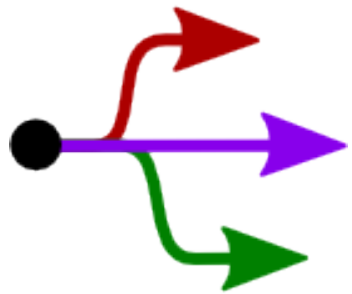
Separation Processes

ChE 4M3



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Overall revision number: 77 (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)

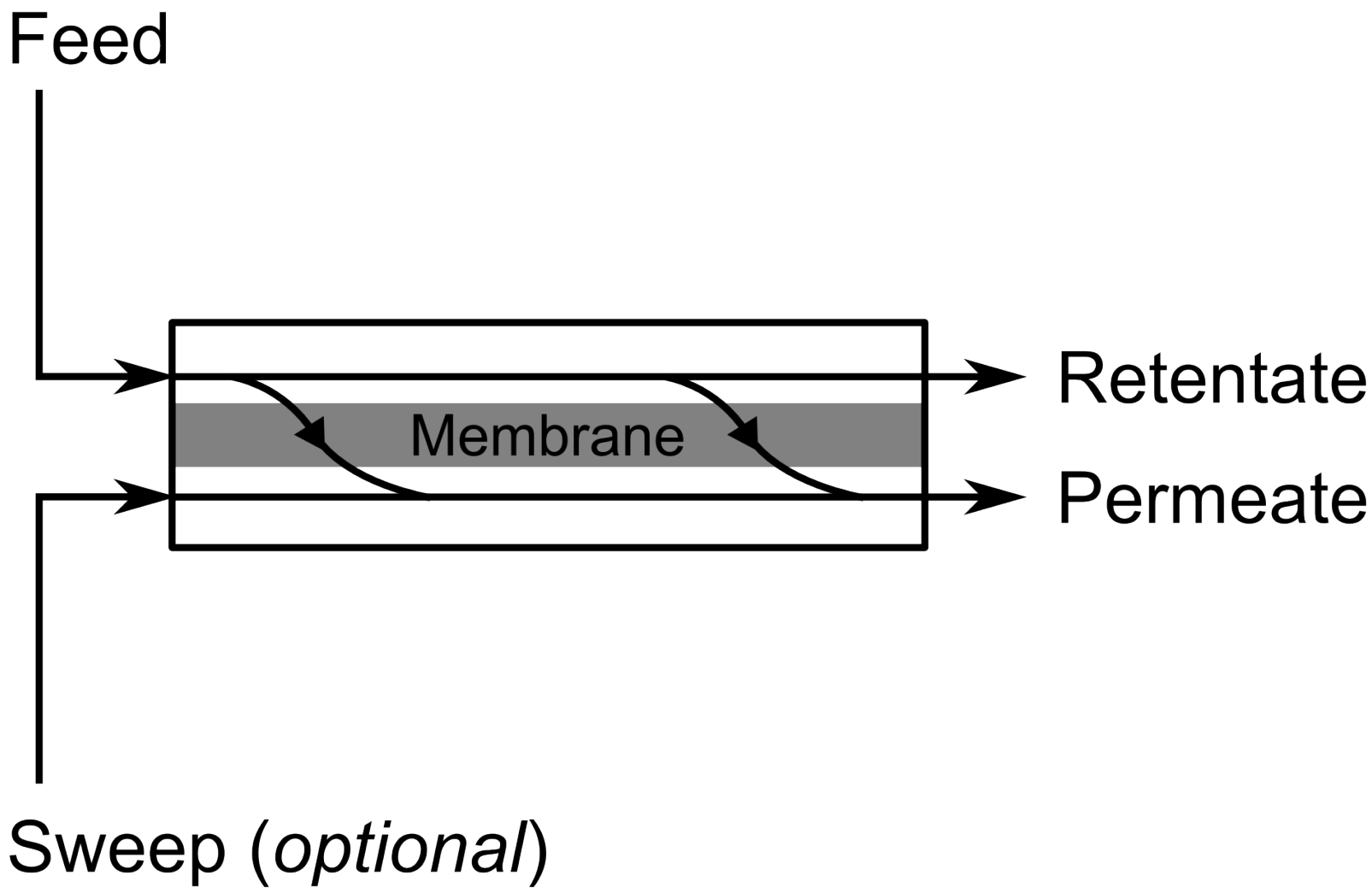
Market size

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

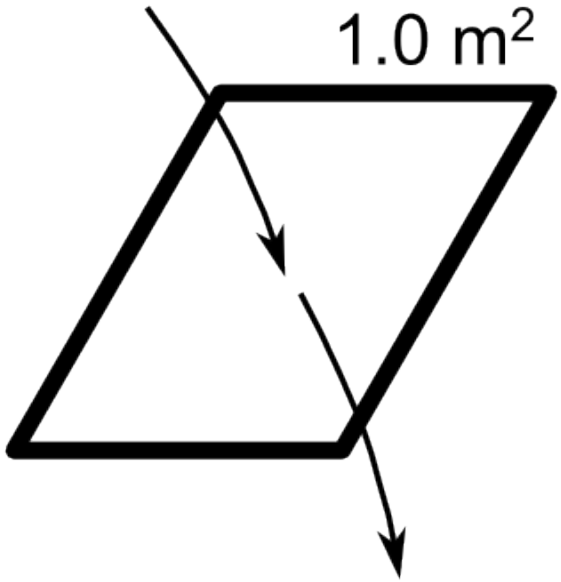
energy separating agent: the applied pressure (pressure drop)

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

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

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

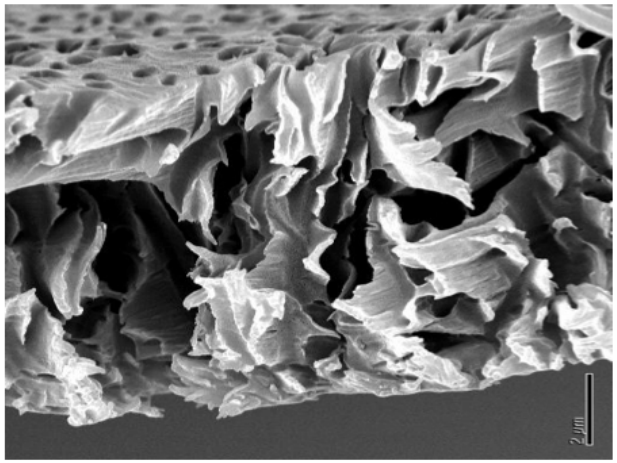
Symbolically:

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

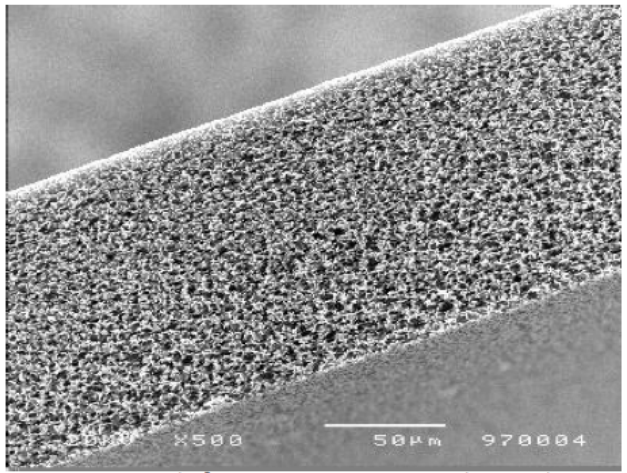
- $\text{permeance} = \dfrac{\text{permeability}}{L} = \dfrac{1}{\text{resistance}} = \dfrac{1}{R} =$ "mass transfer coeff"
- permeance: easier to measure
- permeance units: depend on choice of (driving force) and J
- resistance $= f$(thickness, viscosity, porosity, pore size)
- we will specifically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



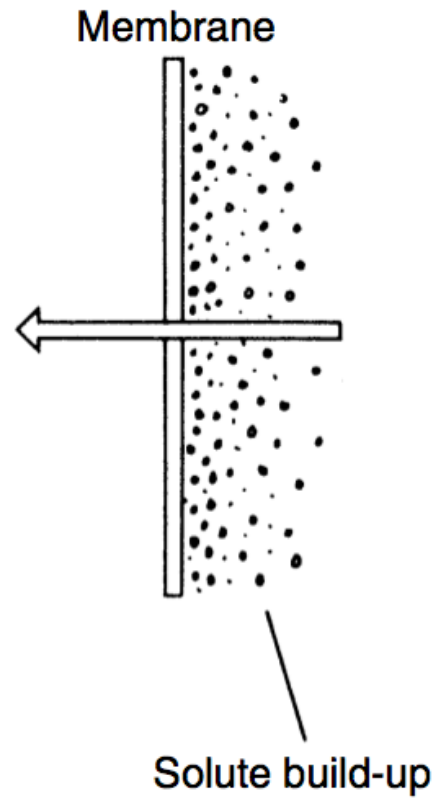
symmetric spongy structure

[Henk Koops' slide]

General modelling equation applied

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

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

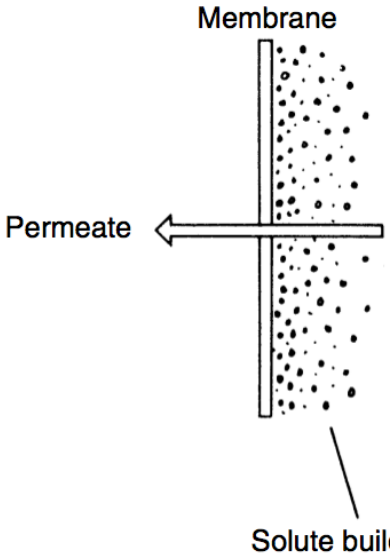


J	$[\text{kg.s}^{-1}.\text{m}^{-2}]$	permeate flux
μ	$[\text{kg.m}^{-1}.\text{s}^{-1}]$	permeate viscosity
ΔP	$[\text{Pa}] = [\text{kg.m}^{-1}.\text{s}^{-2}]$	TMP varies for different applications
R_m	$[\text{m.kg}^{-1}]$	resistance through membrane (small)
R_c	$[\text{m.kg}^{-1}]$	resistance through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

[Illustration from Richardson and Harker, Ch8]

