



Membrane technology for water treatment

J-C SCHROTTER

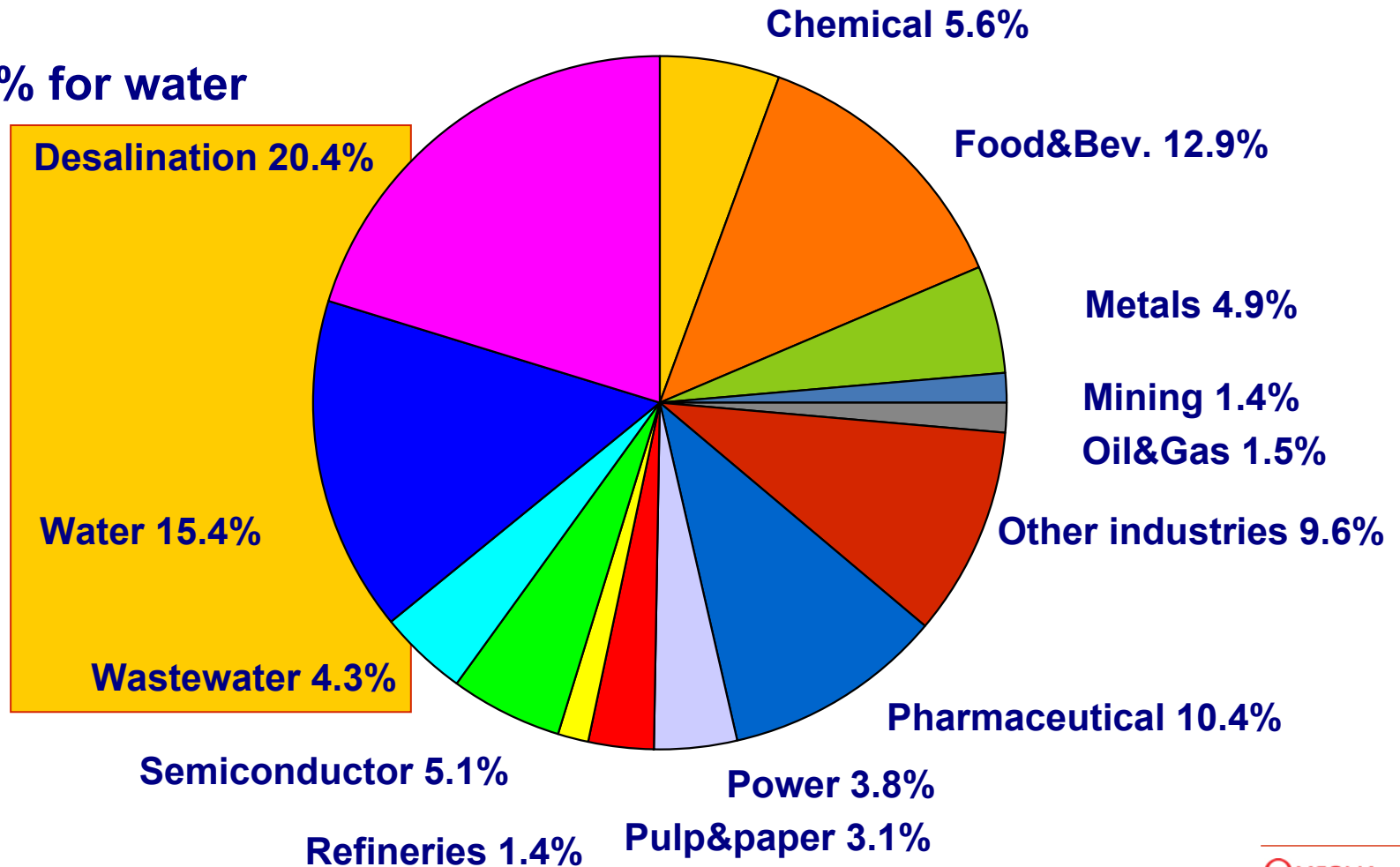
Membrane Research Manager

- 1956 - early 1980s : RO desalination, no commercial MF/UF for drinking water
- mid-1980 - early 1990s : Development of Memcor (MF), Aquasource (UF), clean waters & small capacities (1993 - Milwaukee- cryptosporidium crisis)
- mid-1990 - 2002: Start of market growth, new competitors (Zenon, Xflow, Hydranautics, Pall, Ionics) with second generation membranes/modules) Use on not so clean waters Start of immersed MBR products
- Now Large plants > 200000m³/d Strong growth of RO desalination market

Global Membrane Market share 2004 (overall \$6.46 Billion)

Source : The McILVAINE COMPANY (2004)

40% for water



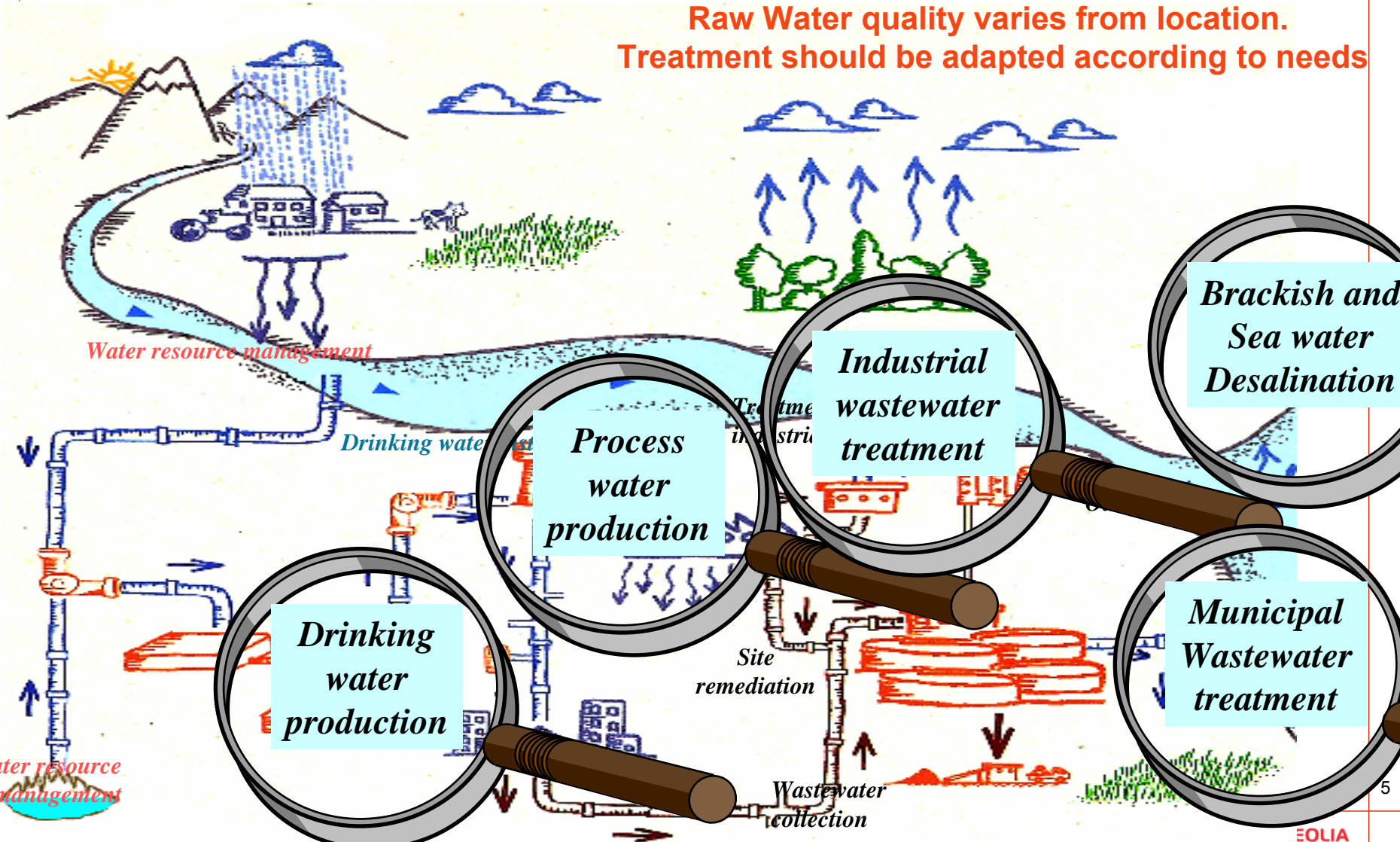
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Use of membrane for water treatment

Raw Water quality varies from location.
Treatment should be adapted according to needs



Brackish and Sea water Desalination

Industrial wastewater treatment

Process water production

Drinking water production

Municipal Wastewater treatment

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Sludge treatment and recycling

EOLIA ENVIRONNEMENT

◆ General trends are:

● O&M Cost

➤ River water

- 0.05- 0.2 \$/m³

➤ Brackish water

- 0.2-0.35 \$/m³

➤ Seawater

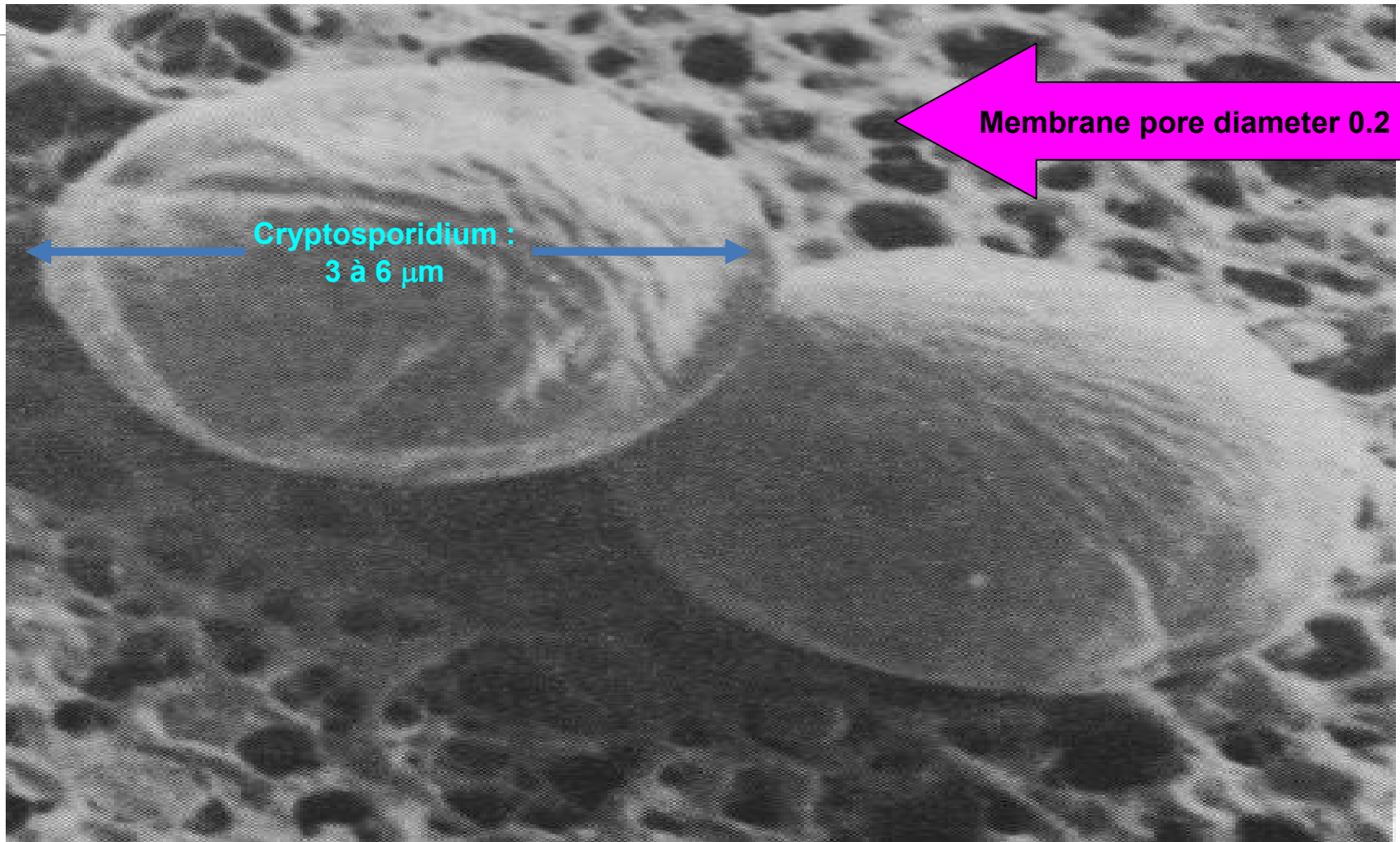
- 0.53-1.3 \$/m³

● Investment Cost from \$100 / m³/d to more than \$2000 / m³/d

Example in UK for drinking water :

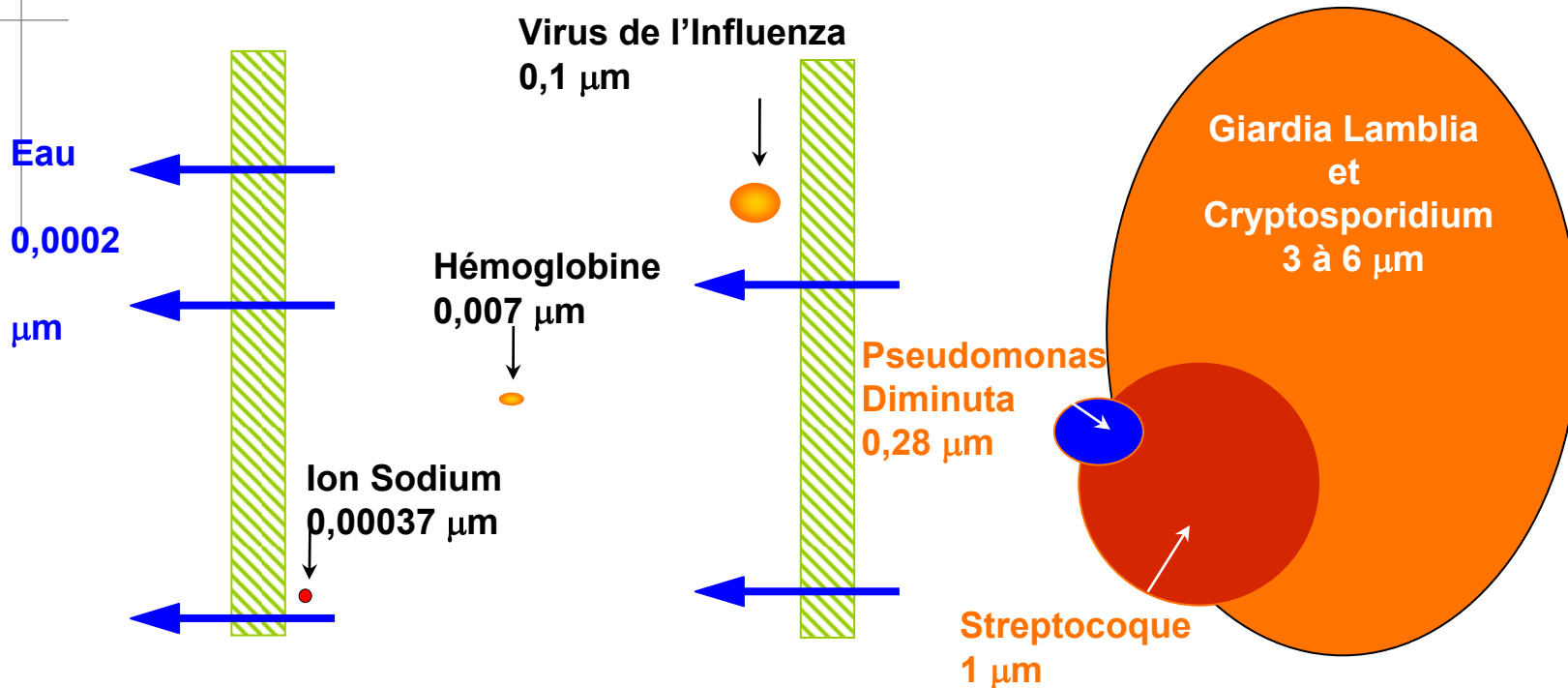
- ◆ New regulations in 2003 for Cryptosporidium (>1 oocysts/10 litres)
- ◆ New specifications have also been put in place on
 - Lead (25µ/L by 2014 and 10µ/L by 2024)
 - Benzene (1µ/L)
 - Nitrate (50mg/L)
 - Nitrite (0.1mg/L)
 - **THM (Trihalomethanes) (100 µ/L)**
 - Bromate (10µ BrO₃/L)
 - Arsenic (10µ/L)
- ◆ High standards required on
 - **Pesticides (0,5µg/l)**
 - **Bacteria (5-6 Log removal)**
 - **Viruses (4log removal)**

