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Texas Desal 2014

Reverse Osmosis – Membrane Basics

How and Why Membranes Work

Dan Muff - Toray

Spiral Module History 1960's - 2012

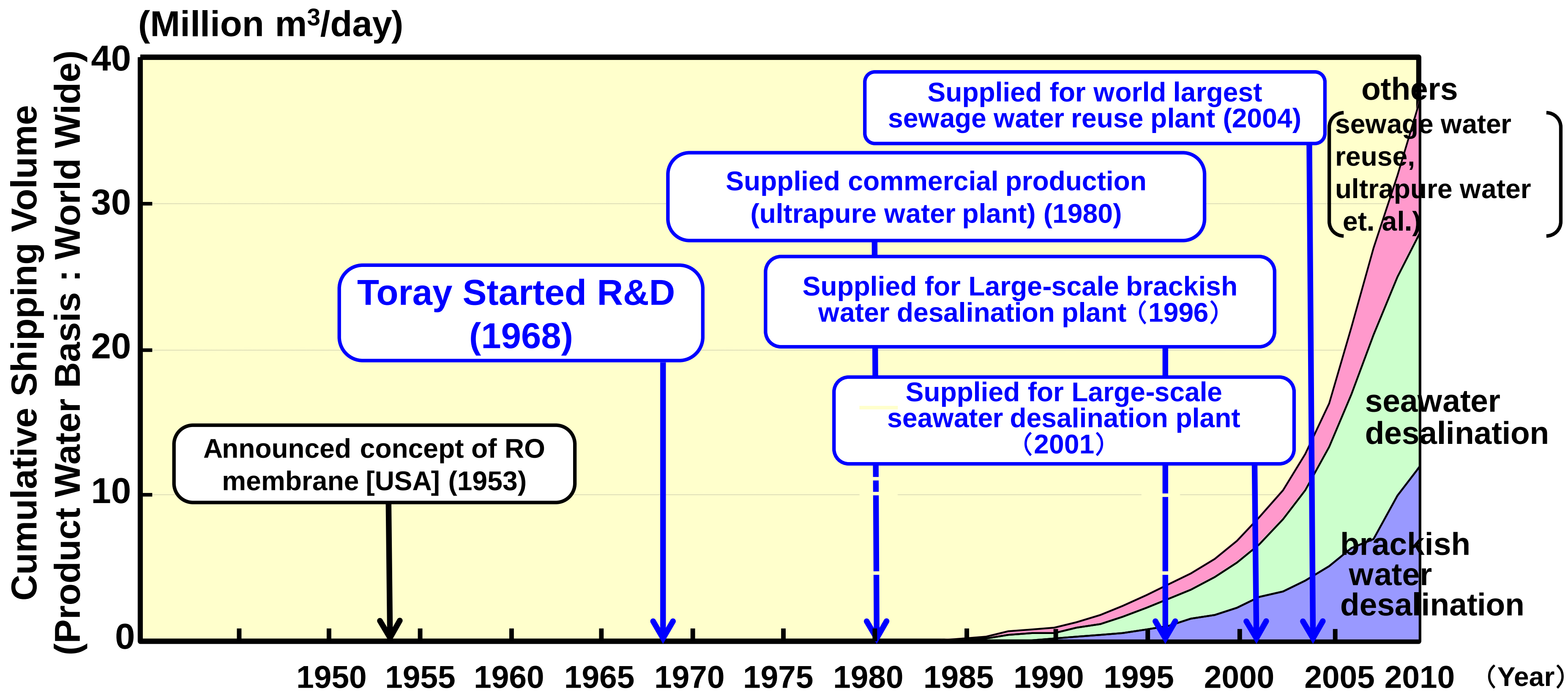
- 1964 - Spiral Wound Module Patented
- 1969 - Global RO Module Sales $1 million
- 1978 - First Large SWRO
- 1979 - TFC Polyamide Membrane Patented
- 1980 - DuPont Market Leader with HFF
- 1983 - Dow Purchased Filmtec
- 2000 - 98% of all RO Modules Spiral Wound
- 2001- Toray/Ionics Joint venture in the USA
- 2010 - Global RO Module Sales $600 + million

Spiral Wound Element Design

First spiral wound element developed in 1964 at General Atomic Co.

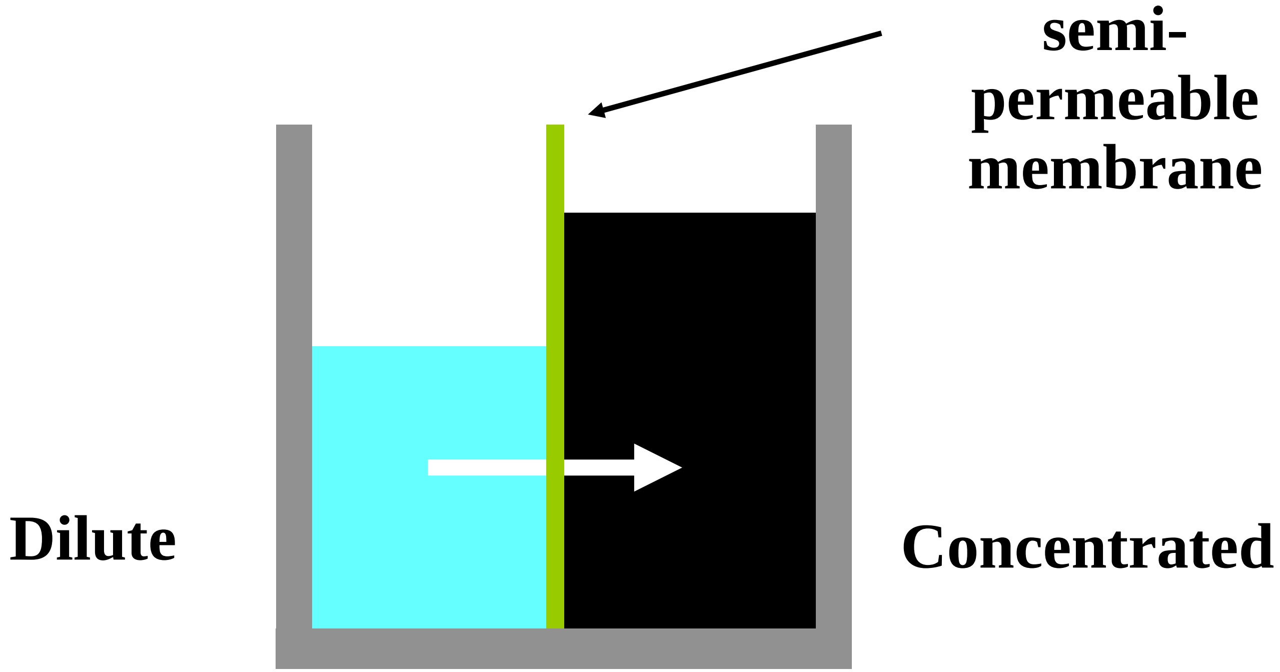
(San Diego, CA)

Toray History in Reverse Osmosis



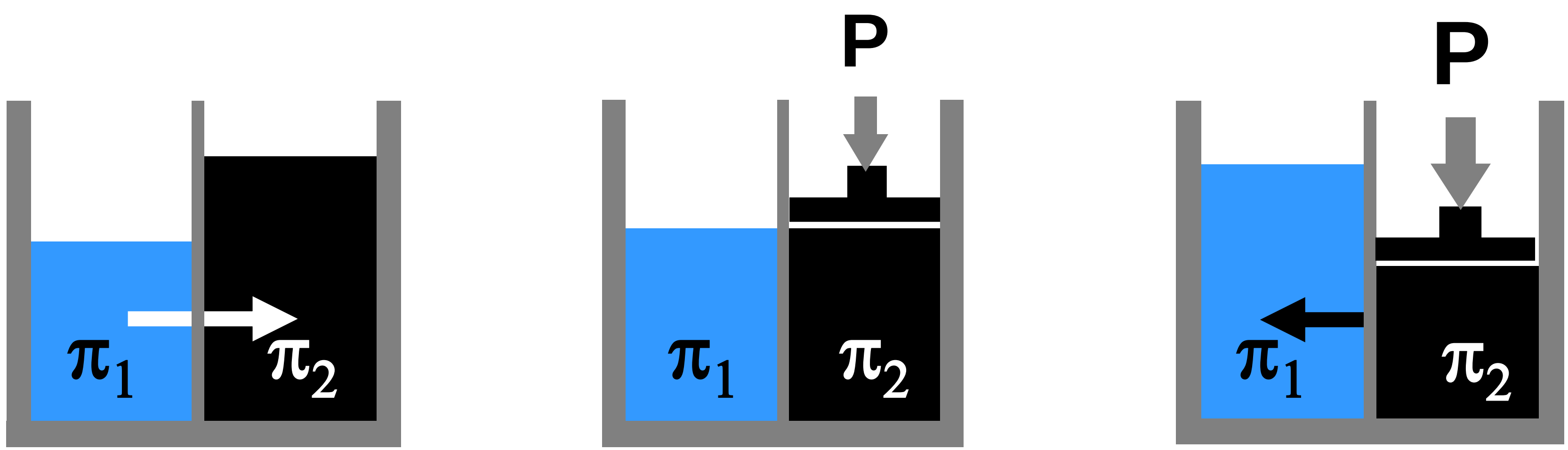
RO is an advanced technology to solve a global water shortage and water pollution.

