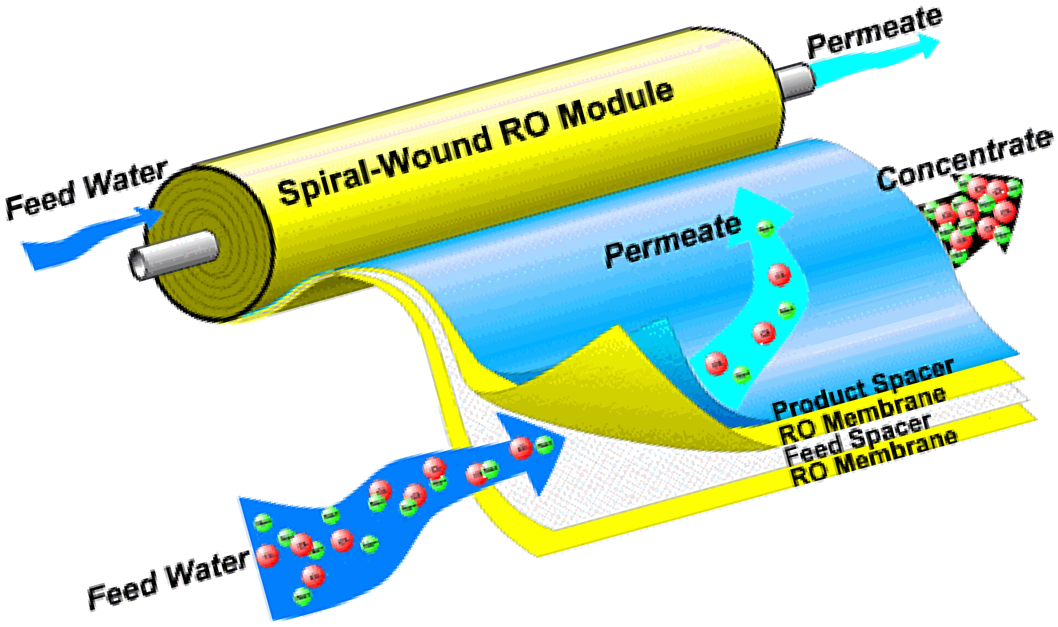
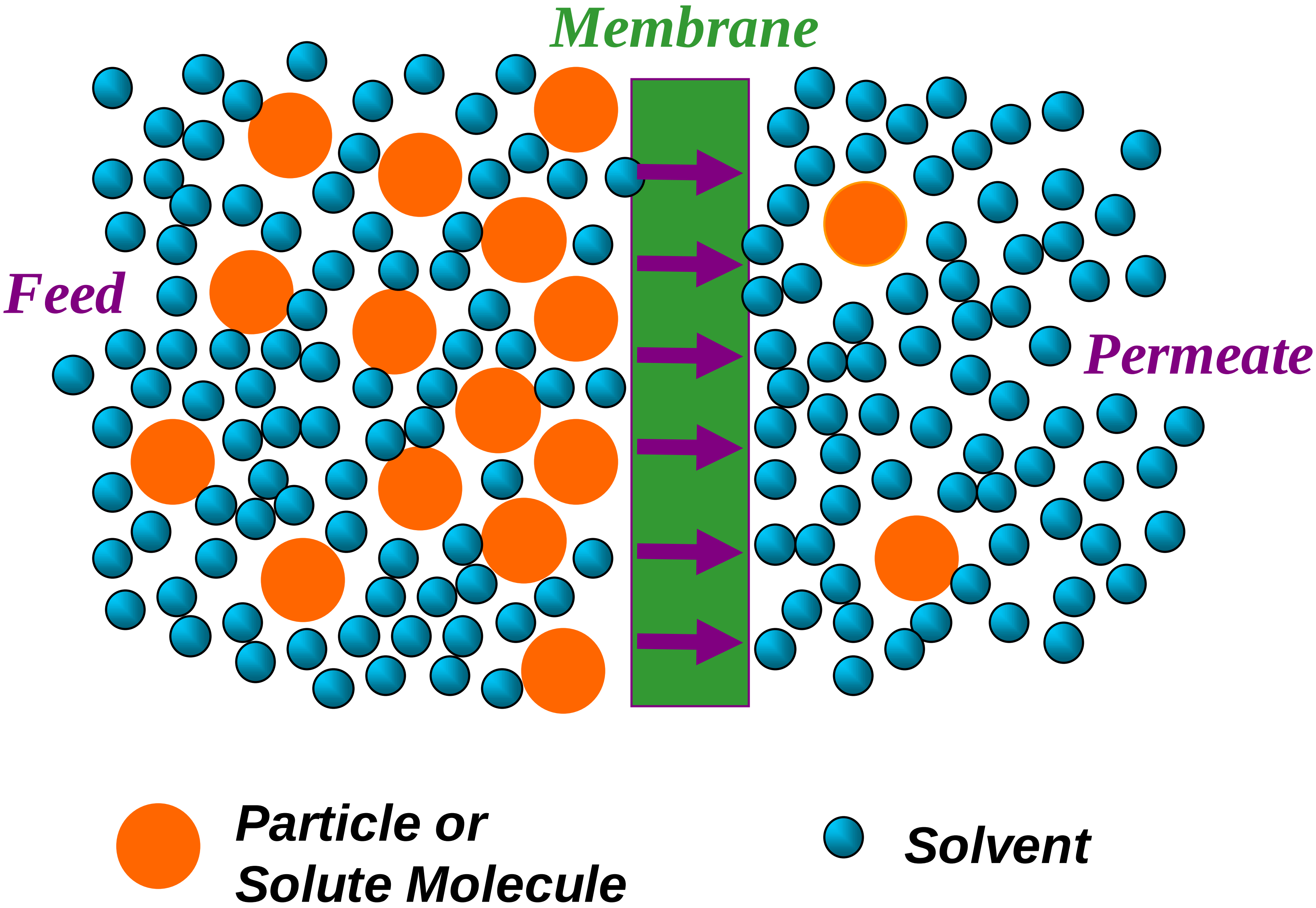
Water Treatment Membrane Processes - Introduction -

COLORADOSCHOOLOFMINES
EARTH ENERGY ENVIRONMENT



Membrane Separation



Definition of Membrane Process

- In a membrane separation process, a feed consisting of a mixture of two or more components is partially separated by means of a semipermeable barrier through which one or more species move faster than the other species
- In water and wastewater treatment applications, membrane processes are used as a solid/liquid separation process. In this case, water is more readily transported through the membrane than solids (both suspended and dissolved)

Classification of Membrane Operations

- Driving force
- Mechanism of separation
- Membrane structure
- Phases in contact

Classification of Membrane Operations

- Pressure-driven membrane operations
- Permeation operations
- Dialysis operations

Pressure-driven Operations

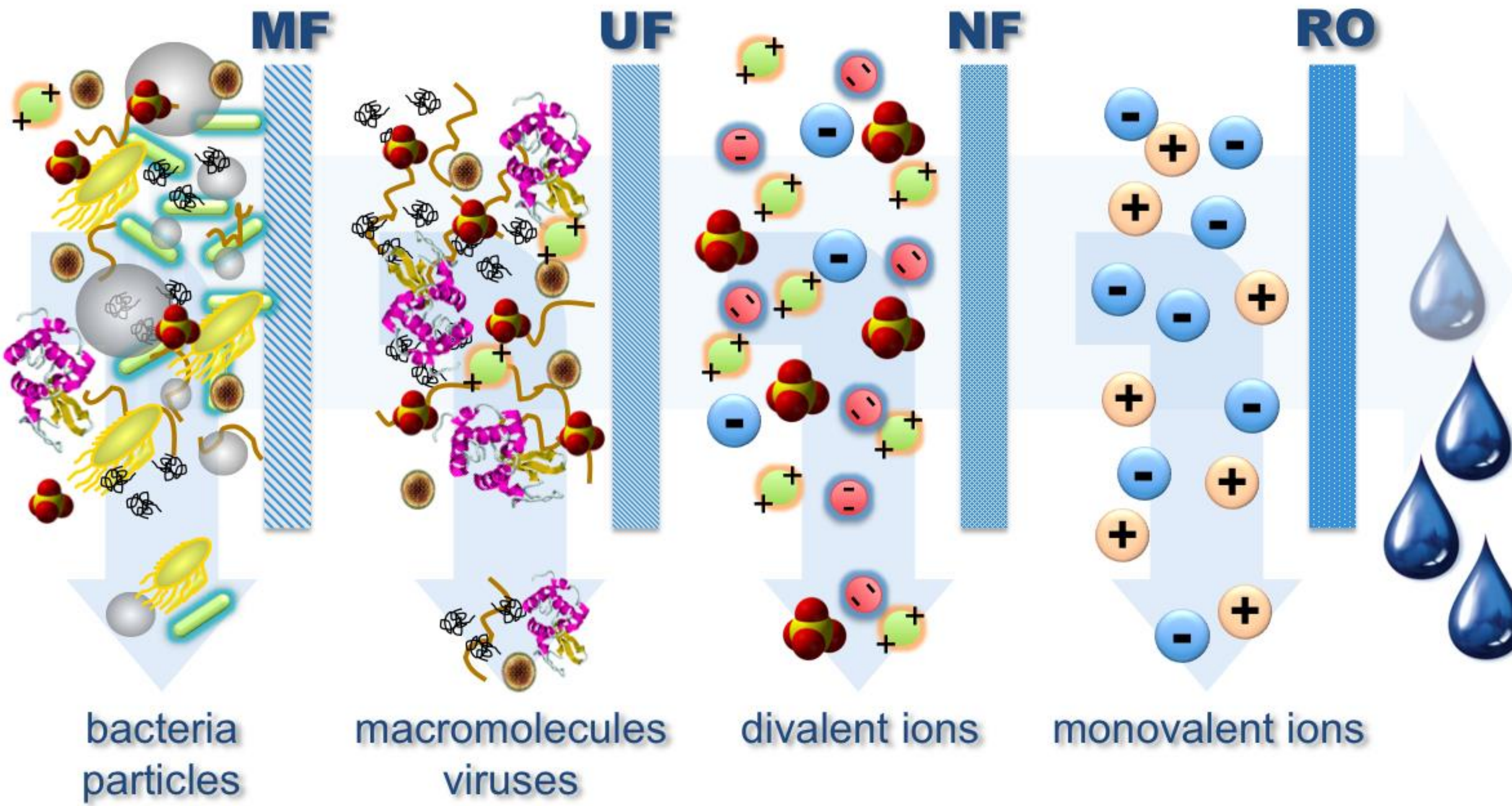
Microfiltration (MF)

Ultrafiltration (UF)

Nanofiltration (NF)

Reverse Osmosis (RO)

Pressure-driven Membrane Processes



Pressure-driven Membrane Processes

RO

- The solvent is transferred through a dense membrane tailored to retain salts and low-molecular-weight solutes
- To produce "pure" water from saline solution, feed pressure must exceed the osmotic pressure of the feed solution
- In order to obtain economically viable flows, at least twice the osmotic pressure must be exerted as hydraulic pressure (e.g., 50-80 bars (700-1,100 psi) for seawater)

Pressure-driven Membrane Processes

NF

- Sometimes referred to as low-pressure RO or membrane softening process
- Lies between RO and UF in terms of selectivity of the membrane
- Designed to remove multivalent ions but can remove sodium and chloride fairly well
- Looser NF membranes are more like UF and tighter NF membranes more closely resemble RO
- Recently has been employed for organic control
- Typical operating pressure: 5-14 bar (70-210 psi)

Pressure-driven Membrane Processes

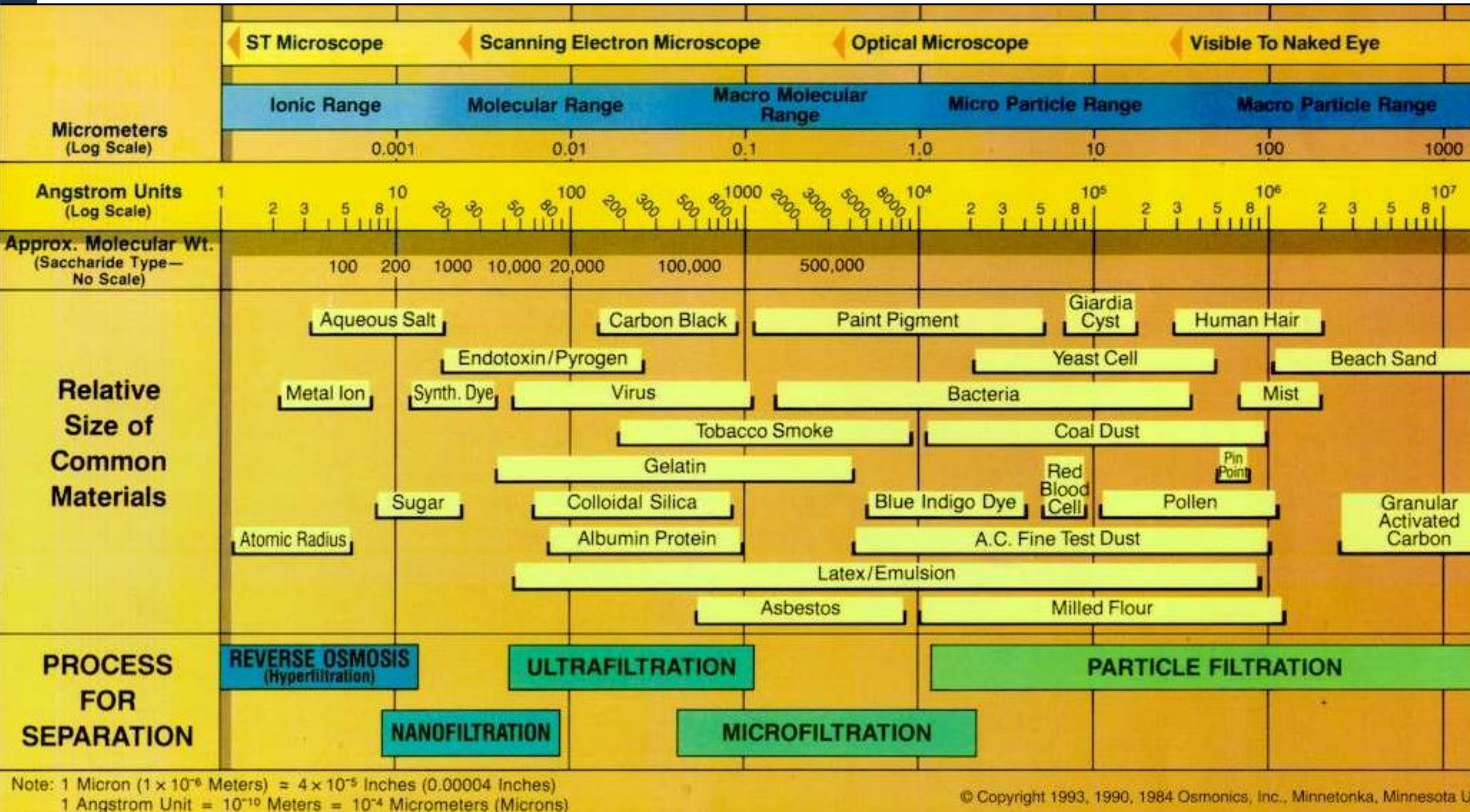
UF

- Considered as a clarification and disinfection operation
- Membrane is porous and rejects most macromolecules, microorganisms, and all types of particles
- Osmotic pressure effects are negligible
- Typical operating pressure: 0.5-5 bar (7-70 psi)