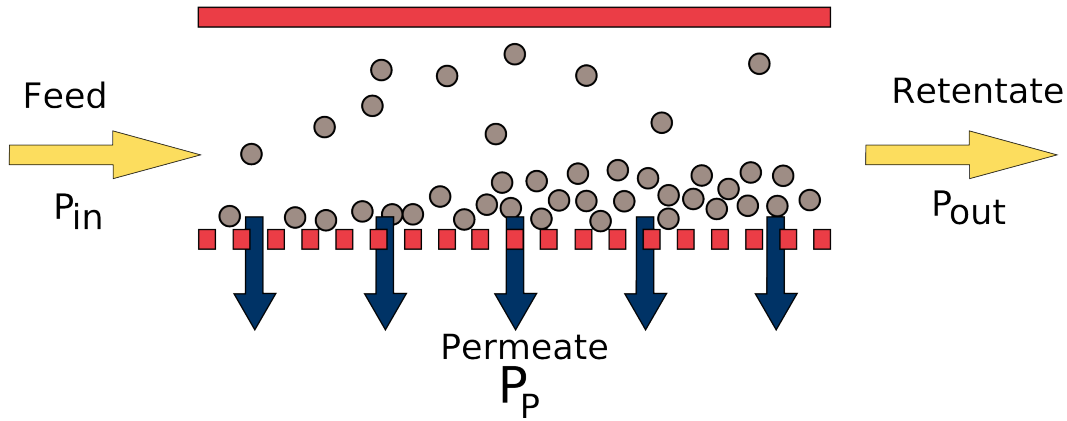
Flow patterns for microfiltration

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
- $\Delta P = \frac{P_{in} + P_{out}}{2} - P_P$

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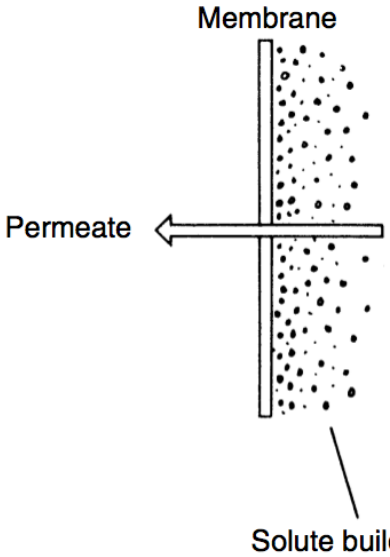

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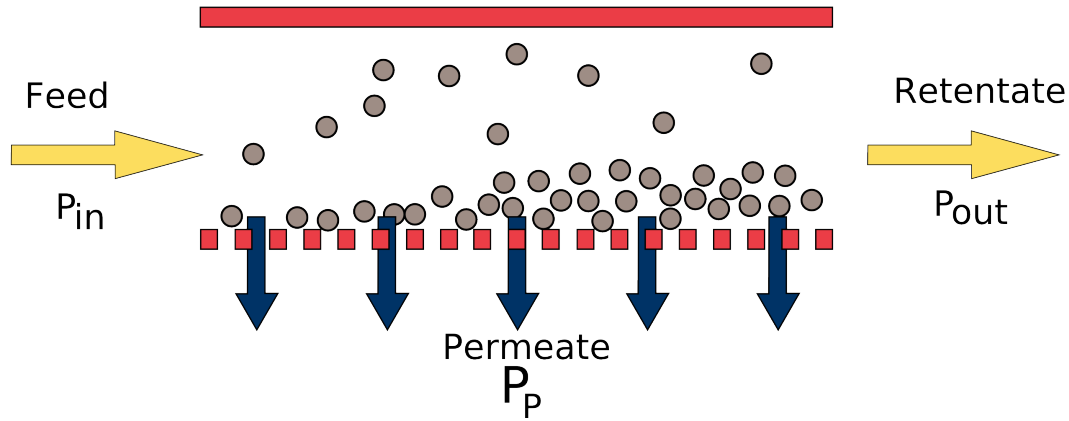

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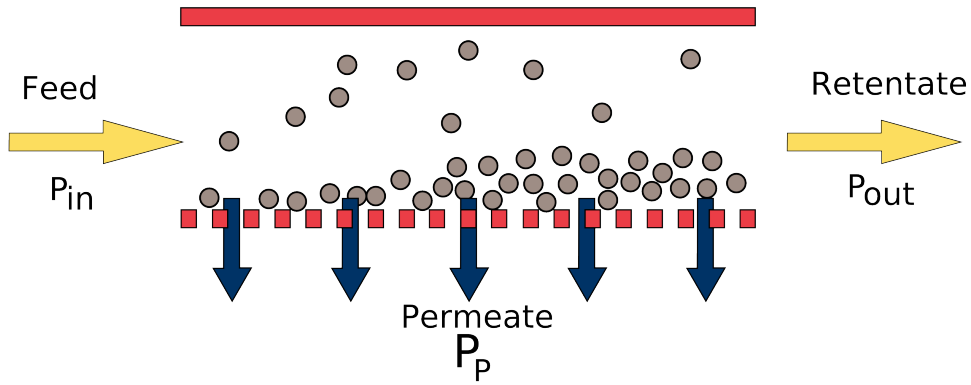
Dead-end flow vs cross-flow geometries

Dead-end flow

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

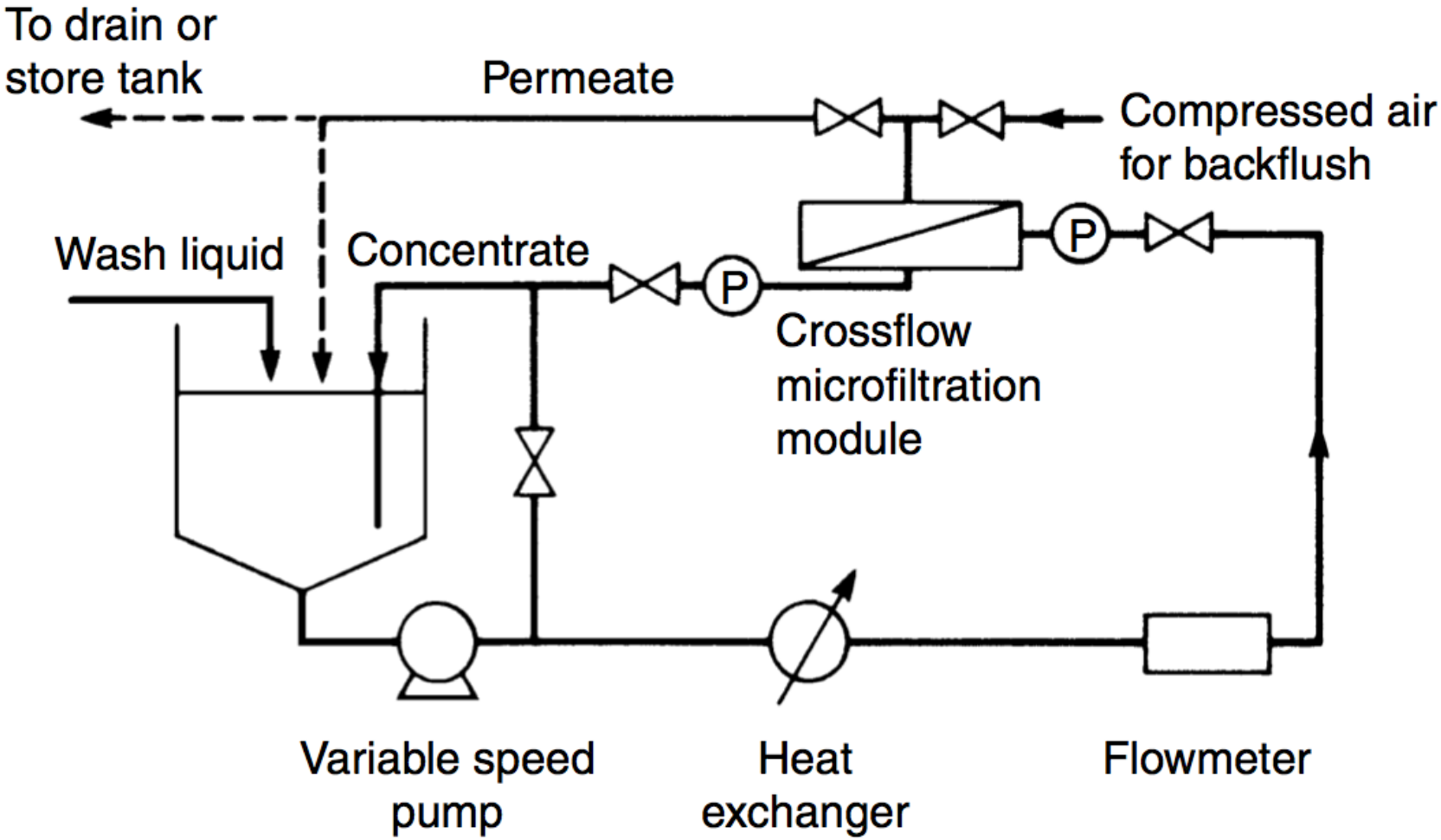
$$J = \frac{\Delta P}{\mu\left(R'_m + R_c L_c\right)}$$