Osmosis



The spontaneous flow of water from a dilute solution to a concentrated solution, when the two solutions are separated by a semi-permeable membrane.

Reverse Osmosis (RO) & Nanofiltration (NF)



osmosis

$\pi_1 < \pi_2$

equilibrium

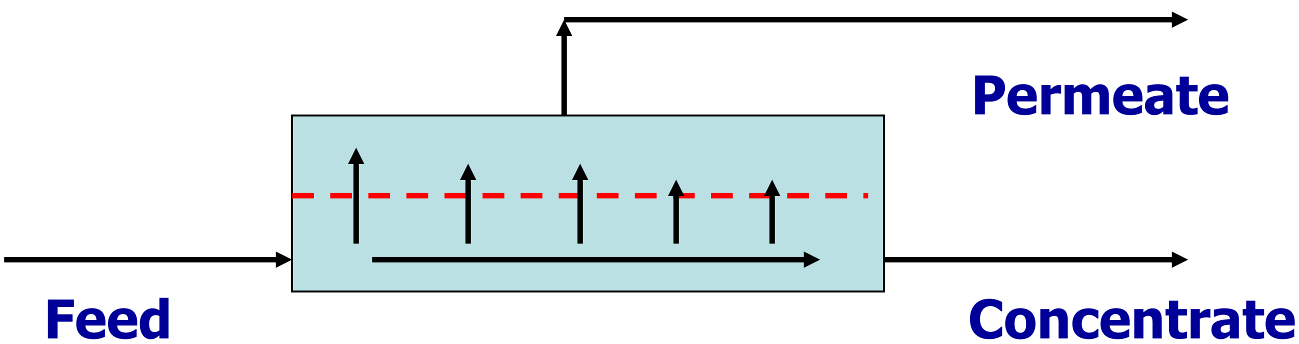
$P = \Delta\pi$

Reverse Osmosis

$P > \Delta\pi$

What is a Reverse Osmosis Membrane Element?

- A device with no moving parts for removing dissolved salts from a liquid stream



- What a Reverse Osmosis Membrane is NOT good at:
  - Removing particulates/undissolved matter of any type:
    - Clays/silts/scale/biological material
- **AN RO ELEMENT IS A VERY POOR SOLIDS SEPARATOR!!**

Various Type of Membrane and Membrane Products of Toray

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Size	0.001 µm		0.01 µm	0.1 µm	1 µm	10 µm
Separation materials	Ion, Low molecule weight organics		High molecular weight polymer	Colloid	Clay	
	Trihalomethane; Monovalent Ions	Agricultural & Organic Material; Multivalent Ions		Bacteria	Coliform	Cryptosporidium
Types	RO/NF Membrane		Low Pressure Membrane			
	Reverse Osmosis [RO]	Nanofiltration [NF]	Ultrafiltration [UF]		Microfiltration [MF]	
Membrane products	Ultrapure Water, Seawater Desalination, Advanced Water Treatment	Softening, Removal of Toxic substance	Municipal Drinking Water, Reuse of Wastewater, Pretreatment for RO Process		Sewage Water Treatment	

RO membrane

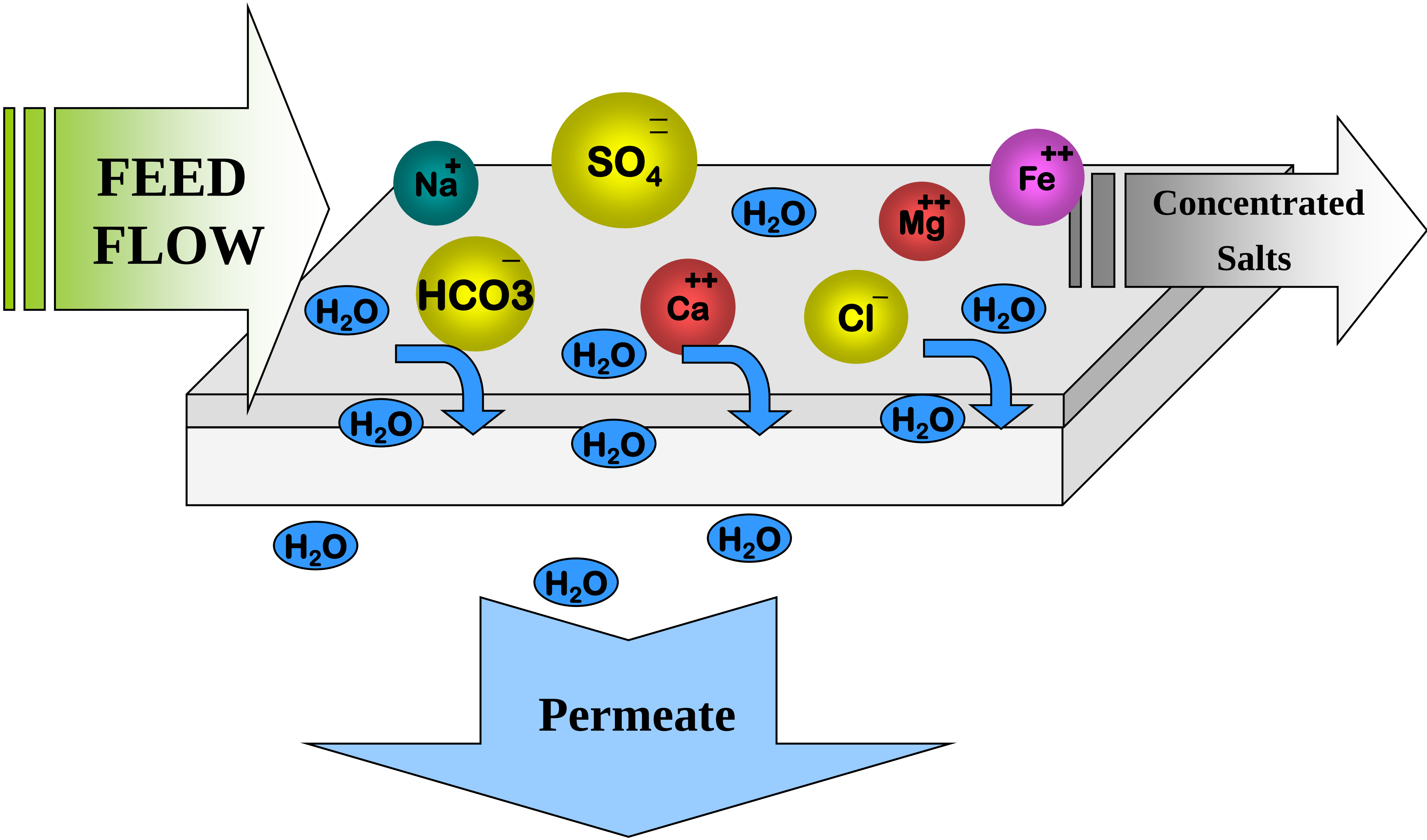
NF membrane

UF membrane (PVDF Hollow Fiber)

MF membrane (PVDF Hollow Fiber)

PVDF Immersed membrane for MBR

RO/ NF Membrane Separation Mechanism



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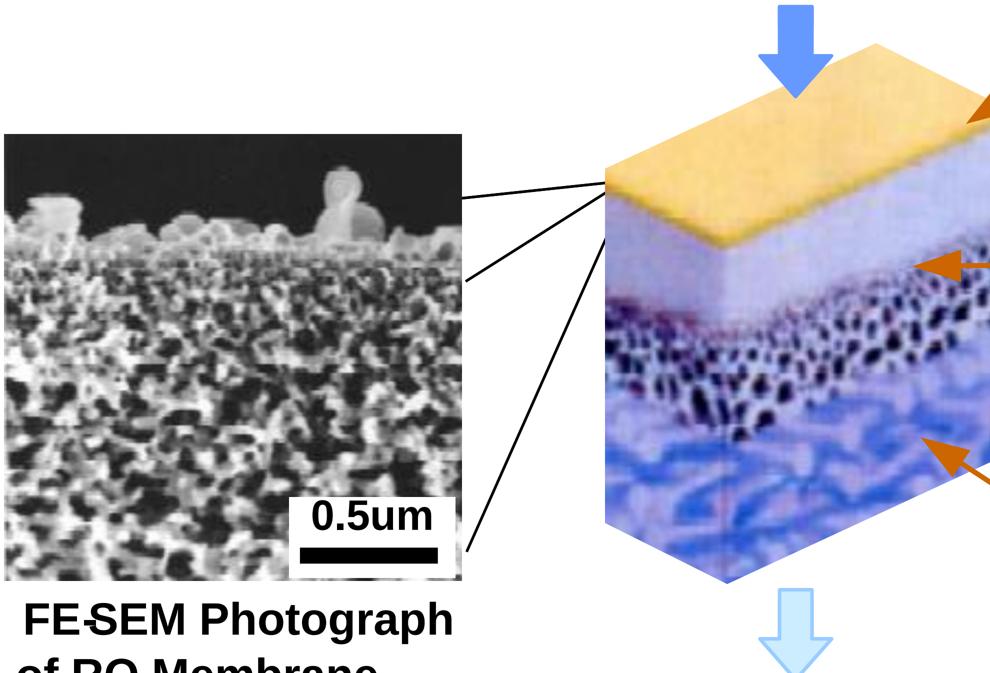
Reverse Osmosis Membrane

