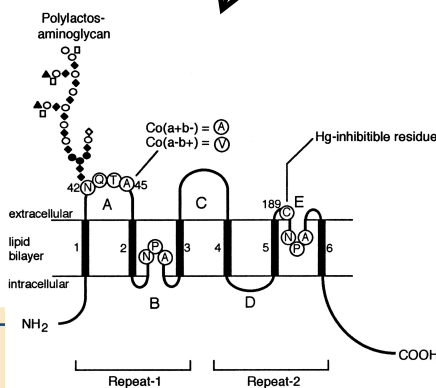


FIGURE 6 The dependence of water flux on the applied pressure difference. Values of pressure differences and water fluxes are taken from Tables 1 and 3, respectively. A line with the best-fit slope for the four data points is also shown in the figure.

Biomimetic membranes

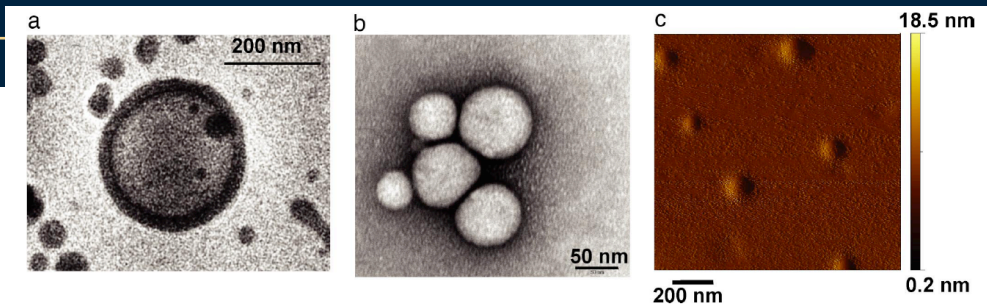


Fig. 1. Examination of polymer vesicles by using microscopy. The cryogenic transmission electron microscope images were used for size determination because regular transmission electron microscopy and atomic force microscopy influence the structure of the observed vesicles. (a) Cryogenic transmission electron micrograph of an ABA polymer vesicle. (Scale bar: 200 nm.) (b) Electron micrograph of a cluster of vesicles. (Scale bar: 50 nm.) (c) Atomic force micrograph of vesicles on mica in nontapping mode shows that a film of polymer is formed on the hydrophilic mica surface with vesicles located in the film. (Scale bar: 200 nm.)

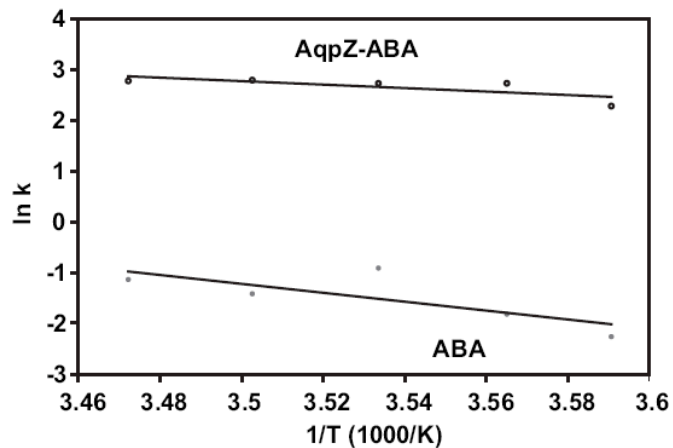


Fig. 3. Arrhenius plots for calculation of activation energy for osmotic transport of water across polymer membranes with incorporated AqpZ (AqpZ-ABA) and pure polymer membranes (ABA).

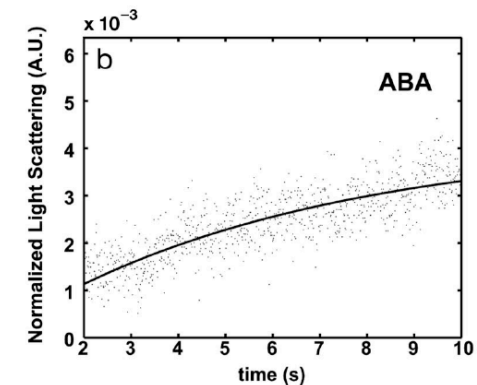
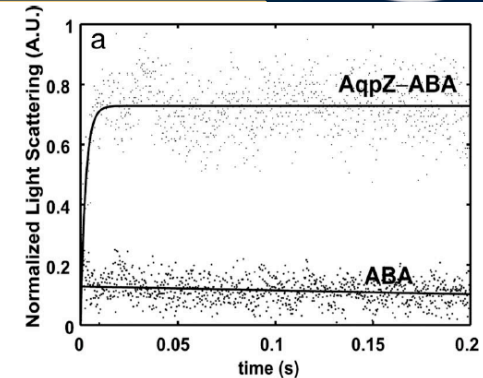


Fig. 2. Stopped-flow light-scattering experiments. (a) Increase in relative light scattering with and without reconstituted AqpZ into the ABA polymer at 5.5°C at a molar ratio of 200:1 (polymer:protein). Fits are shown as guides. The initial rise rates were used to calculate the permeability. As seen from a, a rise cannot be calculated for the pure ABA polymer vesicles. (b) Shown is the rise in scattering between 2 and 10 s for the ABA vesicles that was used in calculating permeability at 5.5°C.

M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, and W. Meier /
Aquaporin ZPNAS 2007 104: 20719-20724

Biomimetic membranes

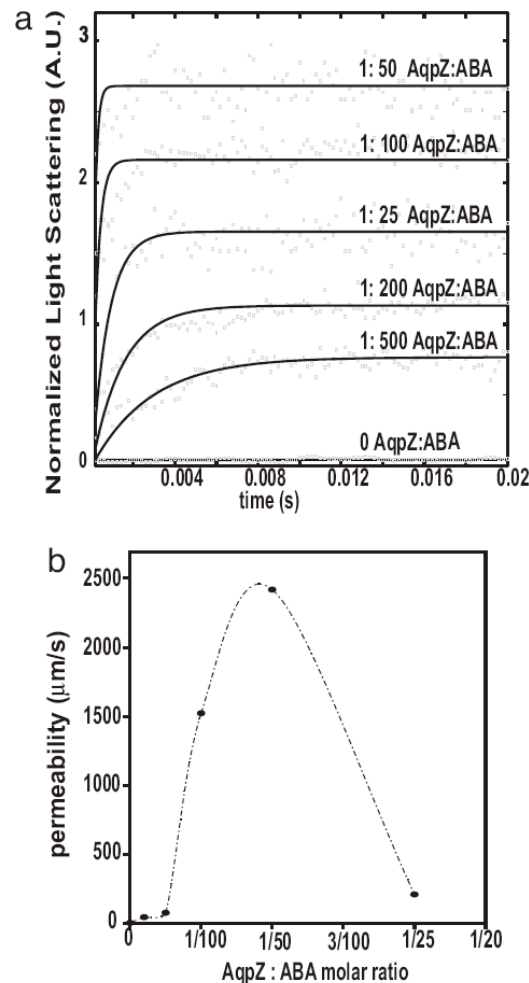


Fig. 4. Effect of increasing AqpZ concentrations on the permeability of ABA polymers. (a) Light-scattering results normalized to fit between 0 and 1. Curves for different ratios have been offset for clarity and fits are shown as guides. Data at 0 AqpZ:ABA ratio shown at a fixed offset. (b) Increase in calculated permeability with increase in protein-to-polymer molar ratio.

