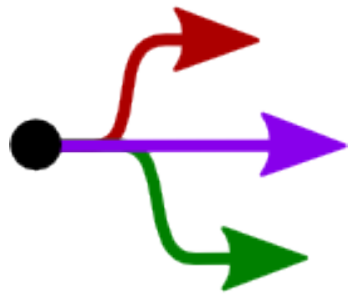
# Separation Processes

## ChE 4M3





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Overall revision number: 73 (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)

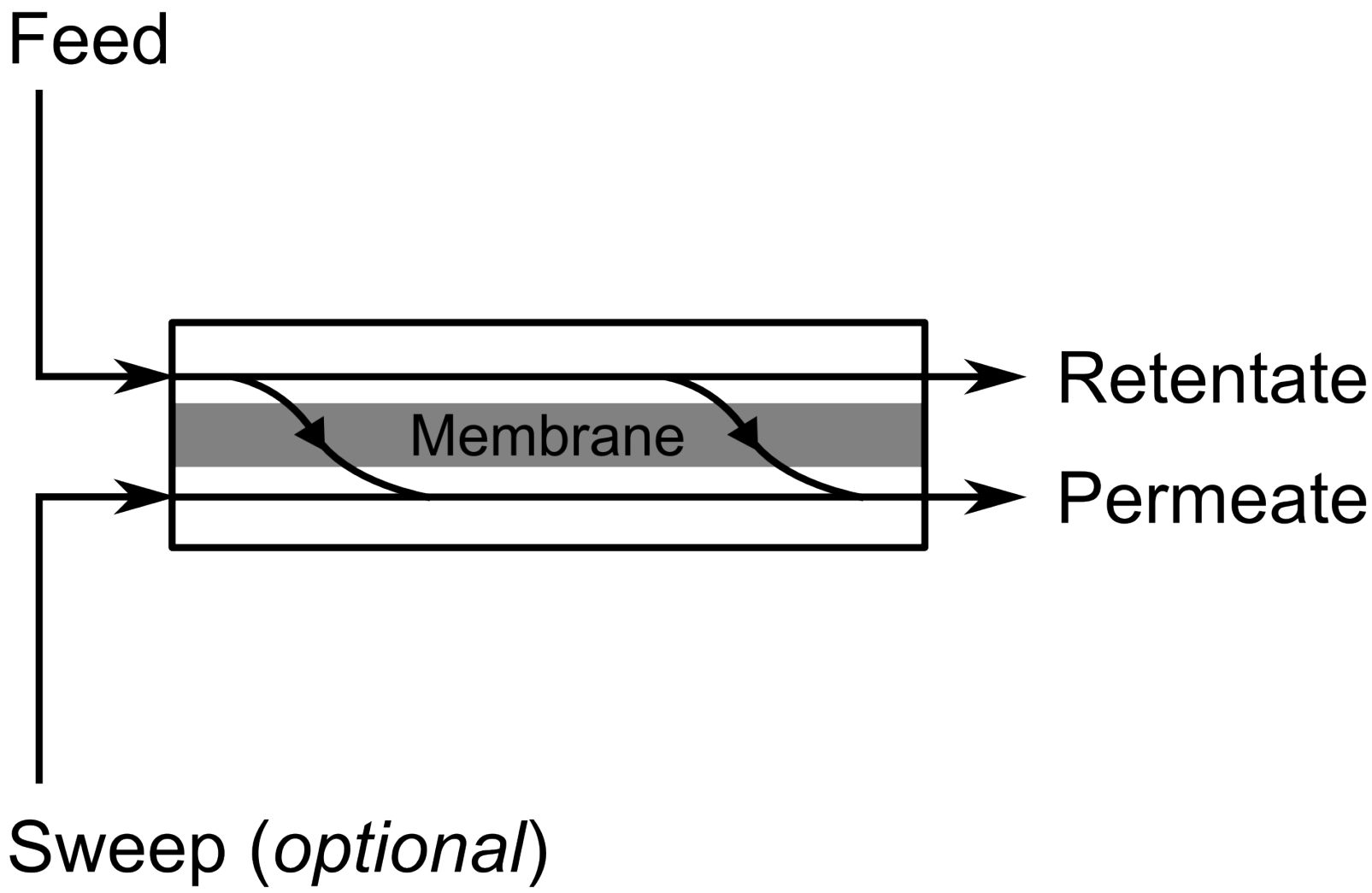
# Market size

**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

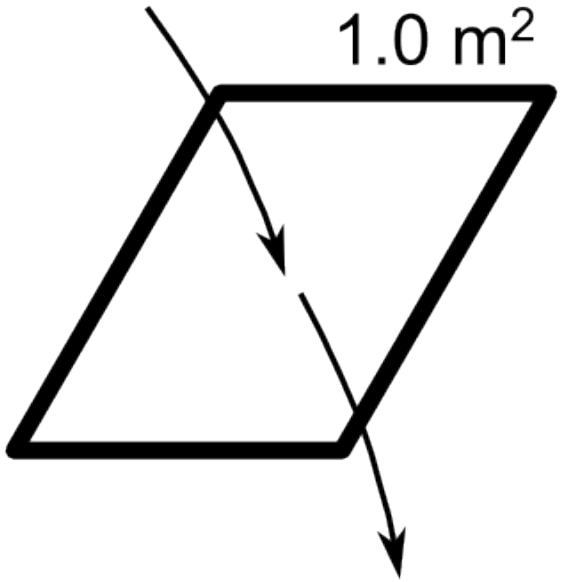
energy separating agent: the applied pressure (pressure drop)

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

# 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 $\text{m.s}^{-1}$




## 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 $\Delta P$ 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

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

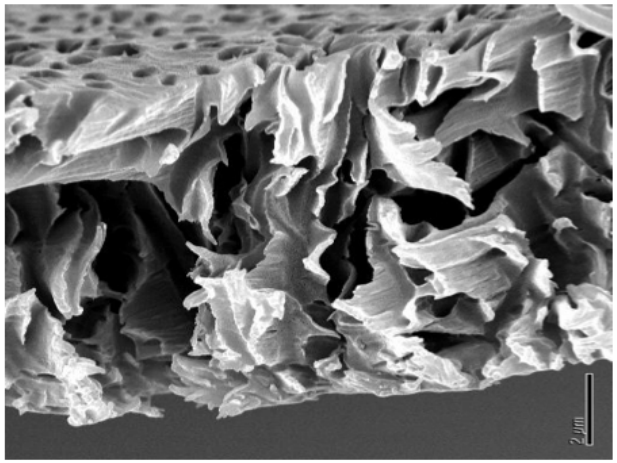
Symbolically:

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

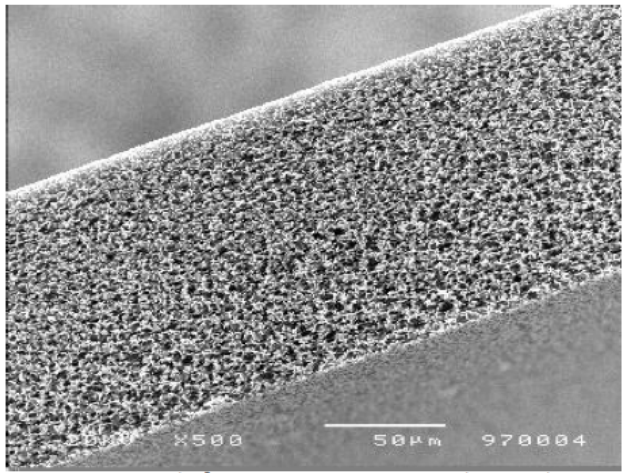
- $\text{permeance} = \dfrac{\text{permeability}}{L} = \dfrac{1}{\text{resistance}} = \dfrac{1}{R} =$ "mass transfer coeff"
- permeance: easier to measure
- permeance units: depend on choice of (driving force) and $J$
- resistance $= f$(thickness, viscosity, porosity, pore size)
- we will specifically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

# Microfiltration

- 0.1 $\mu$m to 10 $\mu$m retained mainly by sieving mechanism
- conventional filters: not effective below $\sim 5$ $\mu$m
- 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



