Membrane technology for water treatment

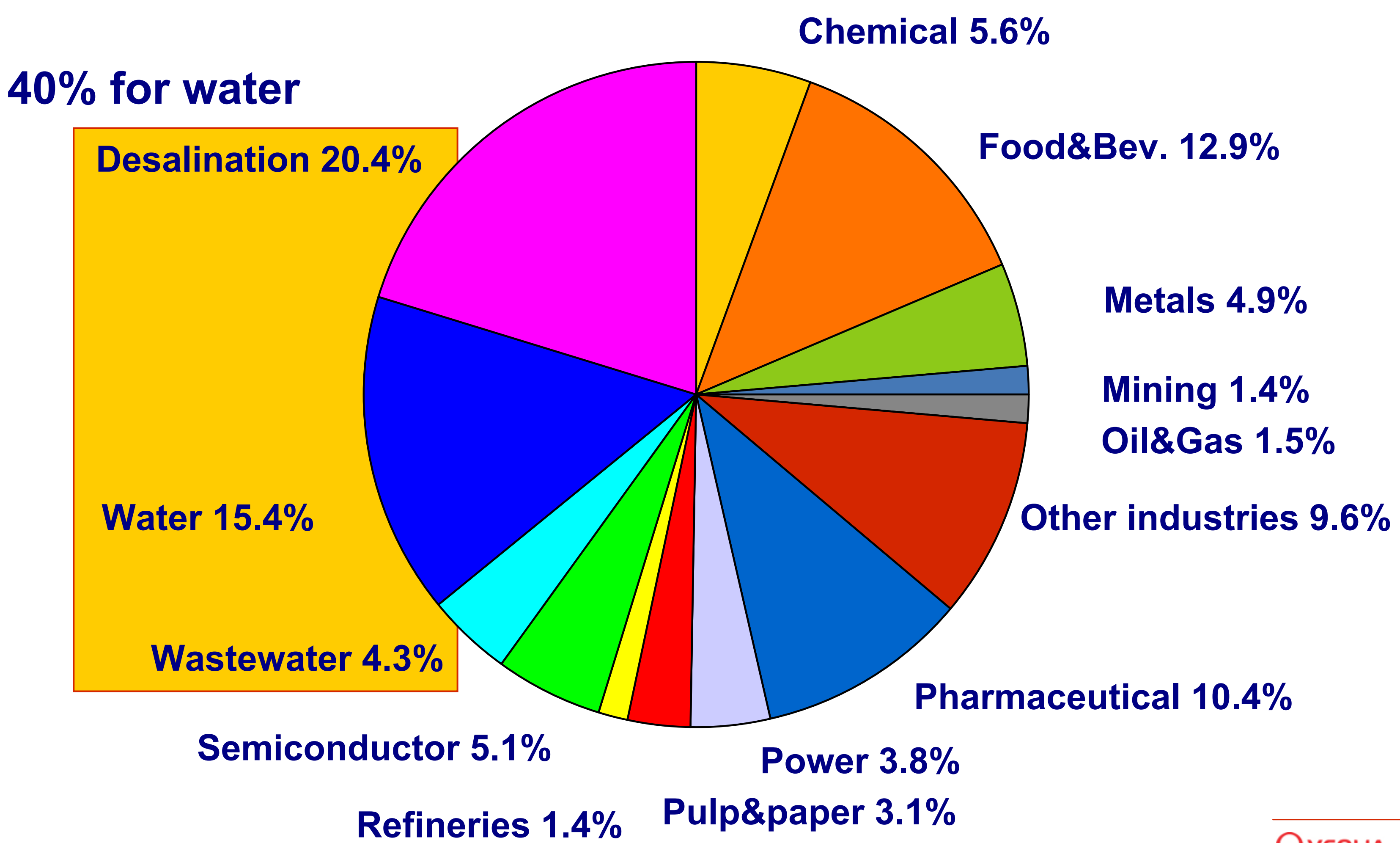
J-C SCHROTTER
Membrane Research Manager

Brief History of Membrane Technology for Water Applications...

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)



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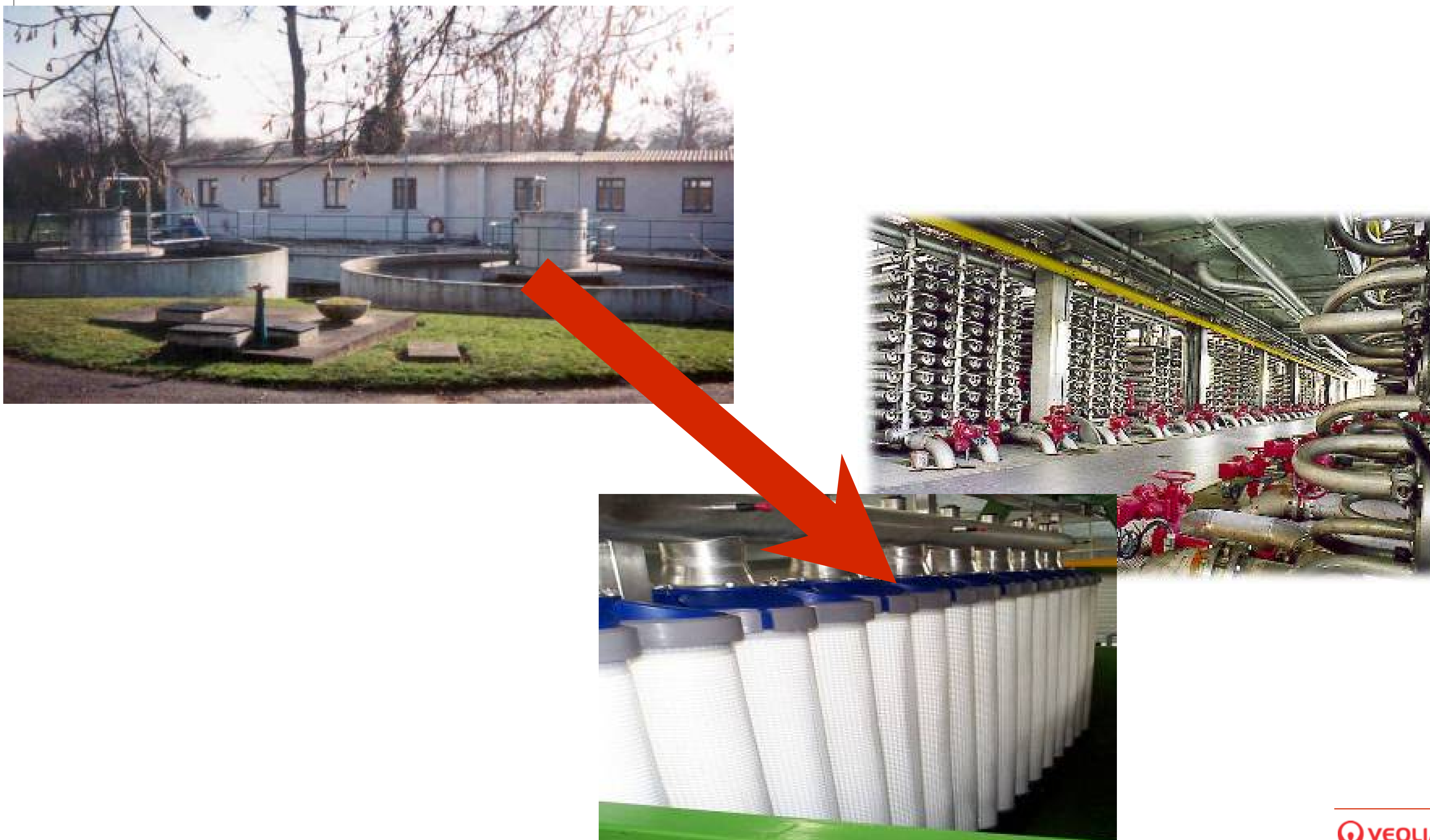
Background : a technical « revolution »in a tight economical context