Microscopic view of a membrane surface



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Pollutant removal by membrane processes



Osmose Inverse	Nano-filtration	Ultra-filtration	Micro-filtration		
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0,0001 μm 0,001 μm 0,01 μm 0,1 μm 1 μm 10 μm 100 μm

Diamètre des pores des membranes

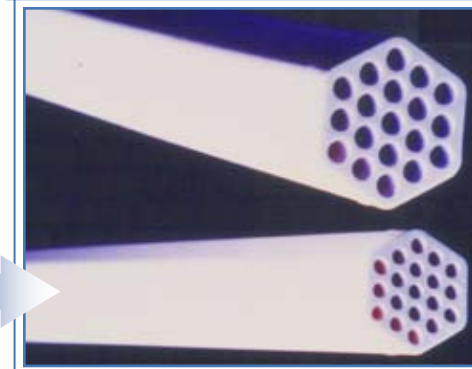
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Differents kind of module

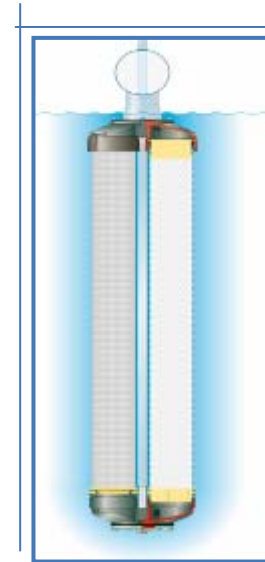


Spiralwounded element

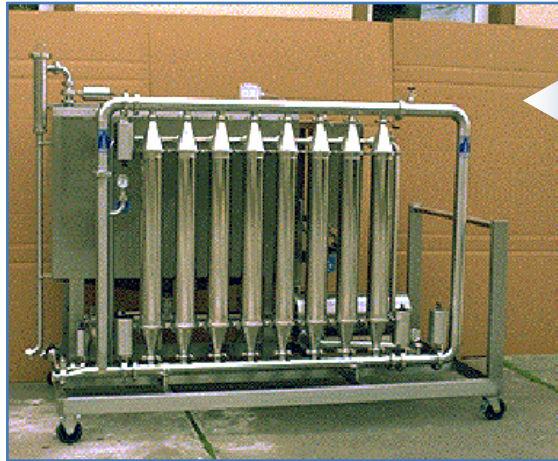
tubular



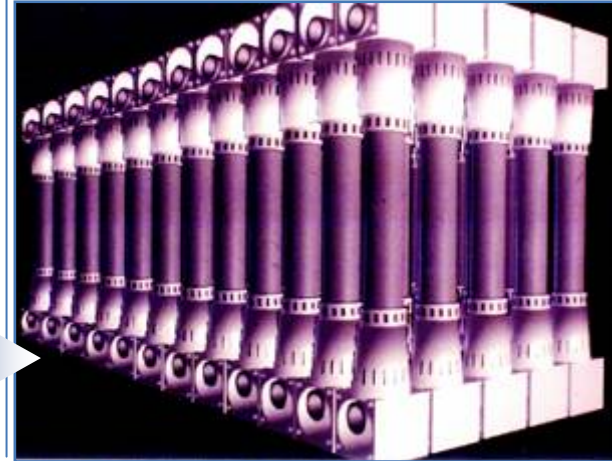
Hollow fibers



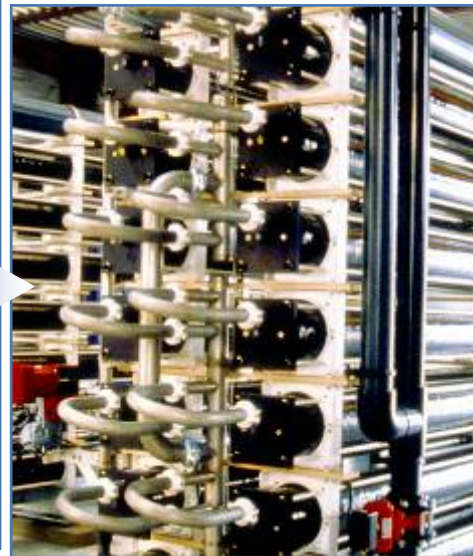
Different kind of systems



Rack



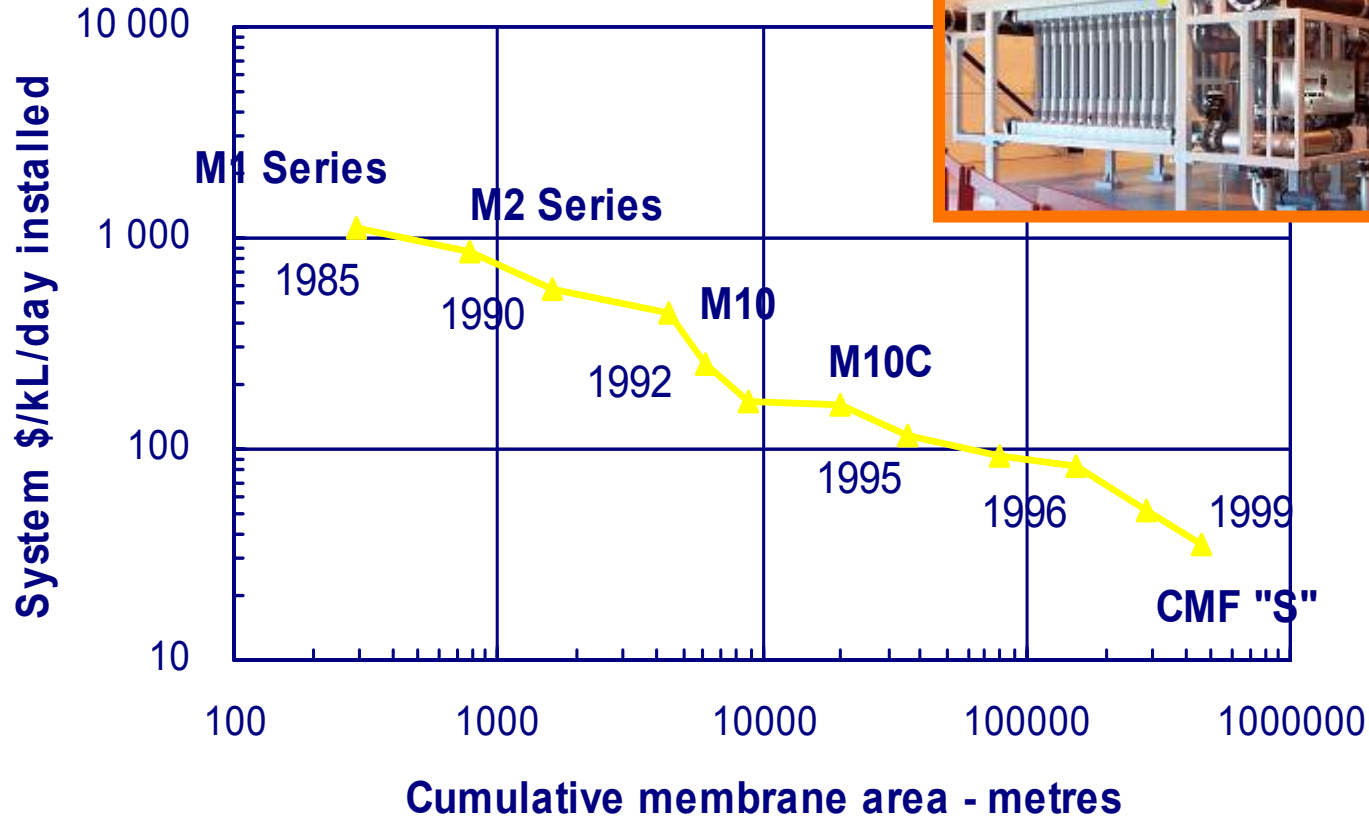
Block



Tube

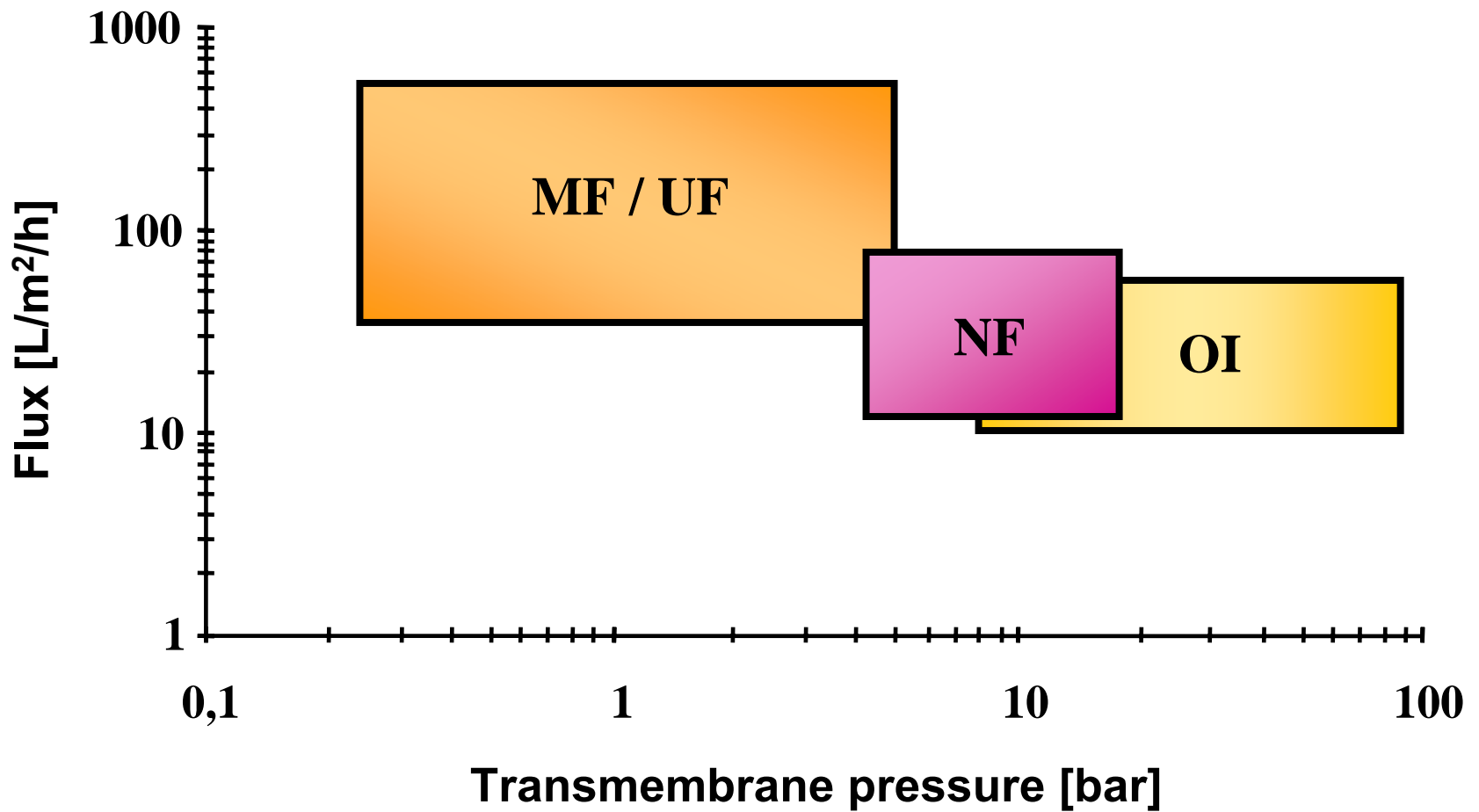
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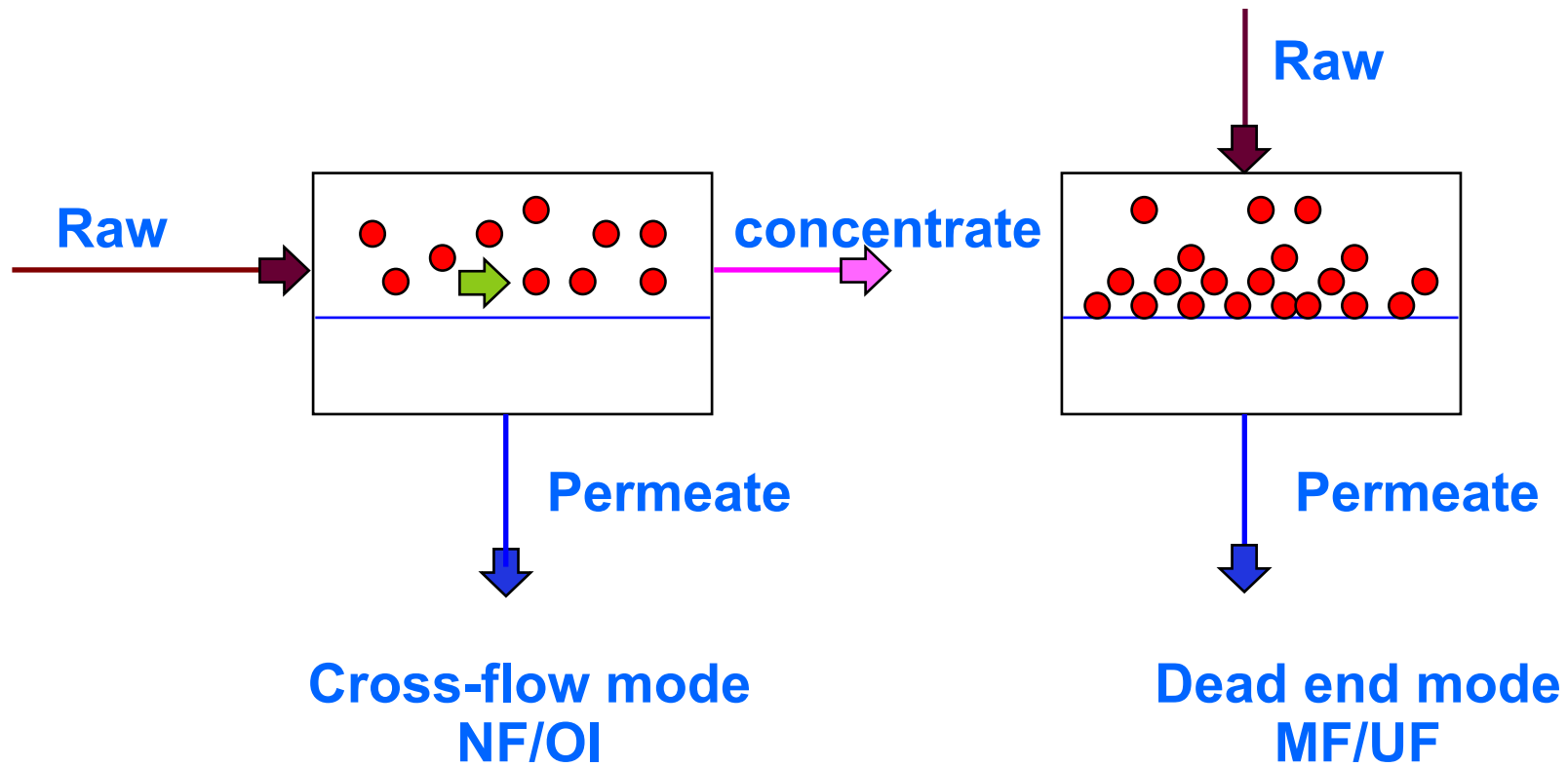
Reduction of membrane cost



