The Development of Reverse Osmosis and Nanofiltration Through Modern Times

Bill Mickols PHD.

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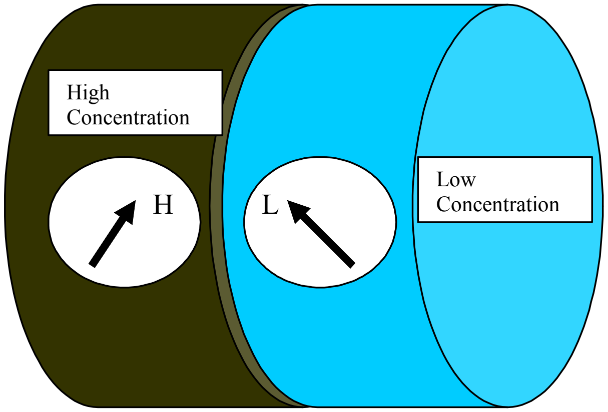
Osmotic Pressure

- Simple Osmotic Pressure

$$\Phi = \frac{-m_A \ln(a_A)}{m_B}$$

- Activity (*a*) is dependent on concentration, temp, other ions.



Control of Solute (Salts) Passage

Solution Diffusion (Lonsdale, 1965)

Water Flux

$J_w = A(\Delta Pressure - \Delta Osmotic\ Pressure)$

Solute Flux

$J_s = B(\Delta[Solute Feed] - \Delta[Solute\ Permeate])$

Coupled Solute Water Fluxes
Irreversible Thermodynamics
(Kedem, 1968)

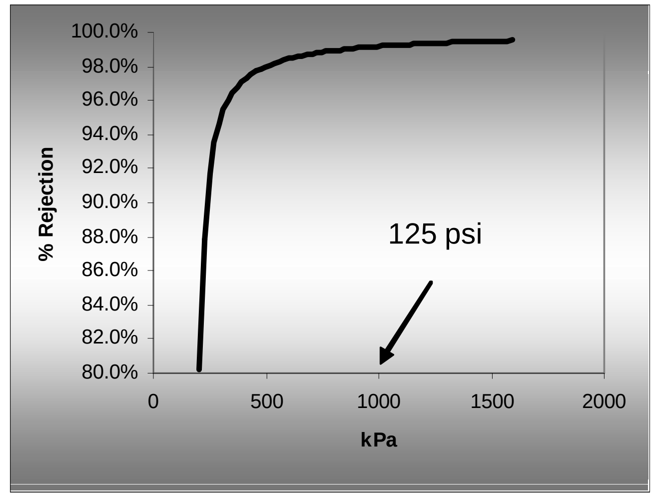
Water Flux

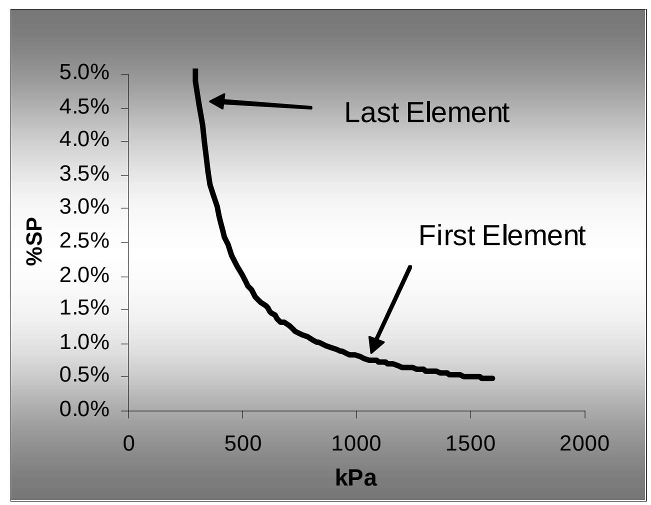
$J_w = A(\Delta Pressure - \sigma \Delta Osmotic\ Pressure)$

Solute Flux

$J_s = (c_m)_{avg}(1-\sigma) J_w +$
$B(\Delta[Solute\ Feed] - \Delta[Solute\ Permeate])$

Passage is very NON-Linear!