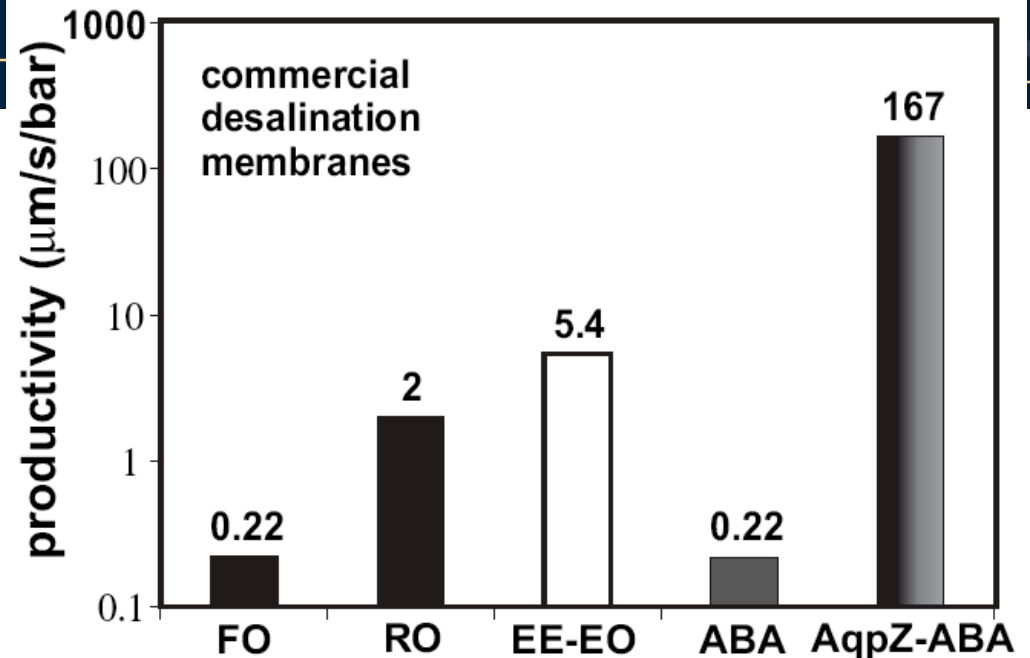


Fig. 5. Comparison of reported permeability values for polymeric membranes to those obtained in this study. FO is a commercial forward-osmosis membrane with data from McCutcheon and Elimelech (37) at 20°C. RO is a commercial reverse-osmosis desalination membrane with data from Matsura (38) at room temperature (assumed 25°C). EE-EO is a polyethylene-polyethylene oxide diblock polymer with data from Discher *et al.* (13) at 20°C. ABA represents the polymer vesicles used in this study with permeability calculated at 20°C. AqpZ-ABA represents the polymer vesicles with incorporated AqpZ at 1:50 molar ratio used in this study at 20°C. Data for ABA and AqpZ were obtained at 5.5°C and calculated at 20°C by using E_a values.

M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, and W. Meier /
Aquaporin ZPNAS 2007 104: 20719-20724

Biomimetic Membranes



- **FIELD OF THE INVENTION**
 - The present invention relates to a novel biomimetic water membrane comprising functional aquaporin channels or tetramers of aquaporin channels, suitable for transporting water from one side of the membrane to the other side, driven by an osmotic pressure gradient. Pressure retarded osmosis will be used in the production of salinity power.
 - By this we use the principles of nature to produce pure and environmentally friendly energy.
- (WO/2007/033675) BIOMIMETIC WATER MEMBRANE COMPRISING AQUAPORINS USED IN THE PRODUCTION OF SALINITY POWER
 - Aquaporin A/S

Aligned-CNT membranes

MATERIALS SCIENCE

Making High-Flux Membranes with Carbon Nanotubes

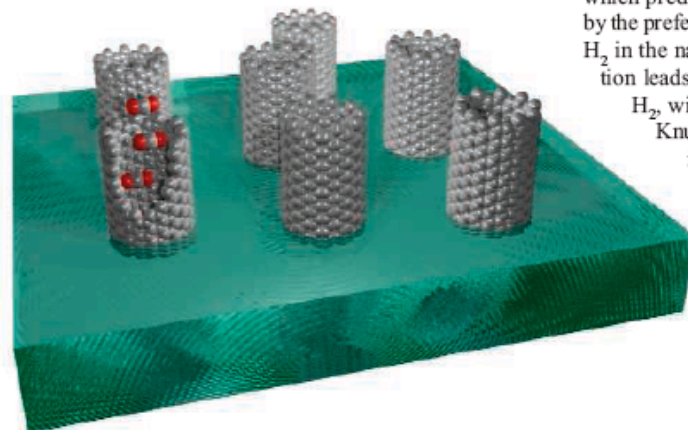
David S. Sholl and J. Karl Johnson

In 1871, James Clerk Maxwell devised a thought experiment whereby a “demon” separates molecules without performing work. The practical realization of such a demon would be extraordinarily useful, because at present, vast amounts of energy and money are expended around the globe separating chemical mixtures. Even separation of very simple molecules can have enormous implications. For example, purifying O_2 and N_2 from air is a multibillion dollar industry, and the ability to economically separate CO_2 from power plant flue gases could revolutionize efforts to reduce greenhouse gas emissions. Efficient membranes are real-world analogs of Maxwell’s demons that can separate chemicals with little (although never zero) work. On page 1034 of this issue, Holt and co-workers (1) describe experiments that are a fascinating step toward the development of highly efficient membranes.

The separation of gases and liquids by membranes can often be more cost and energy effective than traditional separation methods, such as distillation or absorption. An ideal membrane would have excellent stability under a wide range of process conditions, high selectivity for the chemicals of interest, and also produce a large molecular flux with a small driving force. Most membranes in use industrially are poly-

simulations of gas transport inside single-walled nanotubes (3, 4). These simulations predicted that the transport of gases inside nanotubes is orders of magnitude faster than in any other known materials with nanometer-scale pores. These rapid transport rates exist because the walls of nanotubes are much smoother (on atomic scales) than other materials.

These model predictions have now been tested experimentally by Holt *et al.*, who have fabricated the first membranes from aligned



Faster flow. A schematic illustration of a membrane in which single-walled carbon nanotubes (gray) create avenues for transport of molecules (shown as red and gray balls passing through a nanotube) across an otherwise impermeable film (green).

single- and double-walled nanotubes. This work follows similar experiments by Hinds

Separation of gases and liquids into their constituents is crucial for many industrial processes. Membranes that incorporate nanotubes show promise for high selectivity and throughput.

fluxes, but to be useful as membranes, they must also show high selectivity. The experiments to date have only examined single-component transport, so no direct information on this crucial issue is available. As is commonly the case for nanoporous membranes, estimation of membrane selectivities from single-component experiments is not expected to be accurate. Mixture selectivity has been studied with MD simulations of single-walled nanotube membranes for CH_4/H_2 mixtures (8), which predict that the selectivity is dominated by the preferential adsorption of CH_4 relative to H_2 in the nanotubes. This preferential adsorption leads to selective transport of CH_4 over H_2 , with selectivities as high as 10 to 20.

Knudsen transport of this gas mixture, in contrast, would give a selectivity of 2.8, favoring H_2 transport over CH_4 .

The discussion above has focused on gas separations, but the need for efficient liquid separations is just as great. Both Holt *et al.* and Hinds and co-workers have performed experiments assessing water transport through their nanotube membranes. Similar to what is seen with gases, water is observed to move through the membranes extremely rapidly. The transport rates reported by Holt *et al.* are in good agreement with predictions made

Downloaded from www.sciencemag.org on August 13, 2007



Remedy/Jenks Consultants
Engineers & Scientists

National Water Research Institute

Aligned-CNT membranes

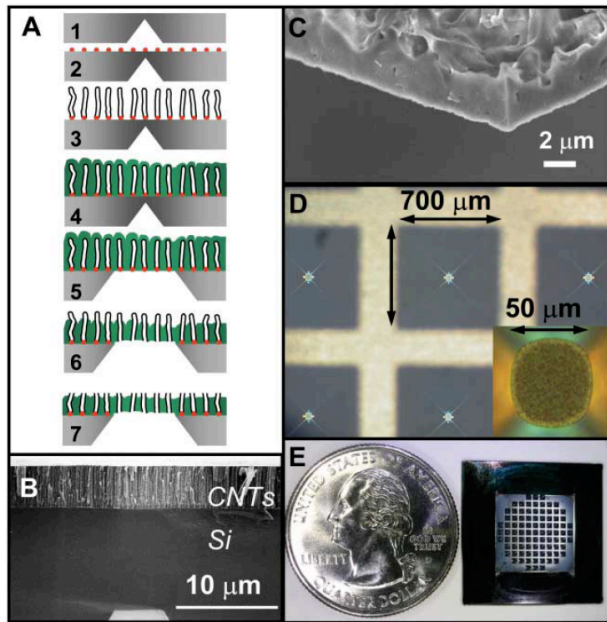
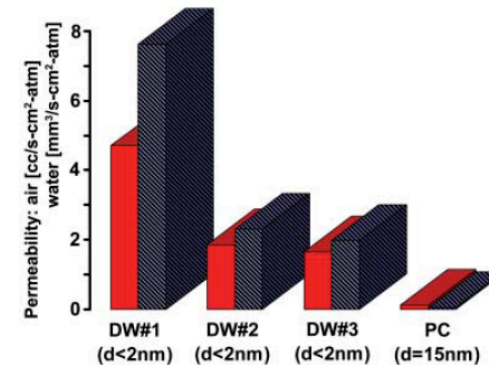


Fig. 1. (A) Schematic of the fabrication process. Step 1: microscale pit formation (by KOH etching). Step 2: catalyst deposition/annealing. Step 3: nanotube growth. Step 4: gap filling with low-pressure chemical vapor-deposited Si_3N_4 . Step 5: membrane area definition (by XeF_2 isotropic Si etching). Step 6: silicon nitride etch to expose nanotubes and remove catalyst nanoparticles (by Ar ion milling); the membrane is still impermeable at this step. Step 7: nanotube uncapping (reactive ion etching); the membrane begins to exhibit gas permeability at this step. (B) SEM cross section of the as-grown DWNTs (CNTs). (C) SEM cross section of the membrane, illustrating the excellent gap filling by silicon nitride. (D) Photograph of the open membrane areas; inset shows a close-up of one membrane. (E) Photograph of the membrane chip that contains 89 open windows; each window is 50 μm in diameter.

