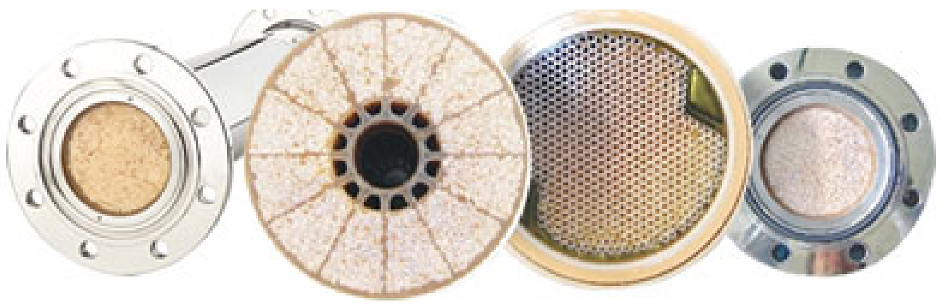
Advanced Membrane Technologies
Stanford University, May 07, 2008

Membrane Separation…Basics

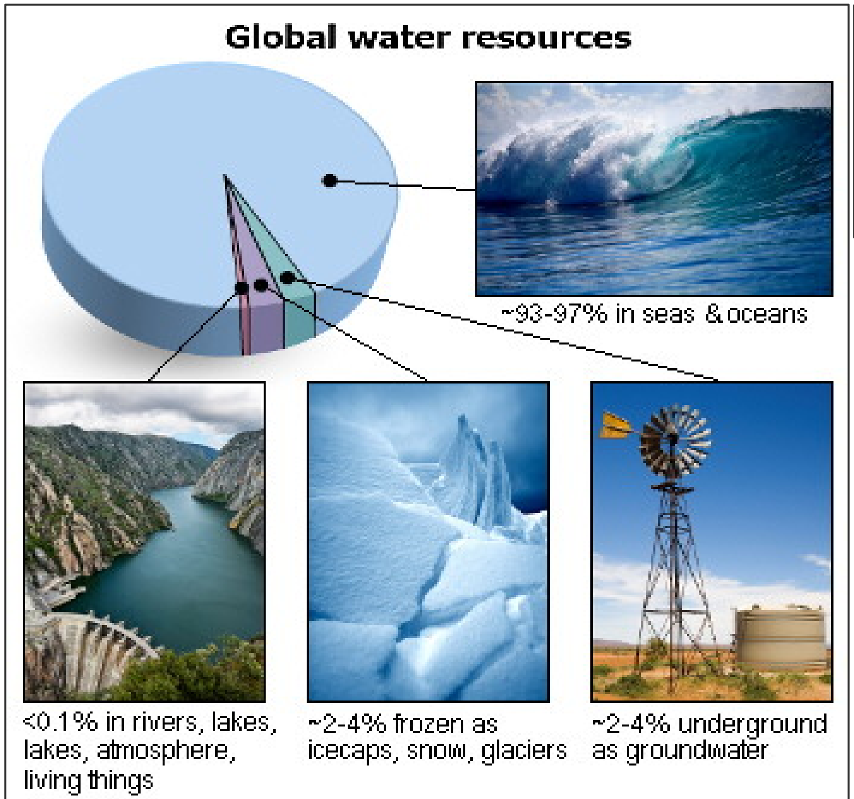


Harry F. Ridgway, PhD

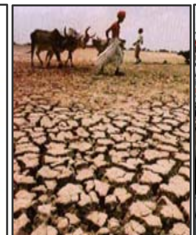
Kennedy/Jenks Consultants
Engineers & Scientists
National Water Research Institute

Global Water Supplies…

> 2 billion lack reliable access to clean water

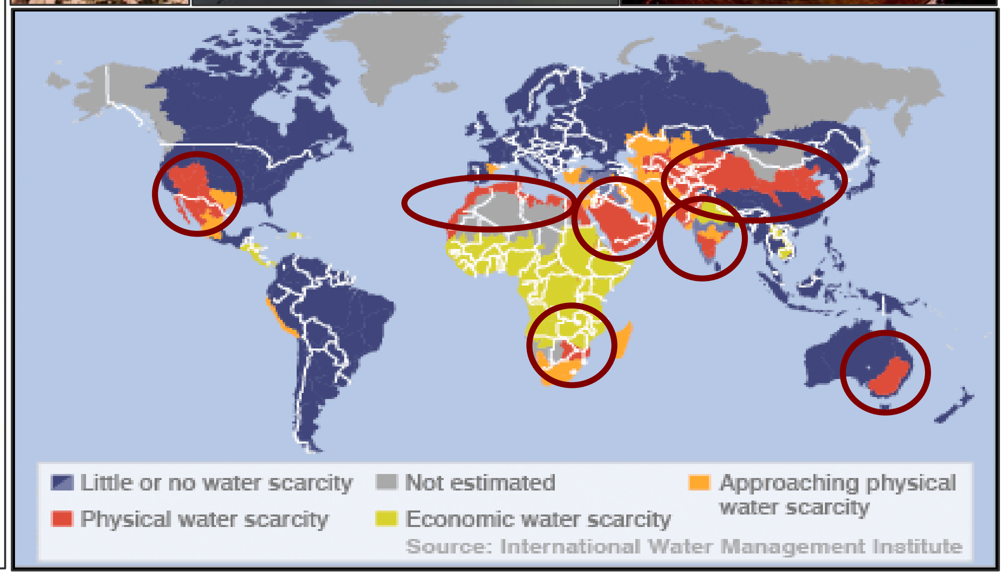


Drought



Pollution

GW Depletion



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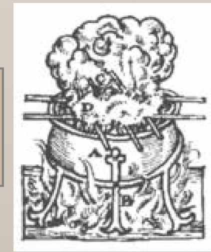
National Water Research Institute

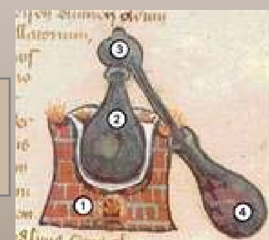
History of Desalination…

400 BC

5th Century BC ~ wool condensator
Earliest distillation process by Greek sailors



3rd Century BC
Aristotle describes water cycle & distillation process



BC

2nd Century BC
Egyptian distillation processes described

AD

17th Century AD ~ first recorded
Japanese sailors ~ distillation earthen pots/bamboo reeds

1700

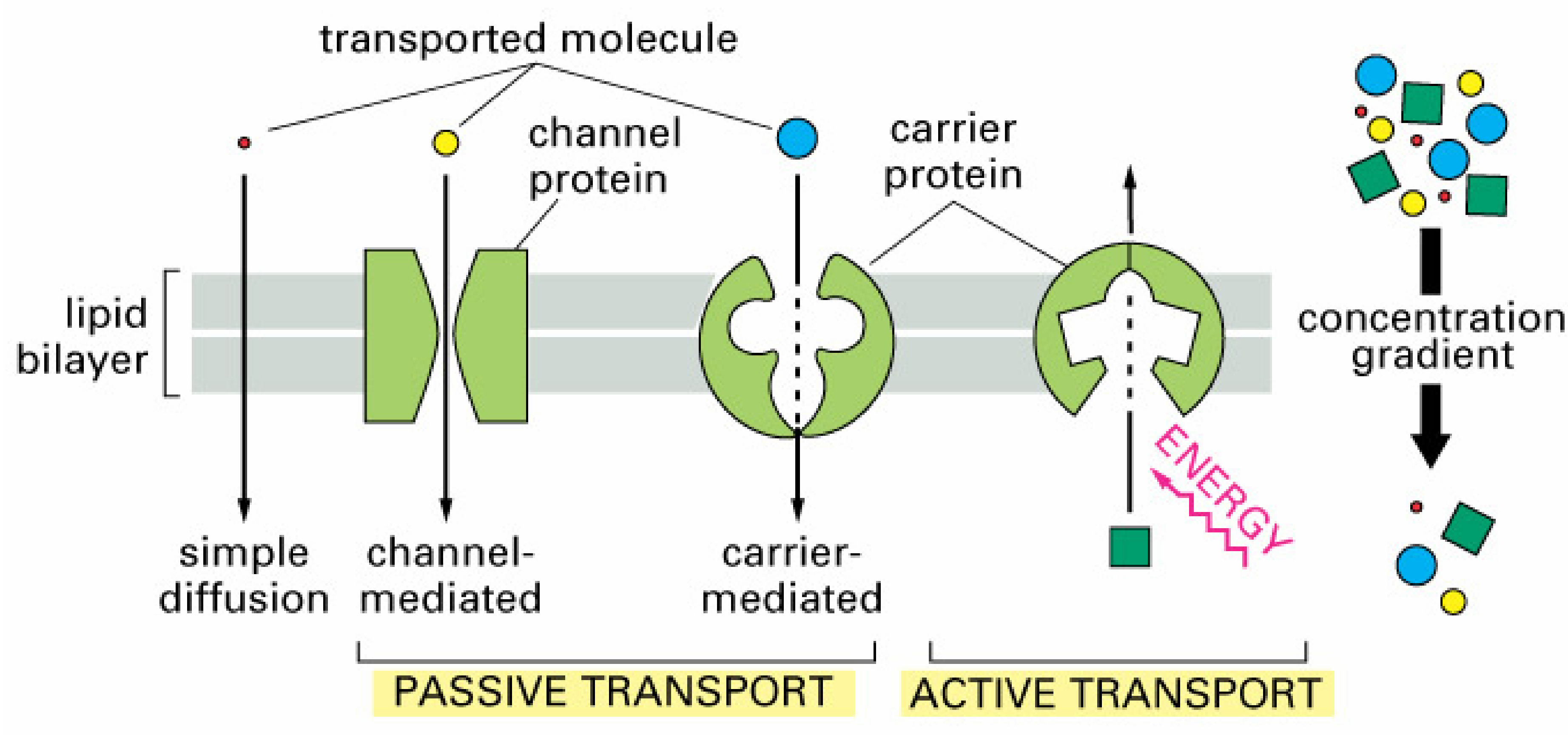
1790's
Thomas Jefferson & Jacob Isaacks
US Navy – Distillation: *"Report on Desalination of Seawater"*

1881
First commercial desal plant
Tigne, Sliema, Malta

1900

1907
Ottoman Turks – Jeddah Distillation Plant
Replaced in 1928

By mid 1900's…Advances in microscopy and cell biology led to concept of the **Lipid Bilayer Membranes** and semipermeable membranes…



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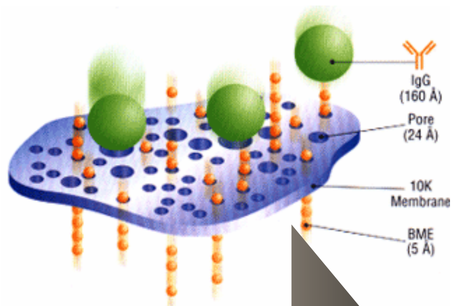
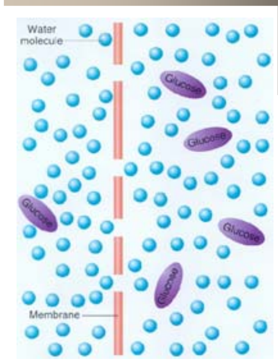
By the 1950s R&D was underway to ID a synthetic permselective membrane…