Feed water



Ultra-thin Salt Rejection Layer
Crosslinked Fully Aromatic Polyamide
0.3um

Supporting Layer
Polysulfone
45um

Base Fabric
Non-woven Fabric
Polyester
100um

FE-SEM Photograph
of RO Membrane
(UHR-FE-SEM)

Product Water

Toray's Patent **Patented: JP1979283, USP4761234, EPC211633 B2**

The RO Membrane

- The membrane layer which makes the separation is extremely thin (approximately 300 Angstrom)
- It is supported on a porous polysulphone backing layer which gives the membrane layer some strength (approximately 45 micron thick)
- The polysulphone is itself supported on a non-woven polyester backing fabric (approximately 100 micron thick)

Basic RO element construction – Single Leaf

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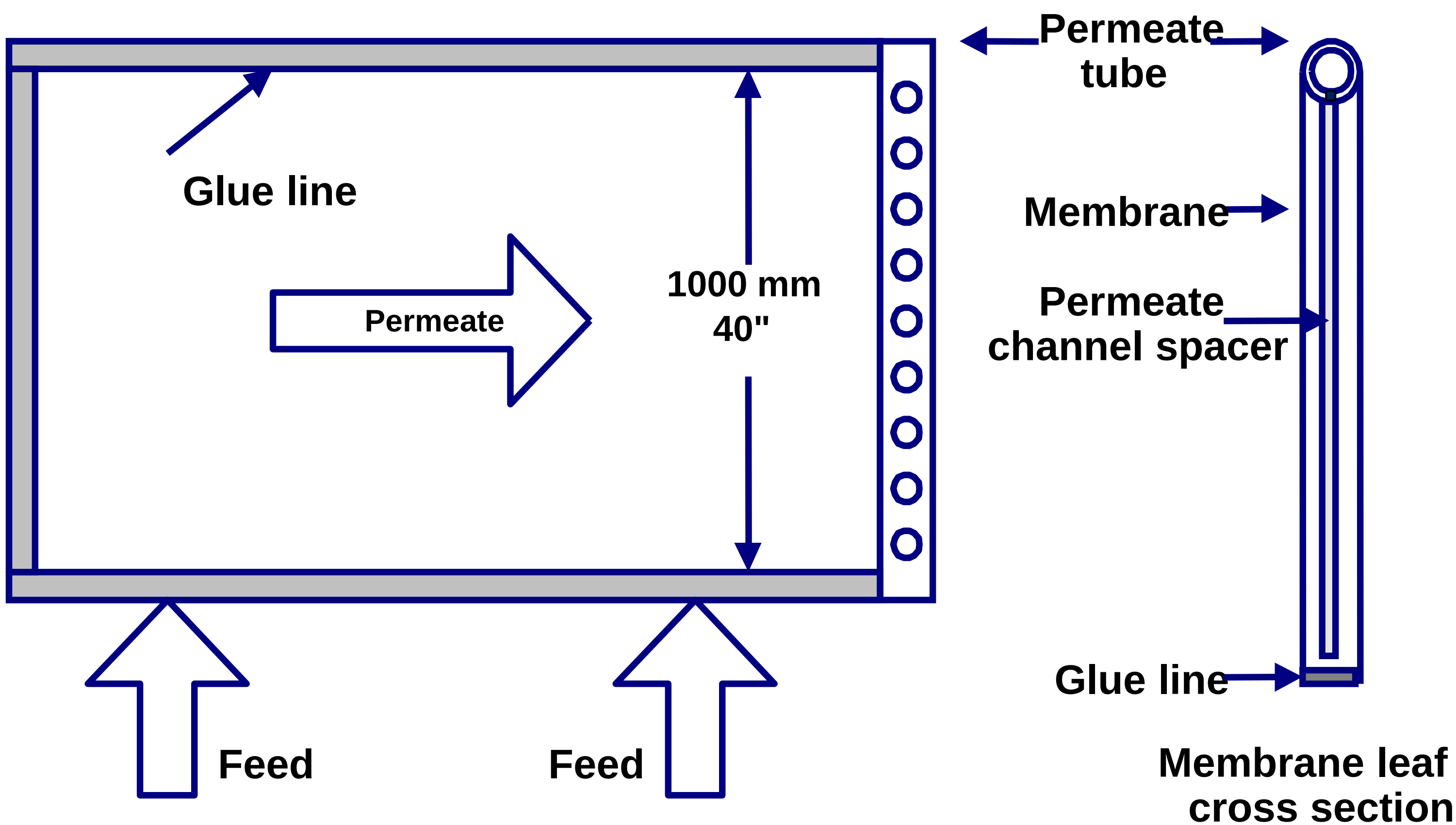
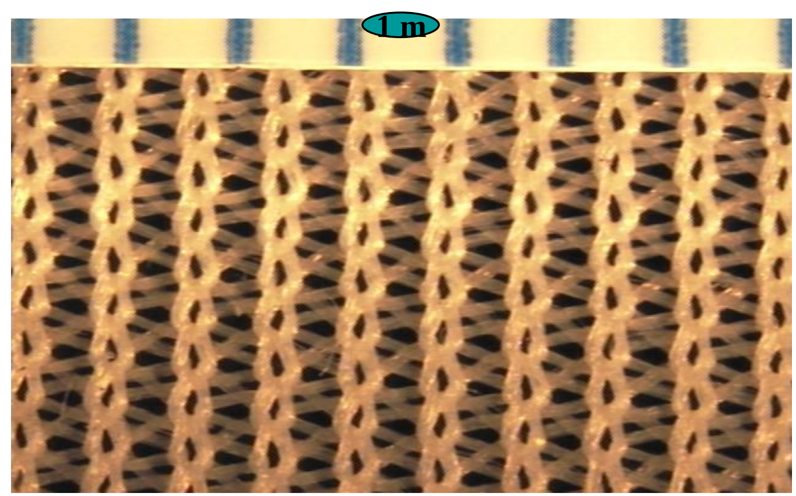


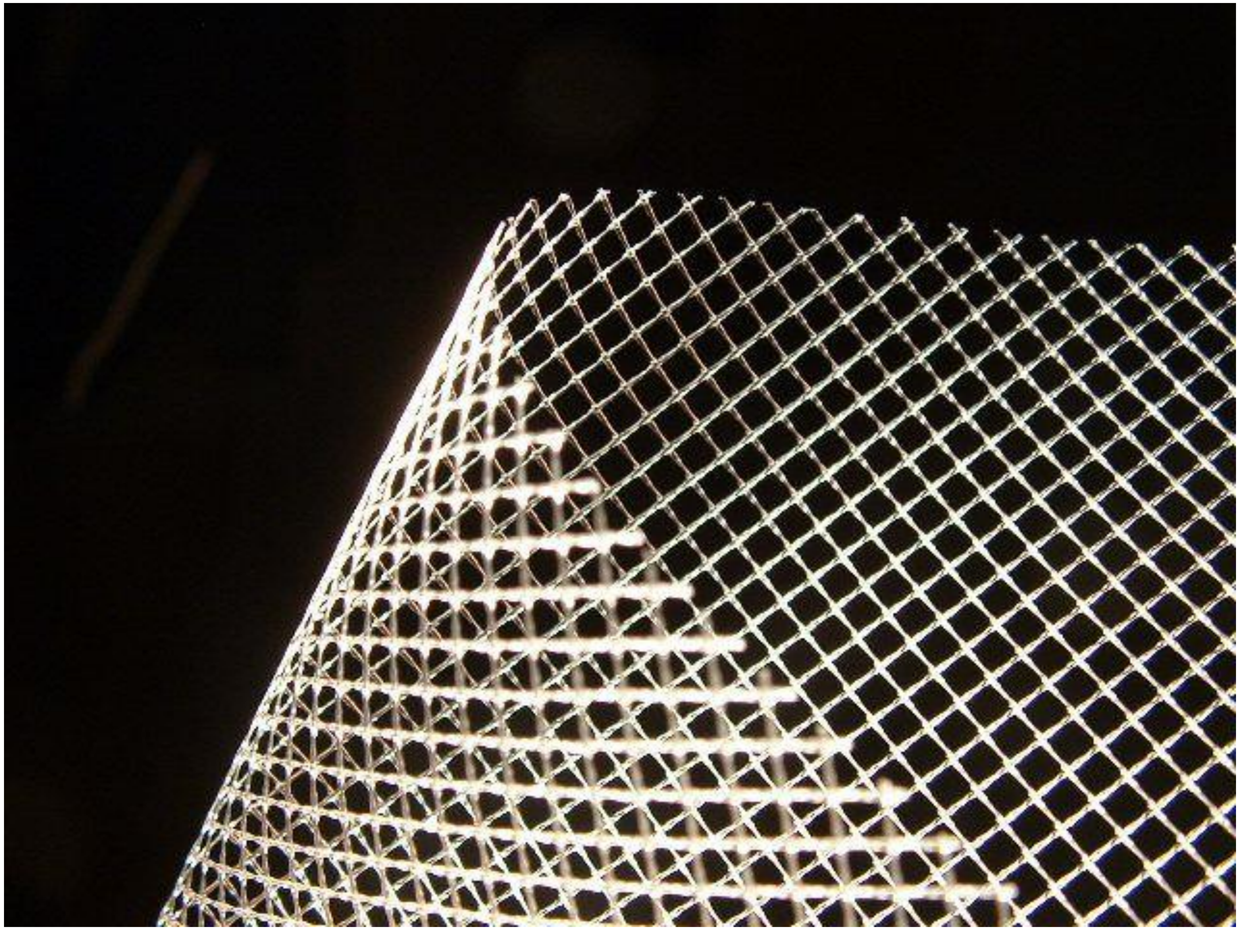
Conventional spiral wound module configuration