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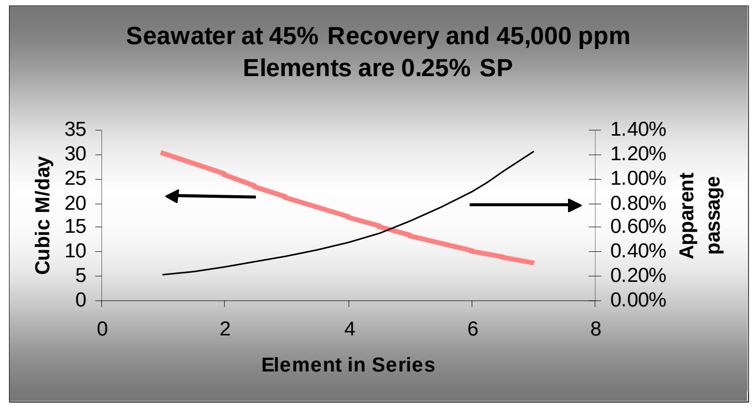
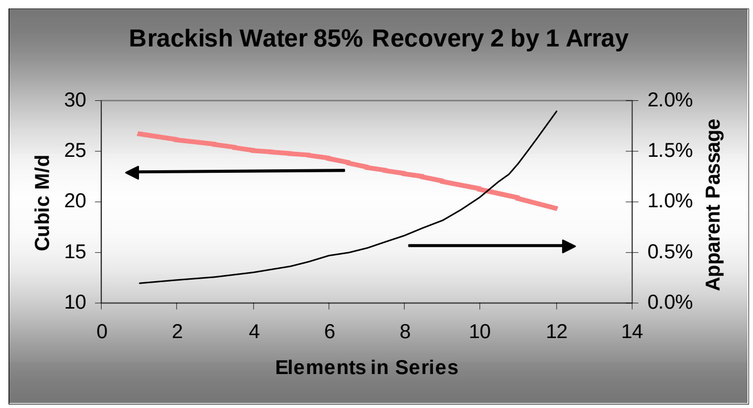
Modern High Rejection Reverse Osmosis Shows Large Changes in Passage vs Within a System

- In brackish water at 85% recovery the first part of the first element operates at 0.9% passage.
- The last element operates at 5-10% passage.
- Seawater fluxes vary by a factor of 4-10 from the beginning to the end of the system.

Flux and Passage of a Brackish Water and Seawater System

- In both Seawater and Brackish water the passage changes by 8-10 fold in the system.
- The flux drops by 4 fold in seawater.
- Membrane efficiency drops by 4 fold.





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Modern RO Elements Use Automated Assembly and Designed Components

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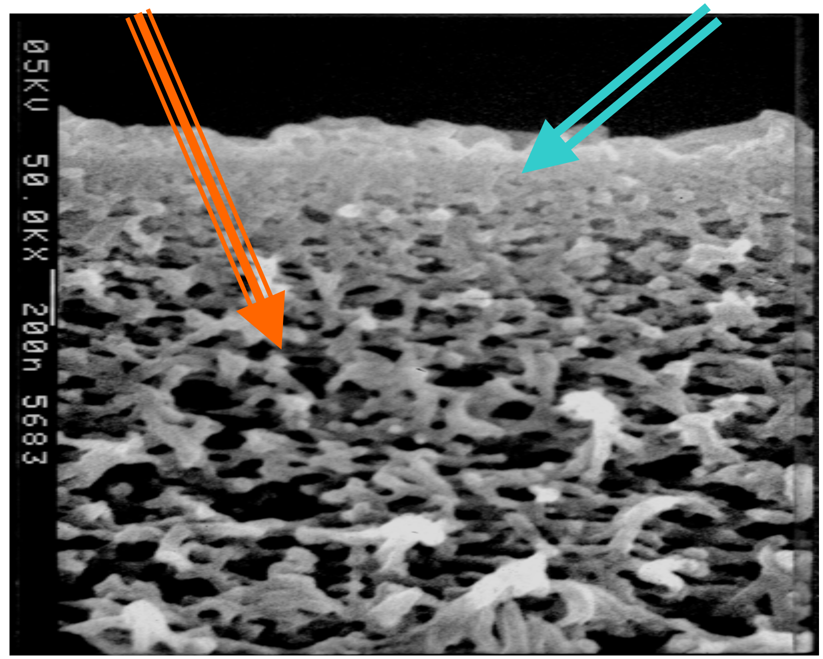
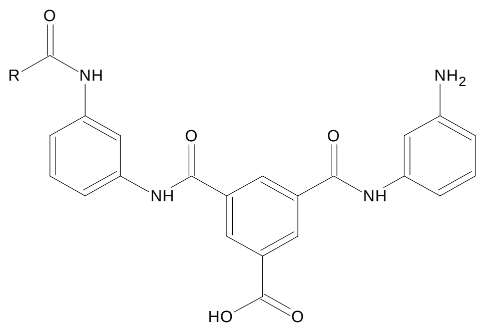
Polysulfone Layer
50 uMeter Thick