…permselectivity



1960, S. Yuster ~ UCLA, Sid Loeb & Souri Sourirajan

…early 1960's…

Commercialization…

"First" Spiral-Wound Element ~ 1963

General Atomic – Fluid Systems

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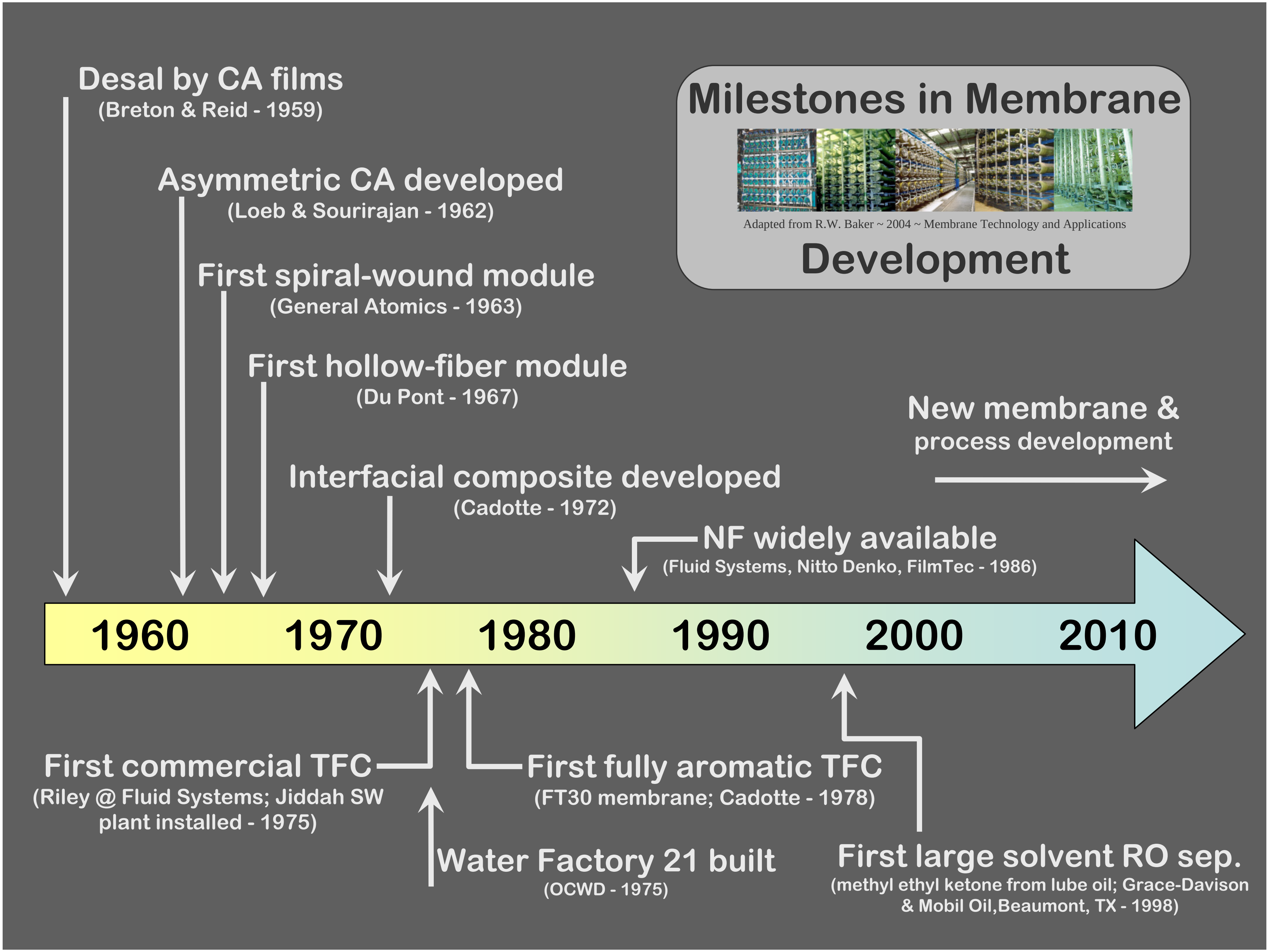
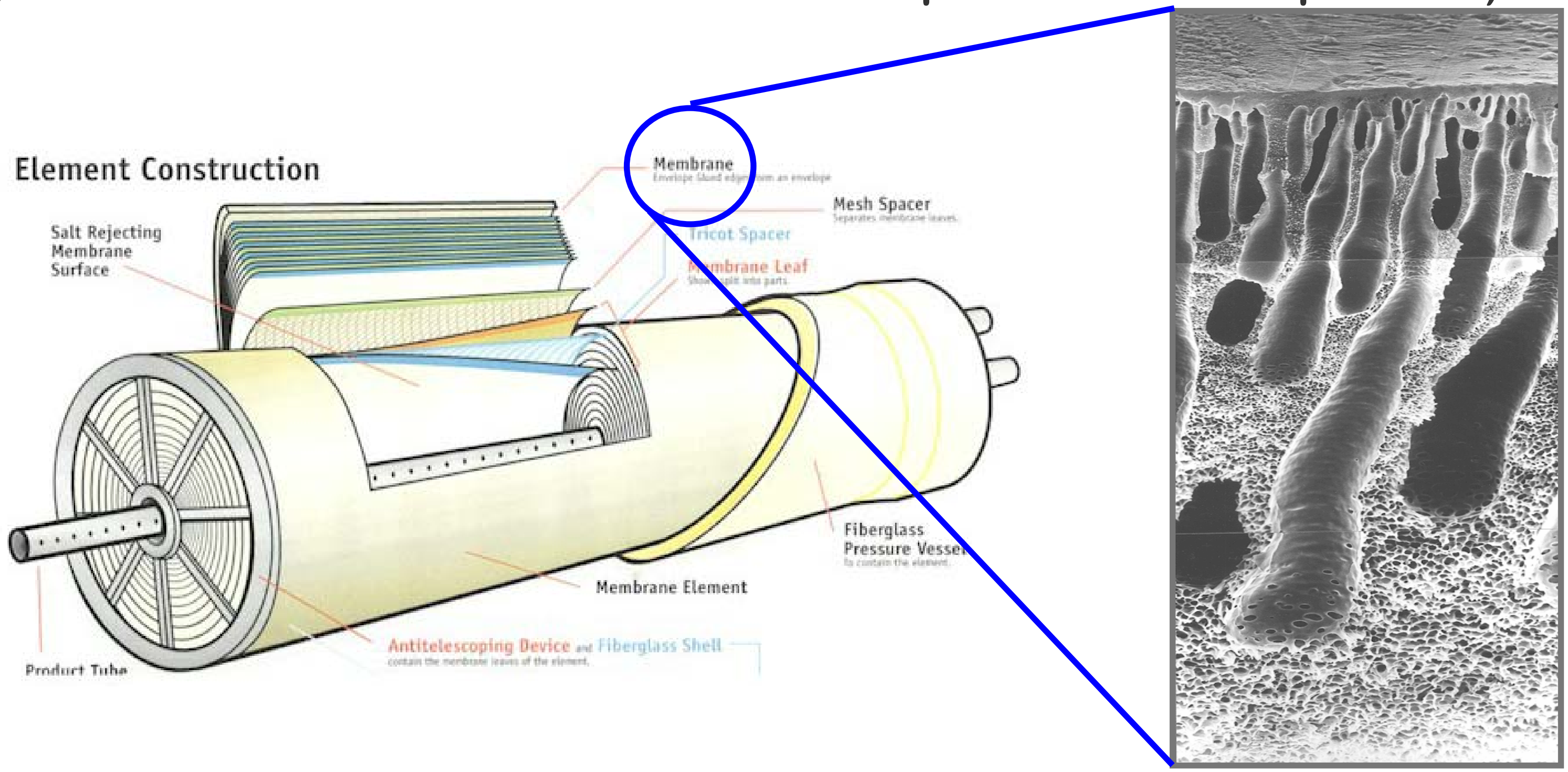
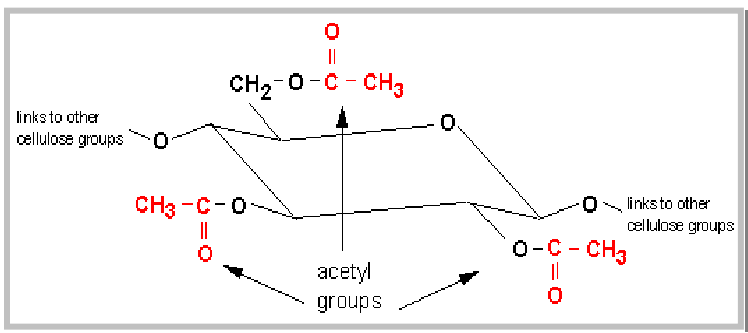
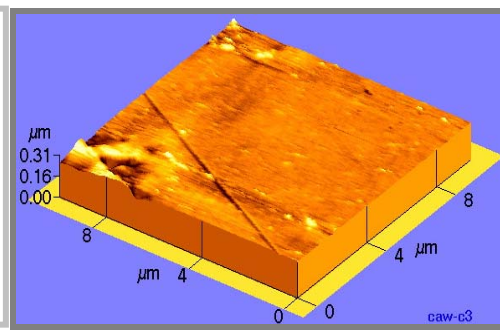

Milestones in Membrane Development
Adapted from R.W. Baker ~ 2004 ~ Membrane Technology and Applications
Desal by CA films
(Breton & Reid - 1959)
Asymmetric CA developed
(Loeb & Sourirajan - 1962)
First spiral-wound module
(General Atomics - 1963)
First hollow-fiber module
(Du Pont - 1967)
Interfacial composite developed
(Cadotte - 1972)
NF widely available
(Fluid Systems, Nitto Denko, FilmTec - 1986)
New membrane & process development
1960
1970
1980
1990
2000
2010
First commercial TFC
(Riley @ Fluid Systems; Jiddah SW plant installed - 1975)
Water Factory 21 built
(OCWD - 1975)
First fully aromatic TFC
(FT30 membrane; Cadotte - 1978)
First large solvent RO sep.
(methyl ethyl ketone from lube oil; Grace-Davison & Mobil Oil,Beaumont, TX - 1998)

"Loeb-Sourirajan" membrane…

(asymmetric cellulose acetate membrane ~ phase inversion process)

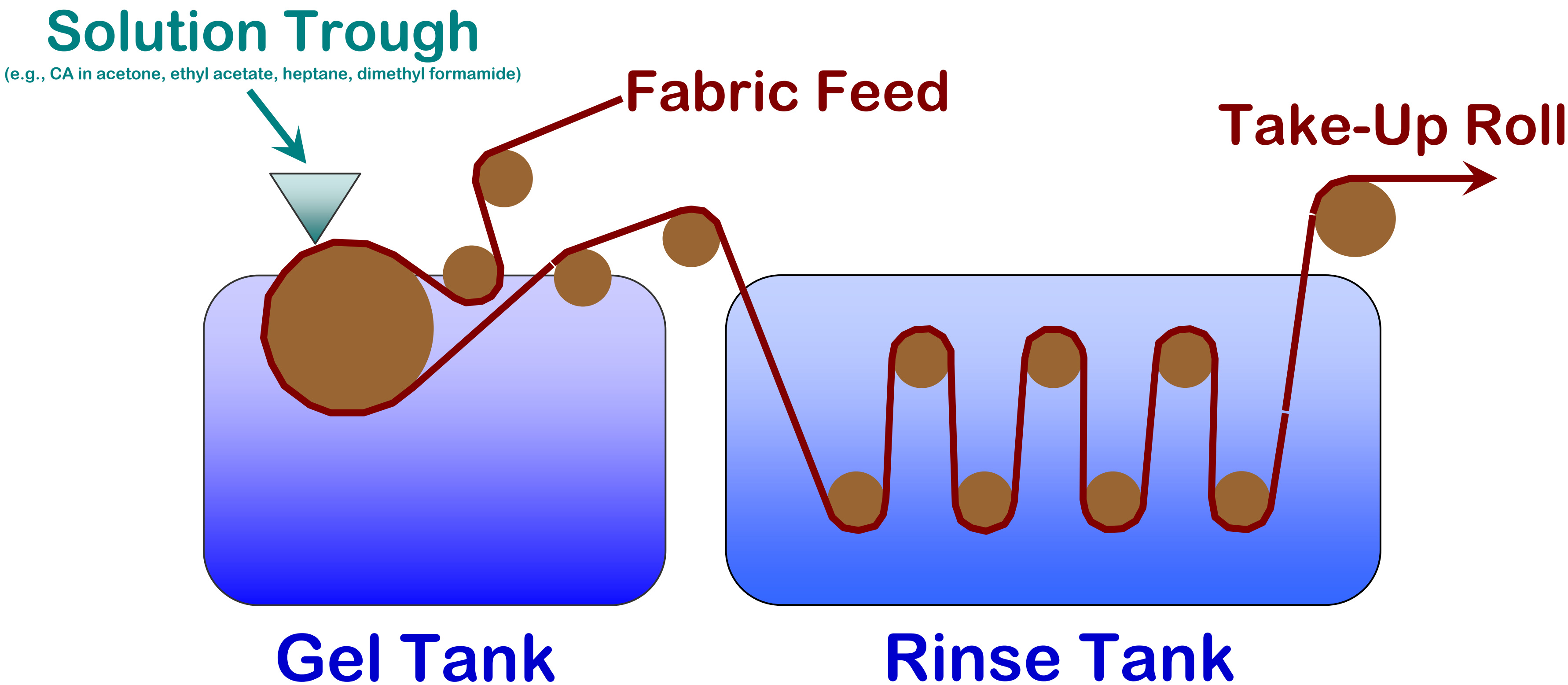






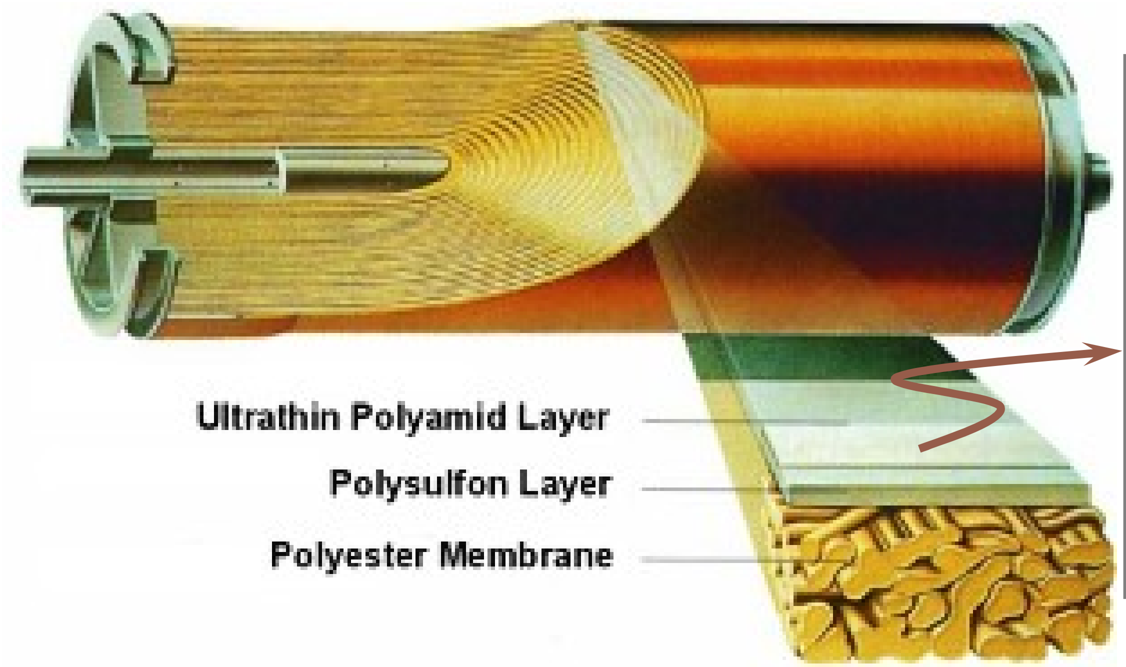
Pressure Range: >150 psi
Flux Range: 5-20 gfd
pH Range: 4 – 6.5
Solute Rejection: 75-95%
Free Chlorine: < 3 ppm

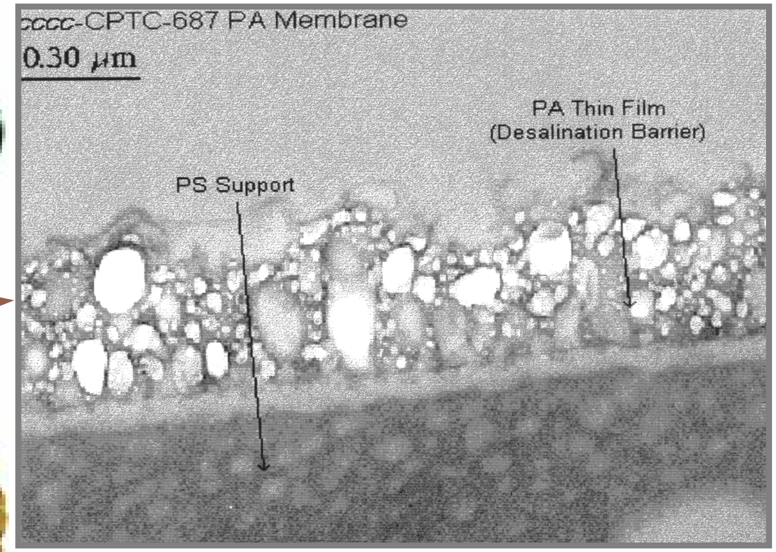
Membrane Synthesis…
Phase Inversion/Separation

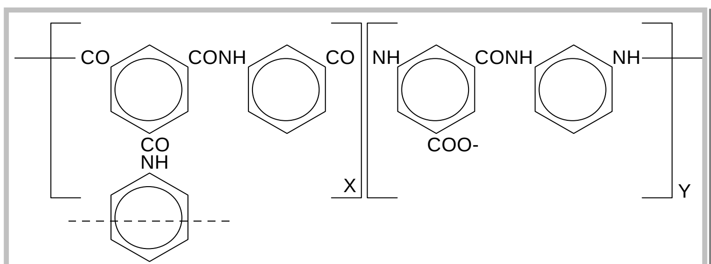


Current “State-of-the-Art” TFC Membranes…

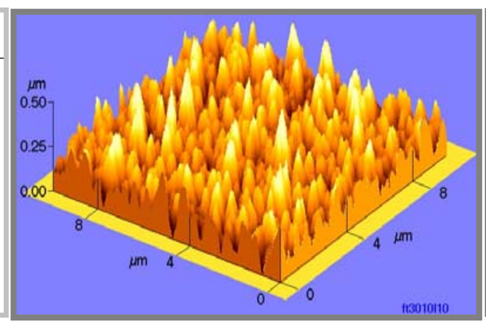
(X-Linked Polyamide, John Cadotte, 1975; interfacial polycondensation reaction)



