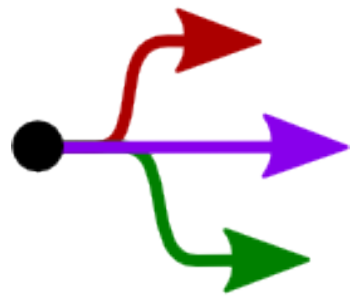
Separation Processes:
Membranes
ChE 4M3



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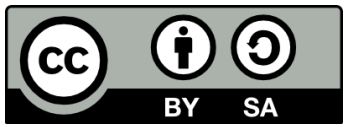

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We appreciate:

- if you let us know about **any errors** in the slides
- **any suggestions to improve the notes**

All of the above can be done by writing to

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If reporting errors/updates, please quote the current revision number: 284

Administrative issues

- Project topics are posted. Due by 12 November 2013
  1. Treatment of dissolved solids in fracking wastewater
  2. Removing CO_2 from a gas phase stream of mixed hydrocarbons
  3. Removing non-valuable particulate solids (dust) from a gas-phase stream
  4. *Challenge Project*: design and operation of a device or method to create drinking-quality water in a region of hardship
     - water is not easily accessible, and is contaminated
     - electricity is not readily available
     - consumers of the water would have little/low money to pay for your water
     - the device/method must not require technical sophistication to operate

Membranes

[Flickr: 21182585@N07/2057883807]

[Flickr: 21182585@N07/3574729377]

Quick activity

On a sheet of paper write

- bullet points *and/or*
- draw a diagram *and/or*
- describe

"what you know about membranes"

References

- Perry's Chemical Engineers' Handbook, 8th edition, chapter 20.
- Wankat, "Separation Process Engineering", 2nd edition, chapter 16.
- Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", chapter 2.1.
- Seader, Henley and Roper, "Separation Process Principles", 3rd edition, chapter 14.
- Richardson and Harker, "Chemical Engineering, Volume 2", 5th edition, chapter 8.
- Geankoplis, "Transport Processes and Separation Process Principles", 4th edition, chapter 7 (theory) and chapter 13.
- Ghosh, "Principles of Bioseparation Engineering", chapter 11.
- Uhlmann's Encyclopedia, "Membrane Separation Processes, 1. Principles", DOI:10.1002/14356007.a16_187.pub3

Why use membranes?

Some really difficult separations:

- finely dispersed solids; density close to liquid phase; gelatinous particles
- dissolved salts must be removed
- non-volatile organics (e.g. humic substances)
- biological materials: sensitive to the environment
- biological materials: aseptic operation is required
  - cannot centrifuge
  - cannot sediment

It is usually worth asking:

How does nature separate?

- energy efficient
- effective
- maybe slow?

Why use membranes?

Relatively new separation step ("new" meaning since 1960 to 1980s)

- often saves energy costs over alternative separations
  - ambient temperature operation
- often easier to operate and control
- more compact
- lower capital cost than alternatives

Modules:

- feed stream split into parallel units
- easier to maintain and replace parts
- can be expanded as needs grow

[Henk Koops' slides, GE Water and Process Technologies]

Challenges in membrane design

Challenges that still remain:

- withstanding high pressure differences but still have a thin membrane
- dealing with fouling and cleaning
- increasing selectivity (separation factor) for specific application areas
- uniformity of pore sizes
- temperature stability (e.g. steam sterilization)

Membrane manufacture is a complex area: very fruitful area for polymer engineers

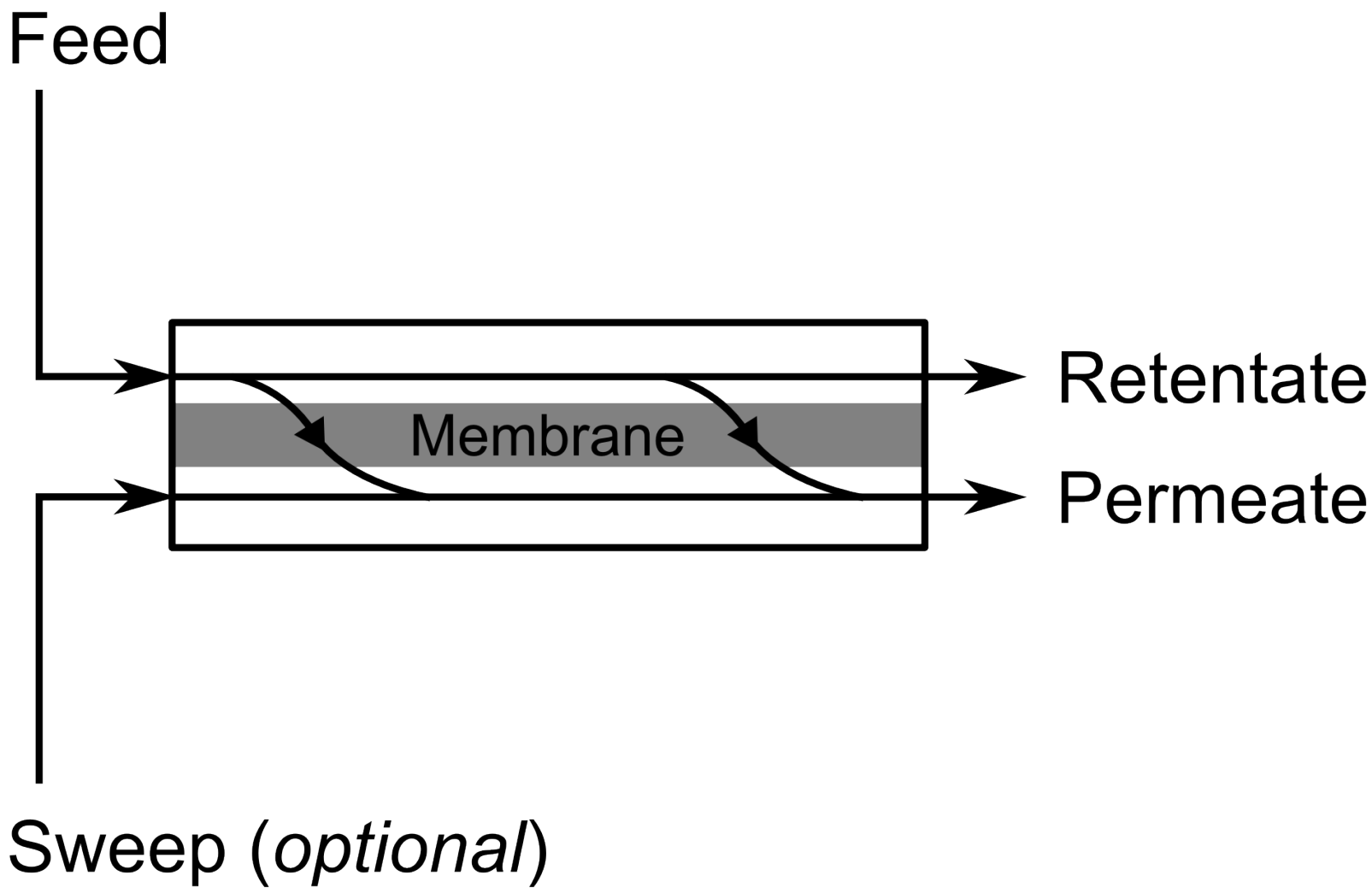
Market size

TABLE 20-16 Membrane Market in 2005

Segment	$M/yr Size	Applications	Characteristics
Dialysis	~2,000	Medical	Mature growing 5%
Reverse osmosis	~500	Water treatment	Growing 10%
Microfiltration	~500	Water, food, pharm.	
Ultrafiltration	~400	Water, food, pharm.	Growing 10%
Gas separation	~500	Nitrogen	
Electrodialysis	~100	Water	
Pervaporation	~5	Solvent/water	Nascent
Facilitated transport	0	None	In development

[Perry's: chapter 20, 8ed]

Let's formalize some terminology



[Seader, Henley and Roper, p 501]

More terminology

semipermeable: partially permeable, e.g. your skin allows certain size particles in, but not others

mass separating agent: the membrane itself

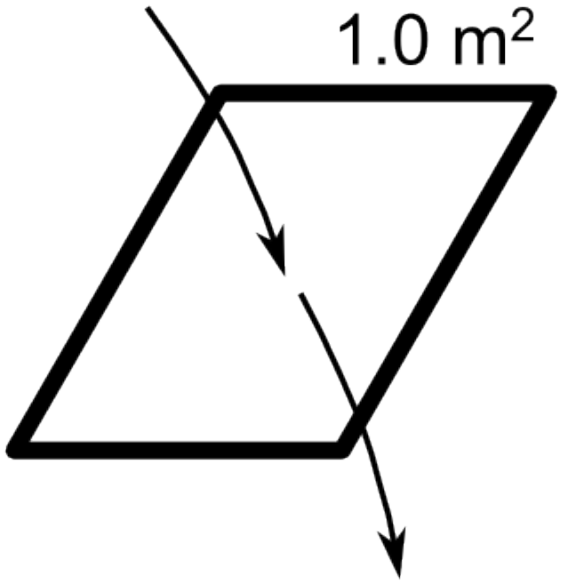
energy separating agent: the applied pressure (pressure drop)

$$\text{porosity} = \frac{\text{area of open pores}}{\text{total surface area}}$$

What is flux?

The (volumetric) or (molar) or (mass) flow per unit time for 1 unit of area

- $J = \text{flux} = \dfrac{\text{transfer rate}}{\text{transfer area}}$
- e.g. 42 $\text{mol.s}^{-1}\text{.m}^{-2}$
- never simplify the units: write 13 $\left(\text{m}^3\text{.s}^{-1}\right)\text{.m}^{-2}$
- you may, and probably should, omit the brackets: 13 $\text{m}^3\text{.s}^{-1}\text{.m}^{-2}$
- do not write 13 m.s^{-1}



General principle

For a given unit area, we want the highest flux possible (at the lowest possible cost)

Membrane classification

Table 8.1. Classification of membrane separation processes for liquid systems

Name of process	Driving force	Separation size range	Examples of materials separated
Microfiltration	Pressure gradient	10–0.1 μm	Small particles, large colloids, microbial cells
Ultrafiltration	Pressure gradient	<0.1 μm–5 nm	Emulsions, colloids, macromolecules, proteins
Nanofiltration	Pressure gradient	~1 nm	Dissolved salts, organics
Reverse osmosis (hyperfiltration)	Pressure gradient	<1 nm	Dissolved salts, small organics
Electrodialysis	Electric field gradient	<5 nm	Dissolved salts
Dialysis	Concentration gradient	<5 nm	Treatment of renal failure

[Richardson and Harker, p 438]

Transport through a membrane

Why study theoretical models?

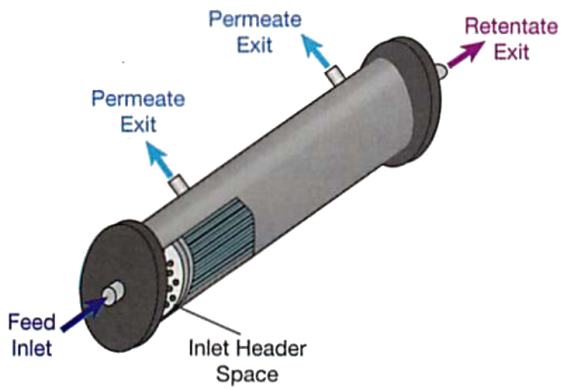
All forms of membrane applications rely to some extent on the same equation **structure**. The details will change.

Will allow us to:

- troubleshoot problems with the process
- predict expected impact of improvements/changes to the process
- used for crudely sizing the unit (order of magnitude estimates)

Examples you will be able to solve

1. how long should we operate unit at constant ΔP to achieve desired separation?
2. what is the mass transfer coefficient through the lab membrane?
3. what pressure drop (and therefore pump size) do I expect?
4. how many cassettes (area) does this application require?