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

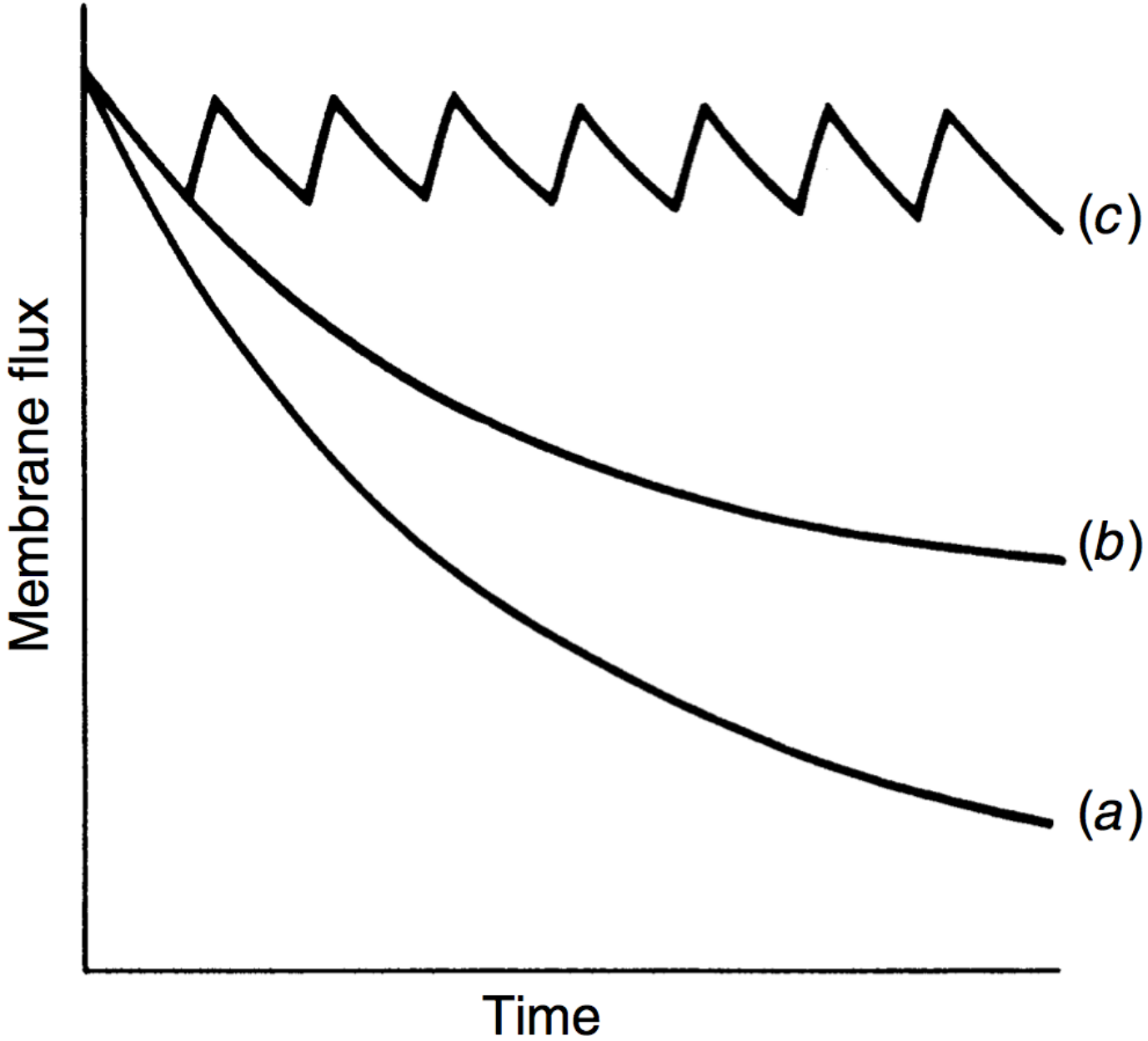


How to pressurize the unit?

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

[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 ΔP
- $R'_c = R_c L_c$: obtained from a plot of J_f vs ΔP_f
  - set different ΔP_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 216×10^{-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.

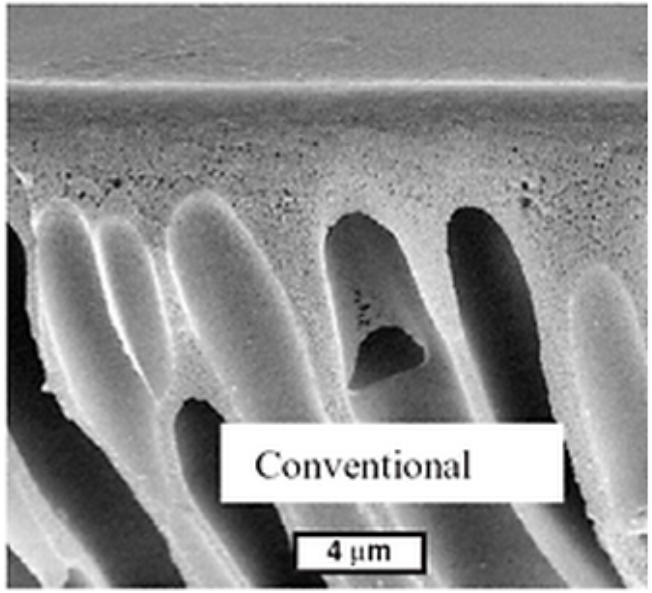
Water microfiltration

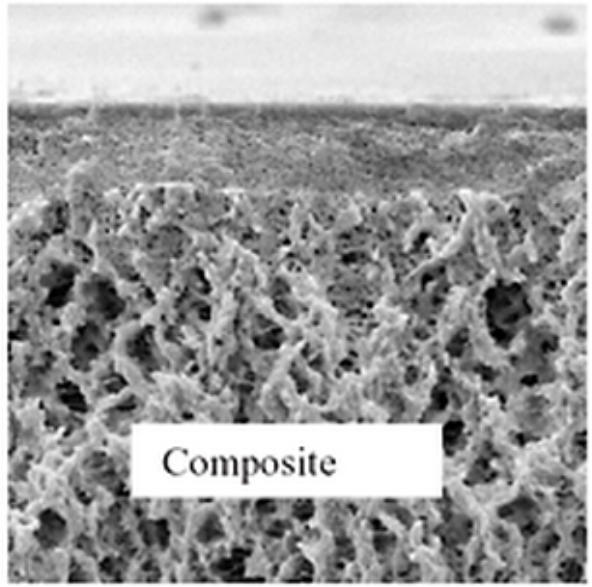
- Constant $\Delta P = 50$kPa applied in cross-flow membrane set up
- Membrane area $= 50\text{cm}^2 = 0.005\text{m}^2$
- Pure water at this ΔP produced a flux of 1.0 $\text{kg.s}^{-1}\text{.m}^{-2}$
- Feed at this same TMP produced a flux of 0.065 $\text{kg.s}^{-1}\text{.m}^{-2}$ permeate
- What is 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]

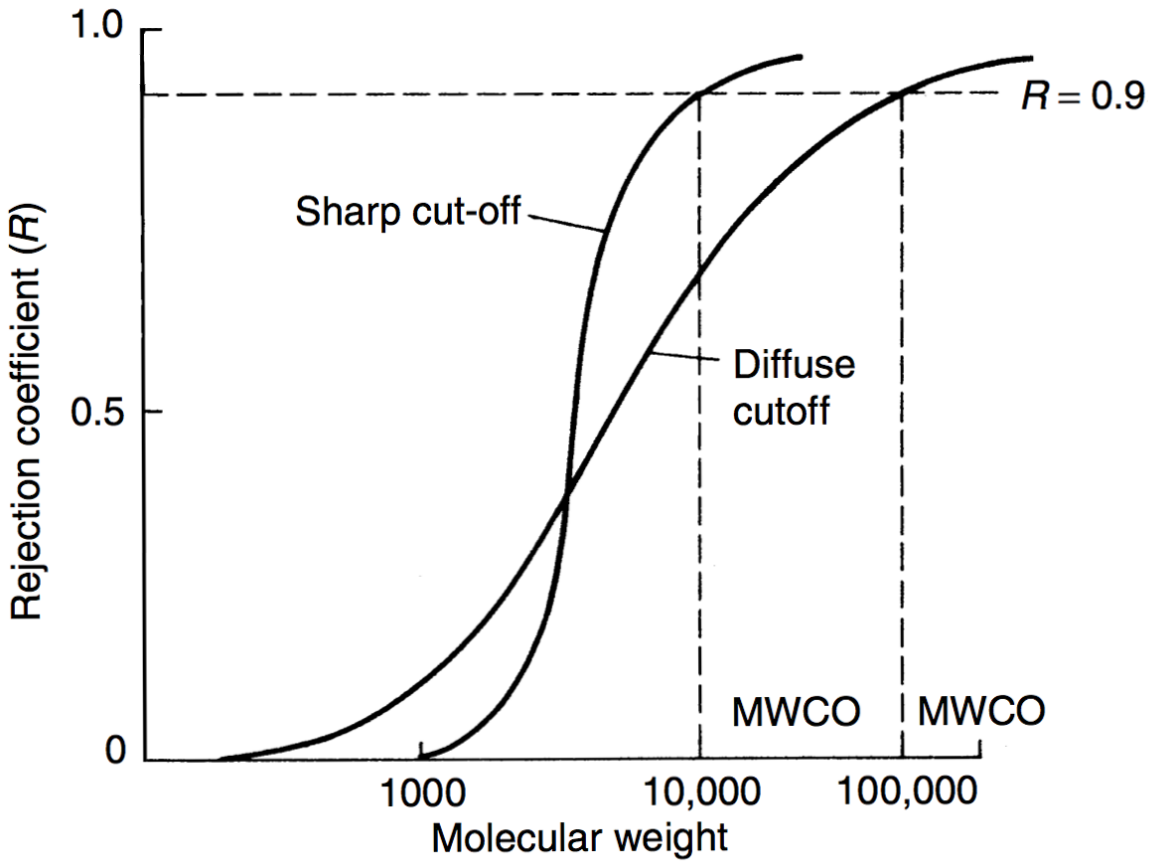
Ultrafiltration applications

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



[Richardson and Harker, Ch8]