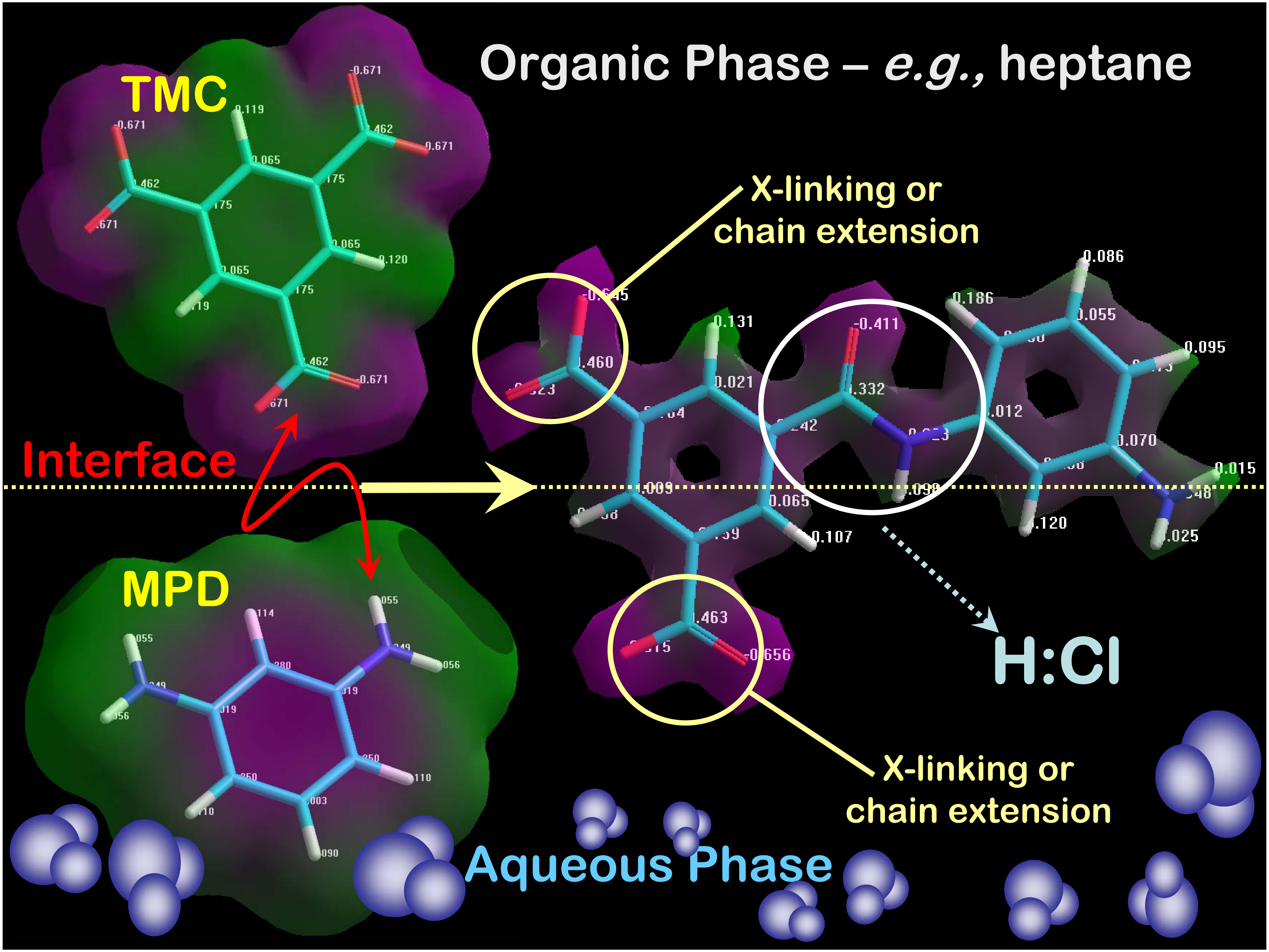




aromatic cross-linked polyamide

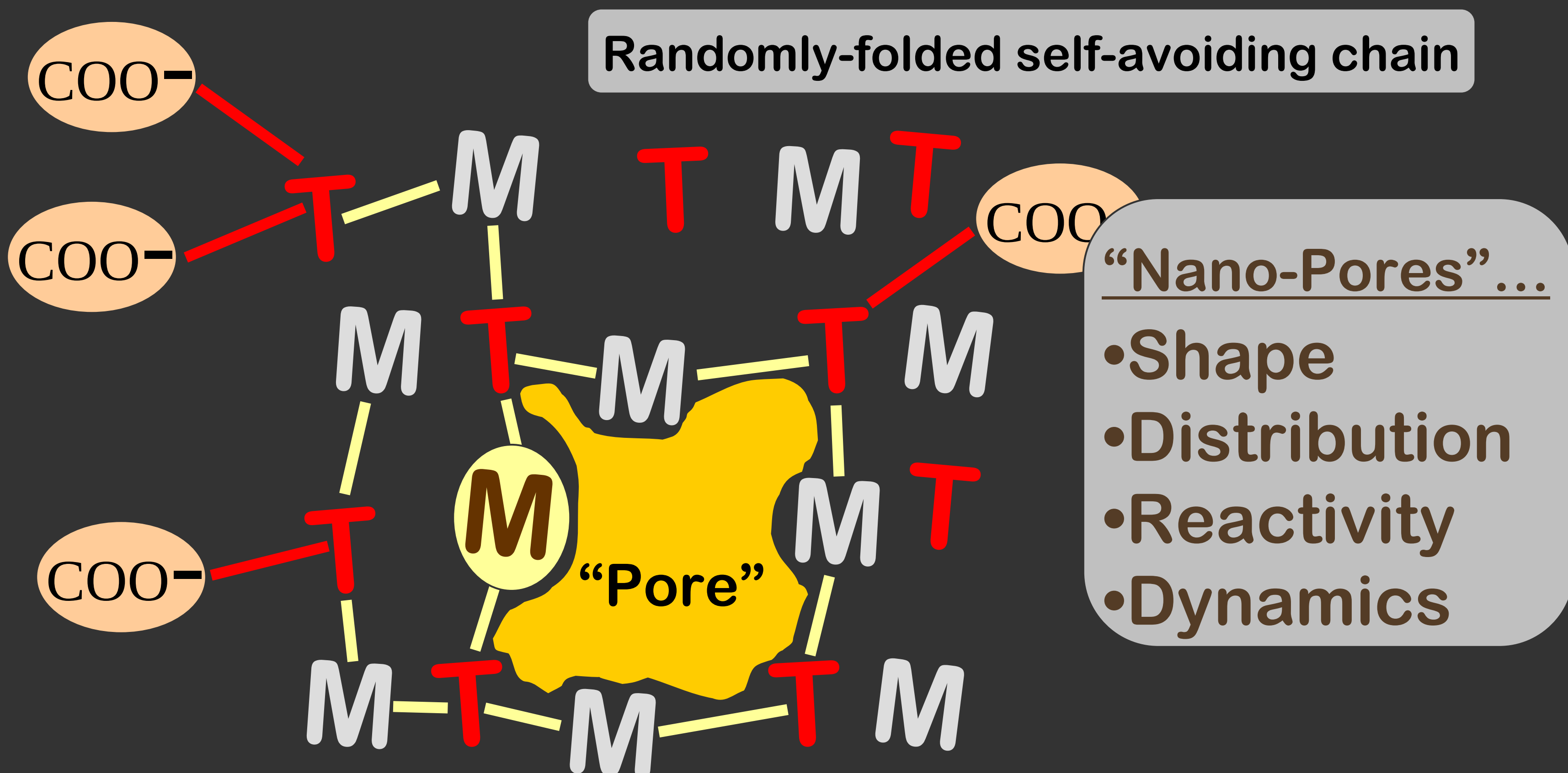


Pressure Range: 100-150 psi
Flux Range: 10-40 gfd
pH Range: 2 - 11
Solute Rejection: 97 - 99%
Free Chlorine: <0.1 ppm



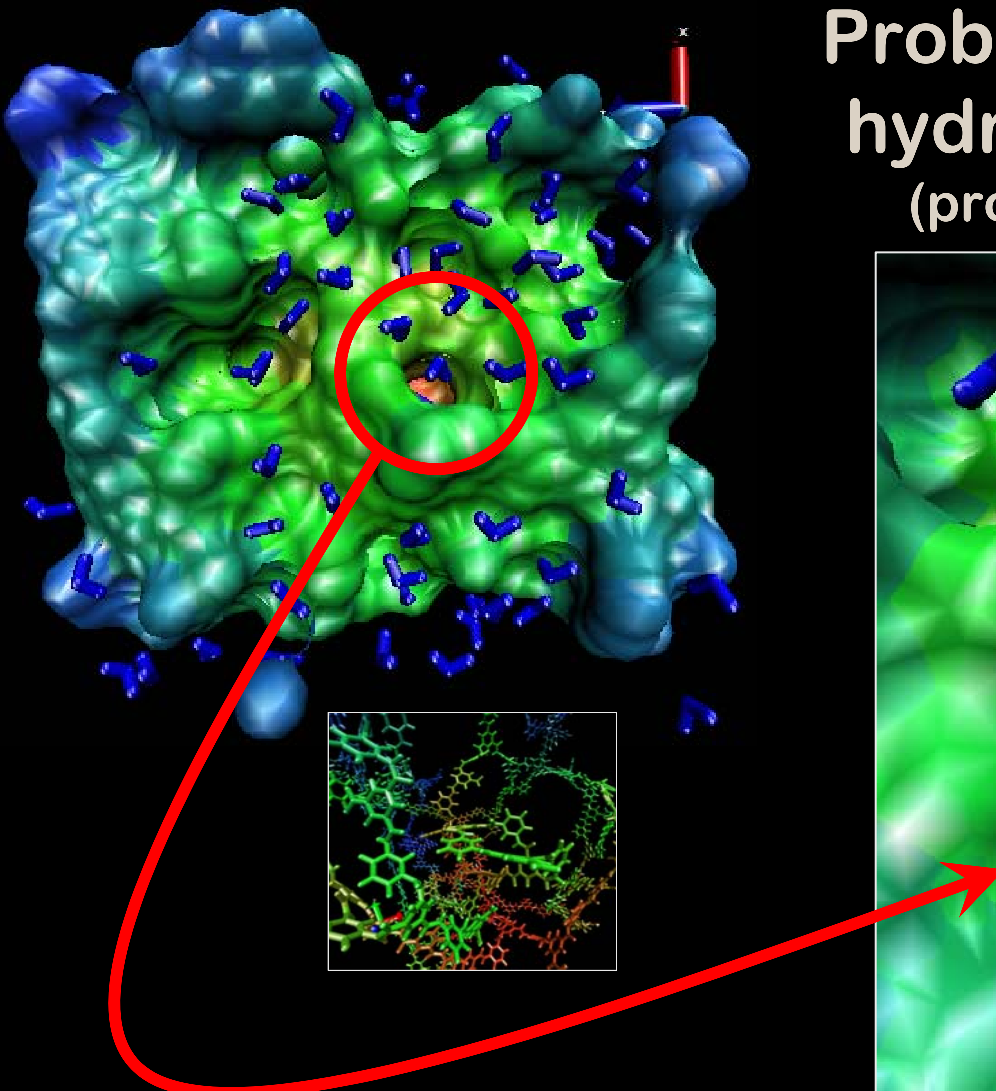
Organic Phase – e.g., heptane
TMC
X-linking or
chain extension
Interface
MPD
H:Cl
Aqueous Phase
X-linking or
chain extension

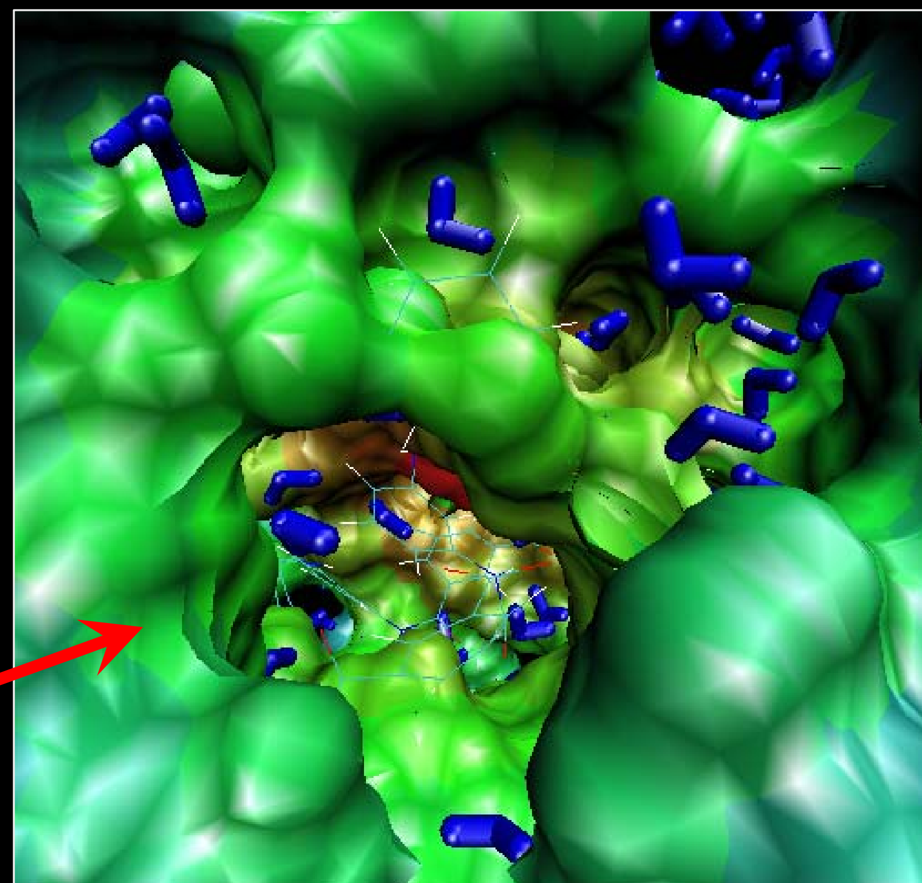
Nano-pore formation resulting from X-linking…



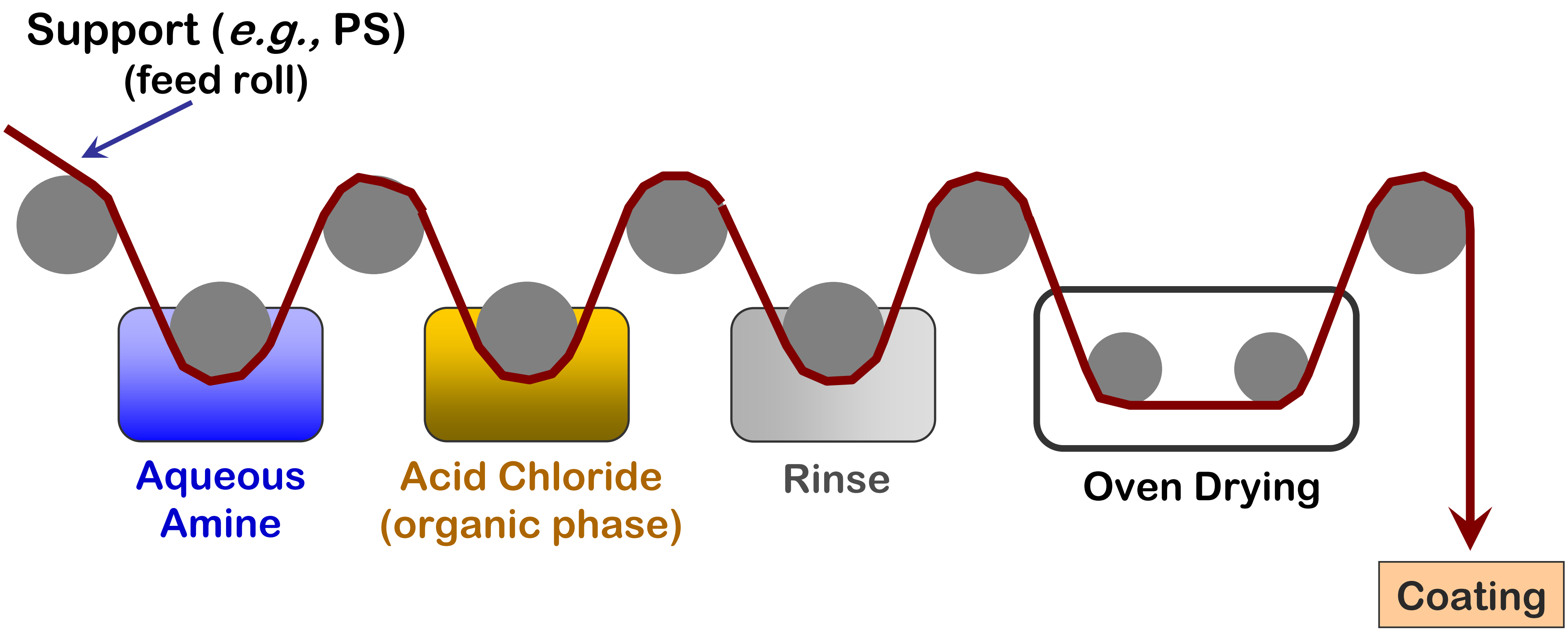
Probe surface rendering of hydrated FT30 Membrane