The general equation

$$\frac{\text{transfer rate}}{\text{transfer area}} = \text{flux} = \frac{(\text{permeability})(\text{driving force})}{\text{thickness}} = \frac{\text{driving force}}{\text{resistance}}$$

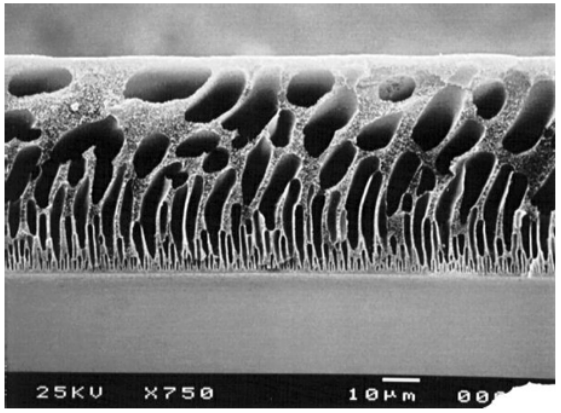
Symbolically:

$$\rho_f \frac{Q_p}{A} = \frac{\rho_f}{A} \cdot \frac{dV}{dt} = J = \frac{(\text{permeability})(\text{driving force})}{L} = \frac{\text{driving force}}{R}$$

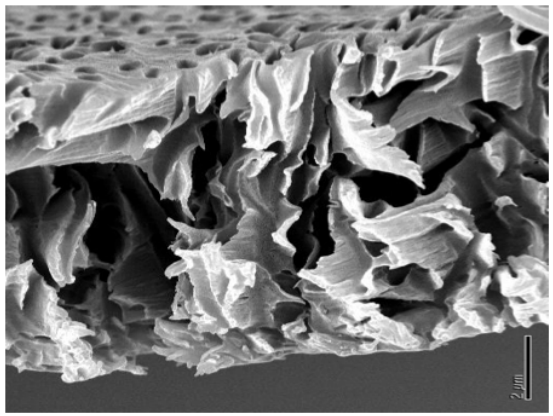
- $\text{permeance} = \dfrac{\text{permeability}}{L} = \dfrac{1}{\text{resistance}} = \dfrac{1}{R} =$ "mass transfer coeff"
- permeance: easier to measure
- permeance units: depend on choice of (driving force) and J
- resistance $= f$(thickness L, viscosity, porosity, pore size)
- we will specifically define resistance in each case

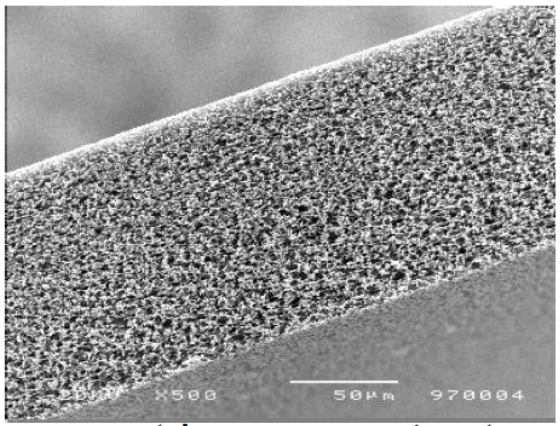
Microfiltration

- 0.1μm to 10μm pores: sieving mechanism
- conventional filters: not effective below ~ 5 μm
- microfiltration membranes: generally symmetric pores
- polysulfone membrane
- (surface) porosity as high as $\epsilon = 0.8$
- driving force $= \Delta P$: 100 to 500 kPa
- high fluxes at low TMP (trans-membrane pressure)
- application areas:
  - yeast cells harvesting
  - wine/beer/juice clarification
  - bacteria and virus removal
  - air filtration
  - cytology: concentrate up cells



finger like structure


symmetric open structure

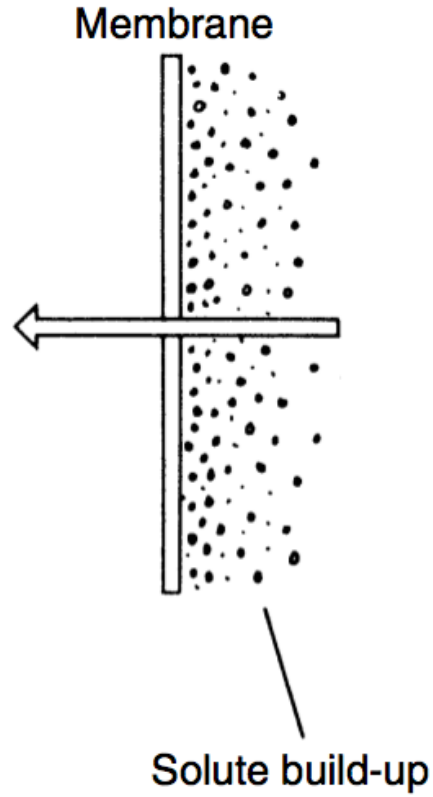


symmetric spongy structure

General modelling equation applied

$$\frac{\rho_f}{A} \cdot \frac{dV}{dt} = \text{Flux} \quad = J = \frac{\Delta P}{\mu \left(R_m \ell_M + R_c L_c \right)}$$

$$\frac{\rho_f}{A} \cdot \frac{dV}{dt} = \text{Flux} \quad = J = \frac{\Delta P}{\mu \left(R'_m + R'_c \right)}$$

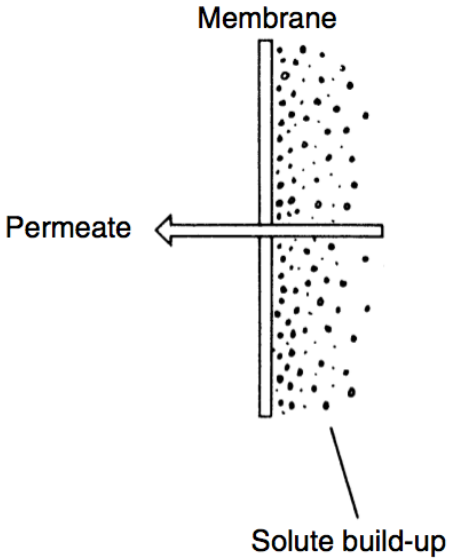


J	$[\text{kg.s}^{-1}.\text{m}^{-2}]$	permeate flux
μ	$[\text{kg.m}^{-1}.\text{s}^{-1}]$	permeate viscosity
ΔP	$[\text{Pa}] = [\text{kg.m}^{-1}.\text{s}^{-2}]$	TMP varies for different applications
R_m	$[\text{m.kg}^{-1}]$	resistance through membrane (small)
R_c	$[\text{m.kg}^{-1}]$	resistance through cake (large)
ℓ_m	[m]	membrane thickness
L_c	[m]	effective cake thickness
ρ_f	$[\text{kg.m}^{-3}]$	fluid density
R'_c	$[\text{m}^2.\text{kg}^{-1}]$	"cake resistance"

[Illustration from Richardson and Harker, Ch8]

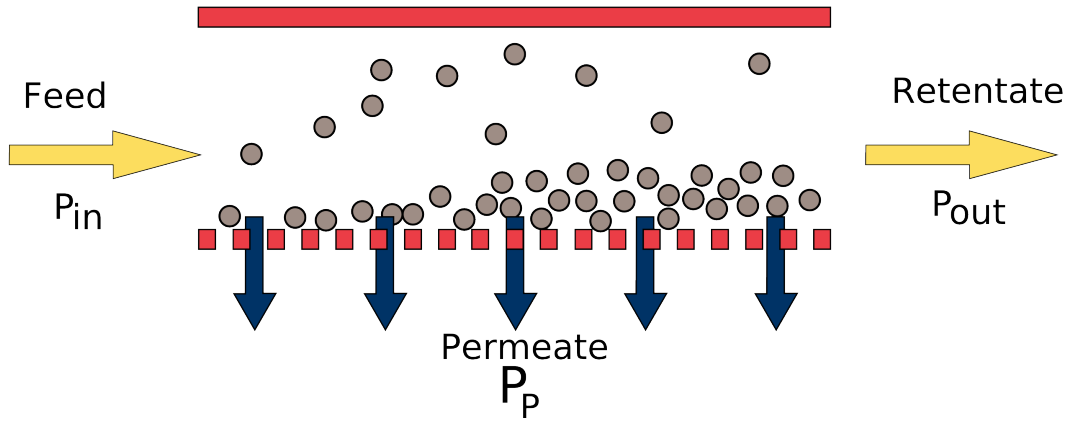
Flow patterns for microfiltration

Dead-end flow



- only for very low concentration feeds
- else becomes rapidly clogged
- air filtration and virus removal applications

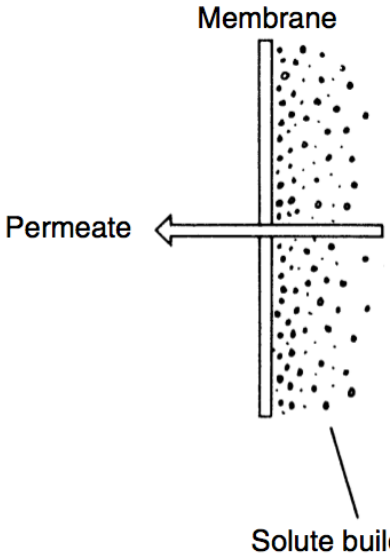
Cross-flow (TFF)



- TFF = tangential flow filtration
- main purpose?
  - microfiltration: tends to have cake build up
  - induces shearing to erode cake
  - mobile slurry for downstream
  - reduces cake resistance, R_c
- $\Delta p = \frac{P_{in} + P_{out}}{2} - P_P$

Flow patterns for microfiltration

Dead-end flow



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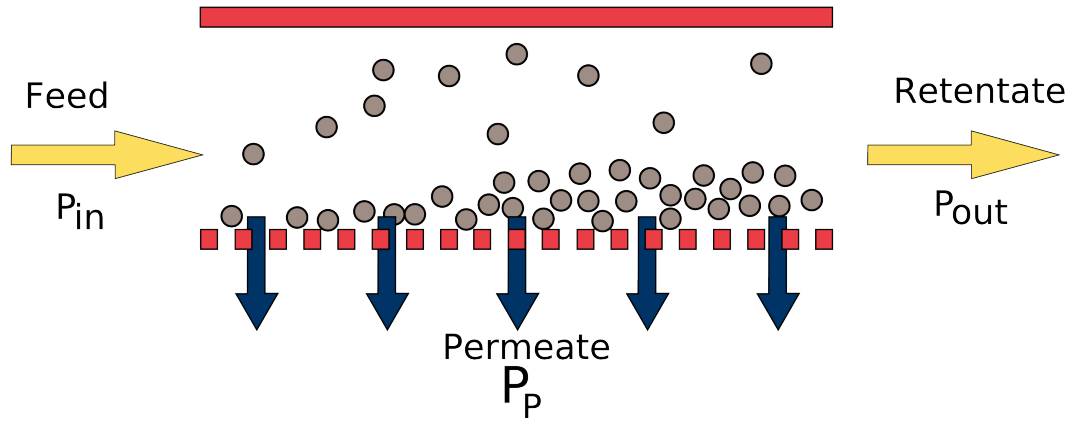

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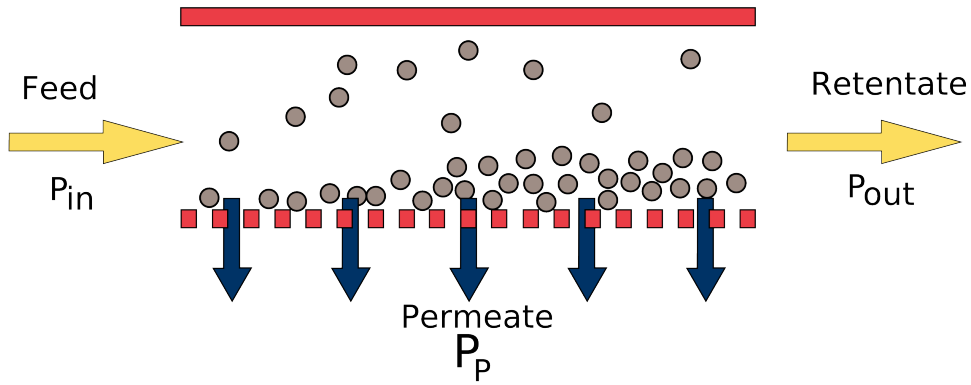
Dead-end flow vs cross-flow geometries

Dead-end flow

- cake thickness increases with time: $L_c(t)$
- implies cake resistance changes with time: $R'_c(t)$
- so for a constant ΔP, implies $J(t)$ falls off

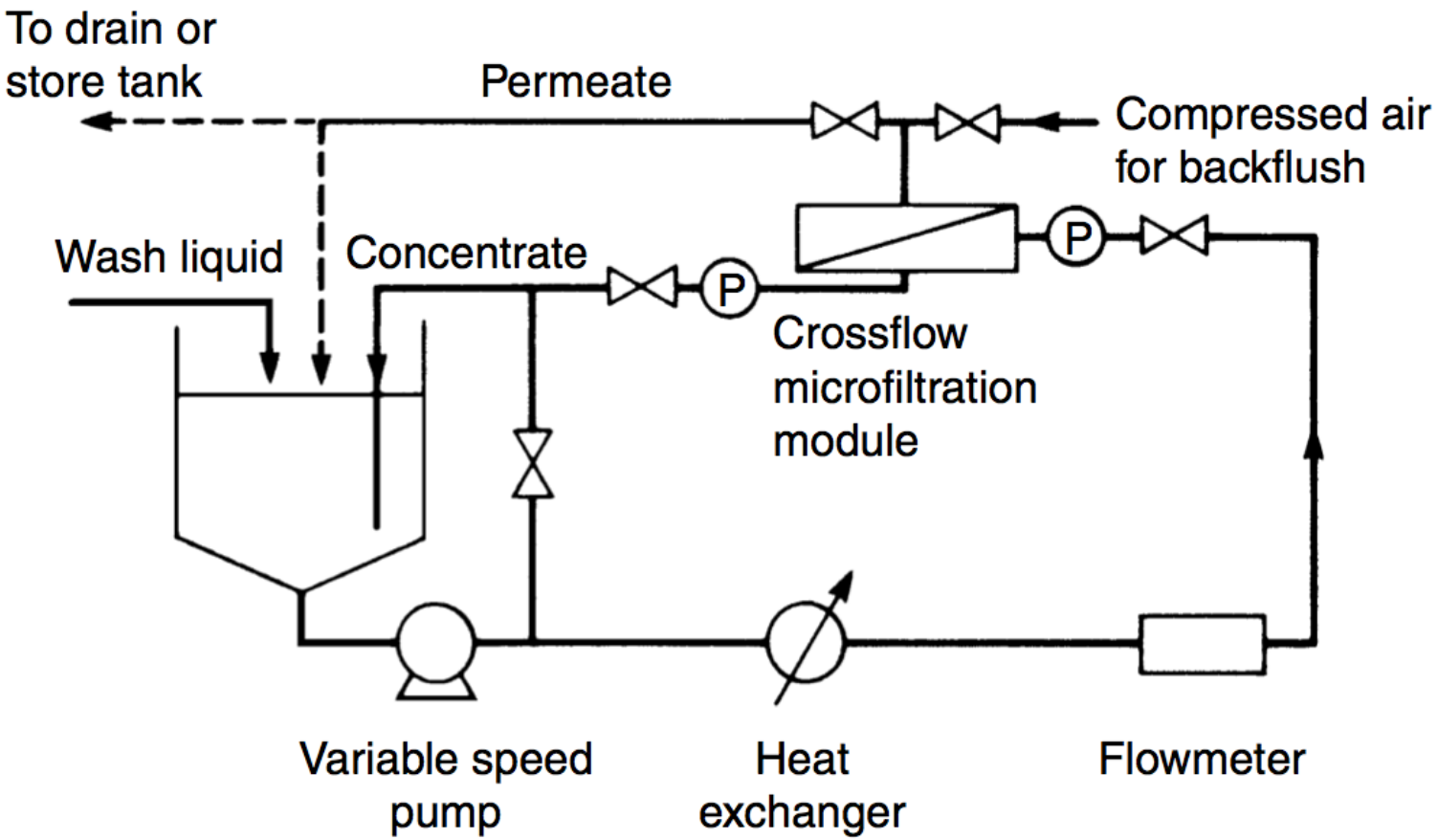
$$J = \frac{\Delta P}{\mu\left(R'_m + R_c L_c\right)}$$