MF

- Major difference between MF and UF is pore size – 0.05-5 micron for MF
- Primary application is particulate removal (clarification)
- Typical pressures like UF

Selection of Membrane Processes



Membranes in Treatment of Drinking Water

- The application of specific pressure-driven membrane process is highly dependent on the characteristics and quality of the source water

  - Surface water: MF, UF, NF
  - Groundwater (fresh): MF, UF
  - Groundwater (brackish): MF/UF pretreatment, NF, RO
  - Seawater: MF/UF pretreatment, NF, RO

Membranes in Treatment of Wastewater

- The application of specific pressure-driven membrane process in wastewater treatment is highly dependent on the characteristics/quality of the source water and the pretreatment process/es used
  - Raw wastewater: MF/UF, MBR, FO (not mainstream…yet)
  - Effluent: MF/UF pretreatment, NF, RO

Membrane Technologies and their Traditional Counterparts

Membrane Separation Technology	Constituents Removed	Comparable traditional Water Treatment Method
MF	Bacteria and large colloids; precipitates and coagulates	Ozonation-UV, chlorination, sand filtration, bioreactors, coagulation-sedimentation
UF	All of the above + viruses, high MW proteins, organics	Sand filter, bioreactor, activated carbon
NF	All of the above + divalent ions, large monovalent ions, color, odor	Lime-soda softening, ion exchange
RO	All of the above + monovalent ions	Distillation, evaporation, ion exchange
ED/EDR	Dissolved ionic salts	Ion exchange

Target Solutes

- **MF:** Microbes (protozoa and bacteria)
  Turbidity (particles and colloids)
- **UF:** Same as MF + viruses, “some” NOM
- **NF:** Same as UF + NOM, SOCs (e.g., Atrazine),
  Divalent cations (Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, etc.),
  Polyvalent anions (SO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, CrO_4^{2-}, etc.)
- **RO:** Same as NF + simple ions (TDS, NO_3^-, ClO_4^-)
- **MF + Coagulant:** viruses, NOM (also fouling reduction)
- **UF + PAC:** SOCs, NOM (also fouling reduction)
- **Submerged MF and UF:** Fe and Mn (aeration),
  NOM (with coagulant), SOCs (with PAC)

Ranges of Pressure and Flux

Membrane Class	Pore Size or MWCO (μm or Dalton)	Pressure		Flux	
		psi	kPa	gfd (gal/ft^2·day)	LMH (L/m^2·hr)
MF	0.1 – 0.5 μm	1.4 - 14	10-100	60 – 120	100 – 200
UF	1 – 100 kD	7.0 - 70	50-500	30 – 60	50 – 100
NF	100 – 500 D	100 - 400	700-2,800	15 – 30	20 – 50
RO	n/a	200 - 1,000	1400-7,000	15 – 30	20 – 50
MF (Immersed)	0.2 μm	-1.4	-10		
UF (Immersed)	0.04 μm	-7.0	-50	20 - 50	35 – 85

conversions

1 atm = 101.3 kPa (kN/m^2) = 14.7 psi

1 kPa = 0.145 psi or 1 psi = 6.90 kPa

1 psi = 0.068 atm

gfd = LMH x 1.7

Ranges of Energy Consumption

Membrane Class	Recovery	Pressure		Energy consumption kWh per	
		psi	kPa	**1,000 gal**	**m^3**
MF	94-98	15	100	0.1	0.4
UF	70-80	75	525	0.8	3.0
NF	80-85	125	875	1.4	5.3
LPRO	70-85	225	1,575	2.7	10.2
RO	70-85	400	2,800	4.8	18.2
ED	75-85			2.5	9.5

Permeation Operations

Gas Permeation (GP)

Gas Diffusion

Pervaporation (PV)

Membrane Stripping (MS)

Membrane Distillation (MD)

Engineered Osmosis (EO)

Other Classifications

Separating Mechanisms

- Separation based on difference in size (sieving)
  - **MF, UF, DIA**
- Separation based on difference in solubility and diffusivity of material in the membrane (solution-diffusion mechanism)
  - **GP, PV, RO, FO**
- Separation based on difference in charges of the species to be separated (electrochemical effects)
  - **ED, EDR**

Rejection Capabilities (pressure-driven processes)

- RO membranes are typically characterized by manufacturers in terms of NaCl rejection, e.g., 96% or 99.9% NaCl rejection
- NF membranes may be characterized in terms of NaCl or $MgSO_4$ rejection or they may be characterized in terms of molecular weight cut-off (MWCO)*, e.g., 98% $MgSO_4$ and 80% NaCl rejection
- UF membranes are typically characterized using MWCO, e.g., 13,000 or 80,000 MWCO
- MF membranes are typically characterized by pore size, e.g., 0.1 or 1 µm

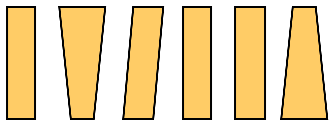
* MWCO is determined by fitting rejection data of acromolecules (e.g., dextrans or proteins)

Porosity

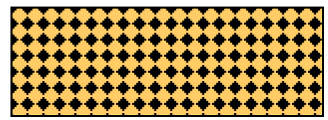
- Porous membranes (MF, UF, NF, DIA)
  - Macroporous: > 50 nm
  - Mesoporous: 2 – 50 nm
  - Microporous: < 2 nm
- Nanoporous membranes
  - Dense media
  - Diffusion of species takes place in the free volume present between the macromolecules chains of the membrane material
- IX membranes
  - Specific type of nanoporous membranes

Morphology

Symmetric



Cylindrical Porous



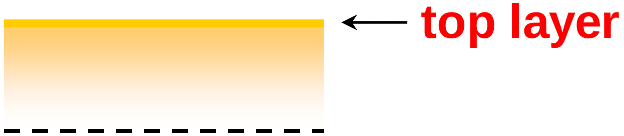
Porous

Homogeneous

(resistance to mass transfer is determined by total membrane thickness)

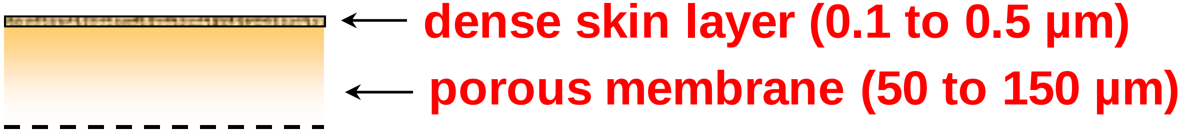
Asymmetric – Single Material

Porous



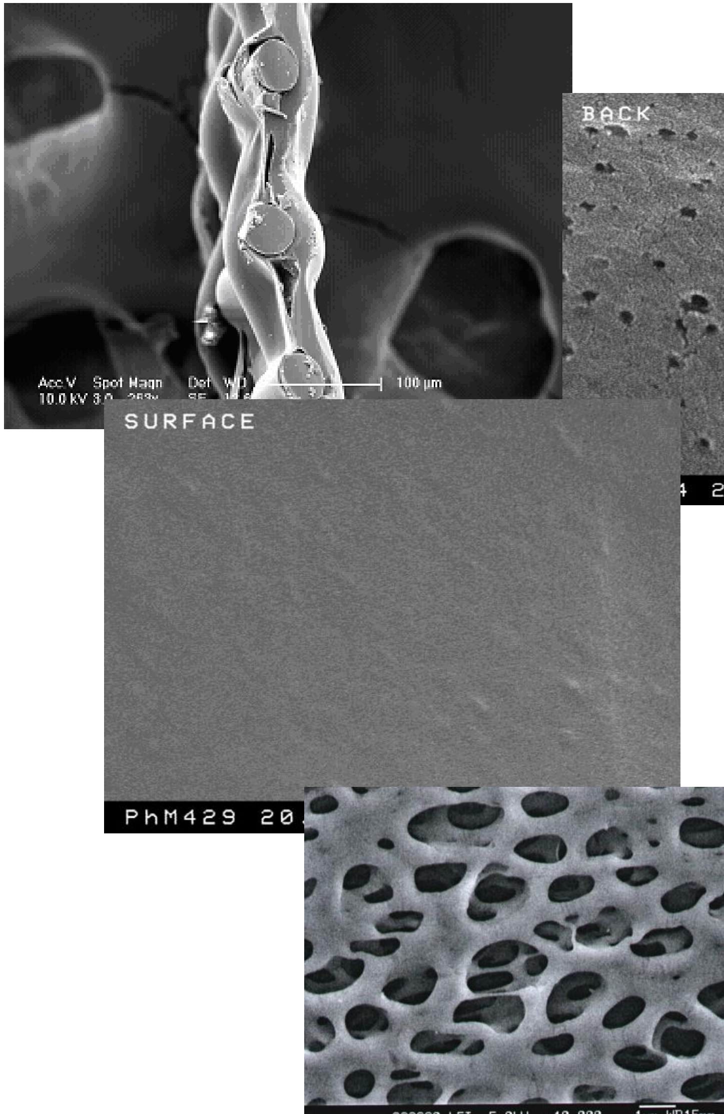
Porous with Top Layer

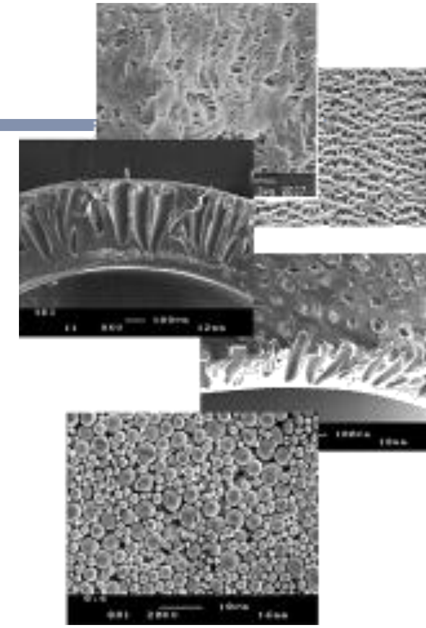
Asymmetric – Composite



(resistance to mass transfer determined by skin layer thickness)