(probe radius = 1.4 Angstroms)

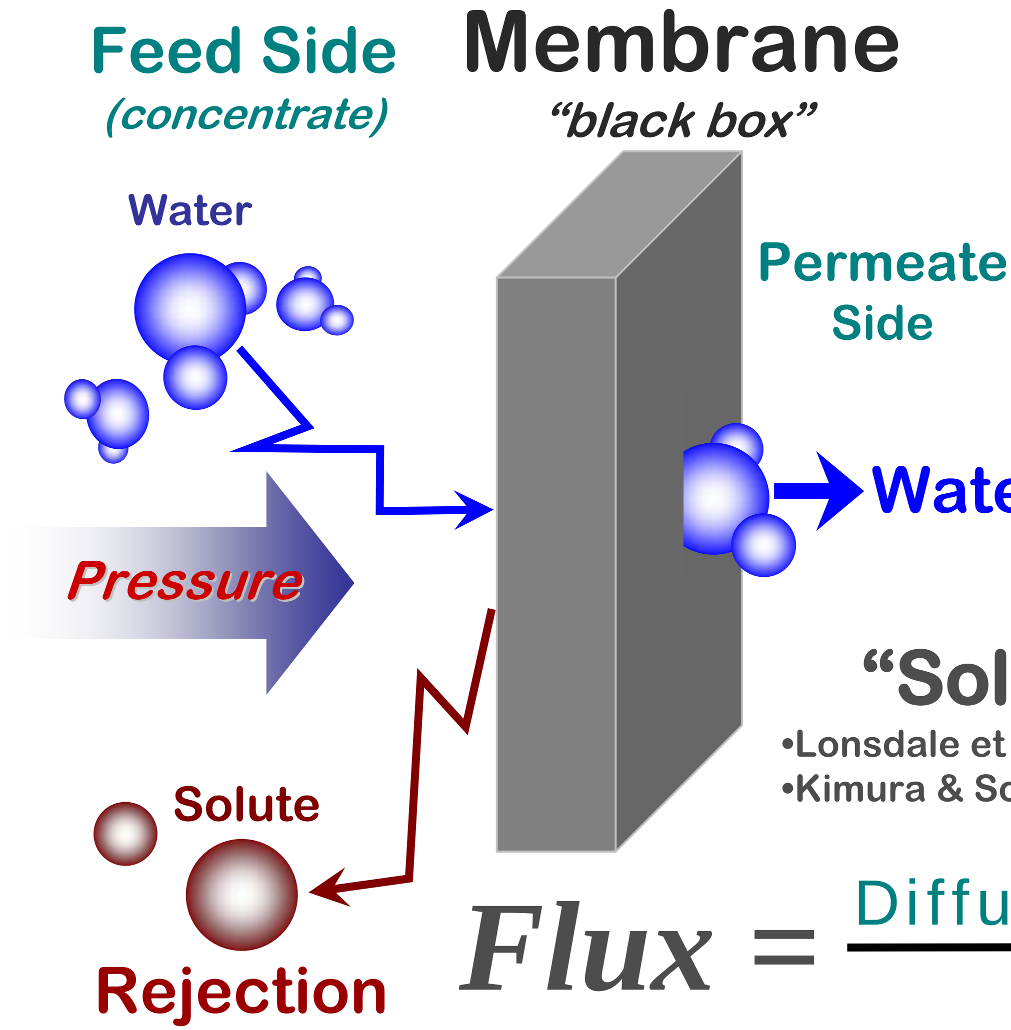


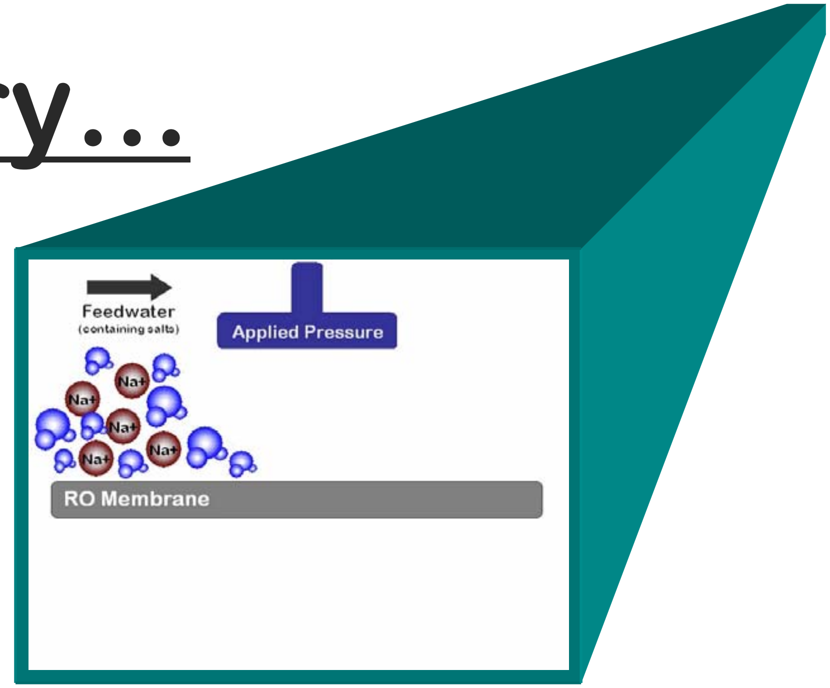


Membrane Synthesis…
Interfacial Polymerization



Membrane Theory…



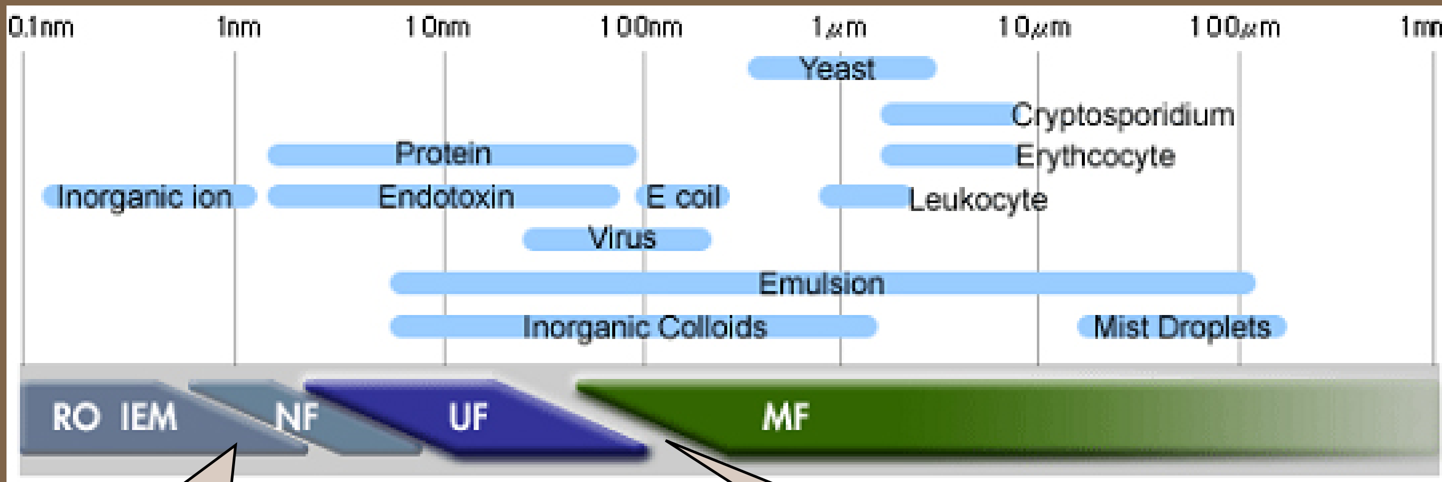


"Solution~Diffusion Theory"

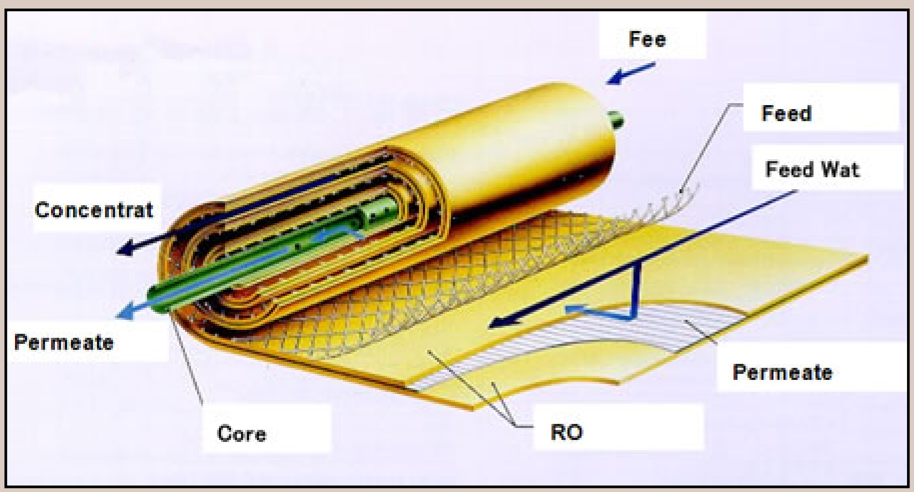
- Lonsdale et al., J. Appl. Poly. Sci., 9, 1341-1362 (1965)
- Kimura & Sourirajan, AIChE J., 13, 497-503 (1967)

$$\mathit{Flux} = \frac{\text{Diffusivity} \times \text{Solubility} \times \text{Force}}{\text{Resistance}}$$

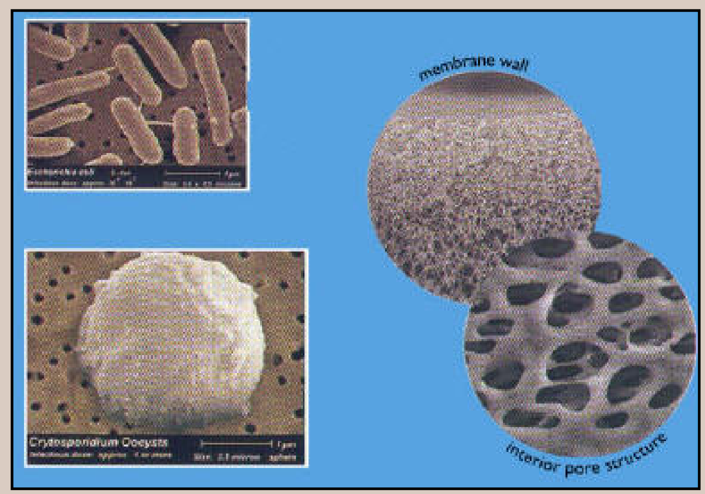
Membrane Categories…



Solution/Diffusion



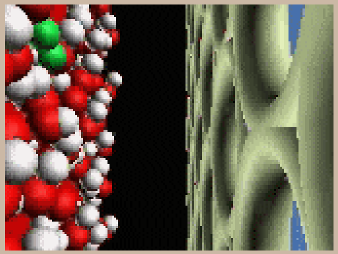
Pore Exclusion



Membrane Separations…

Pressure Driven:
RO, NF, UF, MF, MBR, Gas…

Thermal Driven:
Membrane Distillation…



Osmotic Driven:
Forward Osmosis…

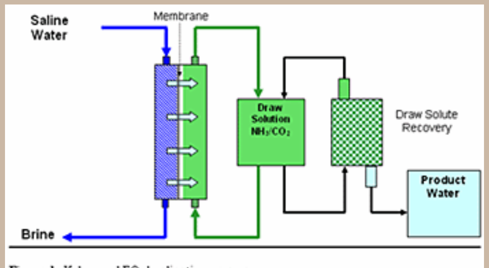
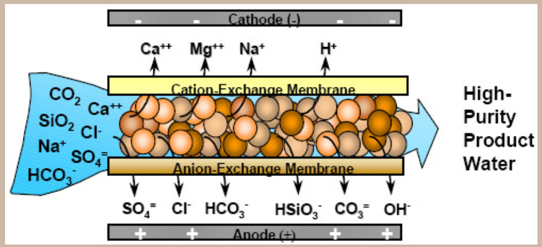
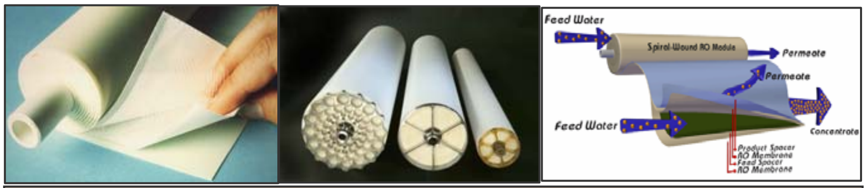


Figure 1: Yale novel FO desalination process

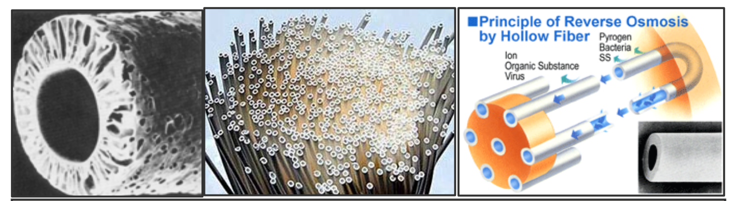
Charge Driven:
Electrodialysis…



Module Configurations…



Spiral-Wound Modules
(brackish, UPW, wastewater, seawater)



Hollow-Fiber Modules
(RO, gas separations)

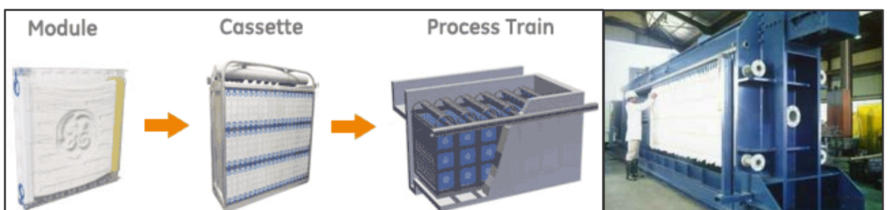


Plate & Frame Modules
(filter presses, laboratory, MBRs)

Membranes are scalable…

LARNACA SWRO WATER DESALINATION PLANT, CYPRUS (54,000 m^3/day)

Advanced Treatment Systems…

Source

UF/MBR System

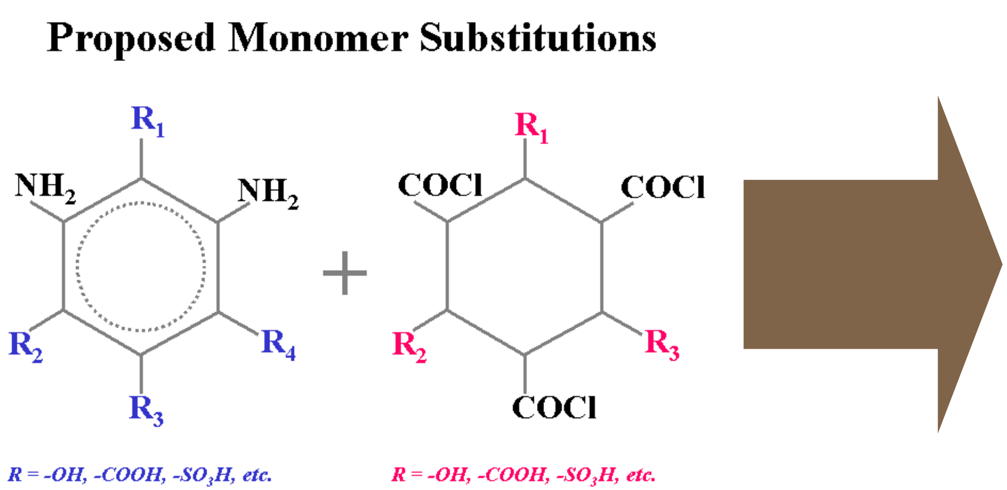
RO System

UV Disinfection

Product

Kennedy/Jenks Consultants
Engineers & Scientists
National Water Research Institute

Novel Membrane Development…



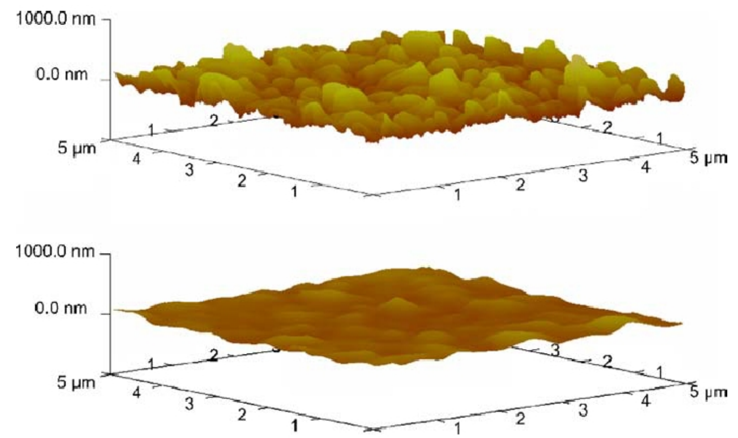


Fig. 3. AFM images of uncoated SWC4 (top) and SWC4 coated with 1 wt.% PEBAX 1657 (bottom).