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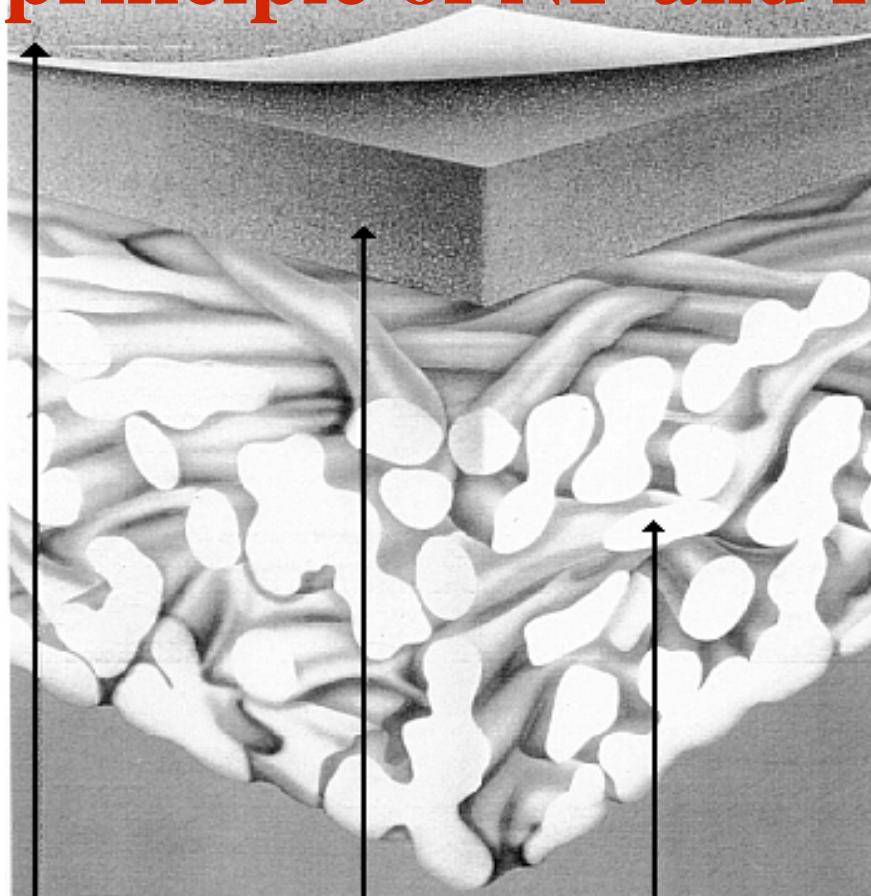
Membrane Operating conditions