Structure of Membranes

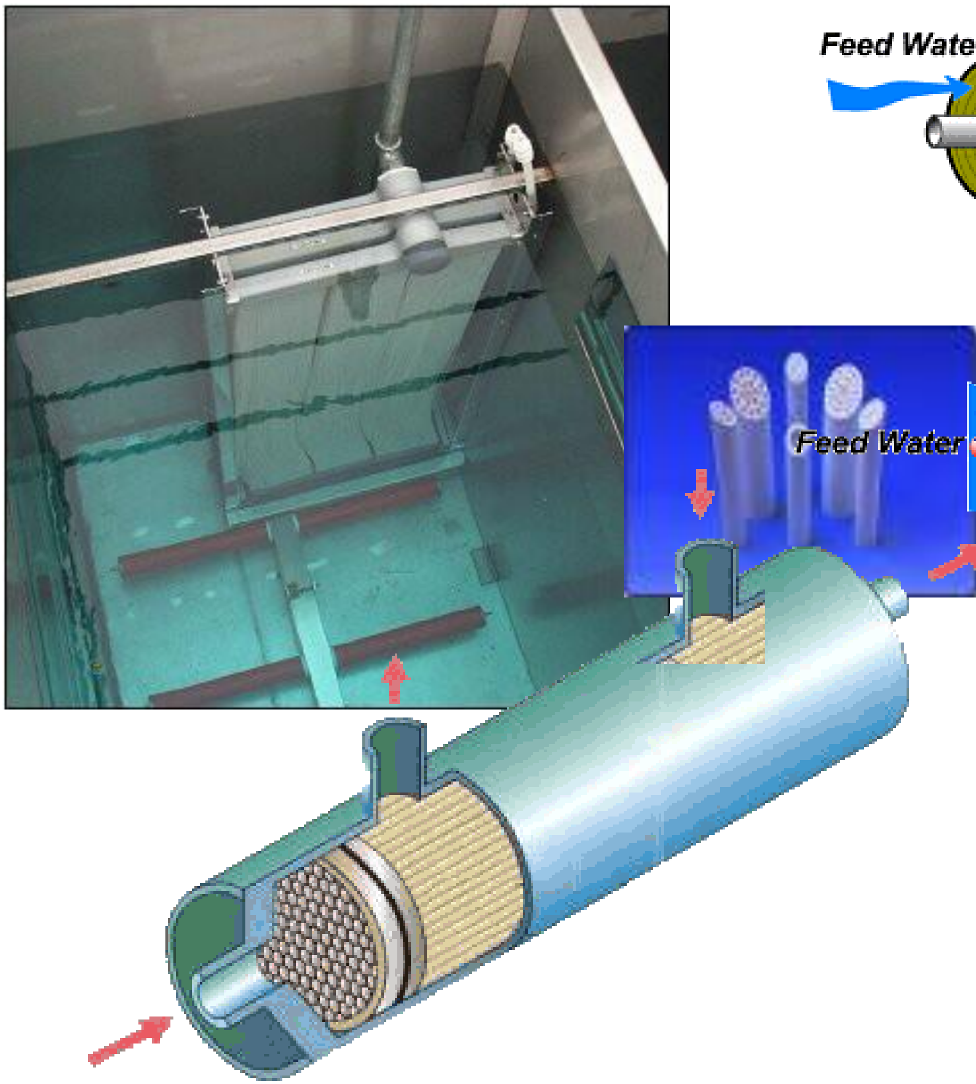


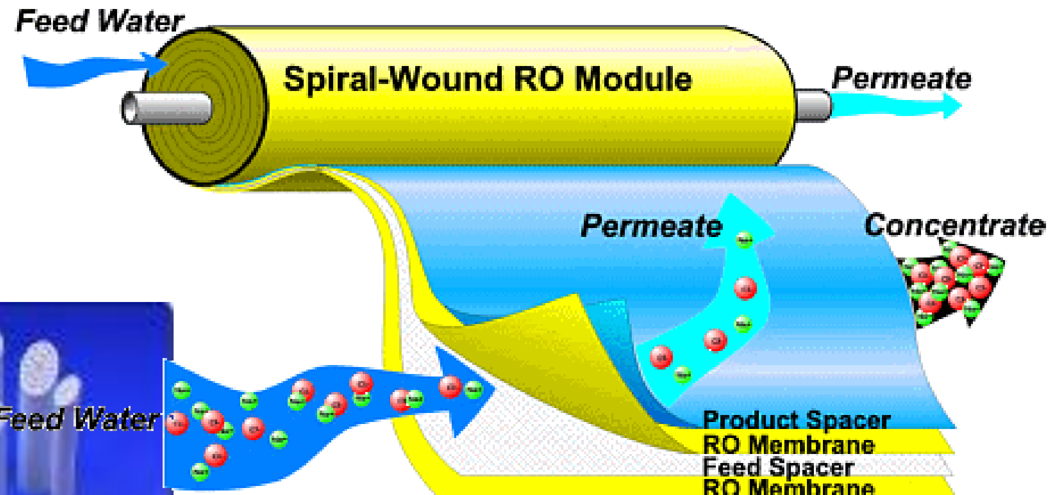


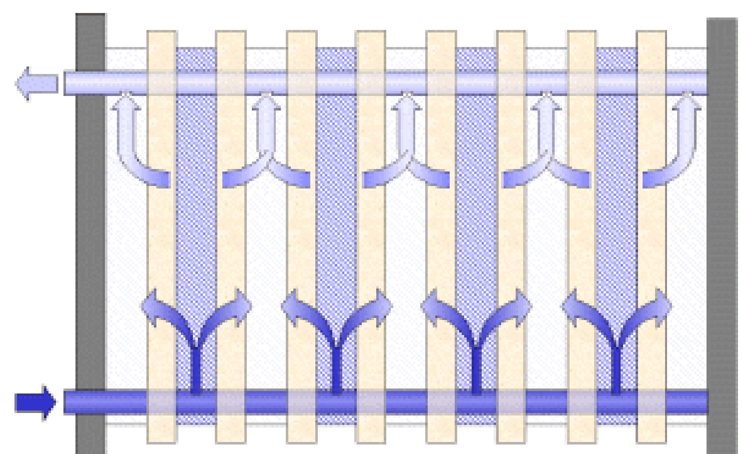
Geometry / Packaging

- Flat-sheet membranes (spiral wound, plate-and-frame)
- Tubular membranes (shell-and-tube, immersed)
  - Tubes
  - Capillaries
  - Hollow fibers

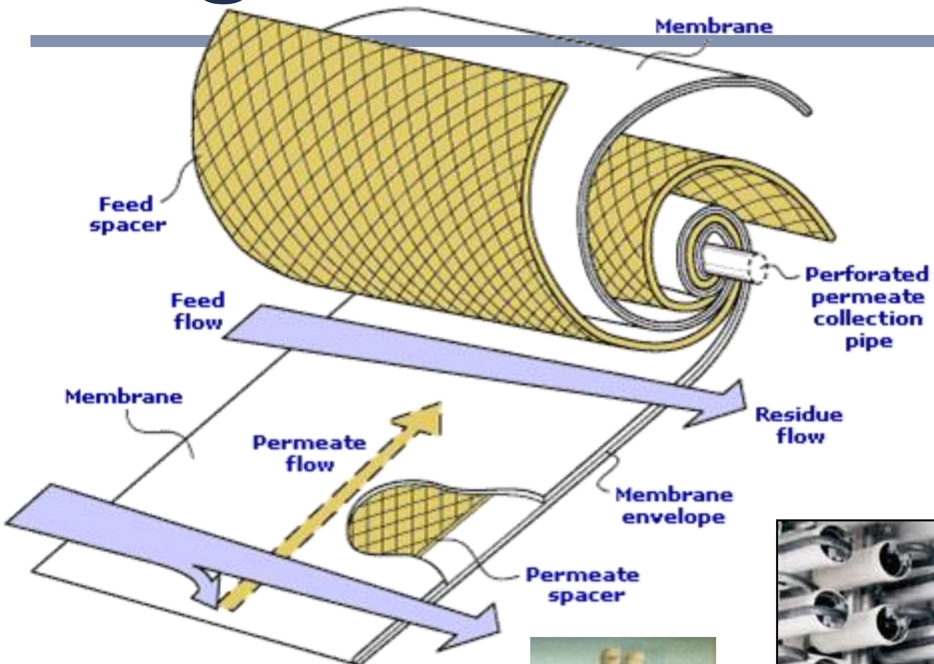
Geometry / Packaging







Spiral Wound Module
Single Element vs. Bank or Array

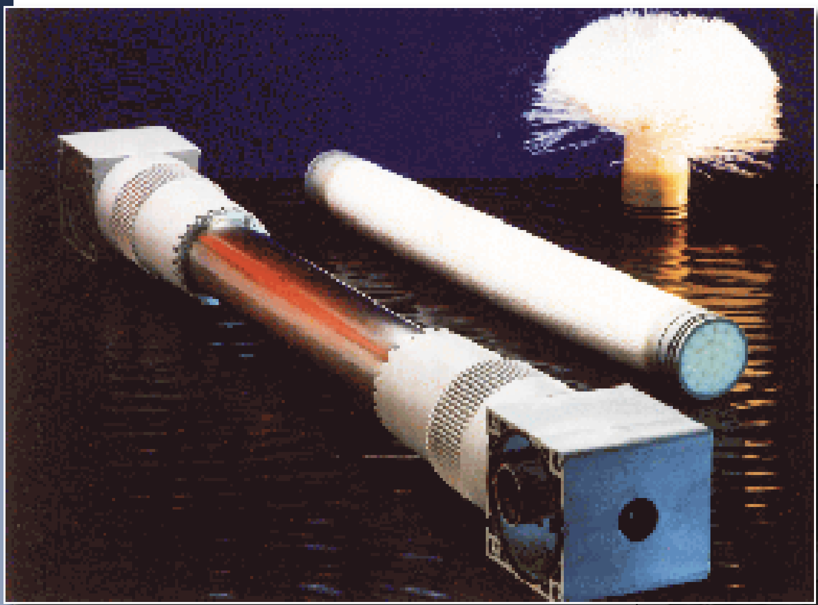


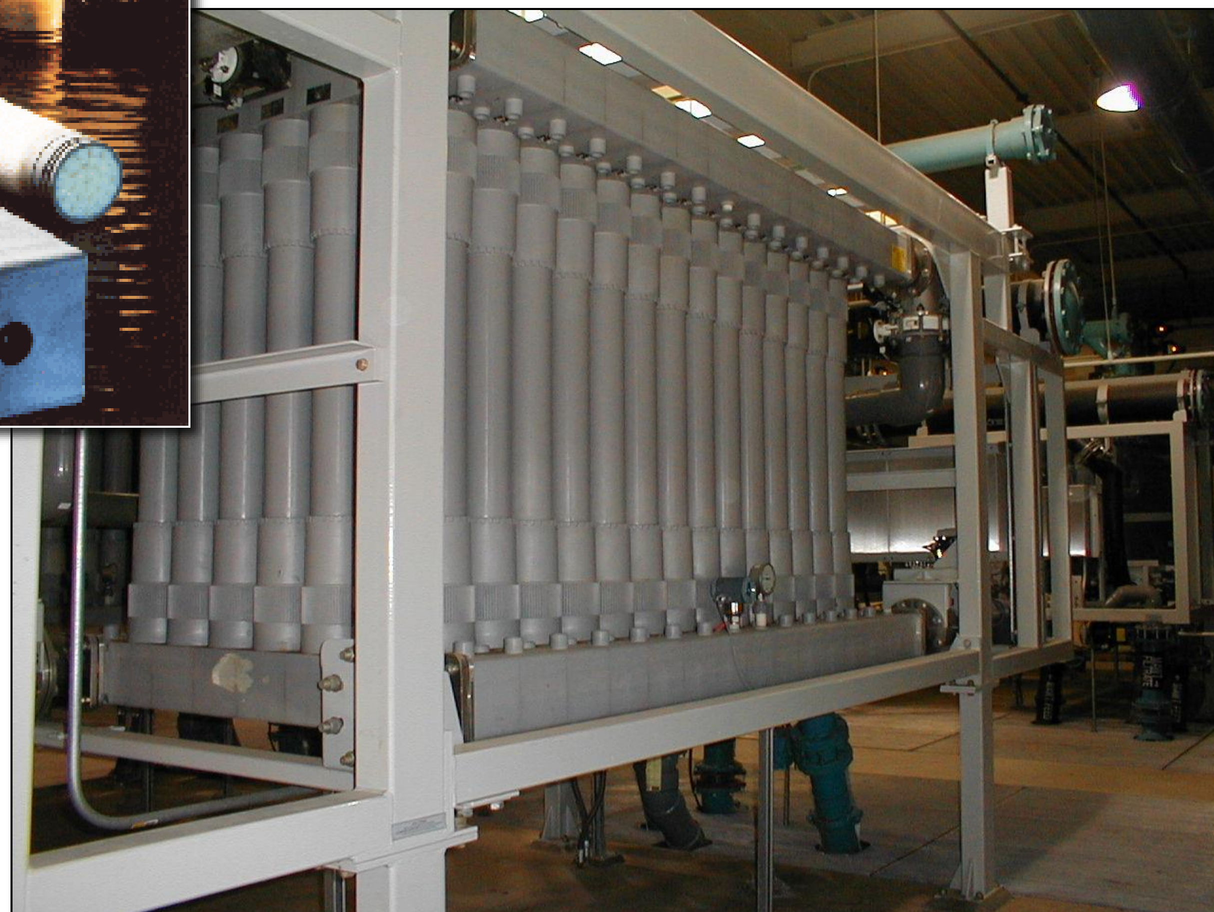
Roga Module 1
ca. 1964

Spiral Wound Module Installation

Hollow Fiber Membrane Single Fiber (left) vs. Module (right)

Hollow Fiber Membrane Module (left) vs. bank (right)

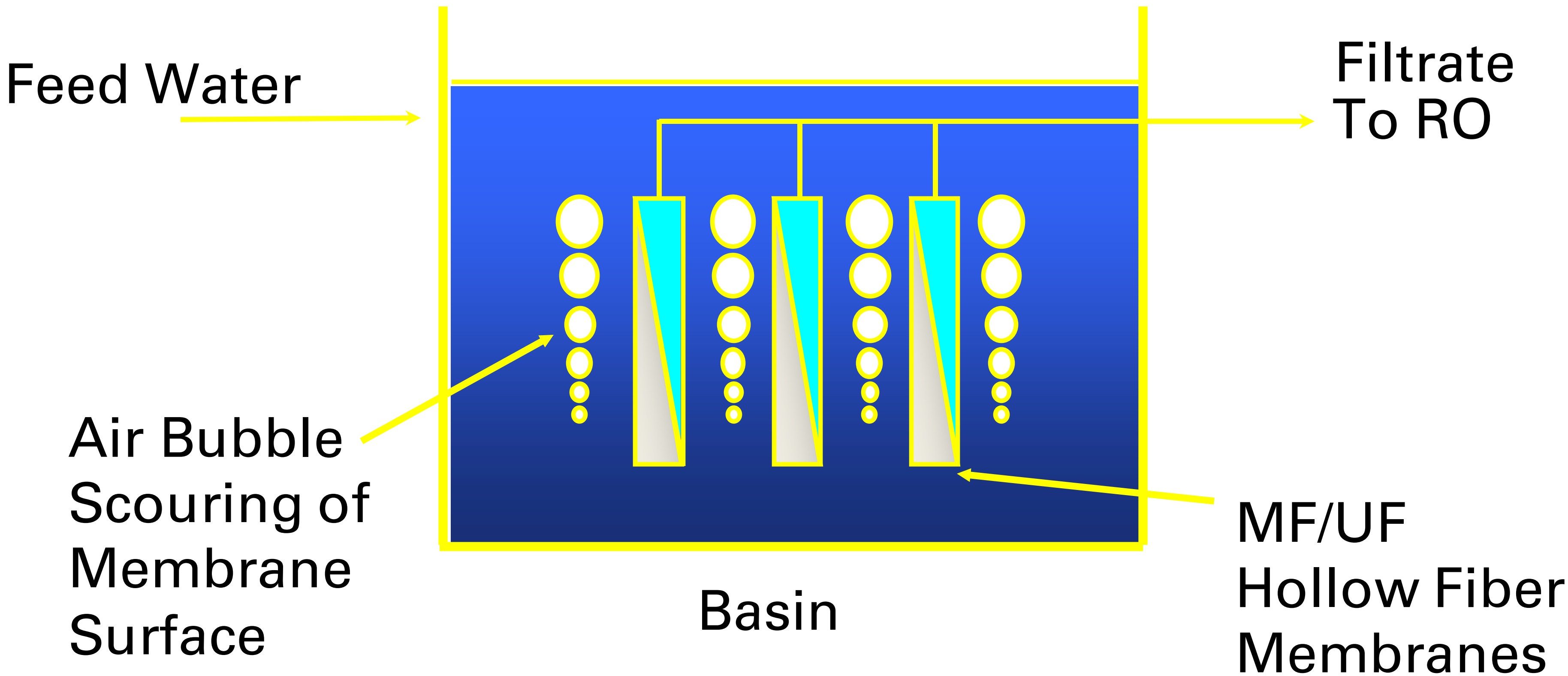




Submerged Membrane – MF/UF

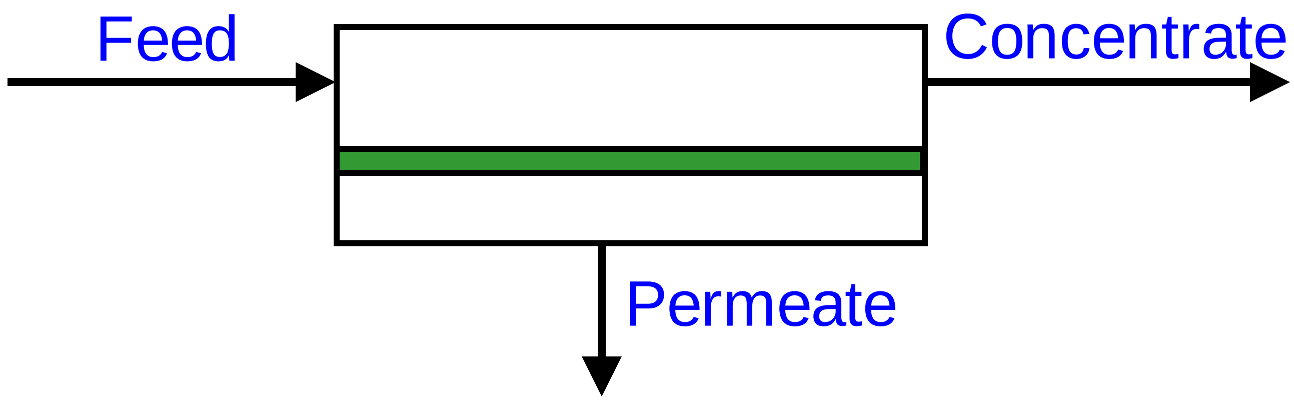
- Uses
  - Surface water treatment
  - Pretreatment for RO
  - Membrane bio reactors (MBR)
  - Filtration for non-potable reuse (add MF after secondary WW treatment and produce water for irrigation)
- Operation
  - Membranes are immersed in basin of feed water
  - Operate under suction
- Advantages
  - Operate at lower pressures than pressurized systems
  - Less fouling potential - good for wastewater treatment
  - Membrane cleaning and fixing