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Welcome to the Database of Zeolite Structures

www.iza-structure.org/databases

Atlas of Zeolite Framework Types

Collection of Simulated XRD Powder Patterns for Zeolites

Catalog of Disordered Zeolite Structures

Schemes for Building Zeolite Framework Models

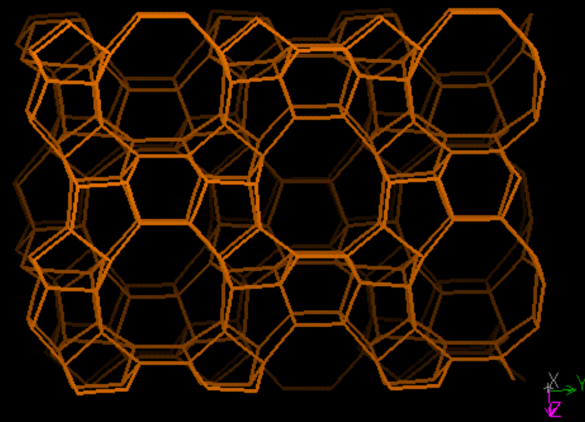
PDF files of IZA-SC Publications

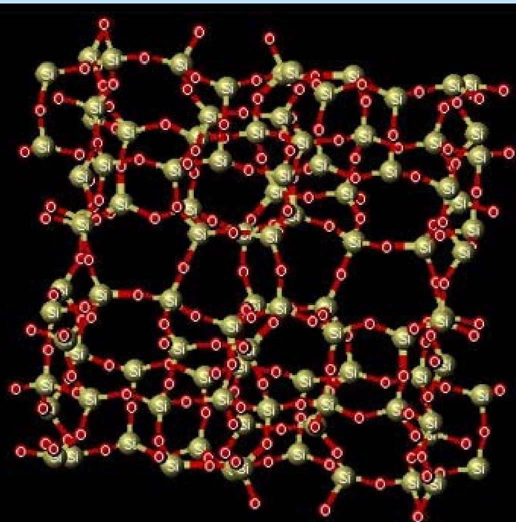
Zeolite Structure References

Hypothetical Zeolites

The database of the Structure Commission of the International Zeolite Association provides structural information on all zeolite structure types. This includes crystallographic data and drawings for all zeolite framework types, simulated powder patterns for representative materials and relevant references.

This is the entry page to the database. Please bookmark only this address (it will 'never' change).





IZA Structure Commission

Database of Zeolite Structures

www.iza-structure.org/databases

Databases
- Introduction
- Structures
  - Advanced Search
  - Explanations
- XRD Patterns
  - Input your Data
  - Explanations
- References
- Disordered Structures
- Model Building

IZA-SC
- Errata
- New Codes
- PDF files

IZA

Credits

Atlas of Zeolite Framework Types

Select a Framework Type Code (FTC)

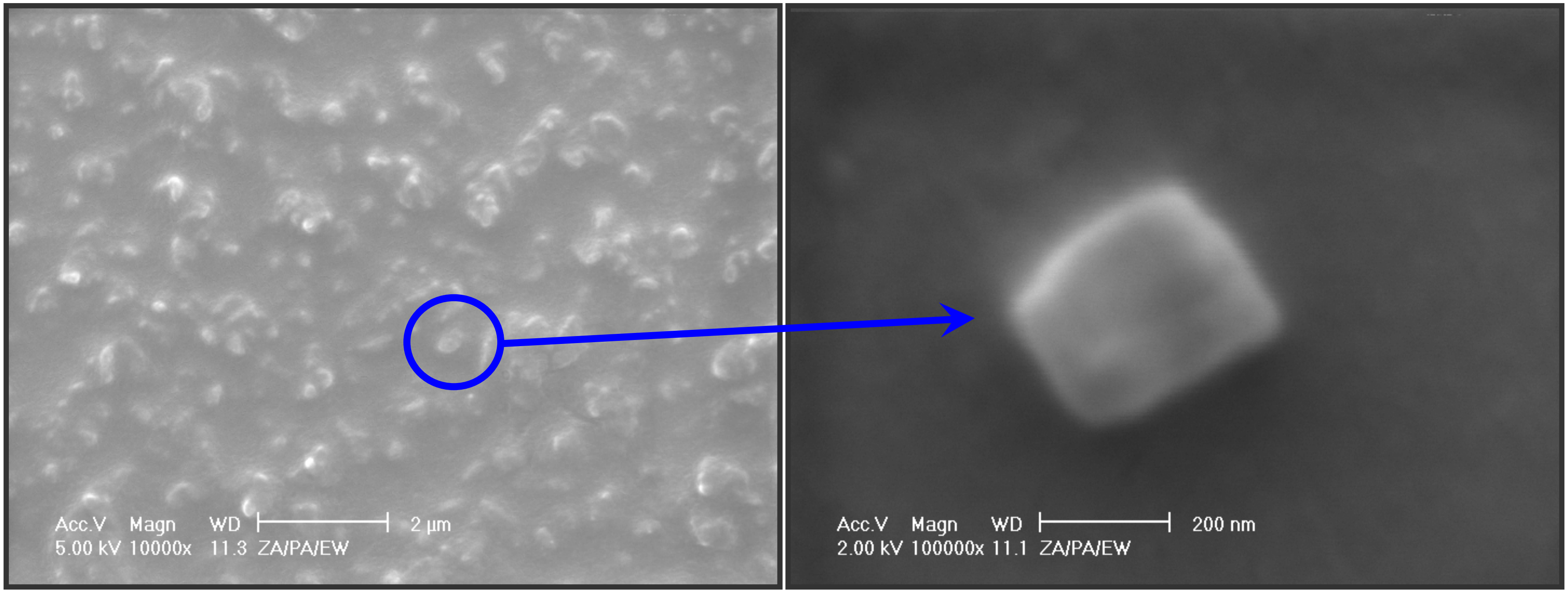
ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS
ATT	ATV	AWO	AWW	BCT	*BEA	BEC	BIK	BOG	BPH	BRE	CAN
CAS	CDO	CFI	CGF	CGS	CHA	-CHI	-CLO	CON	CZP	DAC	DDR
DFO	DFT	DOH	DON	EAB	EDI	EMT	EPI	ERI	ESV	ETR	EUO
FAU	FER	FRA	GIS	GIU	GME	GON	GOO	HEU	IFR	ISV	ITE
ITH	ITW	IWR	IWW	JBW	KFI	LAU	LEV	LIO	LOS	LOV	LTA
LTL	LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI	MFS	MON	MOR
MSO	MTF	MTN	MTT	MTW	MWW	NAB	NAT	NES	NON	NPO	OBW
OFF	OSI	OSO	-PAR	PAU	PHI	PON	RHO	-RON	RRO	RSN	RTE
RTH	RUT	RWR	RWY	SAO	SAS	SAT	SAV	SBE	SBS	SBT	SFE
SFF	SFG	SFH	SFN	SFO	SGT	SOD	SOS	SSY	STF	STI	STT
TER	THO	TON	TSC	UEI	UFI	UOZ	USI	UTL	VET	VFI	VNI
VSV	WEI	-WEN	YUG	ZON							

Or enter the name of a zeolite material

Material Name CONTAINS [ ] start search

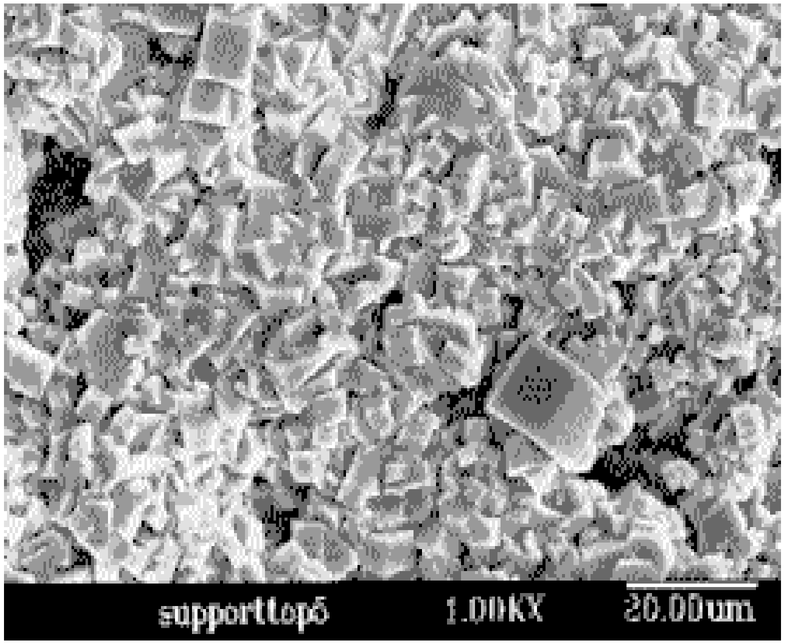
Hybrid Zeolite-Polyamide Nano-Composite

(Byeong-Heon Jeong & Eric Hoek, UCLA &, Yushan Yan, UCR)



http://www.cee.ucla.edu/faculty/ehoek.htm

Other Zeolite Membrane Groups…



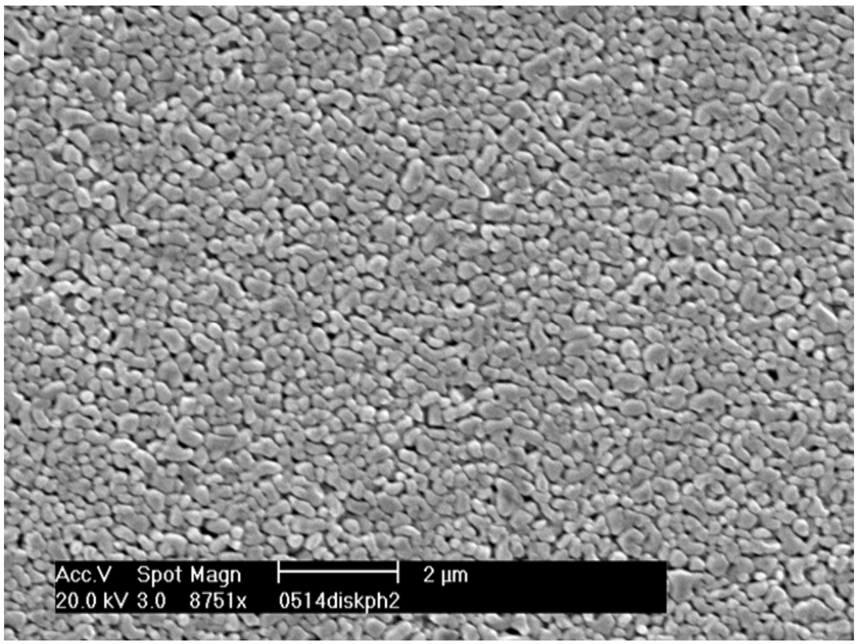
Supported Zeolite RO/NF Memb…
Richard Noble Group…University of Colorado, Boulder

Zeolite RO/Nano-Membranes
Junhang Dong Group, New Mexico Tech…
Socorro jhdong@.nmt.edu

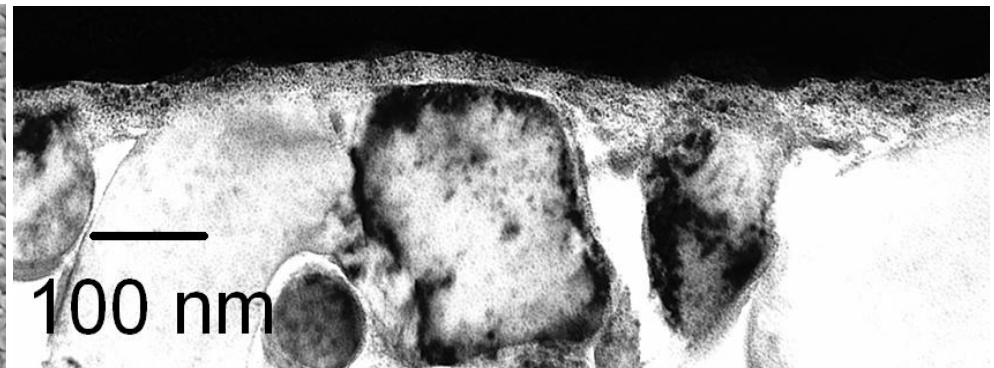
Ceramem Corporation…
http://www.ceramem.com/index.htm

γ-Alumina (Ceramic) Membranes…

Yu, Matthew Mottern, and Henk Verweij , OSU; John Bukowski, and Jennifer Lewis



Quasi-homogeneous α-Al_2O_3 supports



TEM γ-alumina membrane

(Made by dipping supports in nano-particle precursor dispersions, followed by calcination.)

www.mse.eng.ohio-state.edu/fac_staff/faculty/verweij/
http://colloids.mse.uiuc.edu

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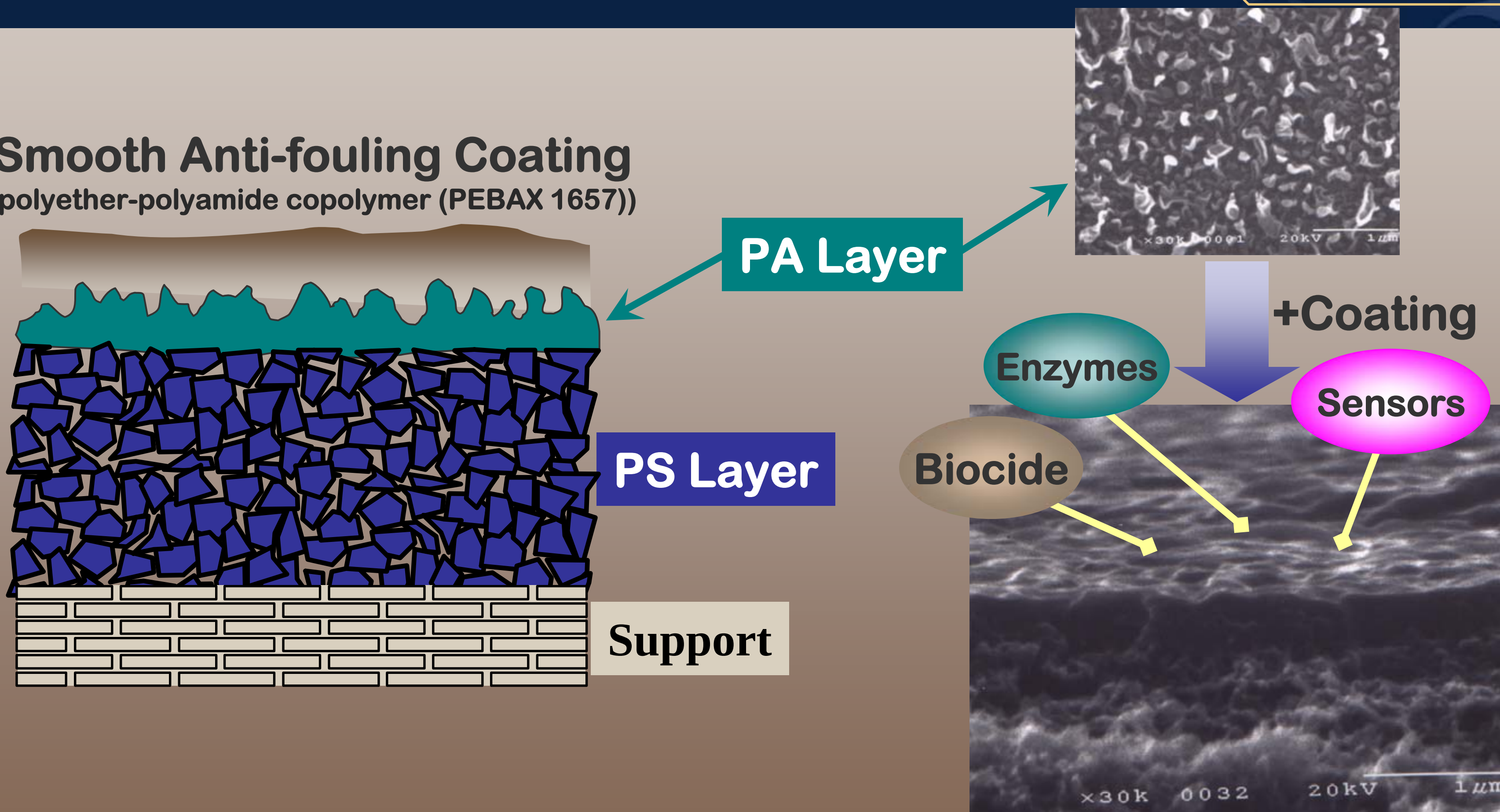
Engineers & Scientists
National Water Research Institute

Synthetic Coating Technologies...