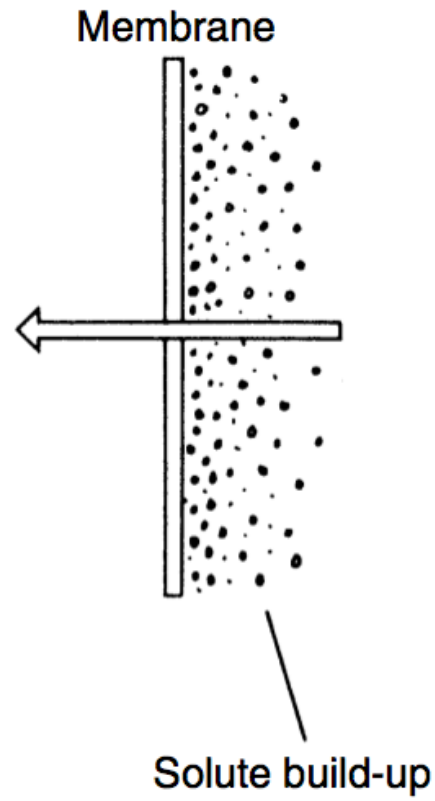

symmetric spongy structure

[Henk Koops' slide]

# General modelling equation applied

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

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

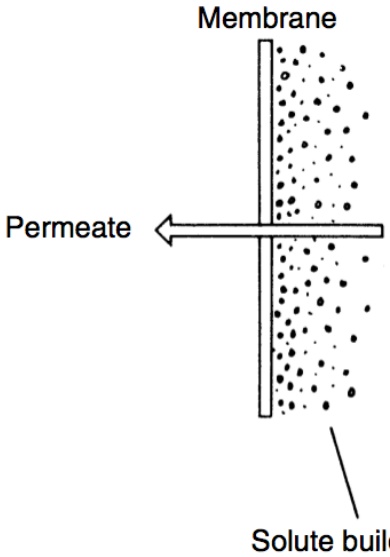



| | | |
|---|---|---|
| $J$ | $[\text{kg.s}^{-1}.\text{m}^{-2}]$ | permeate flux |
| $\mu$ | $[\text{kg.m}^{-1}.\text{s}^{-1}]$ | permeate viscosity |
| $\Delta P$ | $[\text{Pa}] = [\text{kg.m}^{-1}.\text{s}^{-2}]$ | TMP varies for different applications |
| $R_m$ | $[\text{m.kg}^{-1}]$ | resistance through membrane (small) |
| $R_c$ | $[\text{m.kg}^{-1}]$ | resistance through cake (large) |
| $\ell_m$ | [m] | membrane thickness |
| $L_c$ | [m] | effective cake thickness |

[Illustration from Richardson and Harker, Ch8]

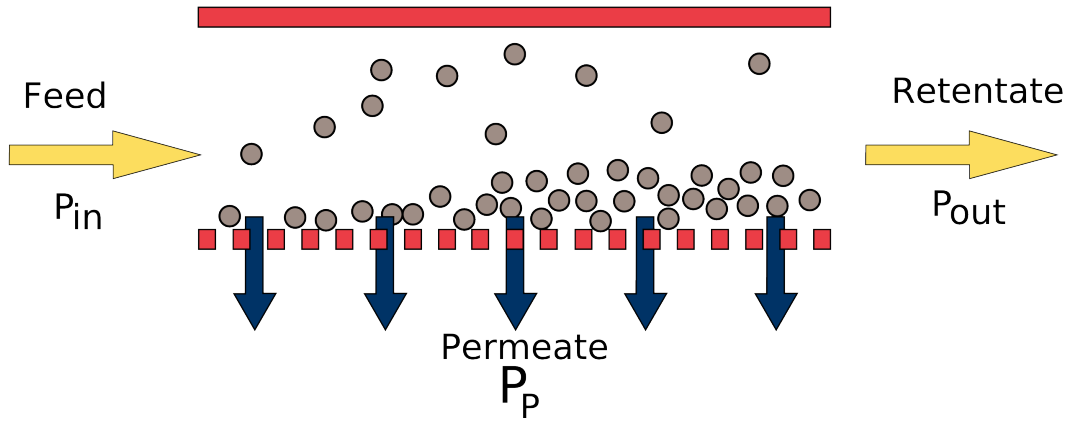
# Flow patterns for microfiltration

## 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
  - cross-flow induces shearing to erode cake
  - reduces cake resistance, $R_c$
- $\Delta P = \frac{P_{in} + P_{out}}{2} - P_P$

# Flow patterns for microfiltration

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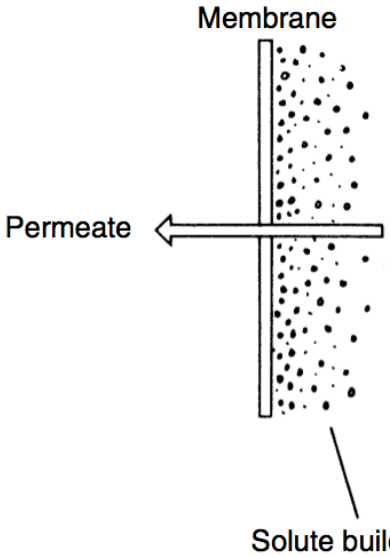


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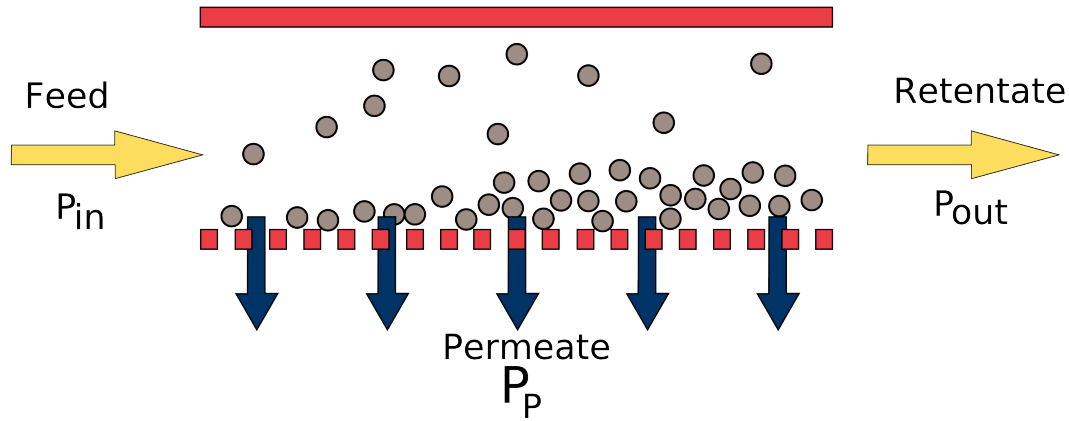


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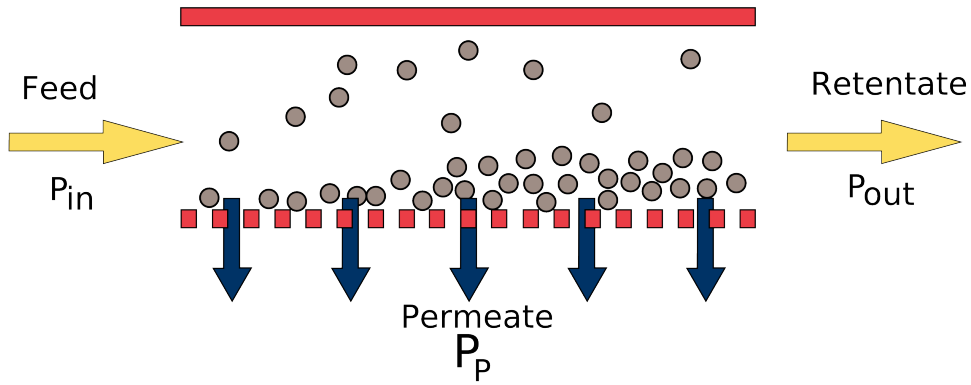
# Dead-end flow vs cross-flow geometries