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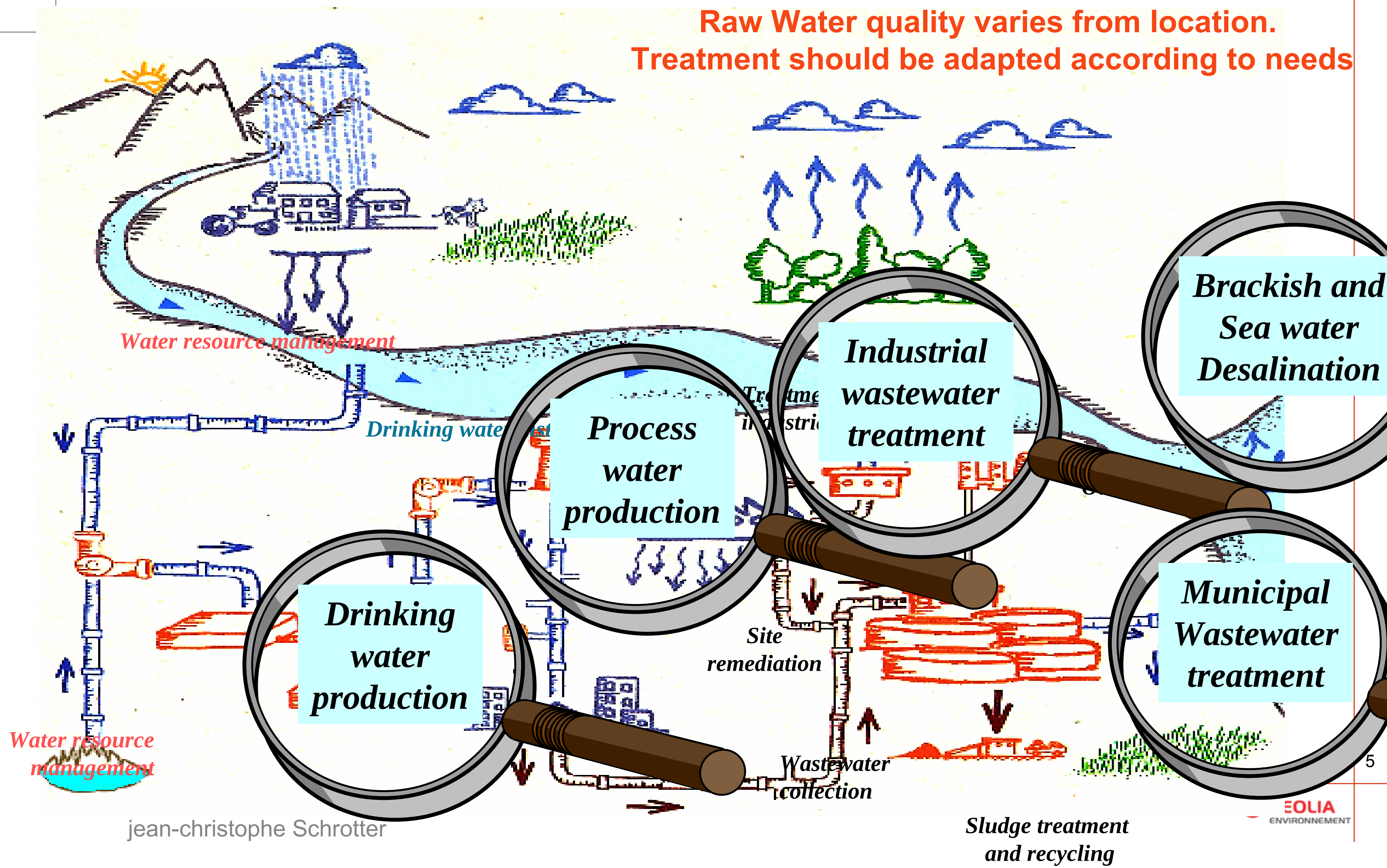
Use of membrane for water treatment

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



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General trends are:

- O&M Cost
  - River water
    - 0.05- 0.2 $\$/m^3$
  - Brackish water
    - 0.2-0.35 $\$/m^3$
  - Seawater
    - 0.53-1.3 $\$/m^3$
- Investment Cost from \$100 / m^3/d to more than \$2000 / m^3/d

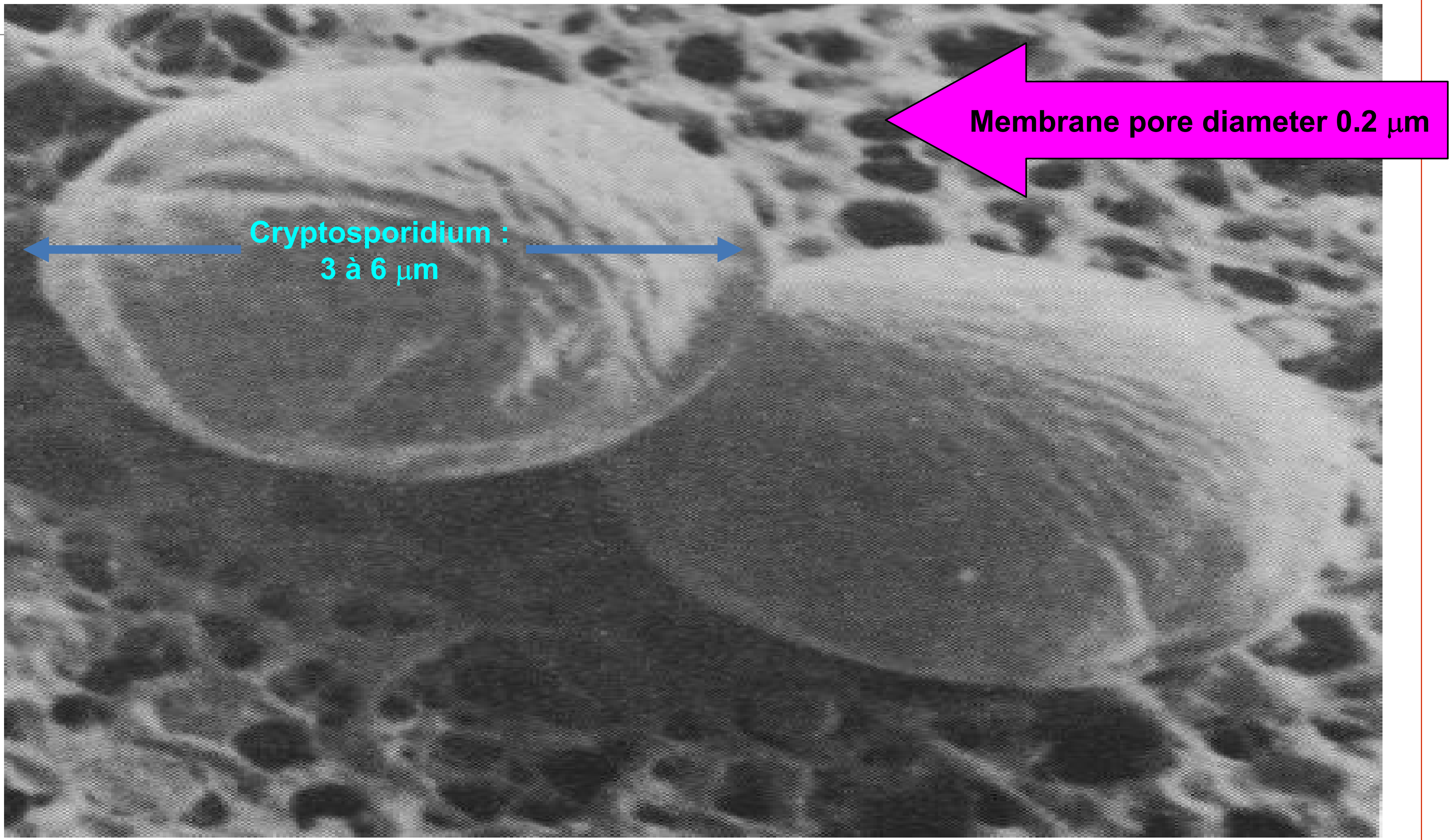
Example in UK for drinking water :