Ingo Pinnau & R. Baker, MTR, Inc., Menlo Park

Louie *et al.* 2006. J. Memb. Sci., 280, 762-770



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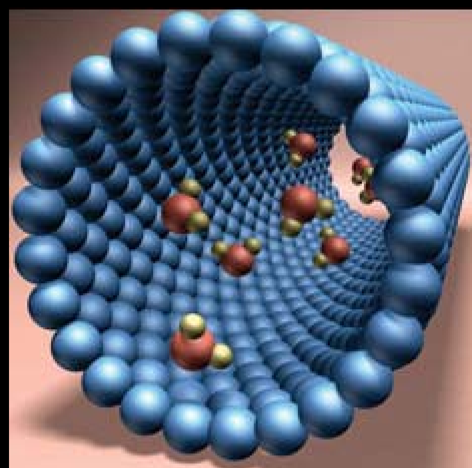
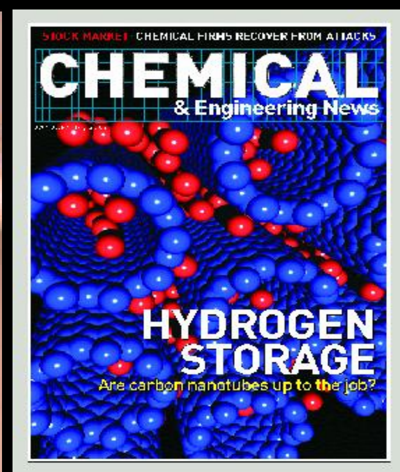
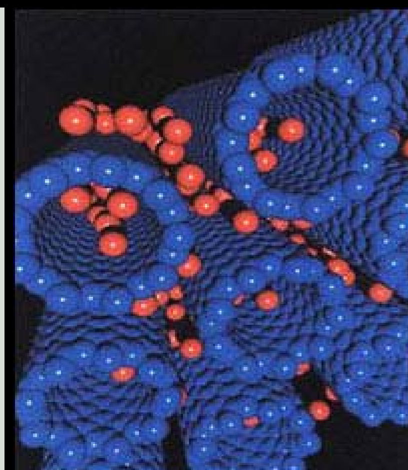
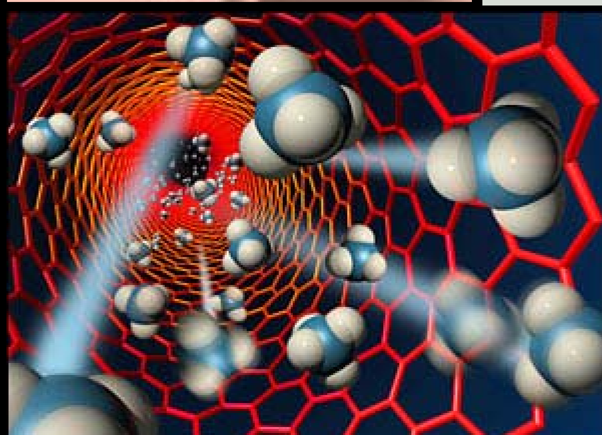
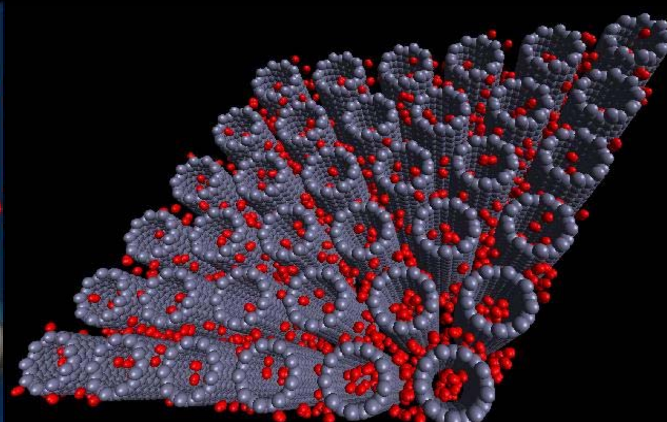
Carbon Nanotube Membranes: Many groups…

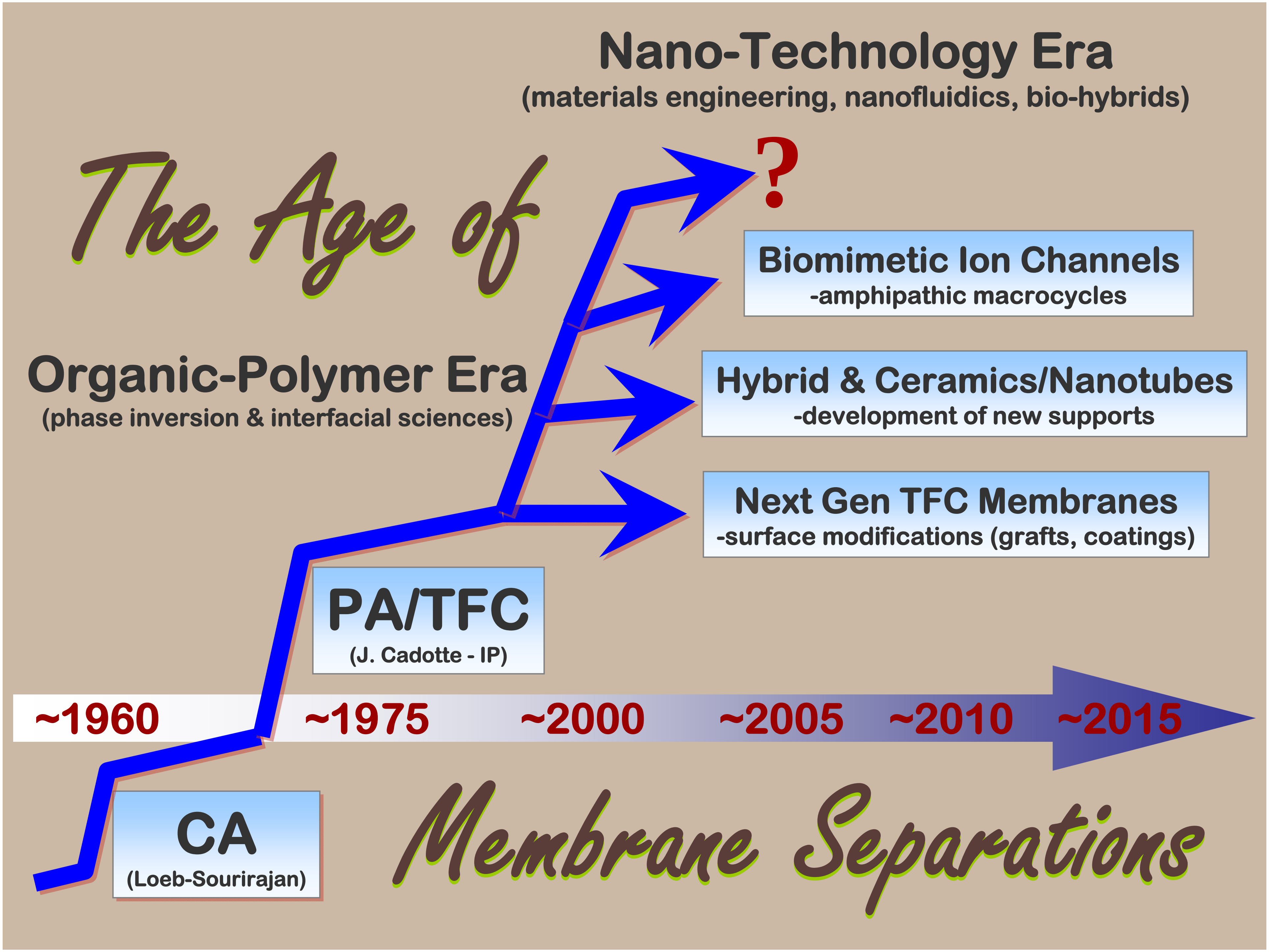








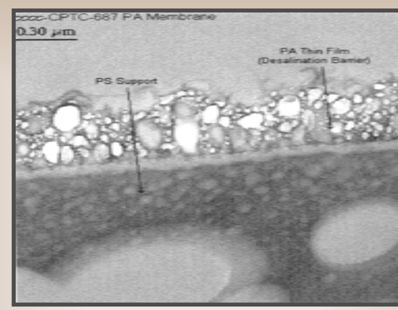




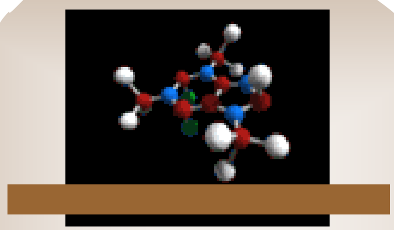
Nano-Technology Era
(materials engineering, nanofluidics, bio-hybrids)
The Age of
?
Biomimetic Ion Channels
-amphipathic macrocycles
Organic-Polymer Era
(phase inversion & interfacial sciences)
Hybrid & Ceramics/Nanotubes
-development of new supports
Next Gen TFC Membranes
-surface modifications (grafts, coatings)
PA/TFC
(J. Cadotte - IP)
~1960
~1975
~2000
~2005
~2010
~2015
CA
(Loeb-Sourirajan)
Membrane Separations

Technical & Scientific Challenges…

Membrane Fouling…



Membrane Integrity…



Trace Organics Rejection…

Module Design…

Kennedy/Jenks Consultants
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Membrane Fouling…

Categories…

- Biofouling
- NOM fouling
- Mineral scaling
- Particulate fouling

Mechanisms…

- Kinetics
- Adsorption
- Precipitation

Control…

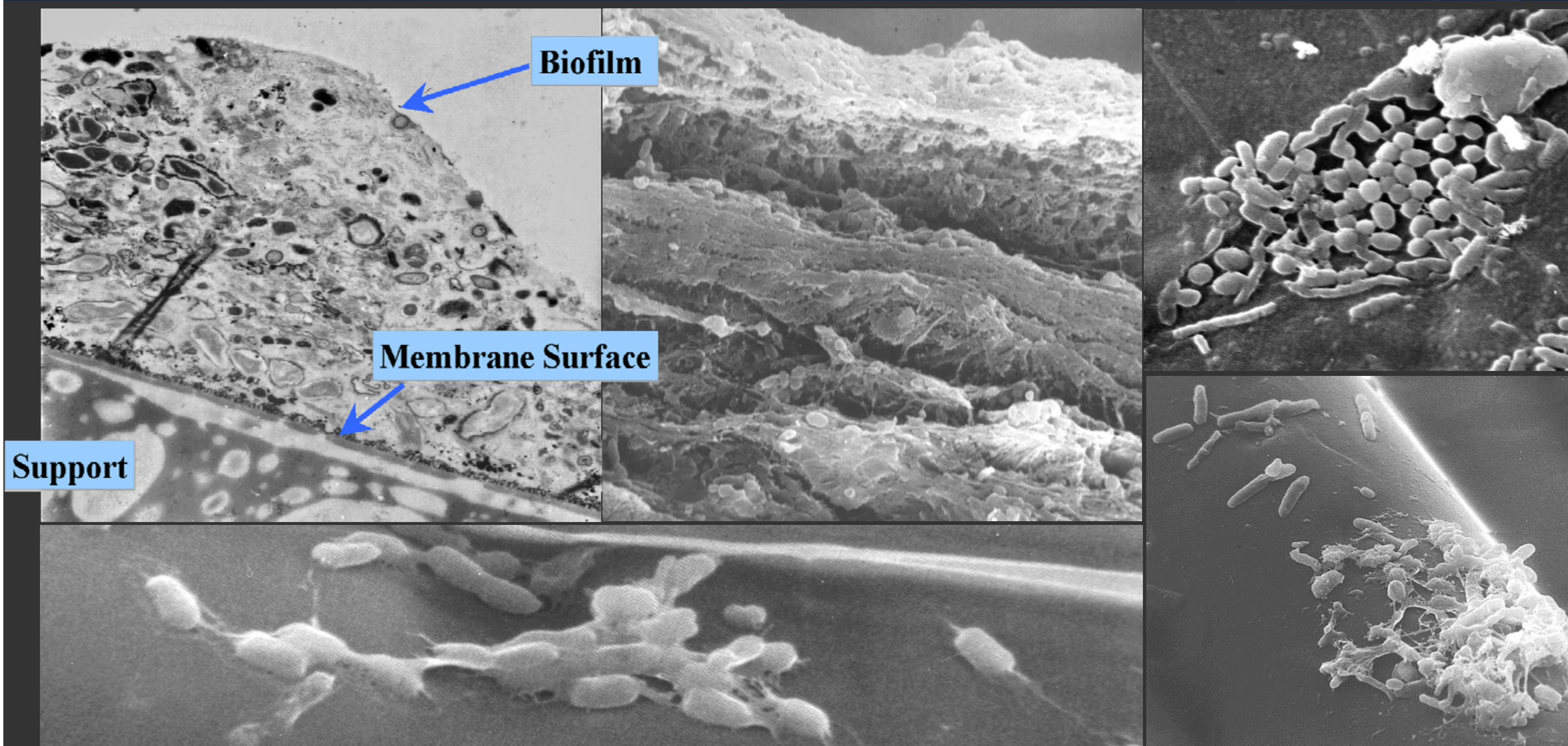
Pretreatment
(filtration, biocides, dispersants)

Membrane/module
(surface mod., spacer/channel design)

Foulant layer
(EPS, porosity, integrity)

Operation
(cleaning, recovery)