Permeate Water Carrier

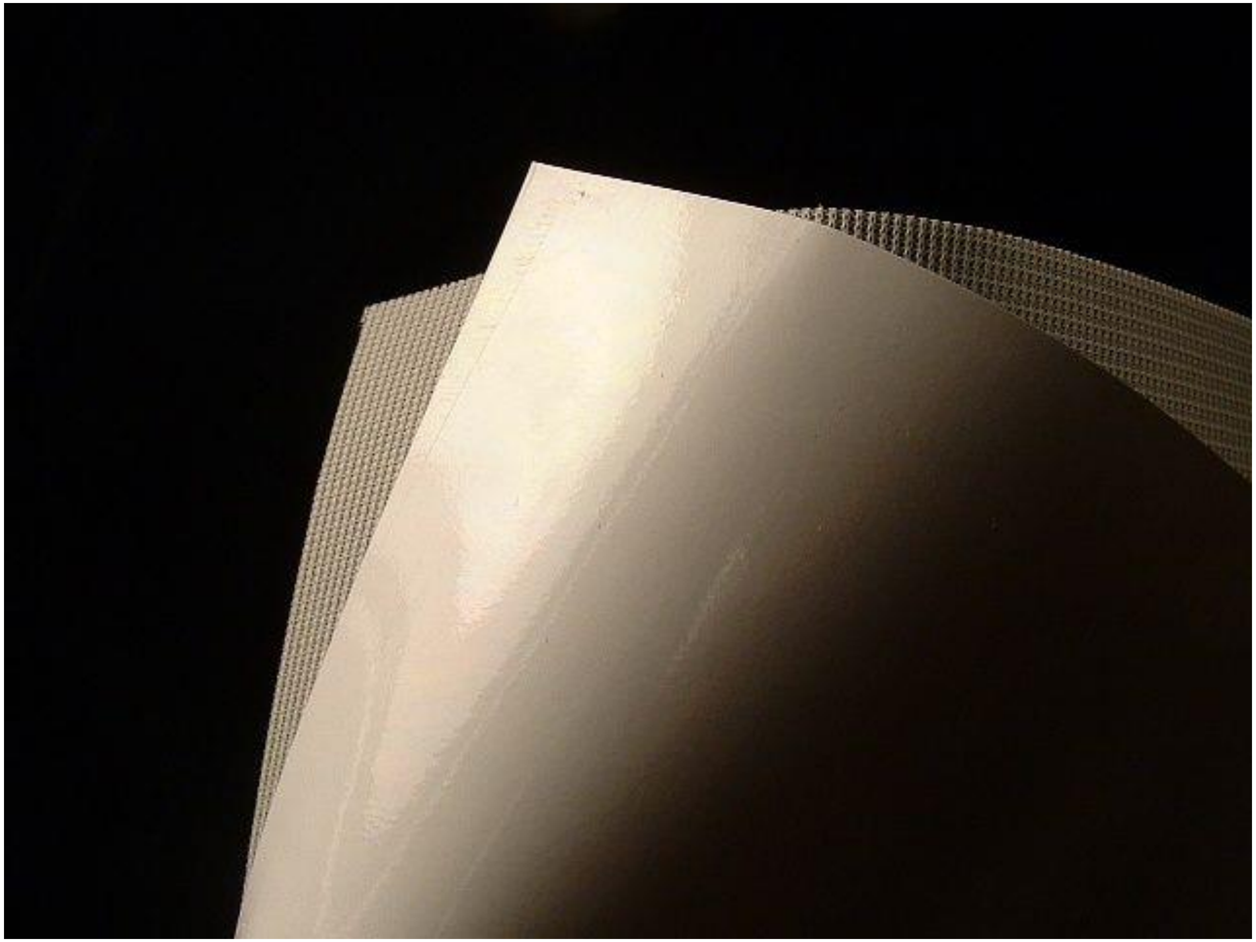
- Provides channel to carry permeate away from the membrane and to the holes in the permeate tube
- Must be capable of withstanding the compressive forces resulting from the operating pressures of the system
- Tricot knit polyester fabric impregnated with epoxy resin and cured



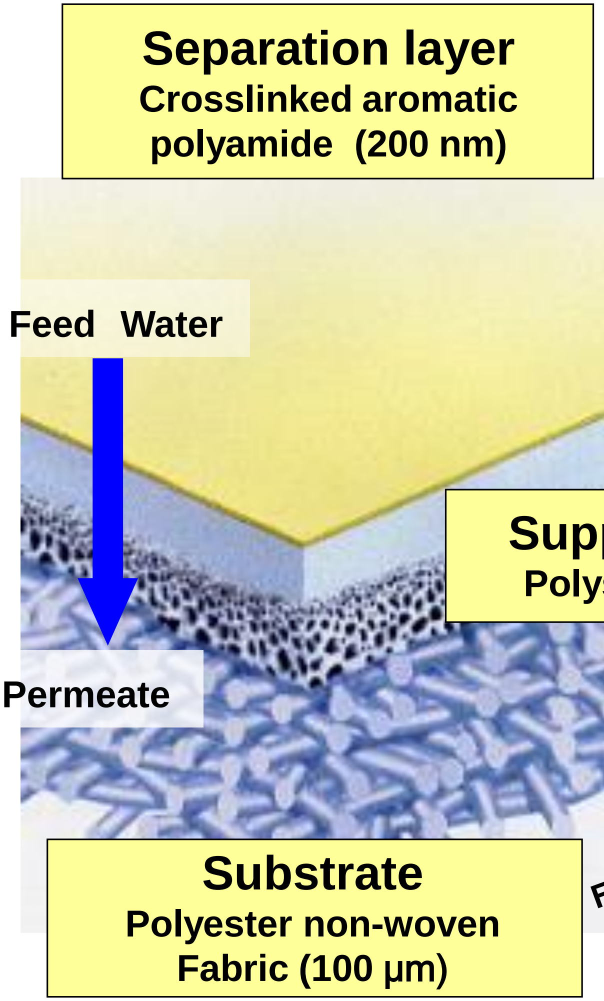
Brine Spacer Material



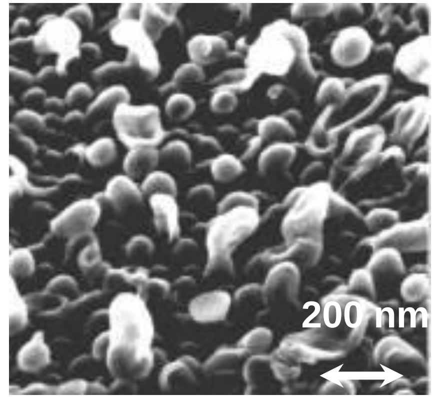
Membrane and Brine Spacer



RO Membrane Element

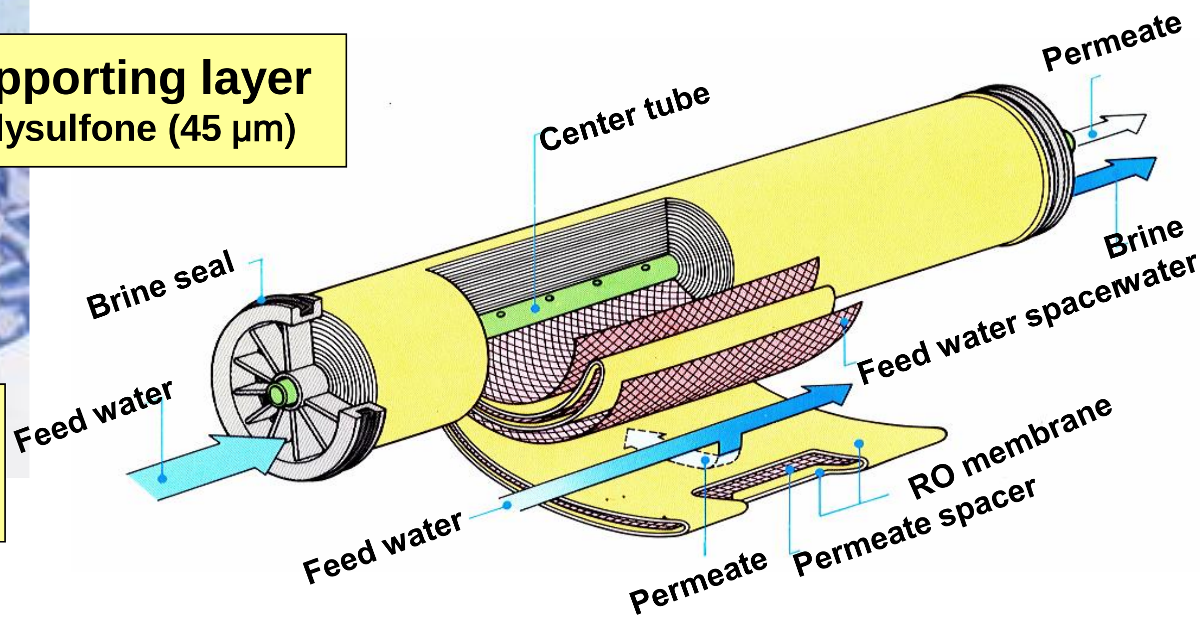


Structure of RO membrane



Surface structure of RO membrane

RO Unit



Structure of RO Element

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Reverse Osmosis – Membrane Structure +Separation Mechanism

