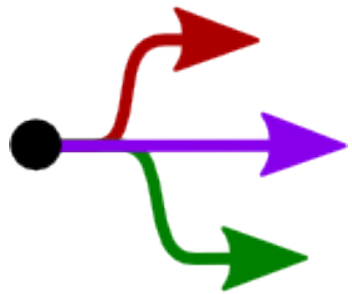
Separation Processes

ChE 4M3



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Overall revision number: 71 (October 2012)

Membranes

On a loose sheet of paper, please list/describe 5 topics related to membranes that you want to learn about in the next 5 classes.

For example:

- the equations to model fluid flow through a membrane
-
-
-
-
-

e.g. recall interesting ideas from Henk Koops' talk; check the internet; talk with the person next to you

Introduction to membranes

Please refer to Henk Koops' slides/video from 28 September 2012 on the course website

Why use membranes?

Some really difficult separations:

- finely dispersed solids; density close to liquid phase; gelatinous particles
- dissolved salts
- non-volatile organics (e.g. humic substances)
- biological materials: sensitive to the environment
  - 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

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:

- withstanding high pressure differences but still have 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)

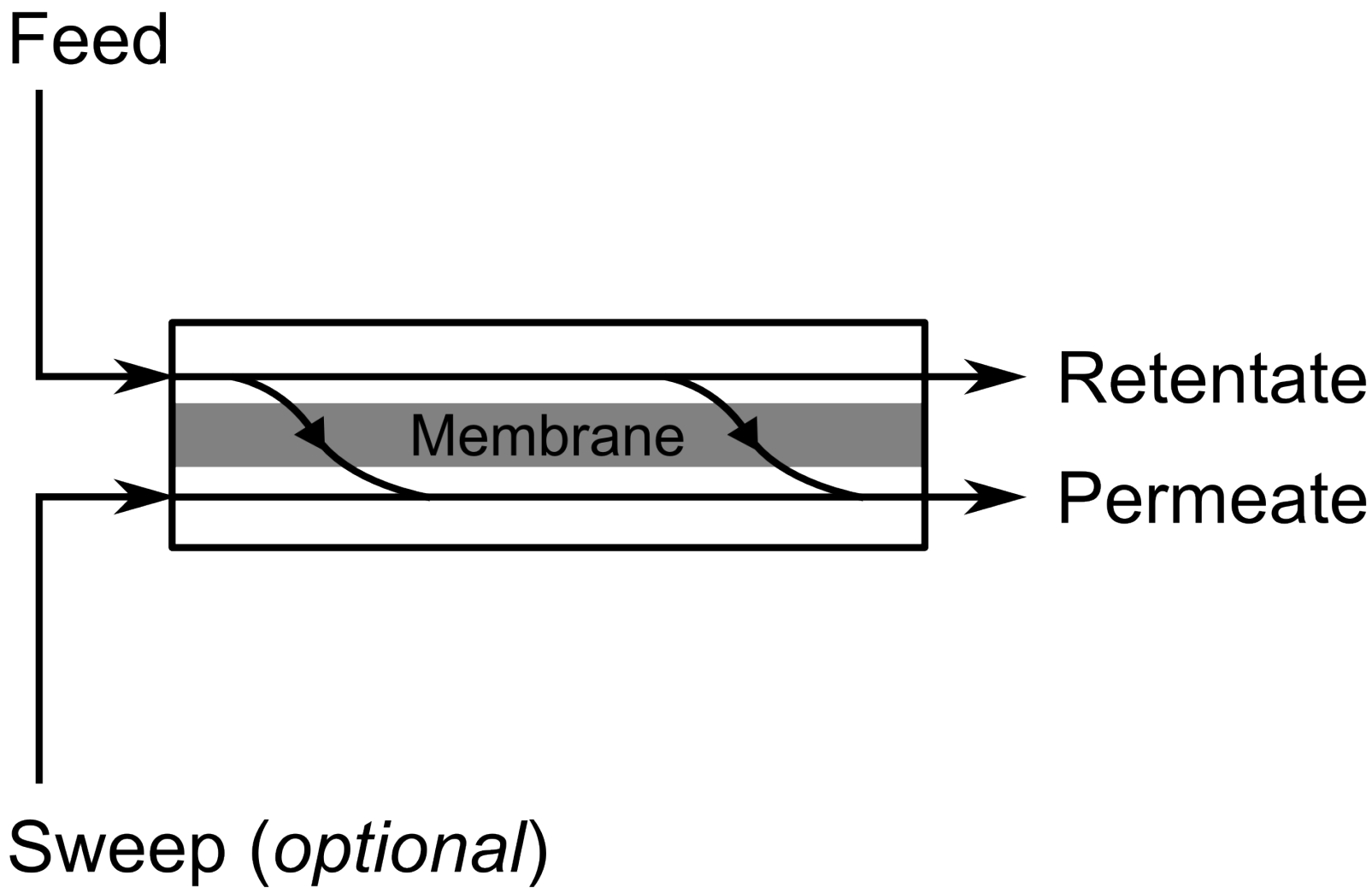
Market size

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

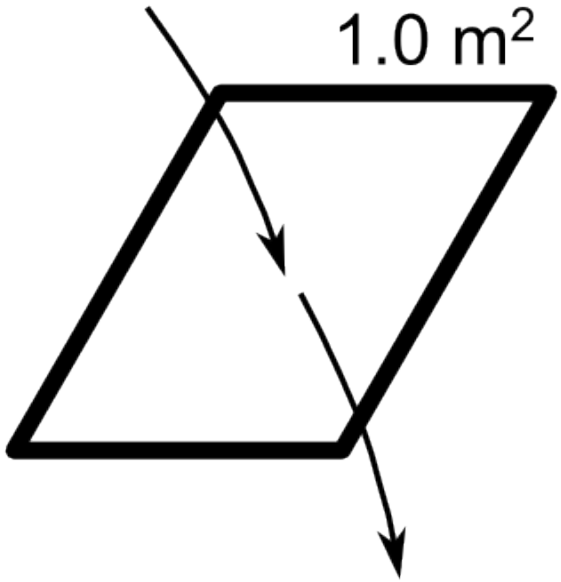
energy separating agent: the applied pressure (pressure drop)

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

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 $\text{m}^3\text{.s}^{-1}\text{.m}^{-2}$
- 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 does this application require?

The general equation

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

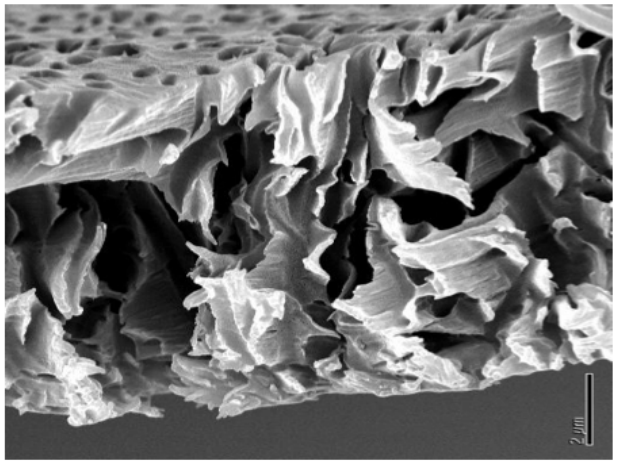
Symbolically:

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

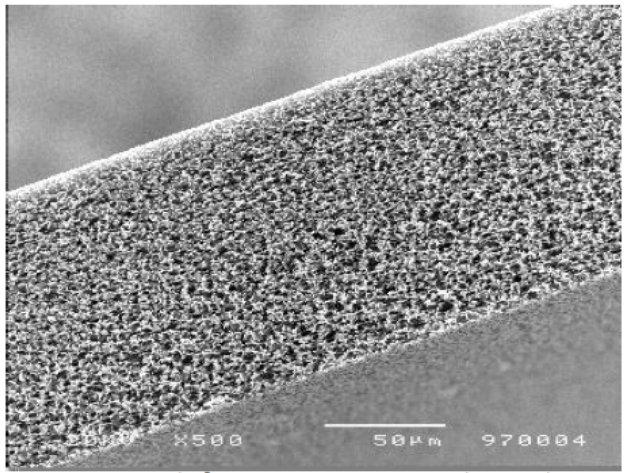
- $\text{permeance} = \dfrac{\text{permeability}}{L} = \dfrac{1}{\text{resistance}} = \dfrac{1}{R} =$ "mass transfer coeff"
- permeance: easier to measure
- permeance units: depend on choice of (driving force) and J
- resistance $= f$(thickness, viscosity, porosity, pore size)
- we will specifically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

Microfiltration

- 0.1 μm to 10 μm retained mainly by sieving mechanism
- conventional filters: not effective below ~ 5 μm
- microfiltration membranes: generally symmetric pores
- polysulfone membrane
- 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



symmetric open structure



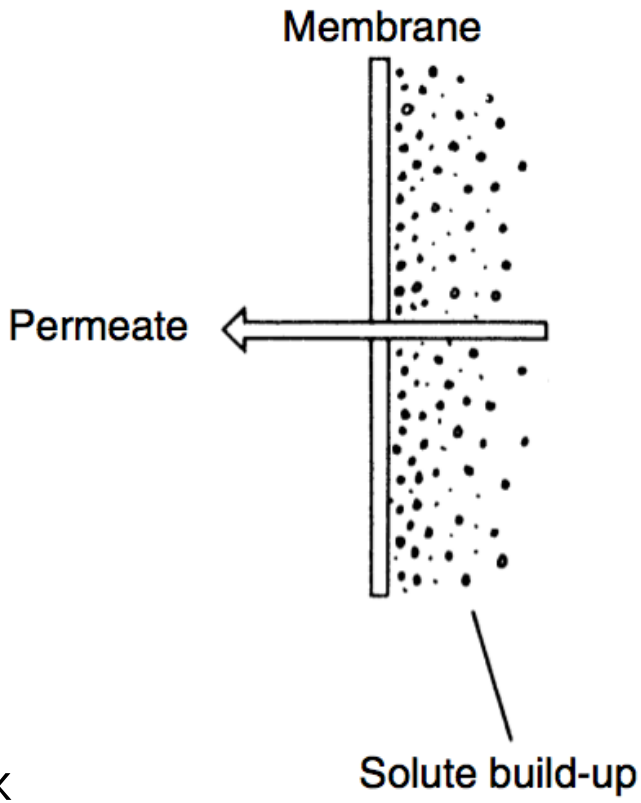
symmetric spongy structure

[Henk Koops' slide]

General modelling equation applied

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

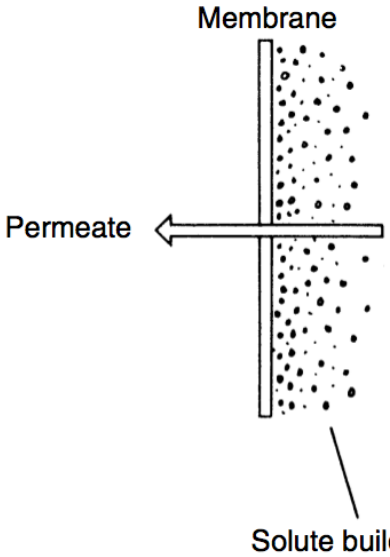
$$\frac{\rho_f}{A} \cdot \frac{dV}{dt} = \text{Flux} \quad = J = \frac{\Delta P}{\mu \left(R'_m + R'_c \right)}$$



