Membrane technology

Fausto Gallucci, Inorganic Membranes and Membrane Reactors

Chemical Engineering and Chemistry, Sustainable Process Engineering

Outlines

Membrane: Why?

Membrane: What?

Membranes: How many?

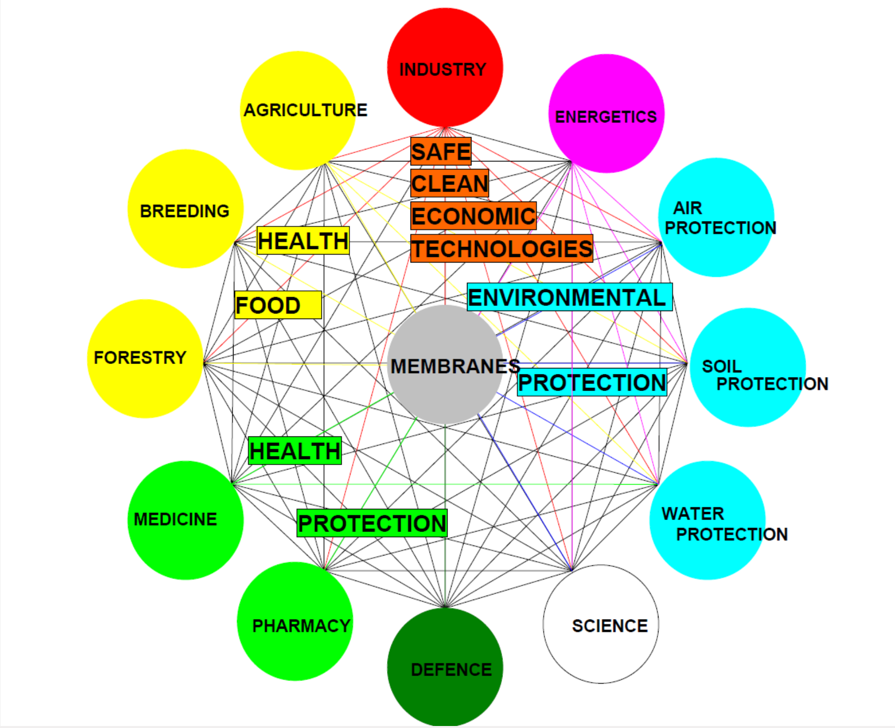
Membrane separation: How?

Membrane production

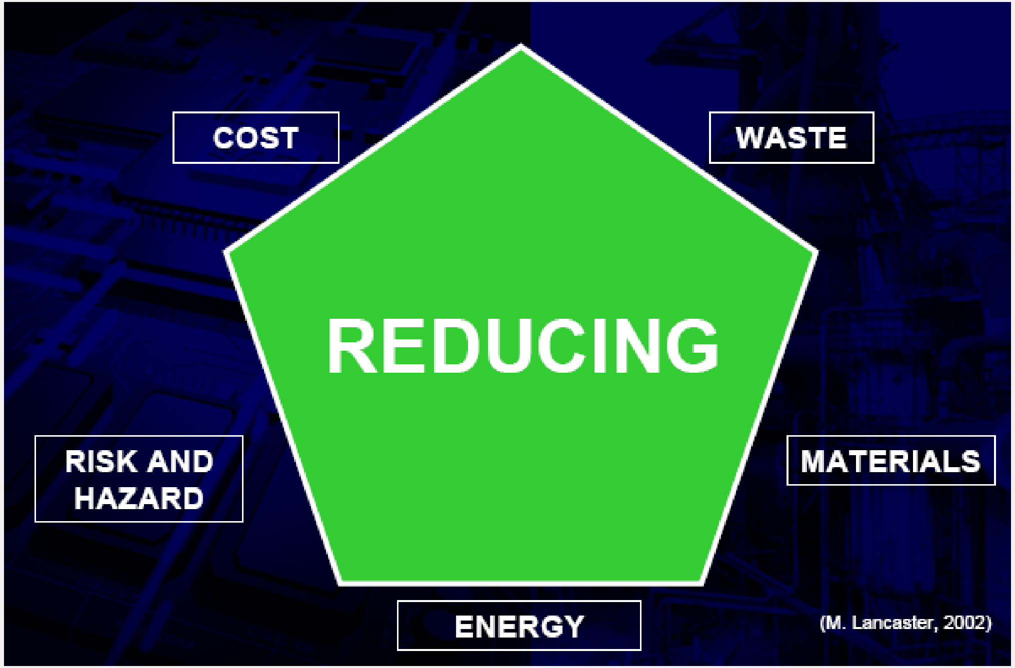
Membrane modules

Application of Membranes in Water treatment

Application of membranes



Introduction - PI



Introduction

Process Intensification

Equipment

Equipment for Carrying Out Chemical Reactions

- Spinning disk reactor
- Static mixer reactor
- Static mixing catalysts
- Monolithic reactors
- Micro reactors
- Heat exchange reactors
- Supersonic gas/liquid reactor
- Jet-Impingement reactor
- Rotating packed-bed reactor

Equipment for Operations without Chemical Reactions

- Static mixers
- Compact heat exchangers
- Micro channel heat exchangers
- Rotor/stator mixers
- Rotating packed beds
- Centrifugal adsorber

Methods

Multi-functional Reactors

- Reverse-flow reactors
- Reactive distillation
- Reactive extraction
- Reactive crystallization
- Chromatographic reactors
- Periodic separating reactors
- Membrane reactors
- Reactive extrusion
- Fuel cells

Hybrid Separations

- Membrane absorption
- Membrane distillation
- Adsorptive distillation

Alternative Energy Sources

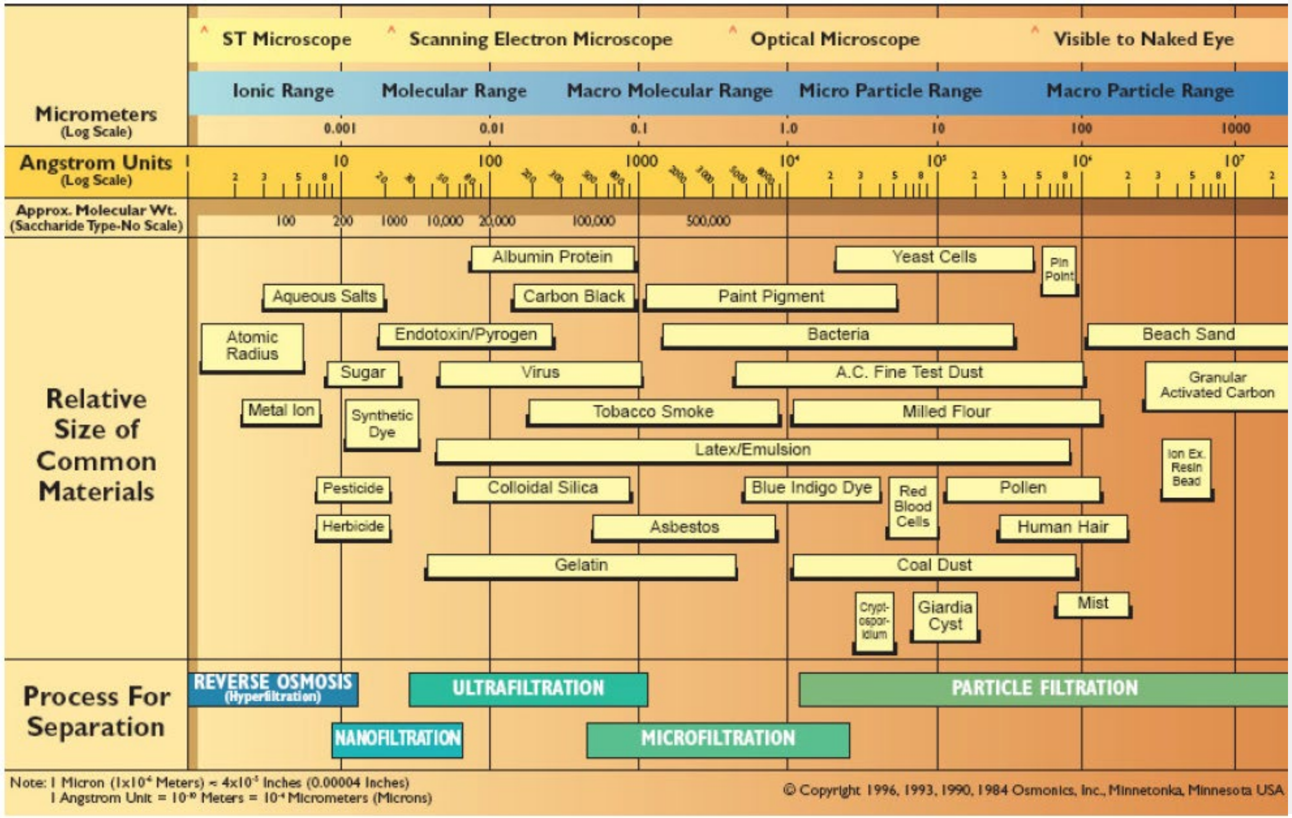
- Centrifugal fields
- Ultrasound
- Solar energy
- Microwaves
- Electric fields
- Plasma technology

Other Methods

- Supercritical fluids
- Dynamic (periodic) reactor operation

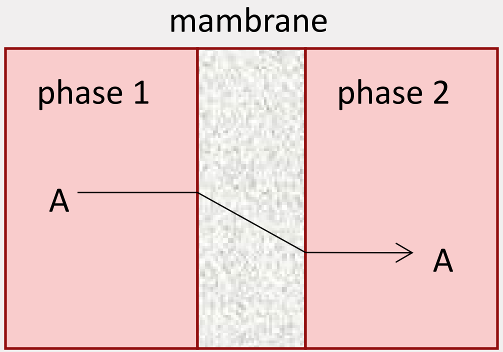
Recreated from:
A.J. Stankiewicz and J.A. Moulijn,
Chem. Eng. Progr., Jan. 2000, 22-34.