Cross-flow (TFF)



- fluid velocity: 1 to 8 $m.s^{-1}$ tangentially
- keeps mass transfer resistance low
- for a given ΔP: TFF allows us to obtain higher fluxes than dead-end (usually ΔP is 100 to 500 kPa)
- cannot take lab test results with a filter cloth dead-end and apply it to cross-flow situation

Cross-flow flowsheet



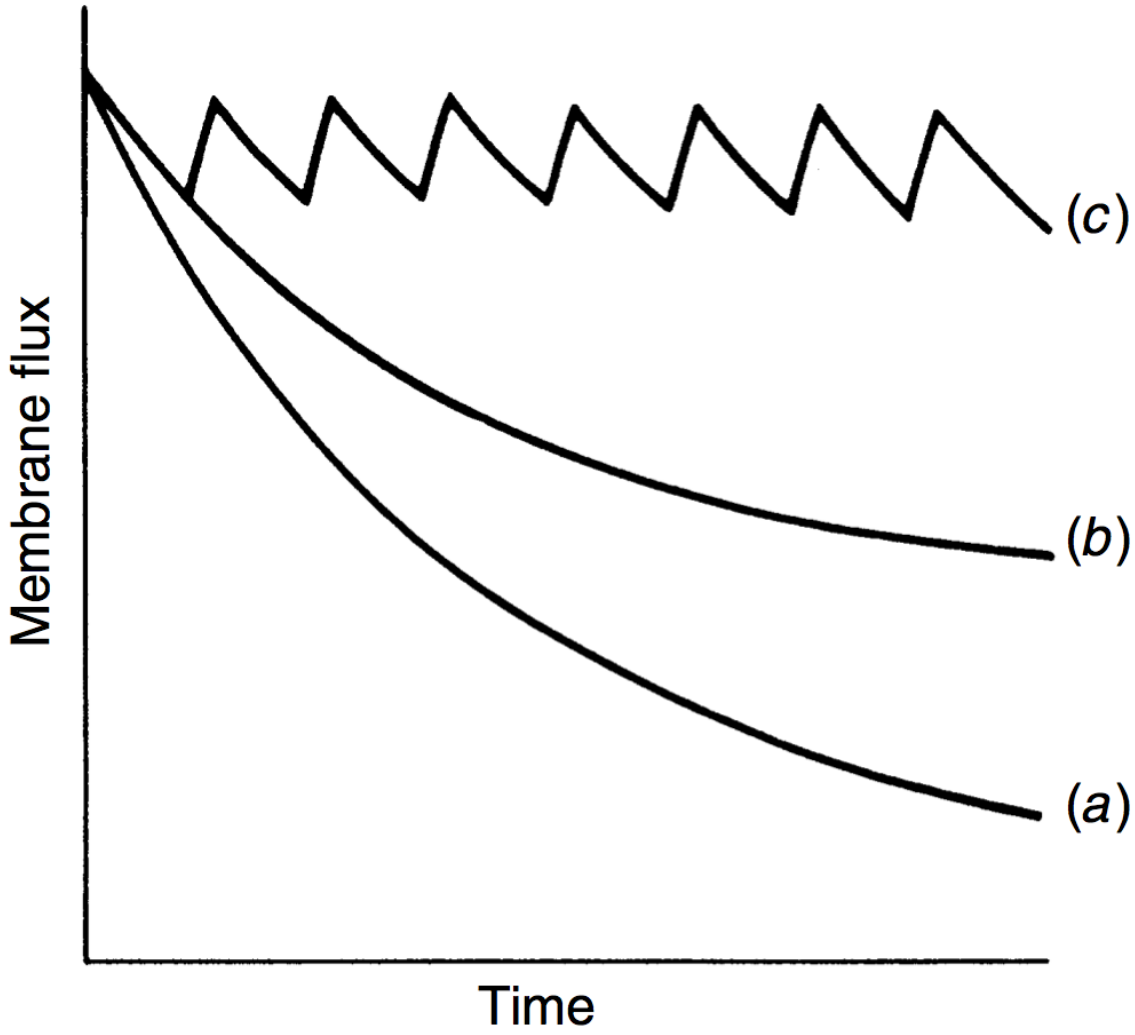
[Illustration from Richardson and Harker, Ch8]

How to pressurize the unit?

1. Supply feed at pressure; valve at retentate to adjust/control ΔP
2. Draw a vacuum at permeate and pull material through membrane

Question: why recycle the retentate stream?

Dealing with fouling



a. slow cross-flow velocity
b. high cross-flow velocity
c. high cross-flow with regular backwashing

[Richardson and Harker, Ch8]

Factors to improve flux

- increase pressure difference
- regular backflush
- choose alternative membrane structure
- feed concentration kept low
- shear rate (velocity in cross-flow): reduces $R'_c = R_c L_c$
- increase temperature of feed
- nature of the solids deposited: affects resistance R_c

Question

A microfiltration membrane operating with pure feed of water produces a flux of 0.06 $kg.s^{-1}.m^{-2}$ when operated with a TMP of 150 kPa.

1. What is the resistance due to the membrane? Specify the units.
2. If operated with a protein-water mixture at a 200 kPa pressure difference, a flux of 0.0216 $kg.s^{-1}.m^{-2}$ is measured at steady state. What is the resistance due to cake build-up? Specify the units.
3. Next, *estimate* the pressure drop required to achieve a flux of 0.035 $kg.s^{-1}.m^{-2}$ [$Ans \sim 325$ kPa].

To consider: are we likely to achieve fluxes of 0.1 $kg.s^{-1}.m^{-2}$ with this membrane? If not, how could we?

A **very crude** estimate of the membrane resistance, R'_m

- Assume the pores are cylinders of diameter D with length ℓ_M
- The velocity in this tube **for pure solvent** is

$$v = \frac{(D^2)(\Delta P)}{32\mu\ell_M} \qquad \text{Hagen-Poiseulle}$$

- Consider a 1 m^2 surface of tube pore openings, where ϵ is the fraction of pore openings of diameter D
- The total flux of solvent through all pores is

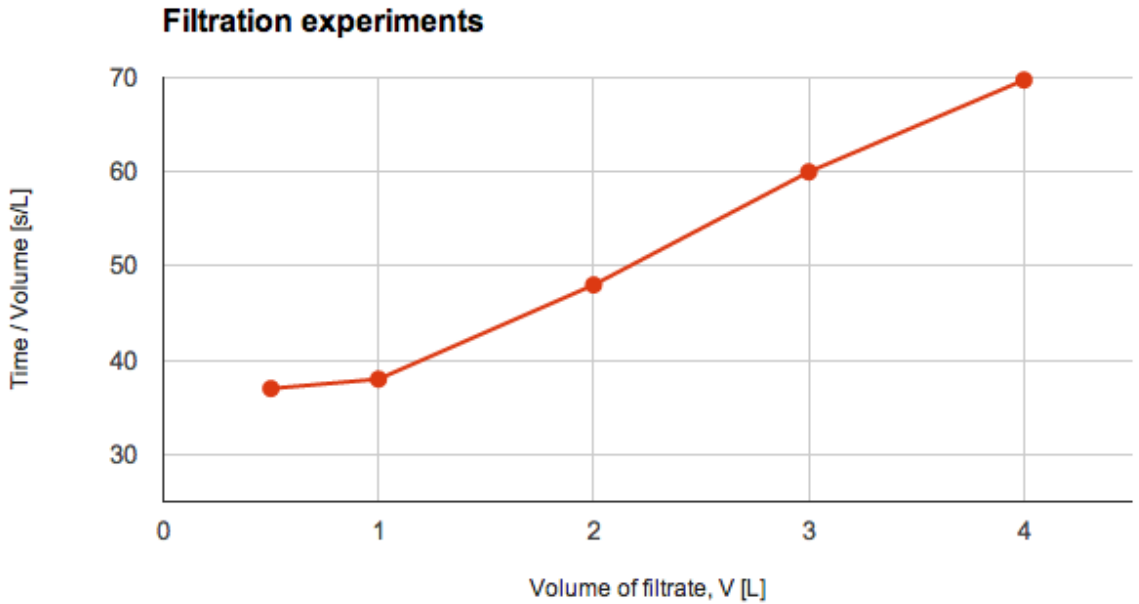
$$J = v\,\rho_f\,\epsilon = \frac{(D^2)(\Delta P)}{32\mu\ell_M}\,\rho_f\,\epsilon = \frac{\Delta P}{\mu\left(\dfrac{32\,\ell_M}{\rho_f D^2\,\epsilon}\right)} = \frac{\Delta P}{\mu\,R'_m}$$

- **Note**: true pores are of different sizes, they are not straight through the membrane; they bend and twist
- **Note**: this R'_m will always be too low

Estimating the cake resistance, R_c: for dead-end filtration

Exactly the same approach as we saw in the filtration section:

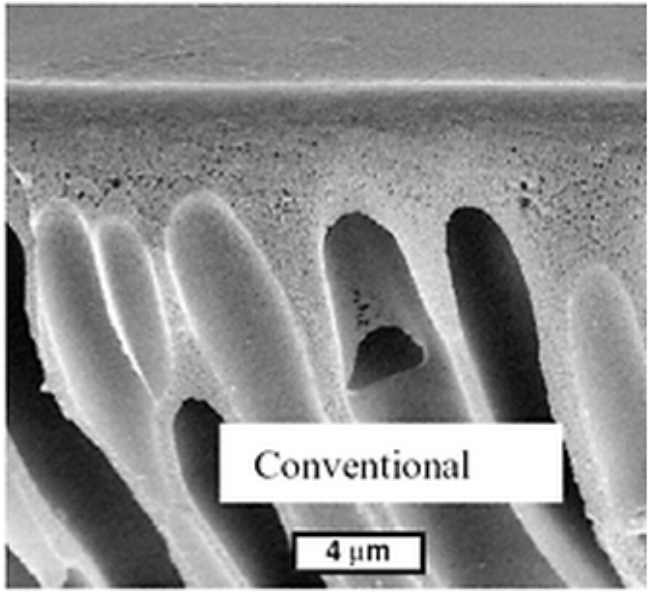
1. Measure V (volume of permeate) against time t at a constant and known ΔP

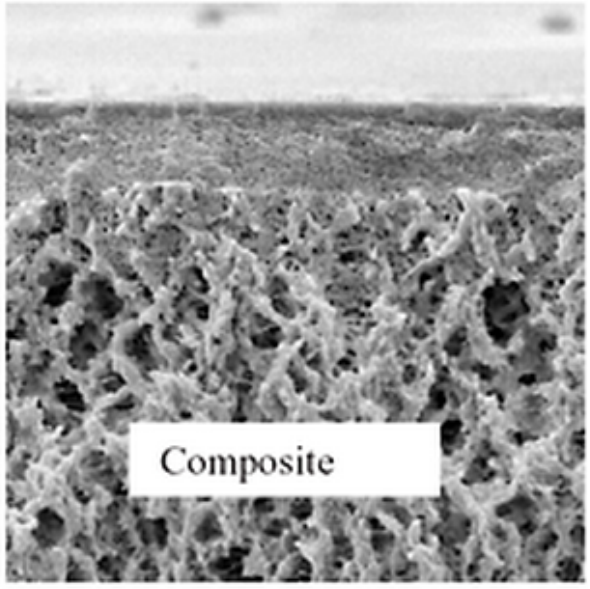


2. The slope is related to α, the specific cake resistance [m.kg^{-1}] (*we defined this in the filtration section*)
3. $R_c'(t) = \dfrac{\alpha C_S}{\rho_f A} V(t)$ will increase over time

Ultrafiltration (UF)

- 5 nm to 100 nm (0.1 μm) particles are retained
- 1 to 1000 kDa particles are retained (move to using molecular weight)
  - 1 dalton = 1 atomic mass unit
  - 1 kilodalton = 1000 dalton = 1000 g/mol
  - particles with lower molecular weight, e.g. most solvents, pass through
- pore sizes: 1 to 20nm
- typical fluxes:
  $J_v = 0.01$ to 0.5 $m^3.m^{-2}.hr^{-1}$
  $J_v =$ 10 to 500 $L.m^{-2}.hr^{-1}$ (LMH)
- asymmetric structure
- almost always operated in TFF (cross-flow filtration)





[Perry's 8ed; Ch20.4]

Ultrafiltration applications

UF: loosely considered: "cross-flow filtration at molecular level"