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

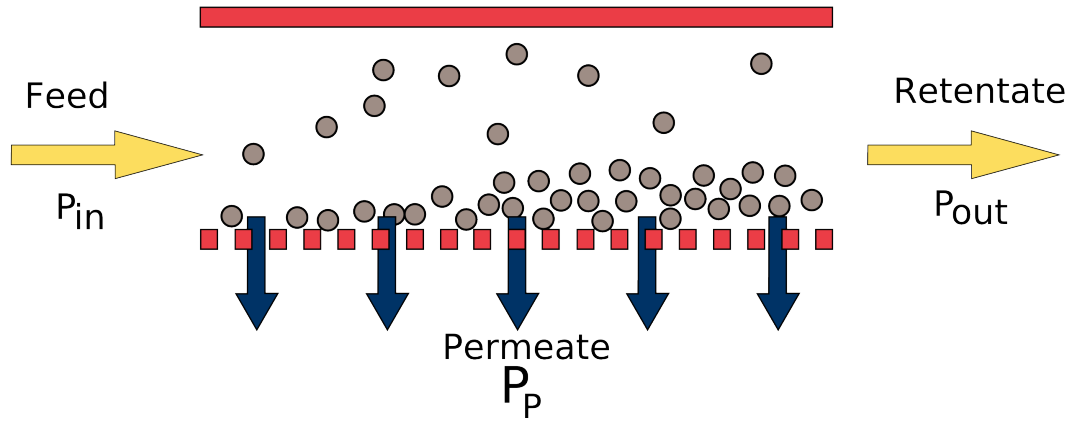
Flow patterns for microfiltration

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?
  -
  -
  -
  -

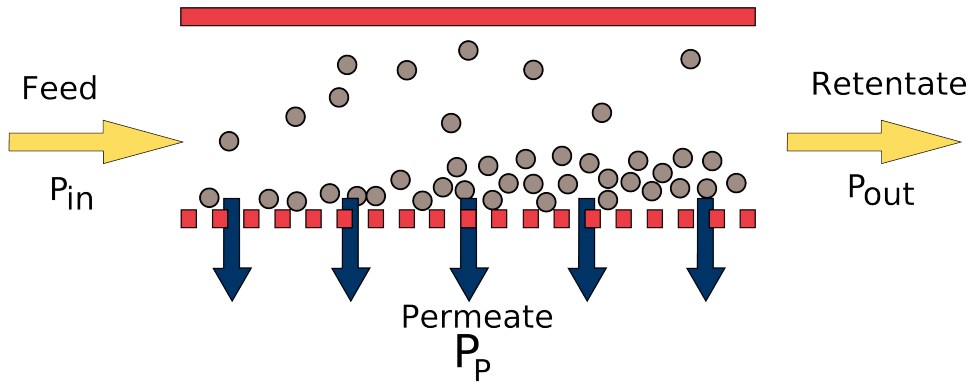
Dead-end flow vs cross-flow geometries

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

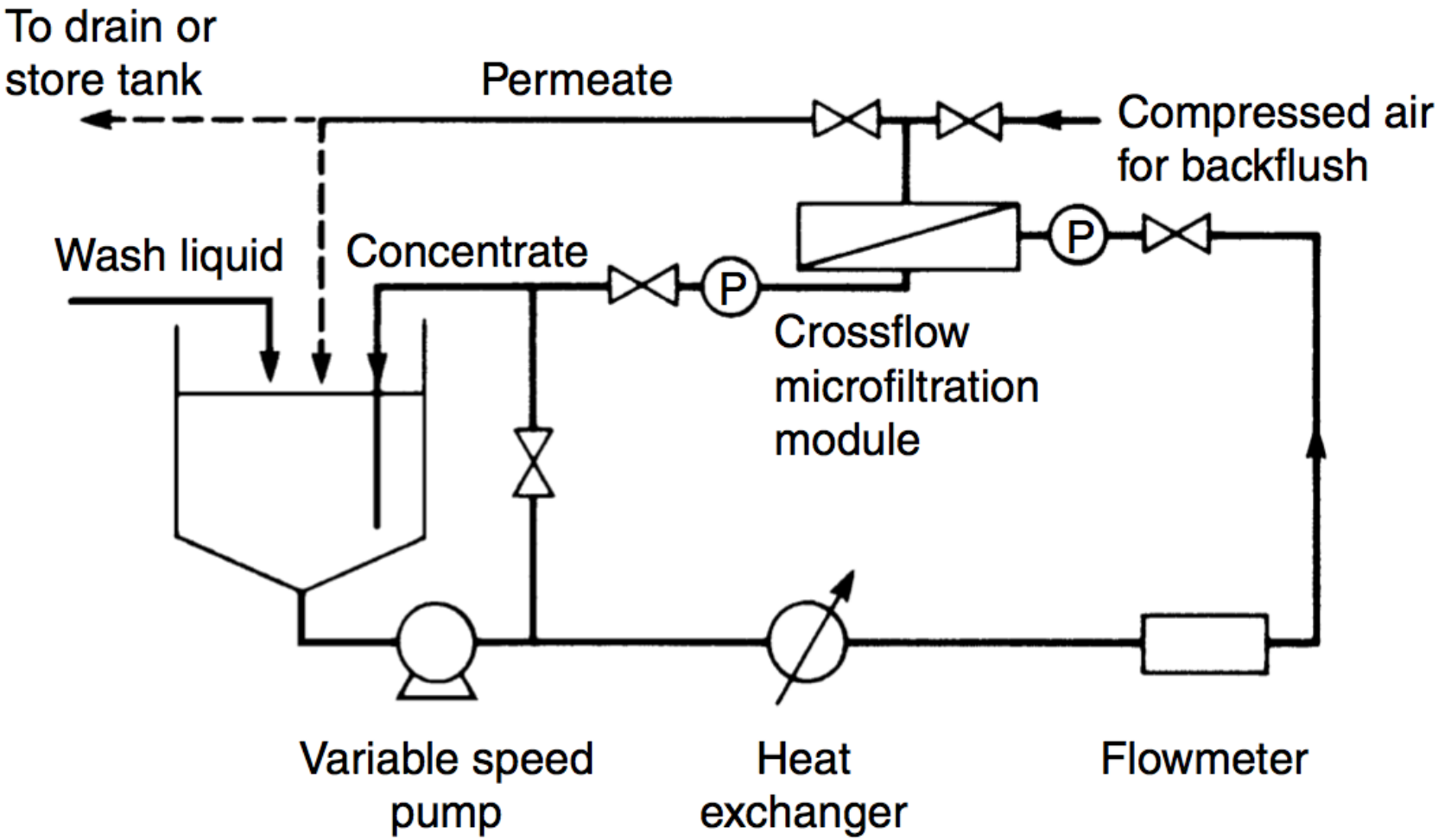
$$J = \frac{\Delta P}{\mu\left(R'_m + R_c L_c\right)}$$

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

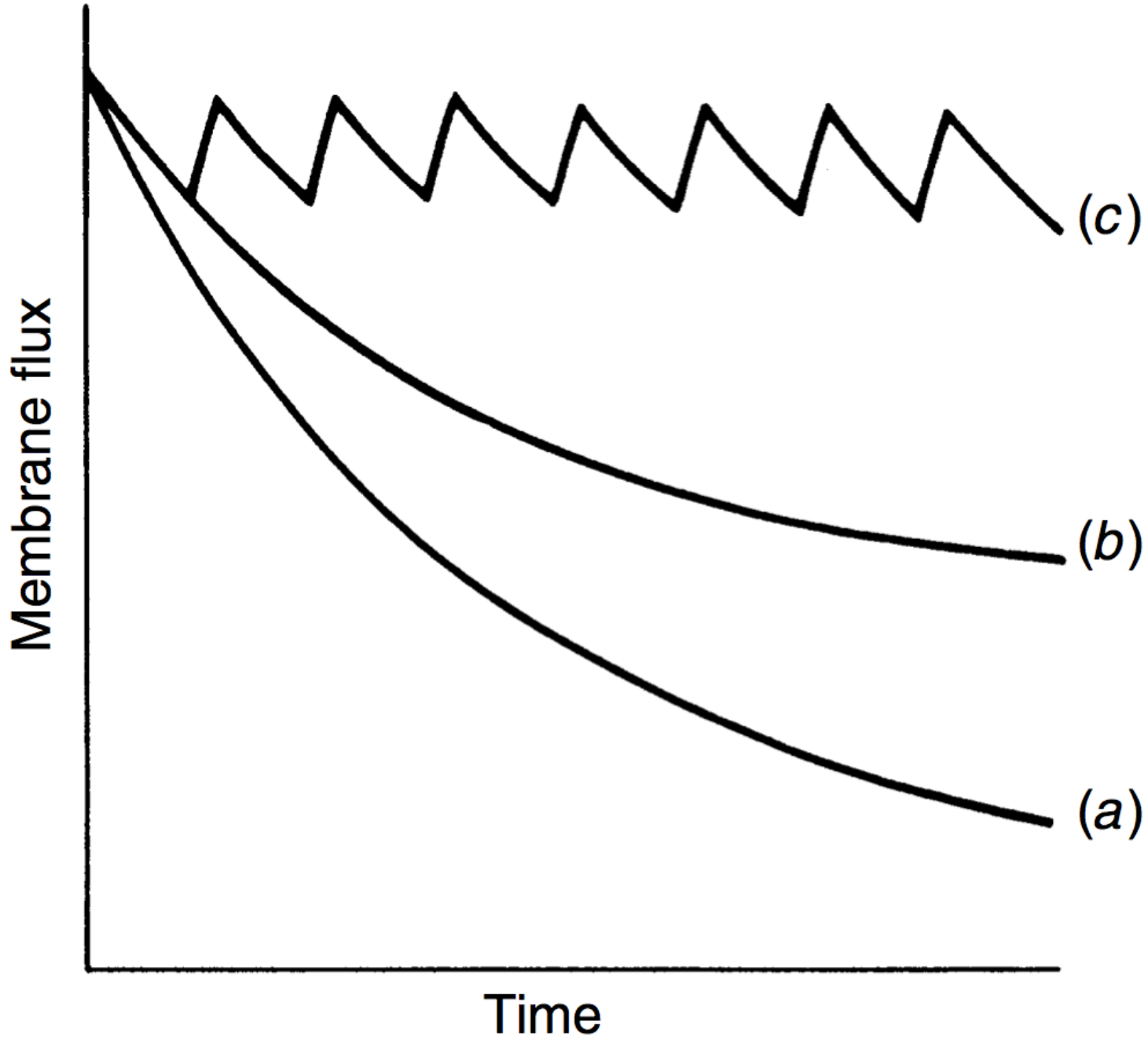
Cross-flow flowsheet



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

Dealing with fouling



A preliminary design

Main aim

Determine the **size** of a membrane for a required **flow rate** of permeate.