High pressure membrane systems NF/OI

Basic principle of NF and RO systems

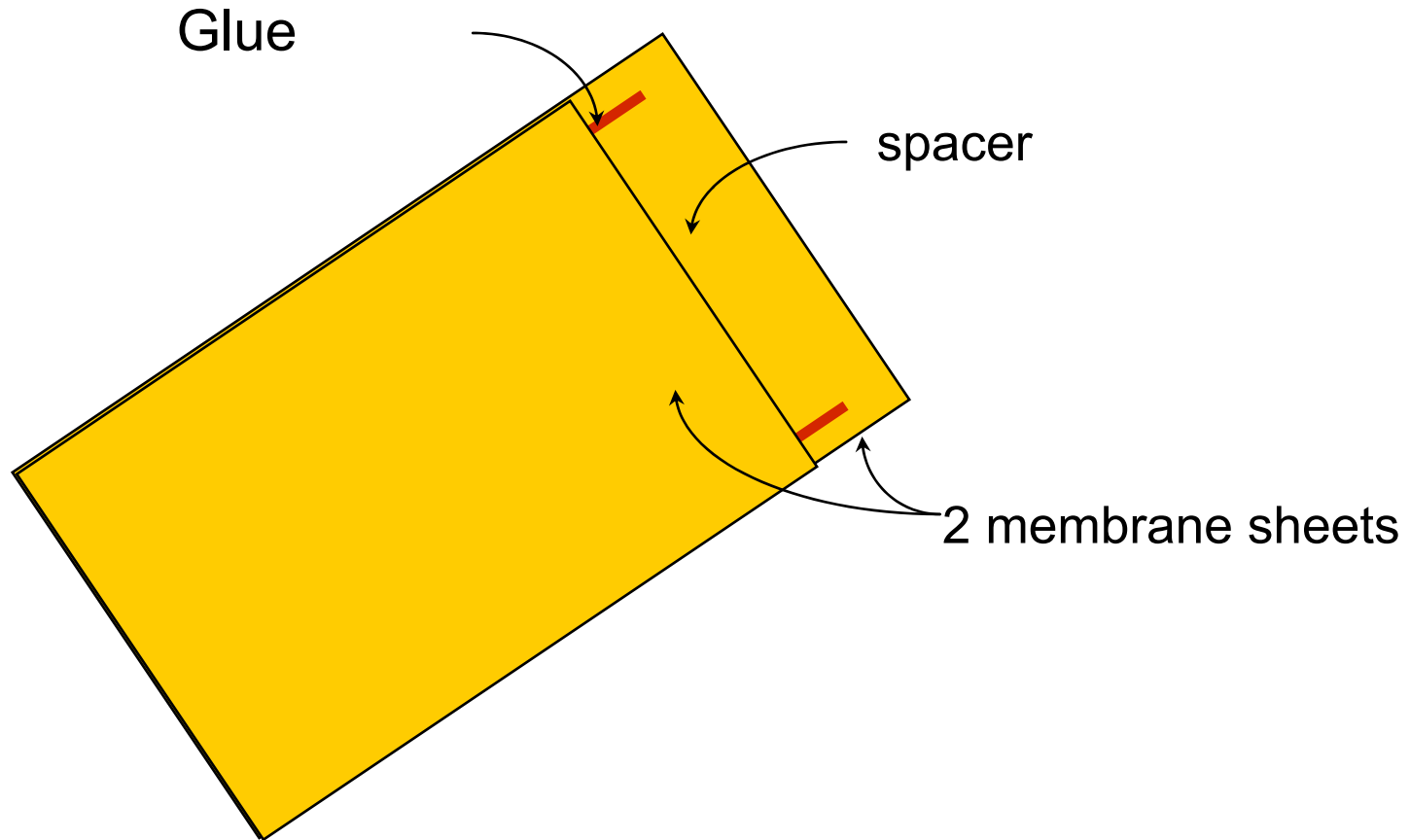


Polyamide
Membrane

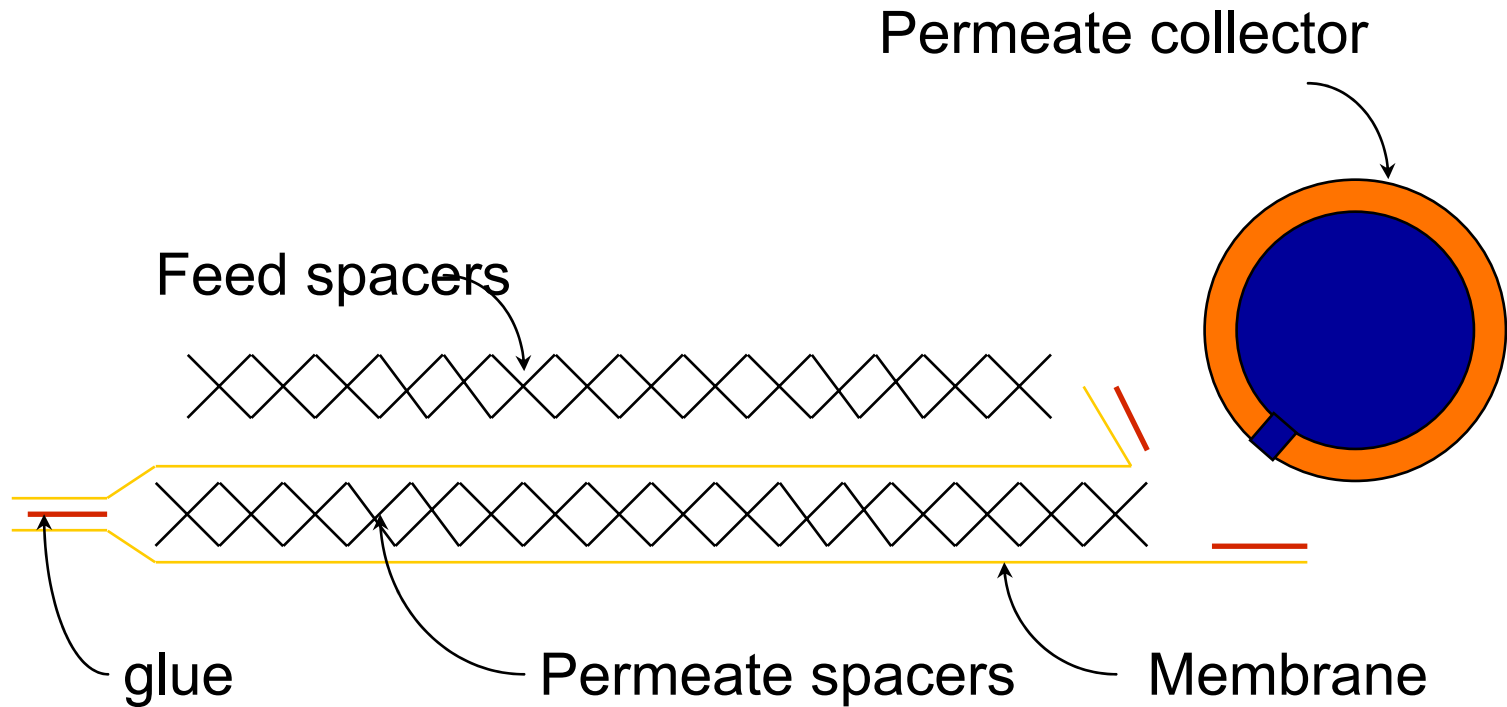
Polysulfone
layer

Polyester
support

Basic principle of NF and RO systems

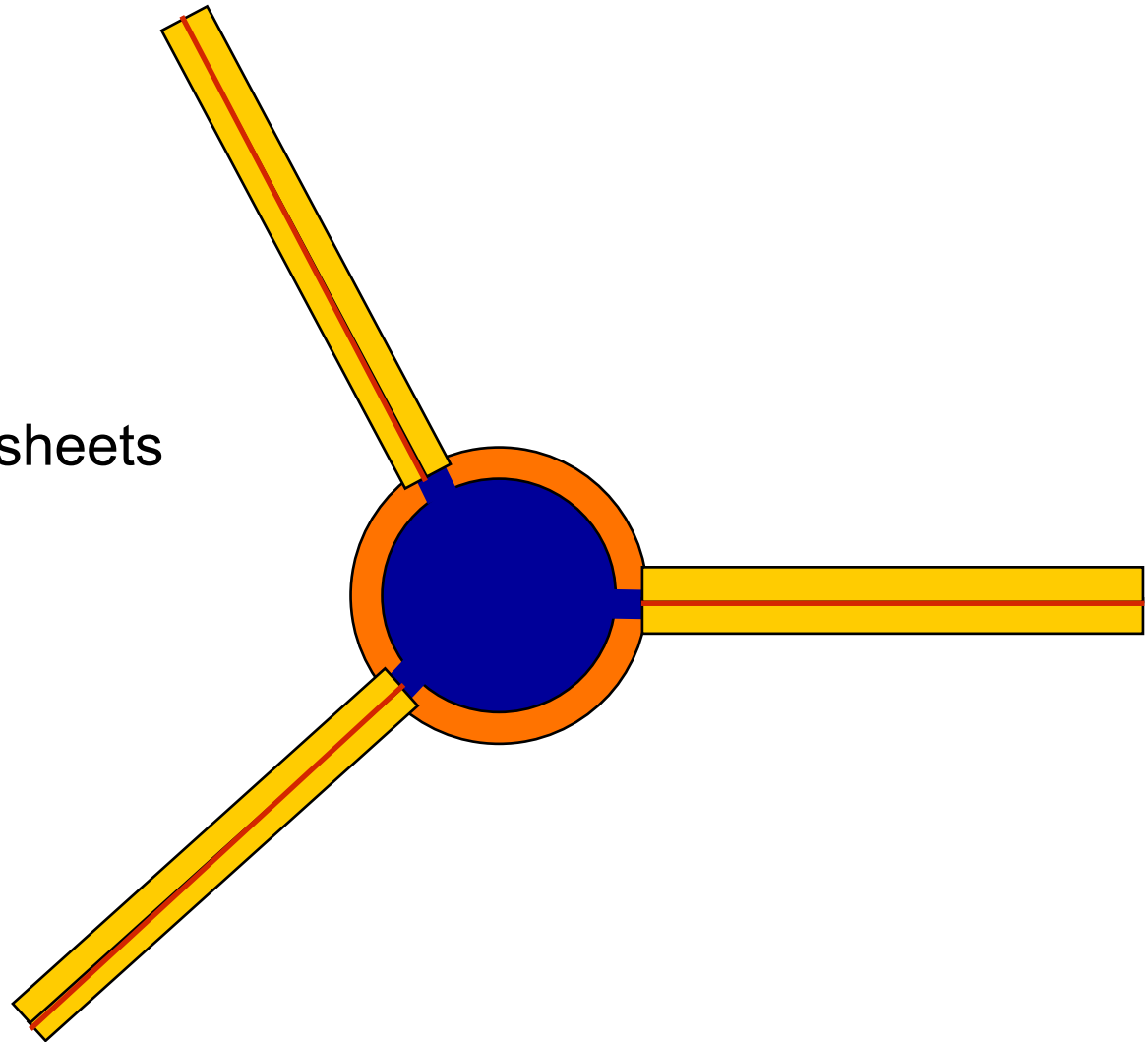


Basic principle of NF and RO systems

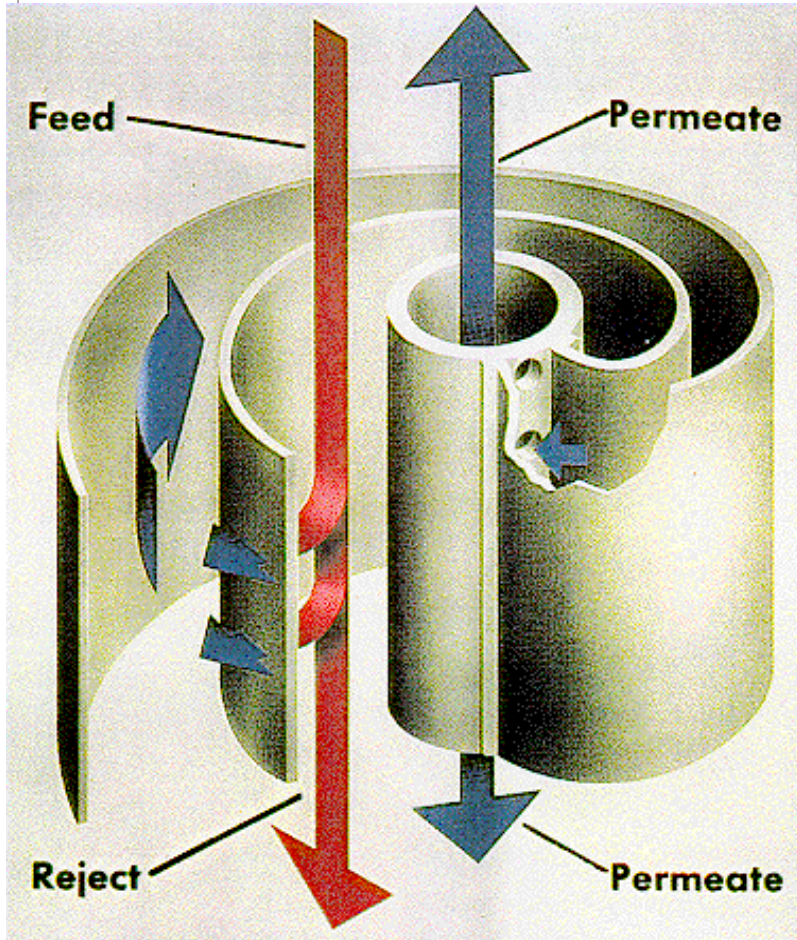


Basic principle of NF and RO systems

Collector with 3 sheets

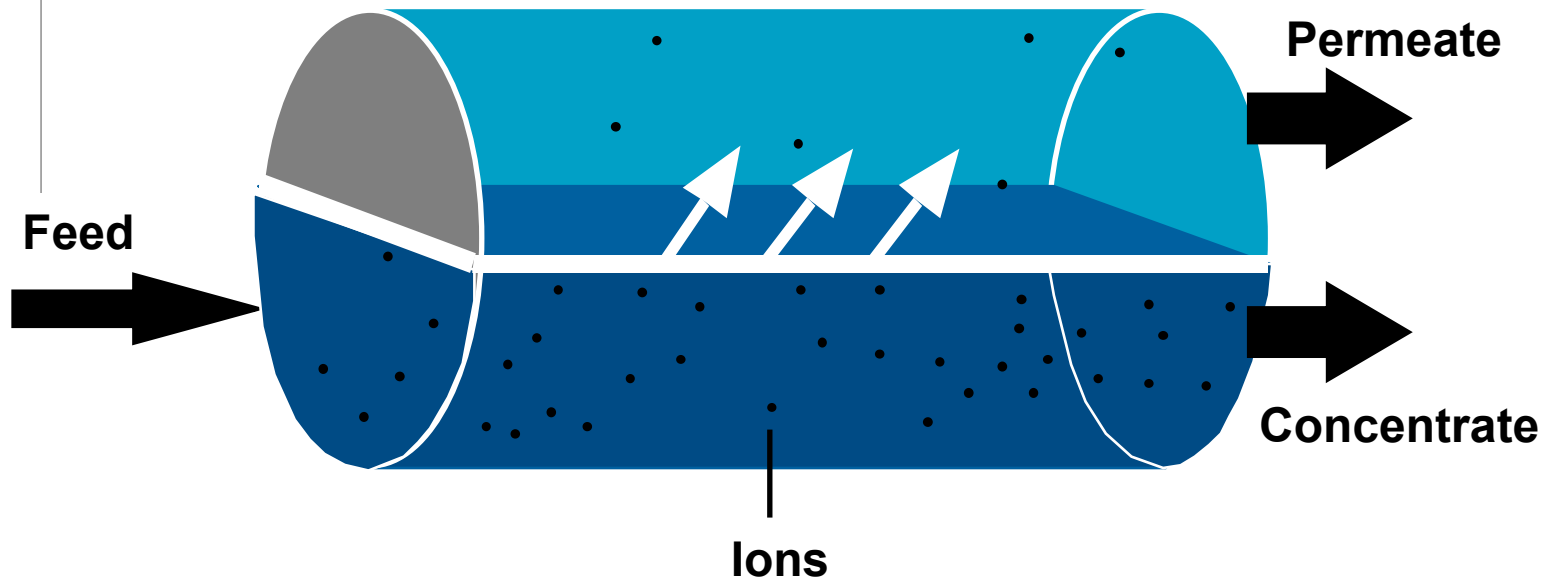


Basic principle of NF and RO systems



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Basic principle of NF and RO systems



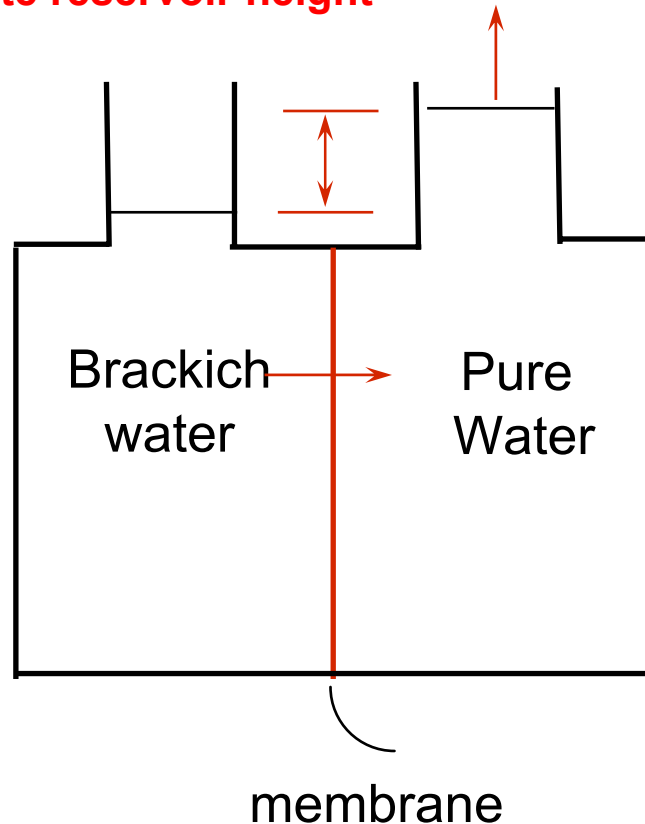
- ◆ Cross-flow filtration with turbulence promoters (feed spacers) to limit polarisation concentration and fouling issues

Basic principle of NF and RO systems

- applied Minimum pressure should counter balance :

:

- Osmotic pressure
- Longitudinal pressure drop
- Permeate reservoir height



Basic principle of NF and RO systems

Osmotic pressure (Van't Hoff Law)

$$\Pi = CRT$$

Avec :

- Π = Osmotic pressure
- C = Ion concentration (mol/m³)
- R = perfect gas constant (= 8,314 J/mol/K)
- T = Temperature (°K)

Basic principle of NF and RO systems

• Osmotic pressure

- 100 ppm TDS \approx 0,068 bar
- 1,000 ppm TDS \approx 0,68 bar
- 35,000 ppm TDS \approx 24,1 bar

Basic principle of NF and RO systems

• Operating pressure

Membrane application	Operating Pressure (bar)
RO	
SW (30 000 - 50 000 mg/l)	50-75
BW (100-10 000mg/l)	10-40
Nanofiltration	5-15

Basic principle of NF and RO systems

- recovery factor

$$\text{recovery factor} = \frac{\text{permeate flow rate}}{\text{Feed Flow rate}}$$

100%
Feed



75%
permeate

25% concentrate

Basic principle of NF and RO systems

$$\Delta p_{tm} = \frac{p_f + p_c}{2} - p_p$$

Transmembrane pressure

$$\Delta \pi_{tm} = \frac{\pi_f + \pi_c}{2} - \pi_p$$

Transmembrane osmotic pressure

$$\Delta p_w = \Delta p_{tm} - \Delta \pi_{tm}$$

Working pressure

$$Q = \frac{\text{flowrate}_p}{S}$$

Permeate Flux
(l/h/m²)

$$L_p = \frac{Q}{\Delta p_w}$$

Permeability
(l/h/m²/bar)

$$Y = \frac{Q_p}{Q_f}$$

Recovery factor

Basic principle of NF and RO systems

- Rejection : R

$$R = 1 - \frac{c_p}{c_f} \quad [\%]$$

$$R_{\text{system}} < R_{\text{module}}$$

- Salt passage

$$P = 1 - R = \frac{c_p}{c_f} \quad [\%]$$

Performance of NF and RO systems

Example : performance of 1 module :

- Recovery = 10%
- Salt rejection = 80%



•Flowrate = 100 m³/h

•TDS = 100 ppm

•Perm flowrate = 10 m³/h
•TDS = 20 ppm

•Perm flowrate = 19 m³/h
•TDS = 21 ppm

•Perm flowrate = 27m³/h
•TDS = 22 ppm

•Conc flowrate = 90 m³/h
•TDS = 109 ppm

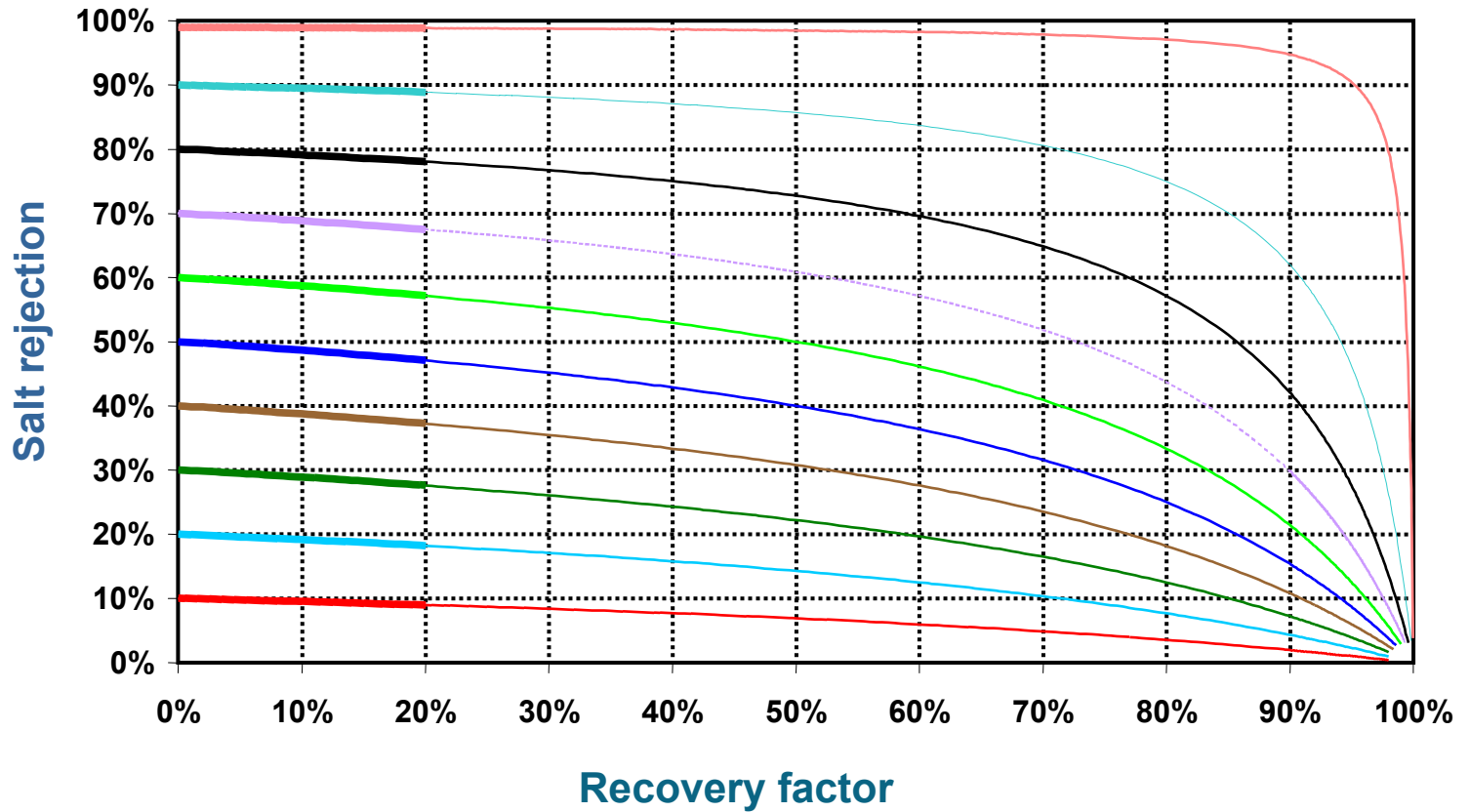
•Conc flowrate = 81 m³/h
•TDS = 116 ppm

•Conc flowrate = 73 m³/h
•TDS = 121 ppm

Performance of the system :

- Recovery factor = 27 %
- Salt rejection = 78 %

Performance of NF and RO systems



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Basic principle of NF and RO systems

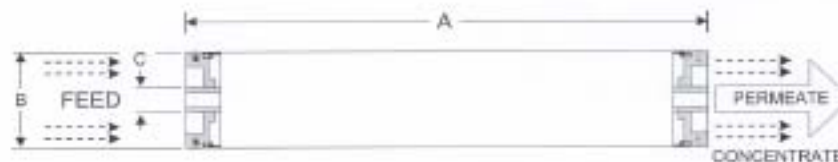


Membrane Element		SWC3
Performance:	Permeate Flow: Salt Rejection: nominal:	5,500 gpd (22.3 m ³ /d) 99.6 %
Type	Configuration: Membrane Polymer: Nominal Membrane Area:	Spiral Wound Composite Polyamide 370 ft ²
Application Data	Maximum Applied Pressure: Maximum Chlorine Concentration: Maximum Operating Temperature: Feedwater pH Range: Maximum Feedwater Turbidity: Maximum Feedwater SDI (15 min): Maximum Feed Flow: Minimum Ratio of Concentrate to Permeate Flow for any Element: Maximum Pressure Drop for Each Element:	1200 psig (8.27 MPa) ≤ 0.1 PPM 113 °F (45 °C) 5.0 - 10.0 1.0 NTU 5.0 75 GPM (17.0 m ³ /h) 5:1 10 psi

Test Conditions

The stated performance is initial (data taken after 30 minutes of operation), based on the following conditions:

32,000 ppm NaCl
800 psi (5.5 MPa) Applied Pressure
77 °F (25 °C) Operating Temperature
10% Permeate Recovery
6.5 - 7.0 pH Range



Core tube ID = 1.125" (28.6 mm)

A, inches (mm)	B, inches (mm)	C, inches (mm)	Weight, lbs. (kg)
43.0 (1092)	7.56 (193.1)	1.50 (38.1)	36 (16.4)

Notes: Permeate flow for individual elements may vary ± 10 percent. All membrane elements are supplied with a center seal, interconnects, and springs. Elements are supplied in a polypropylene bag containing a 1.0% sodium borate solution, and are packaged in a UN-certified box.