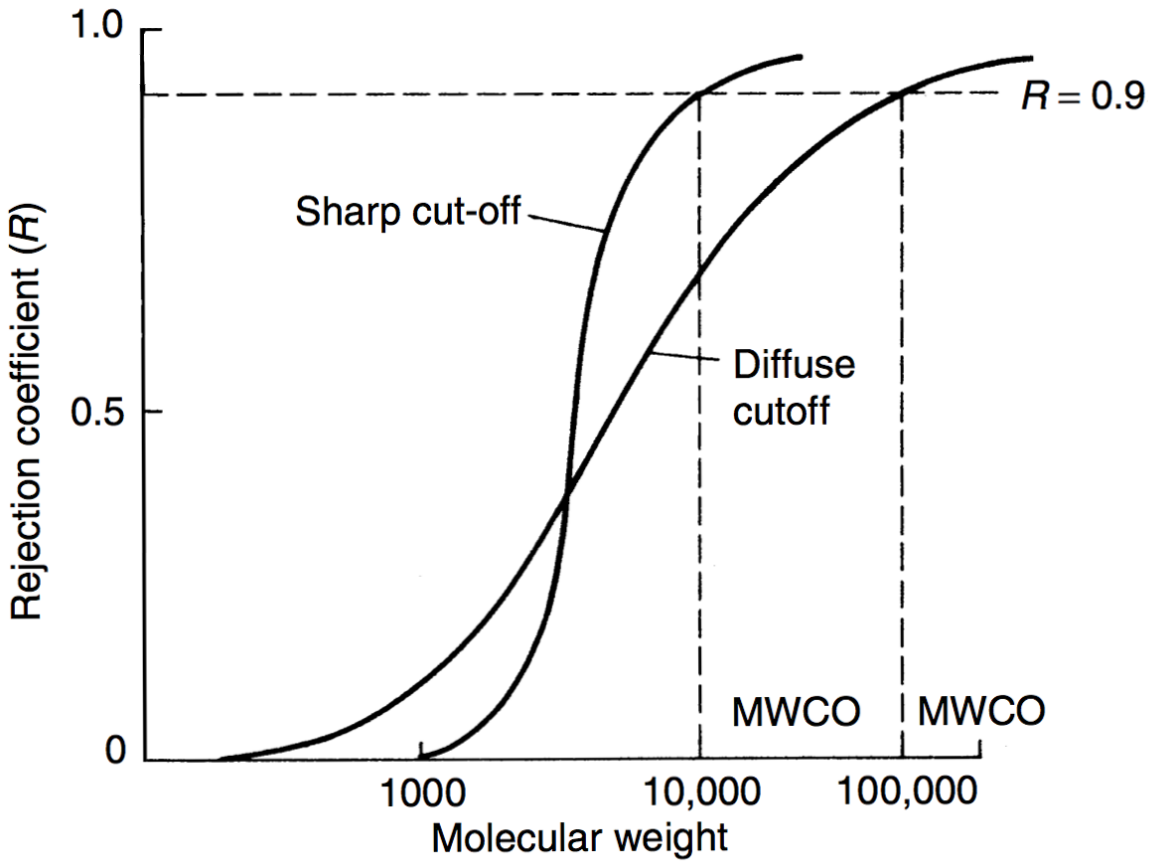
- Recovery of proteins and high molecular weight materials (solute)
- Permanent emulsions: e.g. oil phase will not pass
- Fine colloidal particles: e.g. paint/dyes
- Large molecules of interest might remain in retentate; permeate discarded
- e.g. albumin (egg white) concentration
- e.g whey processing (liquid "waste" after cheese-making):
  - centrifuge $\longrightarrow$ UF $\longrightarrow$ reverse osmosis (RO)
  - valuable proteins retained by UF
  - permeate sent to RO to concentrate smaller molecule sugars and salts
  - that RO concentrated permeate: used for ethanol and lactic acid production

More terminology

- permeate: the material passing through the membrane from feed to outlet side
- retentate: the material retained on the feed-side of the membrane
- solute: most often retained on the inside (feed side) of the membrane and deposited on the membrane wall
- solvent: the liquid phase that carries the solute
- gel effect: buildup of the solute on the membrane wall to form a high concentration gradient "gel"

Ultrafiltration (UF)

- driving force = ΔP of 0.1 to 1.0 MPa
- "tight", low-permeability side faces the TFF to retain particles
- this skin layer is about 10μm thick; provides selectivity, S
- open, high-permeability side mainly for mechanical strength



[Richardson and Harker, Ch8]

$$R = 1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}}$$

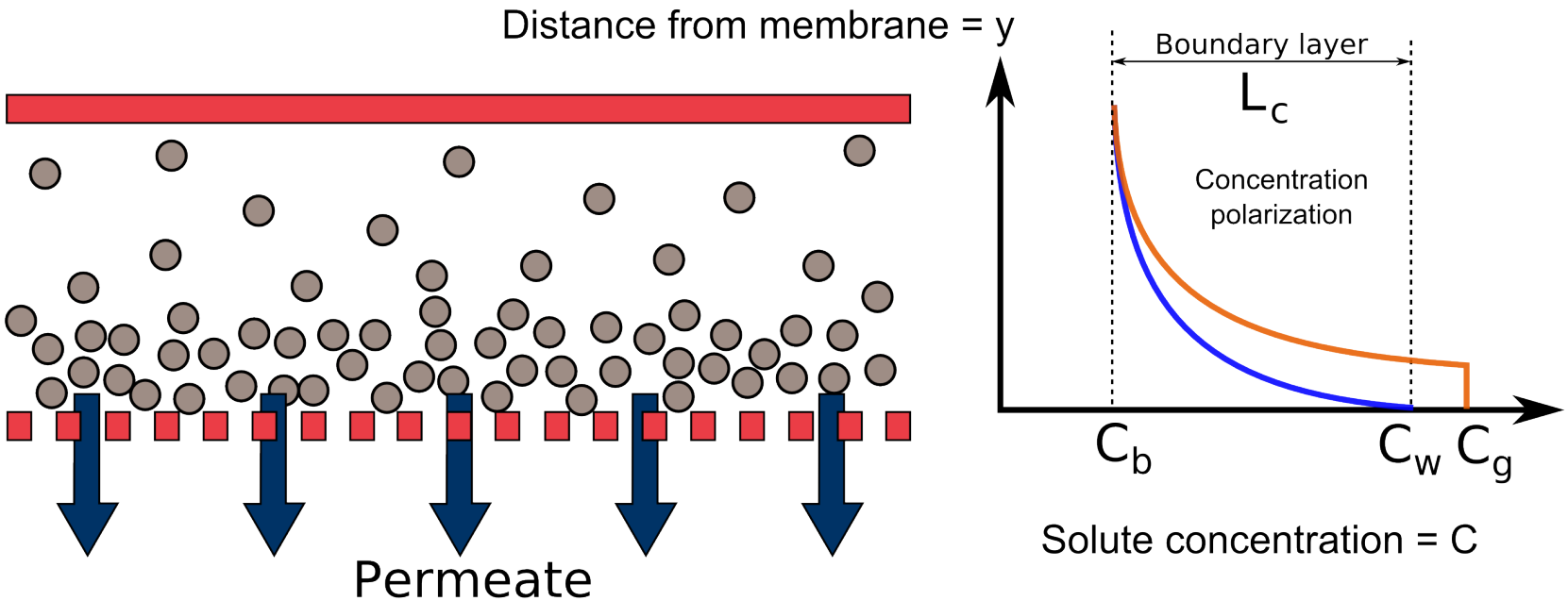
$$R = 1 - \frac{C_p}{C_f} = 1 - S$$

MWCO: molecular weight where $R = 0.9$

i.e. 10% of that molecular weight passes through to the permeate

Transport phenomena in UF

- solute (i.e. particles) carried towards membrane by solvent
- $J = \dfrac{\Delta P}{R_m + R_{cp}}$
- R_m = membrane resistance [m.s^{-1} if J is mass flux]
- R_{cp} = resistance due to "concentration polarization"
- R_{cp} effectively is the resistance due to solute boundary layer
- Mass concentration C_b (in bulk), steadily increasing to C_w (wall)
- Units of C are kg solute per m^3 solvent



Transport phenomena in UF

- **Solute** flux towards membrane: $\frac{J}{\rho_f} \cdot C = J_v C$
- **Solute** flux out of membrane (leakage): $J_v C_{\text{permeate}} \approx 0$

Net transport of solute $= J_v(C - C_p)$

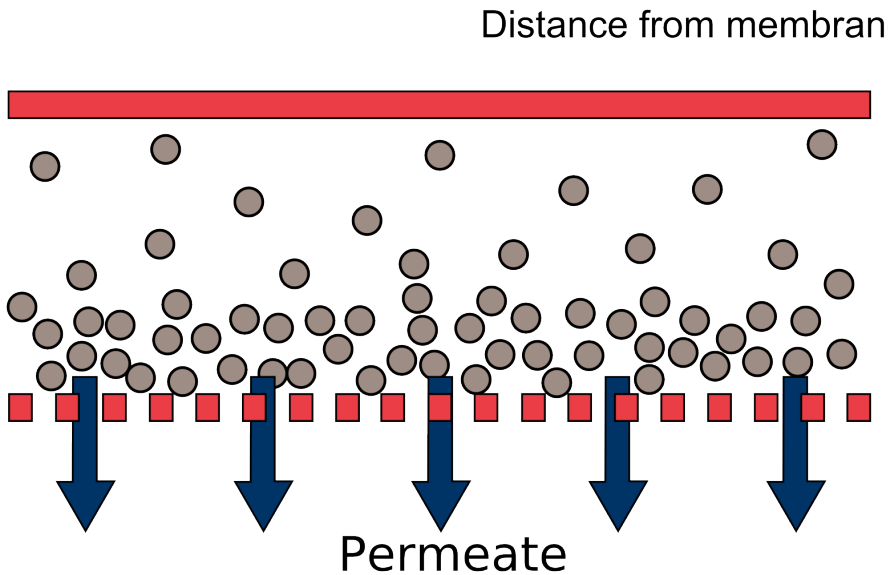
J_v	$\left[\frac{\text{m}^3 \text{ solvent}}{\text{m}^2.\text{s}}\right]$	volumetric flux of the permeate
C	$\left[\frac{\text{kg solute}}{\text{m}^3 \text{ solvent}}\right]$	solute mass concentration at a given point
$J_v C$	$\left[\frac{\text{kg solute}}{\text{m}^2.\text{s}}\right]$	**solute** mass flux towards membrane
$C_p \approx 0$	$\left[\frac{\text{kg solute}}{\text{m}^3 \text{ solvent}}\right]$	solute mass concentration in permeate

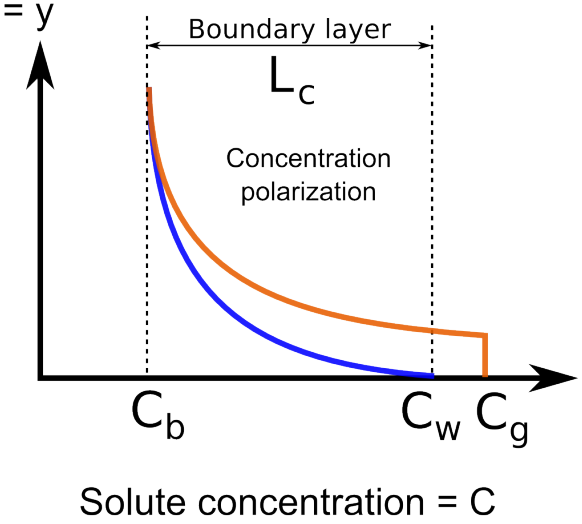
Diffusion term

- **Solute** diffusion away from membrane = $J_{\text{diffusion}}$

$$J_{\text{diffusion}} = -D_{AB}\,\frac{dC}{dy}$$

D_{AB}	$\left[\frac{\text{m}^3\ \text{solvent}}{\text{m.s}}\right] = \left[\text{m}^2.\text{s}^{-1}\right]$	diffusion of solute in solvent
$J_{\text{diffusion}}$	$\left[\frac{\text{kg solute}}{\text{m}^2.\text{s}}\right]$	solute mass flux into bulk





- See animation on Wikipedia

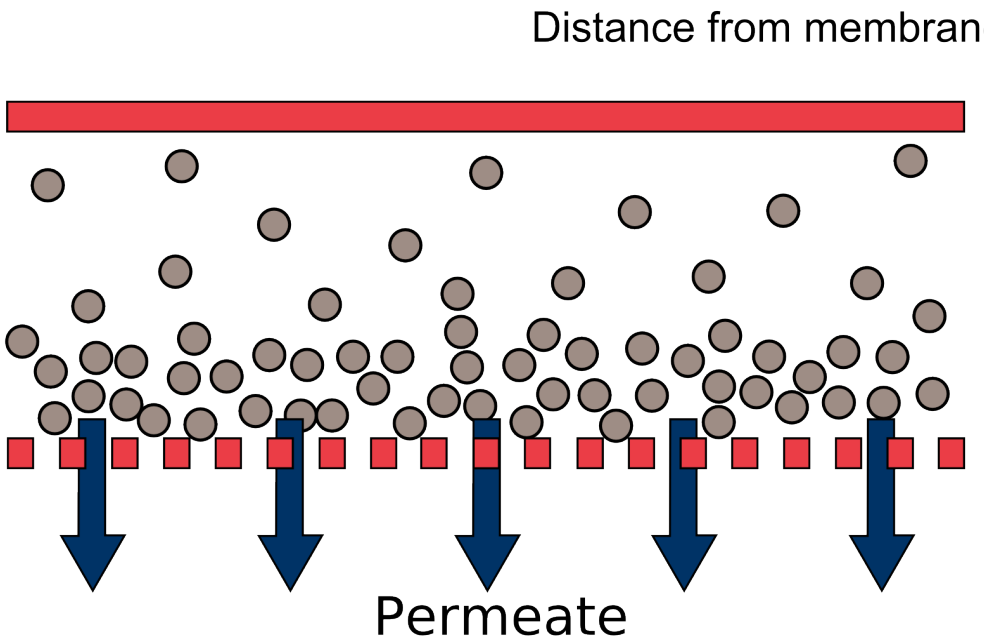
Transport at steady state

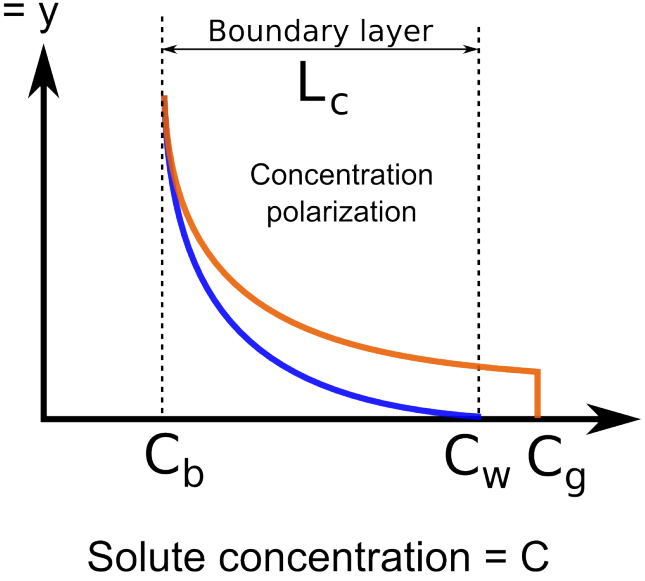
At steady state: transfer *towards* membrane equals diffusion back

$$J_v(C - C_p) = -D_{AB}\frac{dC}{dy}$$

$$-\frac{J_v}{D_{AB}}\int_0^{L_c} dy = \int_{C_w}^{C_b}\frac{dC}{C - C_p}$$

$$\ln\left(\frac{C_w - C_p}{C_b - C_p}\right) = \frac{J_v\, L_c}{D_{AB}} = \frac{J_v}{h_w}$$