- New regulations in 2003 for Cryptosporidium (>1 oocysts/10 litres)

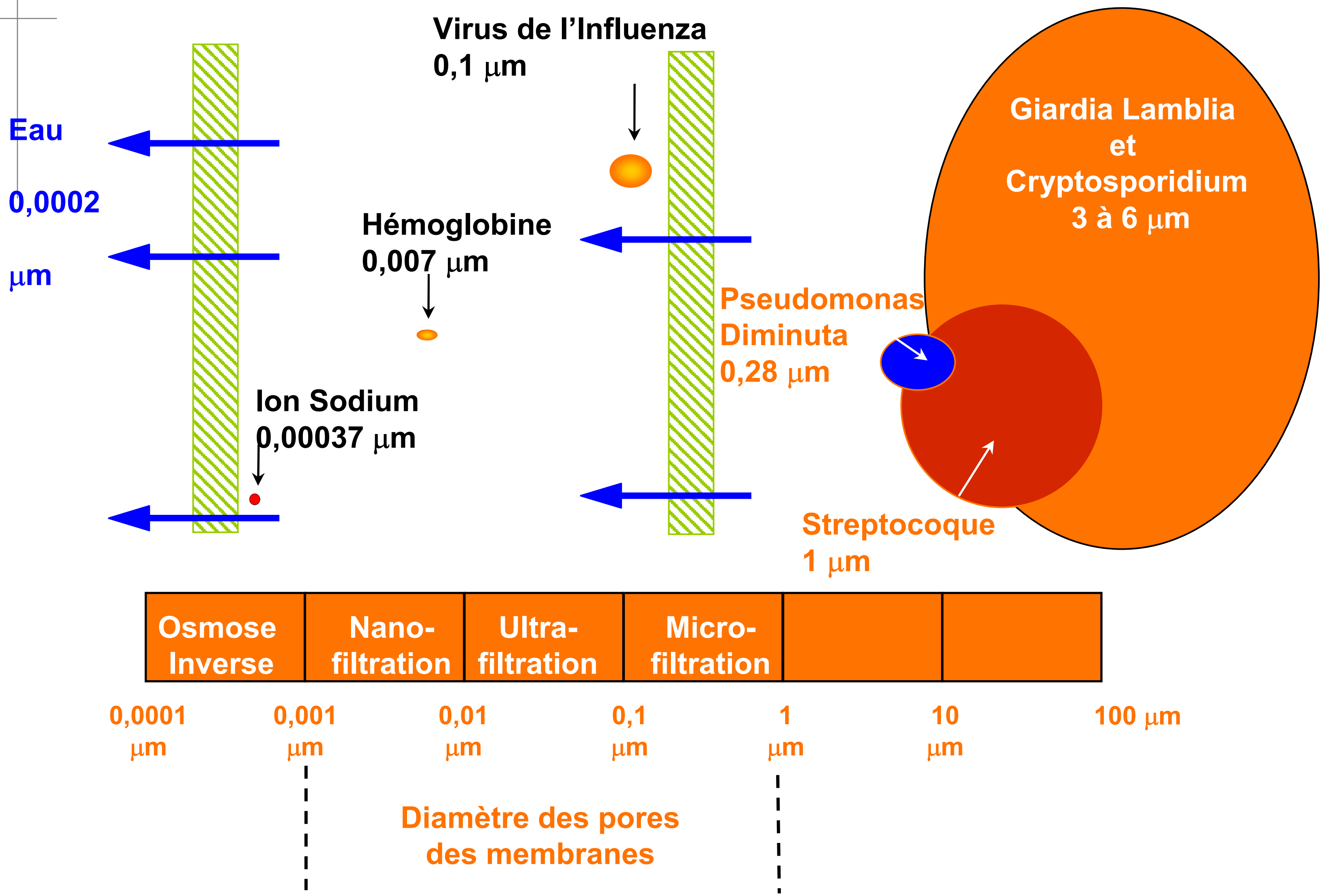
- New specifications have also been put in place on
  - Lead (25µ/L by 2014 and 10µ/L by 2024)
  - Benzene (1µ/L)
  - Nitrate (50mg/L)
  - Nitrite (0.1mg/L)
  - **THM (Trihalomethanes) (100 µ/L)**
  - Bromate (10µ BrO_3/L)
  - Arsenic (10µ/L)

- High standards required on
  - **Pesticides (0,5µg/l)**
  - **Bacteries (5-6 Log removal)**
  - **Viruses (4log removal)**

Microscopic view of a membrane surface



Pollutant removal by membrane processes



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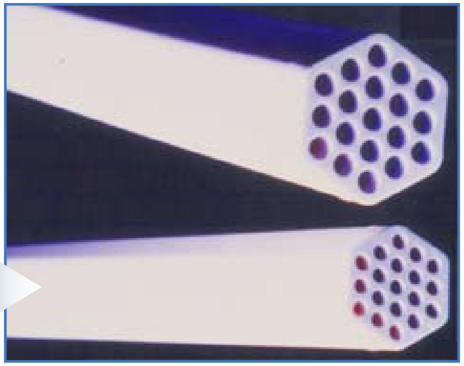
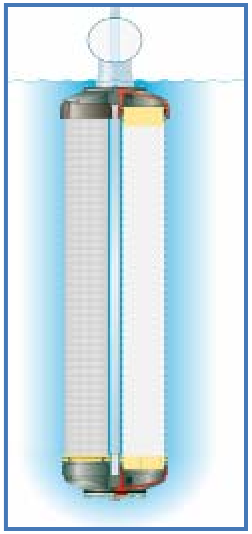
Differents kind of module