Classification of membranes (separation)



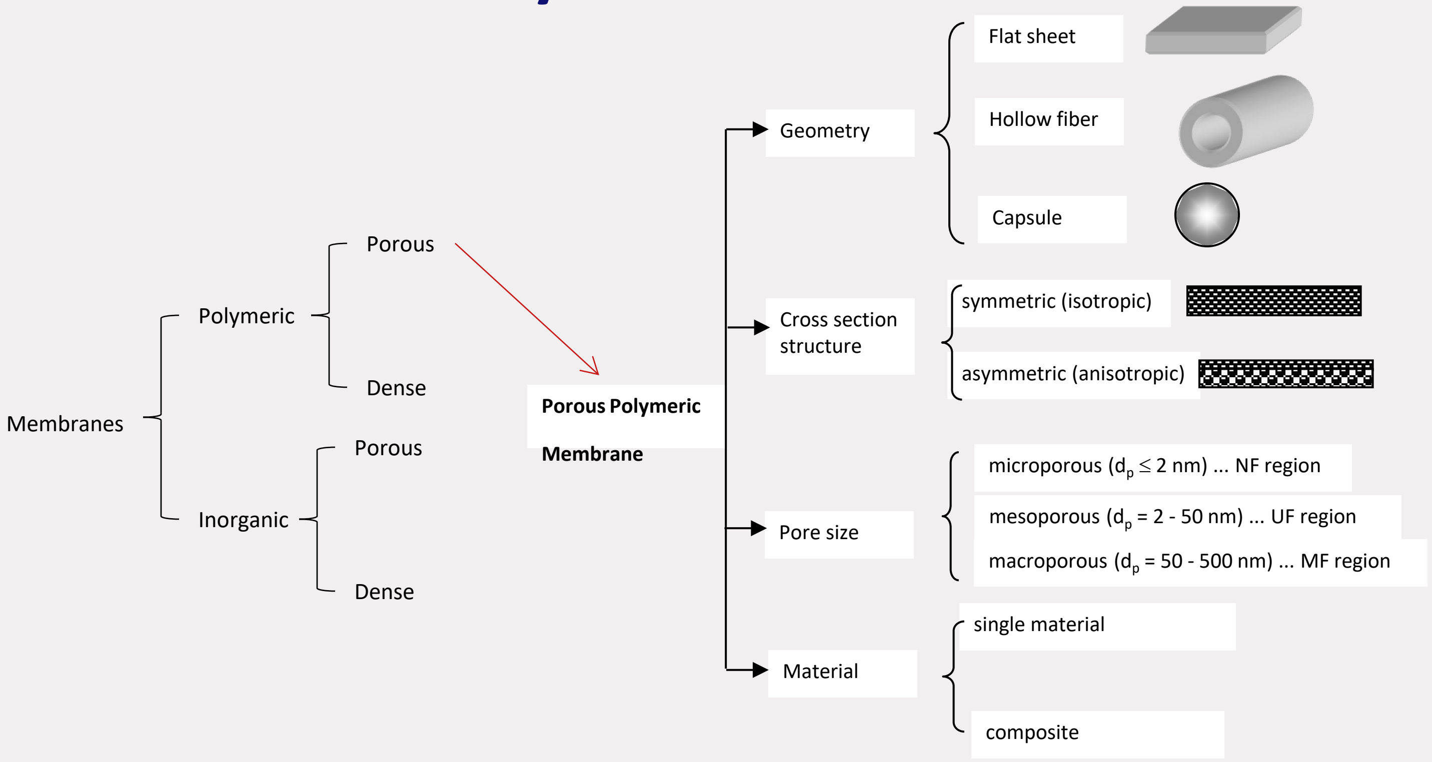
Membrane: what?

Definition: A membrane is a permeable phase acting as a selective barrier.
Transport processes depend on a driving force (gradient of P, pH, C, etc.).

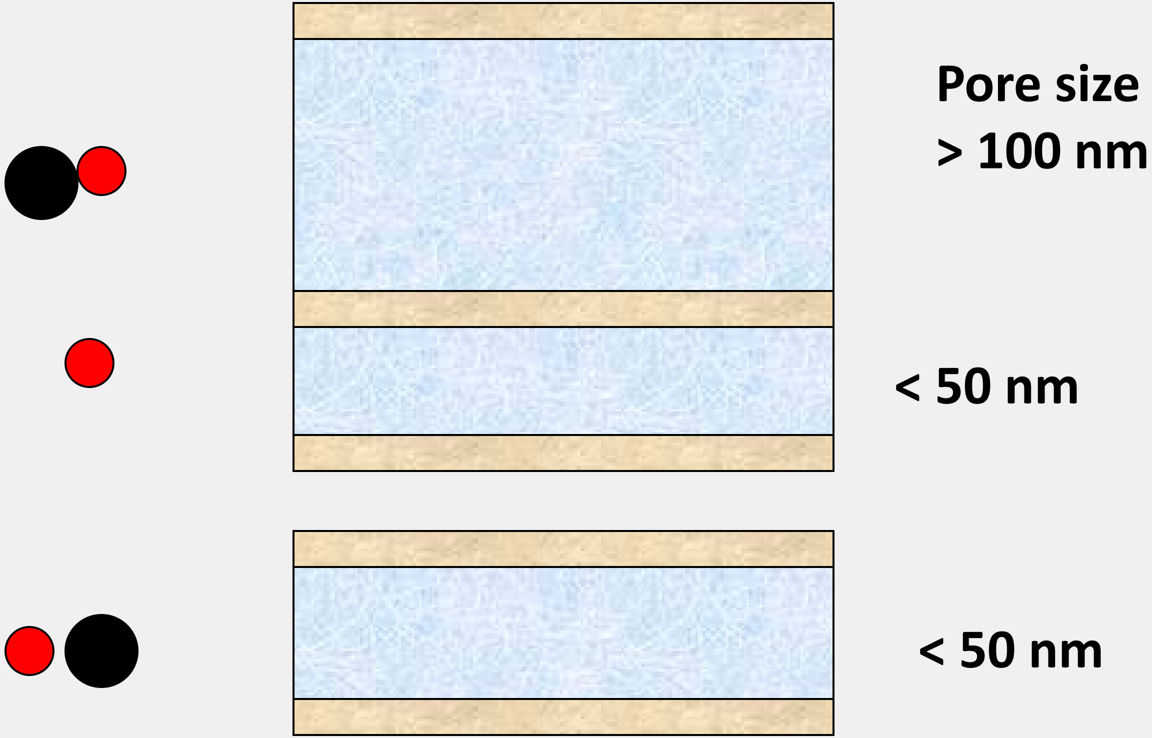


Process	Driving Force	Typical values driving force	Transport mode
Microfiltration	Δp	**0.1-3.0 bar**	Convection
Ultrafiltration	Δp	**1.0-10 bar**	Convection
Reverse Osmosis	Δp ($\Delta \mu_i$)	**10-200 bar**	Diffusion
Dialysis	ΔC(Δa)		Diffusion
Gas separation	Δp (Δf_i)	**Up to 140 bar**	Diffusion
Pervaporation	Δp_i (Δf_i)		Diffusion
Electrodialysis	$\Delta \phi$		Migration

Membrane: How many?

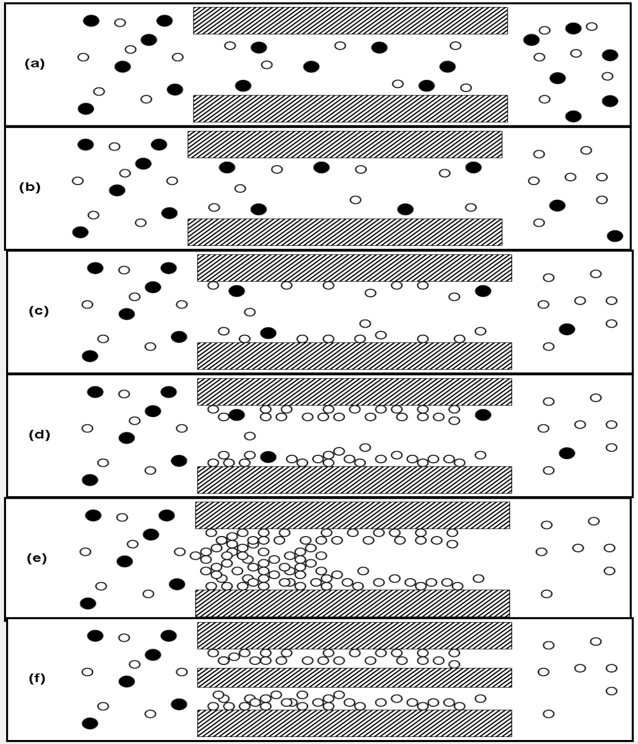


Membrane: How?



Membrane: How?