Polyamide Layer
1000-3000 Angstrom Thick

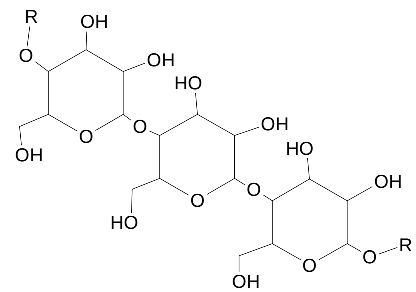


Cellulose and Polyamides Used in RO and NF

pK =3.9, 5

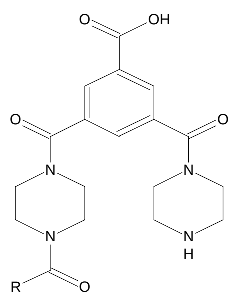


FT-30 Aramide Cadotte



Cellulose Loeb Sourirajan

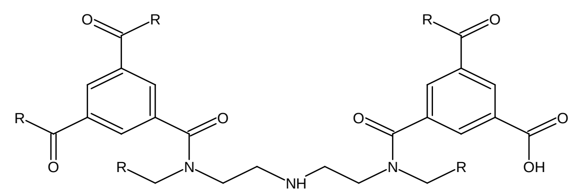
pK =7.5, 3.8



Mixed Aromatic Aliphatic

Trimesic / Piperazine

NF-40 Cadotte



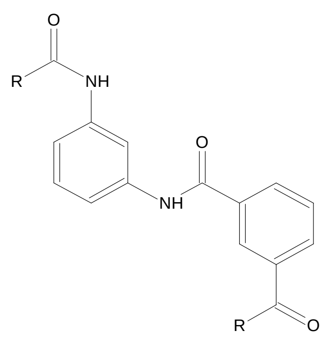
pK=8.5, 3.5

Mixed Aromatic Aliphatic

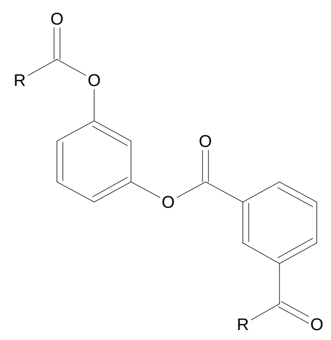
Trimesic / Poly imine

NS200 Cadotte

Other RO/NF Polymers

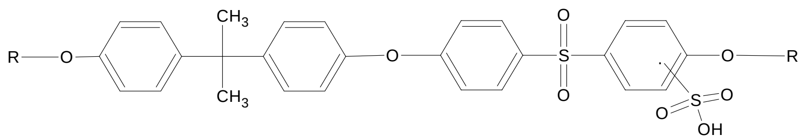


Sundet B-10



Sundet Experimental

Sulfonated Thermoplastics



Sulfonated Polysulfone

The Transition From Cellulose to Aramides Based Membranes

Year	Thin Film Aromatic Polyamide		Cellulose	
Brackish Water	Flow gpd	Rejection	Flow gpd	Rejection
1990	8000	98%	7500	95%
1998	10,000	99.20%	9000	97-98%
2007	11,000	99.80%	~ 10,000	~99%
Sea Water	Flow gpd	Rejection	Flow gpd	Rejection
1990	4000	99.40%	2300	96%
1998	5500	99.5	4000	99%
2007	7500-8000	99.80%	---------	---------

- Cellulose and derivatives operate at 0.1-1 ppm hypochlorite and are cleaned between pH 4-7.
- Aramides (aromatic polyamides) are run on hypochlorite free water and cleaned over a pH of 2-14.
- The spiral element using Aramides membranes have higher rejection and they are easier to clean.

FilmTec Research 1996

J. Cadotte Inventor of FT-30 and Thin Film Composite Polyamides

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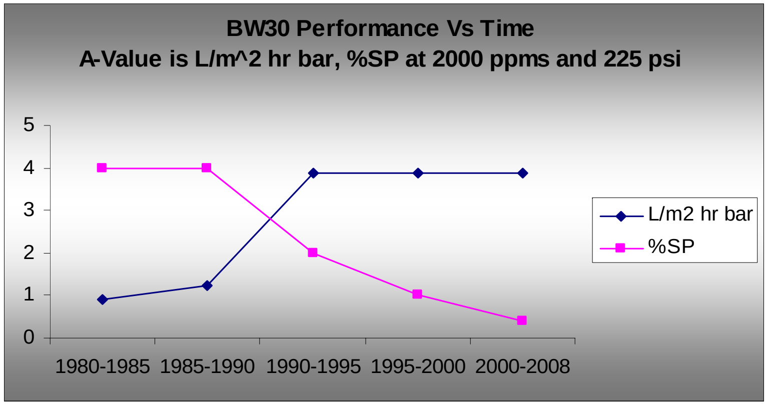
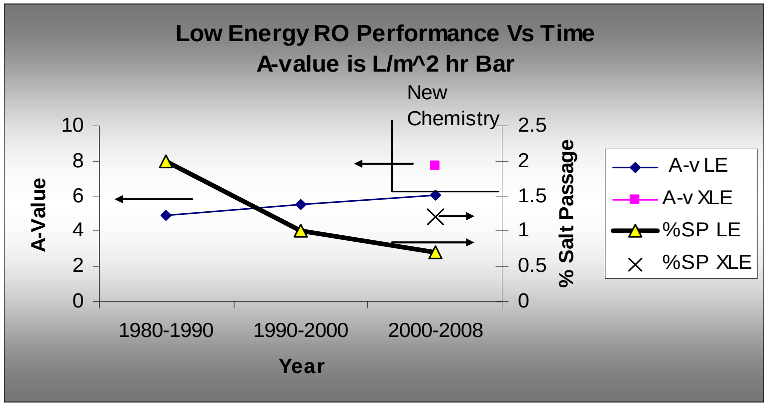
Development of Brackish Water RO from 1980 to 2008