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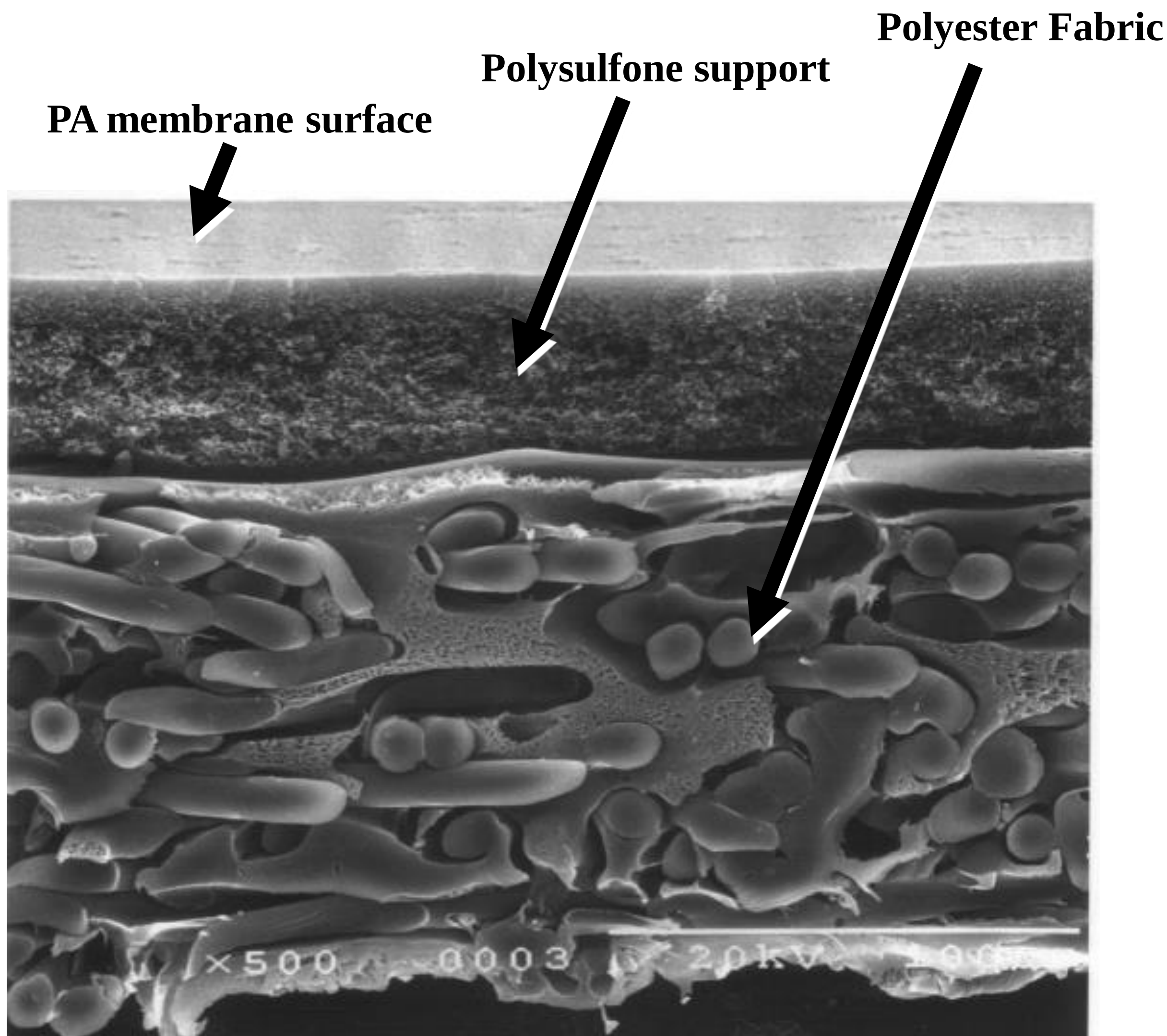
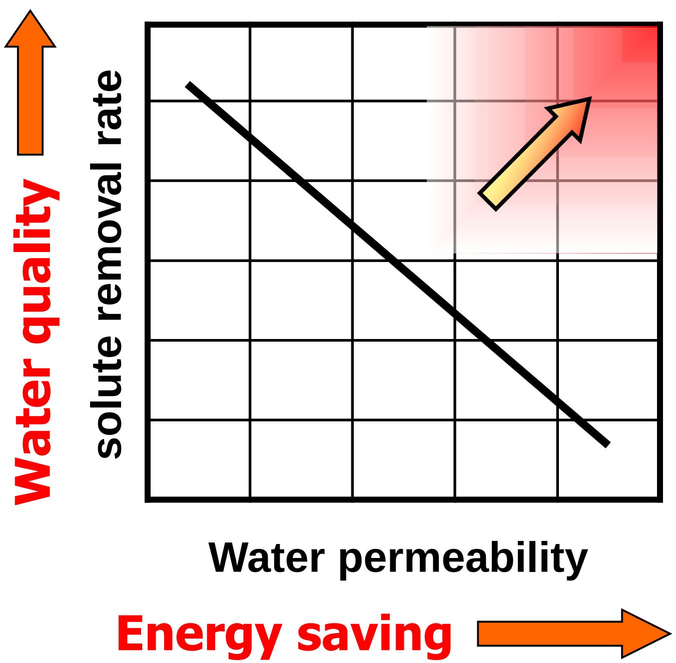
Thin Film Polyamide Membrane



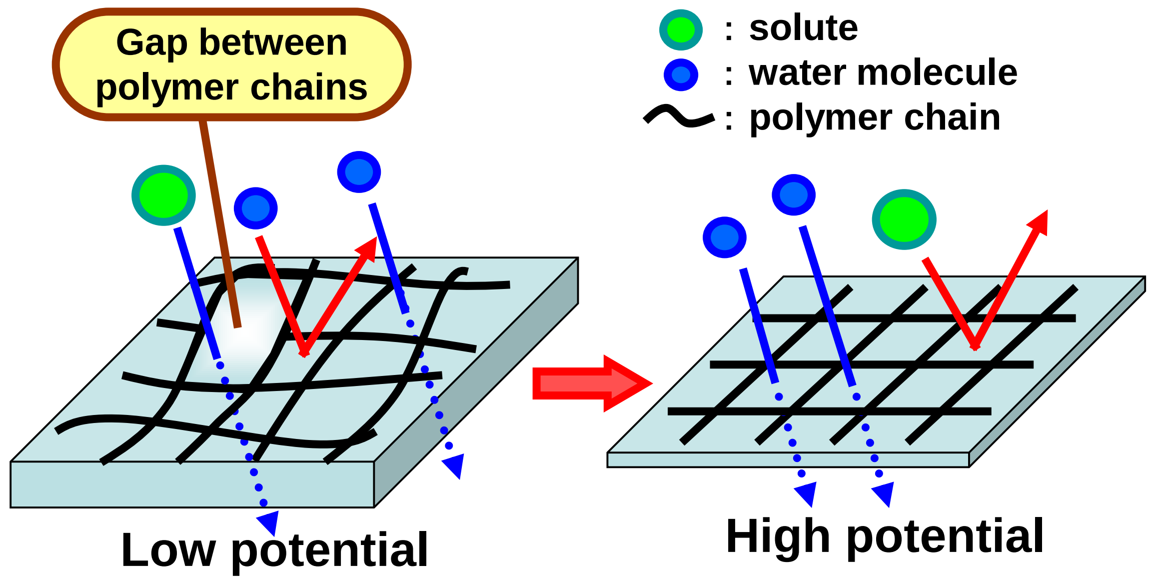
Concept for Innovative RO Membranes

Co-existence of high water permeability and low solute permeability

"Performance improvement" of membrane



Rough sketch of permeation phenomenon through RO membrane



- Molecular design for uniform pores
  ⇒ Selective removal of solutes
- Formation of thinner separation layer
  ⇒ Efficient transport of water molecules

How Membranes Reject Dissolved Solids and Particulates

Size Exclusion (UF and MF)

Membranes contain distinct pores. Water and dissolved solids can travel through the pores of the membrane. Water travels, for the most part, unrestricted, while particulates are restricted mostly by pore size. (Some particulate rejection is due to adsorption and electrostatic repulsion)

Solution – Diffusion (RO and NF)

Water molecules and dissolved solids dissolve into the semi-permeable membrane material, then diffuse, or migrate, across the membrane, going back into solution on the permeate side of the membrane. Dissolved solids, due to their lower solubility and mobility, travel at a much slower rate than the water molecules. (No pores)