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

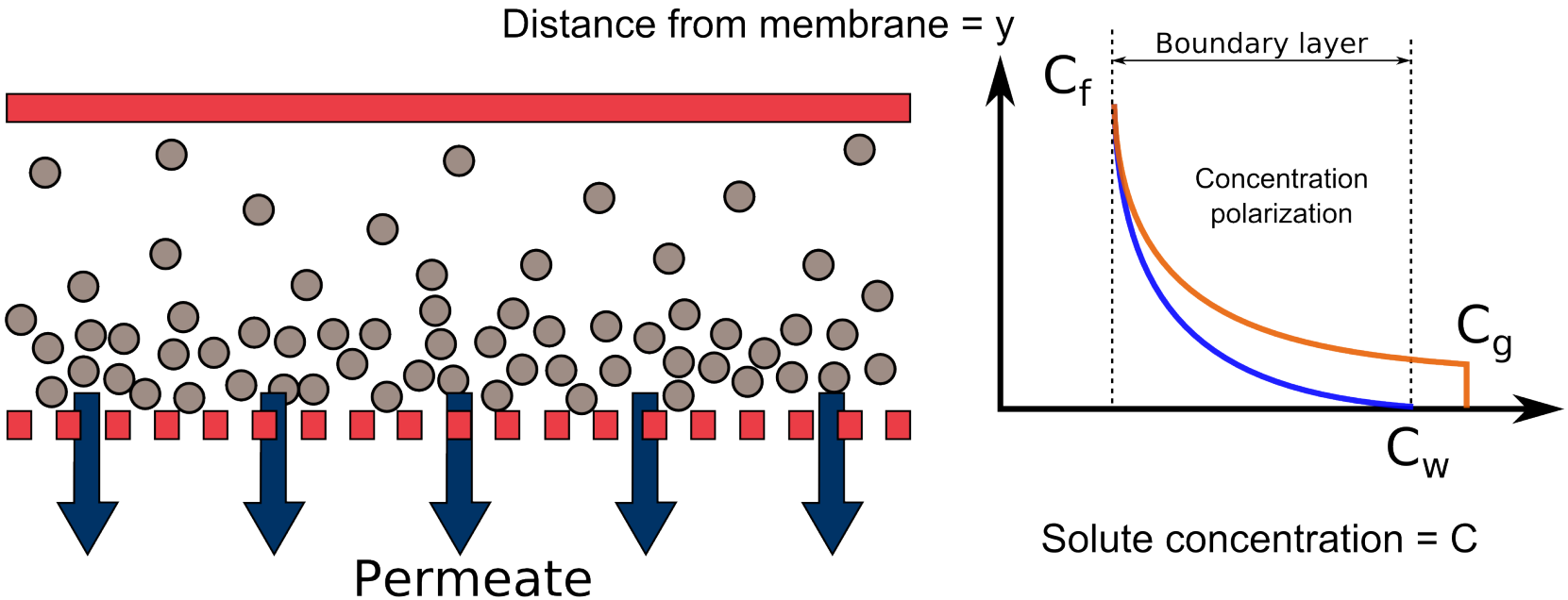
$$R = 1 - \frac{C_p}{C_f} = 1 - S$$

MWCO: molecular weight where $R = 0.9$

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

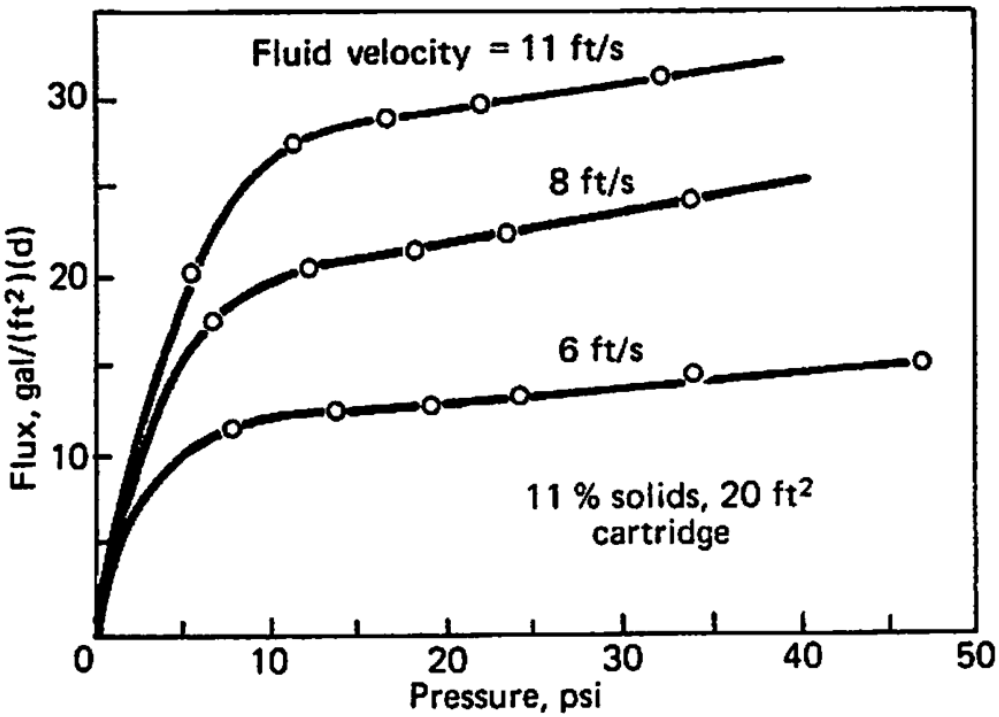
Transport phenomena in UF

- 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 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

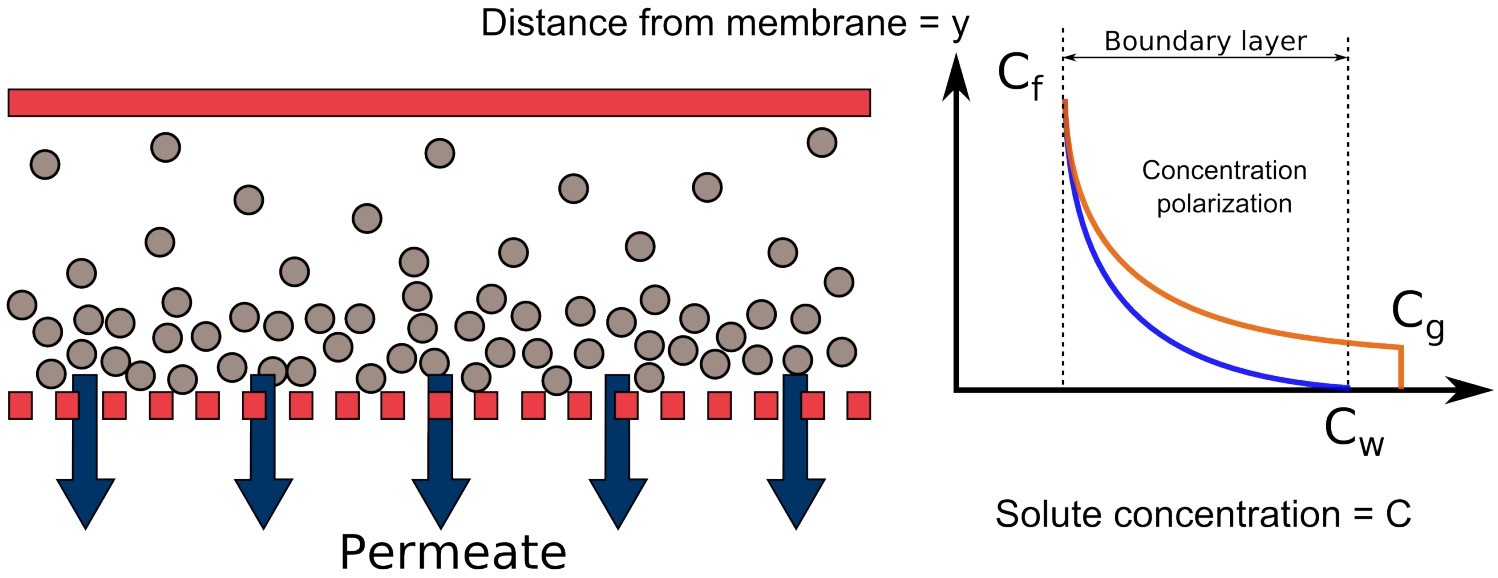
Space for picture

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

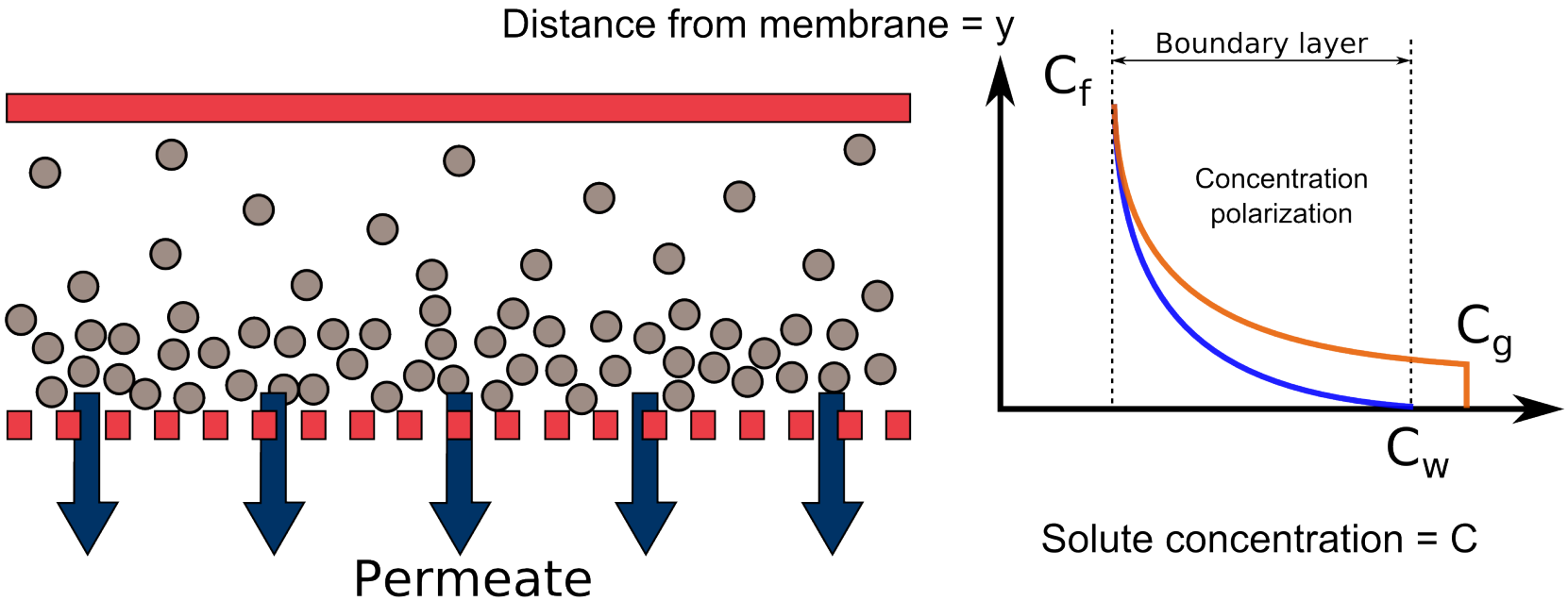
Transport at steady state

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 $kg.m^{-3}$ 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

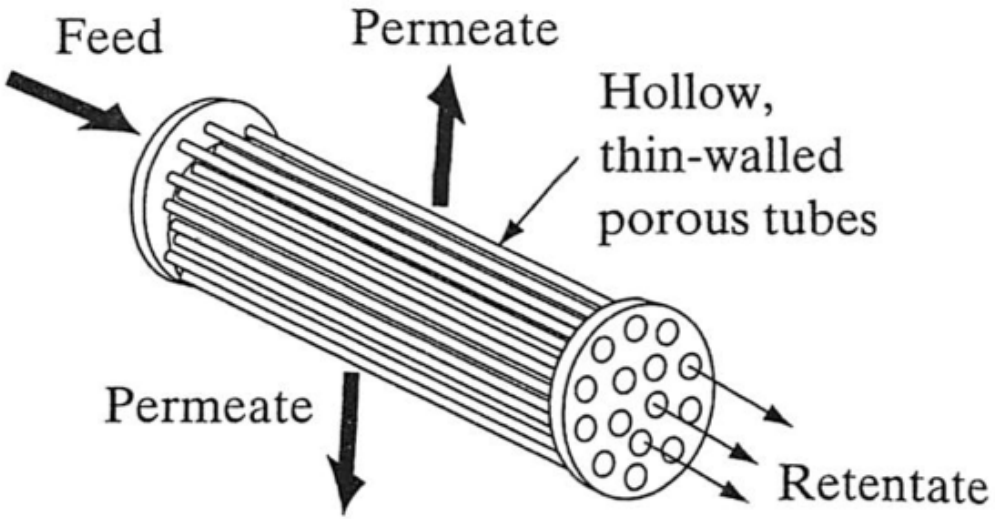
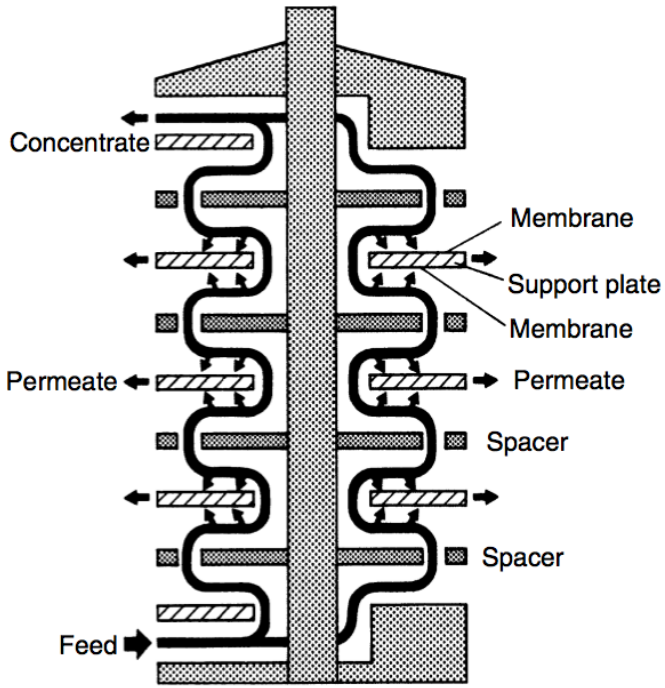