Spiralwounded element

tubular



Hollow fibers



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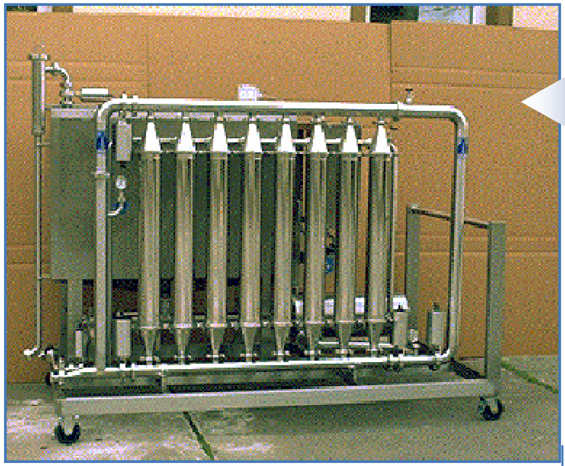
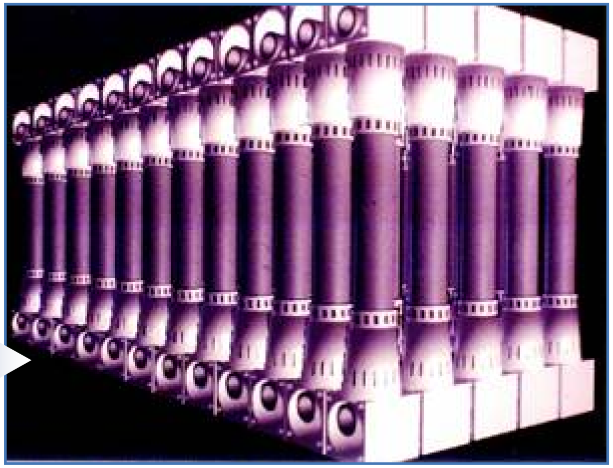
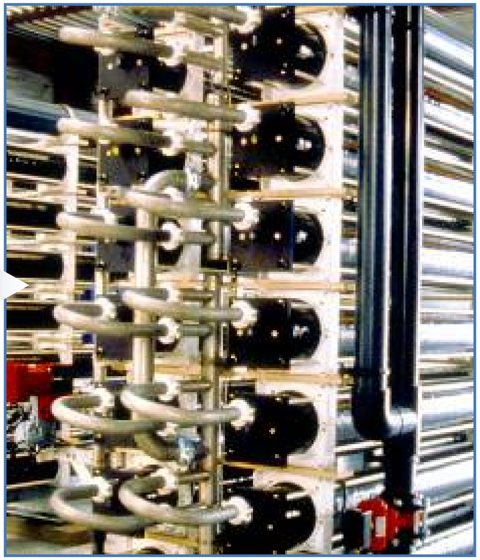
Different kind of systems



Rack



Block



Tube

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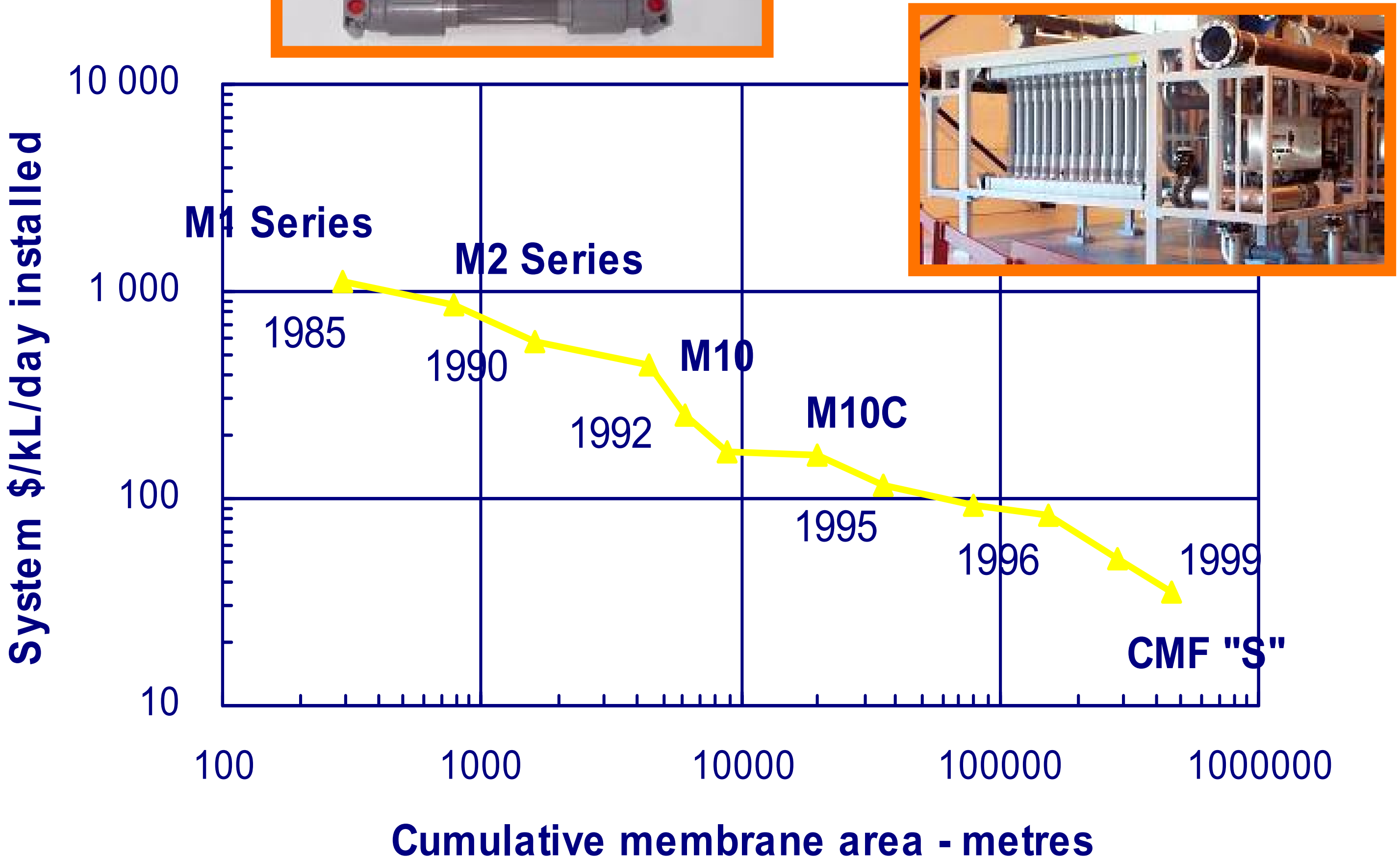
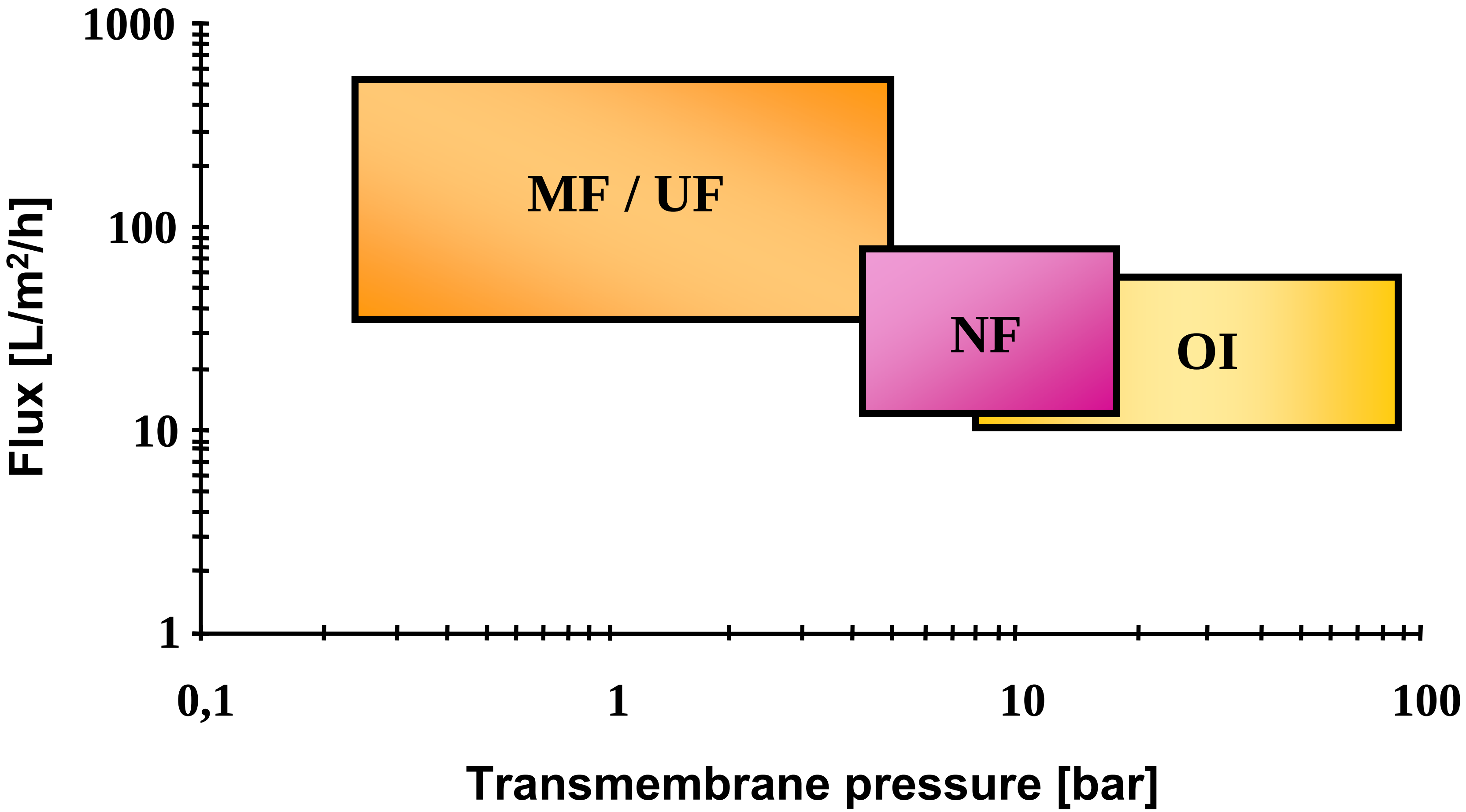
Reduction of membrane cost