## Dead-end flow

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

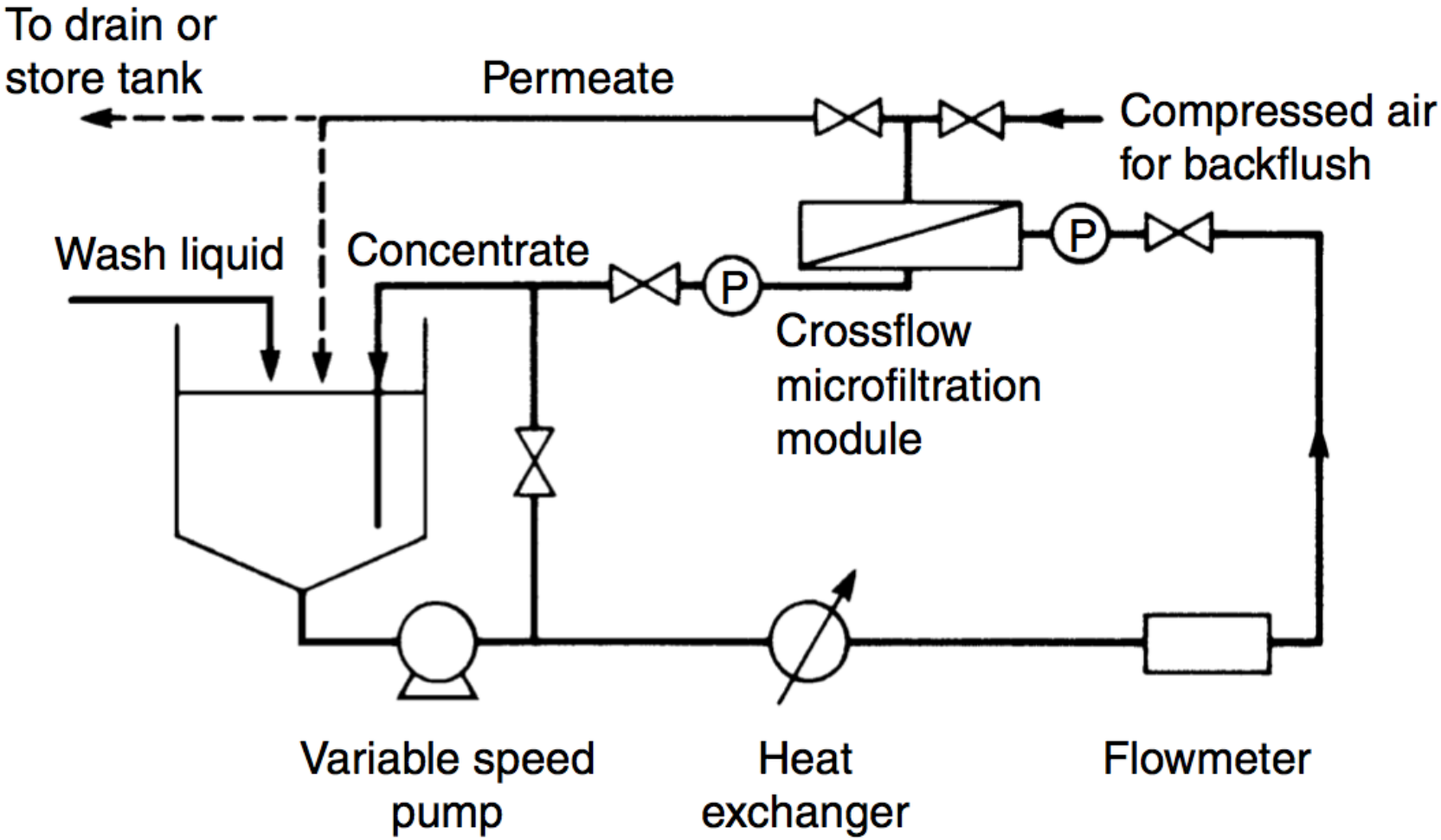
$$J = \frac{\Delta P}{\mu\left(R'_m + R_c L_c\right)}$$

## Cross-flow (TFF)




- fluid velocity: 1 to 8 $m.s^{-1}$ tangentially
- keeps mass transfer resistance low
- for a given $\Delta P$: TFF allows us to obtain higher fluxes than dead-end (usually $\Delta P$ 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

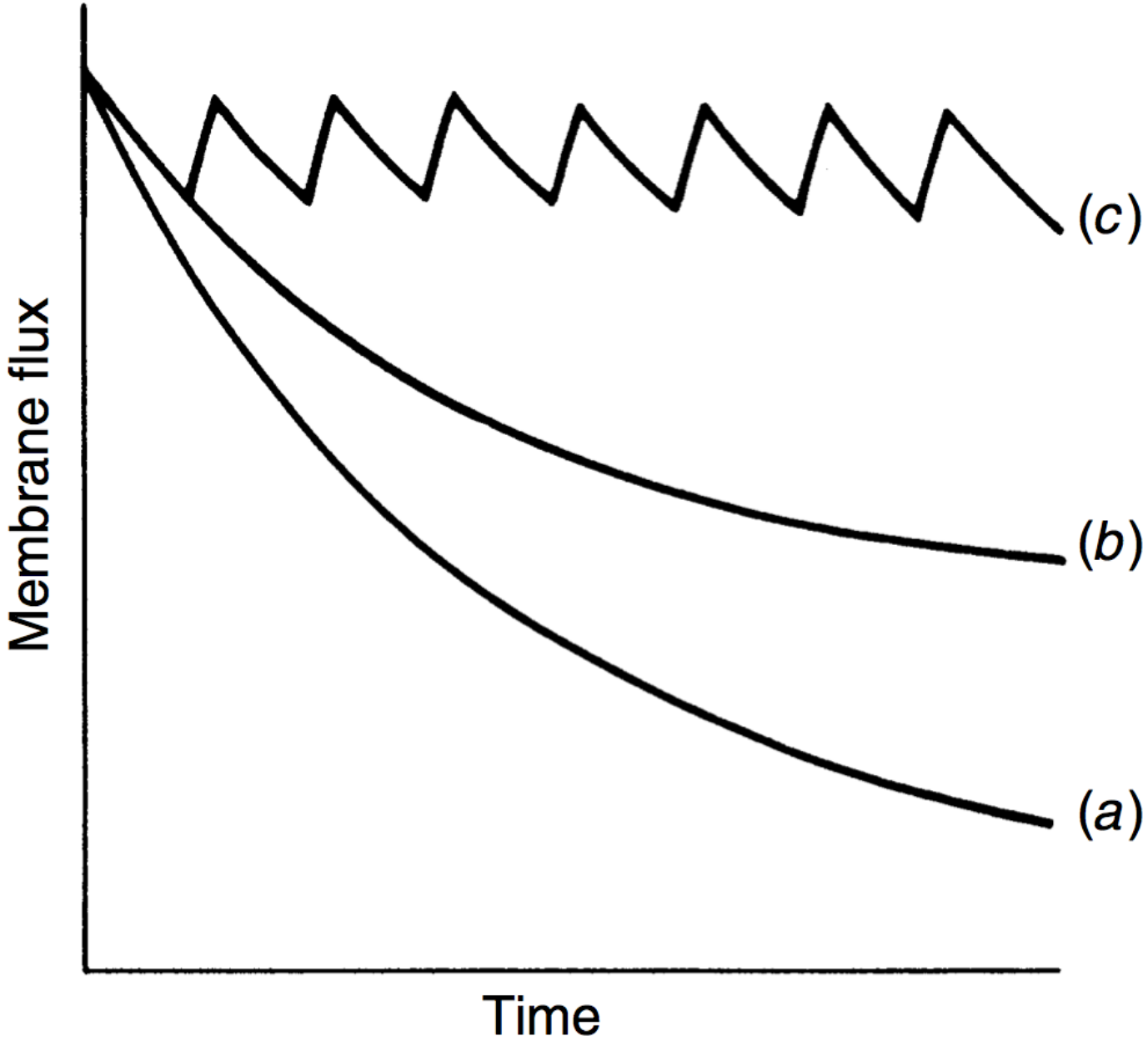



How to pressurize the unit?