UF: mass-transfer key points

Assuming $C_p \approx 0$ (i.e. $R = 1$)

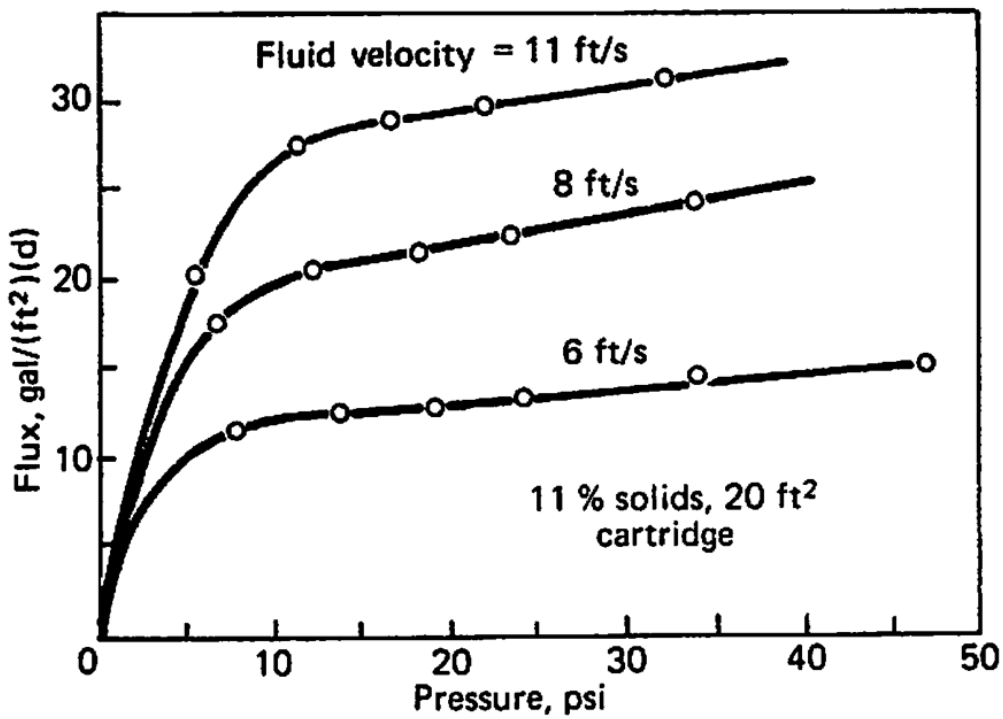
$$\frac{J_v L_c}{D_{AB}} = \frac{J_v}{h_w} = \ln\left(\frac{C_w}{C_b}\right)$$

where h_w is a mass-transfer coefficient, with units of $\mathrm{m.s^{-1}}$

- there are correlations for
  $h_w = f(\text{velocity, temperature, channel diameter, viscosity})$
- when gelling occurs, $C_w = C_g$ at the wall
- the effect of increasing ΔP is
  - increase in solute flux towards boundary layer
  - diffusion increases to oppose it
  - net effect: almost zero (see earlier plot)
  - experiments mostly agree with this theory
- there is a limiting flux $J_{\text{lim}} = f(C_w, C_b, h_w)$
- at higher feed concentrations, lower fluxes if we are at/near the gel polarization state (gelling)
- typical diffusivities: 1×10^{-9} (fast!) to 1×10^{-11} $\mathrm{m^2.s^{-1}}$

Transport phenomena in UF

- Experimental evidence agrees well with theory ... to a point.
- Increasing ΔP leads to compacting this layer, increasing C_w
- So diminishing returns from increasing ΔP
- Also, there is a strong concentration gradient
- Diffusion *away* from membrane due to concentration gradients
- Eventually solute forms a colloidal gel on the membrane, C_g
- Adjusting pressure has little/no effect anymore



[Chemical Engineering Magazine, 8 May 1978]

Example question

An ultrafiltration application is required to treat a waste stream that has 4 $kg.m^{-3}$ waste in the feed. The desired solute concentrate must be 20 $kg.m^{-3}$.

Pilot plant studies show the flux can be expressed as

$$J_v = 0.02 \ln\left(\frac{25}{C_b}\right)$$

in units of $m^3.hour^{-1}.m^{-2}$. Due to gelling and fouling the flux cannot exceed 0.05 $m^3.hour^{-1}.m^{-2}$.

1. What is the flux J_v right at the membrane entrance?
2. What is the flux J_v *for most of the membrane* if we are able to reach our desired end-point?
3. Interesting: what happens if we require a solute concentration of 10 $kg.m^{-3}$?

Geometries for ultrafiltration

Tubes in a shell

- membrane on a porous support
- cleaned with soft sponge balls

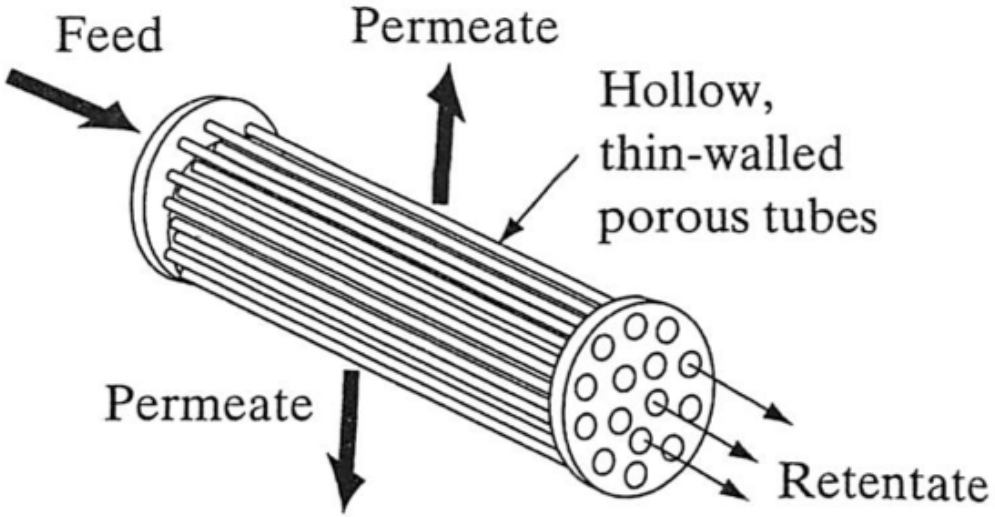
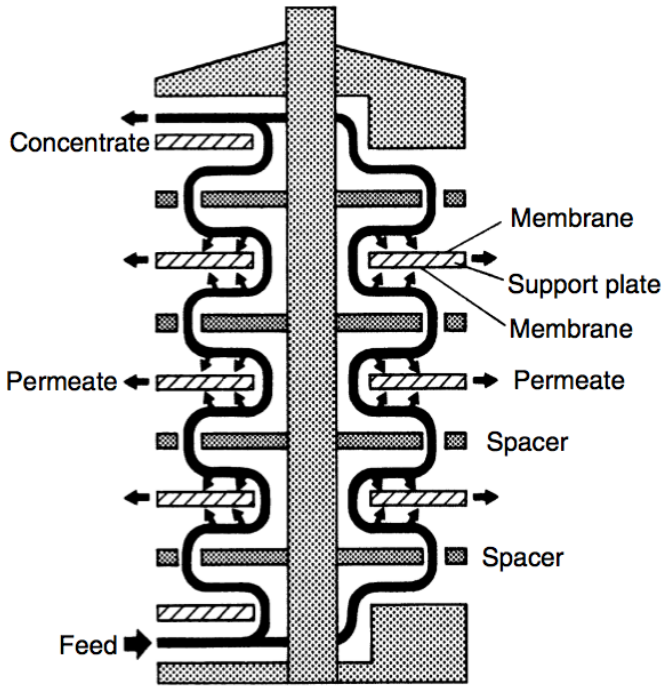


Plate and frame

- batch operation



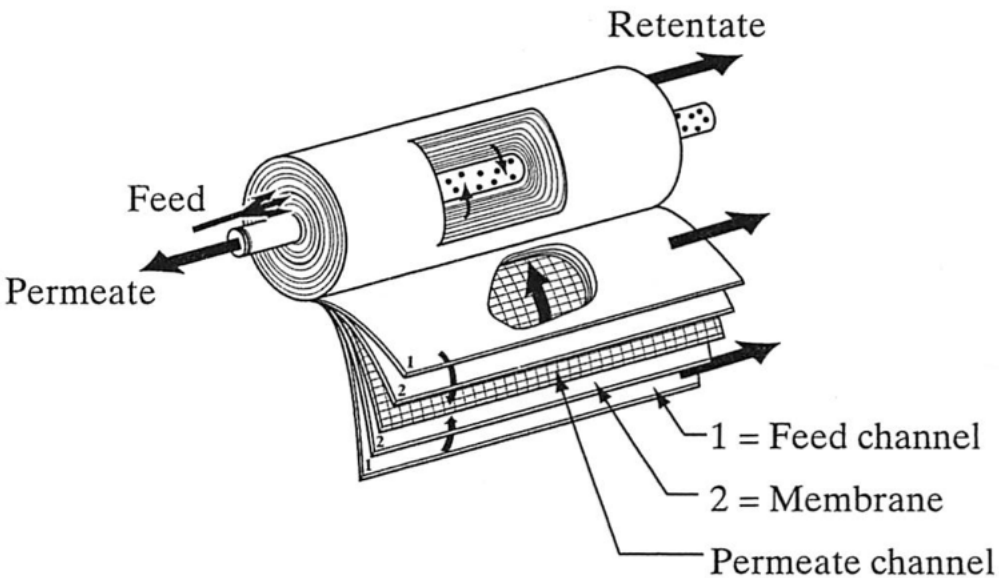
- All these units bought as complete module from supplier
- In fixed sizes; so need to be combined (next section)
- Also as cassettes, tubes and flat sheets run in TFF to increase flux.