Plate and frame

- batch operation



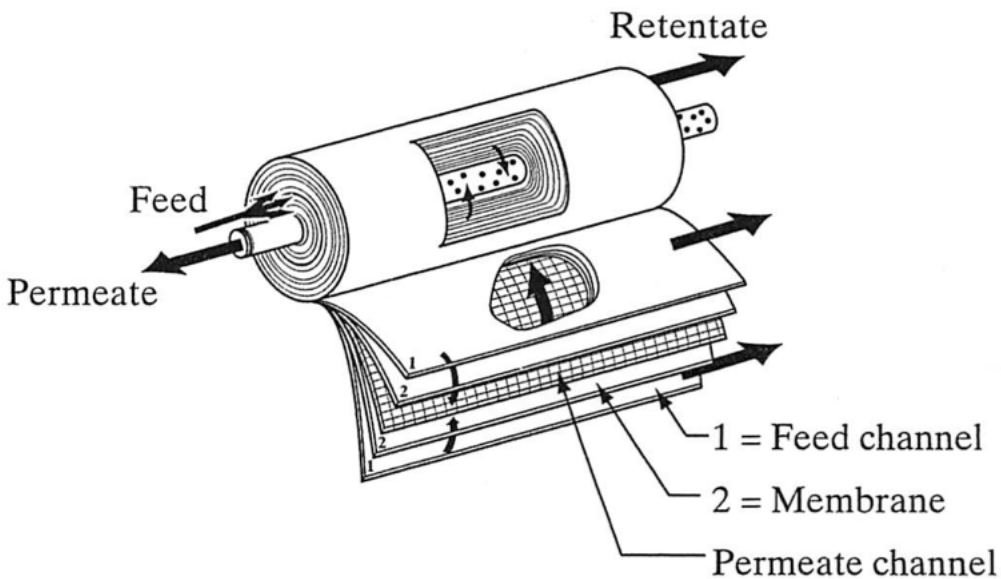
- All these units bought as complete module from supplier
- In fixed sizes; so need to be combined (next section)
- Also as cassettes, tubes and flat sheets run in TFF to increase flux.

[Illustrations from Wankat, 2ed, Ch 16]

Geometries for ultrafiltration (recap)

Spiral wound

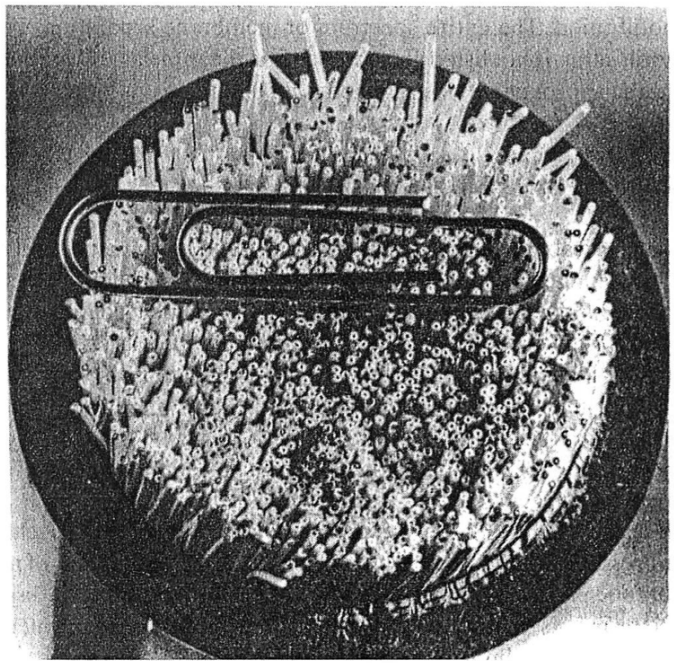
- high surface area per unit volume
- high turbulence, reducing mass transfer resistance

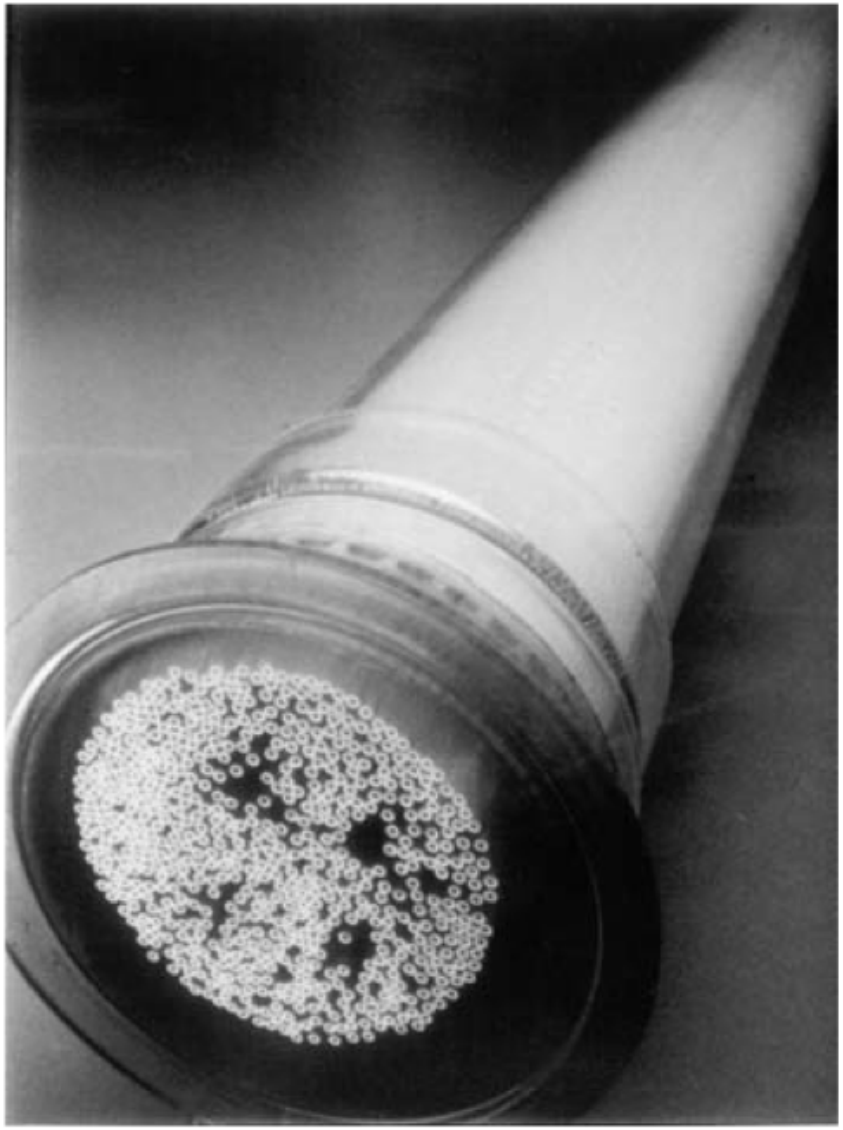


[Illustrations from Wankat, 2ed, Ch 16]

Hollow fibre membranes

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





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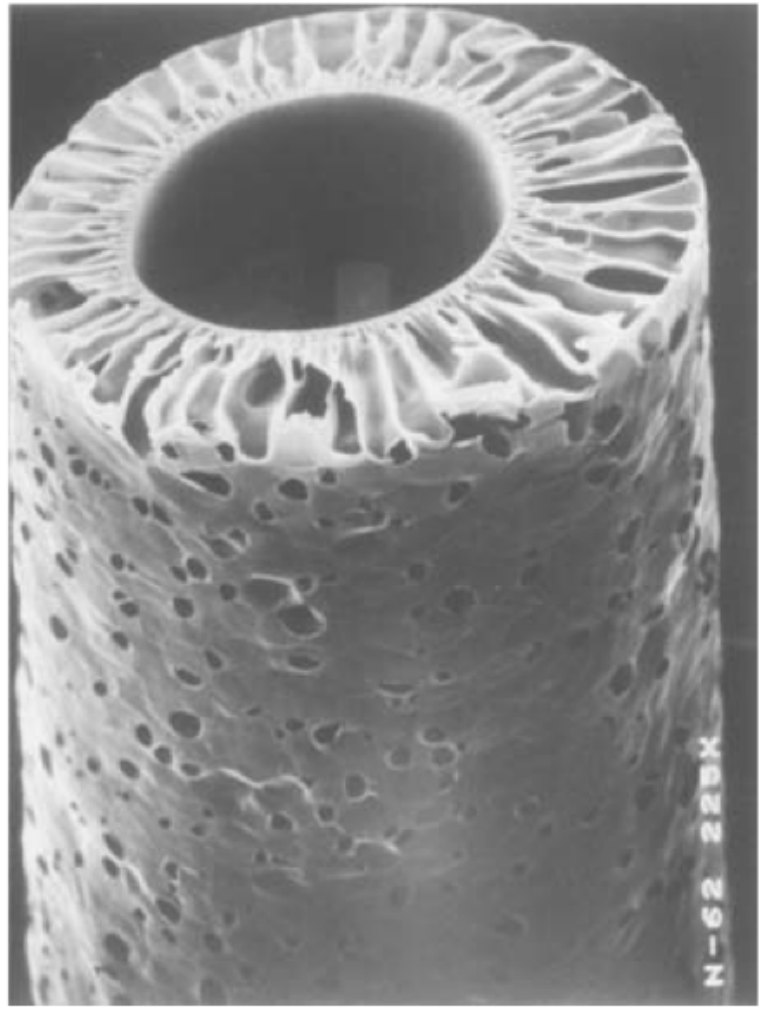


(*b*)

[Richardson and Harker, Ch8]