We have a reasonable budget to purchase equipment, and membrane samples from suppliers.

How would you set up your lab experiment(s) to get the information required?

-
-
-

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

Pop-quiz 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 30 kPa.

1. What is the resistance due to the membrane? Specify the units.
2. If operated with a protein-water mixture at a 20 kPa pressure difference, a flux of 216×10^{-6} $kg.s^{-1}.m^{-2}$ is measured at steady state. What is the resistance due to cake build-up? Specify the units.

Estimating the cake resistance, R_c

- $R'_{c,v} = R_{c,v} L_c = R_{c,v} \dfrac{V_{\text{cake}}}{A_{\text{membrane}}}$
- $R_{c,v} = R_c \cdot \rho_f$ and similarly $R_{m,v} = R_m \cdot \rho_f$
- **Important note**: $R'_{c,v}$ emphasizes that this is a resistance only when $J_v = \dfrac{J}{\rho_f}$, which has units $\left[\left(\text{m}^3.\text{s}^{-1}\right).\text{m}^{-2}\right]$
- Carman relationship: $R_{c,v} = 180 \left(\dfrac{1-e}{e^3}\right)\left(\dfrac{1}{D_p^2}\right)$
- $e =$ porosity of the cake; $e \sim 0.4$ if unknown
- $D_p =$ Sauter mean particle diameter [m]
- $L_c =$ estimated cake thickness [m]
- $R'_{c,v}$ has units of $[\text{m}^{-1}]$
- $R_{c,v}$ has units of $[\text{m}^{-2}]$

Microfiltration example

The previous lab experiment to determine mass-transfer resistance is preferred. But we can estimate it.

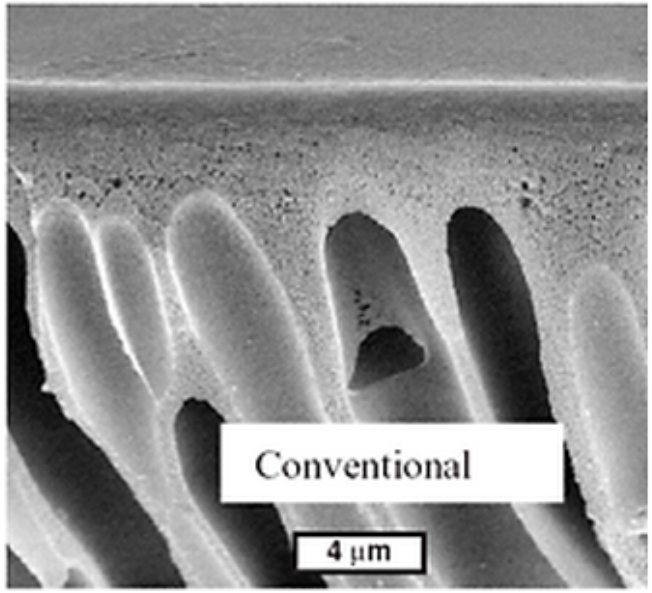
Water microfiltration

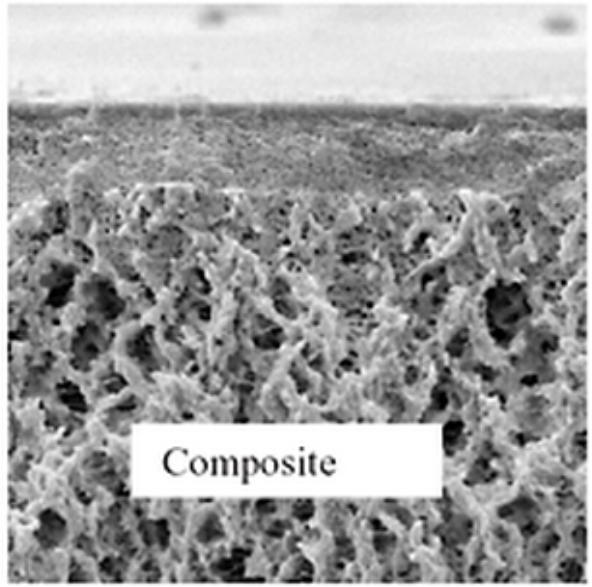
- Constant $\Delta P = 50$kPa applied in cross-flow membrane set up
- Membrane area $= 50\text{cm}^2 = 0.005\text{m}^2$
- Pure water at this ΔP produced a flux of 1.0 $\text{kg.s}^{-1}\text{.m}^{-2}$
- Feed at this same TMP produced a flux of 0.065 $\text{kg.s}^{-1}\text{.m}^{-2}$ permeate
- What is the estimated thickness of the cake build-up if the average particle size diameter is 2μm?

Practical use of this example?

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 $m^3.m^{-2}.hr^{-1}$
  $J_v = \quad 10$ to 50 $L.m^{-2}.hr^{-1}$ (LMH)
- asymmetric structure
- almost always operated in TFF





[Perry's 8ed; Ch20.4]

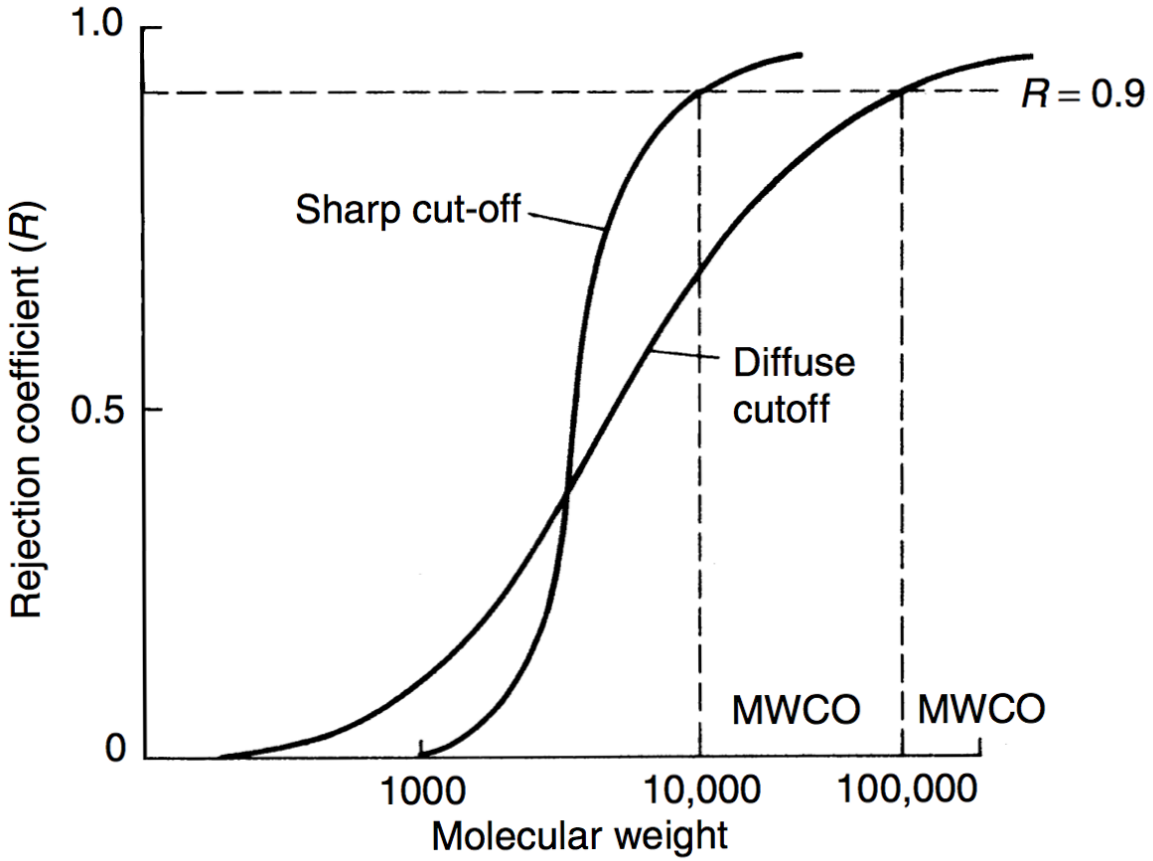
Ultrafiltration applications

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:
  - UF first, followed by reverse osmosis (RO)
  - valuable proteins retained by UF
  - permeate sent to RO to concentrate smaller molecule sugars and salts
  - this concentrated permeate: used for ethanol and lactic acid production