Biofilm Morphology…



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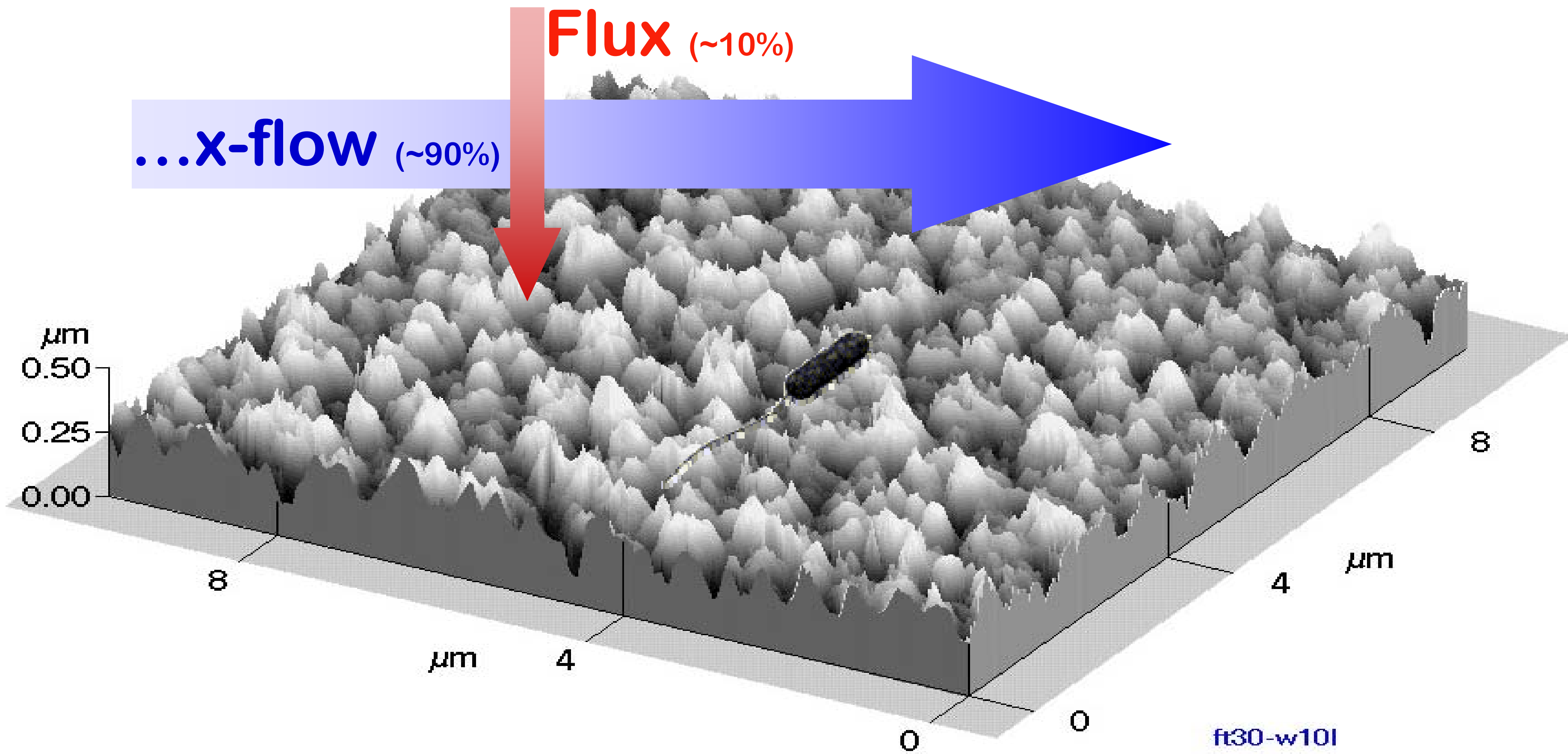
Fouling Mechanisms…



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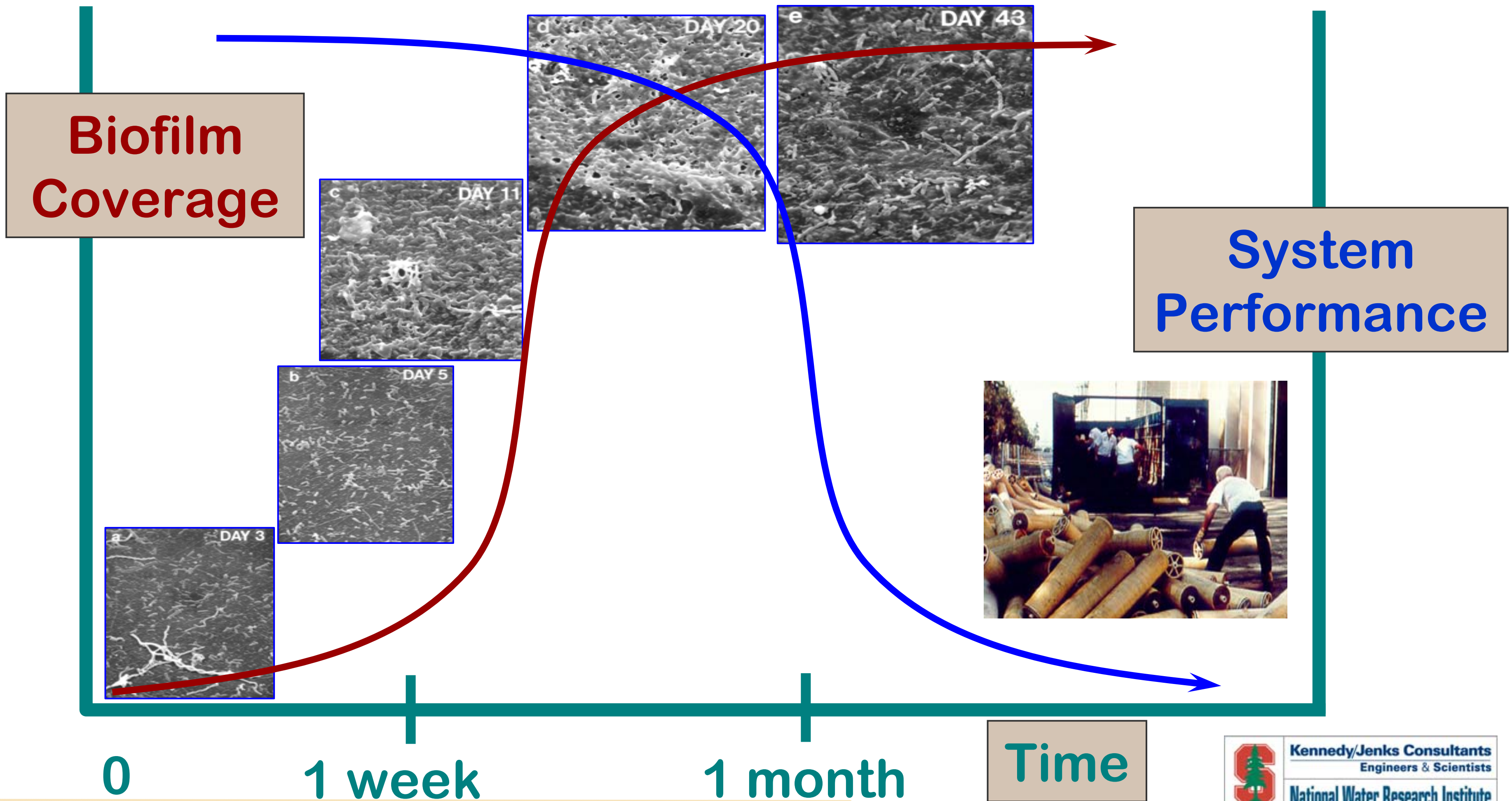

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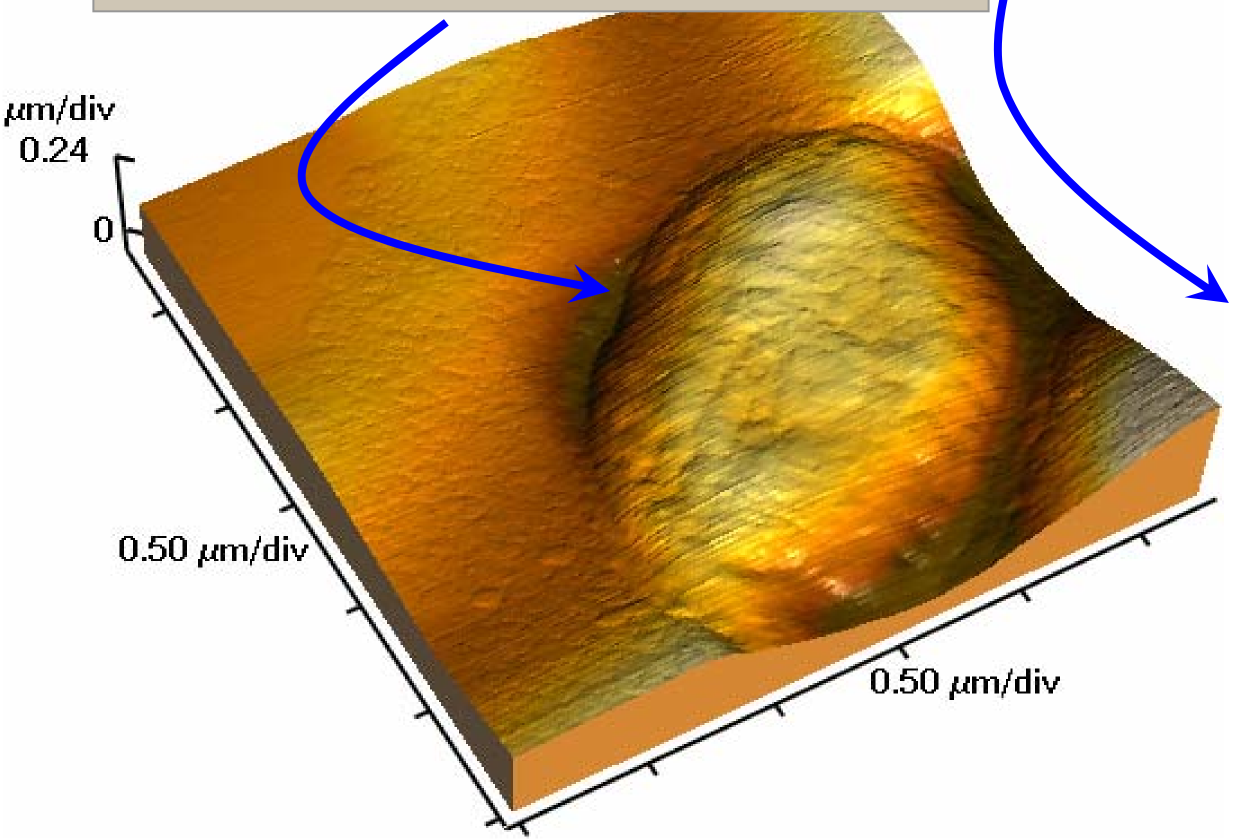
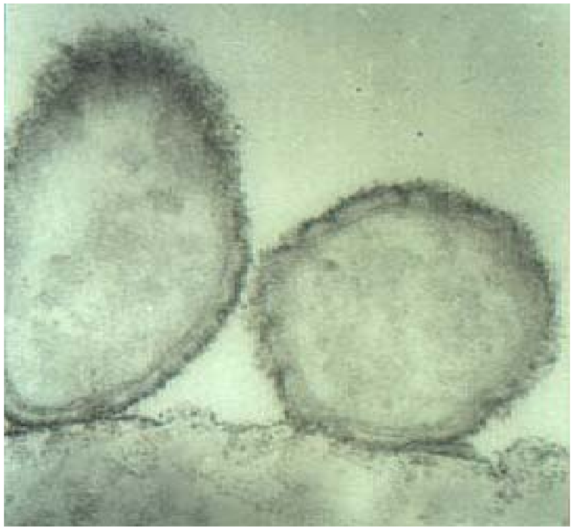
Fouling Mechanisms...

Adsorption interactions

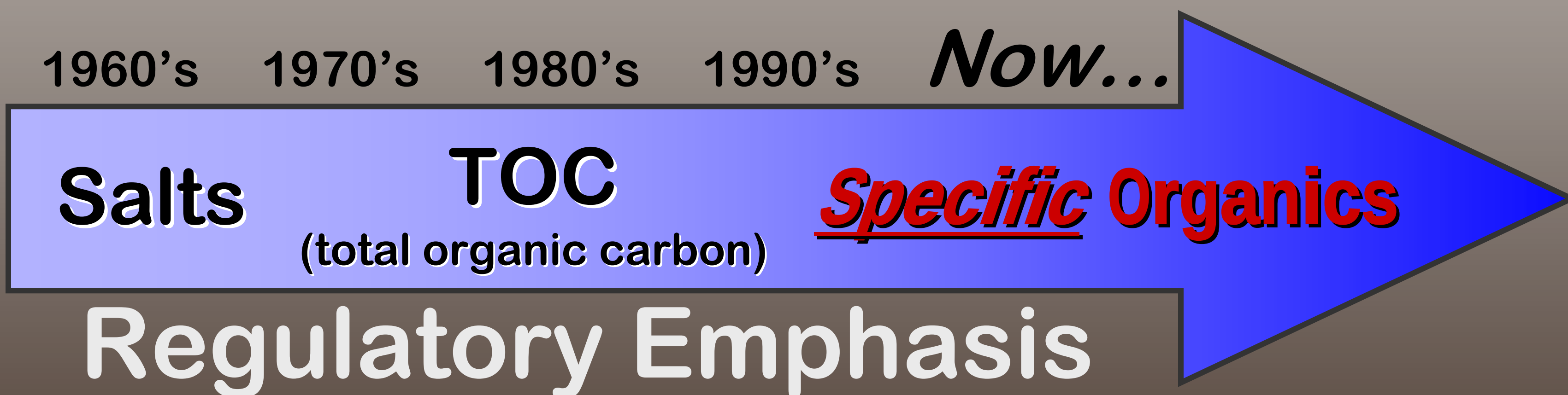




ACS

Organics Rejection…

- RO membranes originally designed to reject salts, ***not organics!***



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Molecular mass is not the whole story!