Fig. 4. Air (red) and water (blue) permeability as measured for three DWNT membranes (DW#1, 2, and 3) and a polycarbonate membrane (PC). Despite considerably smaller pore sizes, the permeabilities for all DWNT membranes greatly exceed those of the polycarbonate membrane.



Jason K. Holt, *et al.*
Science 312, 1034 (2006)

Table 2. Comparisons of experimental air flow rates observed for several DWNT membranes with Knudsen model predictions, and of experimental water flow rates with continuum flow model predictions. The differences among the three DWNT membranes are most likely the result of different numbers of pores opened in the fabrication process. Values for a poly-

carbonate membrane are provided as a reference. Pore diameters were determined from size exclusion measurements, TEM measurements, and (for polycarbonate) manufacturer's specifications. Pore density values are upper limits, as determined from TEM measurements and (for polycarbonate) manufacturer's specifications.

Membrane	Pore diameter (nm)	Pore density (cm ⁻²)	Thickness (μm)	Enhancement over Knudsen model* (minimum)	Enhancement over no-slip, hydrodynamic flow† (minimum)	Calculated minimum slip length‡ (nm)
DWNT 1	1.3 to 2.0	$\leq 0.25 \times 10^{12}$	2.0	40 to 120	1500 to 8400	380 to 1400
DWNT 2	1.3 to 2.0	$\leq 0.25 \times 10^{12}$	3.0	20 to 80	680 to 3800	170 to 600
DWNT 3	1.3 to 2.0	$\leq 0.25 \times 10^{12}$	2.8	16 to 60	560 to 3100	140 to 500
Polycarbonate	15	6×10^8	6.0	2.1	3.7	5.1

*From (18). †From (26). ‡From (29).



Aligned-CNT membranes



1428 *J. Phys. Chem. B*, Vol. 112, No. 5, 2008

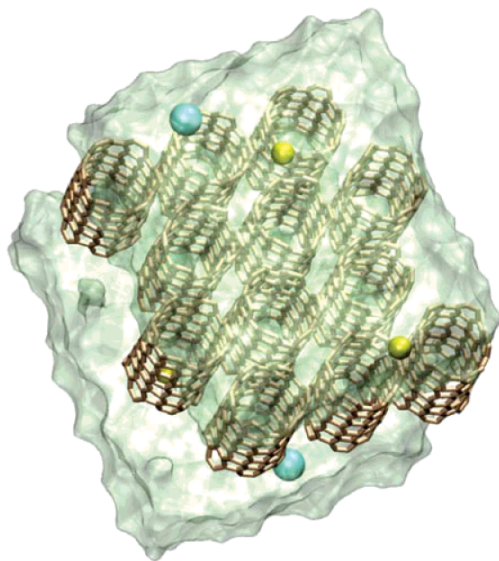


Figure 1. Simulation system. A CNT membrane is formed by hexagonally packing 12 nanotubes in a periodic cell. The full simulation system is formed by placing layers of water on either side of the membrane (light blue surface) and adding ions to the bulk solution.

TABLE 3: Desalination Potential of Carbon Nanotube Membranes^a

size	salt rejection	maximal pore density		2.5×10^{11} pores per cm^2	
		flow rate	improvement	flow rate	improvement
(5,5)	100%	45.2	682	0.16	2.42
(6,6)	100%	78.8	1189	0.27	4.21
(7,7)	95%	119.5	1801	0.42	6.39
(8,8)	58%	182.9	2759	0.65	9.76

^a Numbers assume an operating pressure of 5.5 MPa and allow for an osmotic pressure of 2.4 MPa. Flow rates are measured in $\text{L cm}^{-2} \text{day}^{-1}$. Improvements in efficiency are quoted relative to published values for a FILMTEC SW30HR-380 commercial reverse osmosis membrane.⁵⁷