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Basic principle of NF and RO systems

•Recovery Factor

Procédé	Recovery Factor (%)
RO	
SW (30 000 - 50 000 mg/l)	35 à 45
BW (100-10 000mg/l)	65 à 85
Nanofiltration	75 à 85

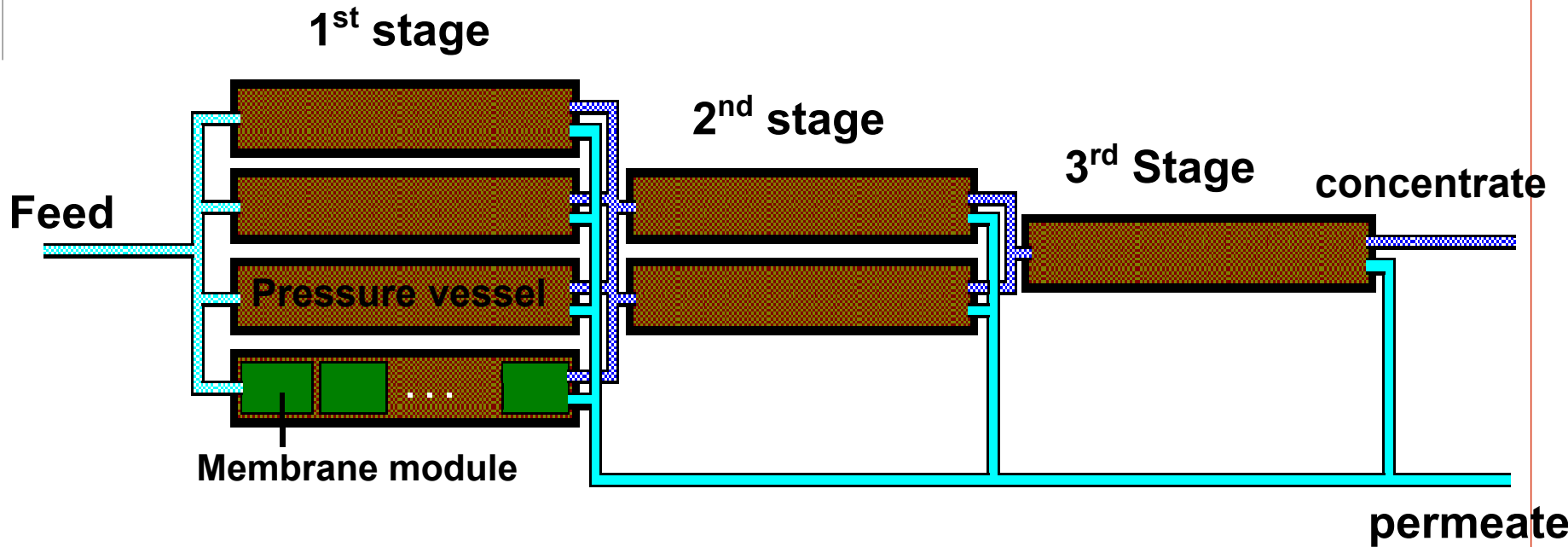
Basic principle of NF and RO systems

- Design Flux

Membrane Application	Design flux (l/h/m ²)
RO	
SW (30 000 - 50 000 mg/l)	10 – 18
BW (100-10 000mg/l)	15 - 25
Nanofiltration	15 - 25

Performance of NF and RO systems

- single pass



Performance of NF and RO systems

- **Double pass**

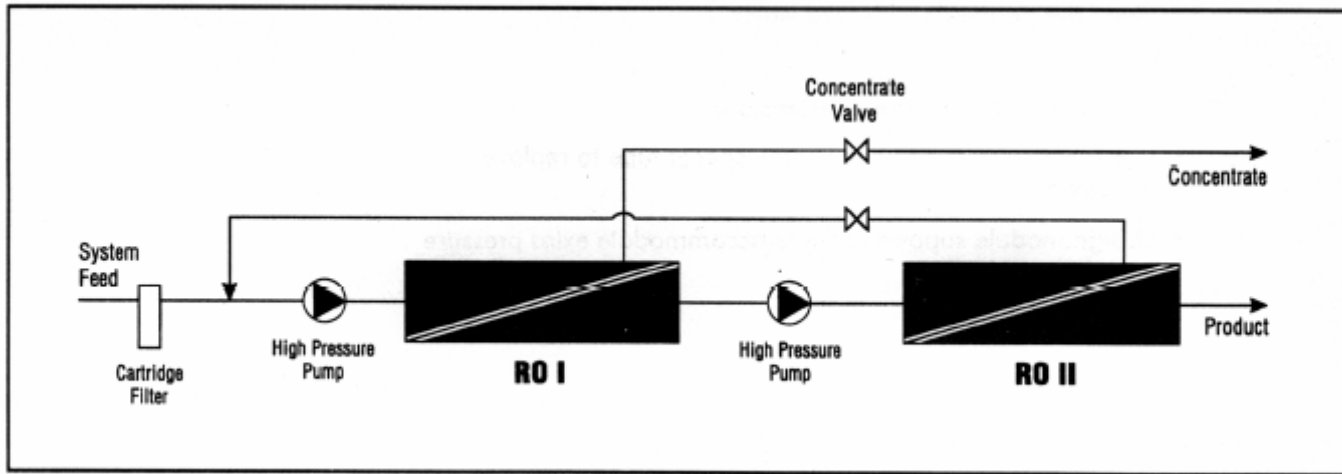


Figure 1: Permeate Staged System

Double pass is necessary when

- ❖ low salinity permeate water is needed
- ❖ Boron should be treated for desalination application
(Boron EC = 1mg/l – WHO = 0,5 mg/l)

Basic principle of NF and RO systems

• Boron species vs pH

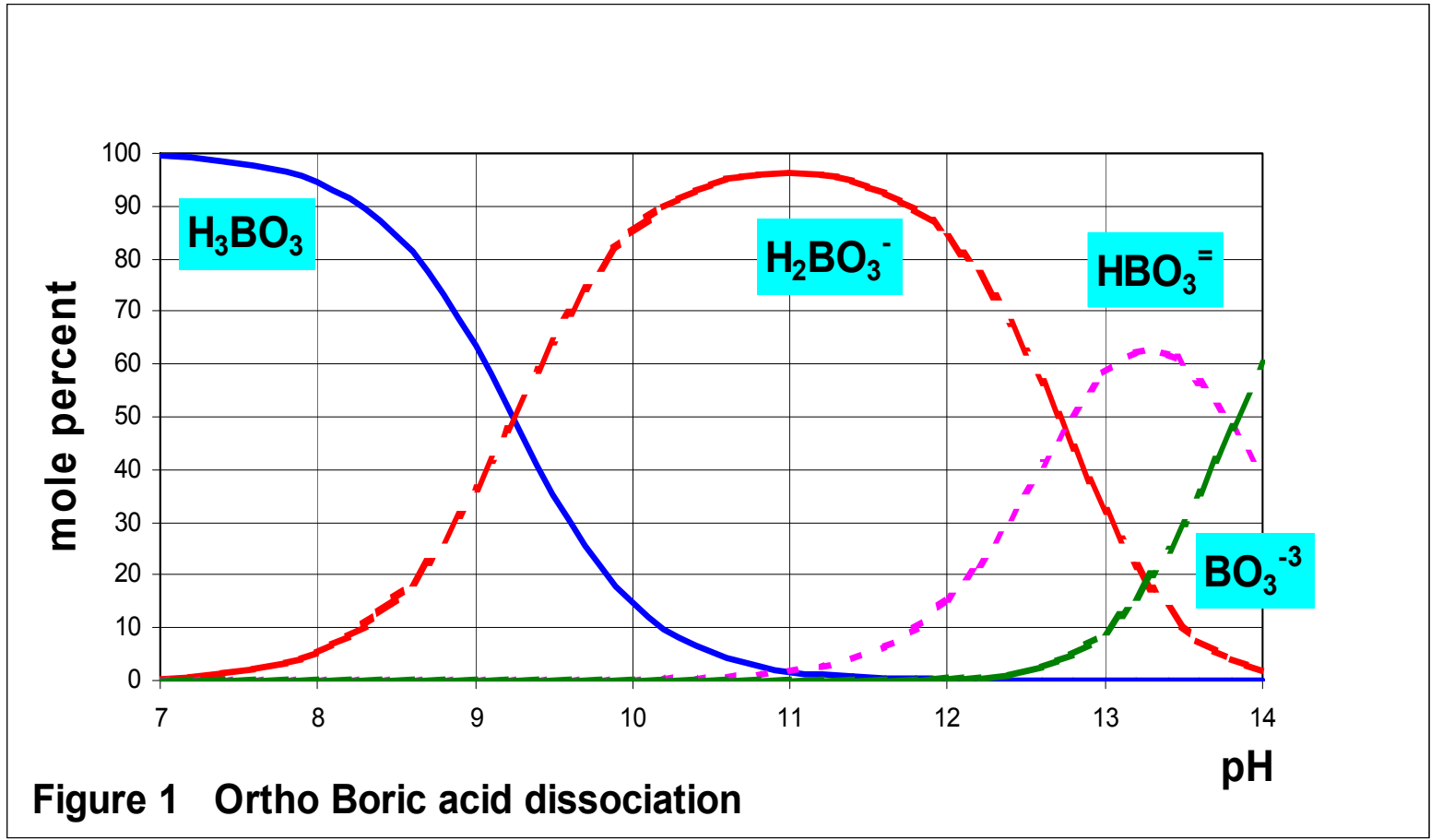


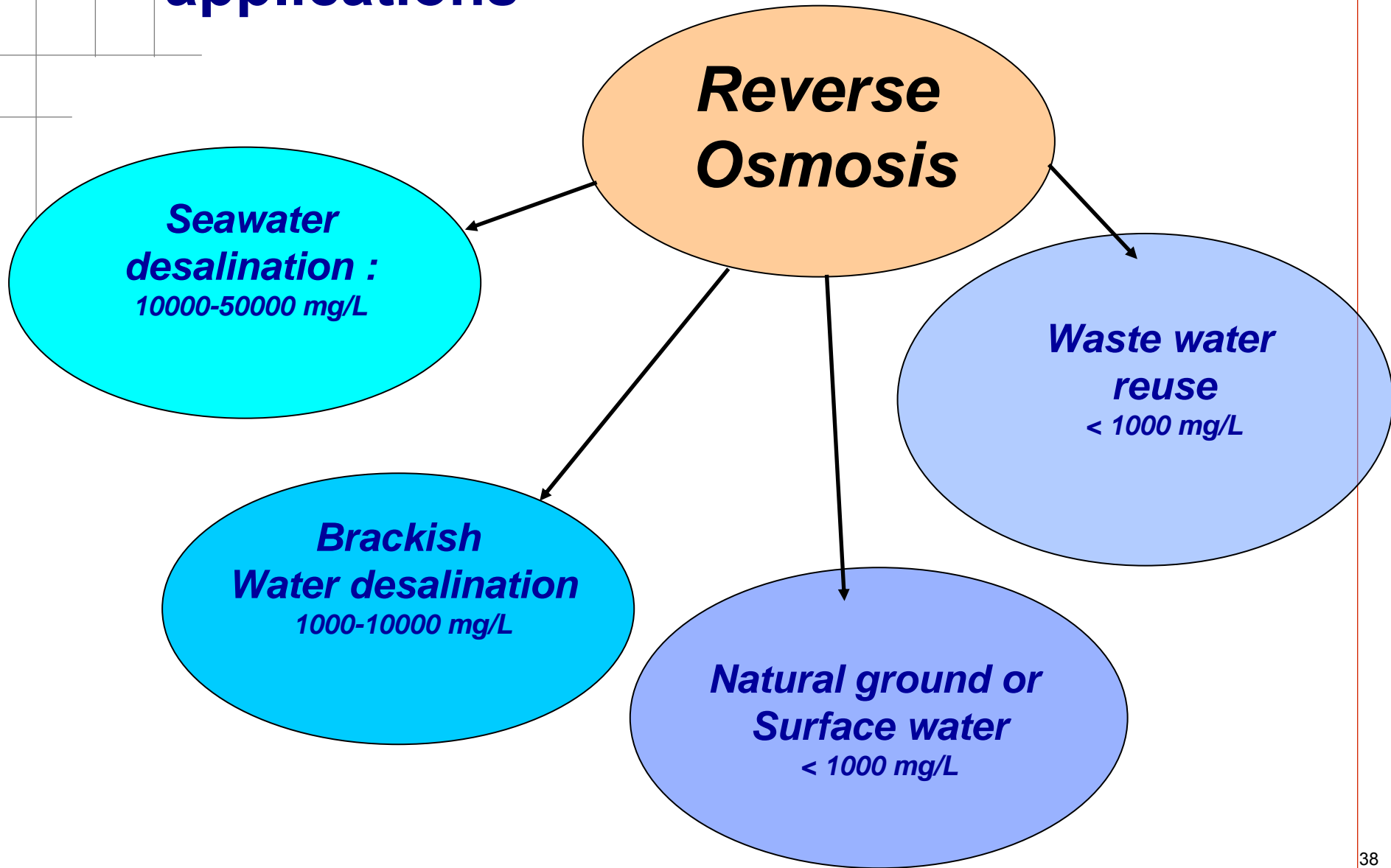
Figure 1 Ortho Boric acid dissociation

NF and RO efficiency

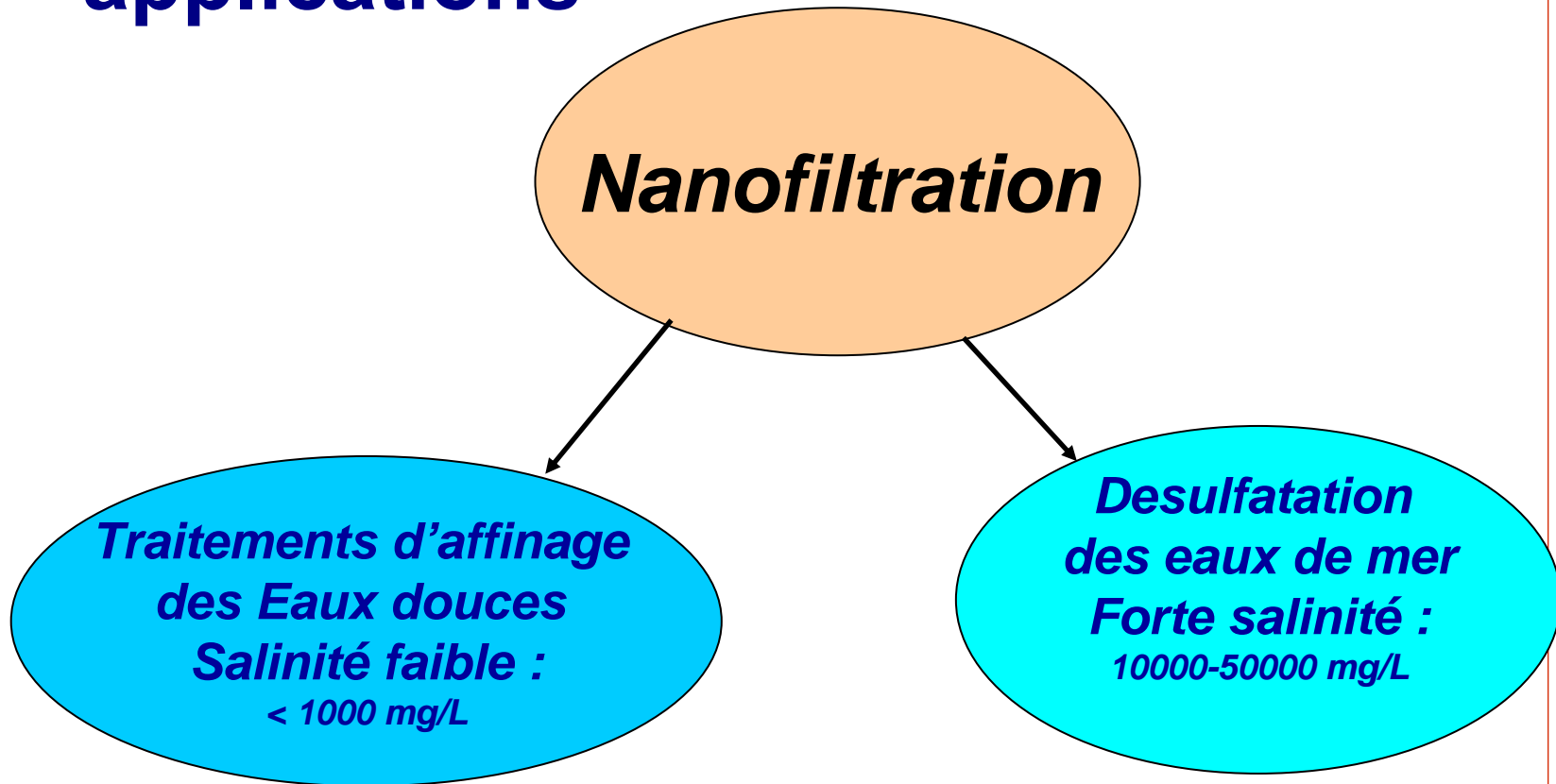
⇒ Removal of :