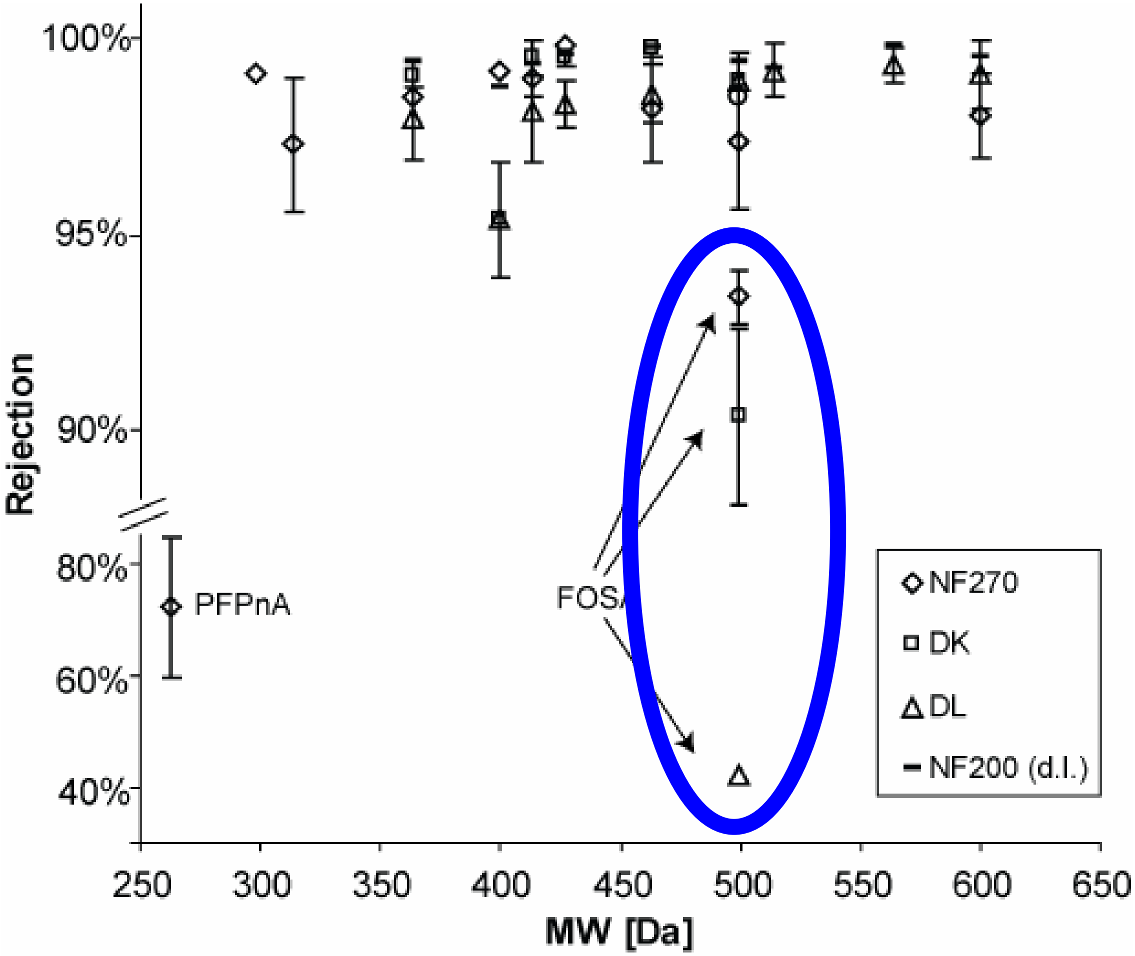
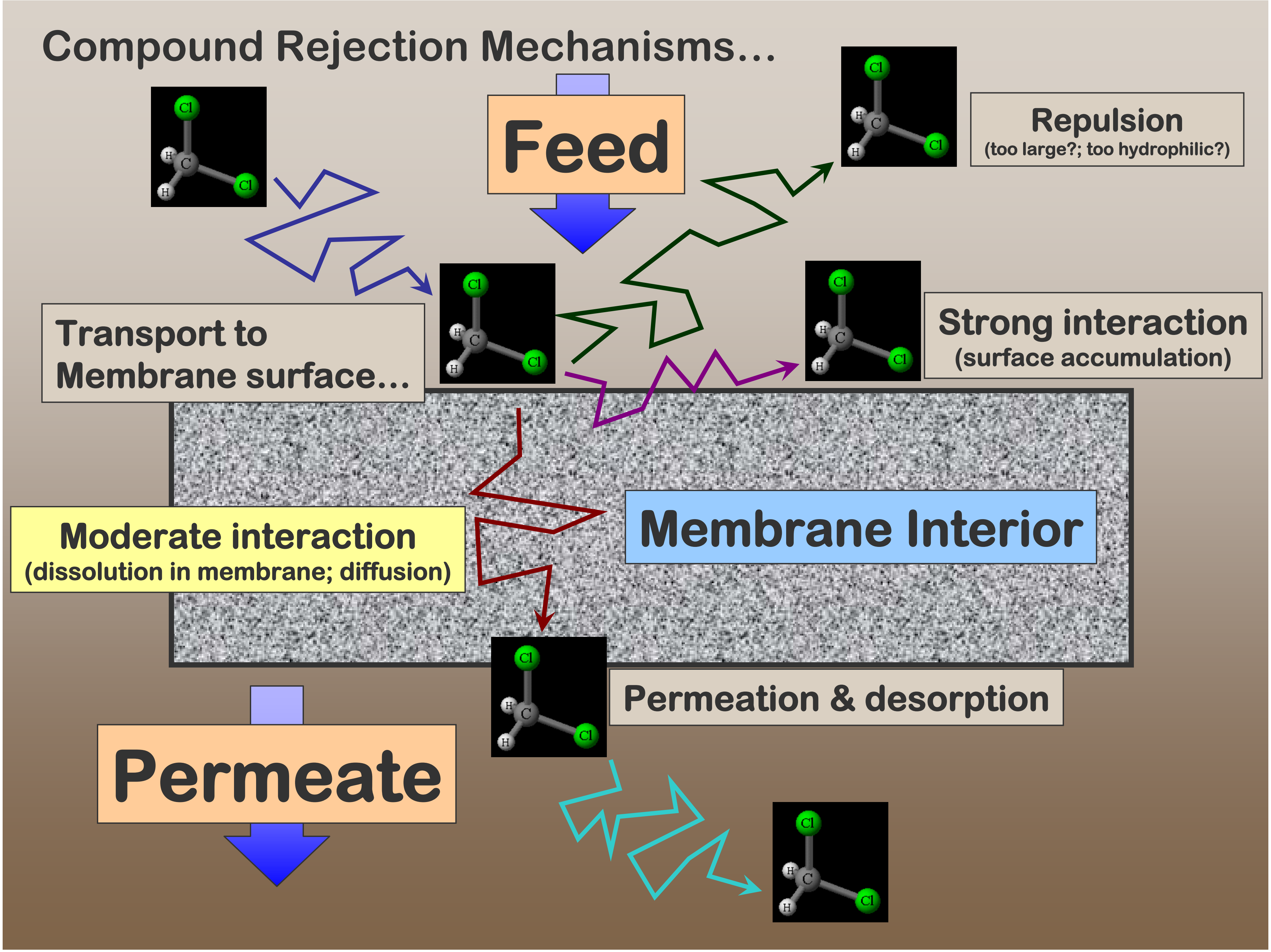
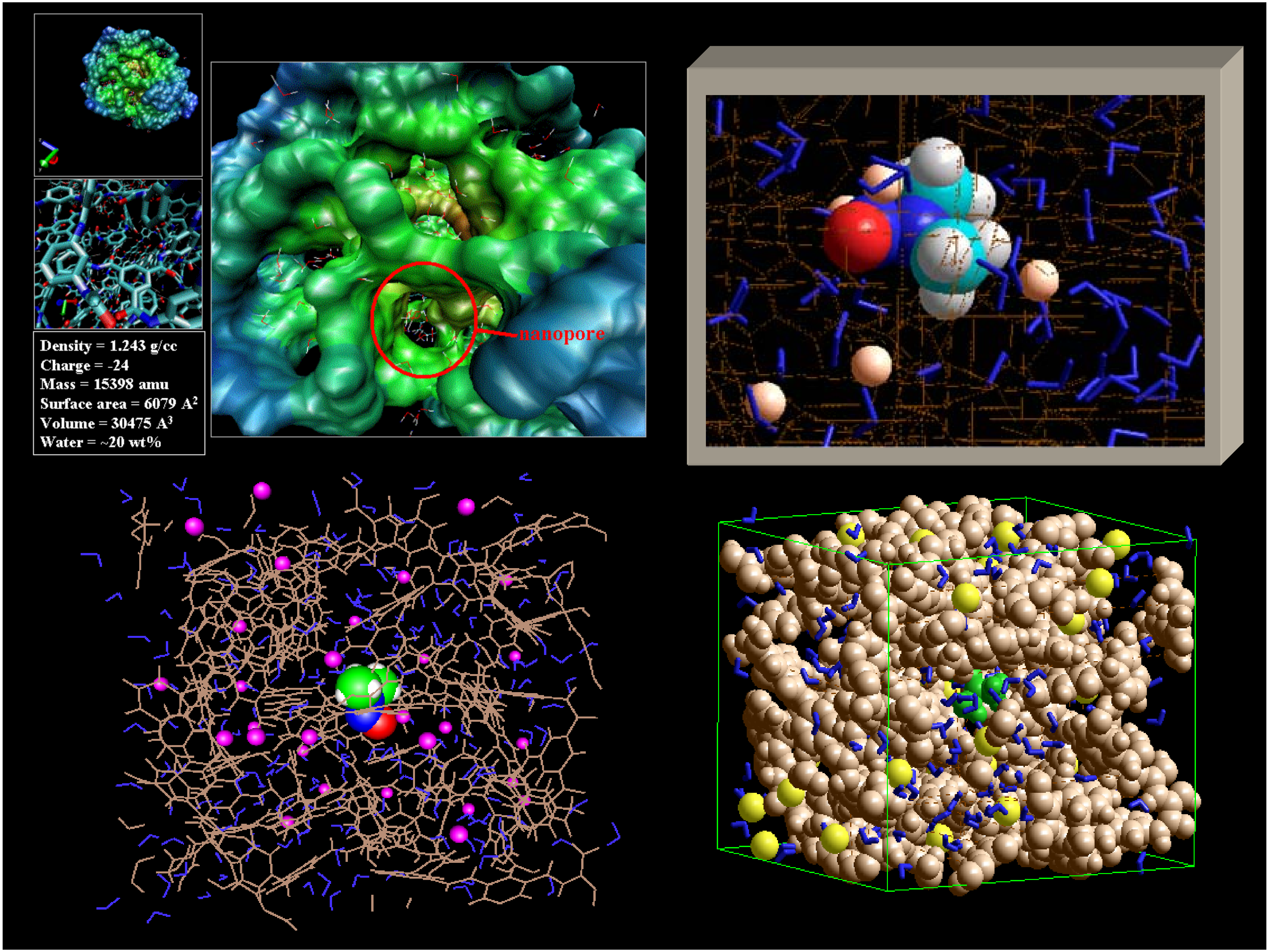
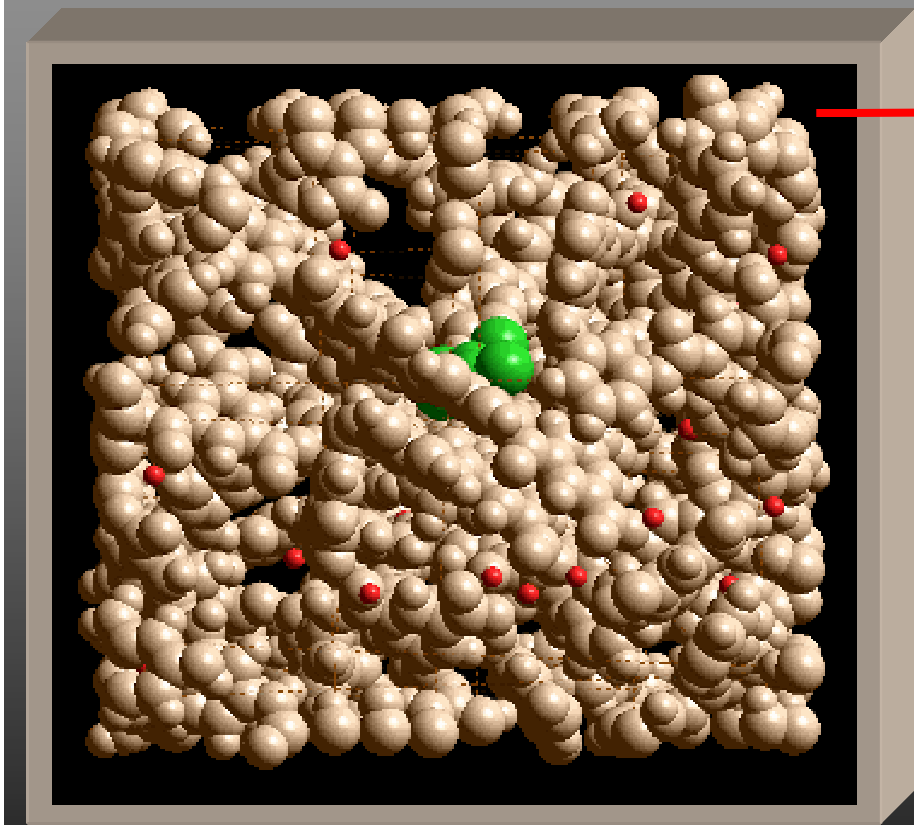


Figure 1 from conditionally accepted PFC paper: Steinle-Darling & Reinhard, Stanford U.


Compound Rejection Mechanisms…
Feed
Repulsion
(too large?; too hydrophilic?)
Transport to
Membrane surface…
Strong interaction
(surface accumulation)
Moderate interaction
(dissolution in membrane; diffusion)
Membrane Interior
Permeation & desorption
Permeate


Density = 1.243 g/cc
Charge = -24
Mass = 15398 amu
Surface area = 6079 A²
Volume = 30475 A³
Water = ~20 wt%
nanopore

Modeling Information…



Trajectories
(coordinates, energies & velocities)

Interactions

System Properties
(statistical mechanical properties)

End…

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PEBAX Coating…

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Effects of polyether–polyamide block copolymer coating on performance and fouling of reverse osmosis membranes

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Abstract

The effects of a water-permeable polymer coating on the performance and fouling of high-flux (ESPA1 and ESPA3) and low-flux (SWC4) polyamide reverse osmosis (RO) membranes were investigated. It was anticipated that the coating would create a smoother hydrophilic surface that would be less susceptible to fouling when challenged with a motor-oil/surfactant/water feed emulsion (used as a model foulant). AFM and FT-IR analyses confirm that a 1 wt.% polyether–polyamide (PEBAX® 1657) solution applied to ESPA and SWC4 membranes produces a continuous polymer coating layer and, thereby, provides smoother membrane surfaces. However, pure-water permeation data combined with a series-resistance model analysis reveal that the coating does not only cover the surface of the polyamide membrane, but also penetrates into its porous ridge-and-valley structure. During a long-term (106-day) fouling test with an oil/surfactant/water emulsion, the rate of flux decline was slower for coated than for uncoated membranes. This improvement in fouling resistance compensated for the decrease in permeate flux for SWC4 over a period of approximately 40 days. However, the coating material is believed to penetrate more deeply into the polyamide surface layer of the high flux, high surface area ESPA membranes relative to the low-flux SWC4, resulting in significant water flux reduction.

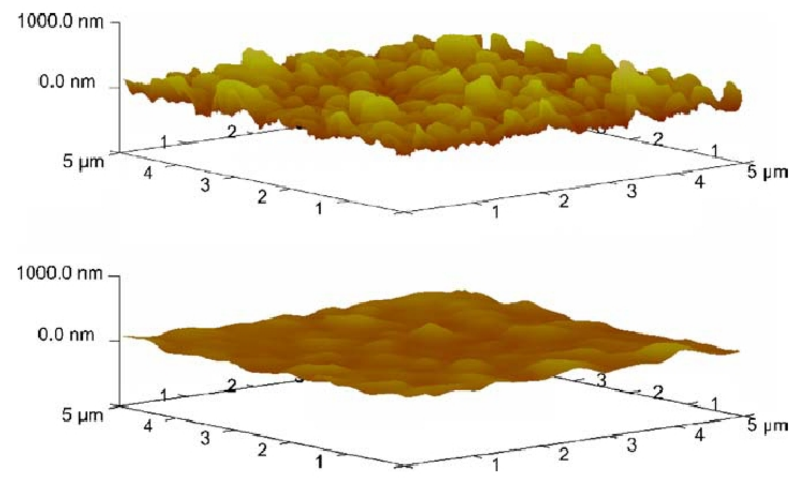
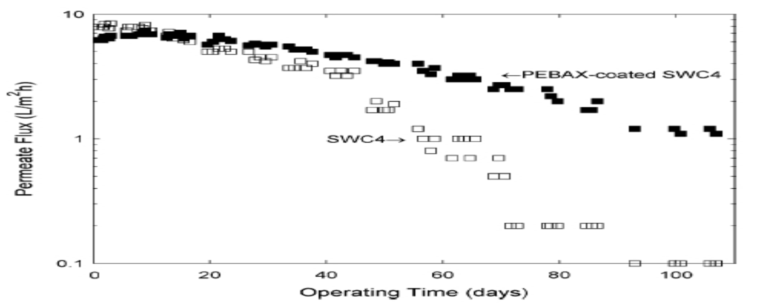


Fig. 3. AFM images of uncoated SWC4 (top) and SWC4 coated with 1 wt.% PEBAX 1657 (bottom).



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