[Illustrations from Wankat, 2ed, Ch 16]

Geometries for ultrafiltration

Spiral wound

- high surface area per unit volume
- high turbulence, reducing mass transfer resistance

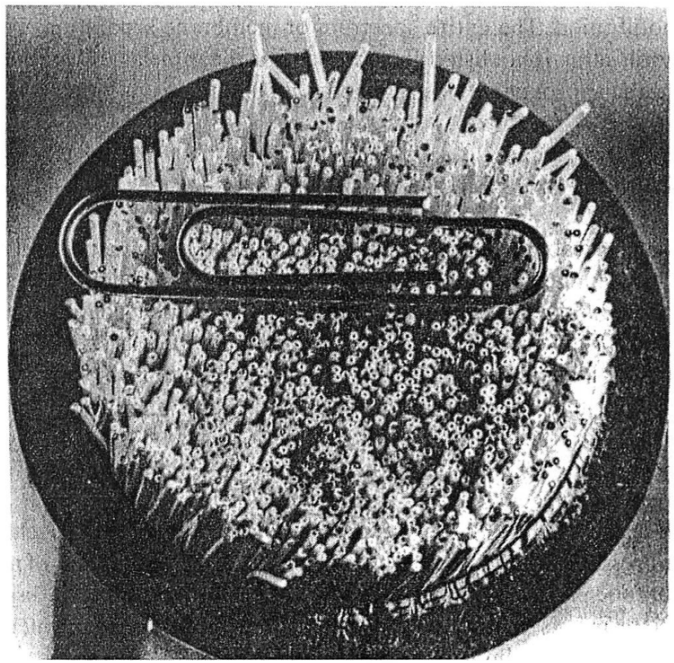


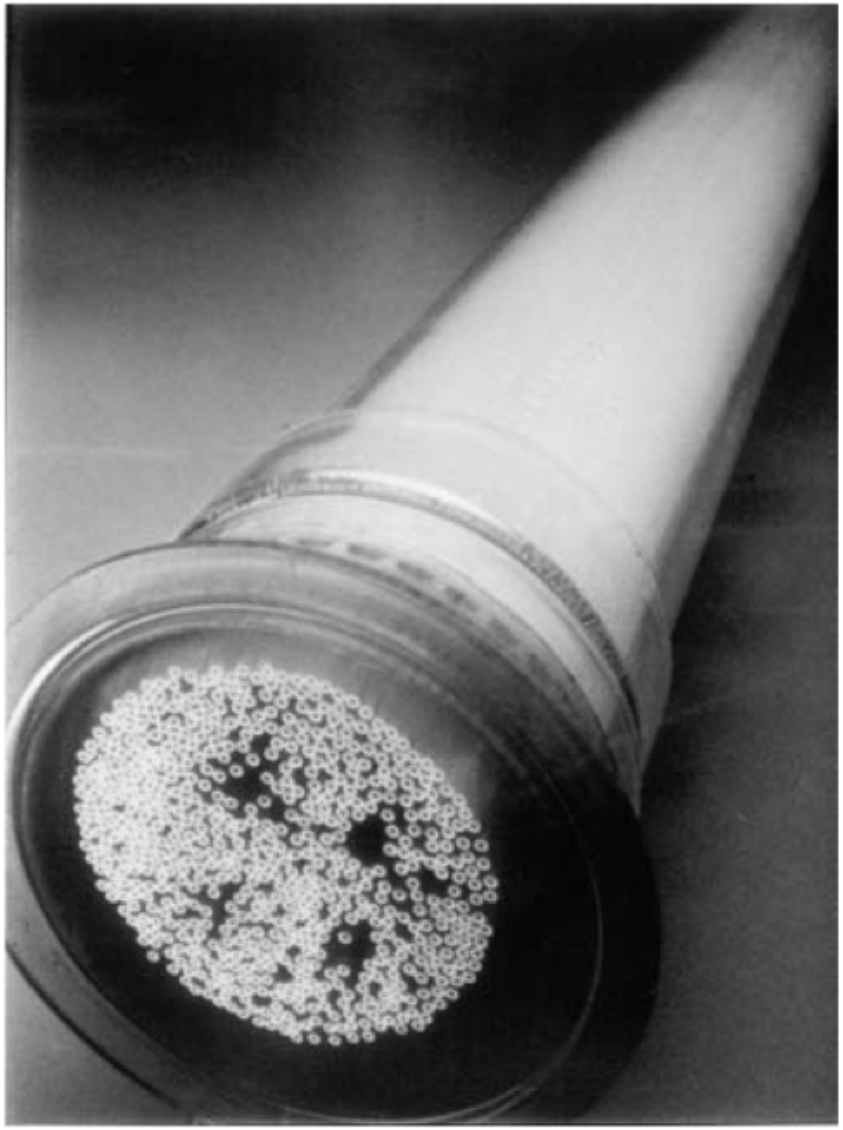
[Illustrations from Wankat, 2ed, Ch 16]

http://www.youtube.com/watch?v=YlMGZWmh_Mw: how spiral membranes are made

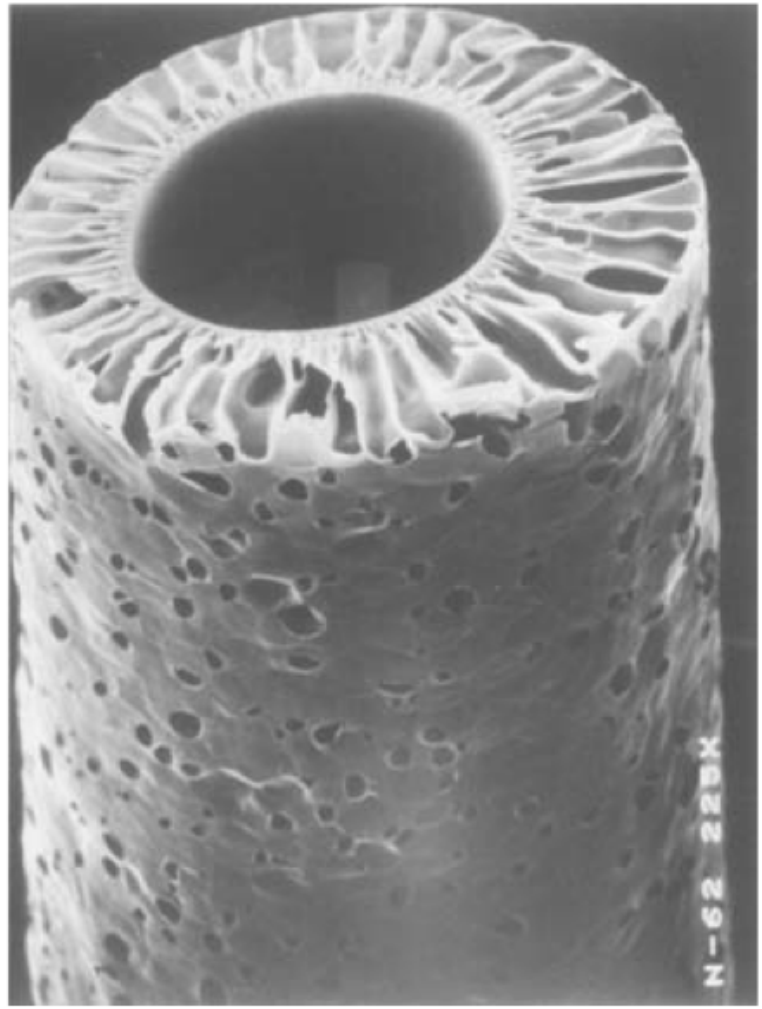
Hollow fibre membranes

- largest area to volume ratio
- fibre inside diameter = 500 to 1100 μm for UF
- UF: feed inside tube, with thin membrane skin on the inside





(*a*)



(*b*)

[Richardson and Harker, Ch8]

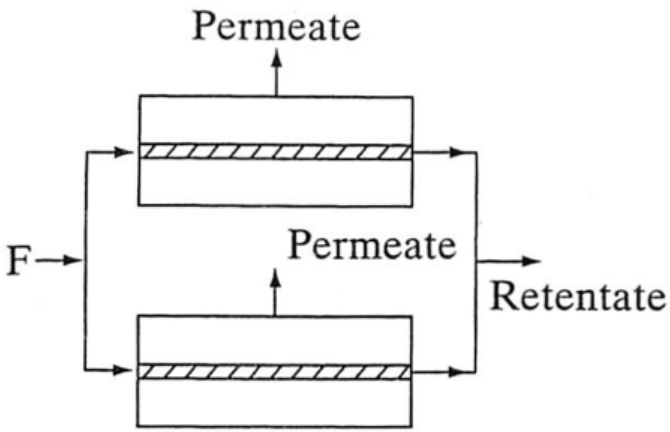
Sequencing membrane modules

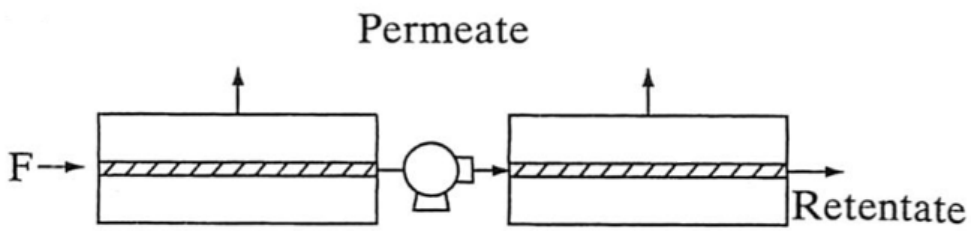
Parallel

- most common configuration
- allows increase in throughput

Series

- used to achieve a desired separation factor (concentration)
- high pressure drop across series circuit
- cannot recover pressure (energy separating agent)





[Wankat, Ch16]

Example of an installation

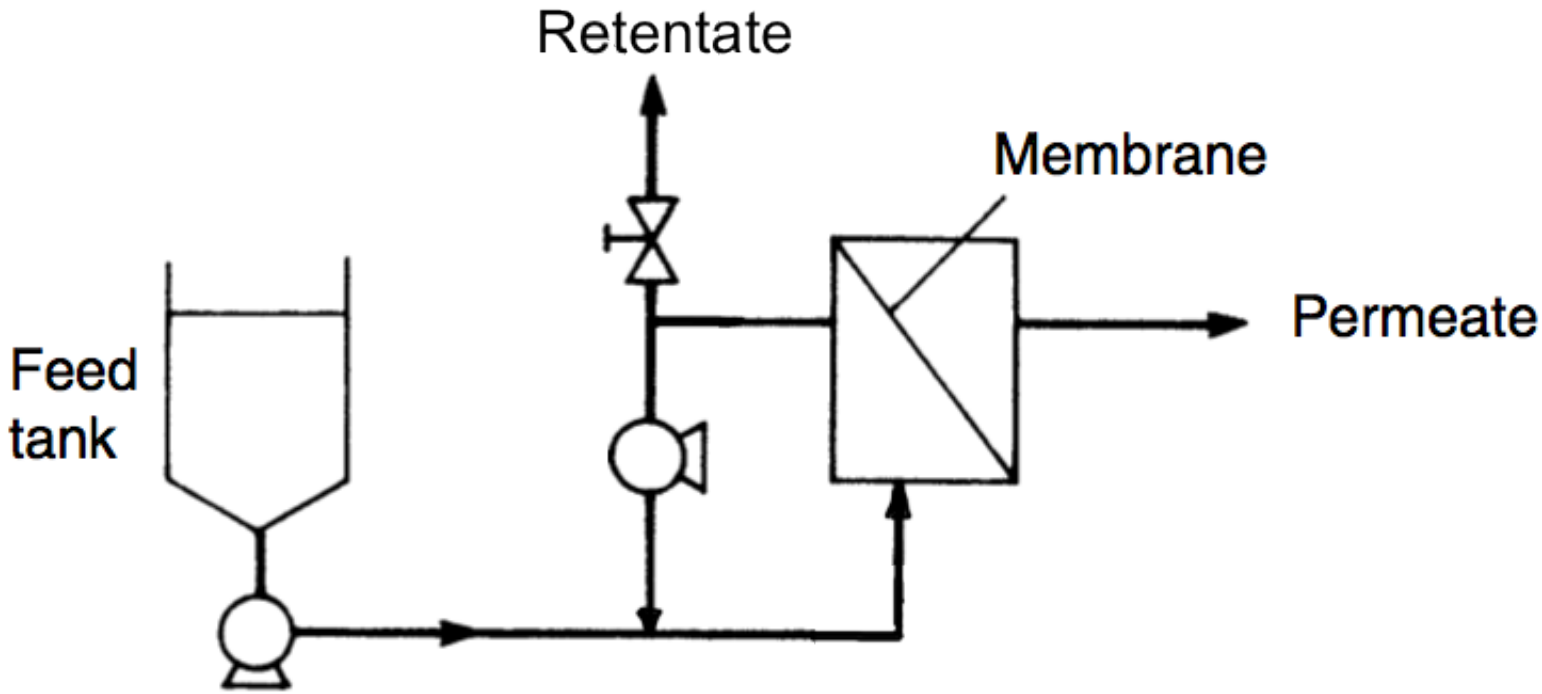
- Larnaca, Cyprus
- Sea-water reverse osmosis membrane, i.e. desalination
- 21.5 million m^3 per year
- parallel and series

[ide-tech.com]

Operating UF units

- Continuous operation provides lower-cost operation
- Batch operation: seldom used, except for start up (see next)
- Biologicals: require batch processing to meet regulatory requirements
- High solids in feed? Require multiple-pass: simply recycle

Recycle operation: "feed plus bleed"



[Modified from Richardson and Harker, Ch8]

- Initially close retentate valve (batch mode operation)
- Fluxes slowly reduce
- Open retentate valve and operate at steady state
- **AIM**: achieve a given concentration in the retentate

Class example

We need to treat 50 $m^3.day^{-1}$ of waste containing a solute at 4.0 $kg.m^{-3}$. The desired solute concentrate must be 20 $kg.m^{-3}$. The plant operates 20 hours per day.

At steady-state the feed-plus-bleed circuit operates with a flux

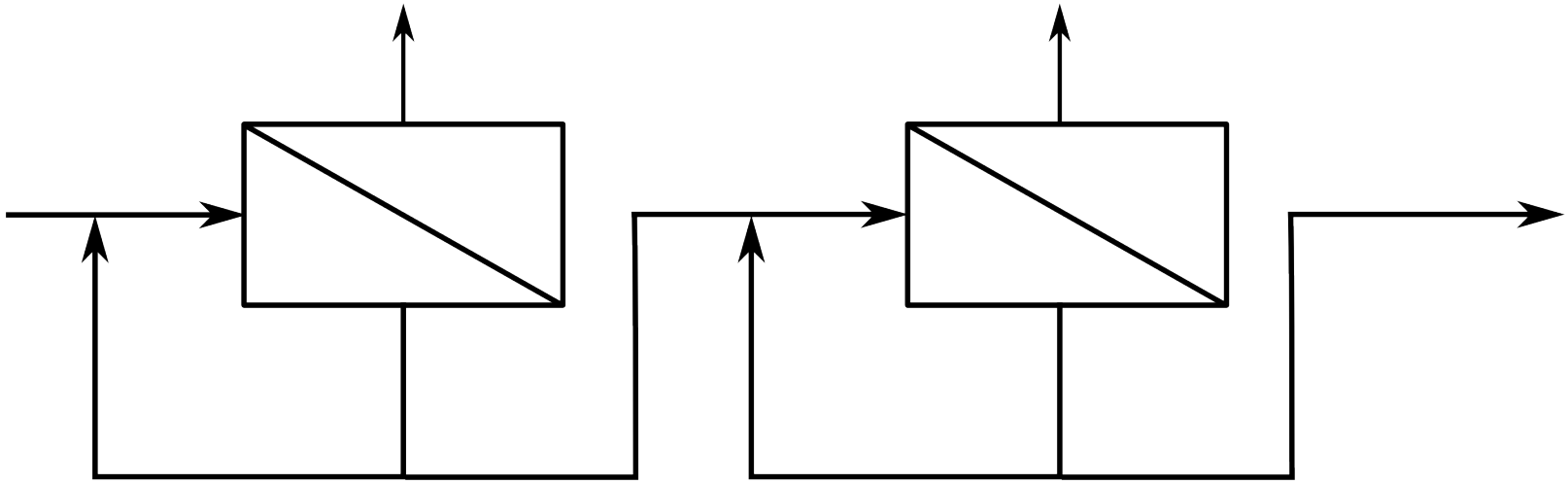
$$J_v = 0.02 \ln\left(\frac{25}{C_b}\right)$$

in units of $m^3.hour^{-1}.m^{-2}$, where C_b is the bulk concentration, measured in units of $kg.m^{-3}$.