- salts
- DOC (Dissolved Organic Carbons)
- pesticides
- microorganisms
- viruses

applications



applications



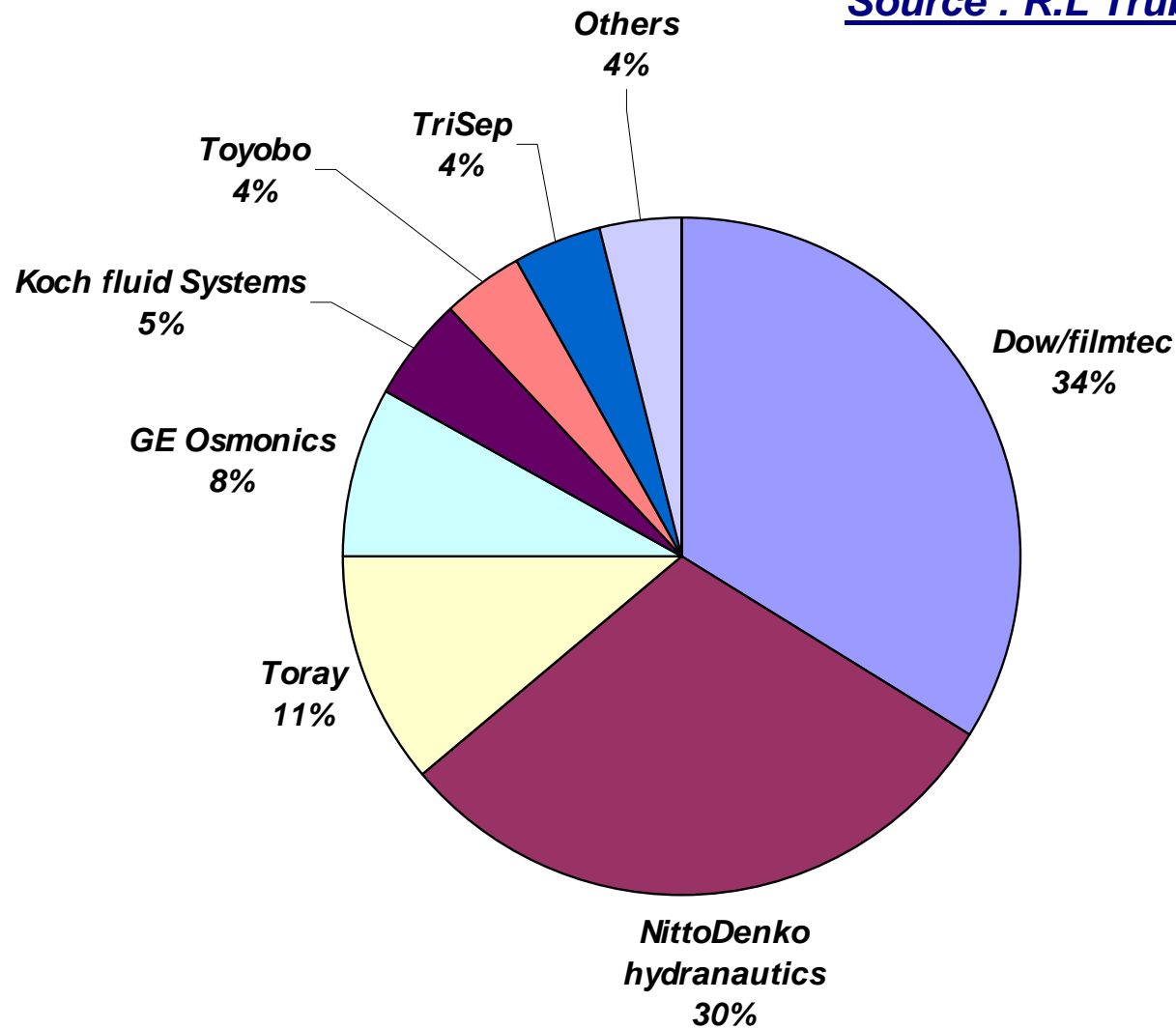
- ◆ NF/RO products dominated by spiral wound elements standardized in 8-inch x 40-inch
- ◆ Price went down over the last 20 years from 40\$/m² to 9\$/m²



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2003 RO/NF Membrane Sales by Competitors

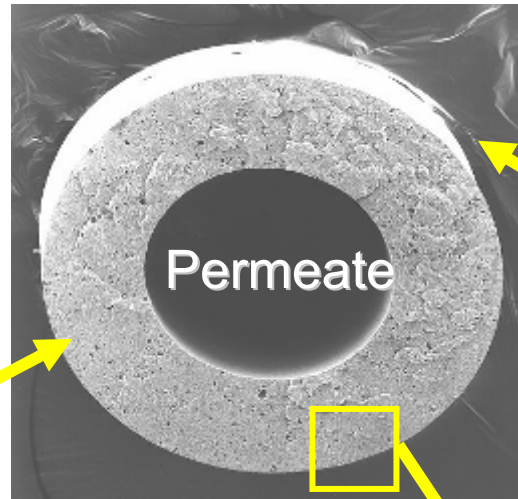
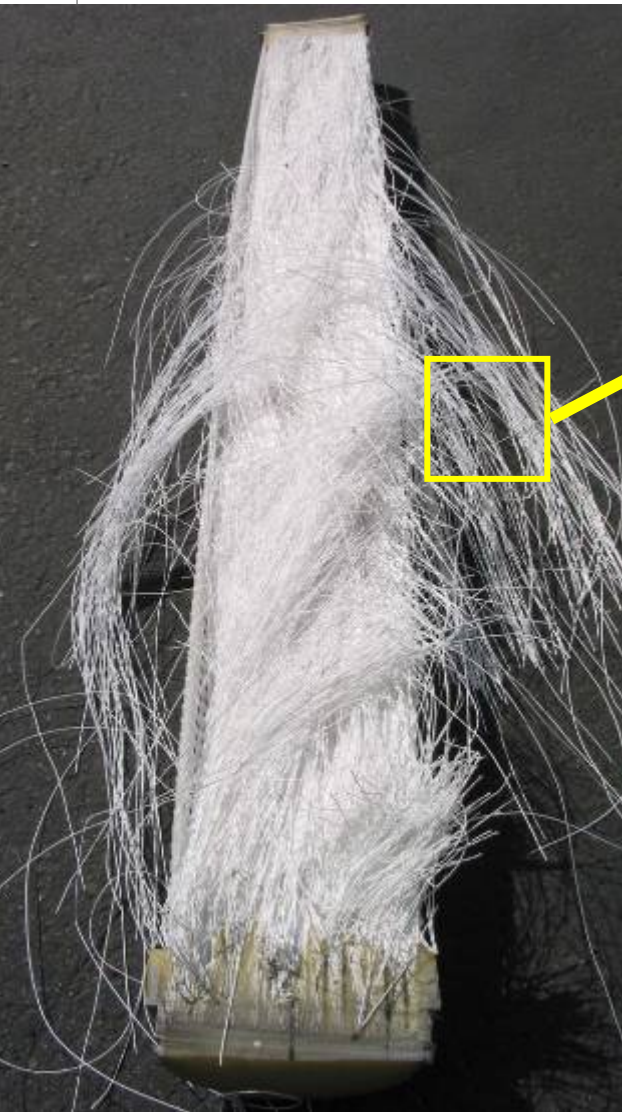
Source : R.L Truby & Associates (2004)



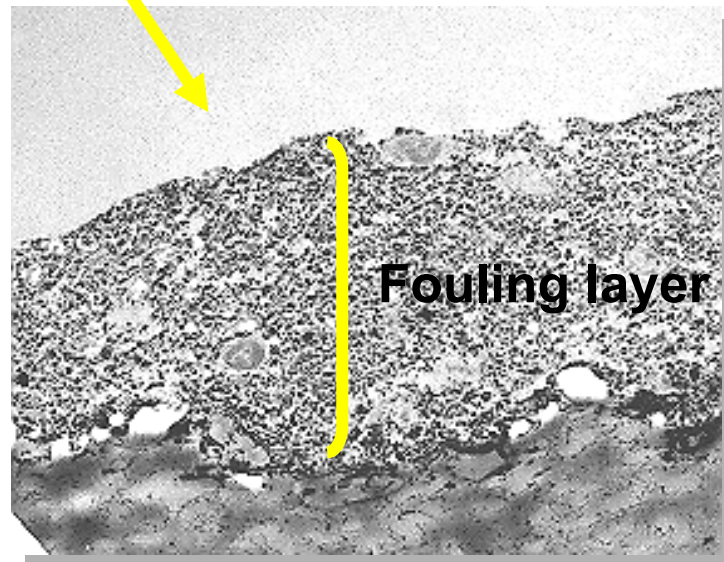
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Low pressure membrane systems MF/UF

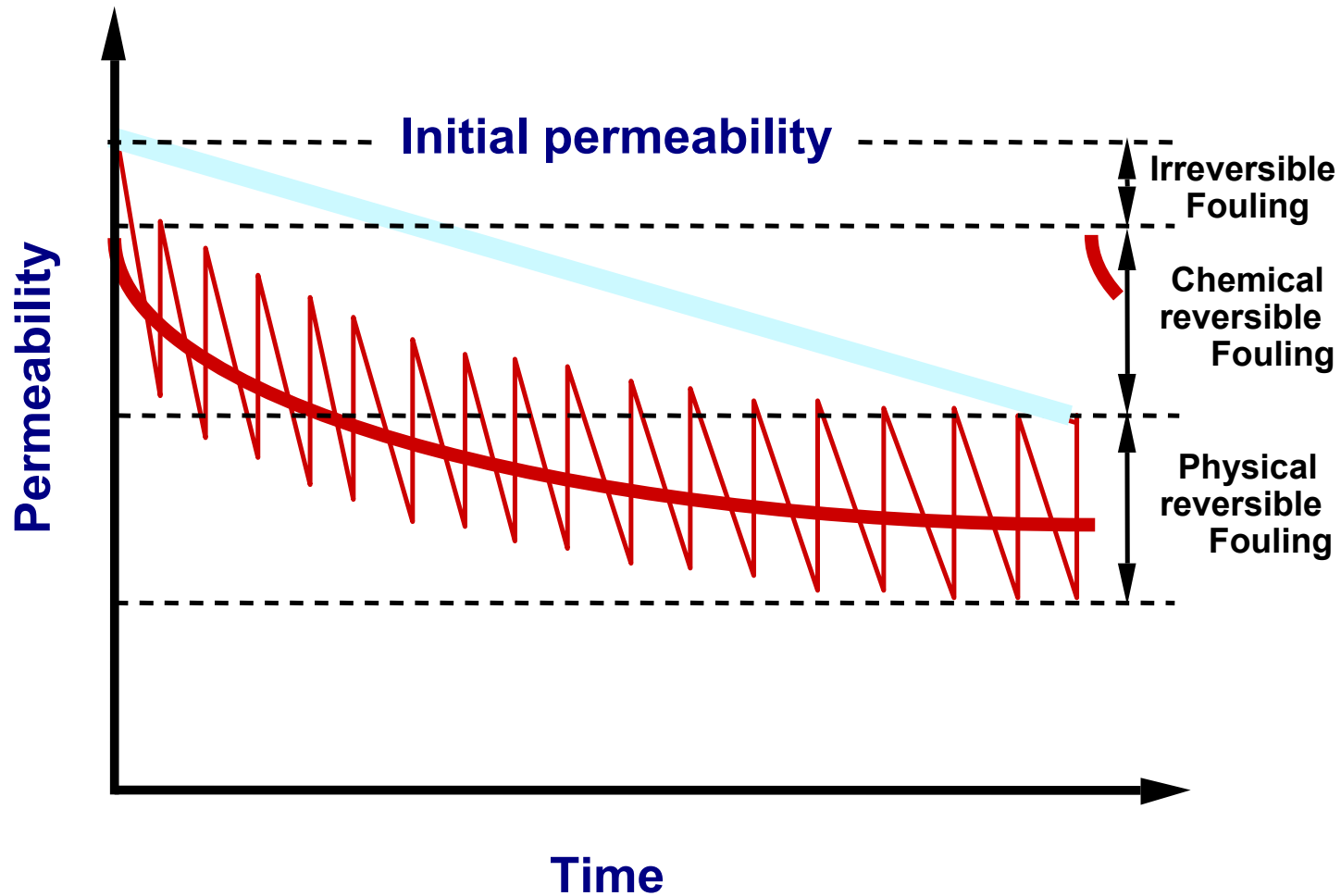
Dominating membrane : Hollow fiber configuration



feed



Fouling affects permeability



Fouling removal

	Physical	Chemical
Action	Fouling particulate Removal	Mineral and organic removal present at the membrane surface
Products used	Water Air	Acid wash for mineral removal Basic wash for organic removal Oxidant for biomass removal