Porous membranes



Poiseuille (viscous) mechanism

Knudsen mechanism

Surface diffusion

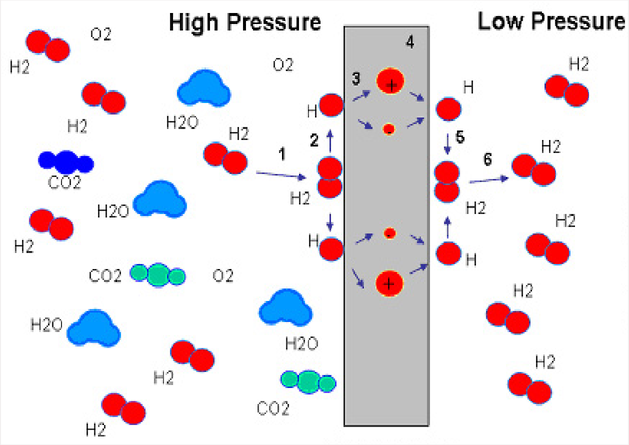
Multi-layer diffusion

Capillary condensation

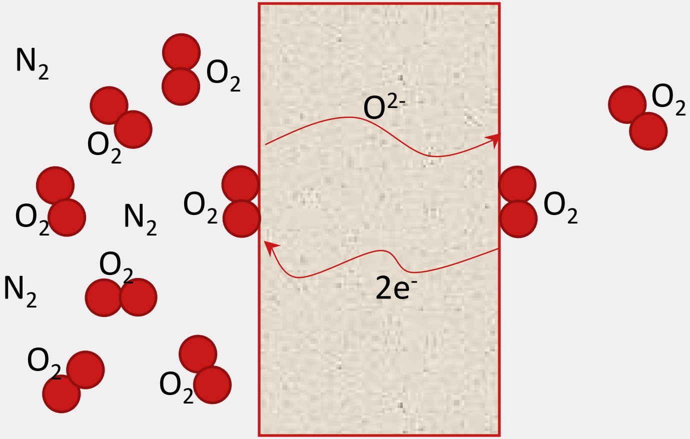
Molecular Sieving

Membrane: How?

Dense membranes



Atomic transport
(metal membranes)



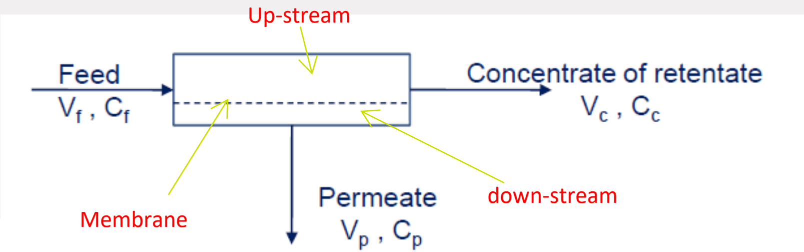
Ionic transport
(solid electrolytes)

Membrane: definitions

Flux, ***Ji,*** *[kmol m^{-2} s^{-1}]:* number of moles, volume, or mass of a specified component i passing per unit time through a unit of membrane surface area

Permeability coefficient ***P_i,*** *[kmol m m^{-2} s^{-1} kPa^{-1}]:* parameter defined as a transport flux, ***Ji,*** per unit trans-membrane driving force per unit membrane thickness

Permeance (pressure normalized flux) *[kmol m^{-2} s^{-1} kPa^{-1}]:* parameter defined as a transport flux, ***Ji,*** per unit trans-membrane driving force



Mass transport in membranes

$$J_i = -P_i \frac{dX_i}{dz}$$

$J_i =$ is the flux through the membrane

$P_i =$ is the permeability coefficient of the membrane

$\frac{dX_i}{dz} =$ is the driving force for mass transfer

TU/e

Mass transport in membranes

the driving force $\frac{dX_i}{dz}$ is related to the gradient of electrochemical potential of the component permeating the membrane $d\eta_i$

$$dX_i = d\eta_i = \overline{V}_i dp + RTd\ln a_i + z_i F d\varphi$$

$$J_i = -P_i \frac{d}{dz}\left(\overline{V}_i dp + RTd\ln a_i + z_i F d\varphi\right)$$

Depending on the driving force the different terms are described with different laws

Mass transport in membranes

A flux of individual components caused by a concentration gradient is described by Fick's law

$$J_i = -D_i \frac{dC_i}{dz}$$

For gases

$$J_i = -\frac{D_i}{RT}\frac{dp_i}{dz}$$

The solution depends on the description of the diffusivity coefficient.

Mass transport in membranes

An expression for diffusivity:

$$D_i = \frac{1}{3}\lambda_i \bar{v}_i$$

Where the mean free path λ is:

$$\lambda_i = \frac{RT}{\sqrt{2}\sigma_i^2 p_{tot} N_{Av}}$$

And where the mean velocity v_i is:

$$\bar{v}_i = \sqrt{\frac{8RT}{\pi M_i}}$$

All together will give:

$$\frac{J_i}{J_j} = \sqrt{\frac{M_j}{M_i}}$$

TU/e

Membrane: definitions

rejection factor, **R:** parameter equal to one minus the ratio the concentrations of a component (i) on the downstream and upstream sides of a membrane $R=1-C_{i,p}/C_{i,r}$

separation factor, **S_F(AB):** ratio of the compositions of components **A and B** in the permeate relative to the composition ratio of these components in the retentate

$$S_F(AB) = \left.\left(\frac{X_A}{X_B}\right)\right|_{permeate} \Bigg/ \left.\left(\frac{X_A}{X_B}\right)\right|_{retentate}$$

stage cut: parameter defined as the fractional amount of the total feed entering a membrane module that passes through the membrane as permeate

Perm-selectivity, **S(AB):** Ratio between the flux of component A and the flux of component B through the membrane

Membrane: the holy grail

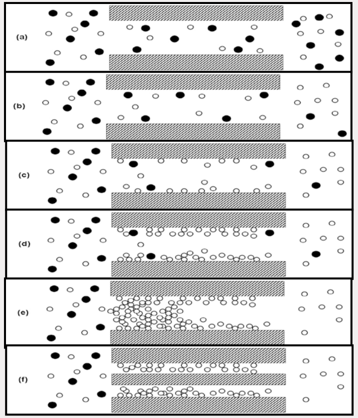
The ideal membrane has a very high flux and a very high perm-selectivity

☹ ☺

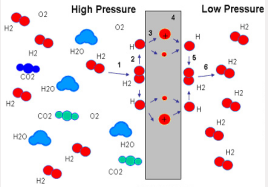
Increasing Perm-selectivity

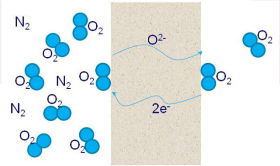
Decreasing Permability

☺ ☹



Porous membranes

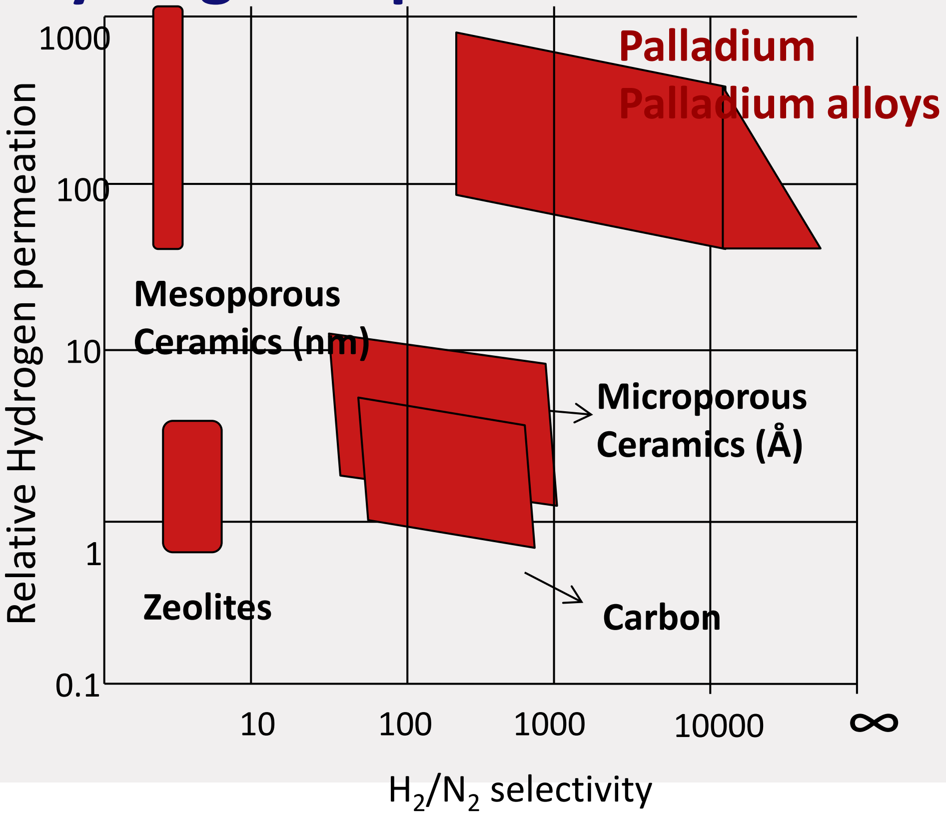




Dense membranes

TU/e

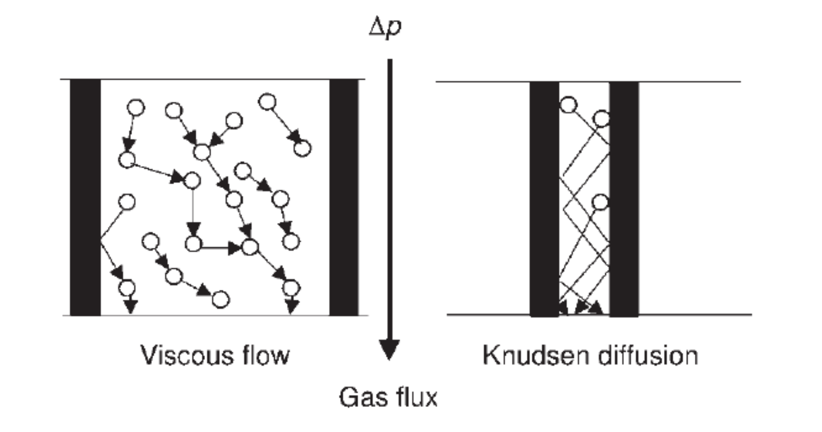
Membrane: Hydrogen separation



TU/e

Membrane principles

Gas Separation in porous membranes



Membrane flux:

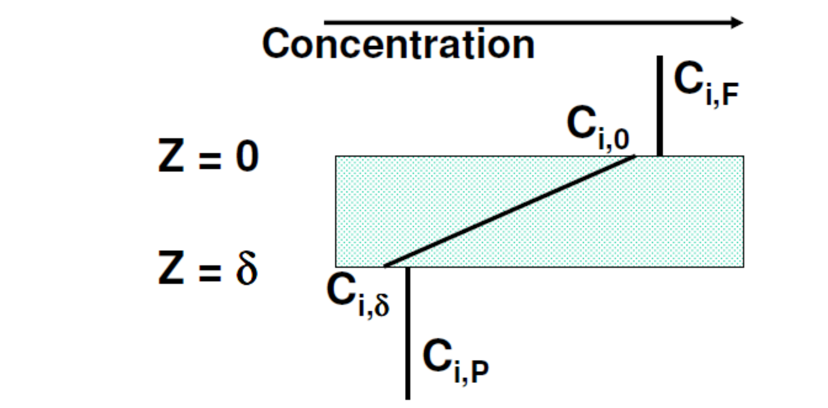
(Dusty-Gas-Model):

$$N_i = \frac{1}{RT}\left(K_0 \frac{4}{3}\sqrt{\frac{8RT}{\pi\langle M\rangle}} + B_0 \frac{\langle p\rangle}{\mu_g} \right) \times \frac{\Delta p_{i,m}}{(r_i+\delta_m)\ln\left(\frac{r_i+\delta_m}{r_i}\right)}$$

Parameters K_0 and B_0 depend on the pore size/structure distributions

Membrane principles

Gas Transport by the Solution-Diffusion Mechanism



$$J_i = -D_i \frac{dC_i}{dz}$$

$$J_i \approx -D_i \frac{C_{i,0} - C_{i,\delta}}{\Delta z}$$

$$K_i = \frac{C_{i,0}}{C_{i,F}} = \frac{C_{i,\delta}}{C_{i,P}}$$

Membrane principles

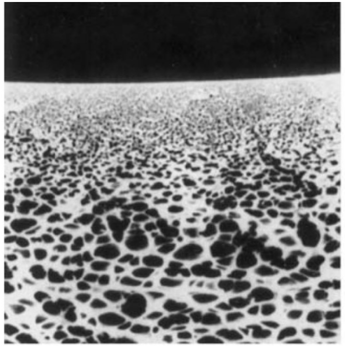
$$J_i = -D_i K_i \frac{C_{i,F} - C_{i,P}}{\Delta z}$$

$$\alpha_{i,j} = \frac{J_i}{J_j} = \frac{K_i}{K_j}\sqrt{\frac{M_j}{M_i}}$$

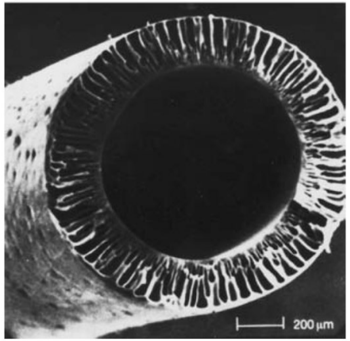
Mem…

Table 1. Porous membranes and their preparation and applications

Membrane type	Membrane material	Pore size, μm	Preparation process	Applications
Symmetric	ceramic, metal, polymer, graphite	0.1 – 20	powder pressing and sintering	microfiltration, gas separation
Symmetric	polymer with partial crystallinity	0.2 – 10	extruding and stretching of films	microfiltration, battery separator
Symmetric	polymer, mica	0.05 – 5	irradiation and etching of films	microfiltration, point-of-use filters
Symmetric	polymer, metal, ceramic	0.5 – 20	template leaching of films	microfiltration
Symmetric	polymer	0.5 – 10	temperature-induced phase inversion	microfiltration
Asymmetric	polymer	< 0.01	diffusion-induced phase inversion	ultrafiltration
Asymmetric	ceramic	< 0.01	composite-membrane gel – sol process	ultrafiltration

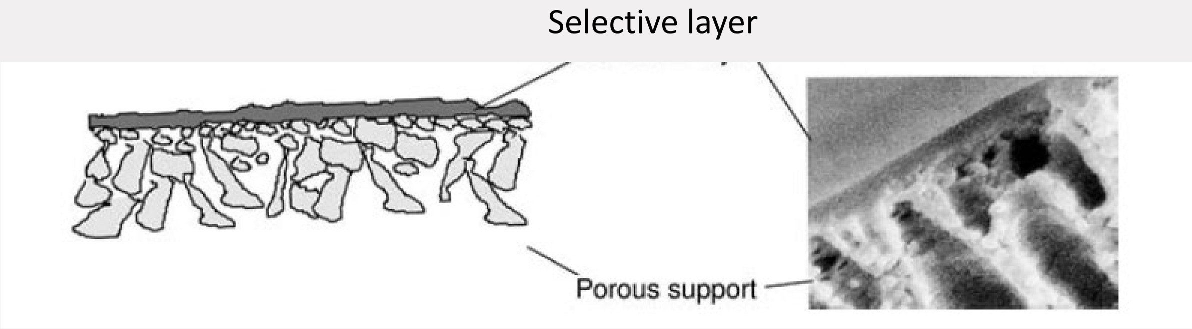


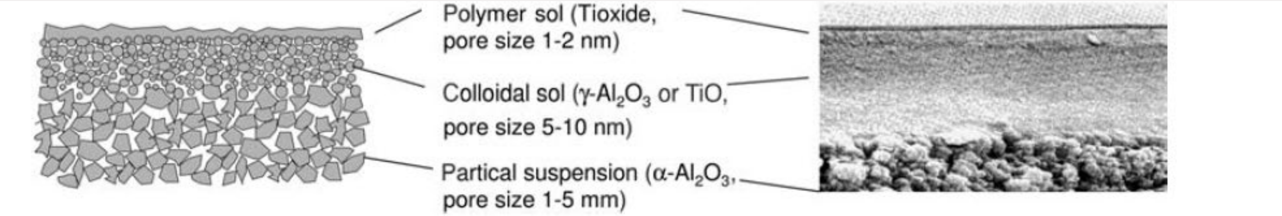
asymmetric reverse osmosis membrane with a graded pore structure



asymmetric ultrafiltration capillary membrane with a finger-type structure

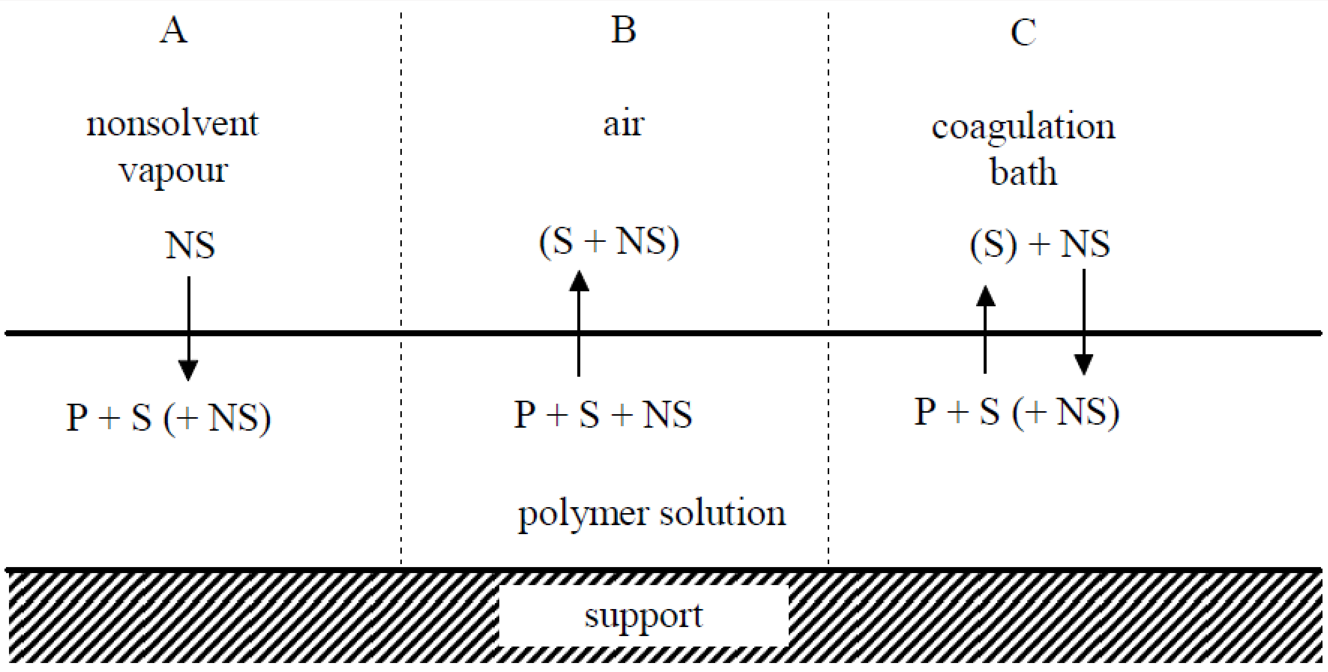
Composite membranes





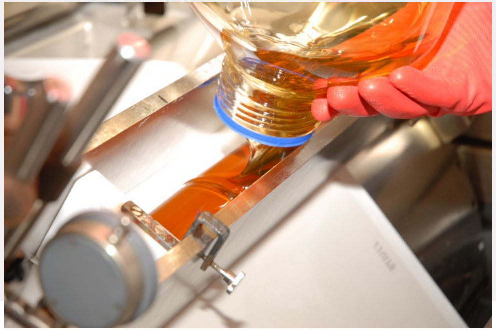
Membrane production

Polymeric membranes mostly produced by phase separation



Schematic representation of three diffusion induced phase separation *processes: A) precipitation with nonsolvent vapor, B) evaporation of solvent, C) immersion precipitation.*