Ultrafiltration (UF)

- driving force $= \Delta P$ 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
- open, high-permeability side mainly for mechanical strength



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

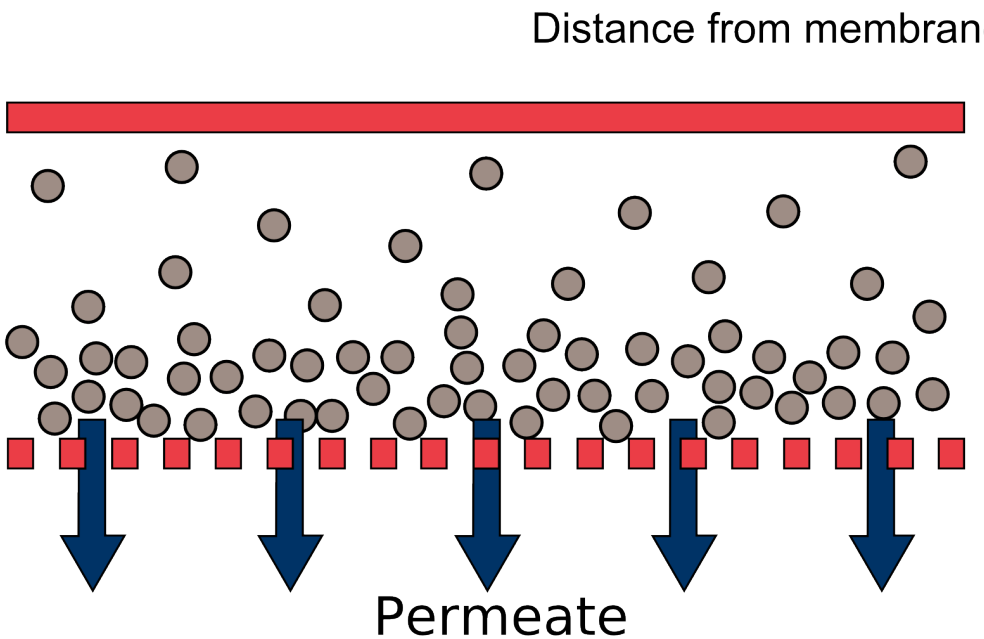
$$R = 1 - \frac{C_p}{C_f} = 1 - S$$

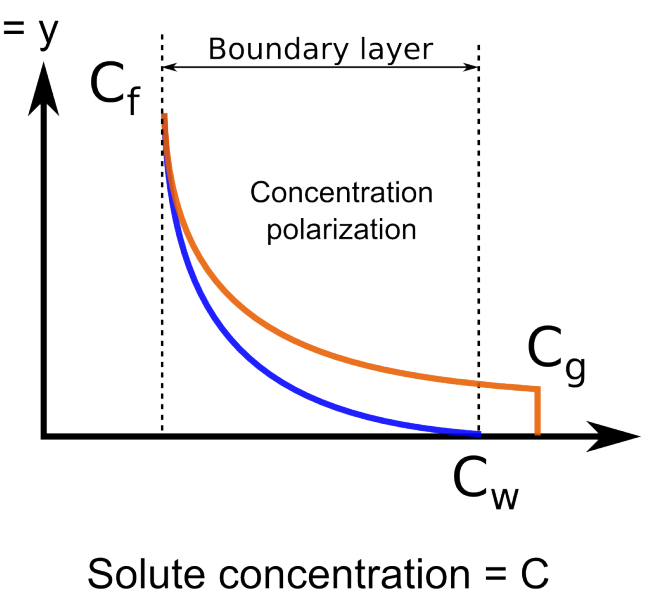
MWCO: molecular weight where $R = 0.9$

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

Transport phenomena in UF

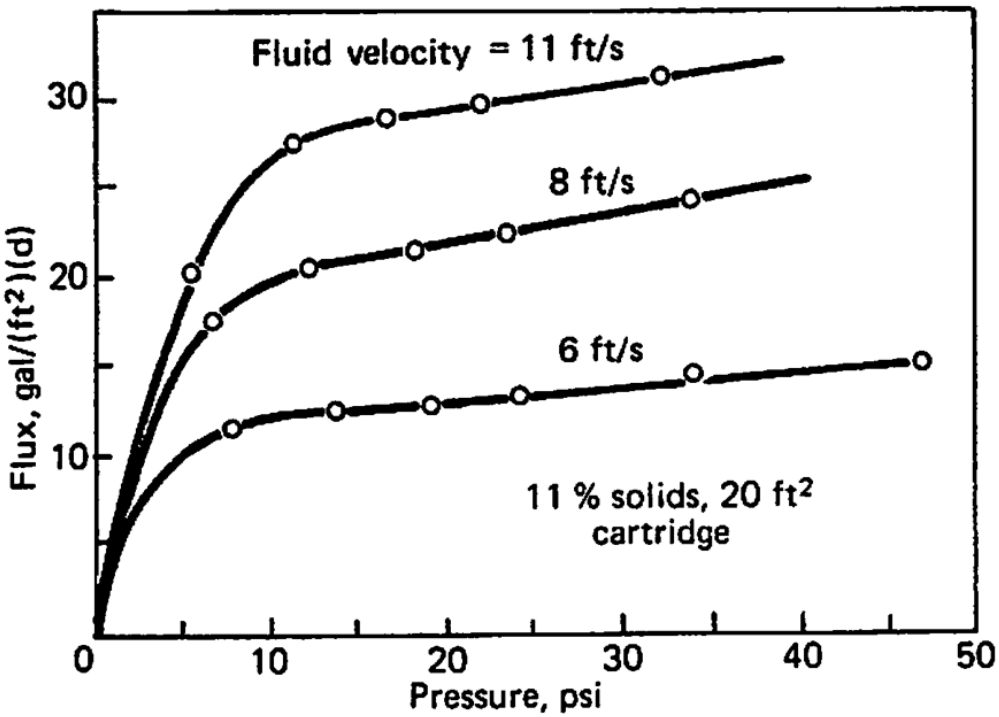
- solute (i.e. particles) carried towards membrane by solvent
- $J = \dfrac{\Delta P}{R_m + R_{cp}}$
- R_m = membrane resistance [m.s^{-1} if J is mass flux]
- R_{cp} = resistance due to "concentration polarization"
- R_{cp} effectively is the resistance due to solute boundary layer
- Mass concentration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