↑

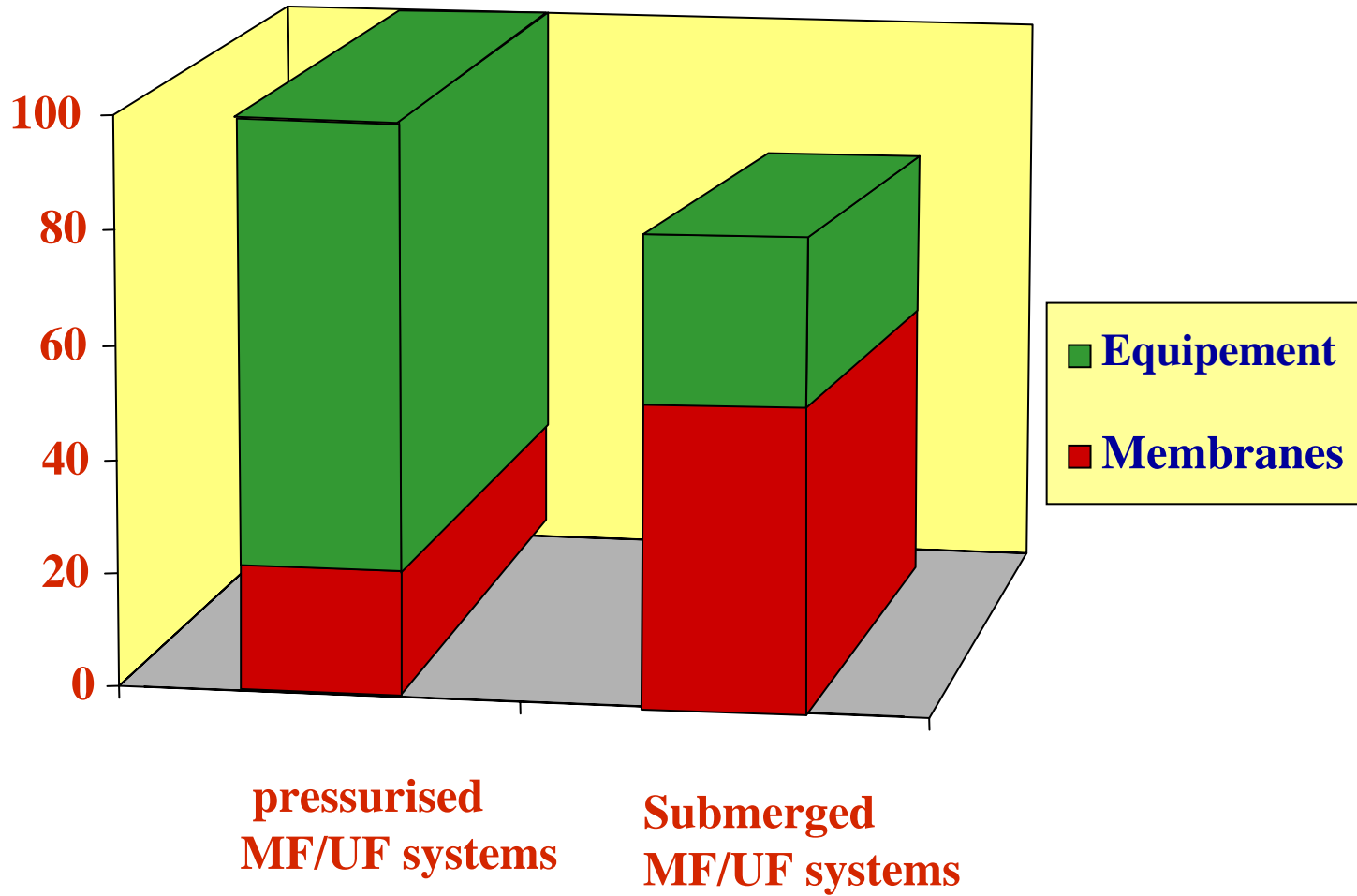
Operating conditions

- **Dead end filtration**
- **Flux : 60 to 140 l/h/m²**
- **Transmembrane pressure: 0,2 to 1,5 bar**
- **Membrane lifetime : 5 years**

Main differences between different type of UF/MF

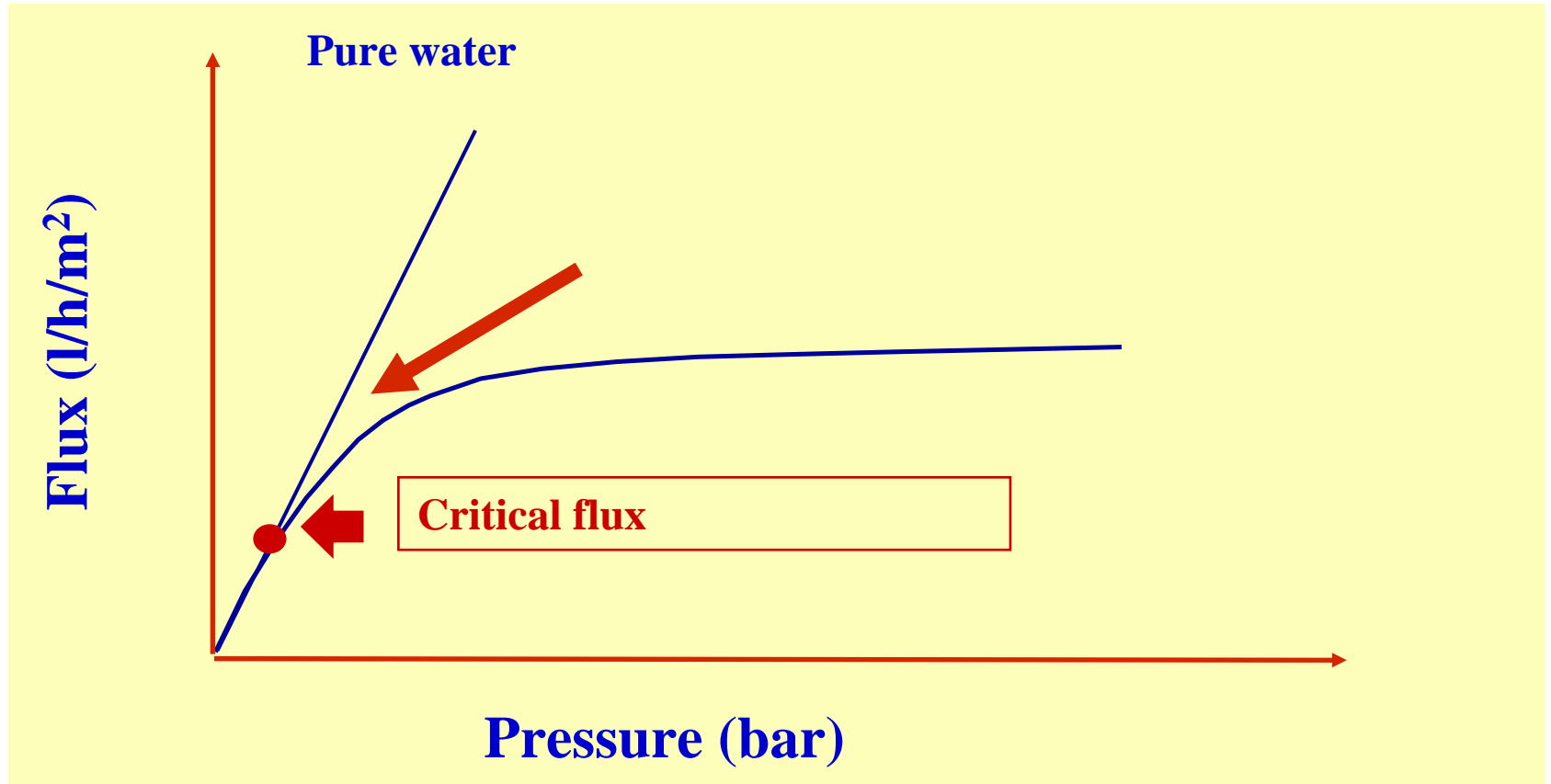
- 1. Molecular Weight Cut Off**
- 2. Inside-out or Outside-in Filtration**
- 3. Cleaning steps**
 - ➔ Backwash water+air
 - ➔ Enhanced Backwash (with chemicals)
 - ➔ Cleaning In Place
- 4. Module surface area (Packing density)**
- 5. Module design**
- 6. Pressurized and suction (Submerged) type**

Submerged systems



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Operating conditions of submerged type



- ◆ Drinking water regulations
 - eg UK cryptosporidium rule: <1 oocyst in 10L of water
- ◆ Membranes provide a physical barrier to these pollutants
- ◆ The ability of a membrane system to remove these pollutants depends on the state of this barrier

INTEGRITY TESTING



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34 million fibres

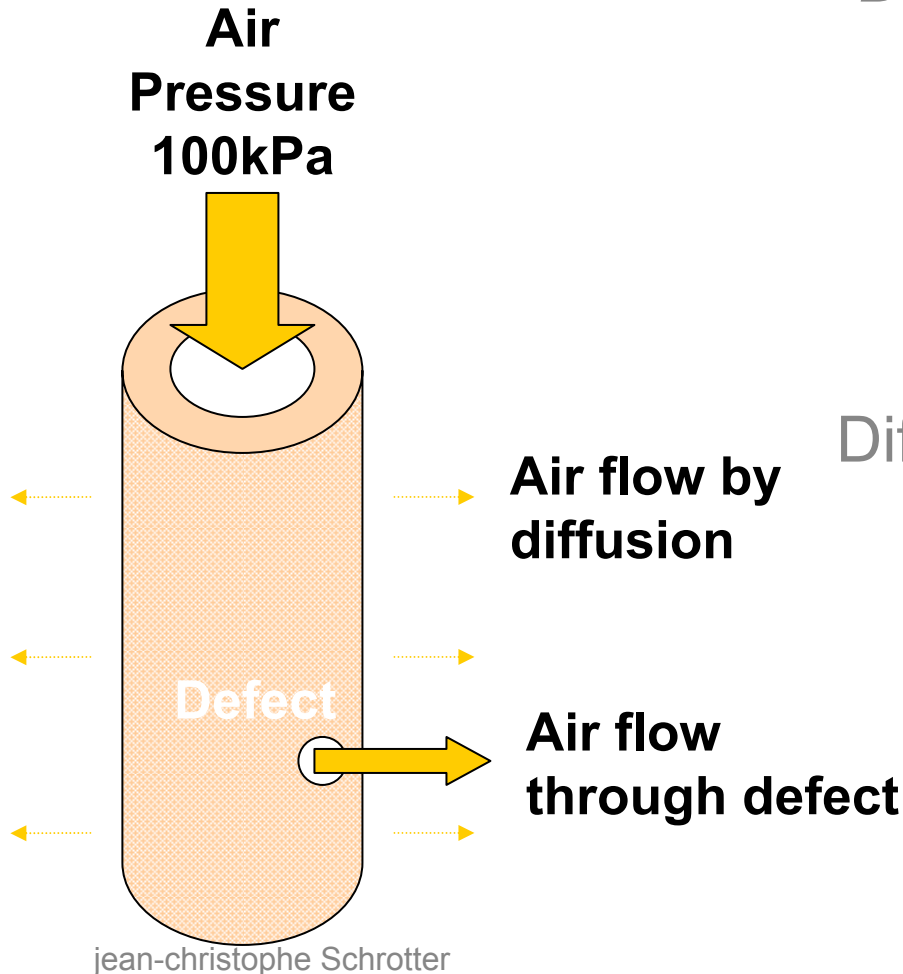


Pressure Decay Test (PDT)
Detection level : Up to Log 5.3

$$\frac{\Delta P}{\text{time}} = f(Q_{\text{air_through_defect}})$$

Diffusive Air Flow Test (DAF)
Detection level : > log 7

$$Q_{\text{water}} = f(Q_{\text{air_through_defect}})$$



Bubble Point Pressure -
where air will pass through
the pores of a wetted
membrane

$$P = \frac{4k\gamma \cos \theta}{d}$$

diameter of
the largest
pore

P = Bubble point pressure (kPa)

K = corrected factor for irregular pores

γ = liquid surfperfacial tension

Θ = contact angle

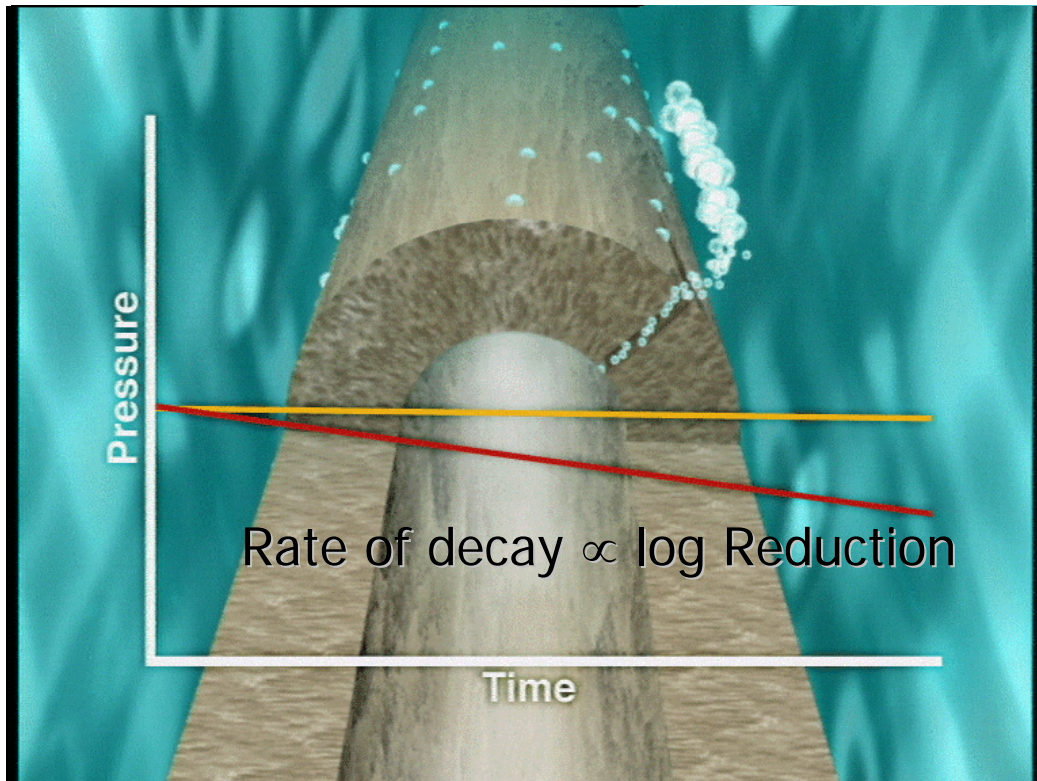
d = pore diameter (microns)

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For hydrophilic membranes, contact angle=0 thus $d = 288/P$

Pore diameter	APPLIED PRESSURE
0,05 μm	$P = 57,6 \text{ bar}$
0,1 μm	$P = 28,8 \text{ bar}$
1 μm	$P = 2,88 \text{ bar}$
2,88 μm	Current on site $P = 1 \text{ bar}$