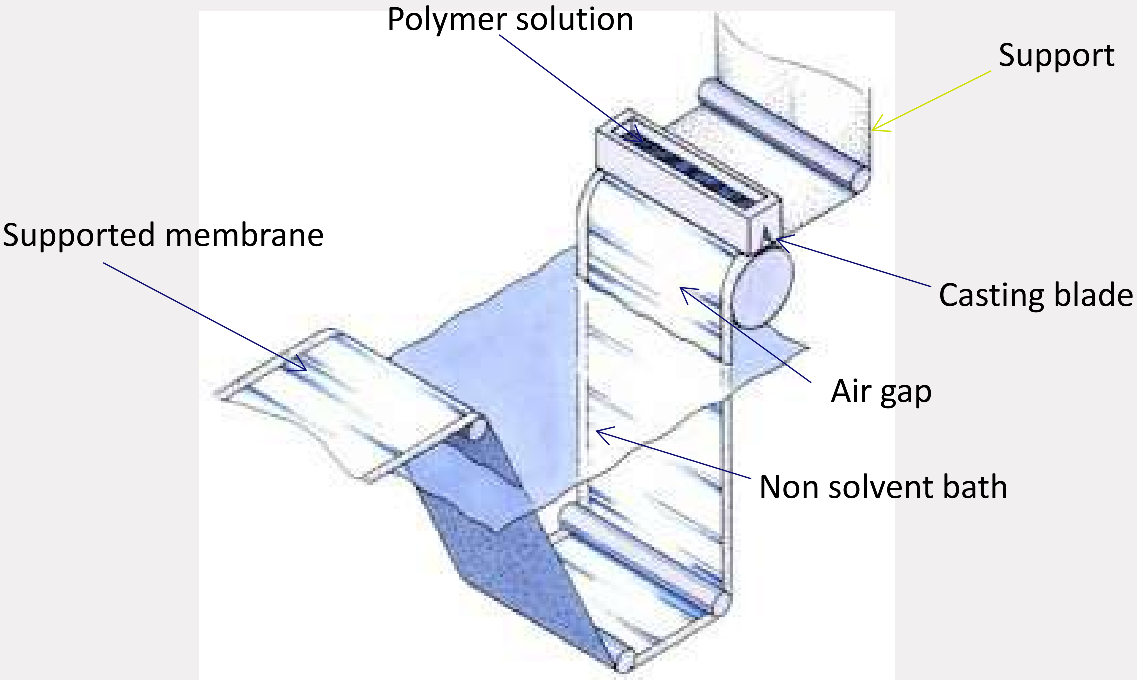
Membrane production



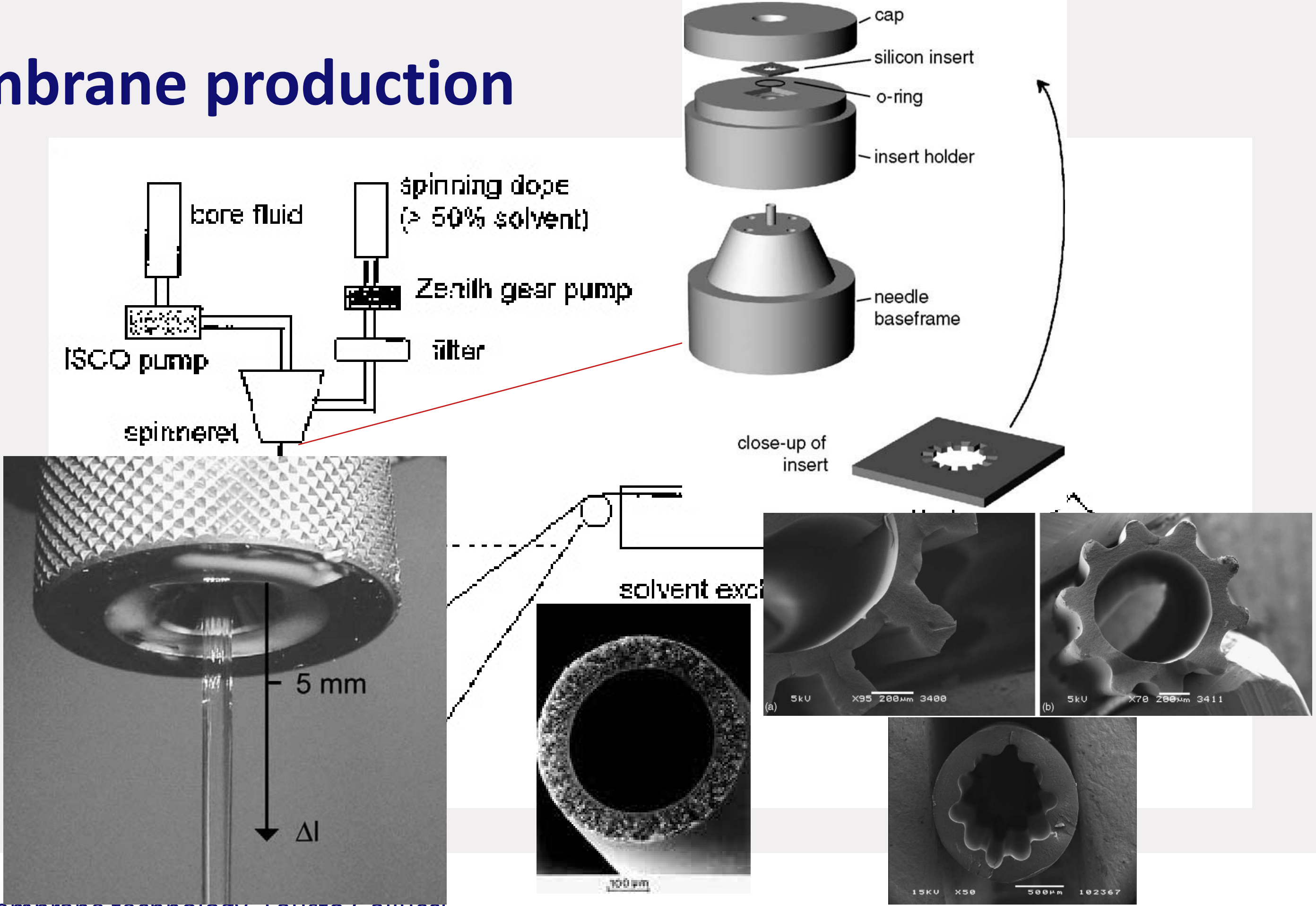
TU/e

Membrane production

Flat membrane casting



Membrane production



TU/e

Preparation of Inorganic membranes

A unique method does not exist mainly due to:

- Different inorganic materials (ceramic, metallic, mixed materials)
- Differences in supported and unsupported
- Differences between dense and porous membranes

Pd-based membranes - Preparation methods

Electroless plating

Support cleaning with ethanol and trichloroethylene

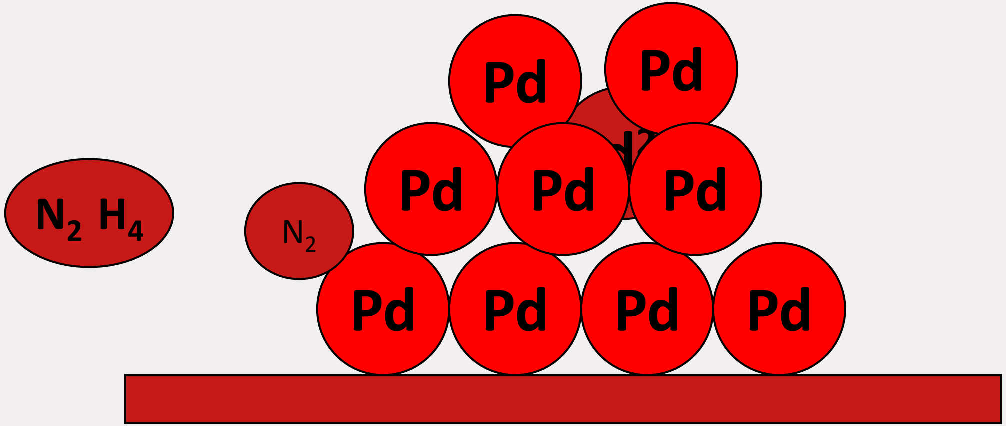
Palladium nuclei formation on the support via alternative stannous chloride and palladium chloride solutions (10 times)

Electroless plating bath containing: tetraammine complex of palladium, EDTA, ammonium, hydroxide and hydrazine (new solution every 1 hr or so)