Submerged Membranes

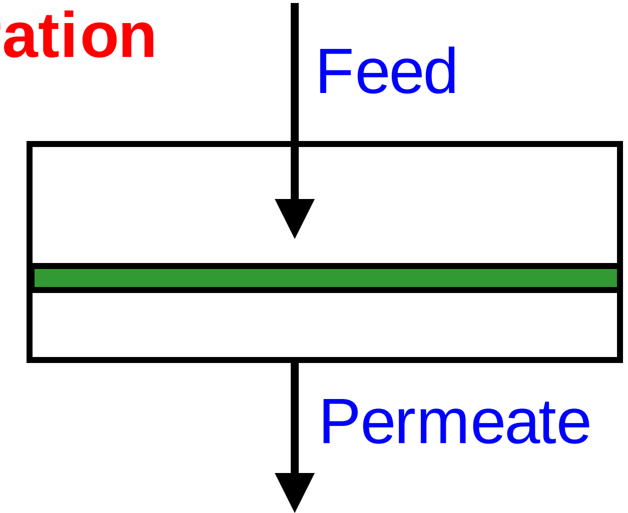


Flow Configuration
Cross Flow vs. Dead End Filtration

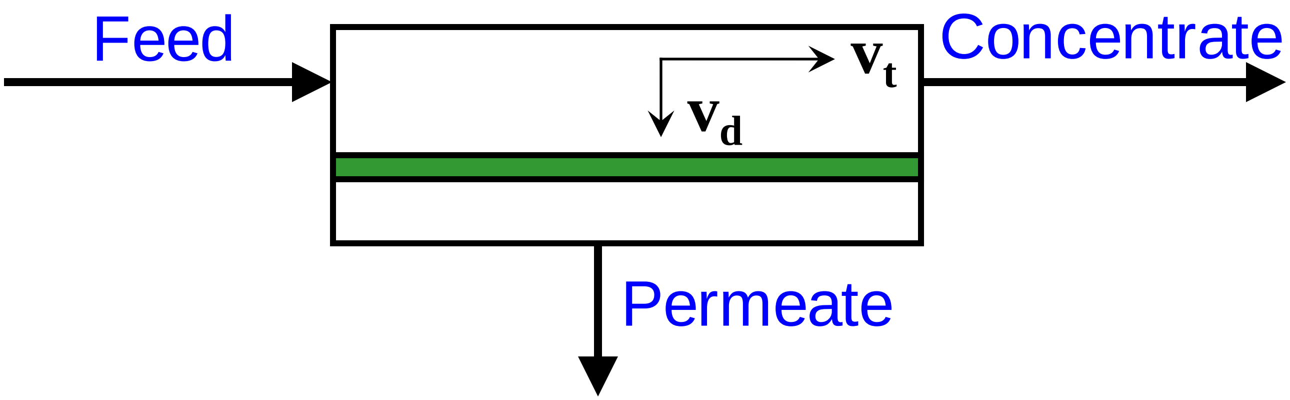
Cross Flow Operation



Dead End Operation

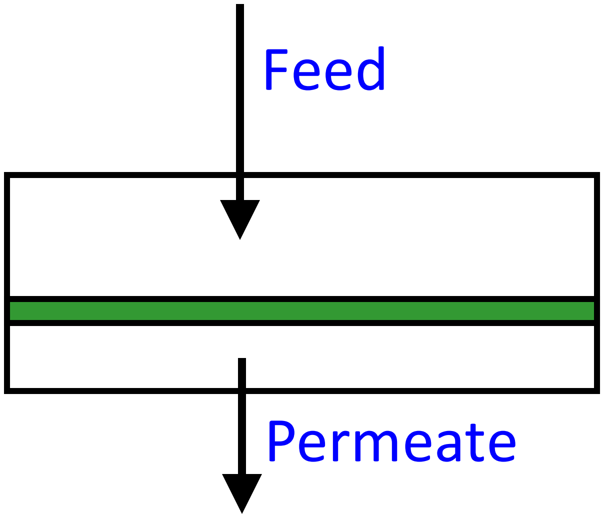


Cross Flow Operation



- Feed flow is parallel to membrane surface
- Retained particles are scoured
- Have concentrate stream
- Preferable for concentrated solutions to control thickness of deposit on membrane (fouling)

Dead End Operation



- Feed flow is perpendicular to membrane surface
- Retained particles form a cake layer on surface
- No concentrate stream
- Preferable for dilute solutions due to lower energy requirements (pumping)

Comparison of Cross-flow Membrane Configurations

	Cost	Packing Density	Operating Pressure Capacity	Membrane Types	Fouling Resistance	Cleanability
Traditional Spiral-Wound	Low	High	High	Many	Fair	Fair
Hollow Fiber	Low	UF-High RO-Very High	UF-Low RO-High	Few	UF-Good RO-Poor	UF-Good RO-Poor
Tubular	High	Low	UF-Moderate	Few	Very Good	Very Good
Plate & Frame	High	Moderate	High	Many	Fair	Fair

Adapted from "Select Engineering Principles of Crossflow Membrane Technology" Osmonics Inc. Technical Paper, P/N 56821

Membrane Materials

- Polymeric membranes:
  - Polysulfone
  - Polyethersulfone
  - Polyphenylsulfone
  - Polyvinylidene Fluoride (PVDF)
  - Polypropylene (PP)
  - Polyethylene (PE)
  - Cellulose and Cellulose acetates (CA)
  - Polyamide (PA)
  - Polyacrylonitrile (PAN)
  - Polytetrafluoroethylene (PTFE)
  - Polycarbonate (PC)
  - Polymethylmethacrylate (PMMA)

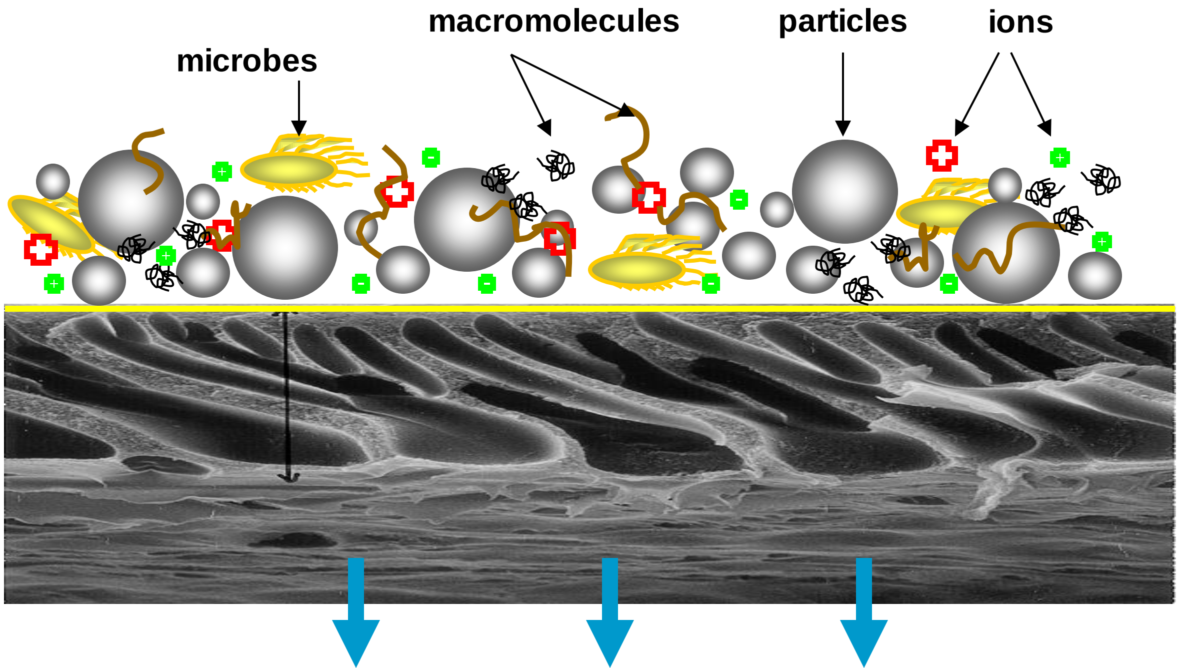
- Ceramic membranes:
  - Aalumina
  - Titania
  - Zirconia
  - ATZ mix

  - chemical, mechanical and thermal stability
  - ability of steam sterilization and back flushing
  - high abrasion resistance
  - high fluxes
  - durable
  - bacteria resistance
  - possibility of regeneration
  - dry storage after cleaning

Membrane Properties

- Pure water permeability (PWP)
- Pore size
- Molecular Weight Cut-Off (MWCO)
- Hydrophobicity/hydrophilicity
- Surface/pore charge
- Surface roughness
- Chemical stability / chlorine tolerance

Principles of Mass Transport and Rejection in Pressure-Driven Membrane Processes



Overview

- RO, NF, UF, and MF have many similarities (geometry, flow configuration, material…)
- Principals of rejection differ substantially
  - In RO, function of relative affinity of solute and solvent to the membrane
  - In MF, mainly due to physical sieving

Membrane Performance

- The performance of a membrane is determined by mainly two parameters, flux and rejection:
  - Flux (J), or permeation rate, is the volume flowing through the membrane per unit area per time (Q/A)
  - Rejection (R), refers to a local relationship between upstream and downstream concentrations
- Another important parameter is recovery (r), which is defined as the amount of material collected as a useful product divided by the total amount of the material entering the process: in membrane separations, the useful product is most often the permeate water

Water and Solute Flux

- Water flux (J_w), or permeation rate, is the volume flowing through the membrane per unit area per time (Q/A)

$$J_w = \frac{Q_{water}}{A_{membrane}} = \frac{V_{water}}{A_{membrane} \cdot time}$$

  - In membrane processes it is a function of driving force, membrane properties, and feed quality

- Specific permeate flux is the water flux calculated above normalized to the applied driving force

$$J_{sp} = \frac{Q_p}{A \times P} \quad [gpd/ft^2 \cdot psi](gfd/psi), LMH/bar]$$

Note: in MF/UF, DP = net applied pressure (NAP)

Water and Solute Flux

- Solute Flux is the mass of solute flowing through the membrane per unit of area per time

$$J_s = \frac{\dot{m}_{solute}}{A_{membrane}} = \frac{mol_{solute}}{A_{membrane} \cdot time}$$

- In membrane processes it is a function of driving force (concentration), membrane properties, and solute/particle properties

Water Recovery Rate (r)

- The ratio of the useful product (permeate) flow rate and the flow rate of feed to the process

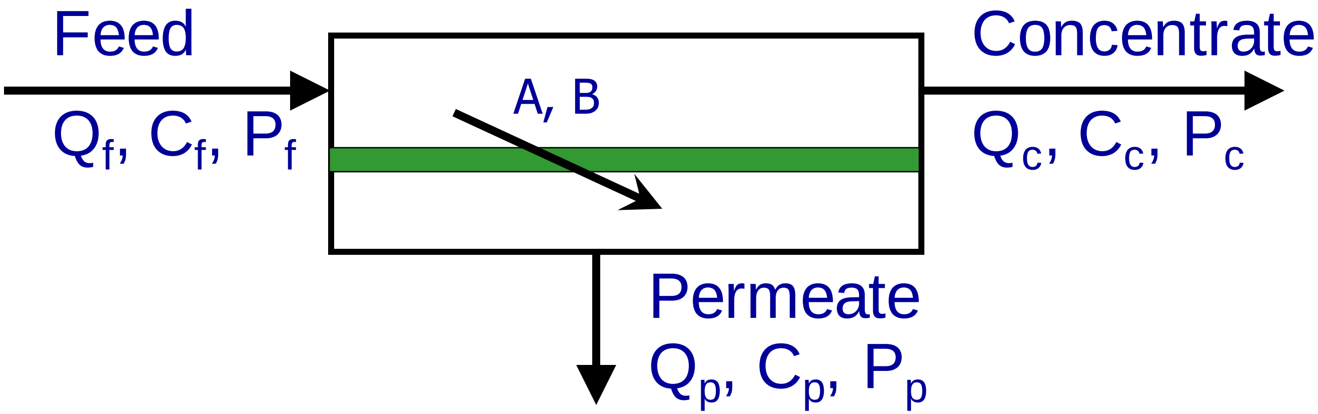
$$r = \left(\frac{Q_p}{Q_f} \right) * 100\%$$

- Global recovery rate:

  - Where Q_p is the product (permeate) flow rate and
  - Q_f is the feed flow rate

- In membrane processes, because of the modularity and various configurations, it is important to distinguish between membrane/module recovery and system recovery