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

[Illustration from Richardson and Harker, Ch8]

# Dealing with fouling




[Richardson and Harker, Ch8]

# 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?

- $J = \rho_f \frac{Q_p}{A} = \frac{\Delta P}{\mu(R_m \ell_m + R_c L_c)} = \frac{\Delta P}{\mu(R'_m + R'_c)}$
- $R'_m$: estimated using pure solvent through membrane at $\Delta P$
- $R'_c = R_c L_c$: obtained from a plot of $J_f$ vs $\Delta P_f$
  - set different $\Delta P_f$; then measure corresponding $J_f$ once steady
  - find $J_f$ (interpolate) that gives required $Q_p$ by varying $A$

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# 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 $216 \times 10^{-6}$ $kg.s^{-1}.m^{-2}$ 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.

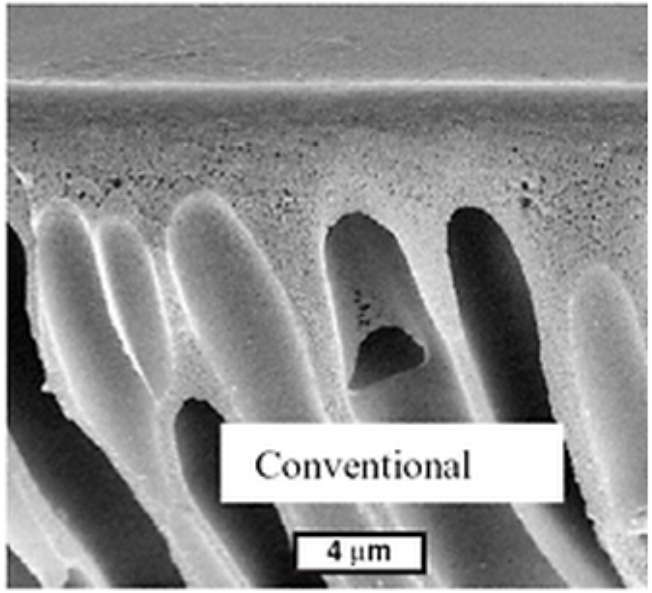
## Water microfiltration

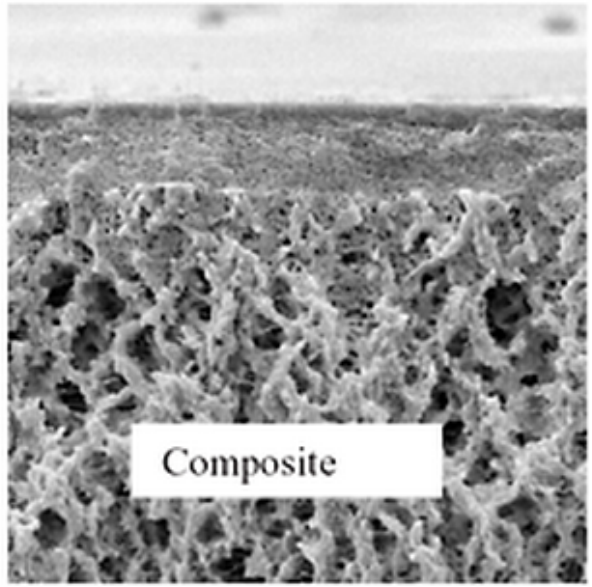
- Constant $\Delta P = 50$kPa applied in cross-flow membrane set up
- Membrane area $= 50\text{cm}^2 = 0.005\text{m}^2$
- Pure water at this $\Delta P$ produced a flux of 1.0 $\text{kg.s}^{-1}\text{.m}^{-2}$
- Feed at this same TMP produced a flux of 0.065 $\text{kg.s}^{-1}\text{.m}^{-2}$ permeate
-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

Practical use of this example?

# Ultrafiltration (UF)

- 5 nm to 100 nm (0.1 $\mu$m) 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]

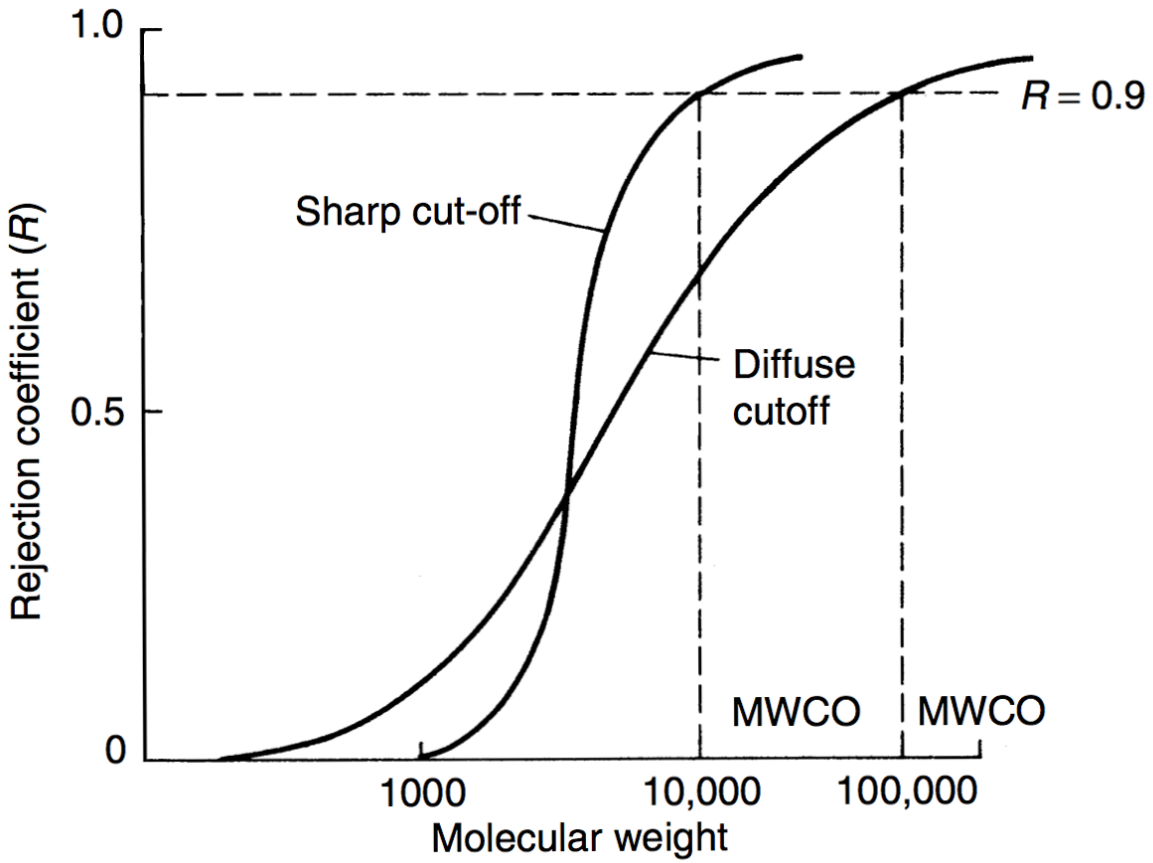
# Ultrafiltration applications

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 $10\mu$m thick; provides selectivity
- open, high-permeability side mainly for mechanical strength




[Richardson and Harker, Ch8]