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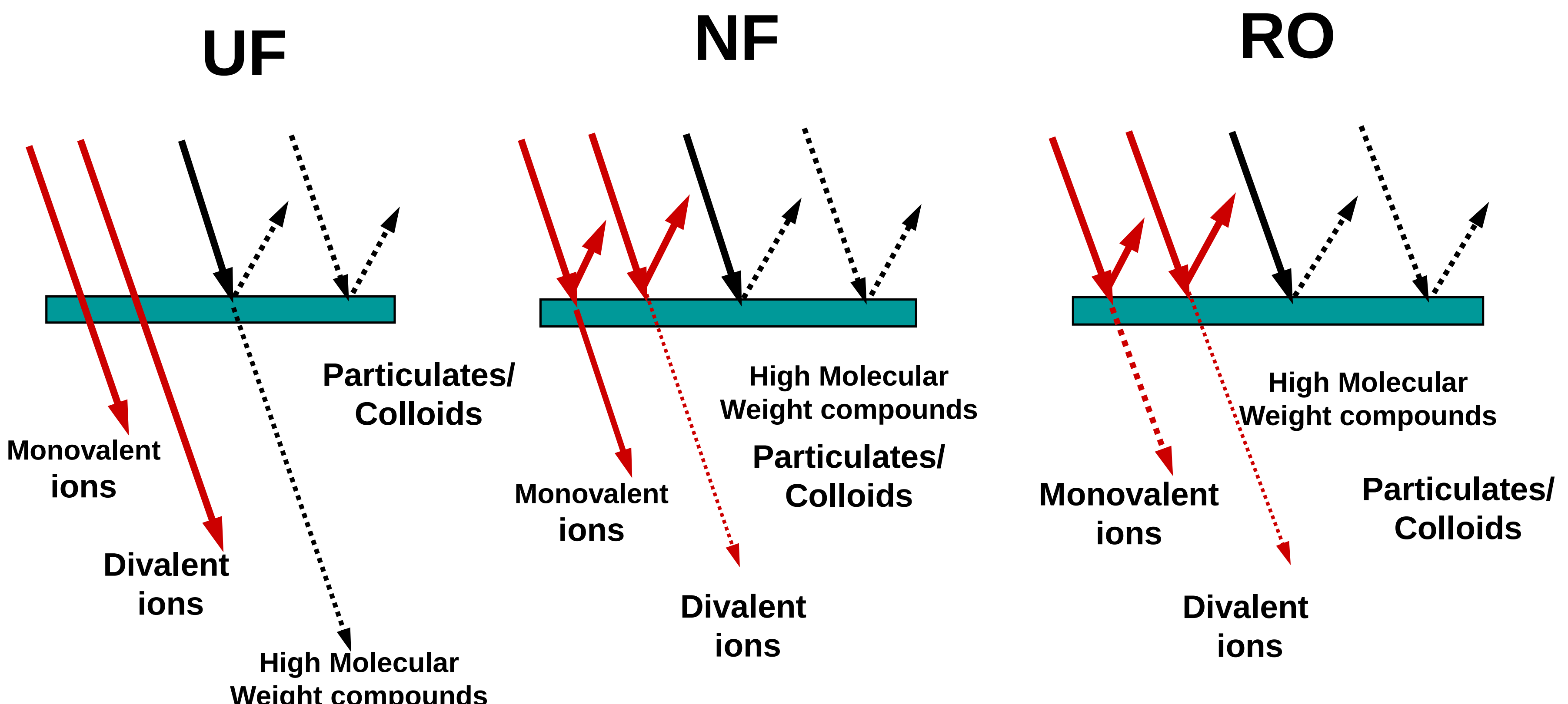
What determines how well a compound is rejected?

- **Primary Separator:**
  - Surface Charge Density of the dissolved ion/compound
  - How easy is it for the ion
    - A) to enter into the membrane polymer chain structure
    - B) to travel through the membrane to the permeate side
- The higher the surface charge density is the more difficult it is to enter and cross the membrane –the better the rejection
- **Secondary Separator (if the surface charge is zero)**
  - Size (molecular weight) and steric effects

What this means

- $SO4^{2-}$ Divalent - High surface charge density (MW 96) – well rejected)
- Cl^{-} Monovalent –lower Surface charge density - lower rejection than Divalent ions
- Rejection of Cl > Br (Both monovalent, but Bromide ion is bigger - lower surface charge
- Dissolved gases: Small (low molecular weight) and no charge so very poorly rejected (CO2, NH3, radon)

SEPARATIONS - WHAT IS THE DIFFERENCE?



<u>RO: Uncharged molecule Rejection</u>

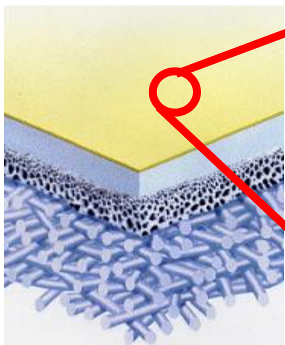
<200 Dalton : poor

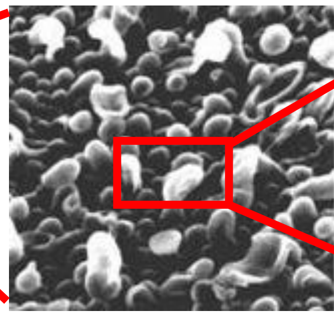
>300 Dalton: good

Morphology Analysis by TEM (Transmission Electron Microscope)

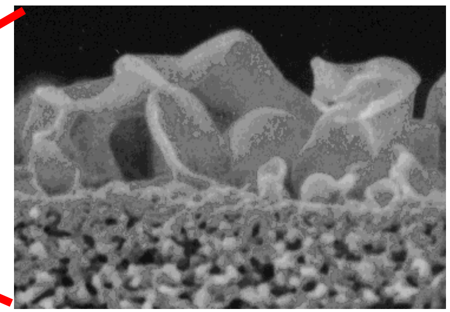
Precise estimation of the "protuberance" structure

Conventional analysis by SEM





Surface (SEM)



Cross section (SEM)

SEM Information from outside appearance

Light Wavelength – 600nm
Electron Wavelength - 6 pm
100,000X better resolution!!

Analysis by TEM with a special treatment of membrane for preserving the structure

Cross section (TEM)

New parameters were estimated:

- Inside structure
- Surface area
- Membrane thickness

Correlation between the morphology of protuberance and water permeability of membrane will be revealed.

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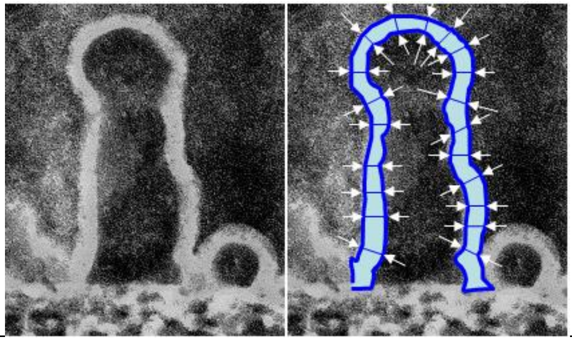
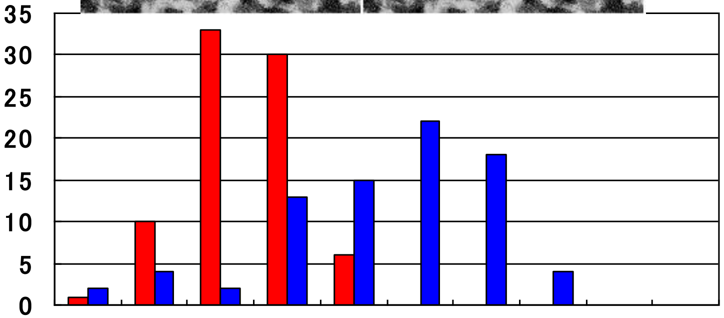
Latest Technology - Quantitative Analysis of Membrane (3D-TEM)

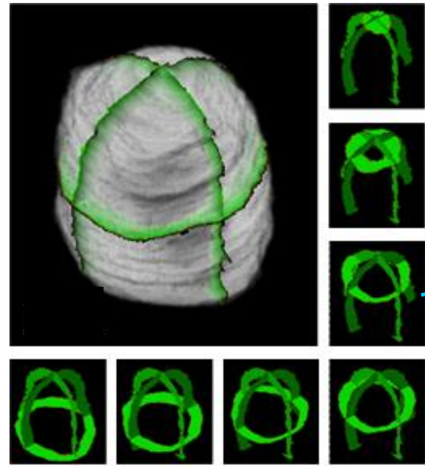
Thickness and Surface area

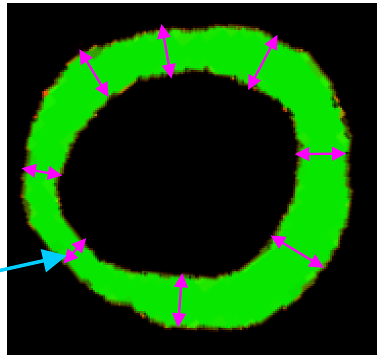
Cross section of protuberance (TEM)





Distribution of Thickness





Multi-direction Quantitative data

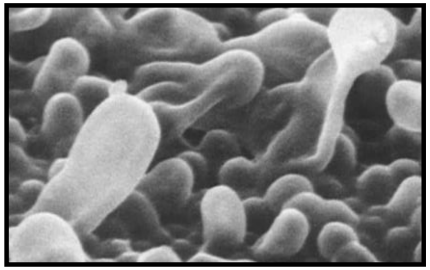
Distribution	Thickness	Surface area
Existing poly-condensation	1	1
Precise poly-condensation	0.6	1.4