Membrane Operating conditions



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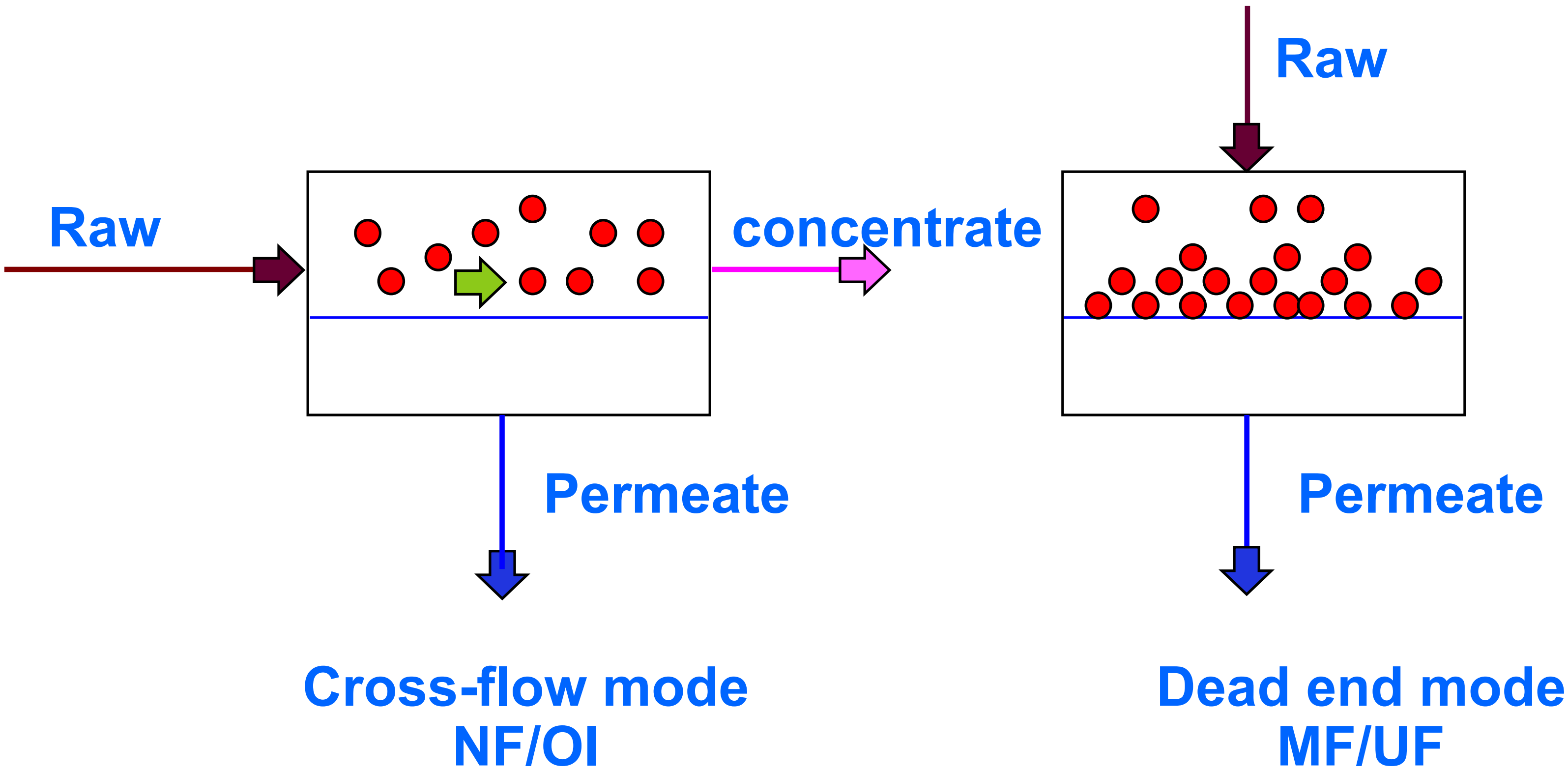
Dead-end and cross-flow mode



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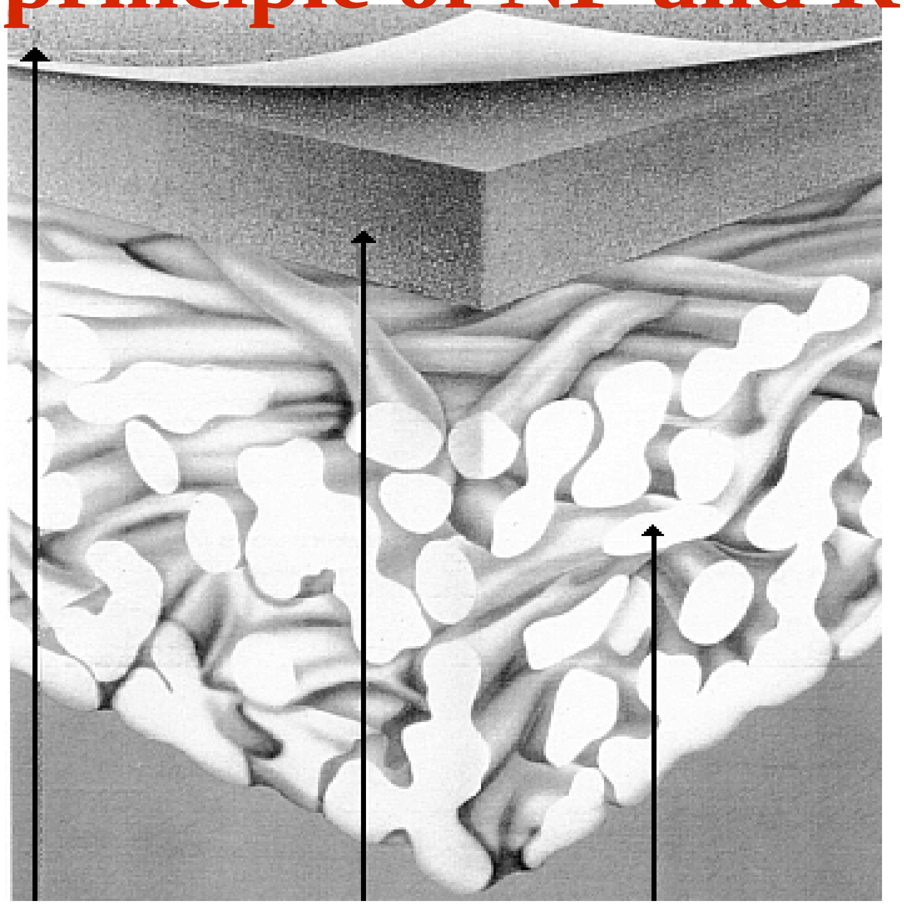
High pressure membrane systems NF/OI