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

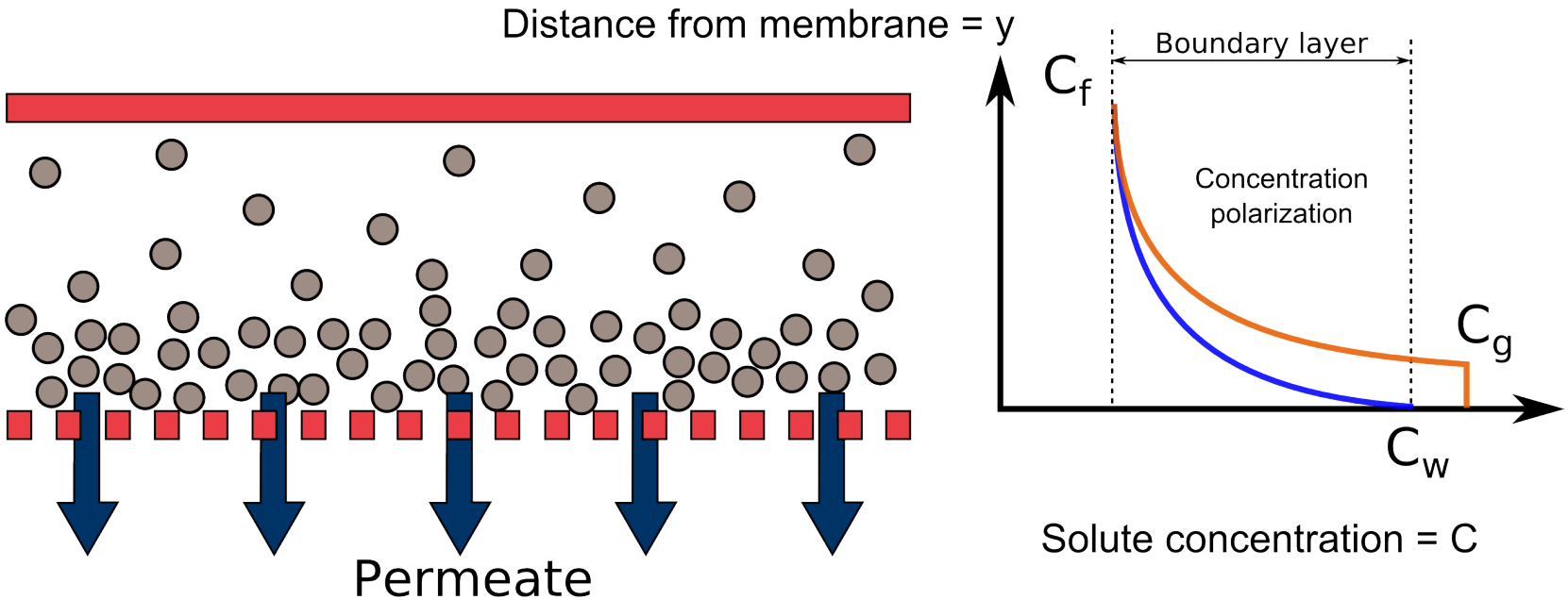
$$R = 1 - \frac{C_p}{C_f} = 1 - S$$

MWCO: molecular weight where $R = 0.9$

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

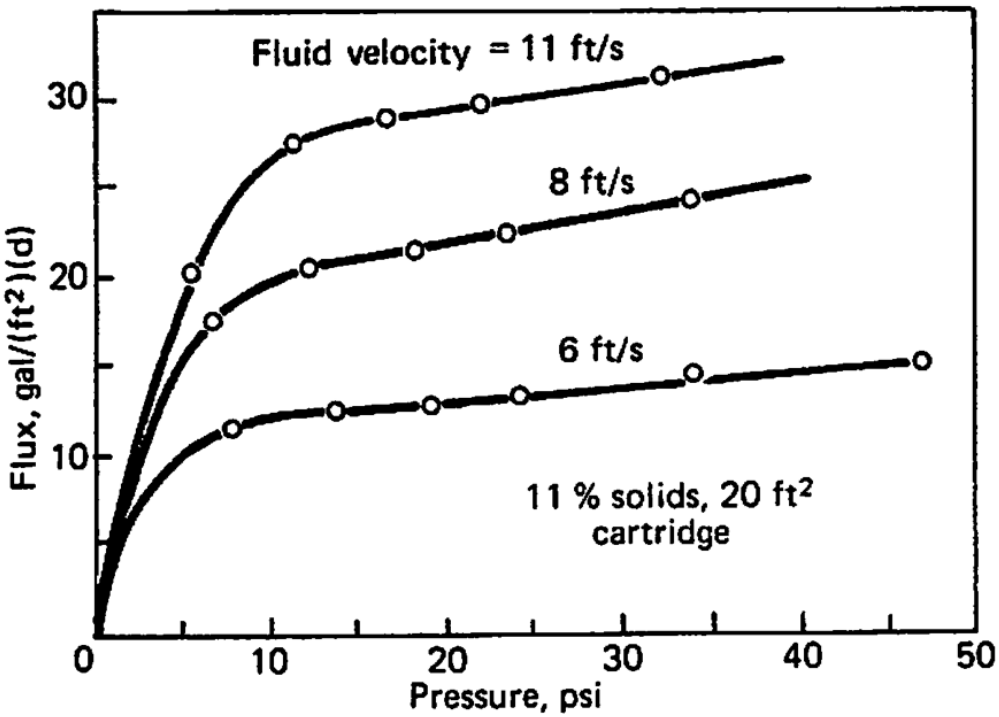
# Transport phenomena in UF

- 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 $C_f$ (in retentate), 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 $\Delta P$ leads to compacting this layer, increasing $C_w$
- So diminishing returns from increasing $\Delta P$
- 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 |