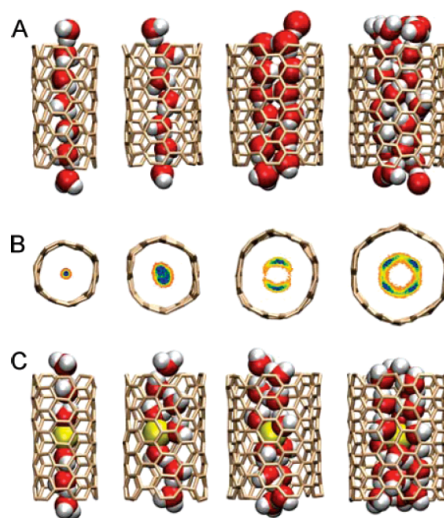
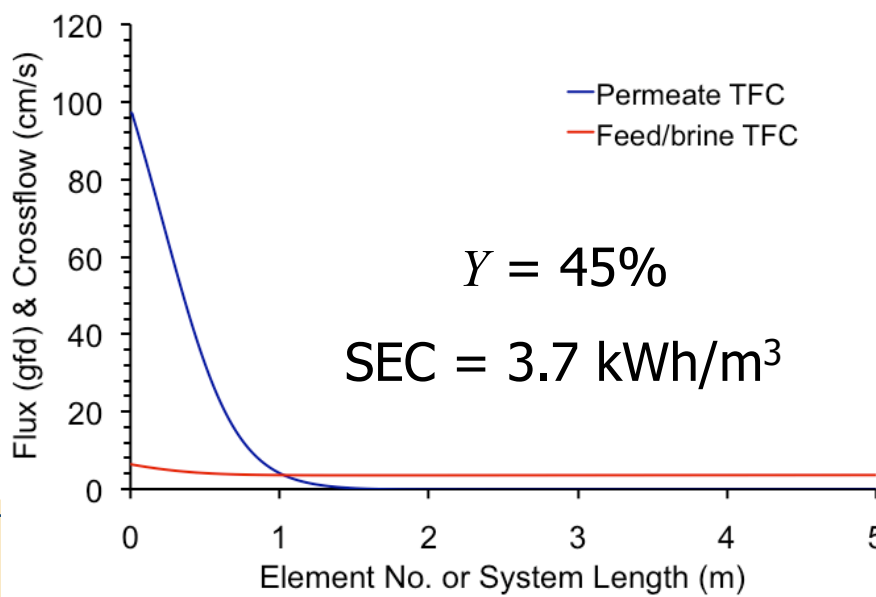
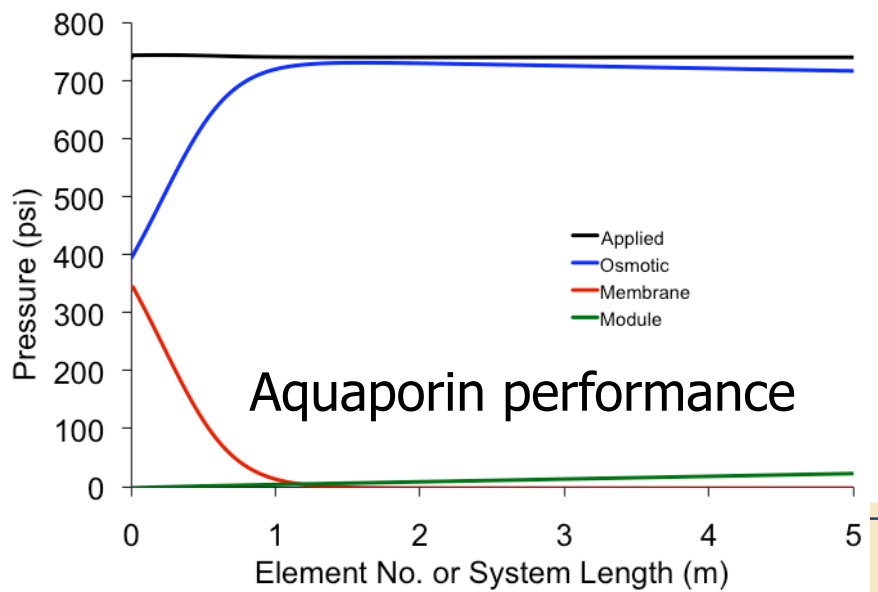
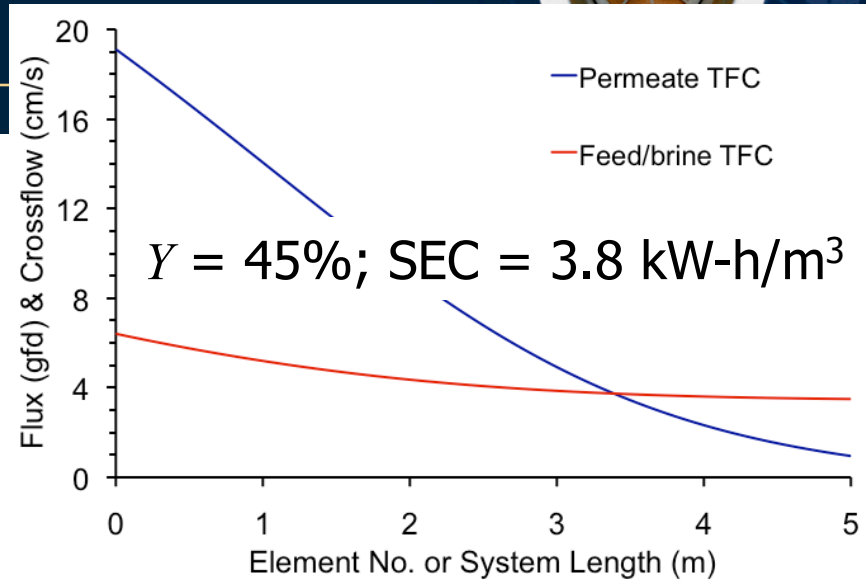
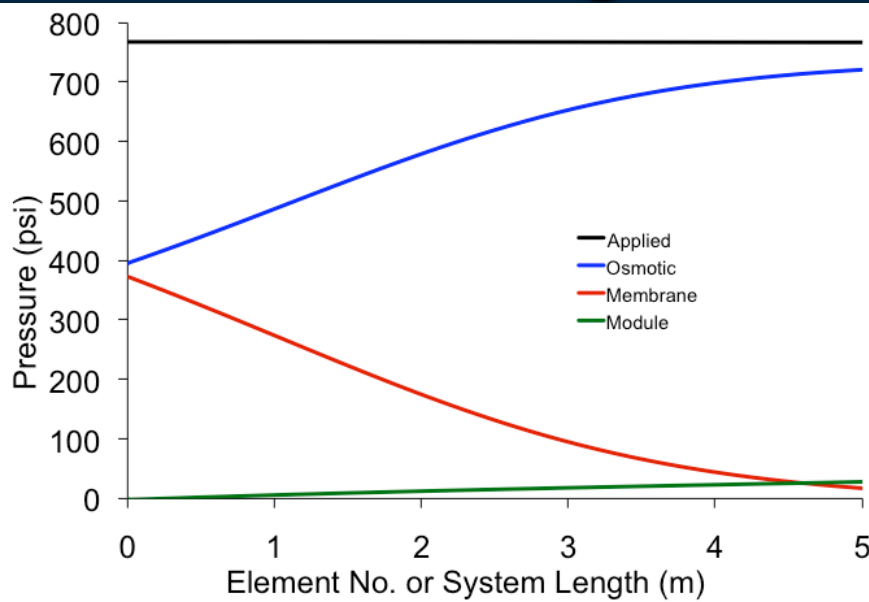


Figure 2. Water and ions in the nanotubes. (A) Snapshots from molecular dynamics simulations showing the configuration of water in each of the (5,5), (6,6), (7,7), and (8,8) CNTs are shown as viewed from the plane of the CNT membrane. (B) Top views of the nanotubes show the differing sizes of the tubes as well as the structure of water in the pores as evidenced from the density of oxygen in the central 7 Å of the pore. Density values range from low (orange) to high (blue). (C) Location and hydration structure of Na^+ ions that are pulled into the center of the pores.

B. Corry / *J. Phys. Chem. B* 2008, 112, 1427-1434

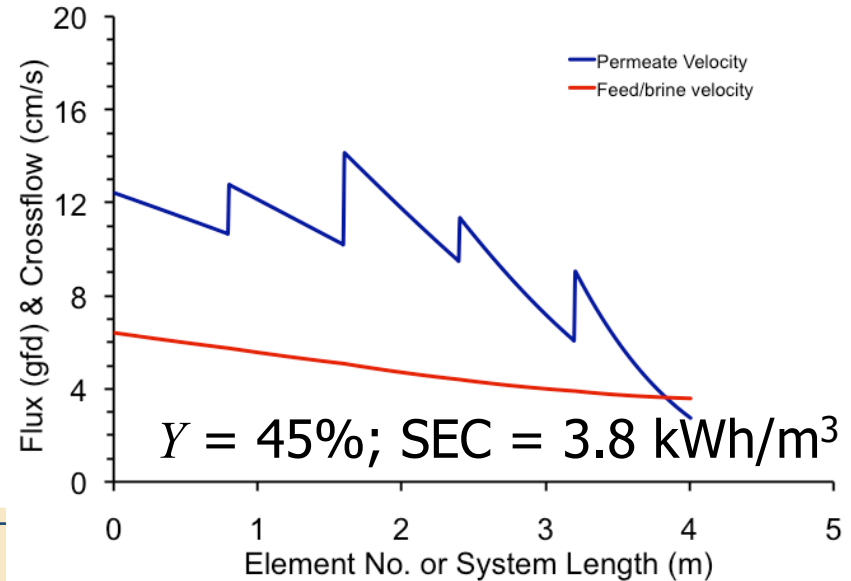
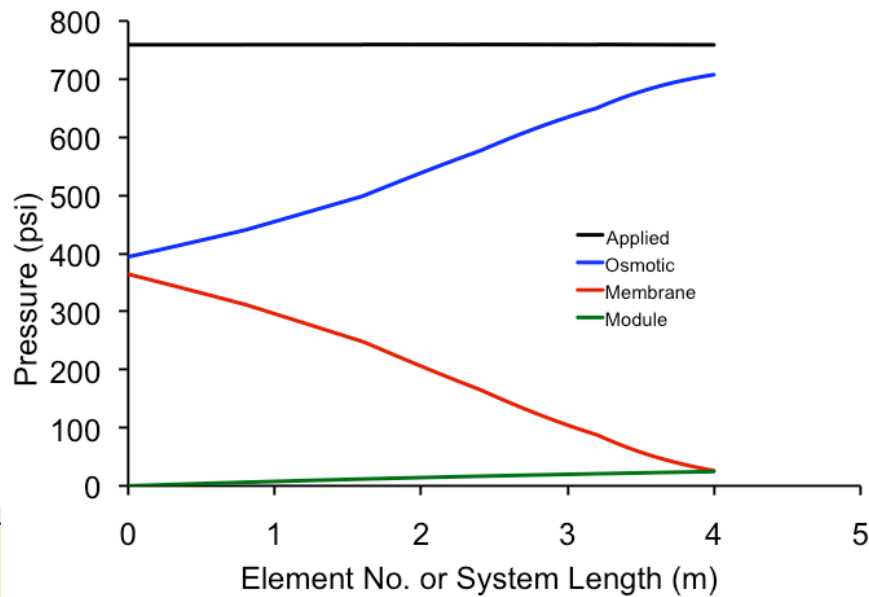
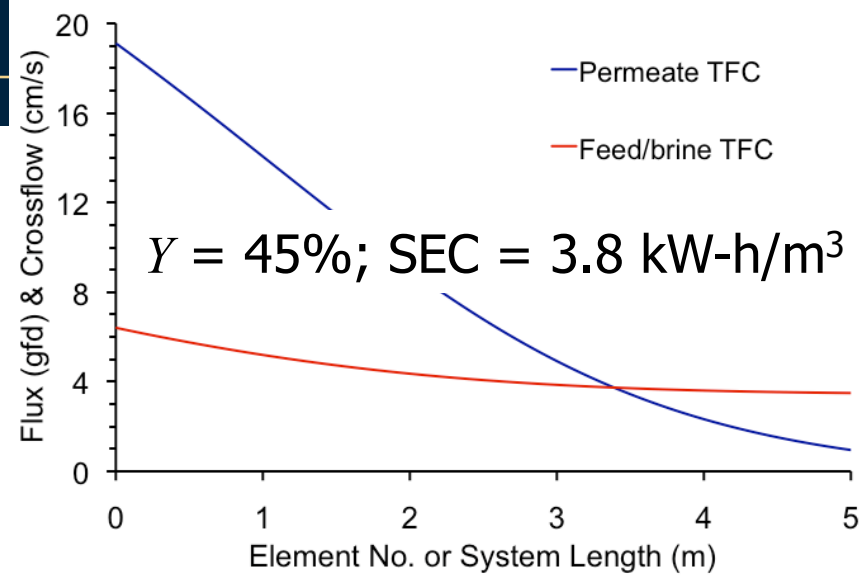
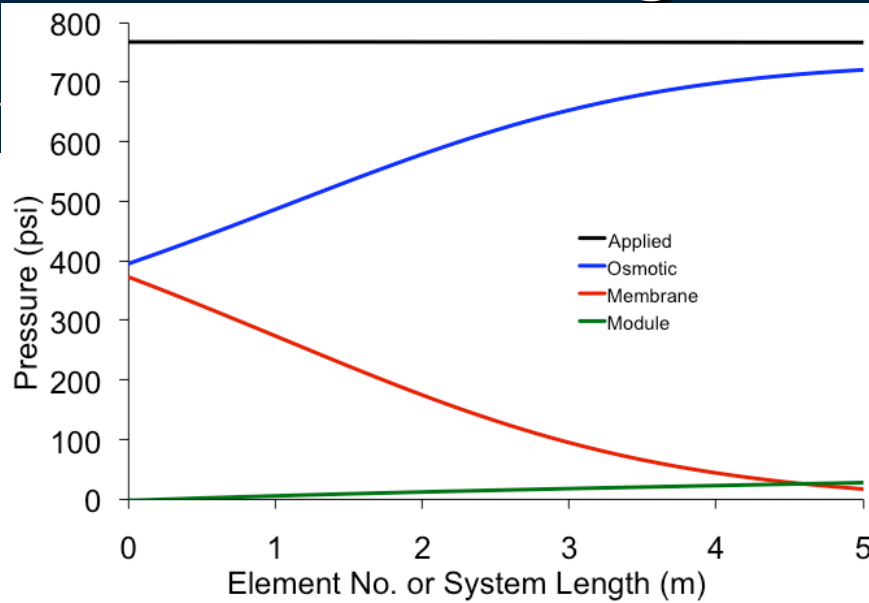