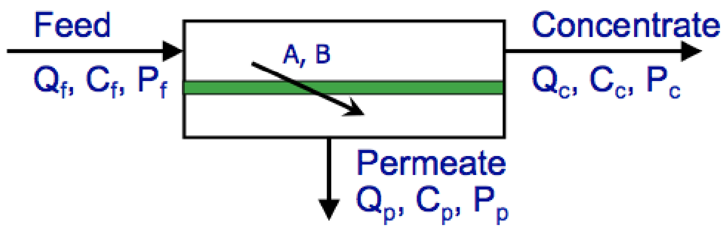
Material Balance in Membrane Separation



Material Balance in Membrane Separation

- Mass balance for water flow

$$Q_f = Q_c + Q_p$$



- Mass balance for solute flux

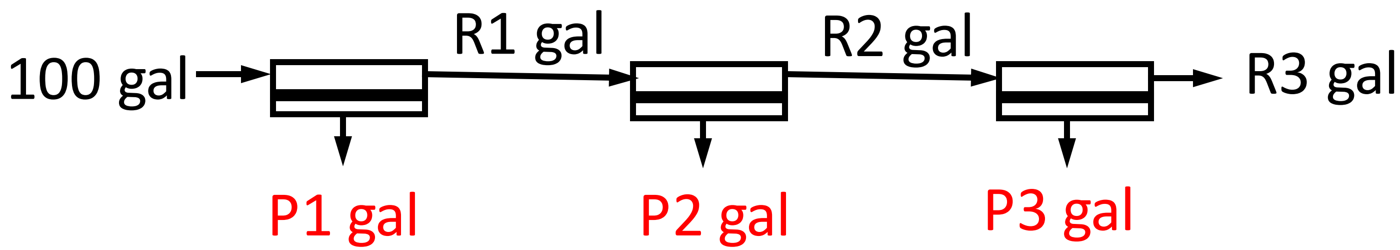
$$Q_f C_f = Q_c C_c + Q_p C_p$$

- Product recovery

$$r = (Q_p/Q_f)\cdot 100\%$$

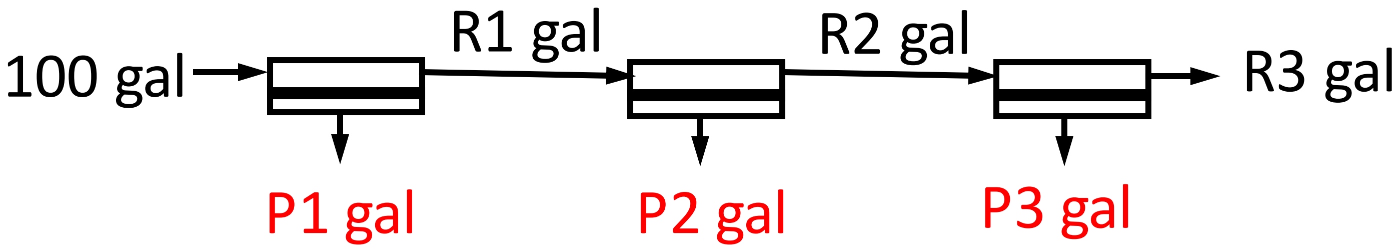
Example of Process Recovery

- Assuming each membrane (or each stage) operated at 20% recovery, what is the total system recovery



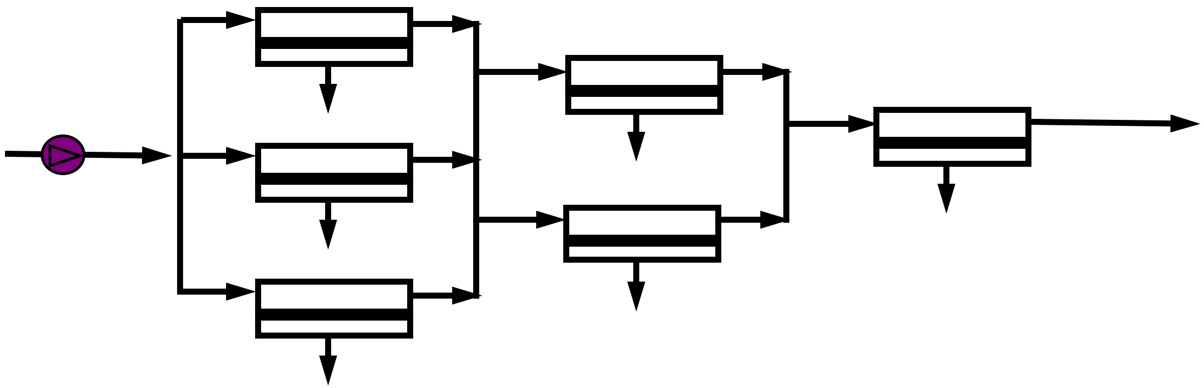
Example of Process Recovery

- Repeat the exercise with 50% recovery per stage, what is the production rate of the third stage?



Staging

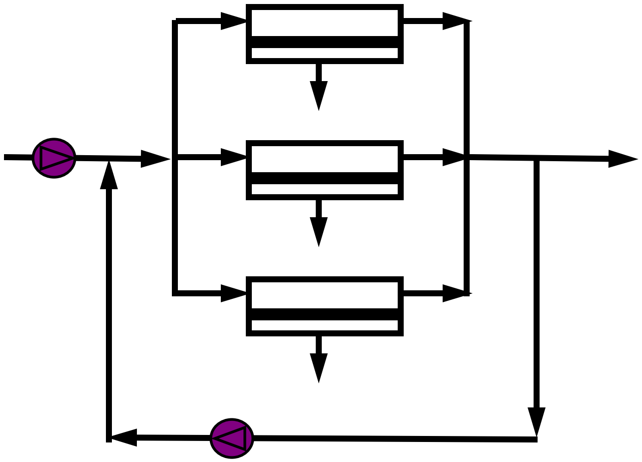
- In RO and NF operations, membranes are often staged



tapered design compensates for loss of feed volume through system

Recirculation

- In MF and UF, some concentrate is often recirculated to the inlet

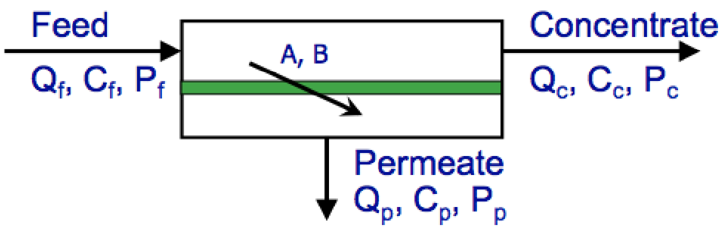


  - Flexible (can control degree of recirculation)
  - Economics (tradeoff between power for recirculation pump and additional recovery)

Material Balance in Membrane Separation

- Mass balance for water flow

$$Q_f = Q_c + Q_p$$



- Mass balance for solute flux

$$Q_f C_f = Q_c C_c + Q_p C_p$$

- Product recovery

$$r = (Q_p/Q_f)\cdot 100\%$$

- Global Rejection

$$R = \left(\frac{C_f - C_p}{C_f}\right)\cdot 100\% = \left(1 - \frac{C_p}{C_f}\right)\cdot 100\%$$

Rejection (R)

- Location-specific ratio of product concentration and feed concentration
- Global rejection…

$$R = \left(1 - \frac{c_p}{c_f}\right) * 100\%$$

where c_p is the solute concentration in the permeate and c_f is the solute concentration in the feed

- Global system rejection…

$$R_{mass} = \left(1 - \frac{c_p}{c_f} r\right) * 100\%$$

  - May yield different value as function of time
  - Variability of feed, permeate $\{C_p = f(R)\}$, membrane condition…

Rejection (R)

- Local rejection due to change in bulk feed concentration in the flow channel

$$R = \left(1 - \frac{c_p}{c_{wall}}\right) * 100\%$$

$$c_{wall} \geq c_{bulk} \geq c_{feed}$$

- If we know the permeate flux and mass transfer coefficient (we will talk about it later), the concentration at the membrane surface can be predicted by calculating a polarization factor (PF)… $c_{wall} = PF \cdot c_{bulk}$

- Apparent rejection calculated based on bulk concentration:

$$R_{apparent} = \left(1 - \frac{c_p}{c_{bulk}}\right) * 100\%$$

Temperature Effects

- Higher transmembrane pressure in the winter, or
- More membranes in the winter to prevent fouling/cleaning
- Water demand difference between summer and winter may offset loss in membrane productivity
- Membrane fouling

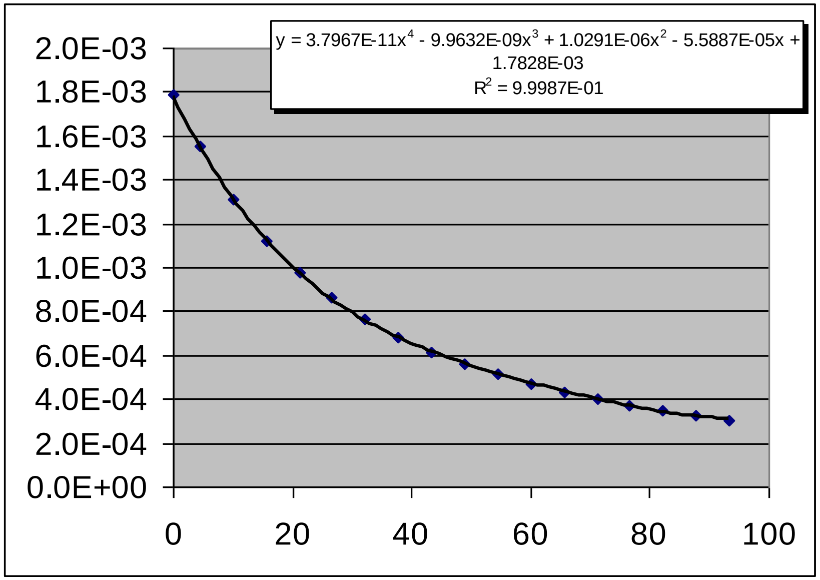
http://watertreatmentguide.com/temperature_correction.htm

Temperature Effects

- Change in temperature may result in a wide range of effects that go beyond the viscosity of the permeate alone
- Different ways to model effects of temperature:
  - Arrhenius equation: $J_T = J_{20} \exp(s/T)$
  - J_{20} = permeate flux at reference temperature of 20 °C
  - s = empirical constant, membrane specific
  - T = temperature
    - For MF and UF: $Flux_{20} = Flux_T (\mu_T/\mu_{20})$; or $\frac{J_T}{J_{25}} = 1.03^{(T-25)}$
  - Temperature Corrected Flux (TCF)

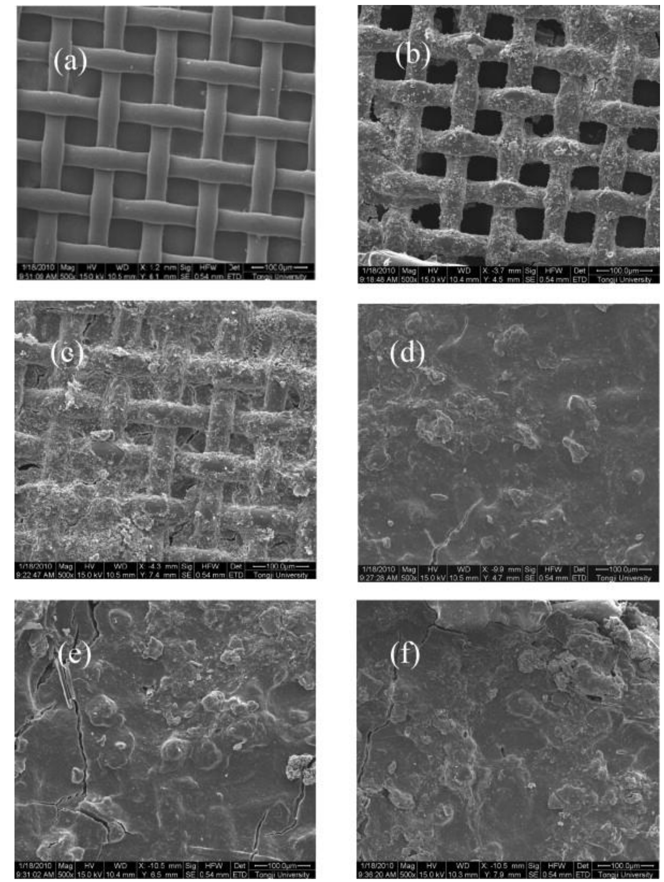
Temperature Effects

- Primary effect due to influence on viscosity
- For temperatures in the range of 0-35 °C
  - μ (centipoise) = $1.777 - 0.052\,T + 6.25\text{x}10^{-4}\,T^2$
  - centipoises = Pa-sec x 1,000
  - μ (Pa-sec) = $3.797\text{x}10^{-11}\,T^4 - 9.963{*}10^{-9}\,T^3 + 1.029\text{x}10^{-6}\,T^2 - 5.589\text{x}10^{-5}\,T + 1.783\text{x}10^{-3}$