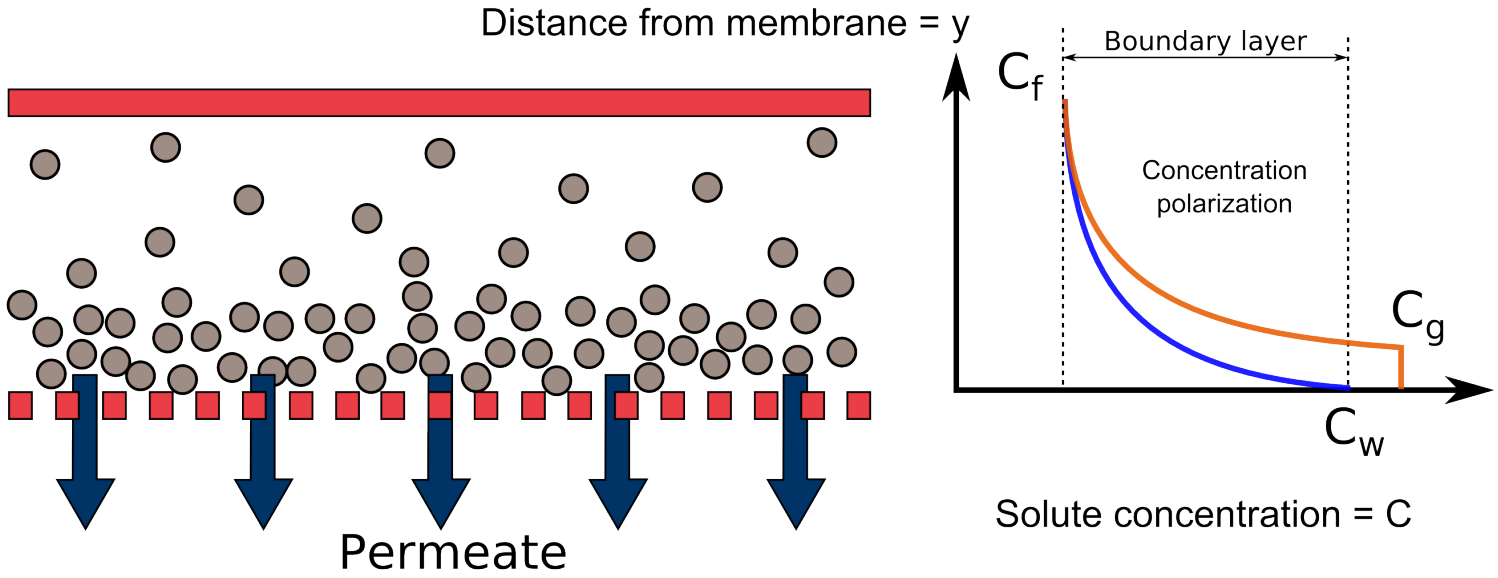
Space for picture

# 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

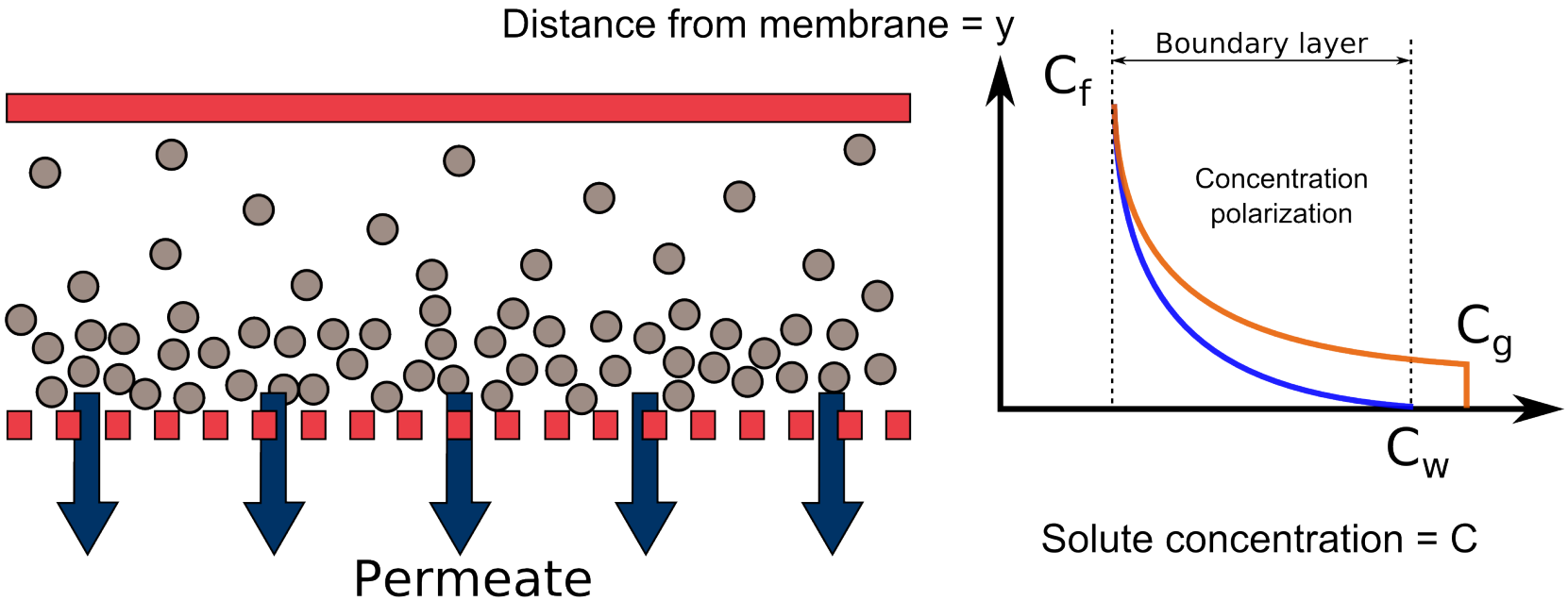
# Transport at steady state

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 $\Delta P$ 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: $1 \times 10^{-9}$ (fast!) to $1 \times 10^{-11}$ $\mathrm{m^2.s^{-1}}$

# Example question

An ultrafiltration application is required to treat a waste stream that has 0.5 $kg.m^{-3}$ 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 $m^3.hour^{-1}.m^{-2}$. Due to fouling the flux from this membrane system never exceeds 0.05 $m^3.hour^{-1}.m^{-2}$.

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

# Geometries for ultrafiltration (recap)

**Tubes in a shell**

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

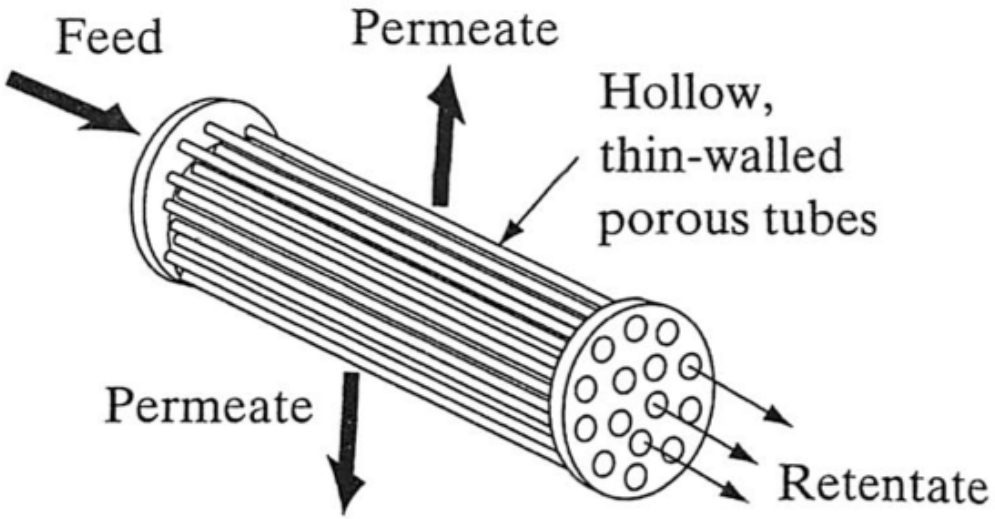
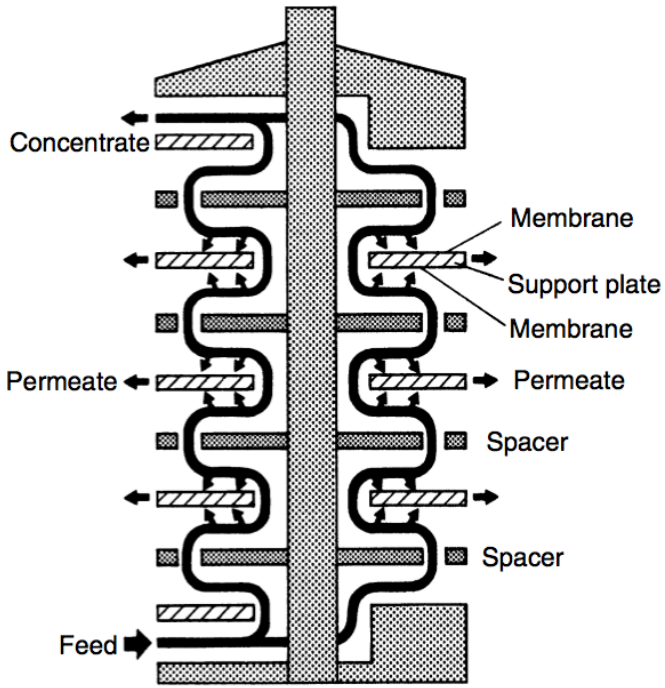



**Plate and frame**

- batch operation



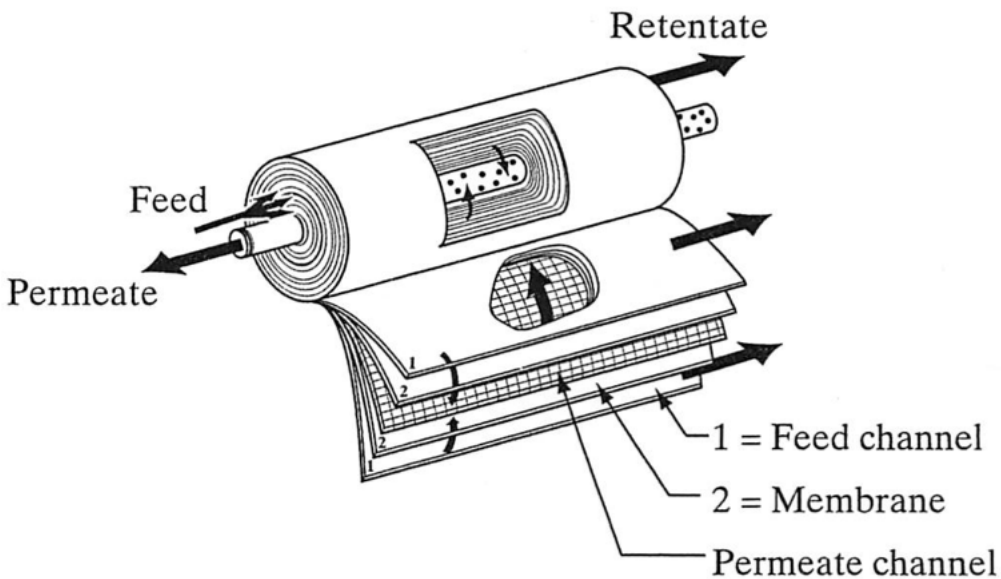

- All these units bought as complete module from supplier
- In fixed sizes; so need to be combined (next section)
- Also as cassettes, tubes and flat sheets run in TFF to increase flux.