Bad Use of High Flux Membranes



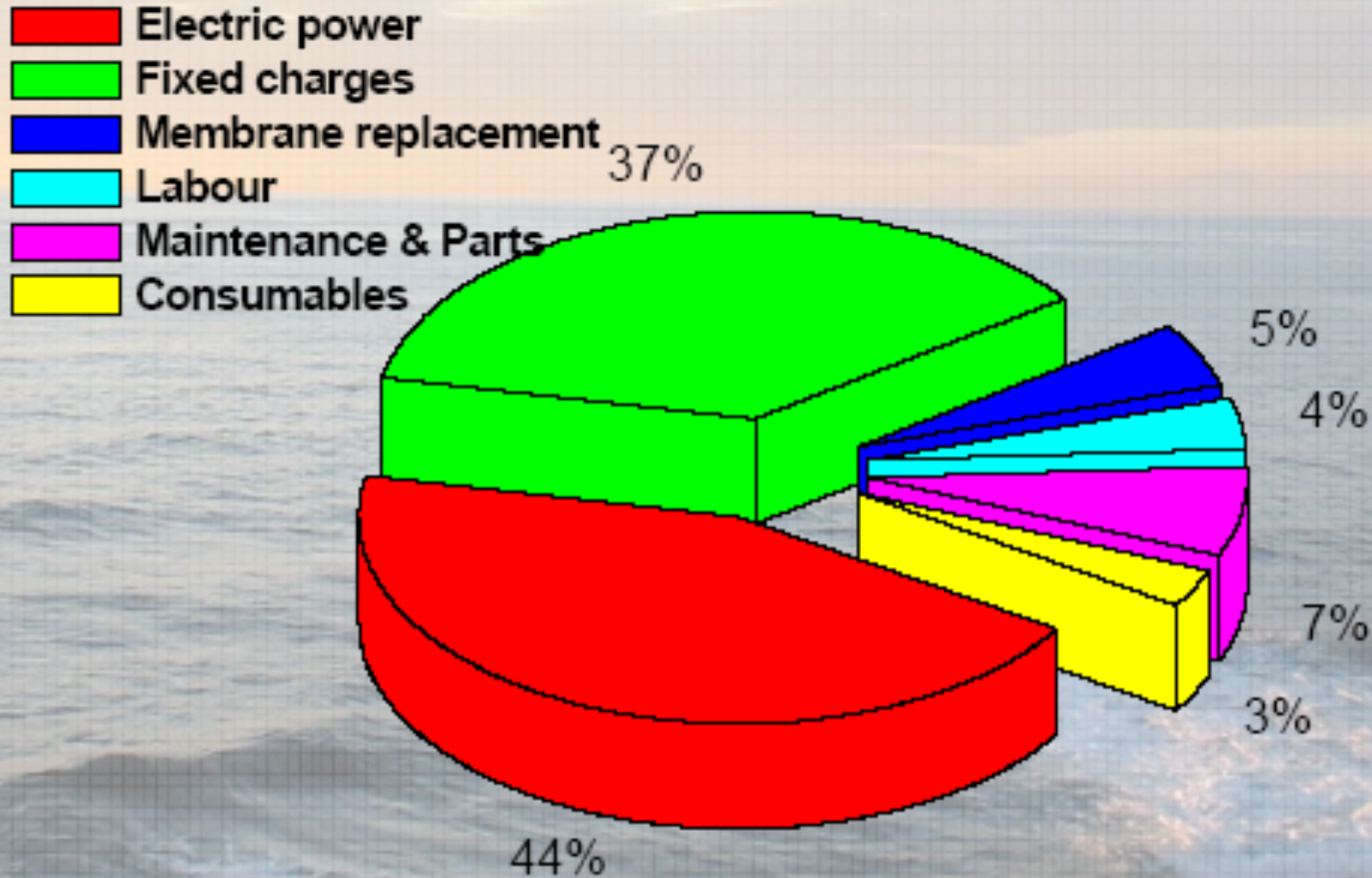


Better Use of High Flux Membranes





Cost of Seawater Desalination



Source: UCLA WaTeR Center

Fouling: the "tail that wags the dog"



Fouling: an undesirable change in separation performance due to accumulation of insoluble matter at membrane surface and/or within membrane pores

$$J_v = \frac{\Delta p_{tot} - \Delta \pi_{mem}^*}{\mu(R_{mem} + r_{dep} \delta_{dep})}; R_s = 1 - \frac{c_p}{CP^* \cdot c_p}$$

Practical

- reversible / irreversible / unrecoverable

Mechanistic

- internal (pore plugging, chemical degradation)
- external (cake, biofilm, and scale formation)

Origin/nature

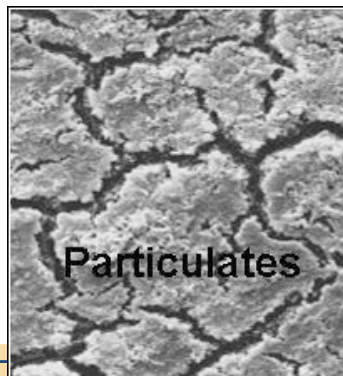
- inorganic (CaCO_3 , CaSO_4 , BaSO_4 , silicates, oxides, clays)
- organic (humic/fulvic acids, biopolymers)
- microbial (bacteria, algae, exopolymers)
- dissolved, colloidal, particulate