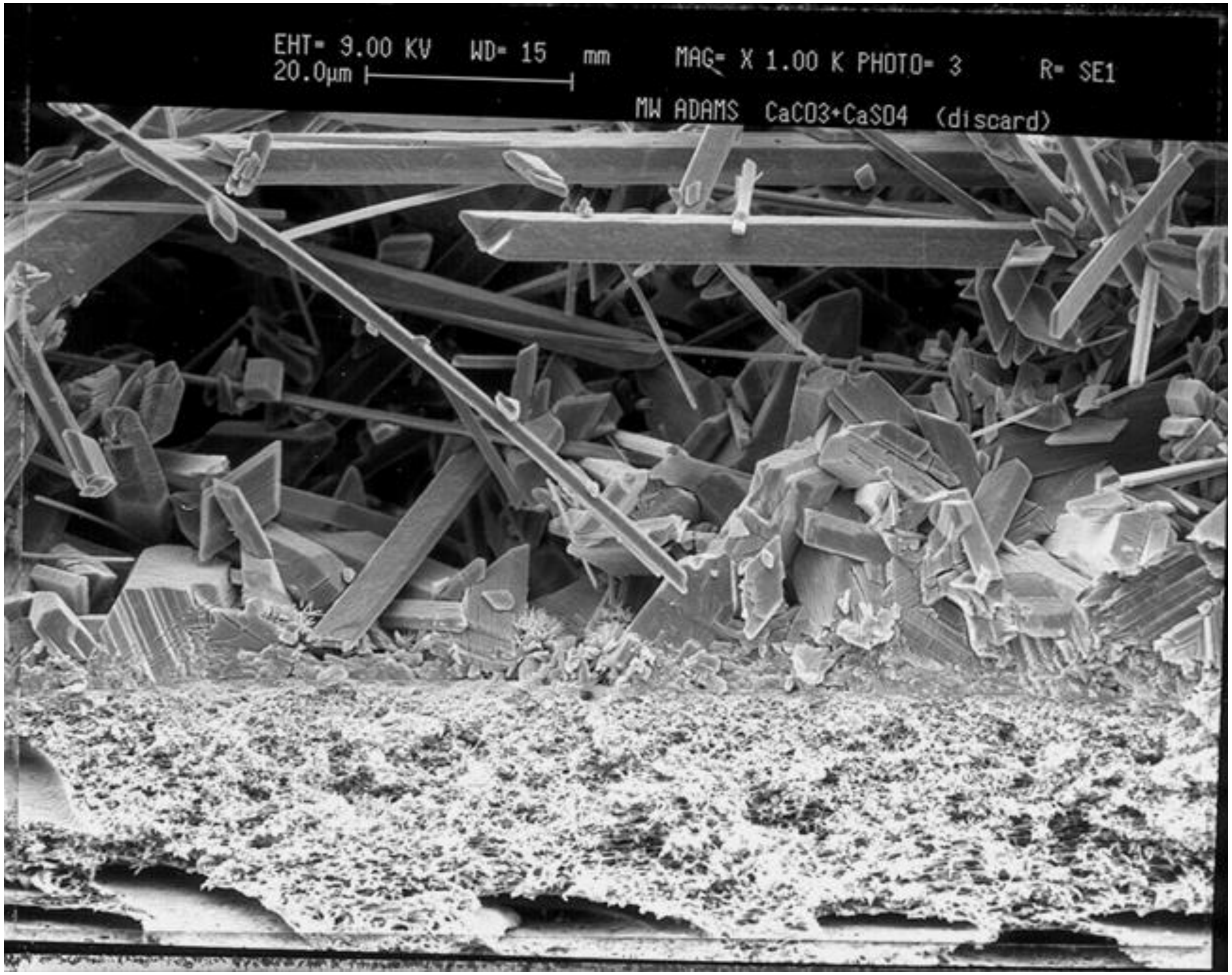


Membrane Fouling

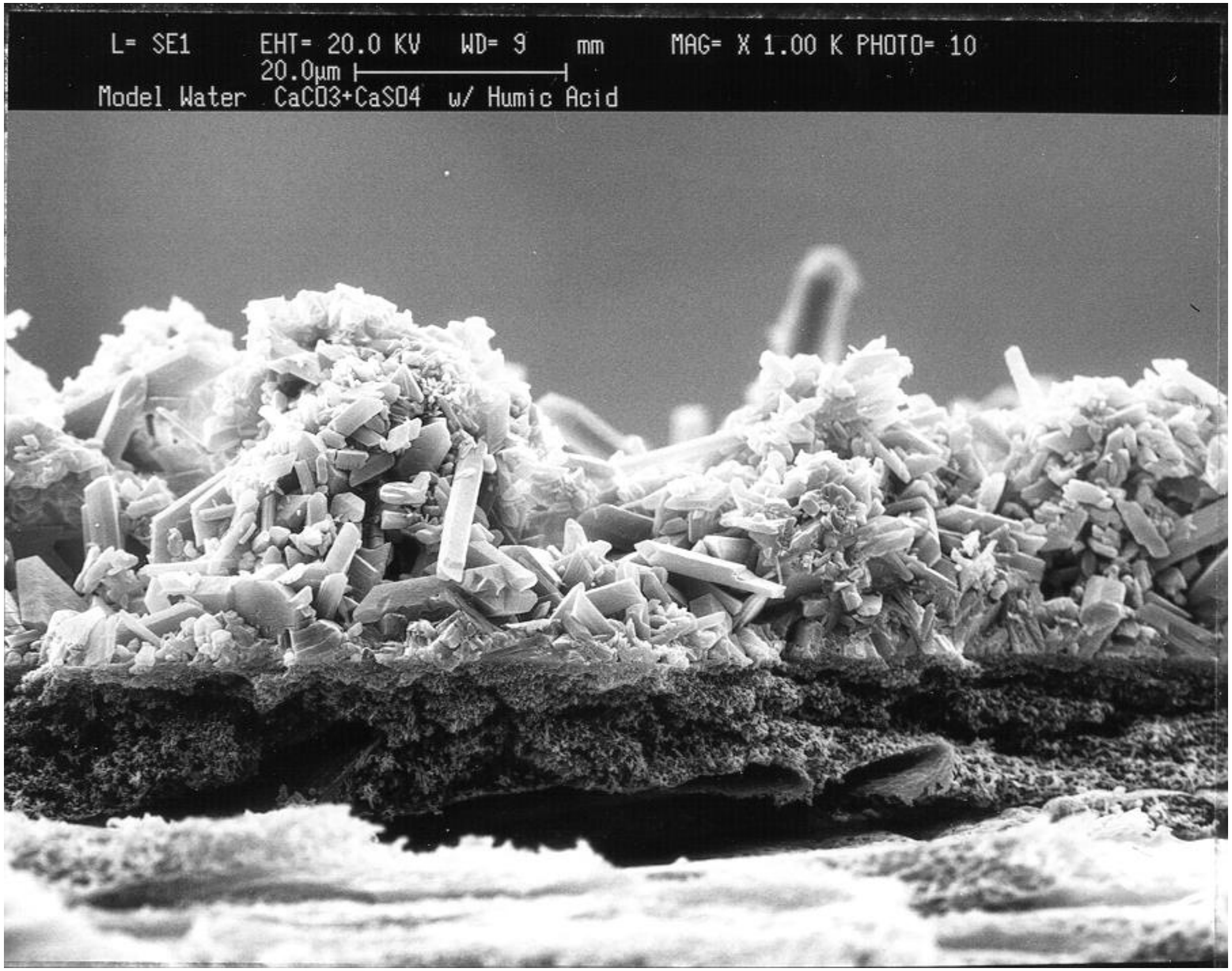
- Deposition
  - Silt and suspended solids
- Scaling
  - Inorganic deposits formed due to concentration of sparingly soluble salts beyond the chemical solubility limit
- Biofouling
  - Microbiological growth entering or within element
- Organic fouling
  - Interactions of natural or synthetic organics



Scaling SEM


EHT= 9.00 KV WD= 15 mm MAG= X 1.00 K PHOTO= 3 R= SE1
20.0µm
MW ADAMS CaCO3+CaSO4 (discard)

Scaling SEM


L= SE1 EHT= 20.0 KV WD= 9 mm MAG= X 1.00 K PHOTO= 10
20.0μm
Model Water CaCO3+CaSO4 w/ Humic Acid

Silt Density Index (SDI)

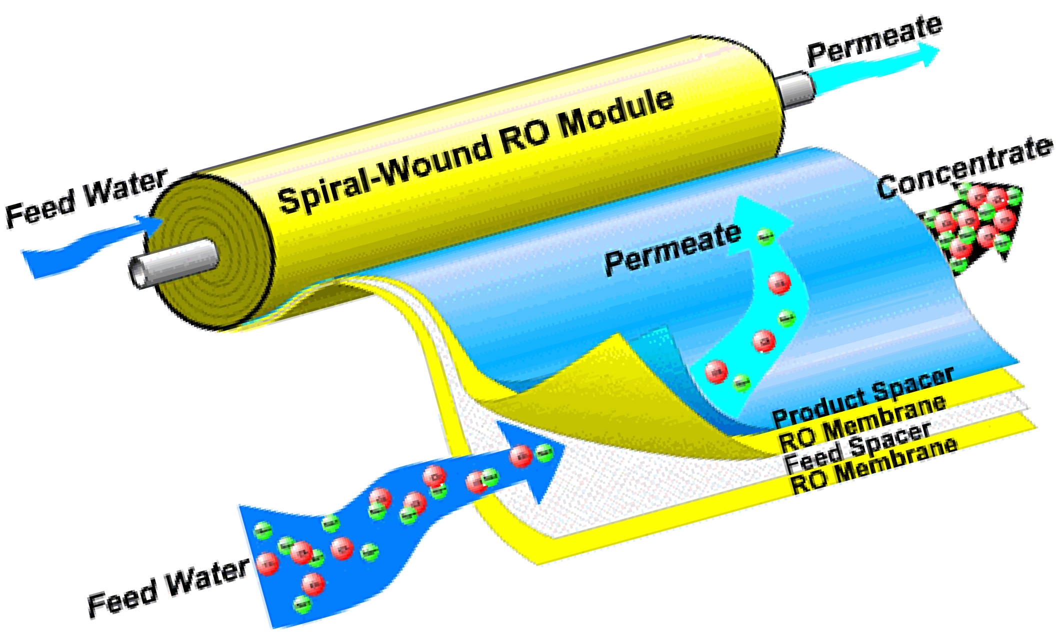
- Empirical test of filterability
- Measures the tendency of a raw water to foul a membrane
  - Use 0.45 µm filter in a dead-end filtration cell
  - t_i – time required to filter a fixed volume of raw water through a clean membrane (~500 ml)
  - t_f – time required to filter the same volume after the membrane has been used for a defined length of time
  - Standard conditions: 47 mm filter, 2 bar (30 psi) transmembrane pressure, total time (t_t) of 900 sec

$$SDI = \frac{100\left(1 - t_i / t_f\right)}{t_t}$$

Water Treatment Membrane Processes

Microfiltration and Ultrafiltration

COLORADO SCHOOL OF MINES
EARTH ▲ ENERGY ▲ ENVIRONMENT



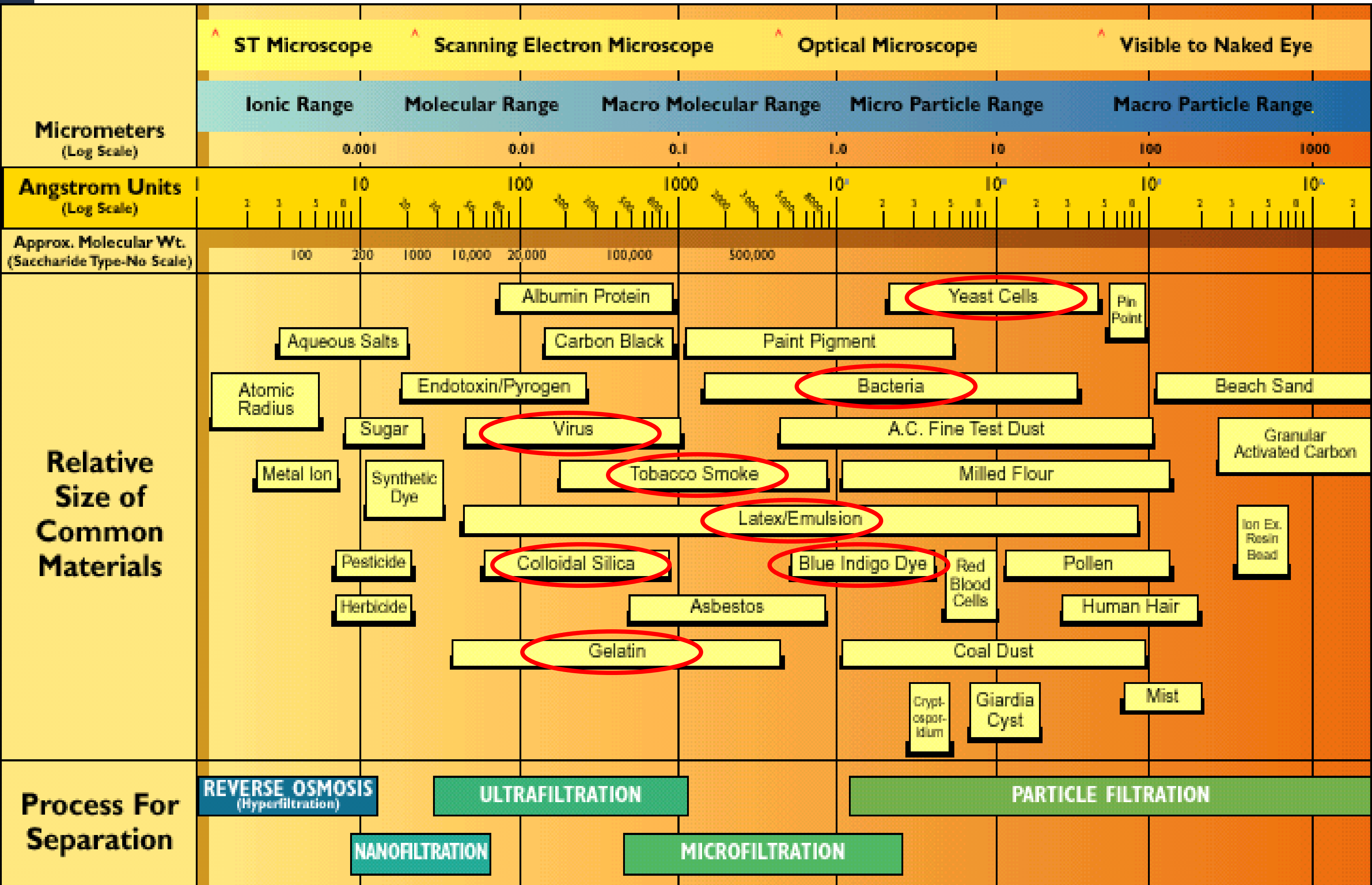
Overview

- Initial use of deep filtration microfilters…disposable, not sustainable…
- MF membranes provide removal by retention of contaminants on the membrane surface
- Lowest pressure membrane process
- Pore size of 0.05 – 5 micron
- Cake filtration provides additional removal capabilities …smaller particles than pore size can be removed

Current Status

- MF and UF generally accepted as being capable of meeting filtration requirements for drinking water production
  - Turbidity removal / disinfection
- MF can resolve the conflict between need to provide primary disinfection and DBP formation
- LT2ESWTR identified membranes as treatment technique for higher level removal of cryptosporidium
- Substantial diversification of membrane processes and configurations