If each membrane module is 30 m^2:

- how many membrane modules are required?
- series or parallel?

Multiple units in series



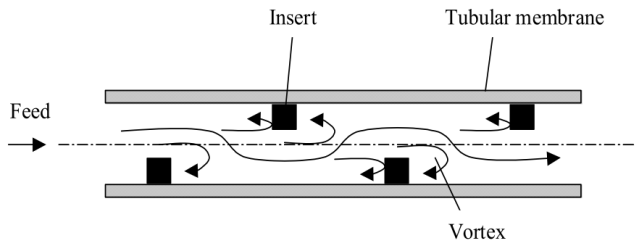
Now consider the previous example.

1. Consider 2 membranes in series of 30 m^2. What are concentration and flow values for unit 1 and unit 2?
   - **Note**: we do not know the outlet concentration, C_{R2} this time!
2. Now try find the optimal areas, A_1 and A_2 for the membranes for a desired outlet C_{R2} concentration.

Hint: use a guess-and-check strategy, bearing in mind the modules can only be purchased in 30m^2 units.

Fouling

- Process feed pretreatment is important.
- e.g. in bio area: prefiltration, pasteurisation to destroy bacteria, or adjust pH to prevent protein precipitation
- Backflushing mostly restores permeation rate (opens pores)
- Can also use pulsated/oscillating feed flows
- Consider adding tube inserts



- Inject air: *sparging* with oxygen or nitrogen
- Oscillating electrical field works on certain feeds
- Chemical cleaning is eventually required [long time], e.g.:
  - flush with filtered water
  - recirculate/back-flush with a cleaning agent at high temperature
  - rinse to remove the cleaning agent
  - sterilize by recirculating weak chlorine solution at high temps
  - flushing with water to remove sterilizing solution

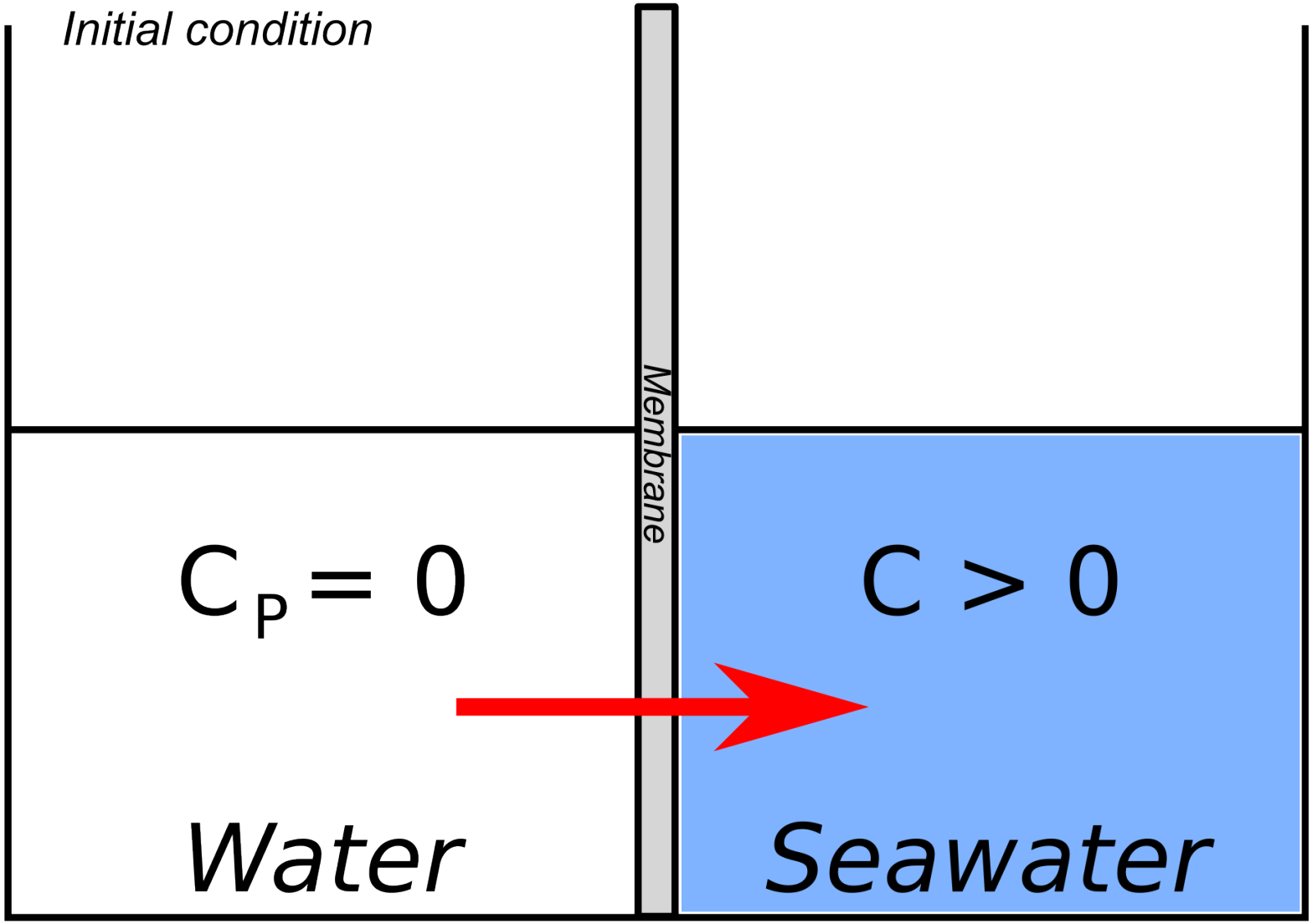
Video

http://www.youtube.com/watch?v=YIMGZWmh_Mw: How spiral membranes are made

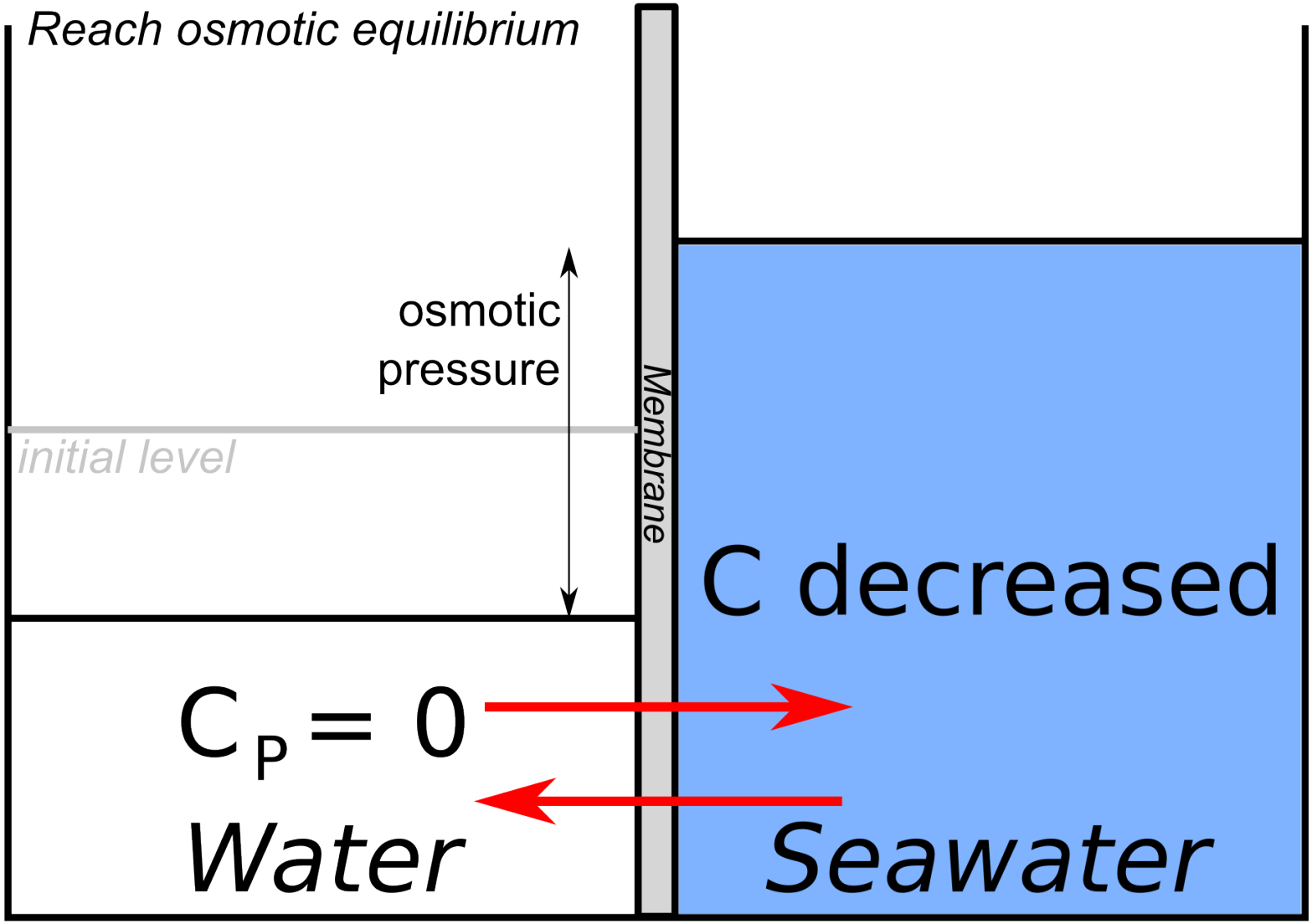
Reverse osmosis

- One the most requested topics (start of the term!)
- One of the largest membrane markets by $ size
  1. Dialysis
  2. Reverse osmosis (water treatment)
- What is osmosis? [Greek = "push"]
- Then we look at reverse osmosis (RO)
- Applications of RO
- Modelling RO