Cake/Biofilm Formation

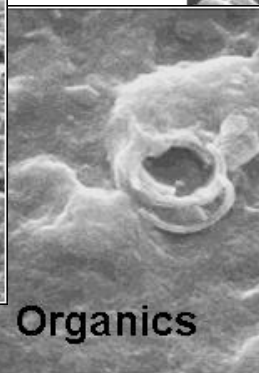
resulting from convective deposition of colloids, organics, and microbes (and growth) on the membrane surface

Scale Formation

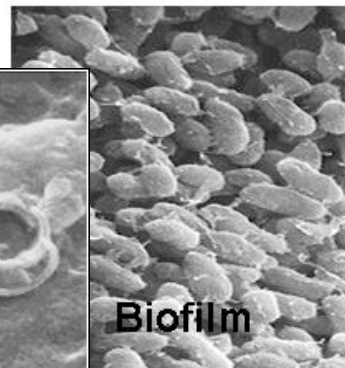
resulting from heterogeneous crystallization of sparingly soluble mineral salts on the membrane surface



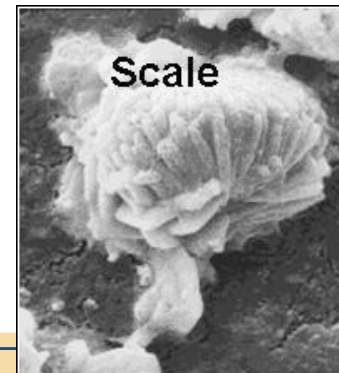
Particulates



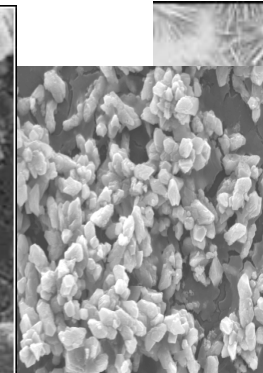
Organics



Biofilm



Scale



SEM images courtesy of UCLA WaTeR Center

Acc.V Spot Magn Det WD
10.0 kV 3.0 10000x SE 13.8

5 μm

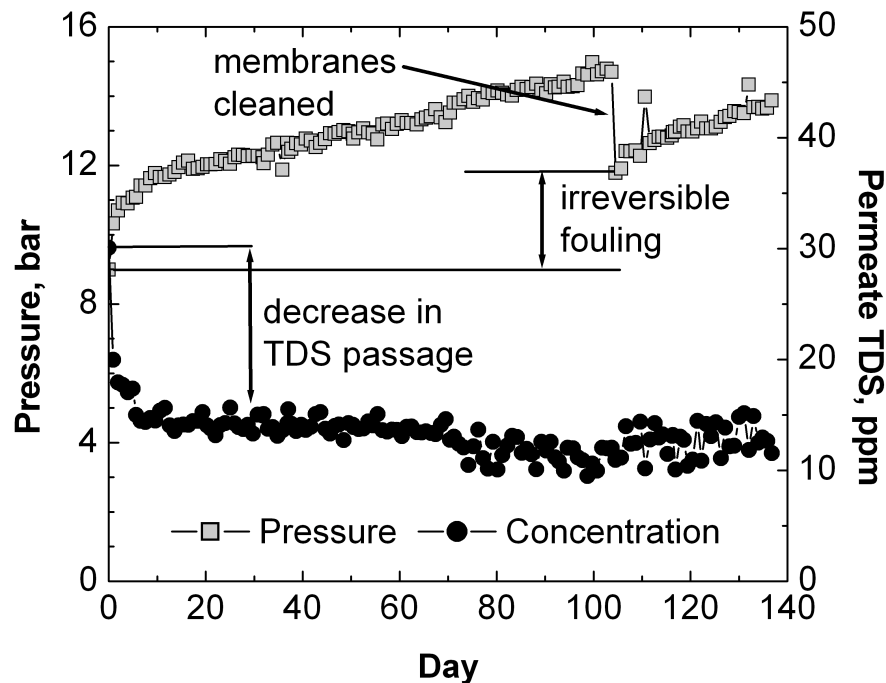
Kennedy/Jenks Consultants
Engineers & Scientists

National Water Research Institute

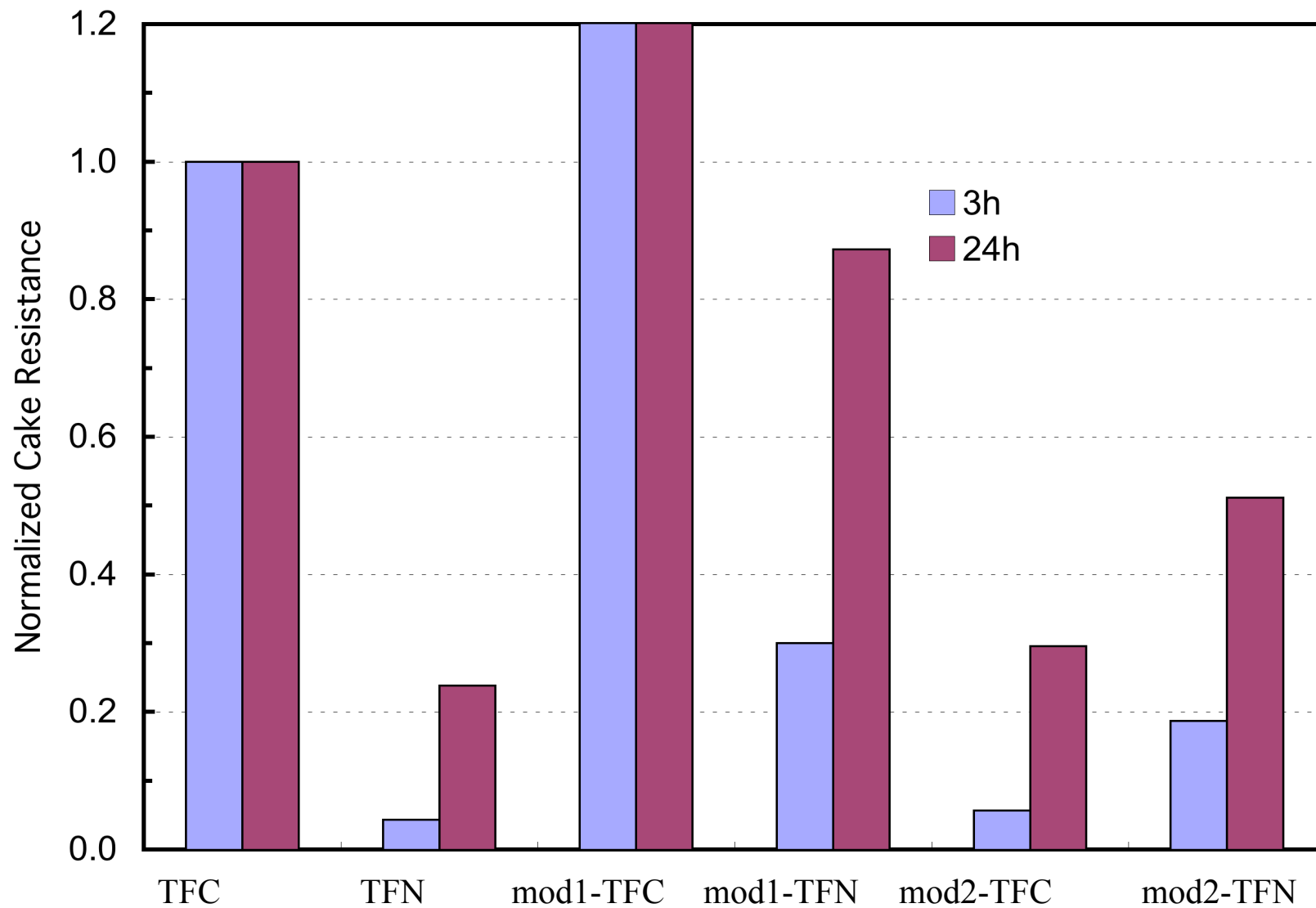
Fouling: the "tail that wags the dog"

AWT System at OCWD (GWRS)