Journal of Membrane Science, 56 (1991) 303-313

Preparation of H_2 membranes by electroless plating

$$Pd^{2+} + 2e^{-} \xleftrightarrow{Pd} Pd$$



Pd-based membranes - Preparation methods

Electroless plating → Most of the supported Pd-based membranes

Example

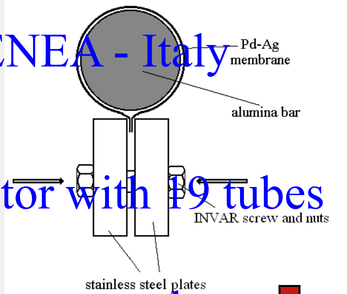
Pd-Ag/ceramic tubes

Module with 13 tubes

Pd-based membranes - Preparation methods

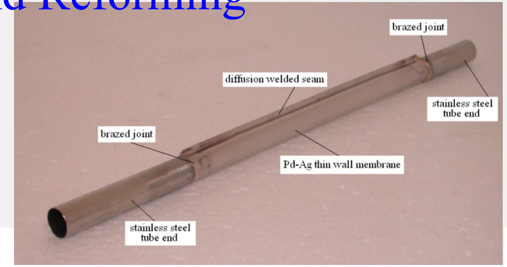
Cold Rolling → Self supported membranes

ENEA - Italy



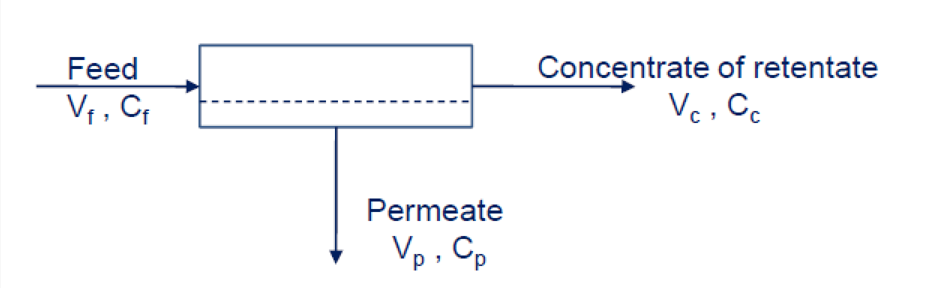
Reactor with 19 tubes

Has been used as reactor for WGS and Reforming



http://www.fusione.enea.it/index.html.en

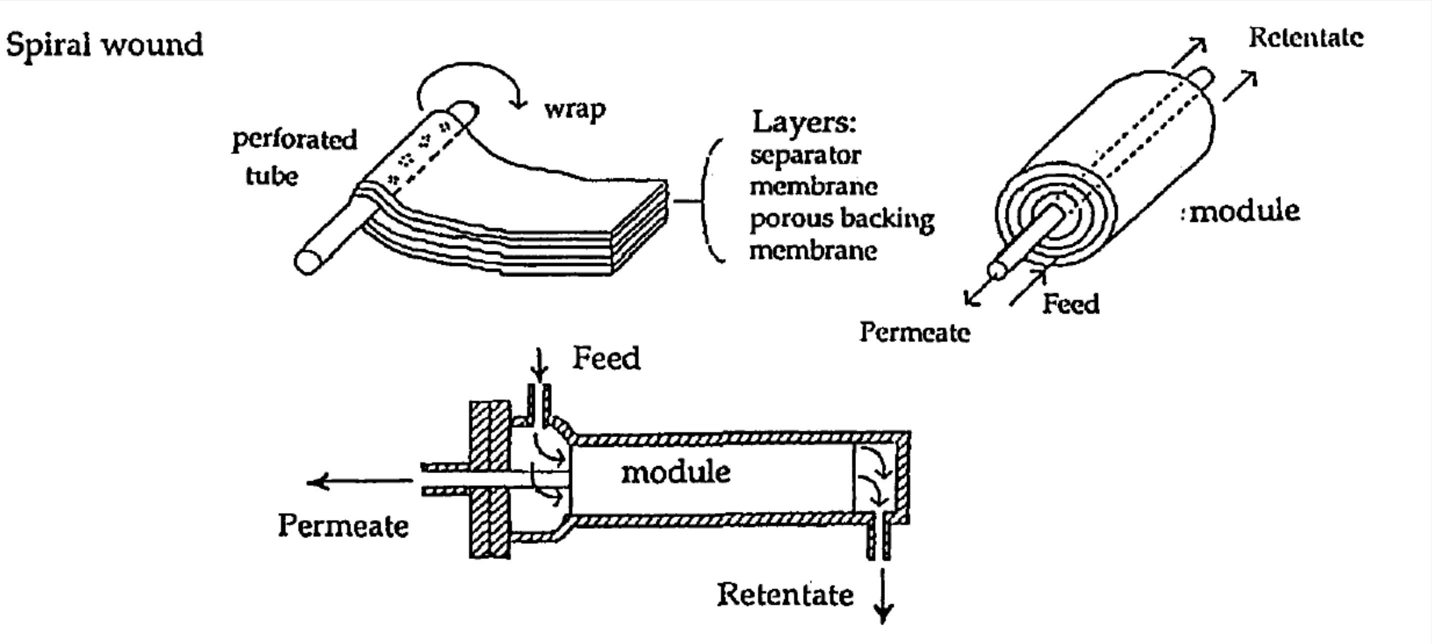
Membrane modules



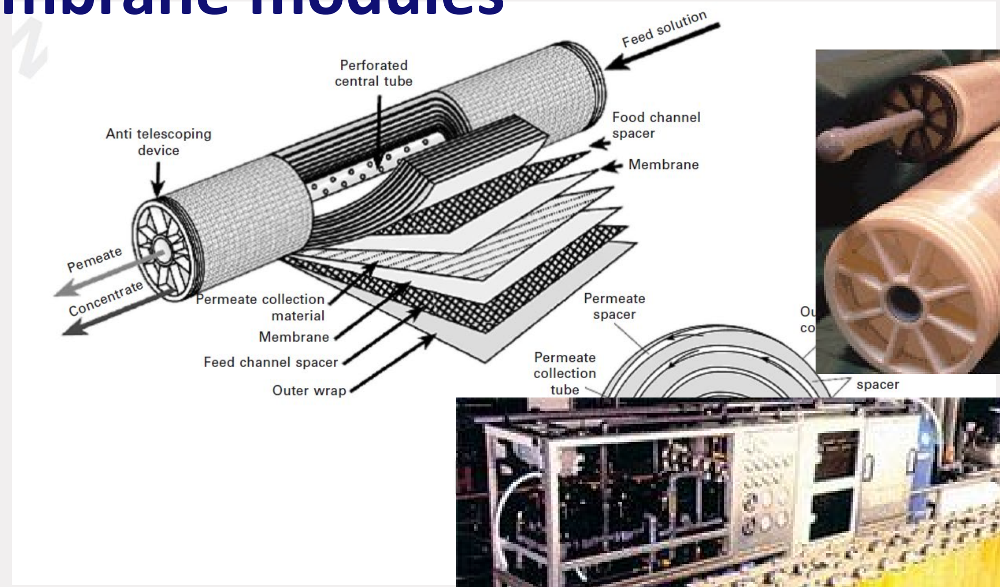
manifold assembly containing a membrane or membranes to separate the streams of feed, permeate, and retentate

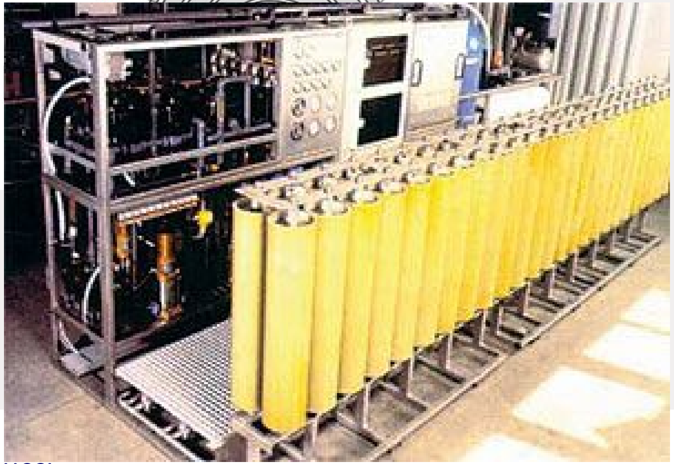
What is important for a membrane module?