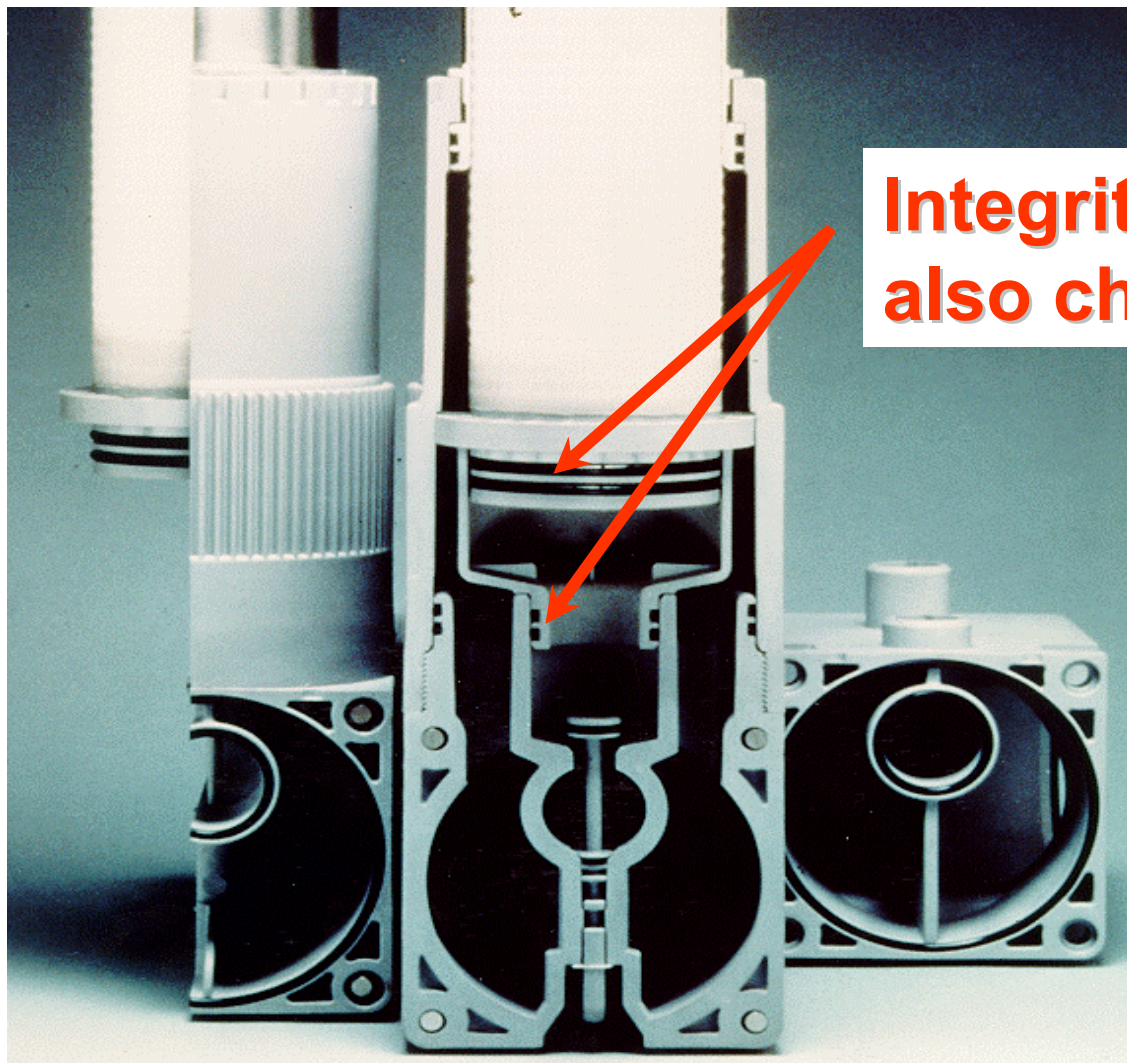
◆ Pressure Decay Test (PDT)



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>Log 4 Crypto Sensitivity

INTEGRITY TESTING



**Integrity methods
also check seals**

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INTEGRITY TESTING : Which Module ?

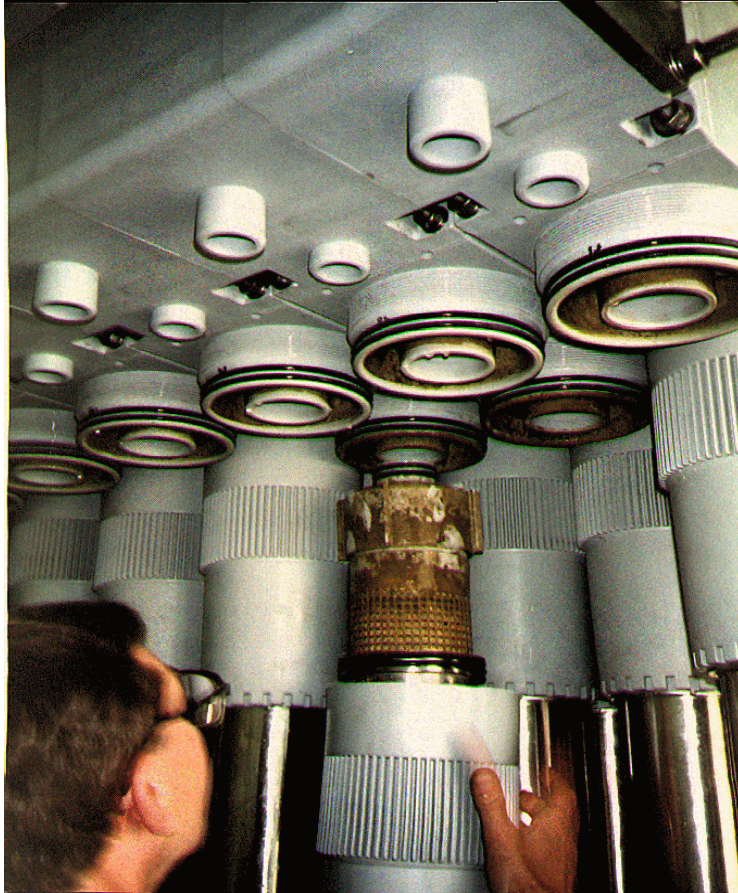


Sonic
Analysis

Will detect
a single
fibre break

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INTEGRITY TESTING : Repairing Broken Fibres



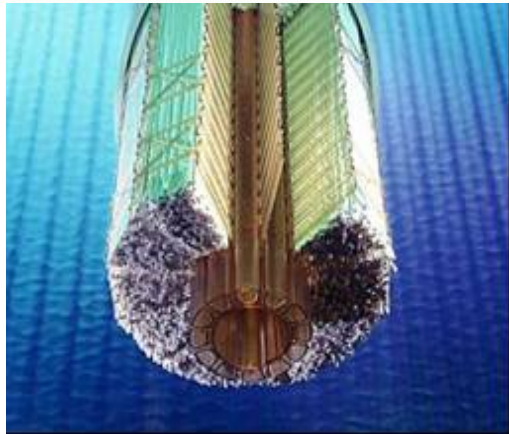
- ◆ Isolate and remove module
- ◆ Immerse in test vessel
- ◆ Pass air through module
- ◆ Locate bubbles in broken fibre
- ◆ Insert pin in top of fibre
- ◆ Check for no more bubbles
- ◆ Re-install module
- ◆ Put module back on line

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Low pressure membrane Keyplayers for Drinking water applications

Pressurized systems vs Submerged systems

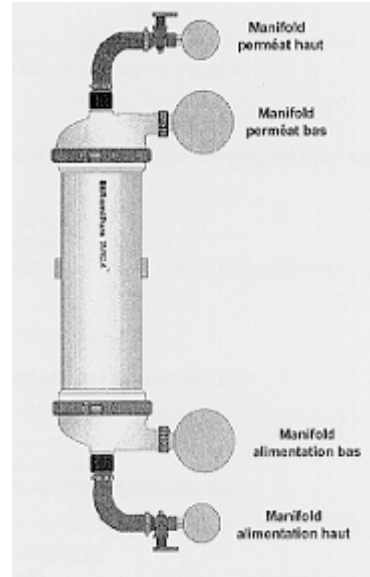
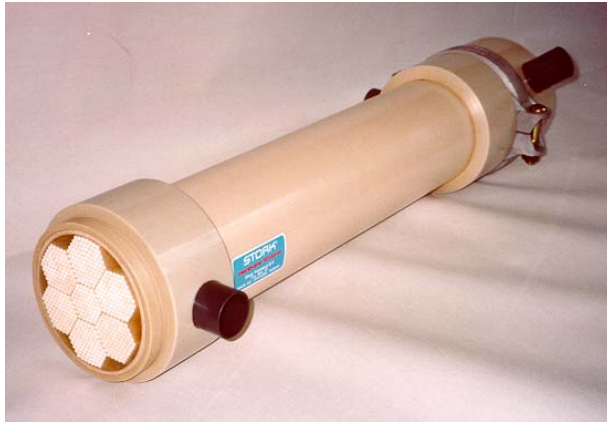


*Pressurized systems
(40% market share)*

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*Submerged systems
(60% market Share)*



Established Players

NORIT

PALL/ASAHI

KOCH

AQUASOURCE

HYDRANAUTICS

MEMCOR (CMF)

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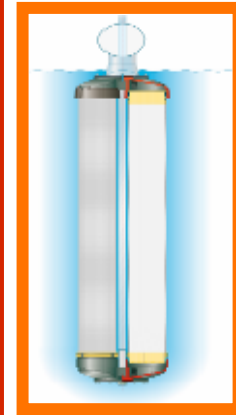
New Entrants

INGE

POLYMEM

DOW/OMEXELL

TORAY



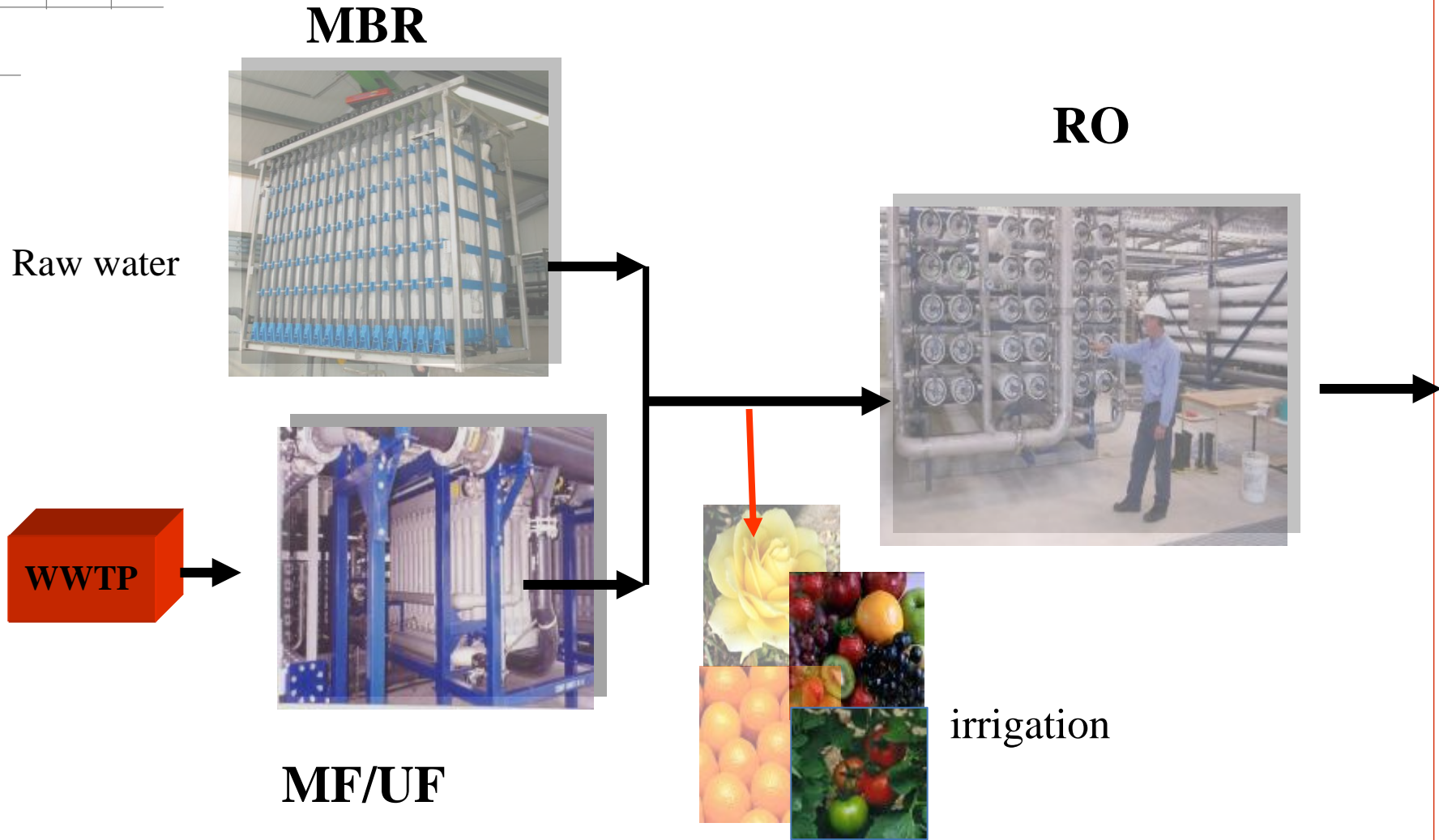
Established Players

ZENON

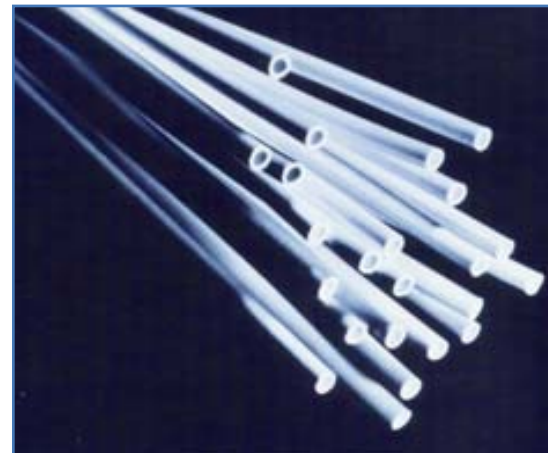
MEMCOR

Low pressure membrane Keyplayers for Municipal waste water applications

- re-use,
- tertiary treatment,
- MBR)



Tertiary treatment and reuse key players

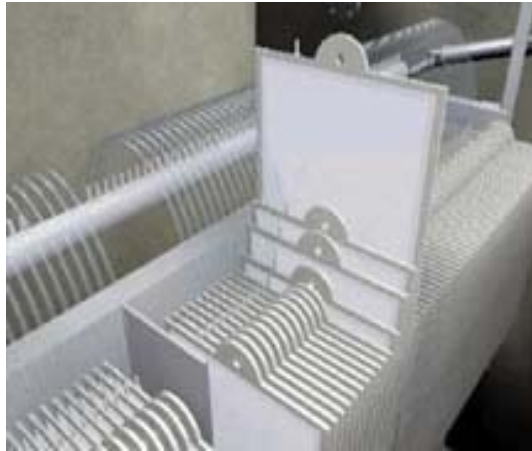


**Hollow fibers
Membranes**

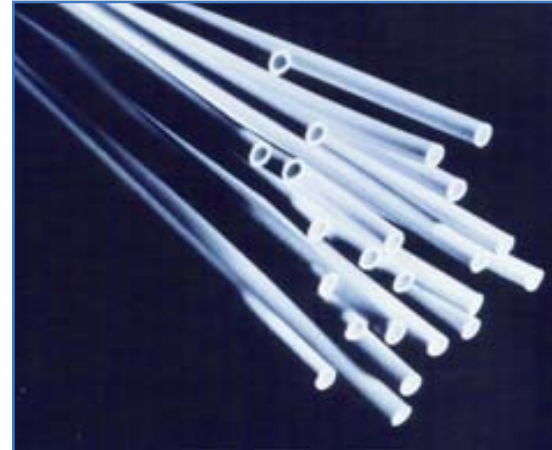
Established Players

Memcor
Norit
Zenon

MBR key players



**Flat sheet
membranes**



**Hollow fibers
Membranes**

Established Players

Kubota

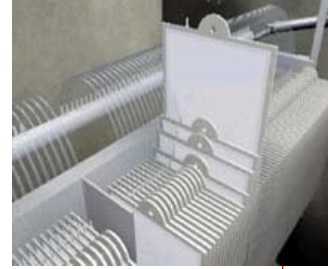
Zenon

New Entrants

Toray

Memcor
Koch
Mitsubishi

Hollow fibers or flat sheet membranes ?



ZENON MEMCOR PURON

mitsubishi HYDRANAUTICS

Hollow fibers		Flat sheet
+	Air consumption	
	S. solids tolerance	+
+	footprint	
	Flux	+
	Membrane resistance	+
+	Integrity testing	
	Pretreatment	+
+	Membrane repaired	
	Simplicity of the process	+

KUBOTA TORAY

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+ la technologie la plus adaptée