Basic principle of NF and RO systems

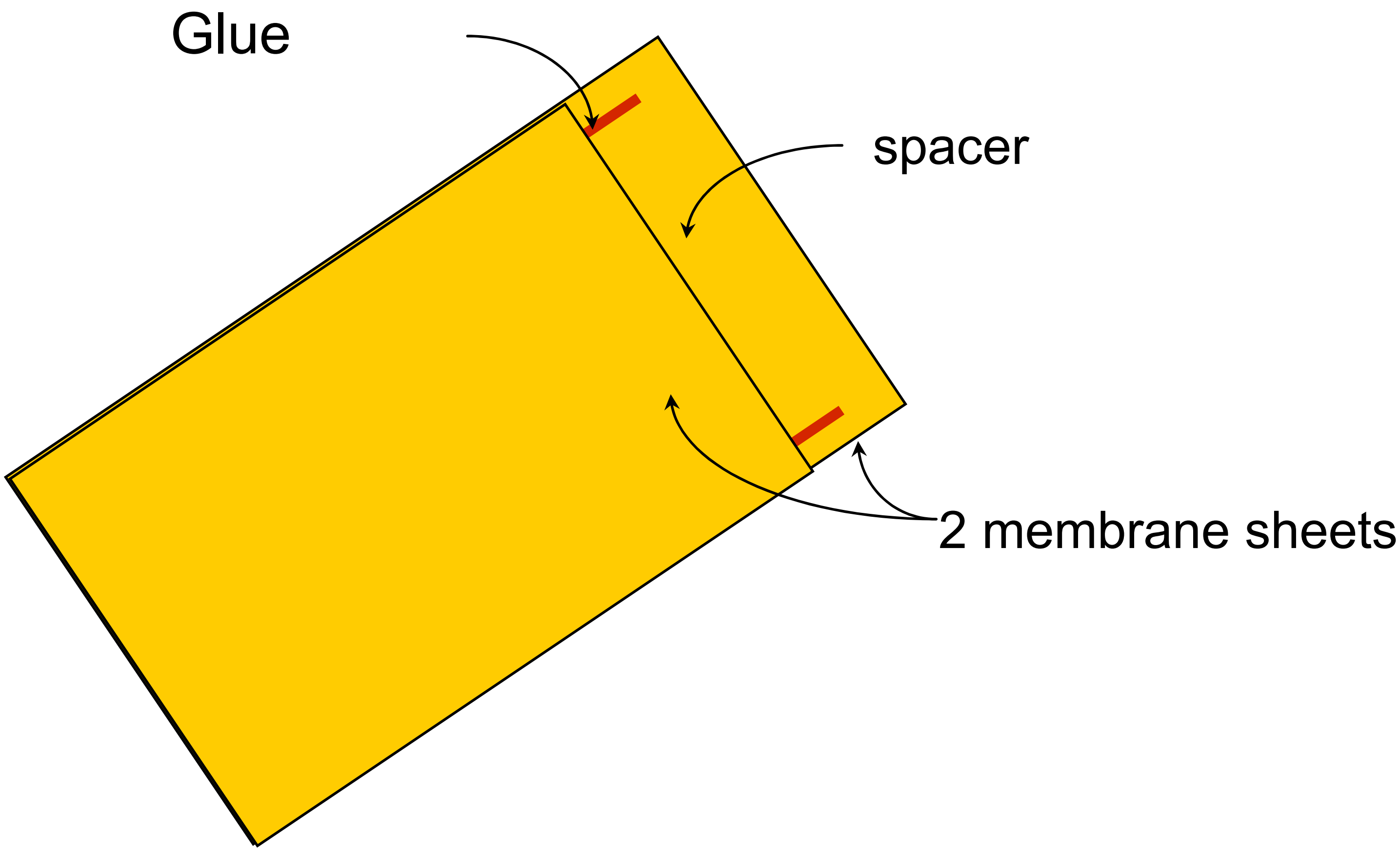


Polyamide Membrane

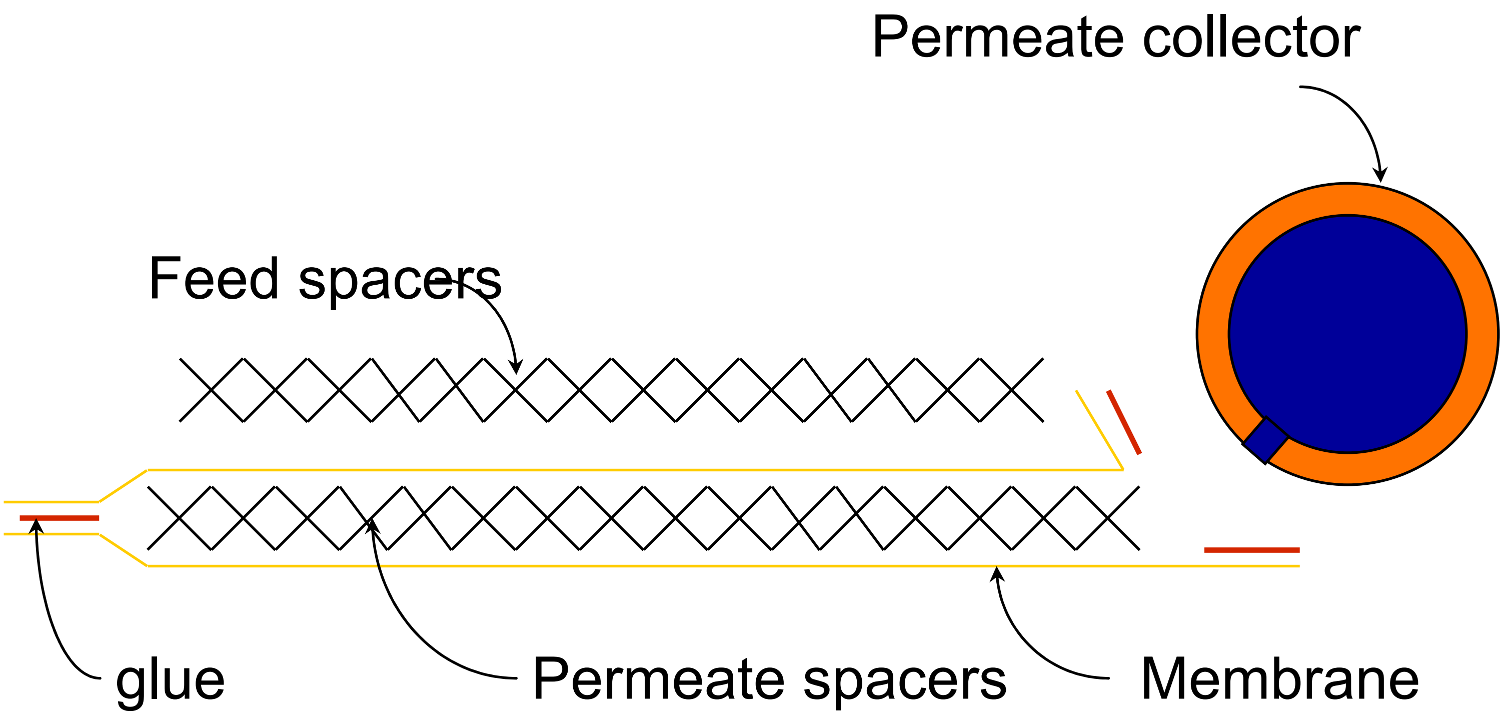
Polysulfone layer

Polyester support

Basic principle of NF and RO systems

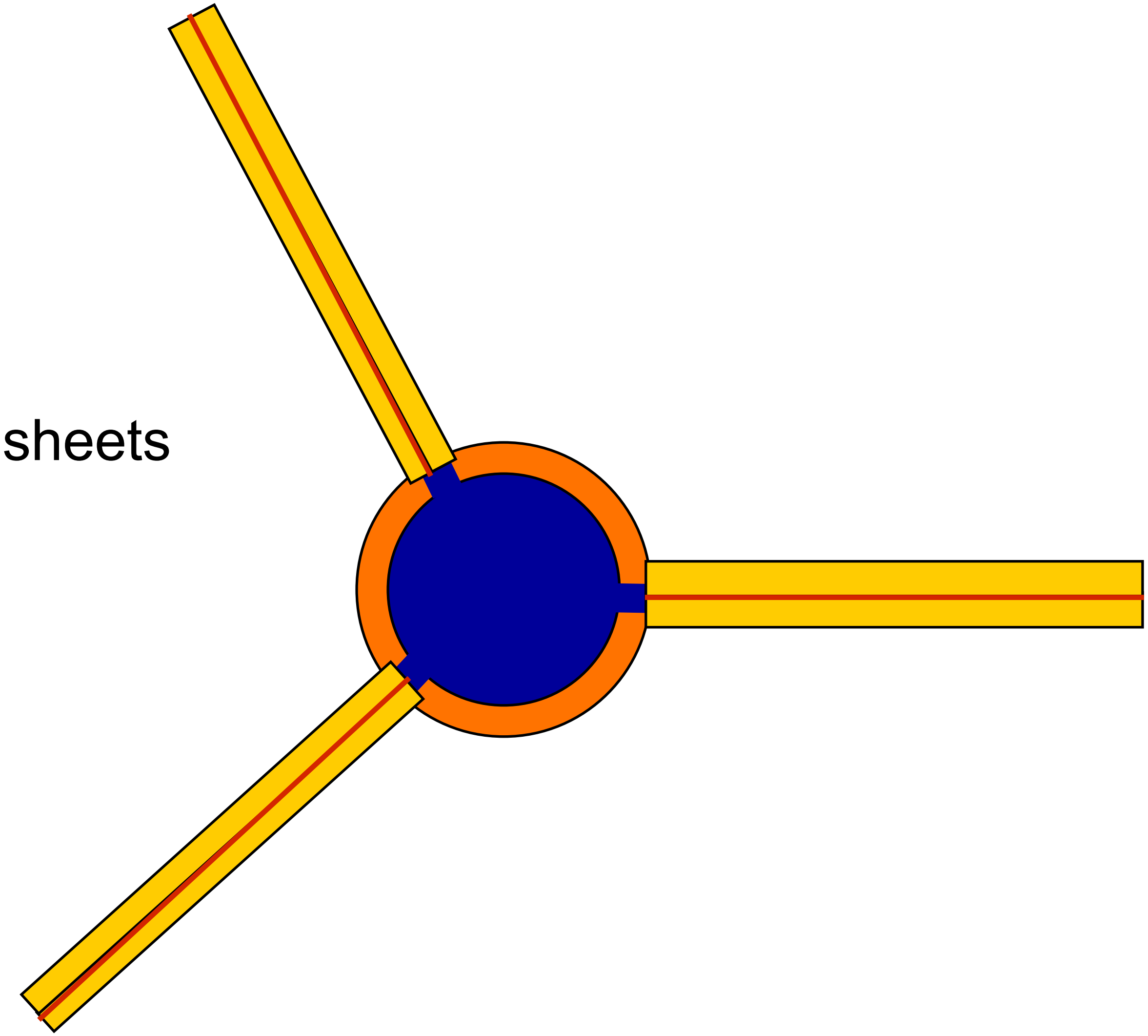