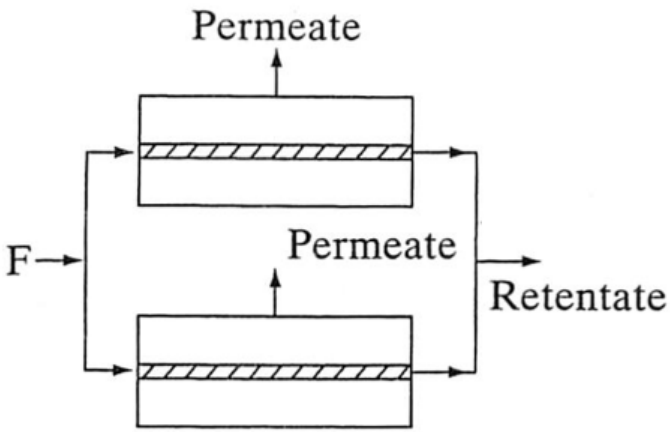
Sequencing membrane modules

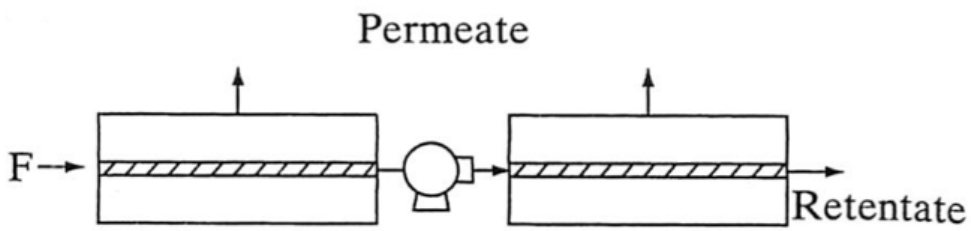
Parallel

- 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

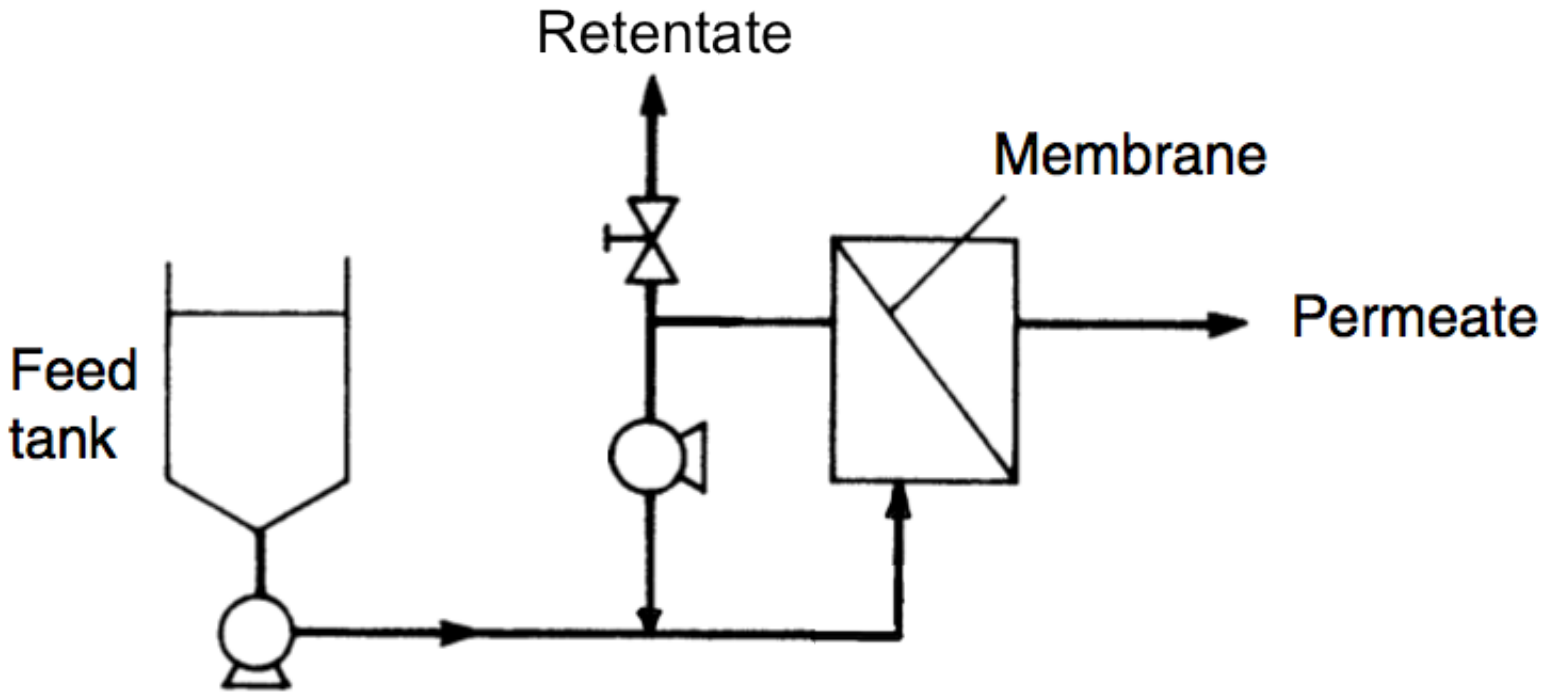
- Larnaca, Cyprus
- SWRO membrane, i.e. desalination
- 21.5 million m^3 per year
- parallel and series

[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

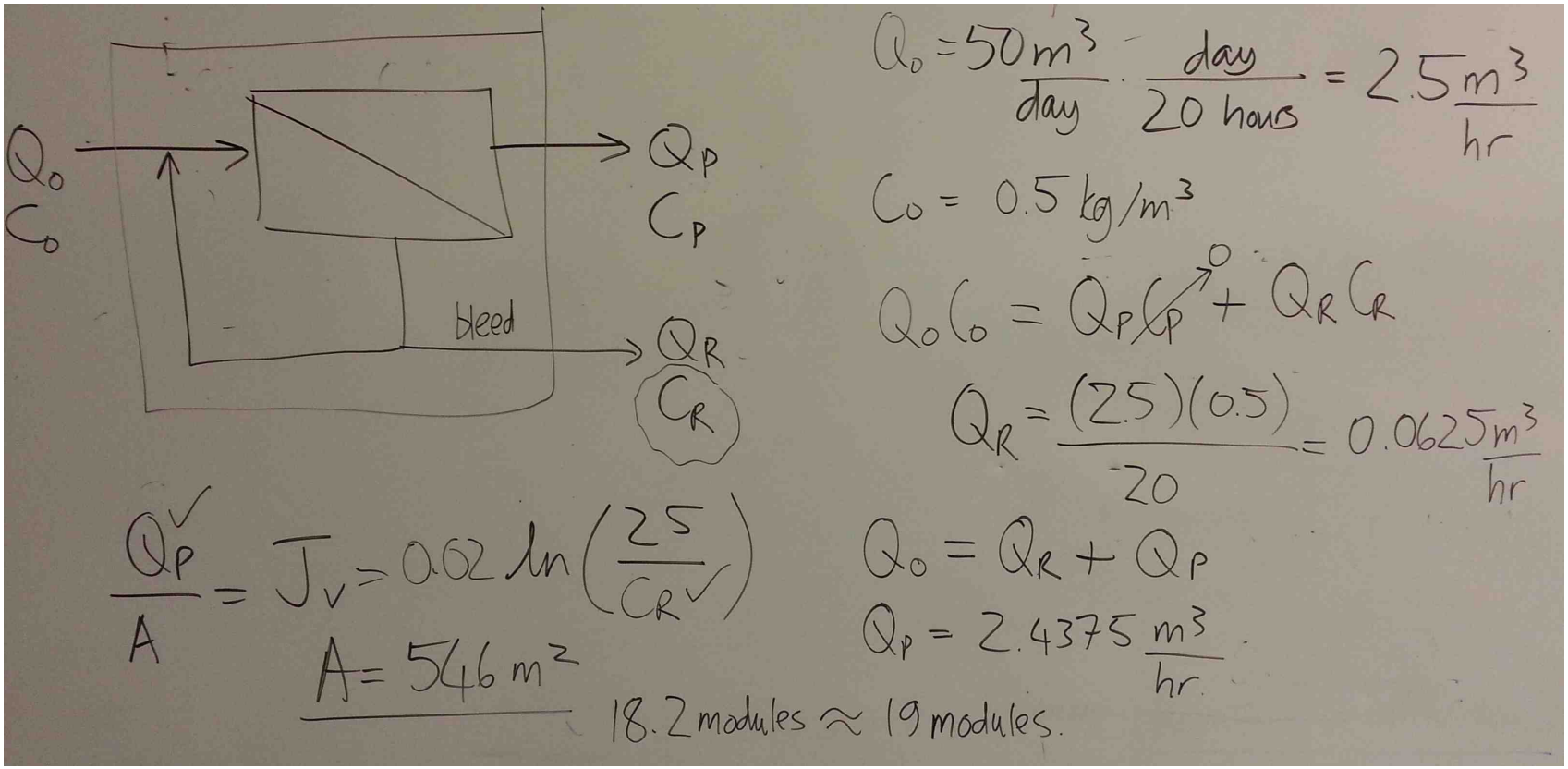
$$J = 0.02 \ln\left(\frac{25}{C_f}\right)$$

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?

Covered in class on 11 October



Administrative

- Assignment 2 (uncollected) at front
- Assignment 3: available on Thursday
- Assignment 4: distributed on 19 October
  - due on 26 October
- Project outline: due on Thursday
  - illustration/photo of unit
  - short description
  - physical principle used for the separation
  - list of references
- Project focus: how is the unit sized
- Side objective: capital and operating costs of the unit

Midterm review

- About 30 messages received via website: 28 anonymous
- General consensus: hard, too long, unfair, vague, unprepared
- Easy way out: divide exam by 85 or 90 instead of 100 and "move on"
- The more I read the emails, the angrier(?) I became as well
  - Simply "moving" on is short-changing your education
  - Let's see why ...