- Different membranes operate at different pressure to produce the same amount of water.
- BW30 Started increasing flux, now improved passage.
- Low energy membranes (LE) are 25-50% higher flux.
- XLE is 100%-150% increased flux.
- Salt passage have been cut by factors of 2-6.





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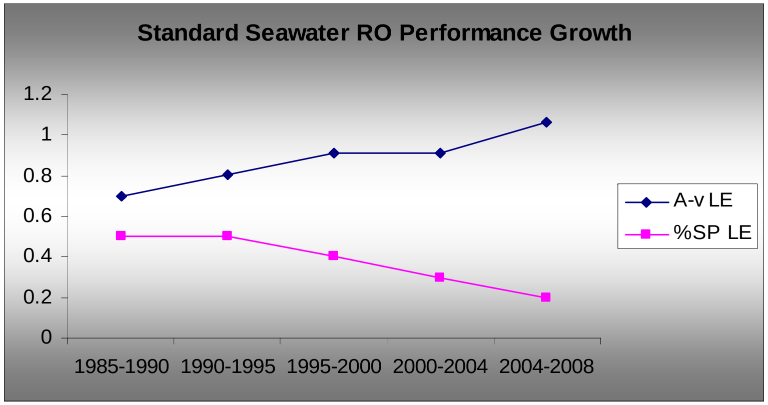
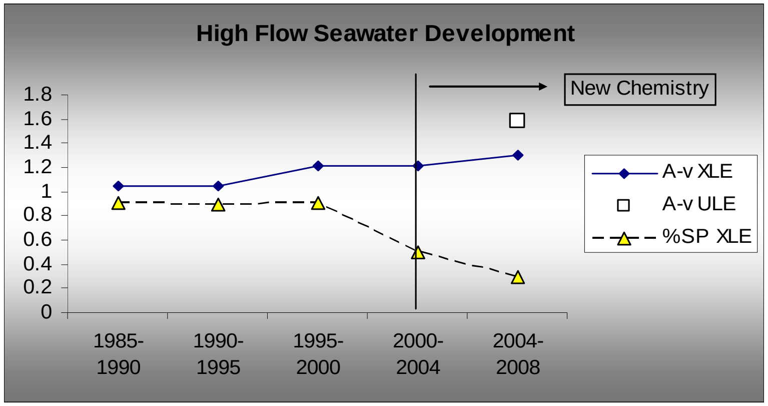
Seawater Development

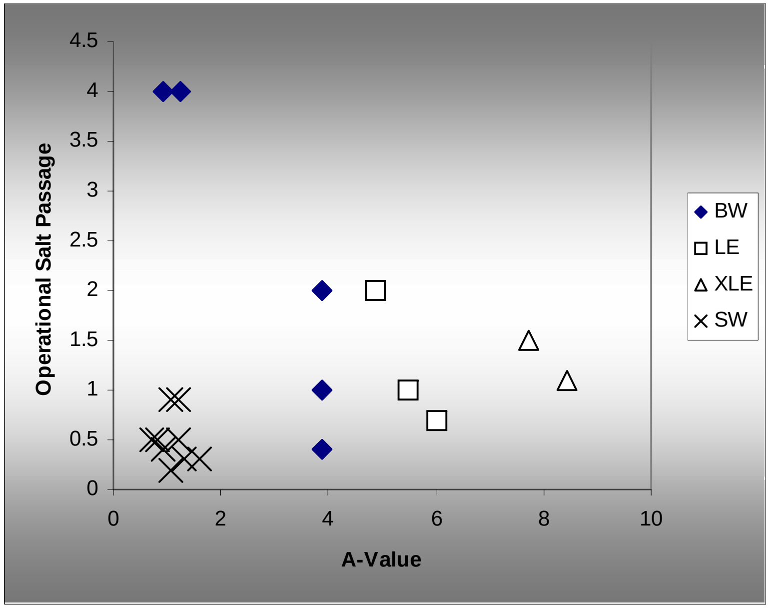
- Salt passage dropped by a factor of over 2. Flux increased by 50%.
- High Flow versions increased permeability another 60% and the salt passage dropped by a factor of 4!
  - A-values are l/m^2 hr bar





Historically Swings in Membrane Development

- Initial work to increase the element flux to a reasonable level.
- Cut Salt Passage by 30-50%.
- Cut Salt Passage again.
- Increase A-value by 50%.
- Repeat of the above.