Filtration Spectrum



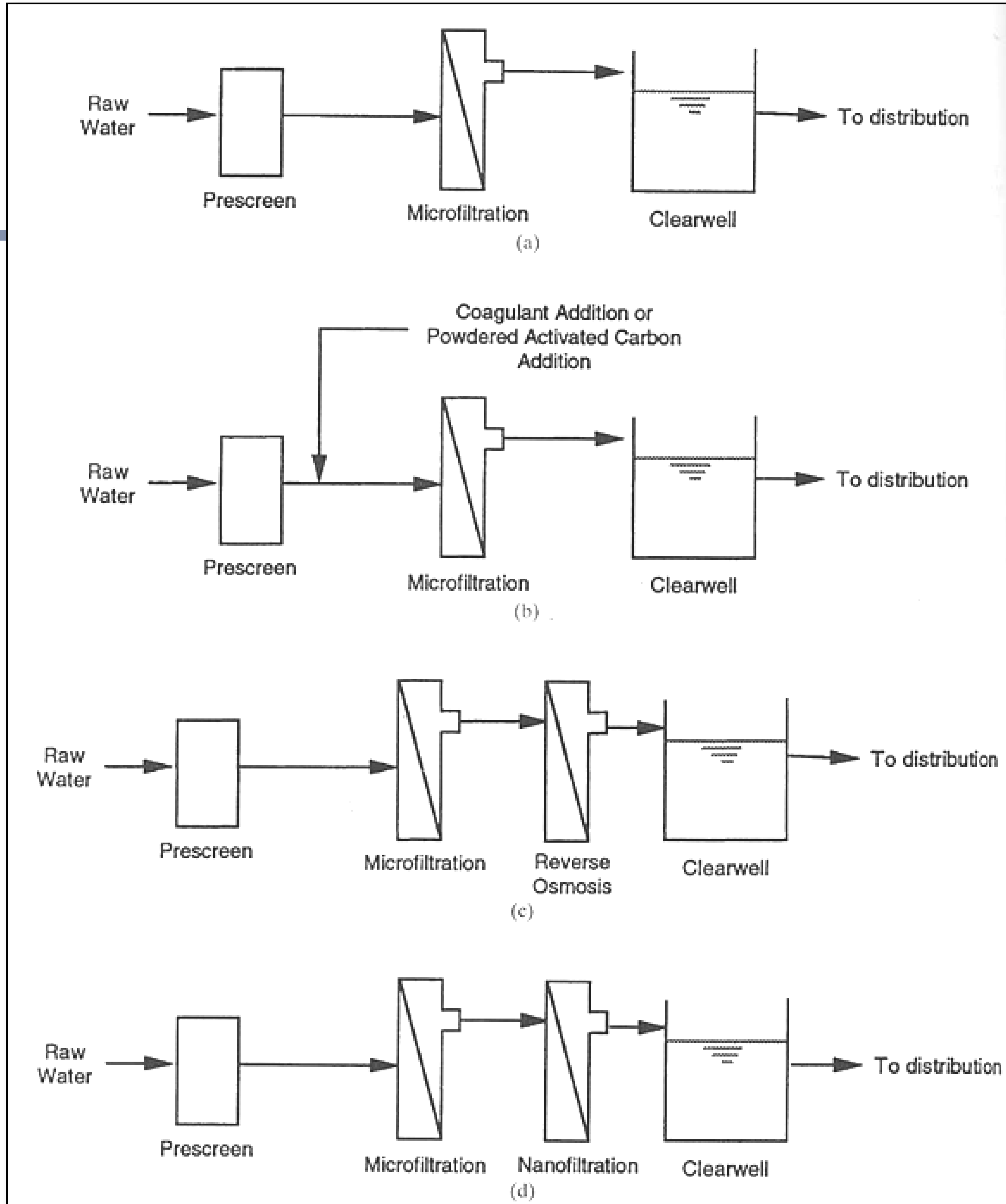
Treatment Capabilities

- Removal of particulate matter
  - Turbidity
  - Particles
  - Microbial control
- Removal of organic and inorganic species when feed water is pretreated (coagulation, adsorption)
  - DOC/DBP precursors
  - color / taste / odor
  - Pesticides
  - Iron / manganese (aeration / chemical oxidation)
  - Arsenic

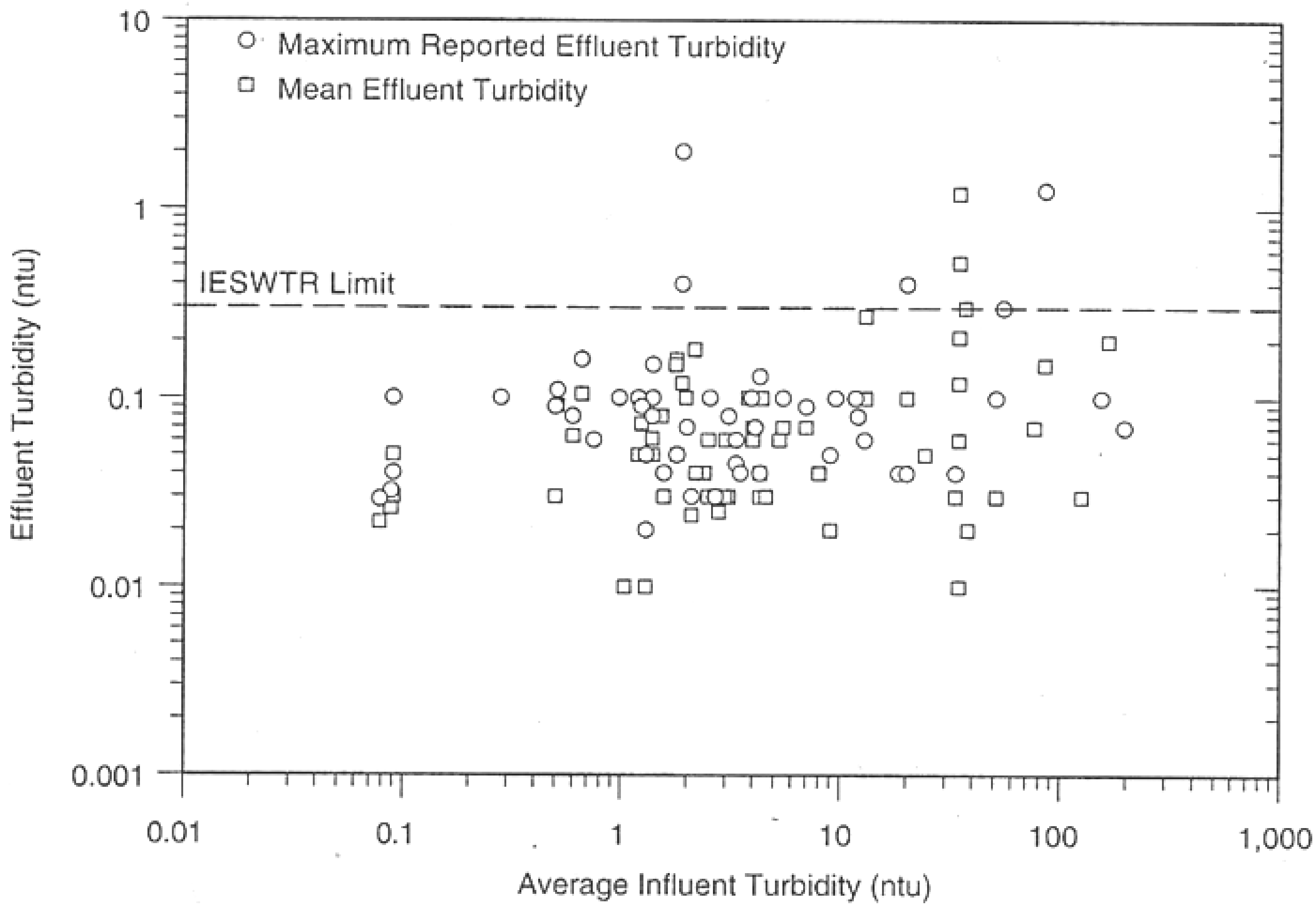
Treatment Capabilities

Parameter		Pretreatment needed for substantial removal	
		MF	UF
Particulate/microbial	Turbidity	None	None
	Protozoa	None	None
	Bacteria	None	None
	Viruses	Coagulation	None
Organic	TOC	Coagulation / PAC	Coagulation / PAC
	DBP precursor	Coagulation / PAC	Coagulation / PAC
	Color	Coagulation / PAC	Coagulation / PAC
	T&O	Coagulation / PAC	Coagulation / PAC
	Pesticides	PAC	PAC
Inorganic	Iron & manganese	Oxidation	Oxidation
	Arsenic	Coagulation	Coagulation
	Hydrogen sulfide	Oxidation	Oxidation

Modes of Application

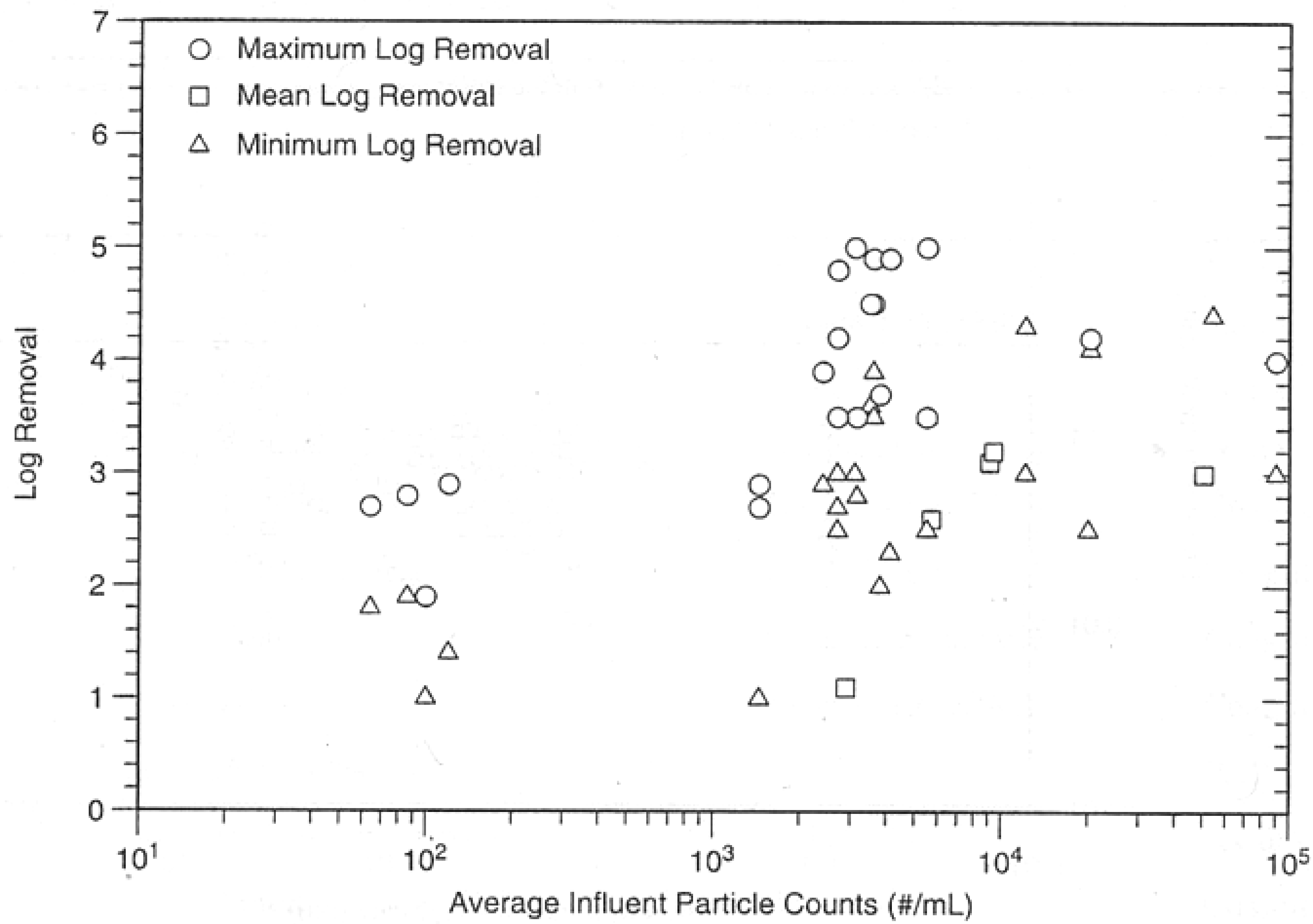


Turbidity Removal



Summarized influent and effluent turbidity results from the literature review

Particle Removal



Summarized MF/UF particle count log removals from the literature review

Water Permeation Across Clean MF/UF Membranes

- Pure water transport through clean porous membrane is:
  - Directly proportional to transmembrane pressure (ΔP)
  - Inversely proportional to viscosity (μ)
- Modeled using modified form of Darcy's Law:

$$J = \frac{Q_{total}}{A} = \frac{\Delta P}{\mu R_m}$$

- R_m ≡ hydraulic resistance of the clean membrane to water permeation (units?)

Example: Membrane resistance

- An MF membrane is tested in the lab by filtering clean, deionized water and the flux is found to be 2,000 LMH (L/m^2-hr) at 20 °C and 0.7 bar. Calculate the membrane resistance coefficient.