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]

Transport phenomena in UF

- Solute flux towards membrane: $\frac{J \cdot C}{\rho_f} = J_v C$
- Solute flux out of membrane: $J_v C_{\text{permeate}} \approx 0$ if membrane retains solute

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

J_v	$\left[\frac{\text{m}^3 \text{ solvent}}{\text{m}^2.\text{s}}\right]$	permeate volumetric flux
C	$\left[\frac{\text{kg solute}}{\text{m}^3 \text{ solvent}}\right]$	solute mass concentration in bulk
$C_p \approx 0$	$\left[\frac{\text{kg solute}}{\text{m}^3 \text{ solvent}}\right]$	solute mass concentration in permeate

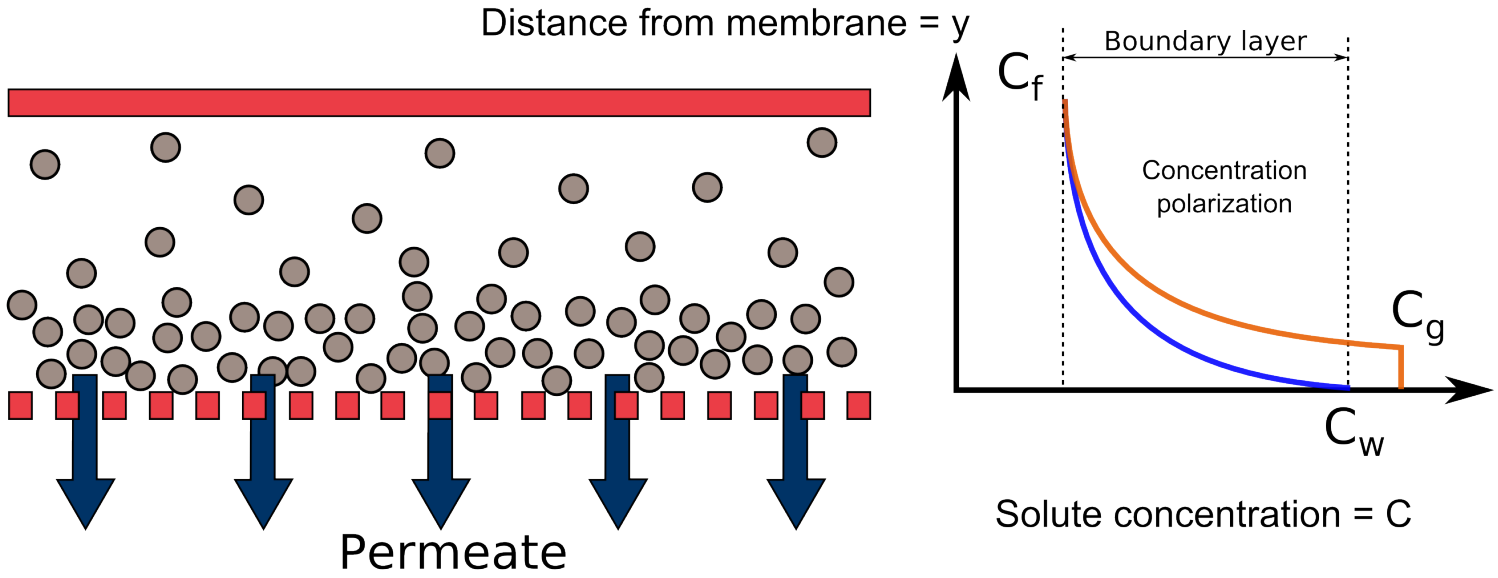
Space for picture

Diffusion term

- Solute diffusion away from membrane

$$J_{v,\text{diffusion}} = -D_{AB} \frac{1}{\rho_f} \frac{dC}{dy}$$

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
$J_{v,\text{diffusion}}$	$\left[\frac{\text{m}^3 \text{ solvent}}{\text{m}^2.\text{s}}\right]$	solvent volumetric flux



- See animation on Wikipedia

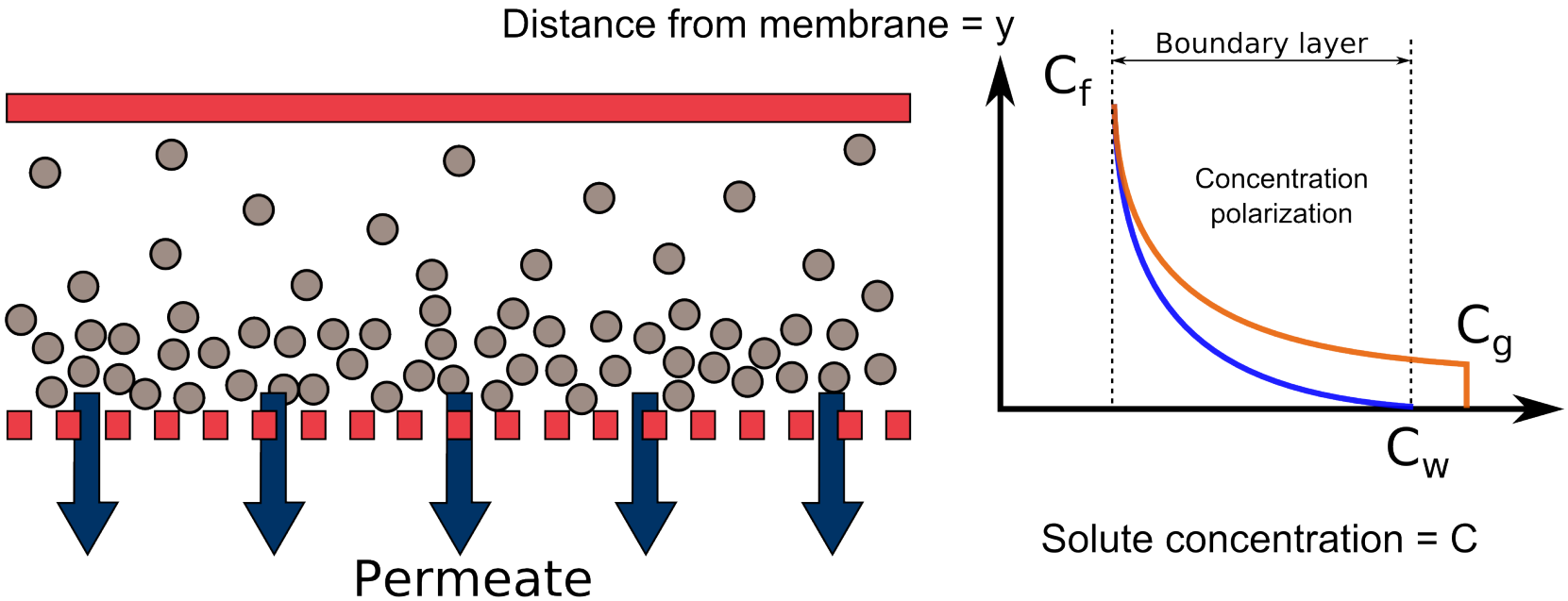
Transport at steady state

At steady state: diffusion back equals transfer through membrane

$$\frac{J(C - C_p)}{\rho_f} = -D_{AB}\frac{1}{\rho_f}\frac{dC}{dy}$$

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

$$\ln\left(\frac{C_w - C_p}{C_f - C_p}\right) = \frac{JL_c}{D_{AB}} = \frac{J}{h_w}$$



UF: mass-transfer key points

Assuming $C_p \approx 0$

$$\frac{JL_c}{D_{AB}} = \frac{J}{h_w} = \ln\left(\frac{C_w}{C_f}\right)$$

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 $J_{\text{lim}} = f(C_w, C_f, h_w)$
- 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} $\mathrm{m^2.s^{-1}}$

Example question

An ultrafiltration application is required to treat a waste stream that has 0.5 $kg^3.m^{-3}$ waste in the feed. The desired solute concentrate must be 20 $kg^3.m^{-3}$.