Membrane modules



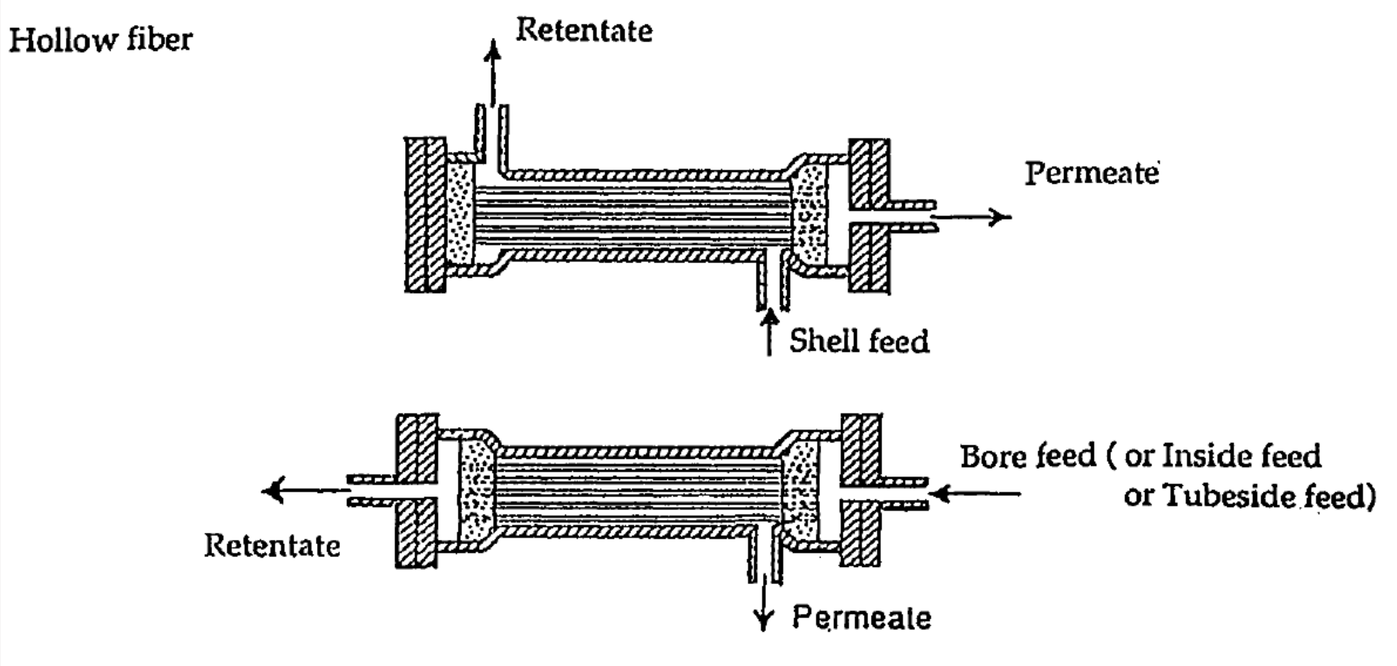
Membrane modules



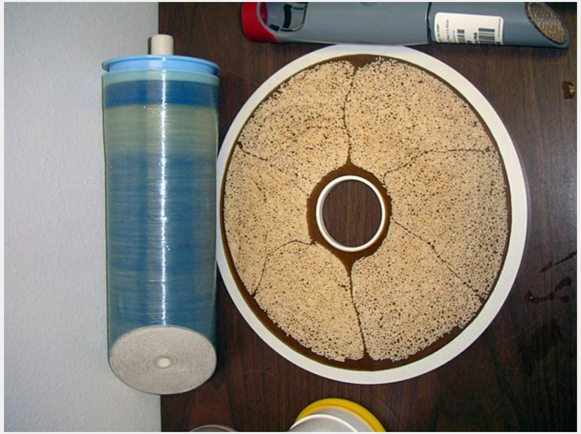


TU/e

Membrane modules



Membrane modules



Applicability of membrane modules

	Tubular	Plate-frame	Spiral wound	Capillary	Hollow fiber
MF	++	+		+	
UF	++	+	+	++	
NF	++	+	++	++	+
RO	+	+	++	+	++
Gas sep.			++	+	++
PV/VP	++	++	+	+	
ED		++			

Characteristics of membrane modules

	Area/vol. m^2/m^3	Fouling tendency	Prefiltration
Plate and frame	100 – 500	little	10 – 25 mm
Spiral wound	300 – 1,000	moderate	10 – 25 mm
Tube >5 mm	100 – 500	low	none
Capillary 0.5 – 5 mm	500 – 4,000	moderate	10 – 25 mm
Fibre <0.5 mm	4,000 – 30,000	high	5 – 10 mm

Membranes in Industry

Industrial Relev.	Membranes Competing with Conv. Processes	Membrane Processes with Clear Adv.	No Alternative to Memb. Processes
State-of-the-art processes			
High	Water desalination (waste)Water treatment	Production of ultrapure water	Artificial kidney, fuel cell separators
Medium	Natural gas treatment Air separation	Down-stream processing of bioproducts	Therapeutic devices for controlled drug release
Low	Dehydration of solvents	Biosensors	Diagnostic devices
Emerging processes			
High	Membrane reactors	Membrane bioreactors	Artificial liver
Medium	Organic/organic separation	Recycling of effluents	Immune isolation of cells
Low	Organic vapor recovery	Affinity membranes	

Strathmann AIChE Journal May 2001 Vol. 47, No. 5

Membranes in Industry

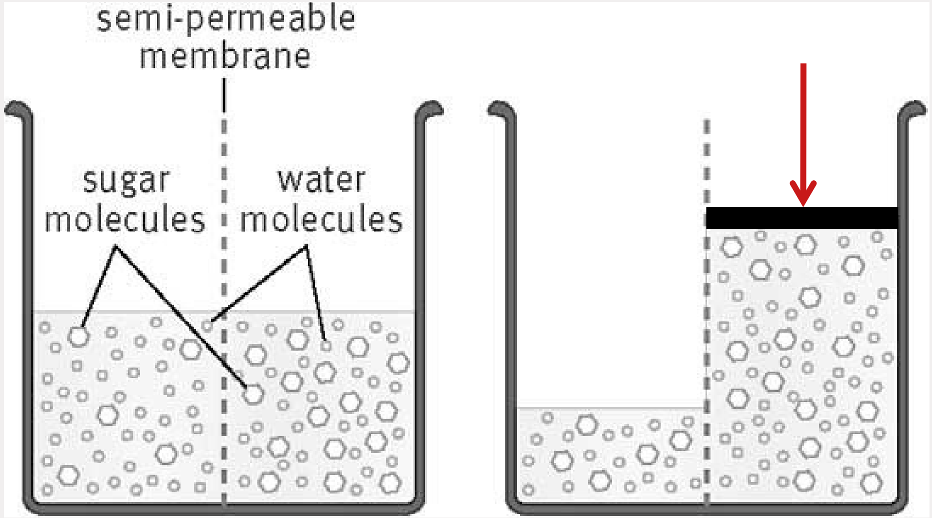
Sales of Membranes and Modules in Various Membrane Processes

membrane process	1998 sales (millions of U.S. dollars)	growth (%/year)
microfiltration	900	8
ultrafiltration	500	10
reverse osmosis	400	10
gas separation	230	15
electrodialysis	110	5
electrolysis	70	5
pervaporation	>10	?
miscellaneous	30	10

WORLD MEMBRANE DEMAND
(million dollars)

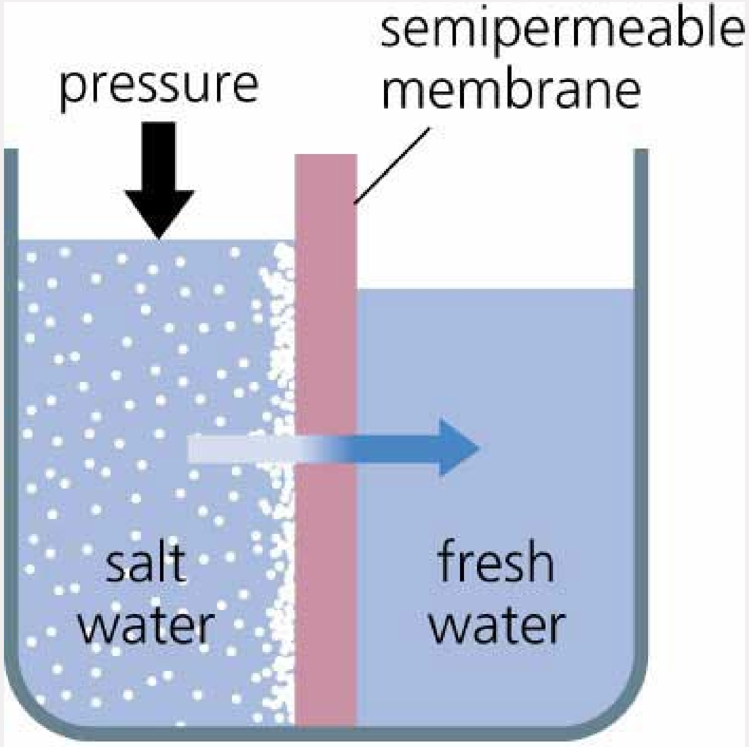
Item	2005	2010	2015	% Annual Growth 2005-2010	2010-2015
World Membrane Demand	8233	12550	19300	8.8	9.0
North America	2741	4080	6070	8.3	8.3
Western Europe	2227	2670	3650	3.7	6.5
Asia/Pacific	2078	3645	6250	11.9	11.4
Other Regions	1187	2155	3330	12.7	9.1

Osmosis



$$\pi = i \cdot C \cdot R \cdot T$$

Reverse Osmosis



Example Reverse Osmosis

$$\pi = i \cdot C \cdot R \cdot T$$

$$c_{NaCl} = 0.1 \text{ mol NaCl / kg } H_2O \text{ bij } 25\,°C$$

$$\rho_{H_2O}(25°C) = 997.0 \frac{kg}{m^3}$$

$$\pi = RT.c = 8.31 \times 298 \times 0.1 \times 997.0 \times 2$$

$$\pi = 494000 \text{ Pa} = 4.94 \text{ bar}$$

Reverse Osmosis

Worldwide Desalination Production Capacity*a*

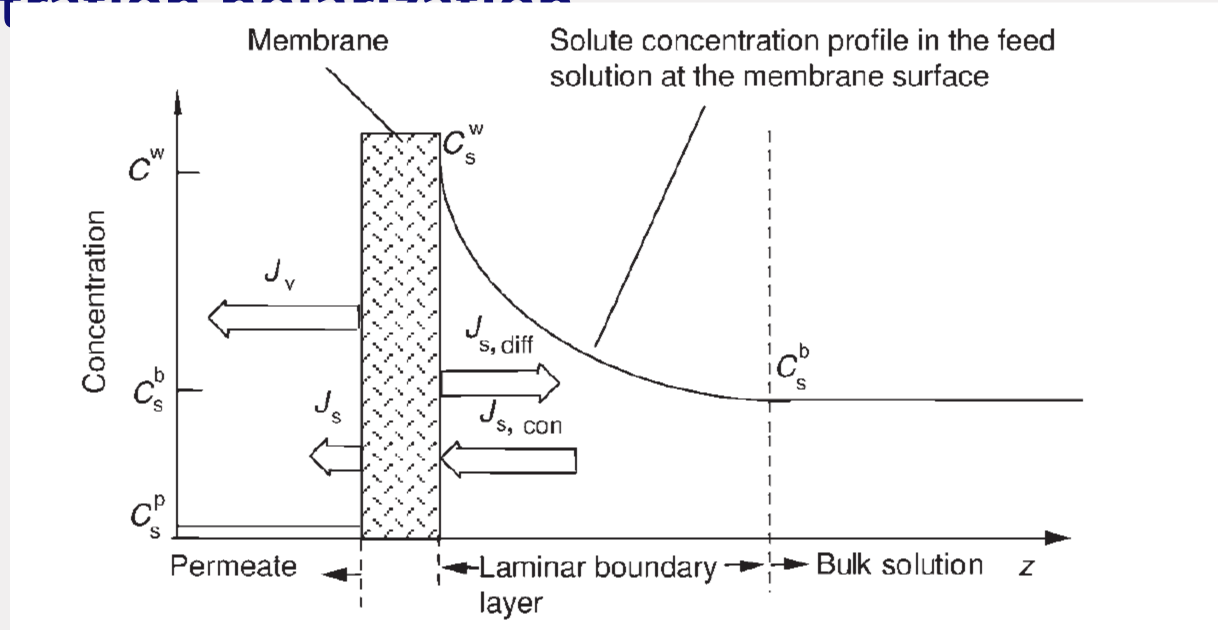
country	total capacity (m^3/day)	% of world production	MSF (%)	MEE (%)	VC (%)	RO (%)	ED (%)
Saudi Arabia	5 250 000	25.9	67.5	0.3	1.2	31.0	1.9
U.S.	3 100 00	15.2	1.7	1.8	4.5	78.0	11.4
United Arab Emirates	2 200 00	10.7	89.8	0.4	3.0	6.5	0.2
Kuwait	1 500 00	7.6	95.5	0.7	0.0	3.4	0.3
Japan	746 000	3.7	4.7	2.0	0.0	86.4	6.8
Libya	685 000	3.4	67.7	0.9	1.8	19.6	9.8
Qatar	570 000	2.8	94.4	0.6	3.3	0.0	0.0
Spain	530 000	2.6	10.6	0.9	15.1	20.4	19.2
Italy	520 000	2.6	43.2	1.9	15.1	20.4	19.2
Bahrain	310 000	1.5	52.0	0.0	1.5	41.7	4.5
Oman	190 000	0.9	84.1	2.2	0.0	11.7	0.0