Basic principle of NF and RO systems



Basic principle of NF and RO systems

Collector with 3 sheets



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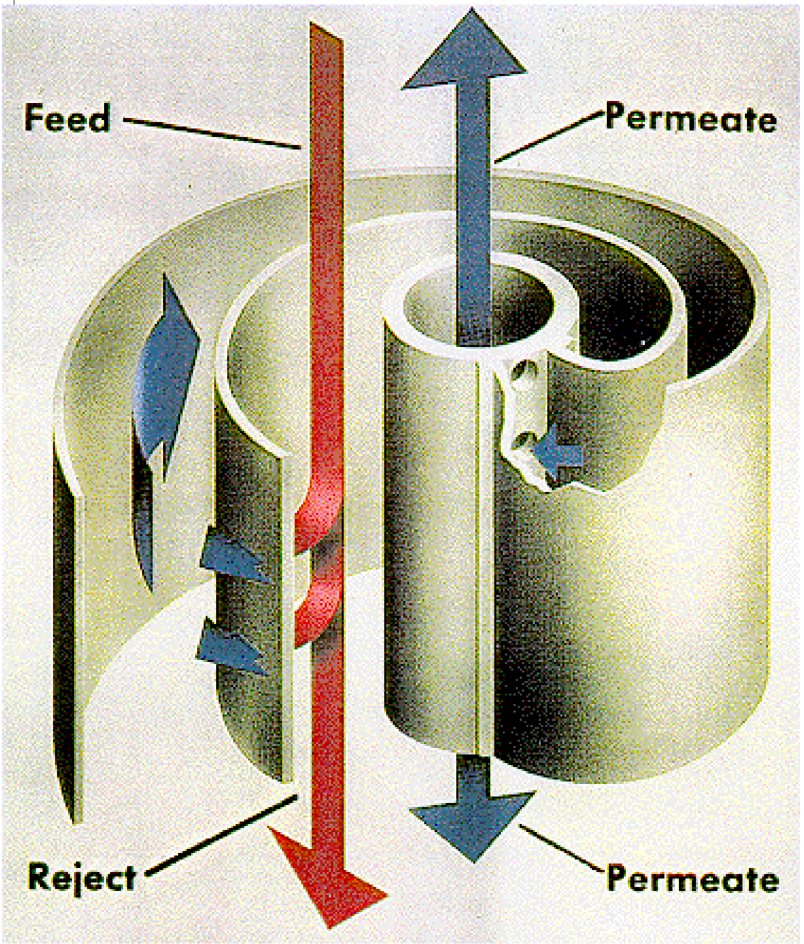
Basic principle of NF and RO systems