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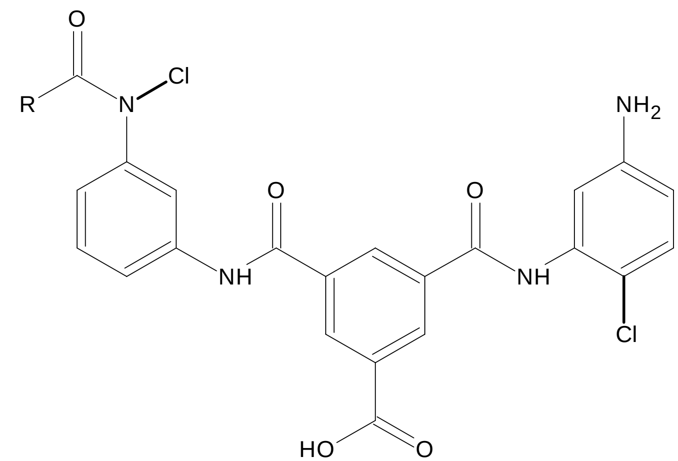
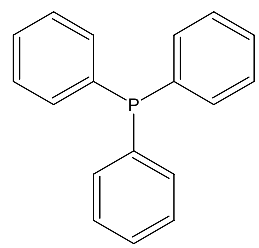
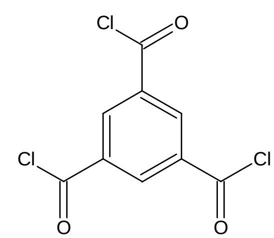
CHANGES IN CHEMISTRY HAS DRIVEN NEW MEMBRANE DEVELOPMENT

- Chlorination of FT-30 can improve the productivity by 50-60% and improve the rejection. John Cadott 1980s
- Addition of alcohols and esters to the reaction. Improvements in flux or rejection. Hirose 1998
- Use of ethers and esters was developed by Toray.
- Organometallic compounds form complexes with our Acid chloride. Mickols et. al. 2002
- New polymers, altered monomers, nano particles.





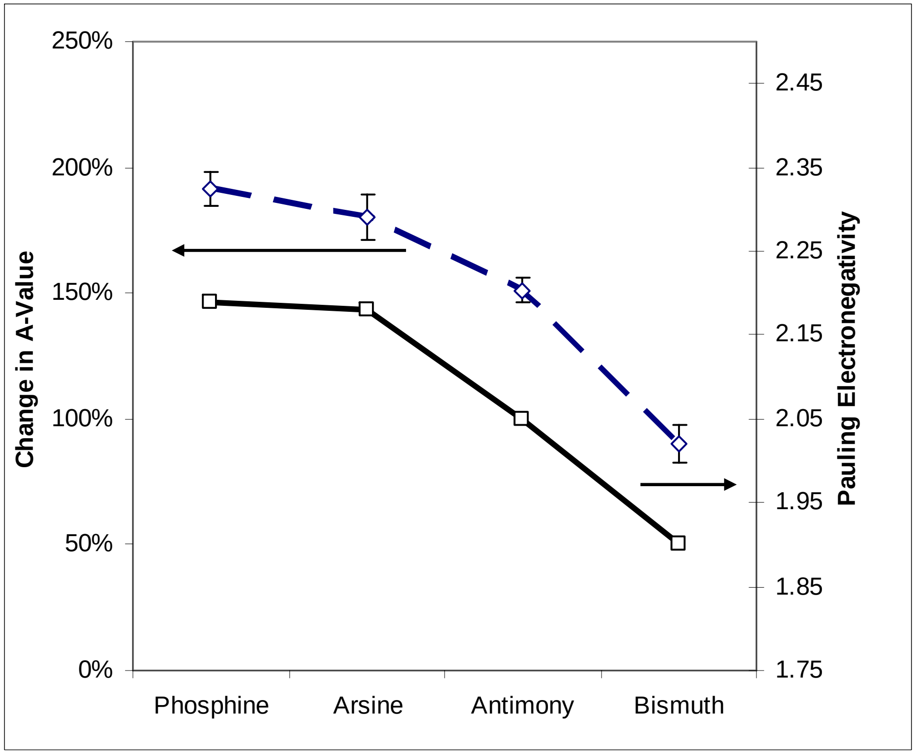
Tri Phenyl Phosphine



TMC

The Effect of Tri Phenyl Group 15 Atom Replacement on FT-30 Performance.

- The effect of the electro negativity of the central atom of the Group 15 elements.
- All structures are Pyramidal.
- Tri-phenyl ammonia is a base and Tri-phenyl Bismuth is acidic.