[Illustrations from Wankat, 2ed, Ch 16]

# Geometries for ultrafiltration (recap)

## Spiral wound

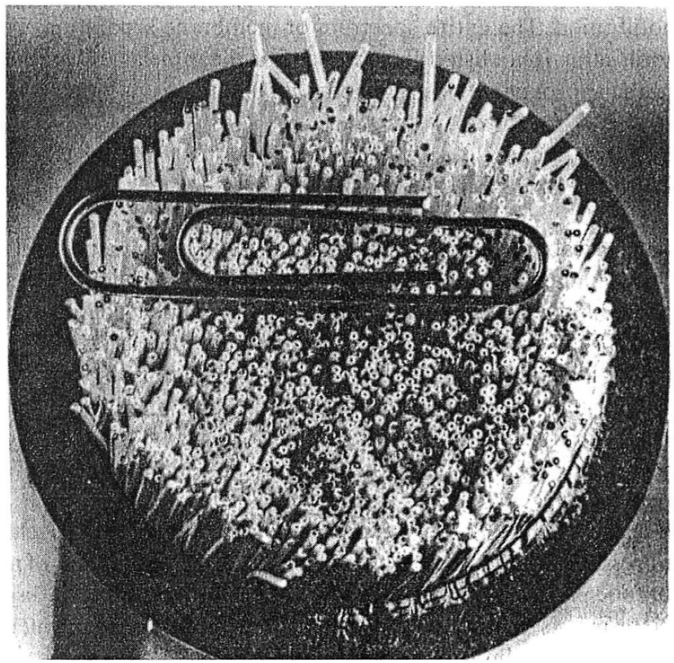
- high surface area per unit volume
- high turbulence, reducing mass transfer resistance

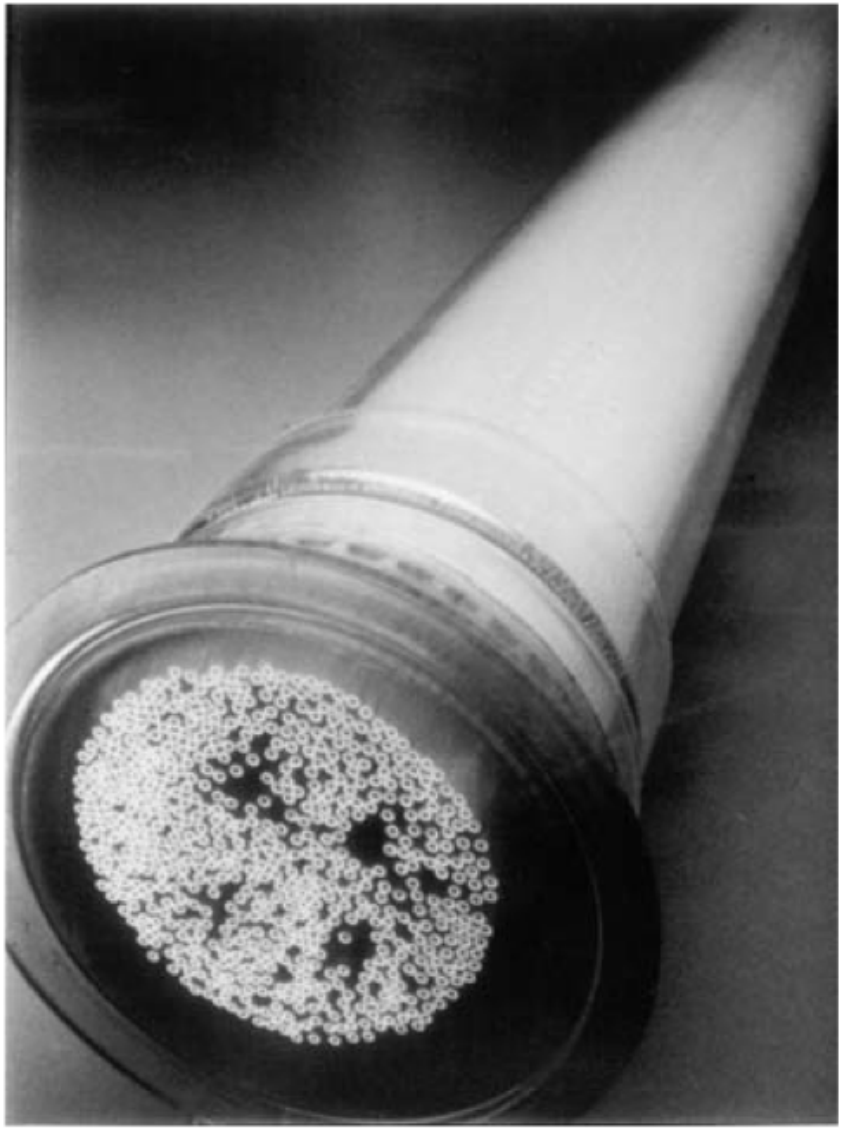



[Illustrations from Wankat, 2ed, Ch 16]

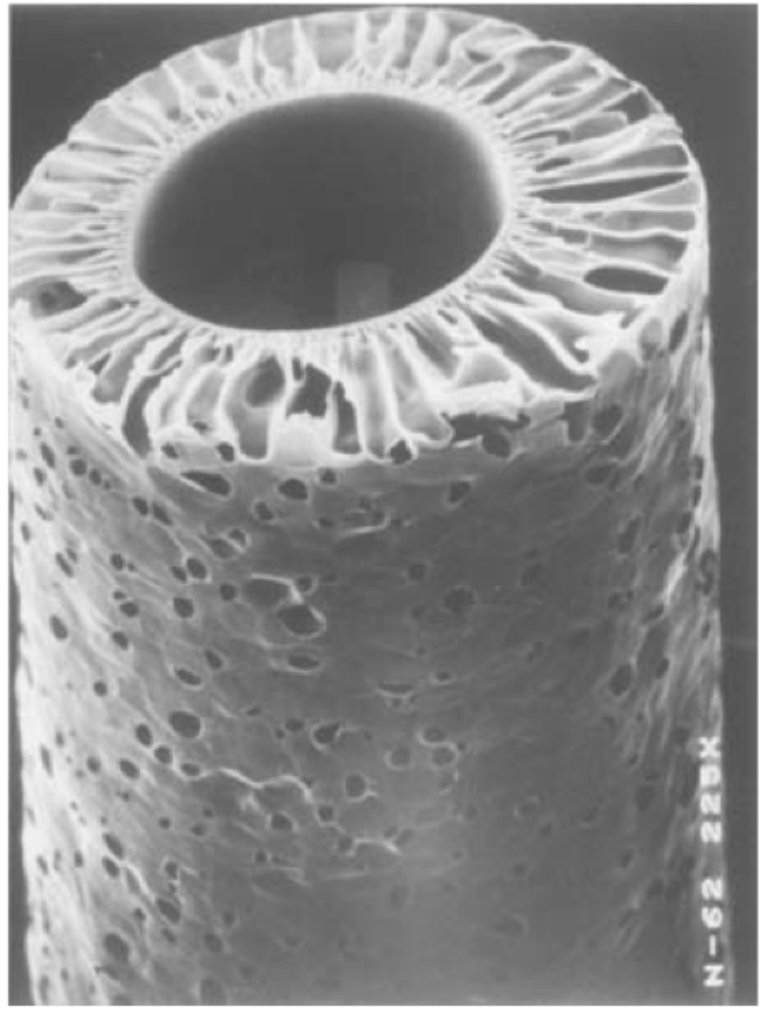
## Hollow fibre membranes

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





(*a*)




(*b*)

[Richardson and Harker, Ch8]