Midterm review

1. "It was hard"
   - It was mainly conceptual
   - You're not used to this (you are probably used to plug & play)
   - Biggest issue: looking around for information in textbooks *etc*
   - In December: you have to be able to say "that's easy"
2. "Questions were vague. It felt like there are multiple answers to the questions"
   - I see this comment on my course evaluations. I really want to improve; (or, confirm my suspicion: "sometimes students don't really read the question")
   - But you must tell me: what **exactly** is "vague"?
   - Please use feedback form to tell me: quote the question and point it out.
   - (Let's go through the questions to see what is vague or unclear.)
   - Note that multiple answers are possible in some open-ended questions: engineers don't have "one correct way" implement something

Midterm review

3. "Too long"
   - Can't compare it to final exam **time** allocation
   - My midterms usually last around 2 to 2.5 hours
   - 15% vs 45% (final) is due to volume of material covered
   - If weight $\propto$ difficulty: then you're in for a nasty final exam!
   - Time management was mentioned to be important.
   - Number of questions in an exam is immaterial
     - Q1, Q2, Q6, Q8 and Q9: 41 marks [$<$ 30 minutes]
     - essentially "free" marks: concepts that must be at the top of your head, little thinking
     - Q4: separation factor required logical analysis [$\sim$ 10 minutes]
     - Q5: plug-and-chug [$\sim$ 10 minutes]
     - Q7: centrifuge: interpret and plug-and-chug [$\sim$ 10 minutes]
     - Total plug-and-chug: 20 marks
     - I don't care too much for plug-and-chug: if that's all you do well, you can be outsourced to a computer
   - Surprising aspect: 65% of students left early
     - lost patience or gave up

Midterm review

4. "Unfair"
   - There was prior notice about question 3
   - Class was cancelled for questions
   - 1.5 days is not too short
   - In practice: **hours** to learn and apply
   - Most of the concepts required for Q3 were covered in **Tuesday**'s class and earlier
     - what is flux (covered 2 weeks ago)
     - where is flux measured: the permeate (covered Tuesday)
     - flux $= \frac{Q_P}{A}$ is obvious, but covered in **Thursday**'s class
     - only "new" material on Thursday: connecting modules in series; recognize the retentate cascades
   - Unfair = "not covered at all" and "beyond capability"
   - Email: "The course this year is very different from the past years making it almost impossible to prepare well for it. All we have is the examples you did in class and the assignments."
     - You should not prepare for something based on how you are going to be tested.
   - Q3: purely mass balances (2nd year); subbing in equations (2nd year[?]); solving single non-linear equation (2nd/3rd year)

Midterm review

5. "Unprepared"
   - Message: "i felt and i feel many others felt that attending the lectures and completing the homework assignments would not have prepared us well for this test ... evidently the test had very little similarity to class examples or assignments"
   - Q1, Q2, Q6: directly from course notes
   - Q3: example covered in class: we solved for area; this time we solve for retentate concentration and flow rate
   - Q4: Use (definition of separation factor) and (design equation for sedimentation): i.e. combine concepts learned in class/assignments
   - Q5: direct application of TSV (see assignment 1 and 2)
   - Q7: uses Σ (assign 3 and covered in class) to calculate Q_{cut}
   - Q8: definition of flocculation (class: MIT video); membrane concepts (class): applications
   - Q9: application of cyclones (class): can you re-interpret what you've learned in a new context?

Question 3: let's break it down

Supposedly confusing, hard, worth too many marks. Let's address this:

- "An asymmetric ultrafiltration membrane is used with the aim of separating dyes from a liquid stream and to achieve a more concentrated dye-water mixture"
  - Here's our **aim**: concentrating up a solute: "the dye"
  - skip ahead to the questions: we are going to find the dye concentration, amongst other things

- The feed waste stream arrives at a flow rate of 2.2 $m^3.hour^{-1}$ with concentration of 1.2$kg.m^{-3}$
  - Some given information

Question 3: let's break it down

- The membrane's operating characteristic was calculated from various experiments:

$$J_v = 0.04 \ln\left(\frac{15}{C}\right)$$

  where the bulk concentration C has units of $\mathrm{kg.m^{-3}}$ and flux is measured in $\mathrm{m^3.hour^{-1}.m^{-2}}$.
- Email: "The description of C, the concentration term in the J_v equation, was that it was the 'bulk concentration'. This confused many people that I talked with, including myself, who took that to mean you were telling us it was the inlet concentration.

  If you give an empirical equation, make sure to either a) specify completely what the terms in the equation mean, or b) tell us explicitly that we have to decide what the term refers to."
- At 4:45 in video on 11 Oct class; and several other times later
- Take a look back at slide 31: "bulk" and "J_v" explicitly defined

Question 3: let's break it down

- It is not an empirical equation: it is derived and has a logarithmic structure.
- Recall from notes: $\frac{JL_c}{D_{AB}} = \frac{J}{h_w} = \ln\left(\frac{C_w}{C_f}\right)$
- If two membrane modules, each of area 25 m^2, are simply placed in series
  - connected in series: what connects to what?
  - draw a picture, if you haven't already

- Now we are ready to answer the questions.

Question 3: let's break it down

1. the dye concentration from the first membrane module?
2. the permeate flow rate from the first membrane module?
3. the dye concentration from the final membrane module?
4. the permeate flow rate from the final membrane module?
5. Then explain whether the above answers seem reasonable.

Please show all calculations, assumptions and relevant details. (*Yes, this question is on new material; it is not hard; just think logically.*)

Solving question 3: on the board

Class example (11 Oct)

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

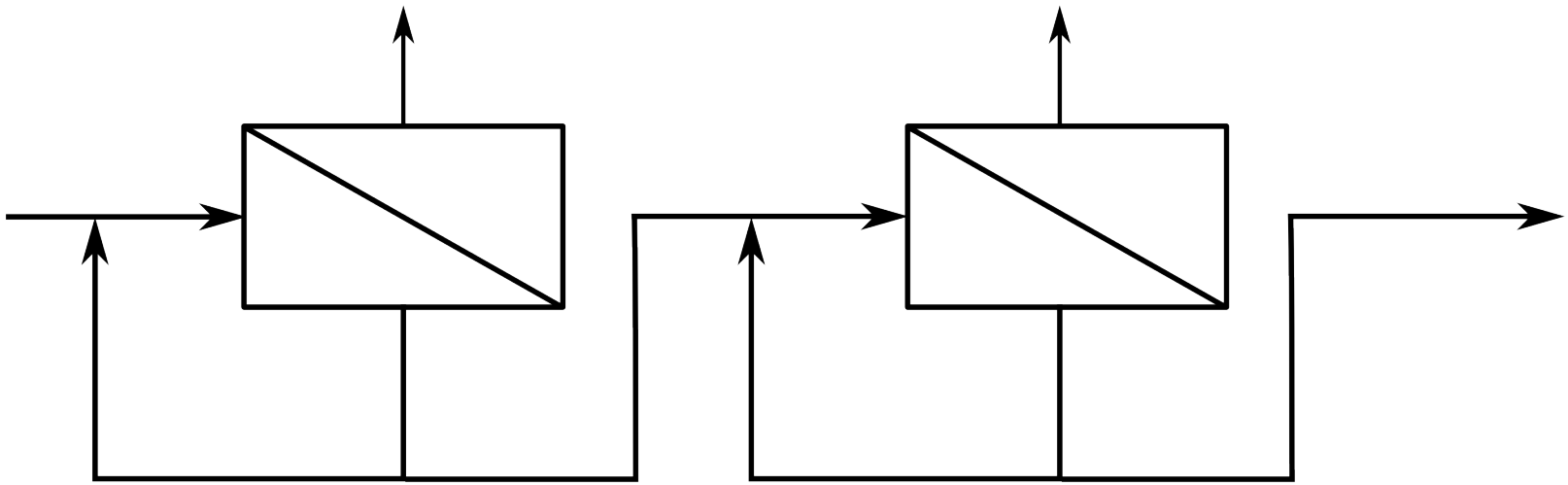
$$J = 0.02 \ln\left(\frac{25}{C_f}\right)$$

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 (will be in Assignment 4)

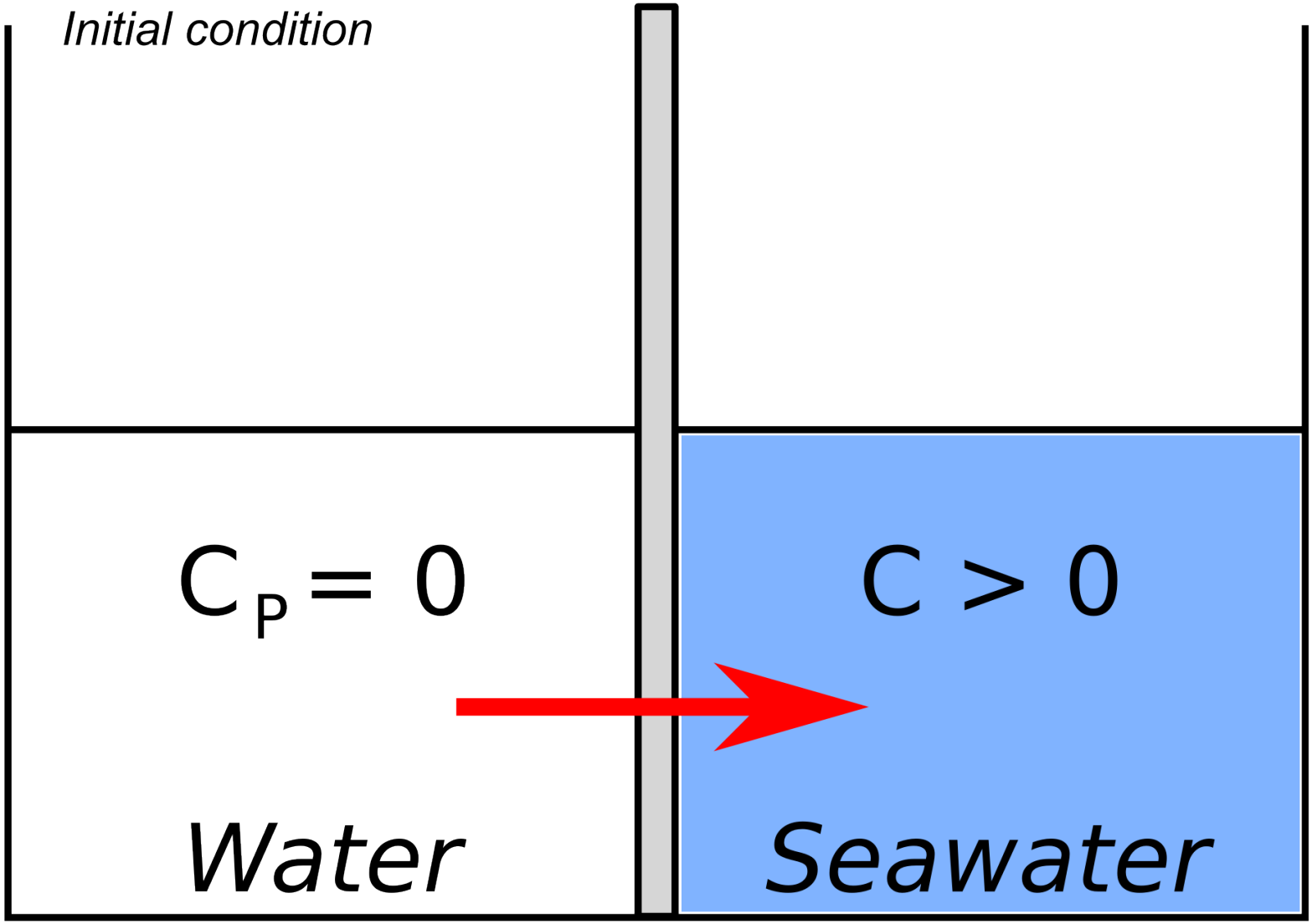


Now consider the previous example. Find the optimal areas, A_1 and A_2 for the membranes.