Water Permeation Across Clean MF/UF Membranes

- Absolute transmembrane pressure vs. pressure gradient
- Typical units of water flux
  - gfd (gal/ft^2-day)
  - LMH (l/m^2-hr)
- LMH x 1.7 = gfd

Flow Through a Cylindrical Pore (Poiseuille's Law)

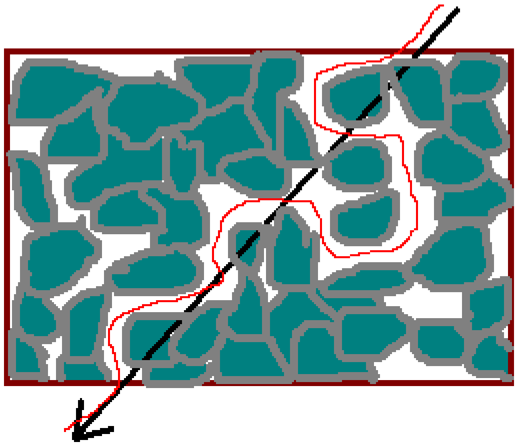
$$Q_{1pore} = \frac{\pi r^4}{8\mu} \frac{\Delta P}{\Delta z}$$

- $\Delta P/\Delta z$ is pressure gradient
- In real membranes pores are not perfectly cylindrical →
  - Dimensionless tortuosity factor (τ) is often introduced

Flow Through Membrane Pores

$$Q_{total} = \frac{\pi r^4}{8\mu\tau}\frac{\Delta P}{\Delta z} A\rho_{pore}$$

ρ_{pore} = #pores/A



$$J = \frac{\pi r^4}{8\mu\tau}\frac{\Delta P}{\Delta z}\rho_{pore} = \frac{\varepsilon r^2}{8\mu\tau}\frac{\Delta P}{\Delta z} \quad \Rightarrow \quad R_m = \frac{8\tau\Delta z}{\varepsilon r^2}$$

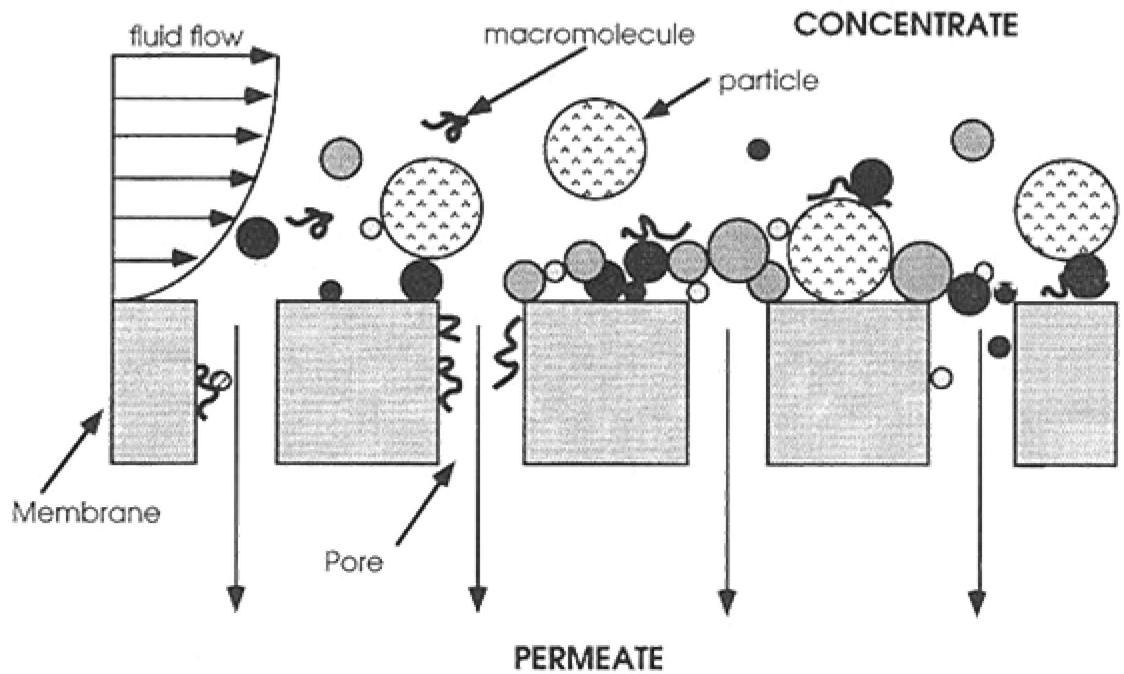
Significant Parameters

- Pore size has the highest effect on resistance to water flow
- Pore size distribution
- Specific flux for membrane comparison
  - Calculated based on area on feed side

$$\Delta P = \frac{P_{Fi} + P_{Fo}}{2} - P_p$$

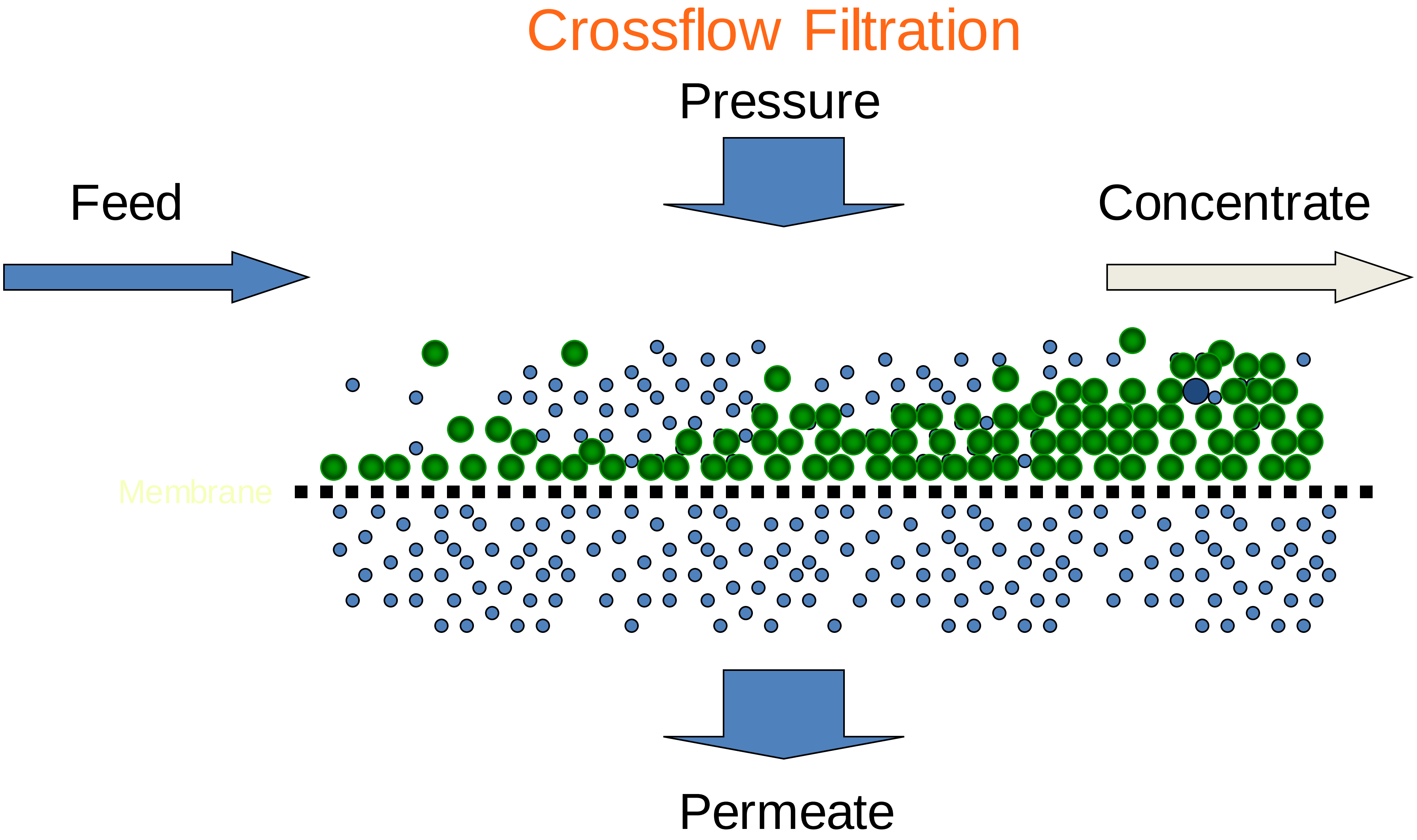
Reduction in Membrane Productivity

- Flux Decline Mechanisms
  - Fouling
  - Concentration polarization
  - Resistance in Series



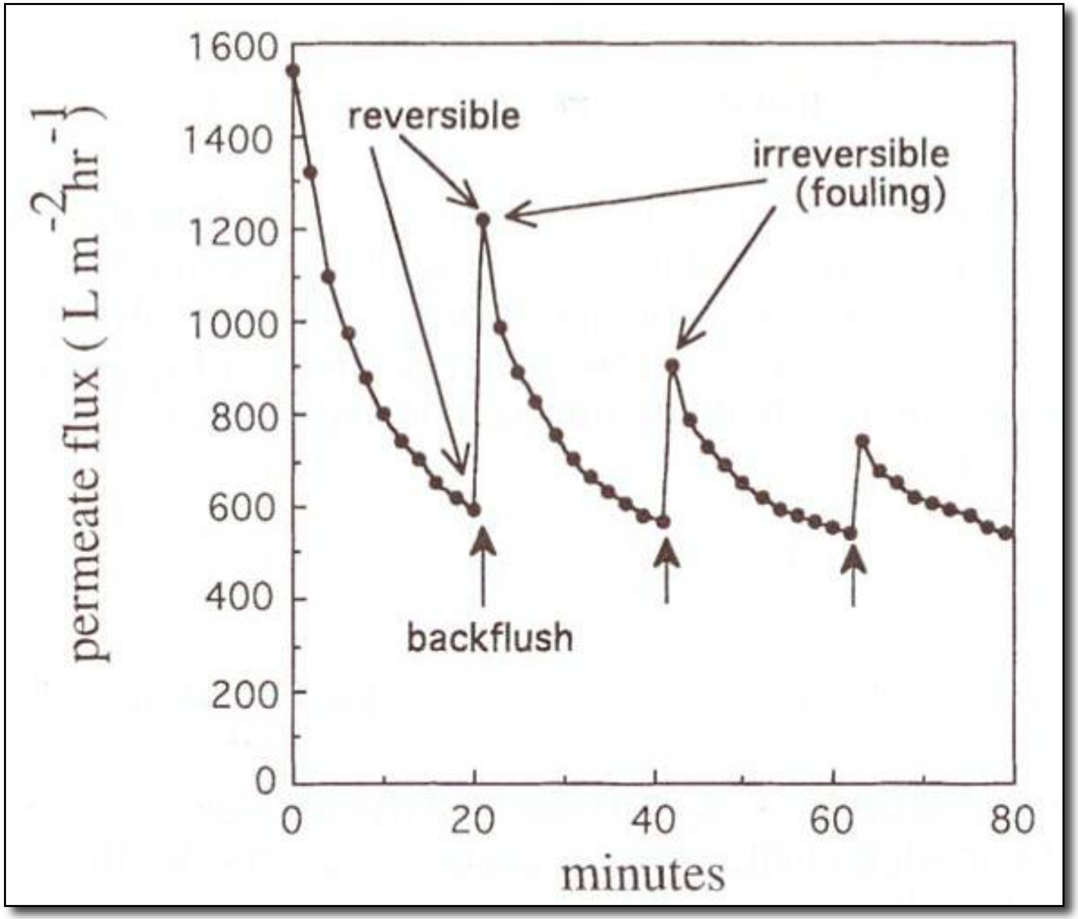
http://books.google.com/books?id=SqHUSd3vk1oC&pg=PA160&lpg=PA160&dq=temperature+correction+factor+ultrafiltration&source=web&ots=21o8VFucPS&sig=hpvbPyECYwEiLkX4BZSi

Reductions in Permeate Flux



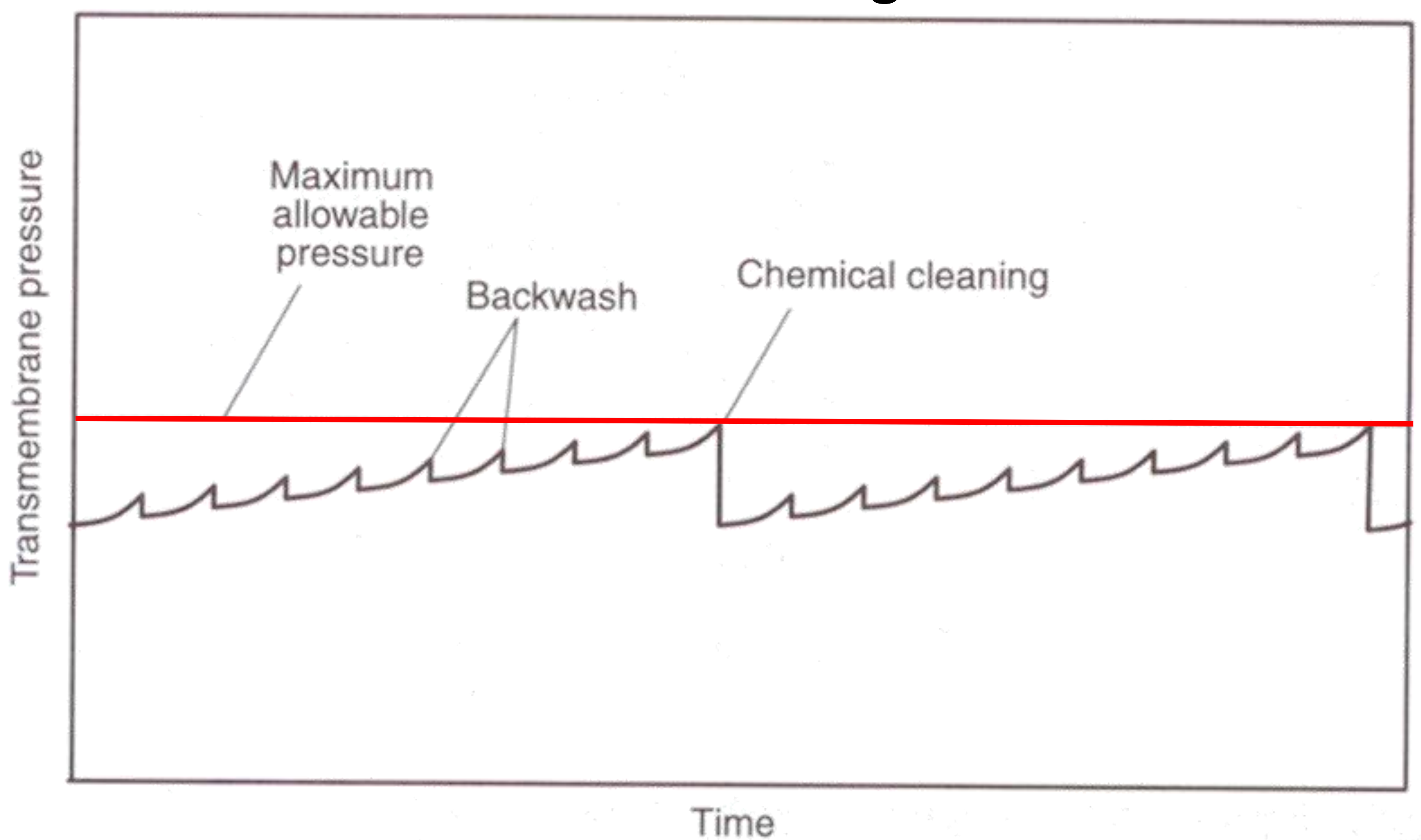
Reduction in Permeate Flux over Time

- Reversible vs. irreversible fouling



Increase in Transmembrane Pressure Over Time

- Reversible vs. irreversible fouling



Classwork: UF Recovery

- Assuming the following operating scenario:
  - UF treatment plant with 48 HydraCap60 membrane elements
  - 20 min operation with average productivity of 55 gfd
  - backwash with product water for 45 sec uses 1500 gal of permeate

- What additional information is needed?
- What is the water recovery rate?
- What is the backwashing flux?

http://www.membranes.com/pdf/HYDRAcap.pdf