[a] Phase-change processes: MSF (multistage flash), ME (multi-effect evaporation), VC (vapor condensation). Single-phase processes: RO (reverse osmosis), ED (electrodialysis).

process[a]	maturity	energy consumption	electric energy equivalent (kWh/m^3)	scale of application	cost for 1 m^3 of freshwater produced (ECU)
MSF	very	thermal	10−14.5	small−large	0.6−1.9
ME	partly	thermal	6−9	small−medium	0.5−2.0
VC	partly	mechanical	7−15	small	0.6−2.4
RO	yes	mechanical	4−8	small−large	0.4−1.4

Reverse Osmosis

Concentration polarization



The material balance for the solute

$$J_S = J_{S,con} - J_{S,diff}$$

Concentration polarization

$$J_S = J_v C_s^P$$

$$J_{S,con} = J_v C_s$$

$$J_{S,diff} = -D_S \frac{dC_s}{dz}$$

$$J_v C_s^P = J_v C_s + D_S \frac{dC_s}{dz}$$

$$C_s = C_s^w \quad \text{for } z = 0$$

$$C_s = C_s^b \quad \text{for } z = Z_b$$

Concentration polarization

$$\frac{J_v Z_b}{D_S} = \ln \frac{C_s^w - C_s^P}{C_s^b - C_s^P}$$

$$R = 1 - \frac{C_s^p}{C_s^w}$$

$$\frac{C_s^w}{C_s^b} = \frac{\exp \frac{J_v Z_b}{D_s}}{R + (1-R)\exp \frac{J_v Z_b}{D_s}}$$

$$\frac{D_s}{Z_b} = k_s$$ Solute mass transfer coefficient

$$\frac{C_s^w}{C_s^b} = \frac{\exp \frac{J_v}{k_s}}{R + (1-R)\exp \frac{J_v}{k_s}}$$

Concentration polarization

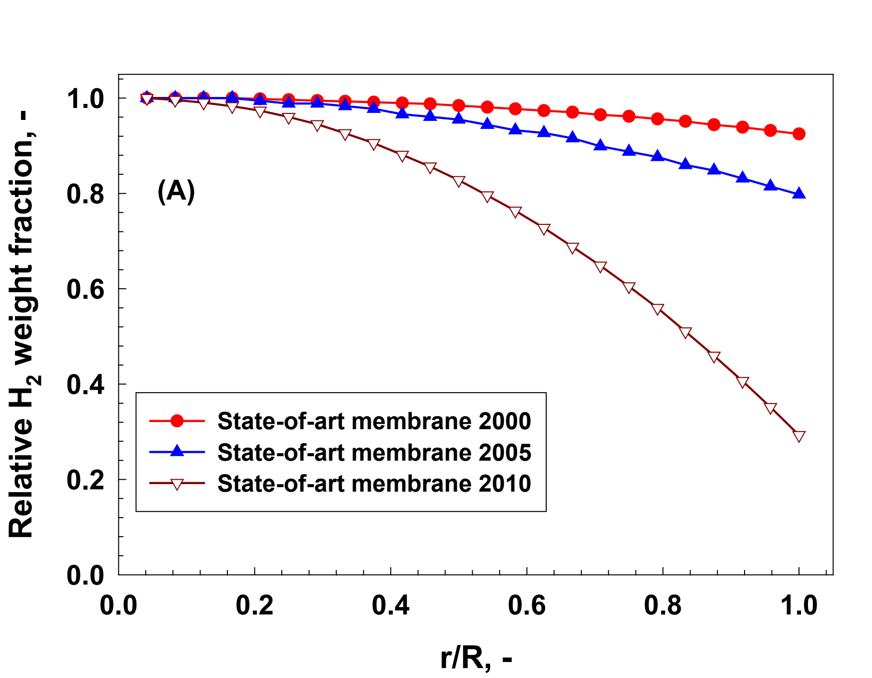
$$Sh = k_s \frac{d_H}{D_s}$$

$$Sh = a\,\mathrm{Re}^b\, Sc^c \left(\frac{d_H}{L}\right)^d$$

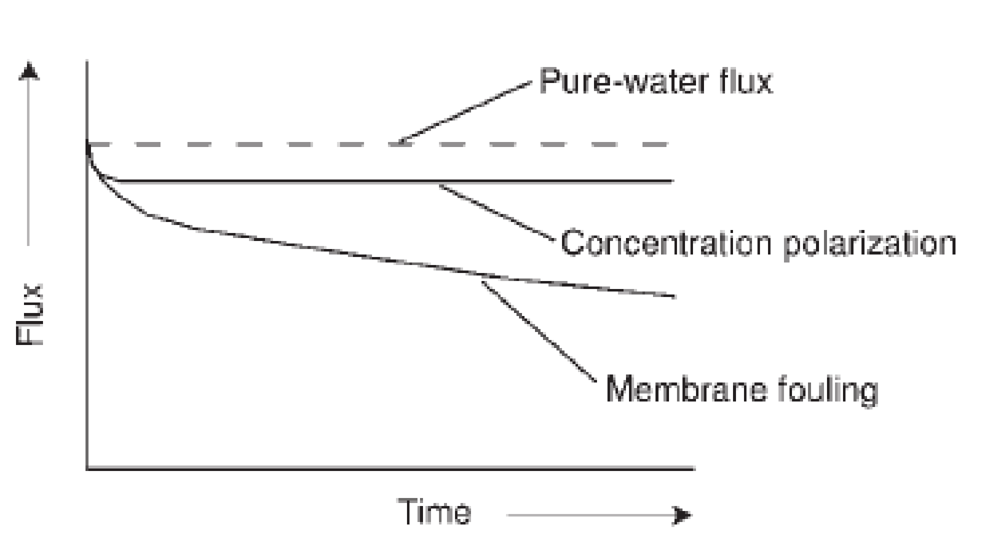
Flow regime	Module geometry	Hydraulic diameter d_H	Characteristic constants			
			a	b	c	d
Turbulent	channel	$\frac{2hw}{h+w}$	0.023	0.8	0.33	0
Laminar	channel	$\frac{2hw}{h+w}$	1.62	0.33	0.33	0.33
Turbulent	tube	r_t	0.023	0.8	0.25	0
Laminar	tube	r_t	1.86	0.33	0.33	0.33

r_t = tube radius, h = channel height, w = channel width.

Concentration polarization in gas separation



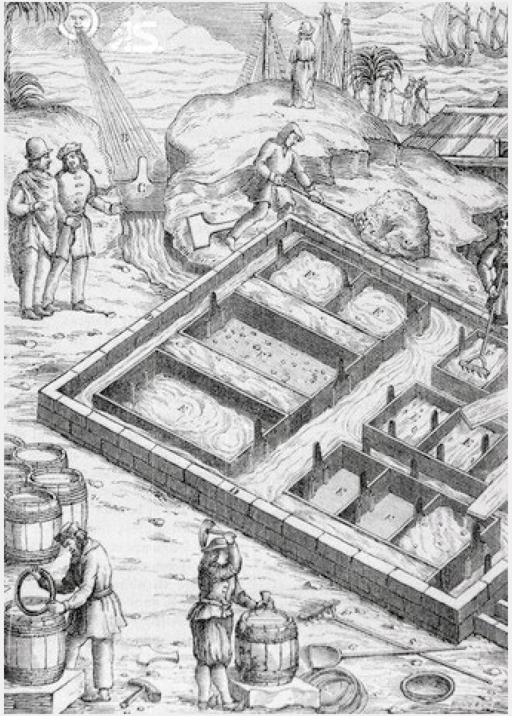
Membrane fouling



Membranes in Industry

Making salt (crystals)

Water treatment



De re metallica – Agricola 1556

Interim Conclusions

Membranes can be made of different materials – from polymers to metals and composites (even inorganic/polymeric mixtures)

Different shapes, modules and hydrodynamic operations are possible

Membranes are used in food industry, pharma, water desalination, water purification, energy etc. etc.

Membranes can be used as stand alone separation units, as integrated separation systems and as integrated operations (membrane reactors like)

Important parameters for membranes are:

Membrane flux

Membrane perm selectivity

Membrane stability

Membrane costs

EINDHOVEN UNIVERSITY OF TECHNOLOGY

Inorganic Membranes & Membrane Reactors

Fausto Gallucci
F.Gallucci@tue.nl