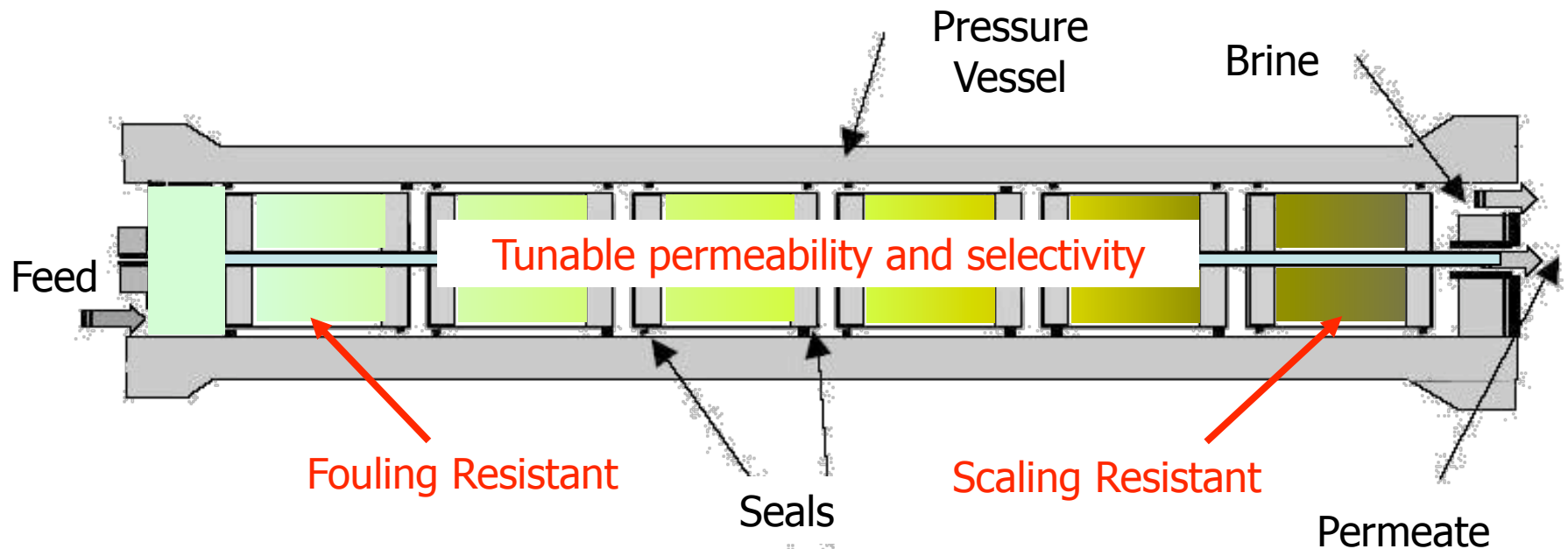
- 1° clarification
 - biological AS
 - 2° clarification
 - b.p. chlorination
 - MF/H₂SO₄/AS
 - RO (3:2:1)
 - UV/H₂O₂
- } @ **OCSD**
- } @ **OCWD**



TFC and TFN fouling resistance



Summary & Concluding Remarks



- Nanotechnology-based membranes offer potential for:
 - New degrees of freedom in designing RO membranes by (independently) engineering polymer and nanoparticle phases
 - Tailoring, independently or in concert, separation performance, interfacial properties, and fouling resistance
 - More efficient and effective process designs by strategically locating tailored elements throughout a RO system

Thank you...questions?



**“If We Could Produce
Fresh Water From Salt
Water at a Low Cost, That
Would Indeed Be A Great
Service to Humanity and
Would Dwarf Any Other
Scientific
Accomplishment”**

John F. Kennedy, 1962

References



Nanocomposite membranes

- Komarneni, S., Nanocomposites. *J. Mater. Chem.* **1992**, 2, 1219-1230.
- Moore, T.T., R. Mahajan, D.Q. Vu, W.J. Koros, Hybrid membrane materials comprising organic polymers with rigid dispersed phases. *AIChE J.* **2004**, 50, 311-321.
- Jeong, B.H., E.M.V. Hoek, Y. Yan, A. Subramani, X. Huang, G. Hurwitz, A. K. Ghosh, A. Jawor, Interfacial polymerization of thin film nanocomposites: A new concept for reverse osmosis membranes. *J. Membr. Sci.* **2007**, 294, 1-7.
- Lee, S.Y., H.J. Kim, R. Patel, S.J. Im, J.H. Kim, B. R. Min, Silver nanoparticles immobilized on thin film composite polyamide membrane: characterization, nanofiltration, antifouling properties. *Polym. Adv. Technol.* **2007**, 18, 562-568.
- Lee, H.S., S.J. Im, J.H. Kim, H.J. Kim, J.P. Kim, B.R. Min, Polyamide thin-film nanofiltration membranes containing TiO₂ nanoparticles. *Desalination* **2008**, 219, 48-56.
- www.nanoh2o.com

Biomimetic membranes

- Tajkhorshid, E., Nollert, P., Jensen, M. O., Miercke, L. J., O'Connell, J., Stroud, R. M., and Schulten, K. (2002). Control of the selectivity of the aquaporin water channel family by global orientational tuning, *Science* 296, 525-530.
- Zhu, F., Tajkhorshid, E. and Schulten, K. (2003). [Theory and simulation of water permeation in aquaporin-1](#). *Biophysical Journal*, 86, 50-57.
- De Groot, B.L., H. Grubmuller, Water permeation across biological membranes: Mechanism and dynamics of aquaporin-1 and GlpF. *Science* **2001**, 294, 2353-2357.
- Murata, K., K. Mitsuoka, T. Hirai, T. Walz, P. Agre, J.B. Heymann, A. Engel, Y. Fujiyoshi, Structural determinants of water permeation through aquaporin-1. *Nature* **2000**, 407, 599-605.
- Zhu, F.Q., E. Tajkhorshid, K. Schulten, Theory and simulation of water permeation in aquaporin-1. *Biophys. J.* **2004**, 86, 50-57.
- Zhu, F., K. Schulten, Water and proton conduction through carbon nanotubes as models for biological channels. *Biophys. J.* **2004**, 85, 236-244.
- Montemagno, C.D., J.J. Schmidt, S.P. Tozzi, Biomimetic membranes, US Patent No. 7208089, 2007.
- Kumar, M., M. Grzelakowski, J. Ziles, M. Clark, W. Meier, Highly permeable polymeric membranes based on the incorporation of the functional water channel protein Aquaporin Z. *P.N.A.S.* **2007**, 105(52), 20723-20728.
- Kedem, O.; Katchalsky, A., Thermodynamic analysis of the permeability of biological membranes to non-electrolytes *Biochim. Biophys. Acta* **1958**, 27, 229-246.
- Spiegler, K.S., O. Kedem, Thermodynamics of hyperfiltration (reverse osmosis): criteria for efficient membranes. *Desalination* **1966**, 1, 311-326.
- Jensen, P.H., D. Keller, C.H. Nielsen, Membrane for filtering of water, Application No.: PA 2005 00740 (US), PCT/DK2006/000278 (International), May 19, 2006.

References



Biomimetic membranes (cont'd)

- Agre, P., M. Bonhivers, and M. J. Borgnia. (1998). The aquaporins, blueprints for cellular plumbing systems. *Journal of Biological Chemistry*, 273, 14659–14662.
- Borgnia, M., S. Nielsen, A. Engel, and P. Agre. (1999). Cellular and molecular biology of the aquaporin water channels. *Annual Review of Biochemistry*, 68, 425–458.
- Burykin and A. Warshel (2003). What really prevents proton transport through aquaporin? Charge self-energy vs. proton wire proposals, *Biophysical Journal* 85, 3696-3706
- Chakrabarti, N., Tajkhorshid, E., Roux, B. and Pommès, R. (2004). Molecular basis of proton blockage in aquaporins, *Structure* 12, 65-74
- de Groot, B. L., and Grubmüller, H. (2001). Water permeation across biological membranes: mechanism and dynamics of aquaporin-1 and GlpF, *Science* 294, 2353-2357.
- de Groot, B. L., Frigato, T., Helms, V. and Grubmüller, H. (2003). The mechanism of proton exclusion in the aquaporin-1 channel, *Journal of Molecular Biology* 333, 279-293.
- Fu, D., Libson, A., Miercke, L. J., Weitzman, C., Nollert, P., Krucinski, J., and Stroud, R. M. (2000). Structure of a glycerol-conducting channel and the basis for its selectivity, *Science* 290, 481-6.
- Ilan, B., Tajkhorshid, E., Schulten, K. and Voth, G. (2004). The mechanism of proton exclusion in aquaporin water channels. *PROTEINS: Structure, Function, and Bioinformatics*, 55, 223-228.
- Jensen, M. O., Tajkhorshid, E., and Schulten, K. (2003). Electrostatic tuning of permeation and selectivity in aquaporin water channels, *Biophysical Journal* 85, 2884-2899.
- Murata, K., Mitsuoka, K., Hirai, T., Walz, T., Agre, P., Heymann, J. B., Engel, A., and Fujiyoshi, Y. (2000). Structural determinants of water permeation through aquaporin-1, *Nature* 407, 599-605.
- Preston, G. M., P. Piazza-Carroll, W. B. Guggino, and P. Agre. (1992). Appearance of water channels in *Xenopus* oocytes expressing red cell CHIP28 water channel. *Science*, 256, 385–387.
- Ren, G., Reddy, V. S., Cheng, A., Melnyk, P., and Mitra, A. K. (2001). Visualization of a water-selective pore by electron crystallography in vitreous ice, *Proc Natl Acad Sci U S A* 98, 1398-1403.
- Sui, H., Han, B. G., Lee, J. K., Walian, P., and Jap, B. K. (2001). Structural basis of water-specific transport through the AQP1 water channel, *Nature* 414, 872-8.
- Jensen, P.H., Biomimetic water membrane comprising aquaporins used in the production of salinity power, Application No. 60/718,890 (US), PCT/DK2006/000520 (International), September 20, 2005.
- http://nobelprize.org/nobel_prizes/chemistry/laureates/2003/public.html
- <http://www.aquaporin.dk>