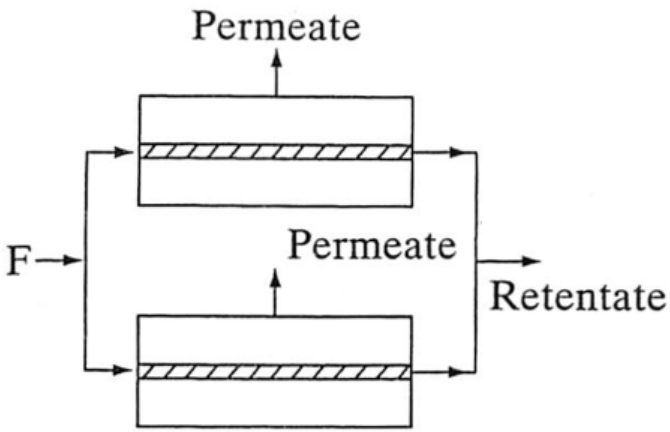
# Sequencing membrane modules

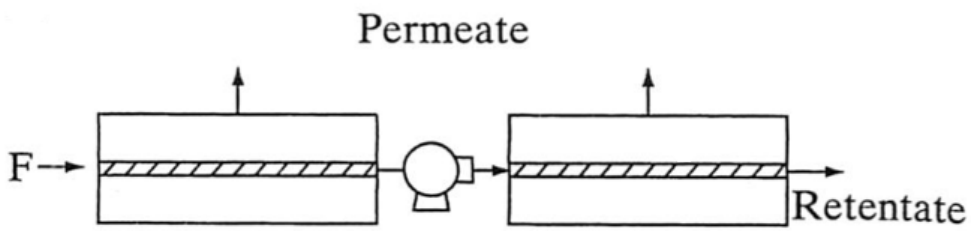
**Parallel**

- 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

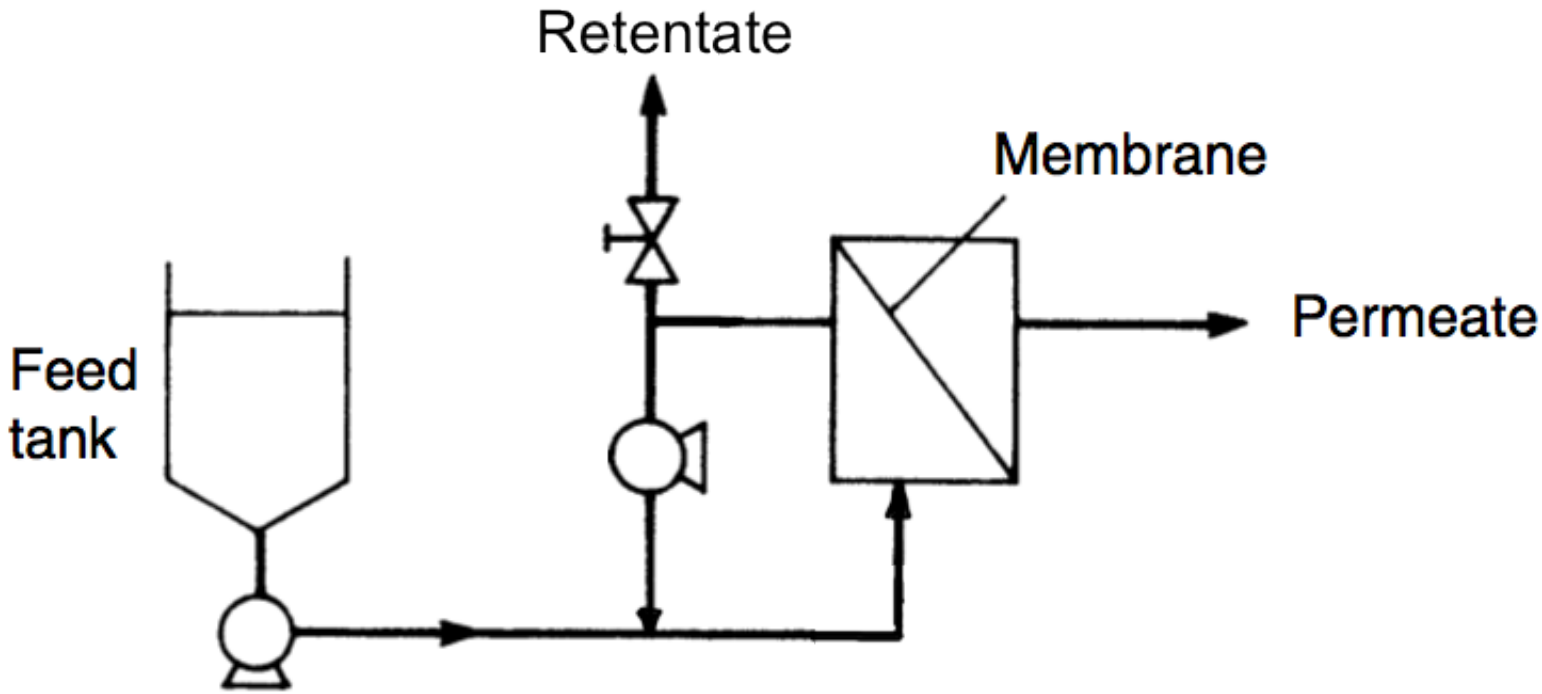

- Larnaca, Cyprus
- SWRO membrane, i.e. desalination
- 21.5 million $m^3$ per year
- parallel and series

[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

# Class example

We need to treat 50 $m^3.day^{-1}$ of waste containing a solute at 0.5 $kg.m^{-3}$. 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

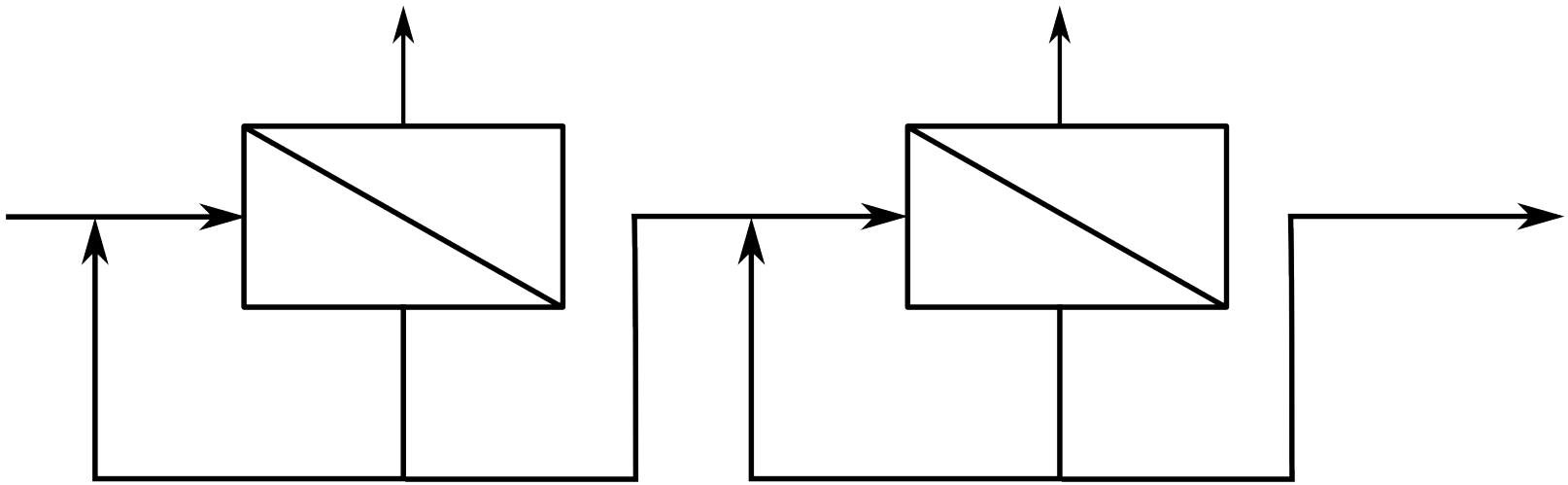
$$J = 0.02 \ln\left(\frac{25}{C_f}\right)$$

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

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.

# References


- Wankat, "Separation Process Engineering", 2nd edition, chapter 16
- Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", Chapter 2.1
- Seader, Henly 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