Pilot plant studies show the flux can be expressed as

$$J = 0.02 \ln\left(\frac{25}{C_f}\right)$$

in units of $m^3.m^{-2}.hour^{-1}$. Due to fouling the flux from this membrane system never exceeds 0.05 $m^3.m^{-2}.hour^{-1}$.

What is the limiting final concentration, C_f? What is the interpretation of it?

Geometries for ultrafiltration (recap)

Spiral wound

-
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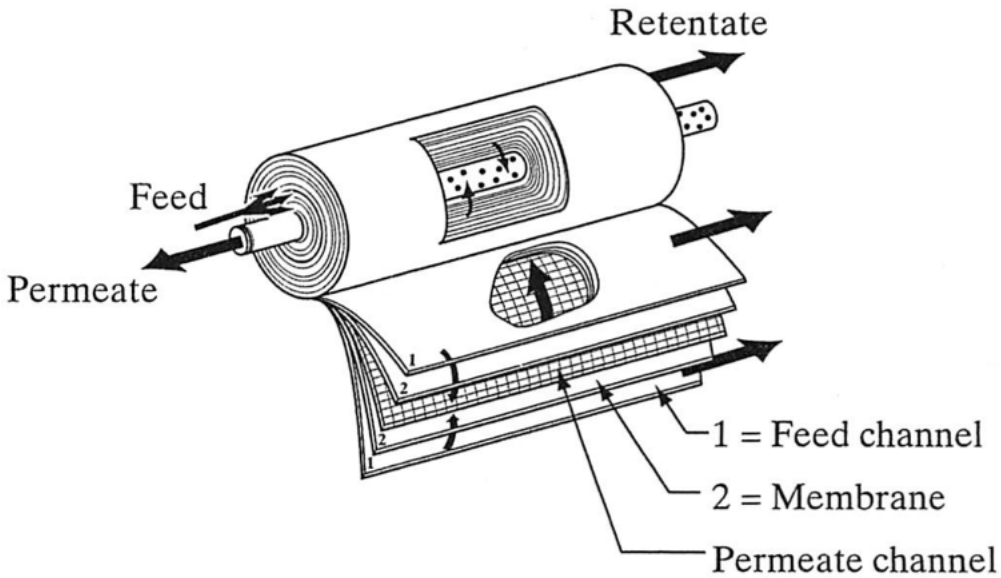
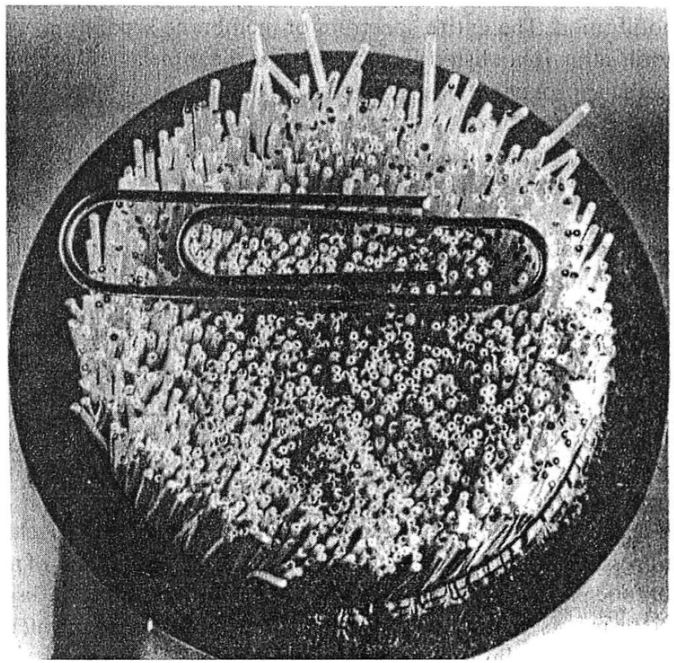


Hollow fibre membranes

- 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



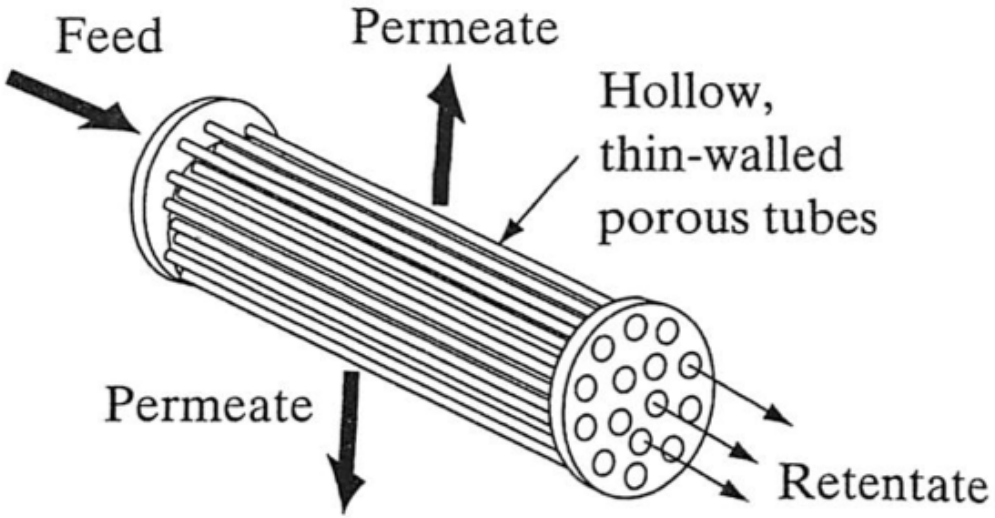
Geometries for ultrafiltration (recap)

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.

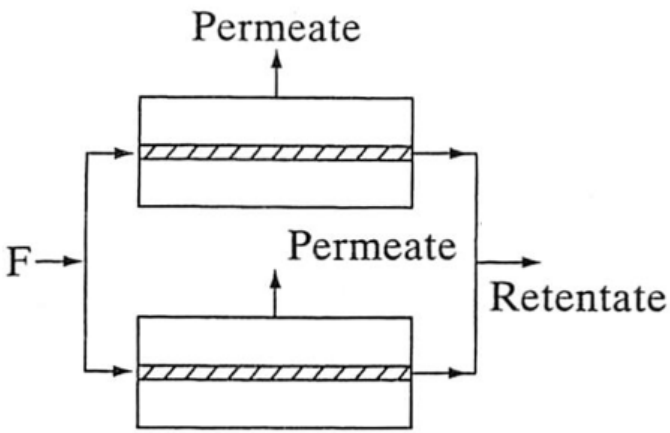
Sequencing membrane modules

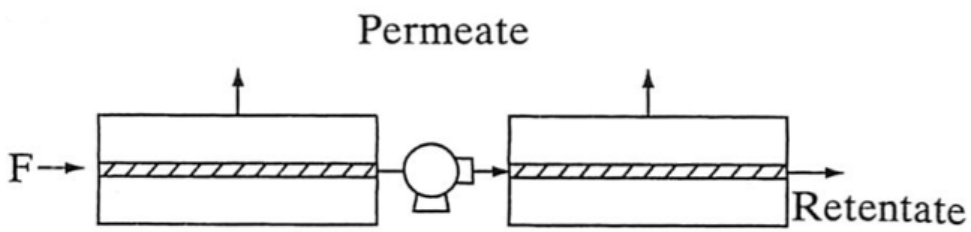
Parallel

- 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)