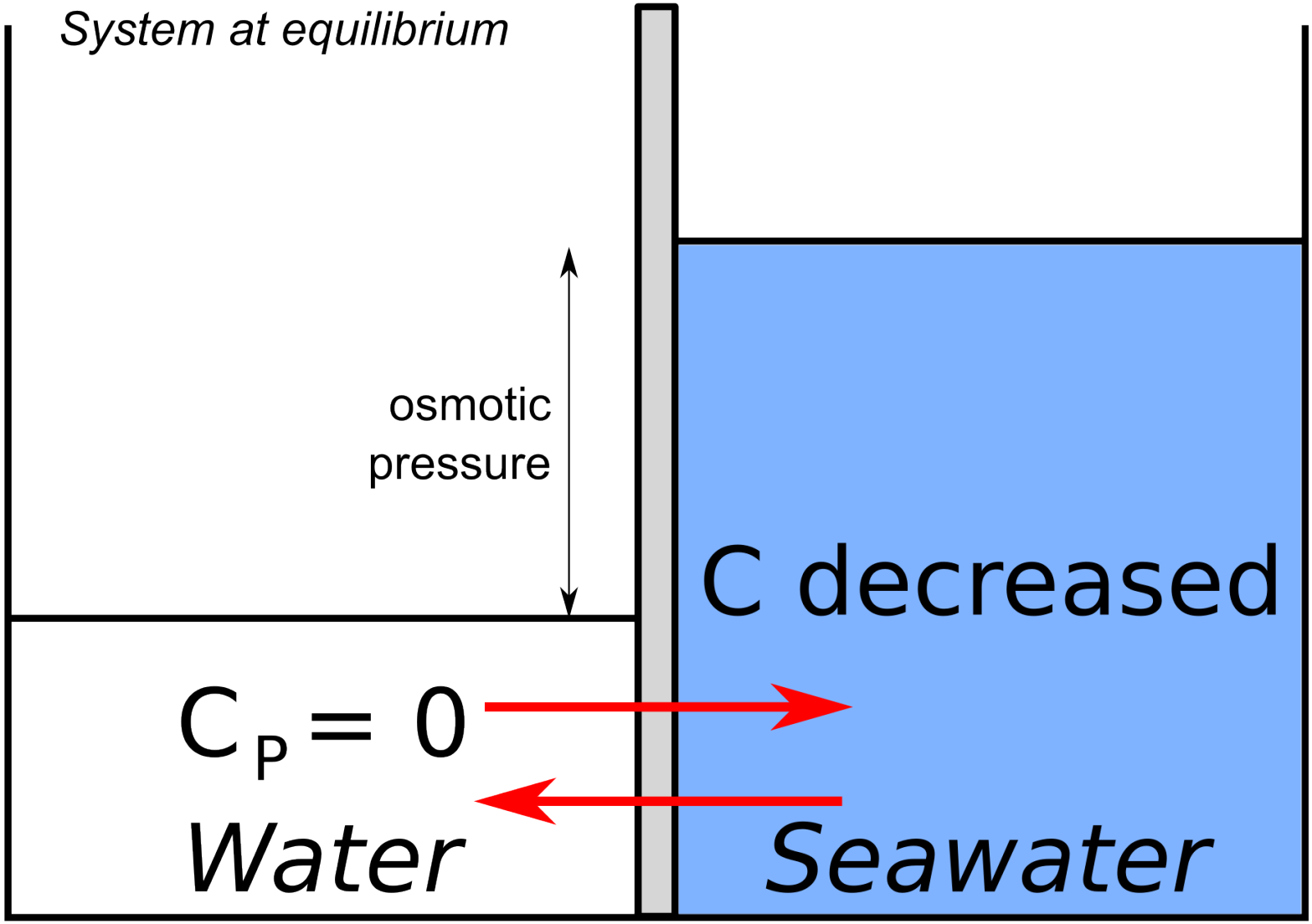
Reverse osmosis

- The **most requested** topic on your list of learning objectives
- Membrane market 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

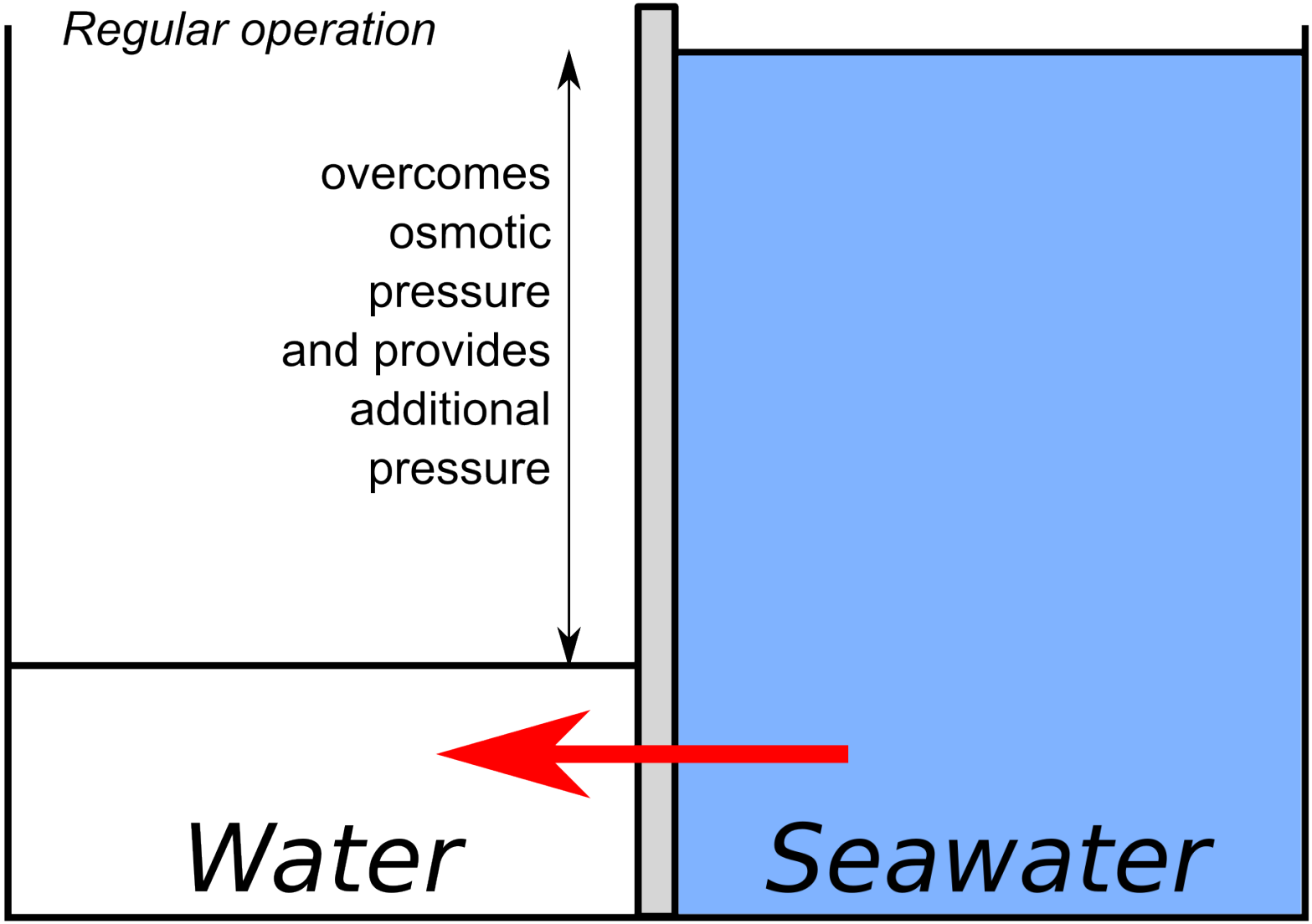
Reverse osmosis principle



Reverse osmosis principle



Reverse osmosis principle

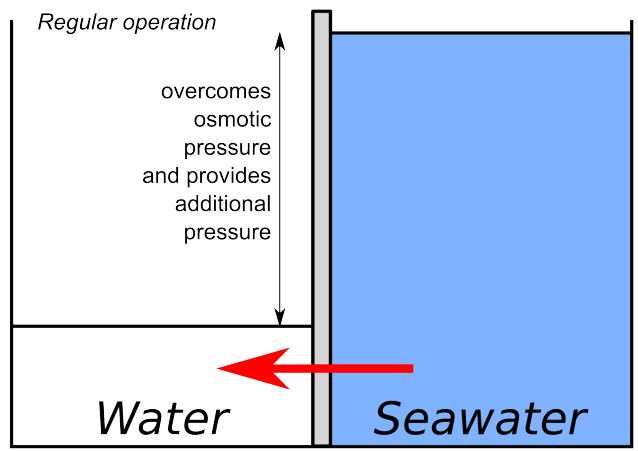


(Reverse) Osmosis principle

- Assume solute barely passes through membrane ($C_p \approx 0$)
- Solvent passes freely
- 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)

(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 = _____



Typical values of osmotic press

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

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 of NaCl dissolved in 1 L of water at 25°C is **4.9 atm**!

- that's almost 500 kPa
- or almost 5m of head for 5.8 g NaCl in a litre of water

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 membranes is pressure difference
- $\Delta P = \pi$ implies we only counteract osmosis
- Reverse osmosis: increase $\Delta P > \pi$
- So the net useful driving force applied: $\Delta P - \pi$
- Ultrafiltration ΔP was 0.1 to 1.0 MPa 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
  - $\Delta\pi = \pi_{\text{feed}} - \pi_{\text{perm}}$
  - $\Delta\pi = C_{\text{ions,feed}} RT_{\text{feed}} - C_{\text{ions,perm}} RT_{\text{perm}}$

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

Videos to watch

In your own time, please watch:

- http://www.youtube.com/watch?v=YIMGZWmh_Mw: how spiral membranes are made
- http://www.youtube.com/watch?v=M3mpJysa6zQ: novel way of recovering pressure energy

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 YouTube video mentioned earlier)

[ide-tech.com]

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 overcome osmotic pressure and membrane resistance

1. **Solvent** flux

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

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

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

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

- Our assumption implies: $C_w = C_{\text{f}} = C_{\text{bulk}} =$ bulk solute conc$^{\text{n}}$
  - how would you enforce this?
- P_{solv} = permeability of the solvent
- C_p = concentration of solute in the permeate
- P_{salt} = permeability of the salt
- ℓ_M = membrane thickness

Example to try at home

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

Conditions on the permeate side are 0.05 wt% NaCl, at same temperature, but 50 psia.

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^3.s^{-1}.m^{-2} for salt is determined experimentally (we won't cover this in the course).

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 for salt.
5. Calculate the separation factor.

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