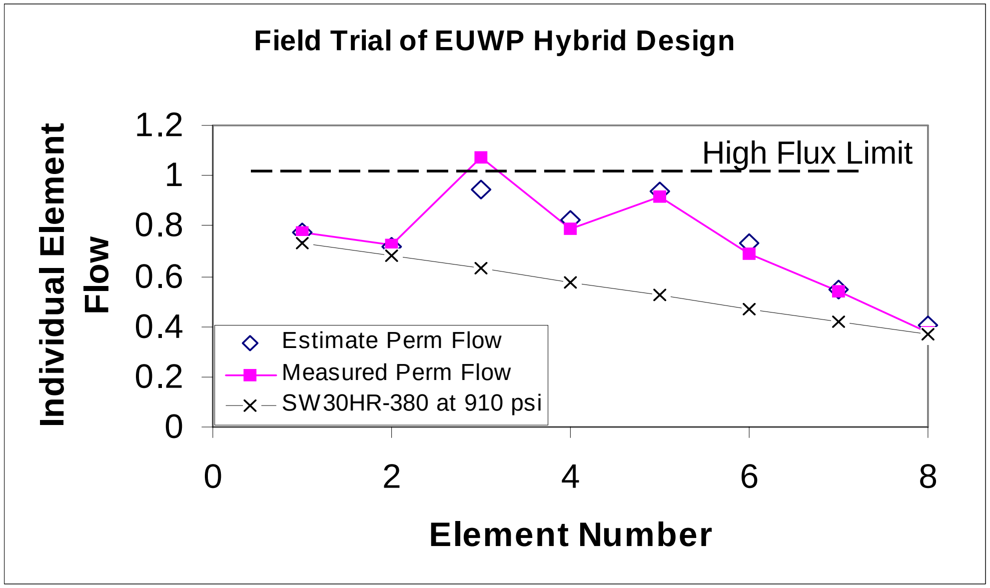


What Use is Increasing Flux by a Factor of Two

- Assuming I can double the flux and keep the same salt passage.
- The membrane would operate at the same flux and HALF the net driving pressure.
- The salt passage DOUBLES.
- I need to operate at about the same passage. Can I convert flux to passage.

EUWP Field Trials 50% Increase in Productivity

- **Operational flux is limited by fouling.**
- **Governmental program to provide Massive Disaster Relief, Mobile Base Camps**
- Field trials began in March 2004 with Mark Miller.
- Three elements types are internally staged. (2xSW30HR-380, 2xSW30XLE-400 and 4xexp 12000 gpd element).



Deployment in Baton Rouge After Hurricane Katrina

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Energy Losses in Seawater Desalination

- Pressure losses through pipes, valves, turns, etc are 5-10%
- Water recovery is 30-55%.
- Energy remaining in reject stream is 40-67%.
- Seawater would cost 30-45% more if the energy were not recovered.

Improvements to the process. Energy Recovery.

- Initial runs with pumps run in reverse. Low efficiency. Darwish 1989
- Pelton wheels (Single and Double) 60-70% energy recovery. Soo-Hoo 1983
- Turbo (Double Turbine Exchanges) High recovery with narrow operating windows.
  - Brine Recovery system. Toray.
- Piston energy exchangers 90-95%. 1989
- Rotating cylinder energy exchangers 90-95%. 2001

Cost of Water from a Standard Seawater Plant

- Electricity for the High pressure pumps is 31%.
- Energy for high pressure pumps is dependent on pressure.
- Capital costs for the RO portion is 13%.
- RO replacement costs are dependent on flux at 5%.
- Depreciation costs are cut in half by bonding.
- **Increased recovery linearly decreases capital, and all costs except energy (69%)!**
- Cost estimates by J. Tonner of Water Consultants International.

	Millions US Dollars
Total Electricity	3.131
Electricity for the High Pressure Pump	*2.841*
Labor and Overhead	0.778
Chemicals	0.887
Cartridge Filter Replacement	0.019
Membrane Replacement	0.379
Repairs and Spare Parts	0.244
Insurance	0.122
Total Depreciation	3.27
RO Depreciation (37%)	*1.210*
Total Annual Costs	**9.028**
Dollars per 1000 gallons/kgal	**1.32**

Mickols Busch

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Higher Water Standards and Contamination of Water Sources Require Higher Rejection of **Different** Solutes

- Lower boric acid from Seawater.
- Recycled and contaminated waters contain high nitrate, nitrite, ammonia, and low molecular weight organics.
- New high rejection needs.
  - Boric acid
  - Arsenic salts
  - Nitrate
  - Endocrine disruptor
  - Trace organics
  - TCE etc.