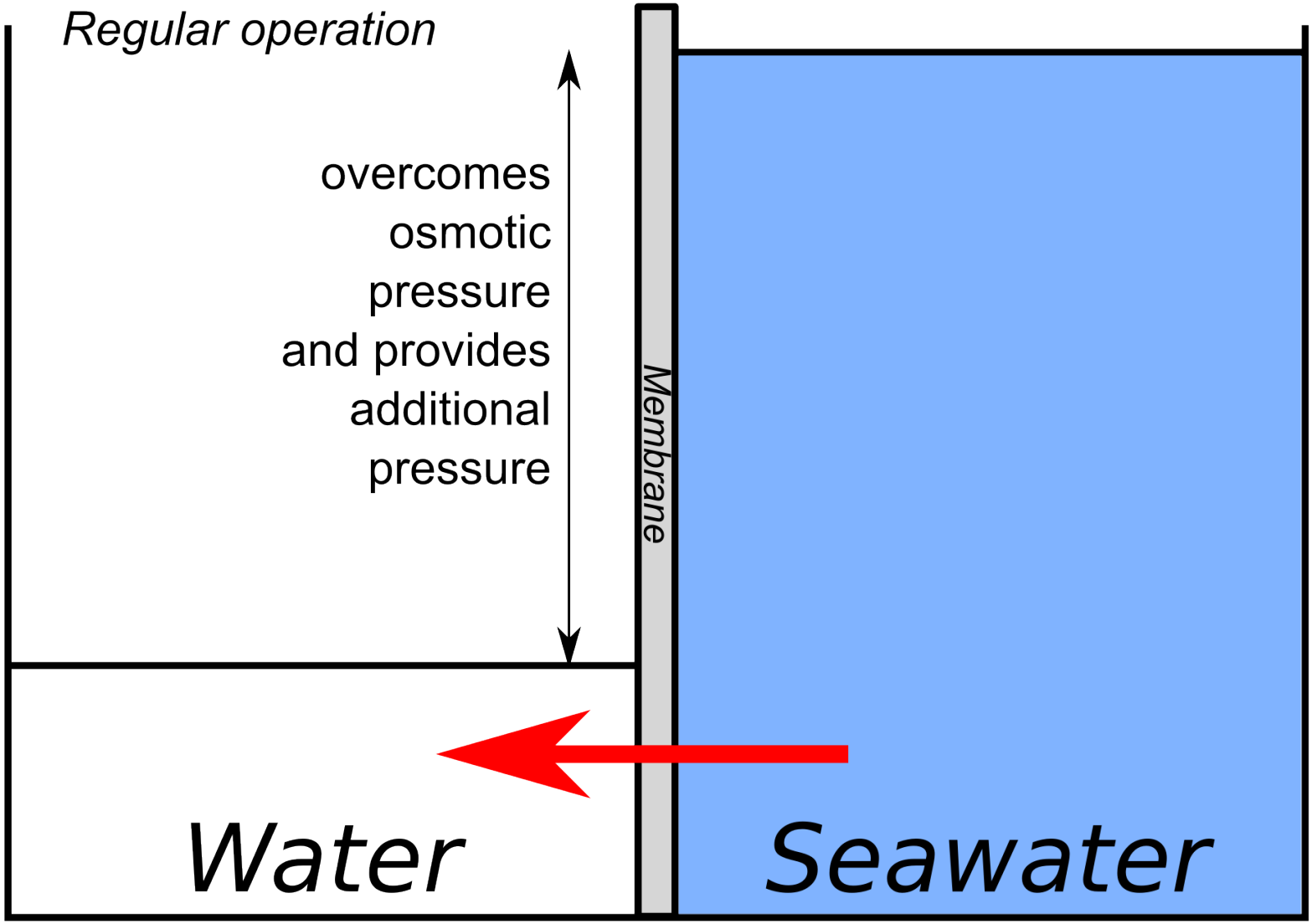
Osmosis principle



Osmosis principle



Reverse osmosis principle

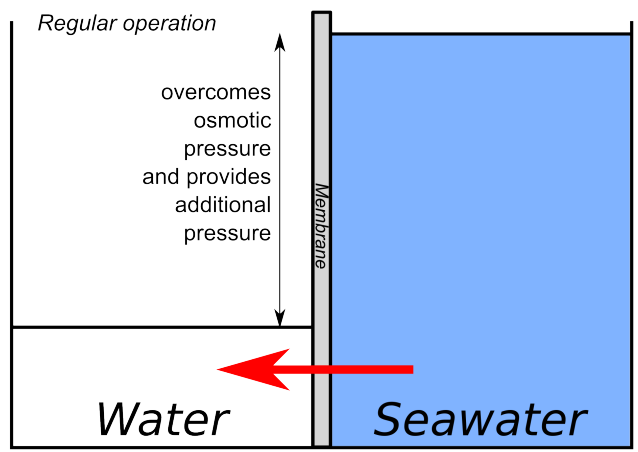


(Reverse) Osmosis principle

- Assume solute barely passes through membrane ($C_p \approx 0$)
- but solvent passes freely: this is why we call it a *semipermeable membrane*
- Chemical potential drives pure solvent (water) to dilute the solute/solvent (mixture).
- This *solvent flux* continues until equilibrium is reached
  - solvent flow to the left equals solvent flow to the right
  - results in a pressure difference (head)
  - called the *osmotic pressure* $= \pi$ [Pa]
  - a thermodynamic property $\neq f$(membrane)
  - a thermodynamic property $= f$(fluid and solute properties), e.g. temperature, concentration, pressure

(Reverse) Osmosis principle

- Osmosis in action:
  - trees and plants to bring water to the cells in upper branches
  - killing snails by placing salt on them
  - why freshwater fish die in salt water and *vice versa*
  - try at home: place peeled potato in very salty water
- If you exceed osmotic pressure you reverse the solvent flow
- Called "reverse osmosis"
- Net driving force in this illustration = _____



Typical values of osmotic press

For dilute solutions

$$\pi \approx \frac{nRT}{V_m} = cRT$$

π	[atm]	osmotic pressure
n	[mol]	mols of **ions**: e.g. Na^+ and Cl^-
R	[m^3.atm.K^{-1}.mol^{-1}]	gas law constant: 8.2057×10^{-5}
V_m	[m^3]	volume of solvent associated with solute
T	[K]	temperature
c	[mol of ions per m^3]	generic concentration

Example

Prove to yourself: 0.1 mol ($\sim$ 1 teaspoon) of NaCl dissolved in 1 L of water at 25°C is **4.9 atm**!

- that's almost 500 kPa
- or almost 50m of head for 5.8 g NaCl in a litre of water
- (recall: 1 atm $\approx$ 10 m of water height)

Other osmotic values

The previous equation is an approximation.

Some actual values:

Substance	**Osmotic pressure [atm]**
Pure water	0.0
0.1 mol NaCl in 1 L water	4.56
2.0 mol NaCl in 1 L water	96.2
Seawater [3.5 wt% salts]	25.2

- Driving force in membrane separation is pressure difference
- $\Delta P = \pi$ implies we only counteract the osmotic pressure
- Reverse osmosis occurs when we increase $\Delta P > \pi$
- So the net useful driving force applied: $\Delta P - \pi$
- Ultrafiltration ΔP was 0.1 to 1.0 MPa (10 atm) typically
- RO: typical ΔP values: 2.0 MPa to 8.0 MPa, even 10.5 MPa

Let's be a little more accurate

- The solute (salt) passes through the membrane to the permeate side
- $C_p \neq 0$
- There is an osmotic pressure, π_{perm} back into the membrane.
- Correct, net driving force $= \Delta P - \Delta\pi$
  - ΔP is the usual TMP we measure
  - $\Delta\pi = \pi_{\text{feed}} - \pi_{\text{perm}}$
  - $\Delta\pi = C_{\text{ions,feed}} RT_{\text{feed}} - C_{\text{ions,perm}} RT_{\text{perm}}$
  - Even more correctly: $\Delta\pi = c_{\text{ions,wall}} RT_{\text{wall}} - c_{\text{ions,perm}} RT_{\text{perm}}$
  - Draw a picture

Key point

There's a natural limitation here: what if we try to recover too much solvent (*high solvent flux*)?

Widest application for RO: desalination

Some quotes:

- "*McIlvaine forecasts that world RO equipment and membrane sales will reach $5.6 billion (USD) in 2012, compared to $3.8 billion in 2008 (actual).*"
- "*Depleting water supplies, coupled with increasing water demand, are driving the global market for desalination technology, which is expected to reach $52.4 billion by 2020, up 320.3% from* **$12.5 billion in 2010**. *According to a recent report from energy research publisher SBI Energy, membrane technology reverse osmosis will see the largest growth, reaching $39.46 billion by 2020.*"

Industrial applications of RO

- demineralization of industrial water before ion exchange
- not primary aim, but RO membranes retain $>$ 300 Dalton organics
- ultrahigh-purity water
  - laboratories
  - kidney dialysis
  - microelectronic manufacturing
  - pharmaceutical manufacturing (purified water)
- tomato, citrus, and apple juice dewatering [$\sim$ 4.5 c/L; 1995]
- dealcoholization of wine and beer to retain flavour in the retentate
- other: keep antifreeze, paint, dyes, PAH, pesticides in retentate; discharge permeate to municipal wastewater

Salt-water reverse osmosis example

- Larnaca, Cyprus [island state near Greece/Turkey]
- Desalination plant: Build, Own, Operate, and Transfer
- 21.5 million m^3 per year
- Seawater intake $\rightarrow$ flocculation and filtration [why?] $\rightarrow$ RO $\rightarrow$ chemical dosing $\rightarrow$ chlorination
- Energy recovery of ΔP (see http://www.youtube.com/watch?v=M3mpJysa6zQ: novel way of recovering pressure energy)

RO costs [Perry's; 8ed], 1992

TABLE 20-23 Representative RO Process Costs

Costs	Seawater
Operating conditions	
Inlet pressure	6.9 MPa
Flux	25 LMH*
Conversion	40%
Total cost, $/1000 gal	4.7
Capital cost	2.1
Operating cost	2.6
Total capital cost, $/(gal/day)	4.5
Direct costs	3.7
Equipment	3.3
Indirect costs	0.8
Total operating cost, $/1000 gal	2.6
Energy	1.6
Membrane replacement	0.4
Chemicals	0.2
Labor	0.3
Other	0.1

Household RO cost:

- $ 0.015 to $0.07/L

Transport modelling of RO

Symbolically:

$$J = \frac{(\text{permeability})(\text{driving force})}{\text{thickness}} = (\text{permeance})(\text{driving force}) = \frac{\text{driving force}}{\text{resistance}}$$

- permeability = $f(\text{membrane properties}, \text{diffusivity}, \text{other physical properties})$
- permeance: easier to calculate:
  - given the driving force (easy to measure)
  - given the flux (easy to measure)
- units are always case specific and must be self-consistent [check!]

Simplified RO modelling

- We don't consider "cake build-up": we assume that solid particles are mostly removed in an upstream separation step
- So ΔP overcomes osmotic pressure and membrane resistance

1. **Solvent** flux

$$J_v = J_{\text{solv}} = \frac{(\Delta P - \Delta\pi)}{R_{m,v} + \cancelto{0}{R_{cp,v}}} = \frac{P_{\text{solv}}}{\ell_M}(\Delta P - \Delta\pi) = A_{\text{solv}}\,(\Delta P - \Delta\pi)$$

$R_{m,v} = f(\ell_M = \text{membrane's thickness, diffusivity of solvent in membrane})$

2. **Solute** (*salt*) flux

$$J_{\text{salt}} = \frac{(\text{permeability})(\text{driving force})}{\text{resistance}} = \frac{P_{\text{salt}}}{\ell_M}\,(C_w - C_p) = A_{\text{salt}}\,(C_w - C_p)$$

- Our assumption: $C_{\text{wall}} \approx C_{\text{bulk}} = \text{bulk solute conc}^{\text{n}} = C_{\text{w}}$
  - how would you enforce this reasonable assumption?
- Crudely assume: $C_{\text{bulk}} \approx C_{\text{feed}}$ [for back-of-envelope calculations]
- $P_{\text{solv}} =$ permeability of the solvent [notation: $P_{\text{solv}} \equiv P_{\text{w}}$]
- $C_p =$ concentration of solute in the permeate
- $P_{\text{salt}} =$ permeability of the salt through membrane

Example to try

Brackish water of 1.8wt% NaCl at 25°C and 1000 psia [68.5 atm] is fed to a spiral wound membrane.

Conditions on the permeate side are 0.05 wt% NaCl, at same temperature, but 50 psia [3.42 atm]

The permeance of water has been established as 1.1×10^{-4} kg.s^{-1}.m^{-2}.atm^{-1} [how would you get this number?] and 16×10^{-8}m.s^{-1} for salt is determined experimentally.

1. Calculate the flux of water in LMH.
2. What is the flux of salt through the membrane?
3. How do these fluxes compare?
4. Calculate the rejection coefficient, R, for salt.

Another example: calculating permeances

At 25 °C in a lab membrane with area $A = 2 \times 10^{-3}$ m^2 we feed a solution of 10 kg NaCl per m^3 solution so well mixed and so rapidly that essentially it has the same strength leaving.

The permeate is measured as 0.39 kg NaCl per m^3 solution at a rate of 1.92×10^{-8} m^3.s^{-1} when applying a constant pressure difference of 54.42 atm.

Calculate the permeance constants for solvent and salt (these were previously given, this example shows how to calculate them experimentally), as well as the rejection coefficient.

Some questions to consider

1. What happens, in terms of osmosis, on a really hot day to fluid flow in a tree?
2. Is P_{solv} going to change if we use a different solute?
3. If we double the pressure drop, will we double the solvent flux?
4. Why did we not take osmotic pressure in account for microfiltration and ultrafiltration?
5. In RO: what will be the expected effect of increasing operating temperature?

Some old and new terminology

Recall from ultrafiltration:

- $R = 1 - \frac{C_P}{C_{\text{feed}}} = 1 - \frac{C_P}{C_0}$
- This rejection coefficient, R, also applies to reverse osmosis.
- A new term = cut = conversion = recovery = $\theta = \frac{Q_P}{Q_0}$ is between 40 and 50% typically

Relaxing the assumption of $C_R = C_{feed}$

1. Usually we specify the desired cut, $\theta = \dfrac{Q_P}{Q_0}$
2. $Q_0 C_0 = Q_R C_R + Q_P C_P$
3. $Q_0 = Q_R + Q_P$
4. $1 = \dfrac{Q_R}{Q_0} + \theta$
5. $C_0 = (1-\theta)C_R + \theta C_P$ from equation (2) and (4)
6. $J_{solv,V} \cdot C_P = A_{solv}(\Delta P - \Delta\pi)C_P =$ salt flux leaving in permeate. [you might have to divide by the solvent density to get $J_{solv,V}$]
7. $J_{salt} = A_{salt}(C_R - C_P) =$ salt flux into membrane

---

- Specify C_0 and θ
- Guess C_P value [how?]
- Calculate C_R from equation 5
- Calculate $J_{solv} C_P$ from equation 6, noting however that $J_{solv} = f(\pi_R, \pi_P)$. So recalculate π_R and π_P
- Note then that equation 6 and 7 must be equal
- Solve eqn 7 for C_P and use that as a revised value to iterate.

Alternative to the above

1. Specify C_0 and θ
2. Guess a reasonable rejection coefficient around 90 to 99%
3. From which you get a reasonable C_P guess
4. Calculate C_R from equation 5
5. Your guesses for C_P and C_R cannot be negative, and C_R must exceed C_0.
6. Calculate $J_{solv,\,V} C_P$ from equation 6, noting however that $J_{solv,\,V} = f(\pi_R, \pi_P)$. So recalculate π_R and π_P
7. Note then that equation 6 and 7 must be equal. So solve eqn 7 for C_P and use that as a revised value to iterate.
8. You should try this on a computer, rather than by hand.

Problem for home

Reverse osmosis with an NaCl-water feed, 2.5 g/L NaCl is being separated into a permeate and retentate stream using a TMP of 27.2 atm at 25 °C.

Through lab experiments the permeance of the membrane with respect to salt is 4.2×10^{-7} m.s^{-1} and solvent is 5.0×10^{-4} kg.s^{-1}.m^{-2}.atm^{-1}. The membrane is operated so the cut is at 40%, producing a permeate stream of 0.38 m^3 per hour.

Calculate the permeate concentration, retentate concentration, rejection coefficient, and separation factor. It is not reasonable to assume that the feed and retentate concentration are the same in this problem: we require accurate estimates.