Nano-scale controlled uniform ultra-thin membrane with high surface area

Production Target: Fine Structure with Precise Poly-condensation

< Existing Poly-condensation >

Membrane surface (SEM)

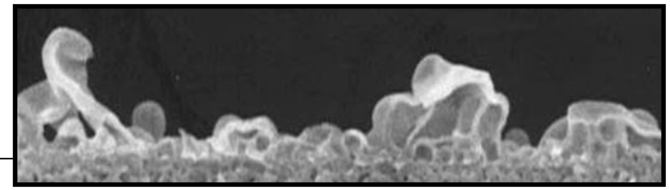


300 nm

Membrane cross section (SEM)

Separation layer

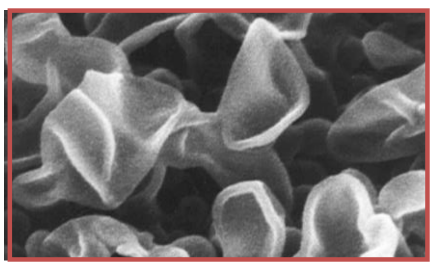
Support layer



300 nm

Large fluctuation of protuberance

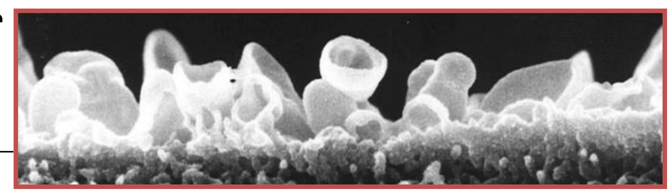
< Precise Poly-condensation >



300 nm

Separation layer

Support layer



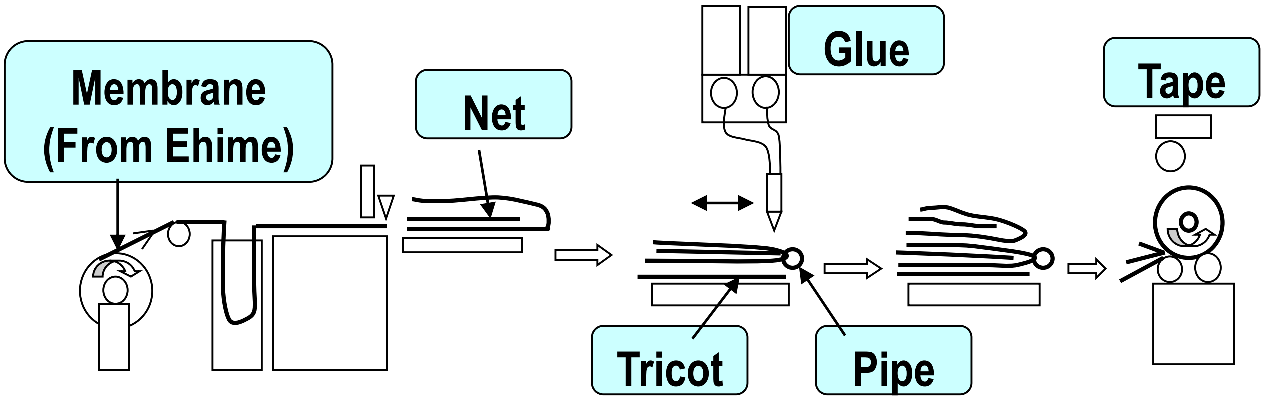
300 nm

Small fluctuation of protuberance

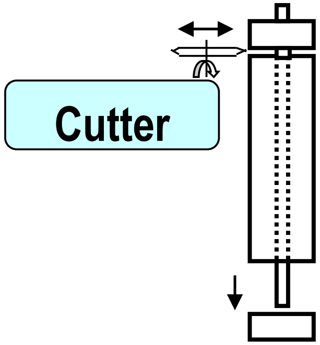
Formation of uniform protuberance

Element Manufacturing Process (1)

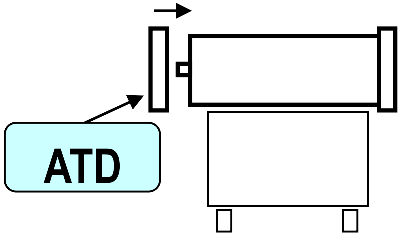
1. Winding



2. Side Cutting

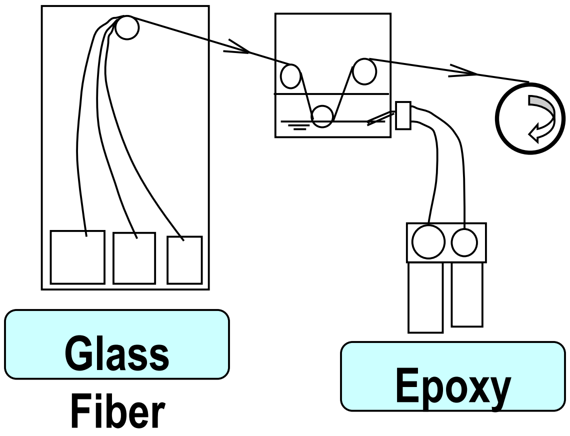


3. ATD Attachment

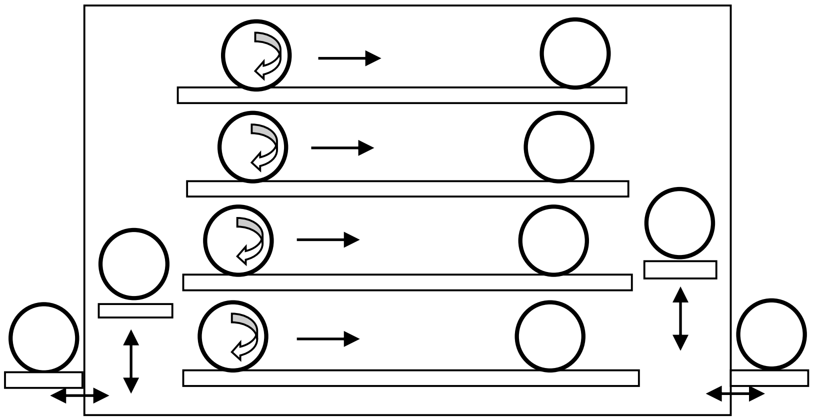


Element Manufacturing Process (2)

4. Filament Winding



5. Curing



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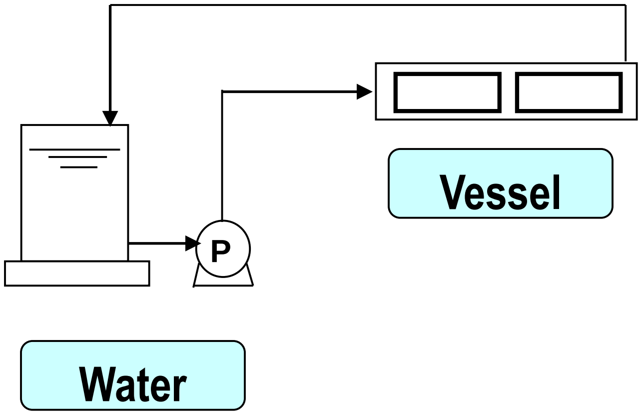
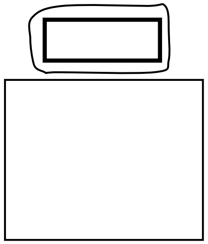
Element Manufacturing Process (3)

6. Evaluation (Wet Test)



7. Preservation Tank

8. Packing



Key RO Concepts: "A" value

- "A" - Water mass transport coefficient
  - units $cm^3/(cm^2.sec.Atm.) = cm/(sec.Atm)$
- Permeate flow per unit membrane area per unit net driving pressure
- Approximate values at wet test conditions:

TMG20-400	"A" = 15.87×10^{-5} cm/(sec.atm)
TM720-400	"A" = 9.01×10^{-5} cm/(sec.atm)
TM820-400	"A" = 3.26×10^{-5} cm/(sec.atm)

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Permeate Flow proportional to "A"

$$Q_W = A\ a\ P_{net}$$

where:

Q_W	=	**Permeate Flow Rate cm^3/sec**
A	=	**Water Permeation Coefficient: ("A"value (cm/sec.Atm))**
a	=	**Membrane Area (cm^2)**
P_{net}	=	**Net Driving Pressure (Atm.)**