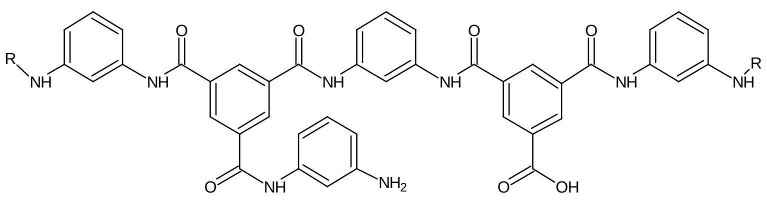
Surface Modification

- Cellulose membrane “repair”.
  - PVA
  - Tannic acid
  - other Colloids

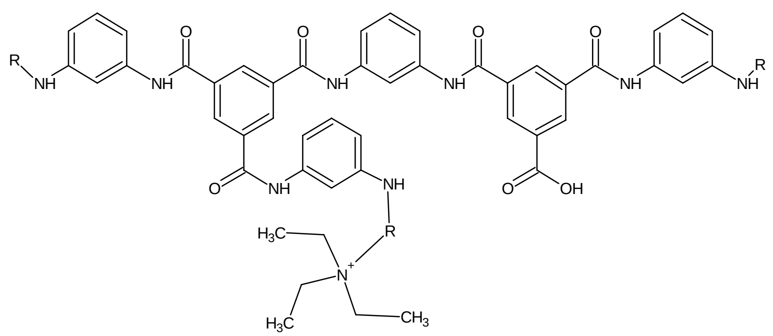
- PVA continues to be used and is commonly used in LF style membranes.
- Quaternary amines have been used to affect the low ionic strength rejection.
- Recent work on boric acid rejection and fouling have used PEGs.

Improvements in Low Ionic Strength Operations

- Ultra pure water membranes. Very low ionic strengths alter rejection based on surface polyelectrolyte effects and concentration of ions at the surface.
- At 1 ppm Na+ standard membranes are 50-70% rejecting
  - Multiple passes using RO membranes with anionic surfaces and cationic surface modifications.
- Commercialized by Toray and Nitto Denko.