References



CNTs and aligned CNT membranes

- Holt, J.K., H.G. Park, Y.M. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* **2006**, 312, 1034-1037
- Sholl, D.S., J.K. Johnson, Making high-flux membranes with carbon nanotubes, *Science* **2006**, 312, 1003-1004.
- Nednoor, P.; Gavalas, V. G.; Chopra, N.; Hinds, B. J.; Bachas, L. G., Carbon nanotube based biomimetic membranes: Mimicking protein channels regulated by phosphorylation. *J. Mater. Chem.* **2007**, 17, 1755-1757
- Nednoor, P.; Chopra, N.; Gavalas, V.; Bachas, L. G.; Hinds, B. J., Reversible biochemical switching of ionic transport through aligned carbon nanotube membranes. *Chem. Mater.* **2005**, 17, 3595-3599
- van Hijkoop, V. J.; Dammers, A. J.; Malek, K.; Coppens, M. O., Water diffusion through a membrane protein channel: A first passage time approach. *J. Chem. Phys.* **2007**, 127, 10.
- Burykin, A., A. Warshel, Membranes assembled from narrow carbon nanotubes block proton transport and can form effective nano-filtration devices. *J. Comput. Theor. Nanosci.* **2006**, 3, 237-242
- Joseph, S., R.J. Mashl, E. Jakobsson, N.R. Aluru, Electrolytic transport in modified carbon nanotubes. *Nano Lett.* **2003**, 3, 1399-1403
- Li, J.Y., X.J. Gong, H.J. Lu, D. Li, H.P. Fang, R.H. Zhou, Electrostatic gating of a nanometer water channel. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, 104, 3687-3692
- Li, J.Y., Z.X. Yang, H.P. Fang, R.H. Zhou, X.W. Tang, Effect of the carbon-nanotube length on water permeability. *Chin. Phys. Lett.* **2007**, 24, 2710-2713
- Liu, H.M., S. Murad, C.J. Jameson, Ion permeation dynamics in carbon nanotubes. *J. Chem. Phys.* **2006**, 125, 14
- Majumder, M., N. Chopra, R. Andrews, B.J. Hinds, Nanoscale hydrodynamics - Enhanced flow in carbon nanotubes. *Nature* **2005**, 438, 44-44
- Majumder, M., N. Chopra, B.J. Hinds, Effect of tip functionalization on transport through vertically oriented carbon nanotube membranes. *J. Am. Chem. Soc.* **2005**, 127, 9062-9070
- Majumder, M., X. Zhan, R. Andrews, B.J. Hinds, Voltage gated carbon nanotube membranes. *Langmuir* **2007**, 23, 8624-8631
- Majumder, S.R., N. Choudhury, S.K. Ghosh, Enhanced flow in smooth single-file channel. *J. Chem. Phys.* **2007**, 127, 5
- Wan, R.Z., J.Y. Li, H.J. Lu, H.P. Fang, Controllable water channel gating of nanometer dimensions. *J. Am. Chem. Soc.* **2005**, 127, 7166-7170
- Wang, Z.K., L.J. Ci, L. Chen, S. Nayak, P.M. Ajayan, N. Koratkar, Polarity-dependent electrochemically controlled transport of water through carbon nanotube membranes. *Nano Lett.* **2007**, 7, 697-702
- Yeh, I.C., G. Hummer, Nucleic acid transport through carbon nanotube membranes. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, 101, 12177-12182.
- Corry, B., Designing carbon nanotube membranes for efficient water desalination. *J. Phys. Chem. B* **2008**, 112, 1427-1434.

References



CNTs and aligned CNT membranes (cont'd)

- Deheer, W.A., W.S. Bacsá, A. Chatelain, T. Gerfin, R. Humphreybaker, L. Forro, D. Ugarte, Aligned Carbon Nanotube Films - Production and Optical and Electronic-Properties. *Science* **1995**, 268, 845-847
- Walters, D.A., M.J. Casavant, X.C. Qin, C.B. Huffman, P.J. Boul, L.M. Ericson, E.H. Haroz, M.J. O'Connell, K. Smith, D.T. Colbert, R.E. Smalley, In-plane-aligned membranes of carbon nanotubes. *Chem. Phys. Lett.* **2001**, 338, 14-20
- Hinds, B.J., N. Chopra, T. Rantell, R. Andrews, V. Gavalas, L.G. Bachas, Aligned multiwalled carbon nanotube membranes. *Science* **2004**, 303, 62-65
- Holt, J.K., A. Noy, T. Huser, D. Eaglesham, O. Bakajin, Fabrication of a carbon nanotube-embedded silicon nitride membrane for studies of nanometer-scale mass transport. *Nano Lett.* **2004**, 4, 2245-2250
- Li, W.Z., X. Wang, Z.W. Chen, M. Waje, Y.S. Yan, Carbon nanotube film by filtration as cathode catalyst support for proton-exchange membrane fuel cell. *Langmuir* **2005**, 21, 9386-9389
- Basheer, C., A.A. Ainedhary, B.S.M. Rao, S. Valliyaveettil, H.K. Lee, Development and application of porous membrane-protected carbon nanotube micro-solid-phase extraction combined with gas chromatography/mass spectrometry. *Anal. Chem.* **2006**, 78, 2853-2858
- Mi, W.L., Y.S. Lin, Y.D. Li, Vertically aligned carbon nanotube membranes on macroporous alumina supports. *J. Membr. Sci.* **2007**, 304, 1-7.
- Casavant, M.J., D.A. Walters, J.J. Schmidt, R.E. Smalley, Neat macroscopic membranes of aligned carbon nanotubes. *J. Appl. Phys.* **2003**, 93, 2153-2156
- Walters, D.A., M.J. Casavant, X.C. Qin, C.B. Huffman, P.J. Boul, L.M. Ericson, E.H. Haroz, M.J. O'Connell, K. Smith, D.T. Colbert, R.E. Smalley, In-plane-aligned membranes of carbon nanotubes. *Chem. Phys. Lett.* **2001**, 338, 14-20.
- de Heer, W.A., W.S. Bacsá, A. Chatelain, T. Gerfin, R. Humphreybaker, L. Forro, D. Ugarte, Aligned Carbon Nanotube Films - Production and Optical and Electronic-Properties. *Science* **1995**, 268, 845-847.
- Li, W.Z., X. Wang, Z.W. Chen, M. Waje, Y.S. Yan, Carbon nanotube film by filtration as cathode catalyst support for proton-exchange membrane fuel cell. *Langmuir* **2005**, 21, 9386-9389.
- Kim, S., J.R. Jinschek, H. Chen, D.S. Sholl, E. Marand, Scalable fabrication of carbon nanotube/polymer nanocomposite membranes for high flux gas transport. *Nano Lett.* **2007**, 7, 2806-2811.
- Wang Y., Z. Iqbal, S. Mitra, Rapidly functionalized, water-dispersed carbon nanotubes at high concentration. *J. Am. Chem. Soc.* **2006**, 128(1), 95-99.