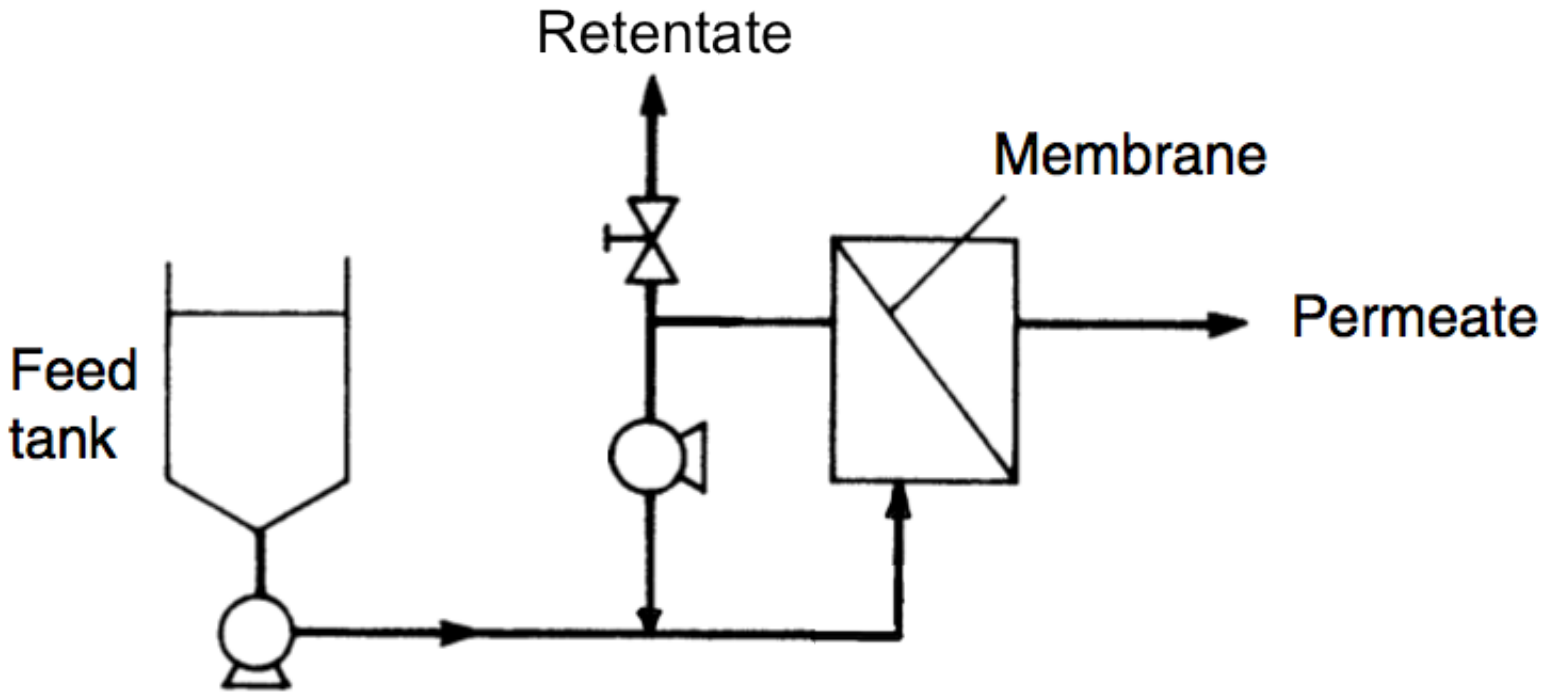
Example of an installation

- Larnaca, Cyprus
- SWRO membrane, i.e. desalination
- 21.5 million m^3 per year
- parallel and series

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"



- Initially close retentate valve (batch mode operation)
- Fluxes slowly reduce
- Open retentate valve and operate at steady state

Class example

We need to treat 50 $m^3.day^{-1}$ of waste containing a solute at 0.5 $kg^3.m^{-3}$. The desired solute concentrate must be 20 $kg^3.m^{-3}$. The plant operates 20 hours per day.

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

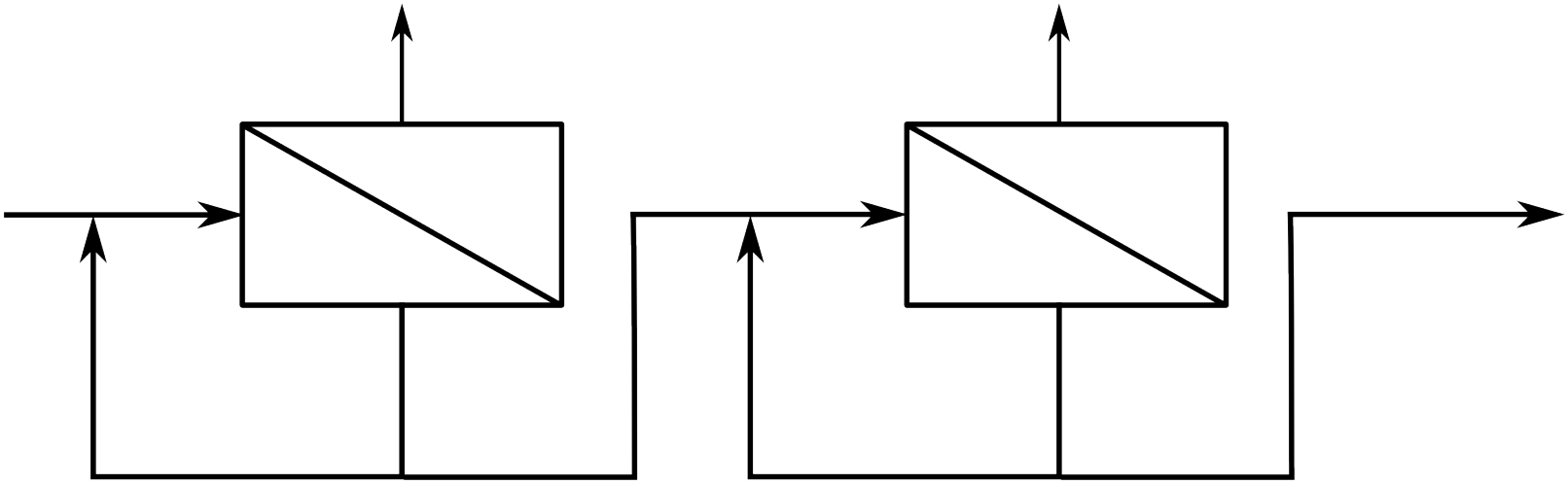
$$J = 0.02 \ln\left(\frac{25}{C_f}\right)$$

in units of $m^3.m^{-2}.hour^{-1}$.

If each membrane module is 30 m^2:

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

Multiple units in series (worked example)



Now consider the previous example. Find the optimal areas, A_1 and A_2 for the membranes.

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- Uhlmann's Encyclopedia, "Membrane Separation Processes, 1. Principles", DOI:10.1002/14356007.a16_187.pub3