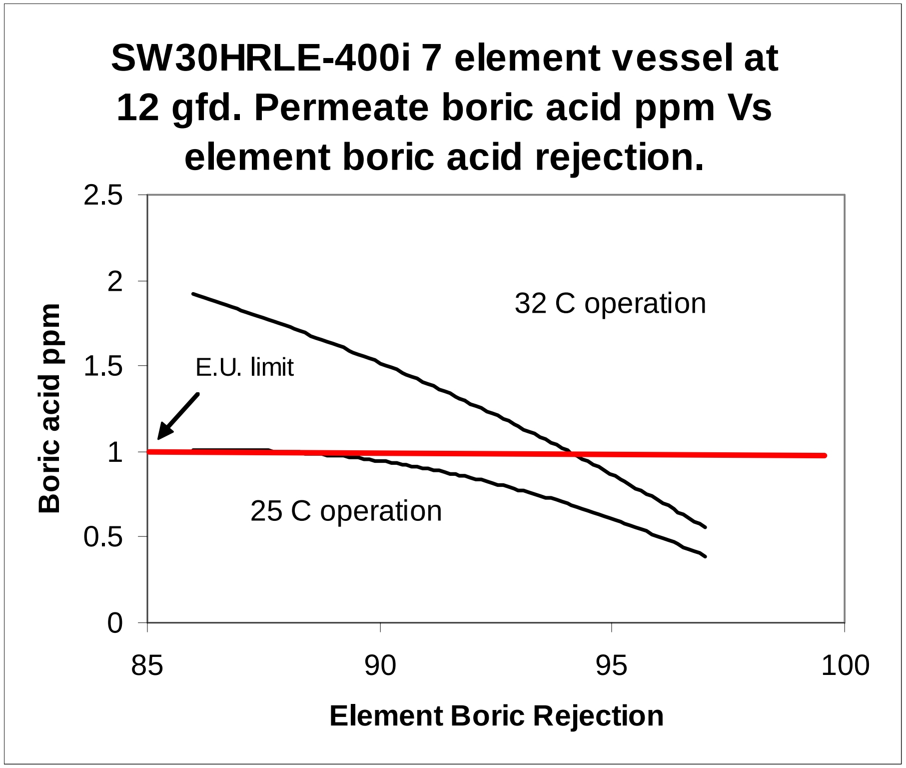
Standard FT-30 Anionic



Cationic Surface Modification

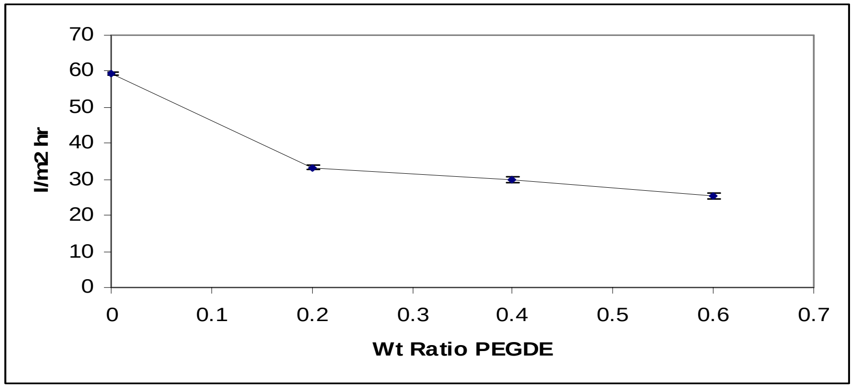
New Solute Requirements for Drinking Water
Boric Acid Requirements

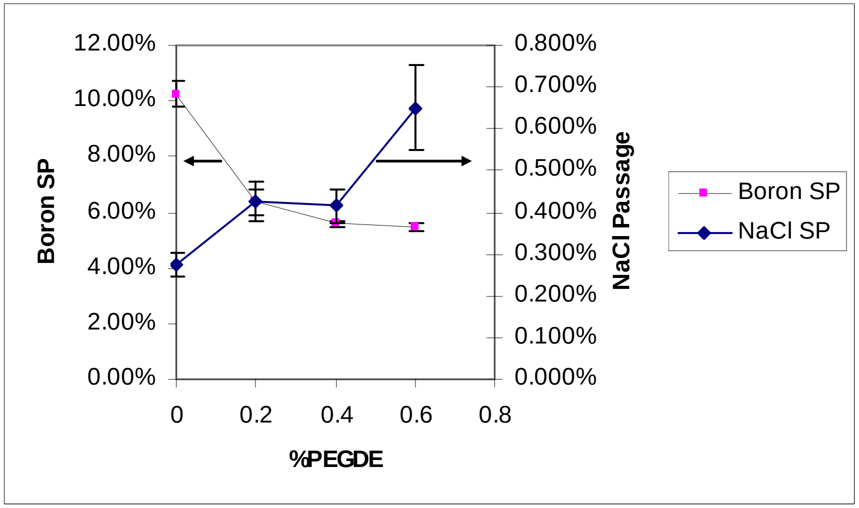
- E.U. recommends 1 ppm Boric acid. Being sequentially implemented across Europe.
- The World Health Organization has established a limit of 0.3 ppm.
- Water for use in certain agricultural areas needs to be below 0.1 ppm.
- Seawater varies from 2-8 ppm while the average is close to 5 ppm.
- Current RO systems produce permeate with 0.8-1.3 ppm.



Surface modifications of FT-30 Using PEG Di Glycidal Ethers (MW 600)

- Testing is at 800 psi (5.58 MPa), 3.2% NaCl, 5 ppm as Boron, pH 8, recovery less than 0.2%.
- Membrane is cleaned in 15% IPA/Water. Soaked in water at 35 C for 2 hr.
- Reacted in water at 60 C for 2 min.
- Large initial changes in performance and then coverage builds slowly.
- Flux Losses, NaCl Passage losses, Boron Passage IMPROVEMENT.





- I Have shown large changes in performance.
- I Have shown specific chemistries which are examples of larger sets of chemistries we developed.
- You can not tell from this presentation which chemistry are in use.

Modified FT-30 with Altered Rejections

- SW30HRLE-400 has 11% boric acid passage, SW30XHR-400 has 6-7% boric acid passage.
- BW30-400 has 99.5% NaCl rejection, XUS has 99.8%.
- BW30-400 has 4-5% Nitrate passage, XUS has 1-1.5% Nitrate passage.

New Needs in the World Fuel RO Membrane Chemistry.

- In the past 20 years water permeability has increased by a factor of 8. The passage has dropped by a factor of 8.
- Improved designs improved the RO efficiency by a factor of 3 with recent doubling.
- Energy recovery cut the energy cost of SW by ~50%.
- Modifications to the membrane to cut “difficult” to remove solute passages by 2-5 fold.
- This will continue for the next 20 years!

Needs of the RO/NF Industry

- Low fouling that works on most fouling waters.
- Another cut in passage by 50% at the same pressure.
- Doubling the flux with half the salt passage.
- New solutes.
  - Operation in partially denitrified waste waters.
  - Elimination of small organics (DBP, Alcohols, nitrosamine, chlorinated solvents).
  - Elimination of silica, As salts, Se.
  - Scaling elimination.

We Stand on the Shoulders of Giants

- Loeb Sourirajan gave us RO.
- Lonsdale/ Kedem gave us the theory.
- Cadotte (Deceased 2007) gave us
  - interfacially polymerized polyamide membranes.
  - 4-5 billion dollar industry.
- Energy recovery cut the cost of Seawater desalination by 30-50%.