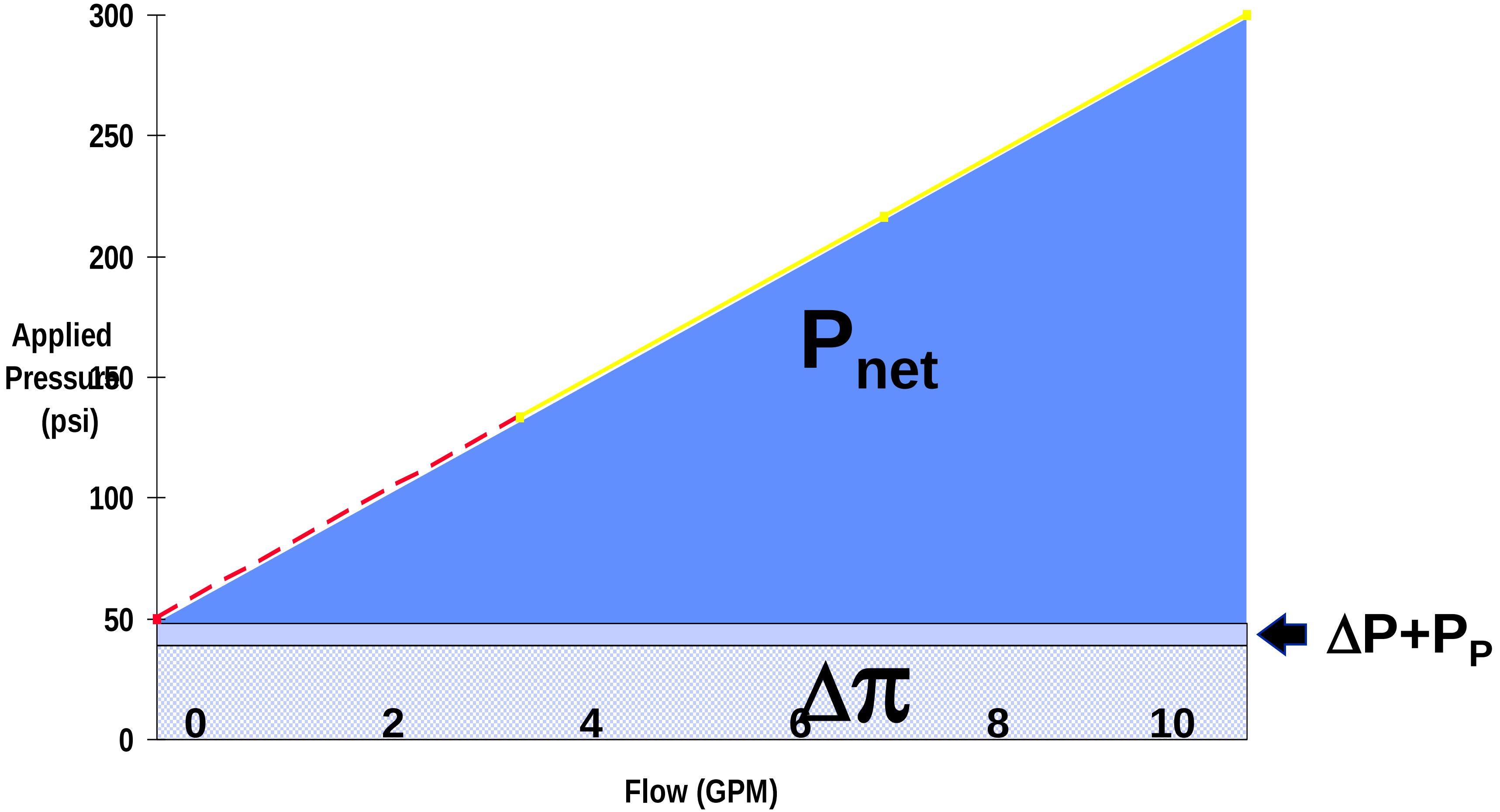
Key concept: Net Driving Pressure

$$P_{net} = P_a - \left(\Delta\pi + \frac{\Delta P}{2} + P_p\right)$$

where:

P_{net}	=	**Net Driving Pressure (Atm.)**
P_a	=	**Applied Pressure (Atm.)**
$\Delta\pi$	=	**Differential Osmotic Pressure (Atm.)**
ΔP	=	**Hydraulic Pressure Losses (Atm.)**
P_p	=	**Permeate Pressure (Atm.)**

Net Driving Pressure – graphical representation



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KEY CONCEPTS: "B" VALUE

- "Salt" mass transport coefficient
  - Units: cm/sec
- Different for each ion species present

Definition

Mass flow of "salt" (gm/sec) per unit area of membrane (cm2) per unit concentration differential across the membrane (feed side to permeate side)

- Typical "B" values (wet test)
  - 100 psi net BWRO: 1.2 x 10-5 cm/sec
  - 200 psi net BWRO 0.5 x 10-5 cm/sec
  - 400 psi net SWRO 0.3 x 10-5 cm/sec

SALT FLOW: “B” VALUE

$$Q_{si} = B_i \, a \, \overline{\Delta C_i}$$

WHERE:

Q_{si} = Salt Flow (g/sec, species “i”)

B_i = Salt Permeation Coefficient (cm/s) for species “I”

a = Membrane Area (cm2)

$\overline{\Delta C_i}$ = Average Concentration Difference across the Membrane (feed side to permeate side) (g/L)

Key Concepts: Flux

Flow of permeate water through a unit area of membrane per unit time.

The most common units of measure are

- ***GFD*** **- Gallons per Square Foot per Day**
- **LMH - liter per (meter)^2 per hour**

- **1 GFD = 1.7 LMH**

Why is Flux Important?

- *Rate of fouling is a function of the flux*
- *Maximum sustainable flux is a function of the water source*

Water Source	System Avge Flux (GFD)
R.O. Perm.	20-25
Deep Well	15-20
Surface (MF/UF pretreat)	14-18
Surface (conv. Pretreat)	12-16
TT sewage effluent (MF/UF pretreat)	10-12.5
TT sewage effluent (conv. Pretreat)	8-11

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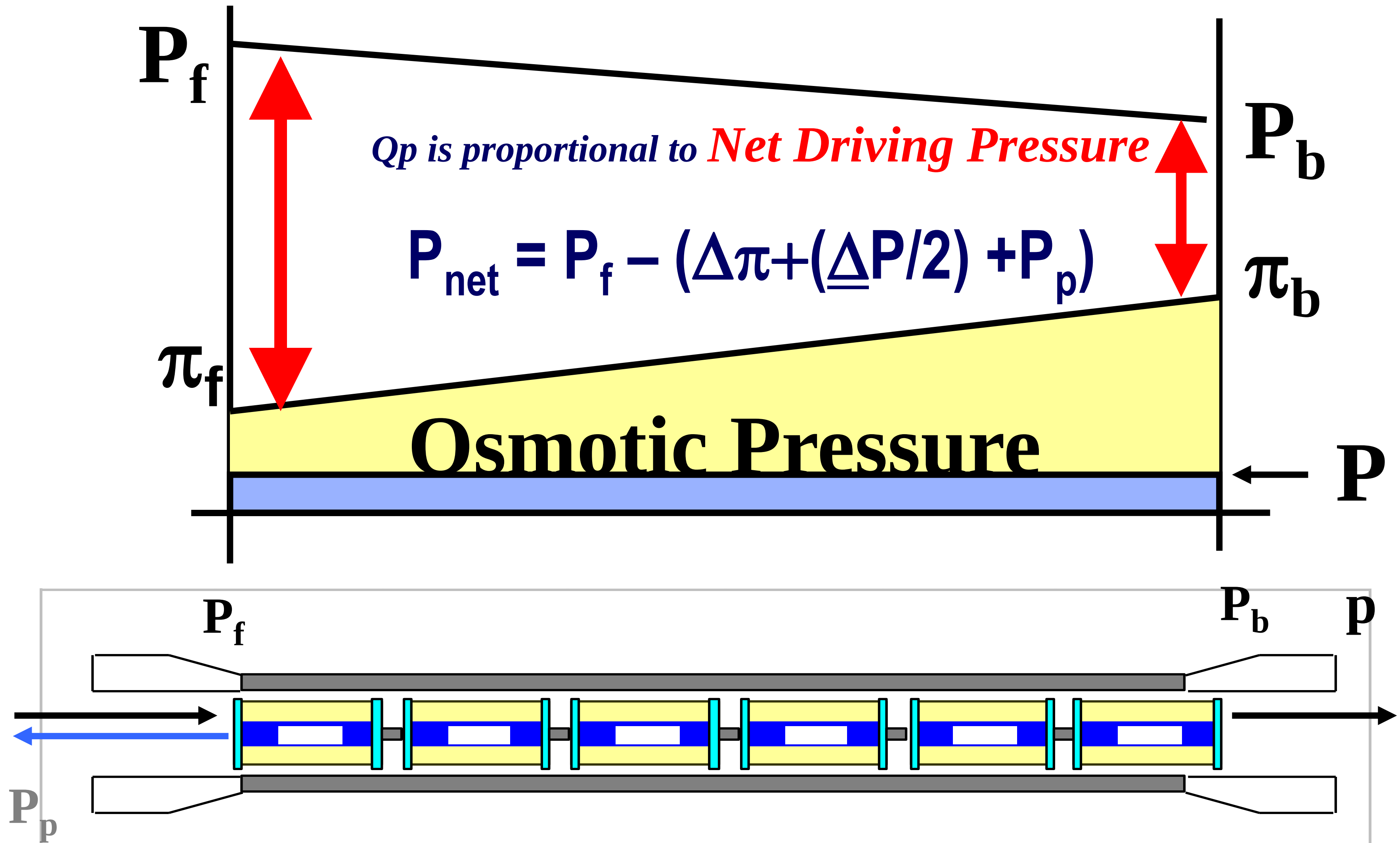
Why Permeate Flow is higher in the lead element-effect of Net Driving Pressure



Key Concept: Lead element Flux

- ***Rate of fouling is a function of the flux***
- Lead element flux is typically the highest flux in the RO unit
- If the lead element flux is too high, then it is likely to foul quickly
- Guideline values are given in the software for all major water types