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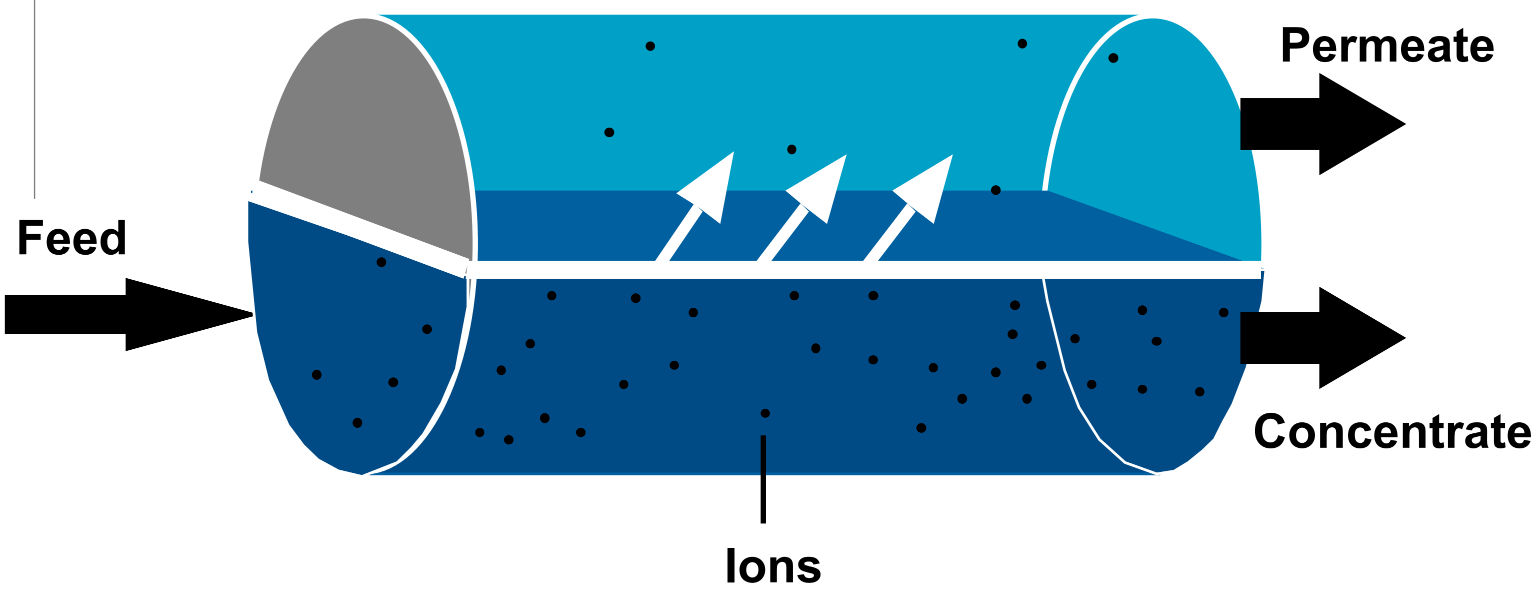
Basic principle of NF and RO systems



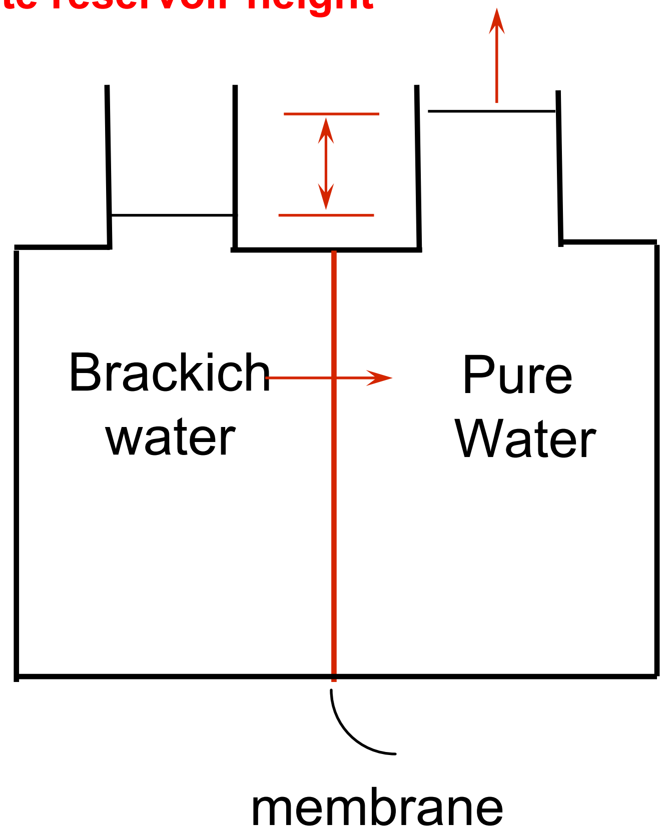
- Cross-flow filtration with turbulence promotors (feed spacers) to limit polarisation concentration and fouling issues

Basic principle of NF and RO systems

- applied Minimum pressure should counter balance :

:

- Osmotic pressure
- Longitudinal pressure drop
- Permeate reservoir height



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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 ≈ 0,068 bar
- 1,000 ppm TDS ≈ 0,68 bar
- 35,000 ppm TDS ≈ 24,1 bar

Basic principle of NF and RO systems

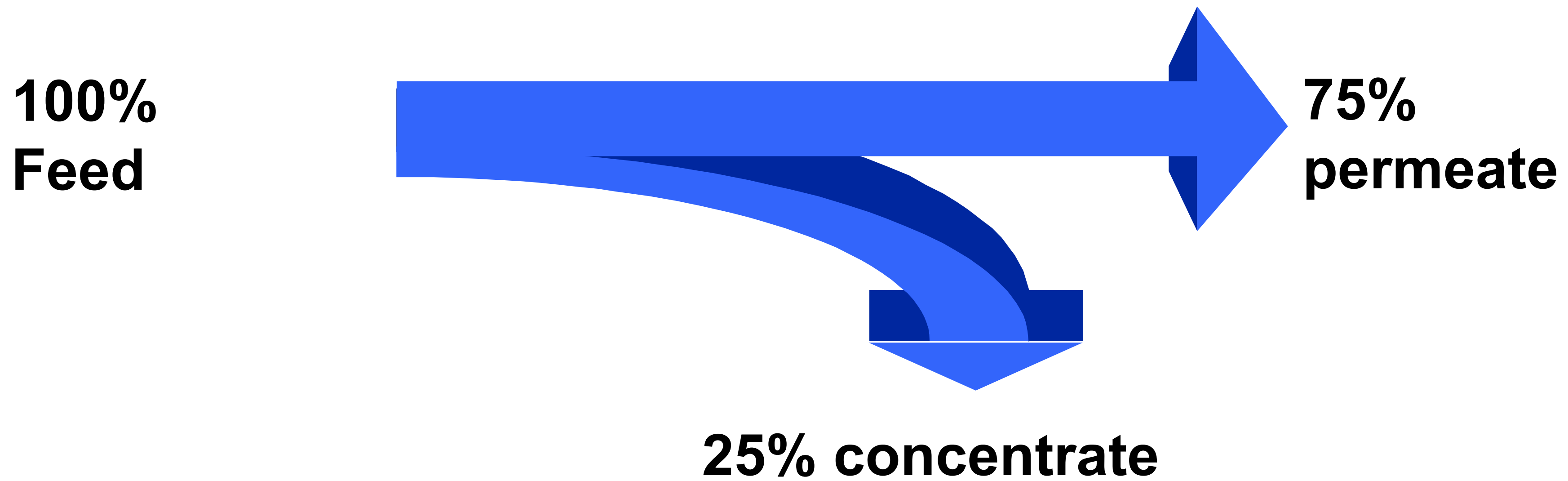
•Operating pressure

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**

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



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

$$Q = \frac{flowrate_p}{S}$$

Permeate Flux ($l/h/m^2$)

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

Permeability ($l/h/m^2/bar$)

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

Recovery factor

Basic principle of NF and RO systems

- **Rejection : R**

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

$$R_{system} < R_{module}$$

- **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**

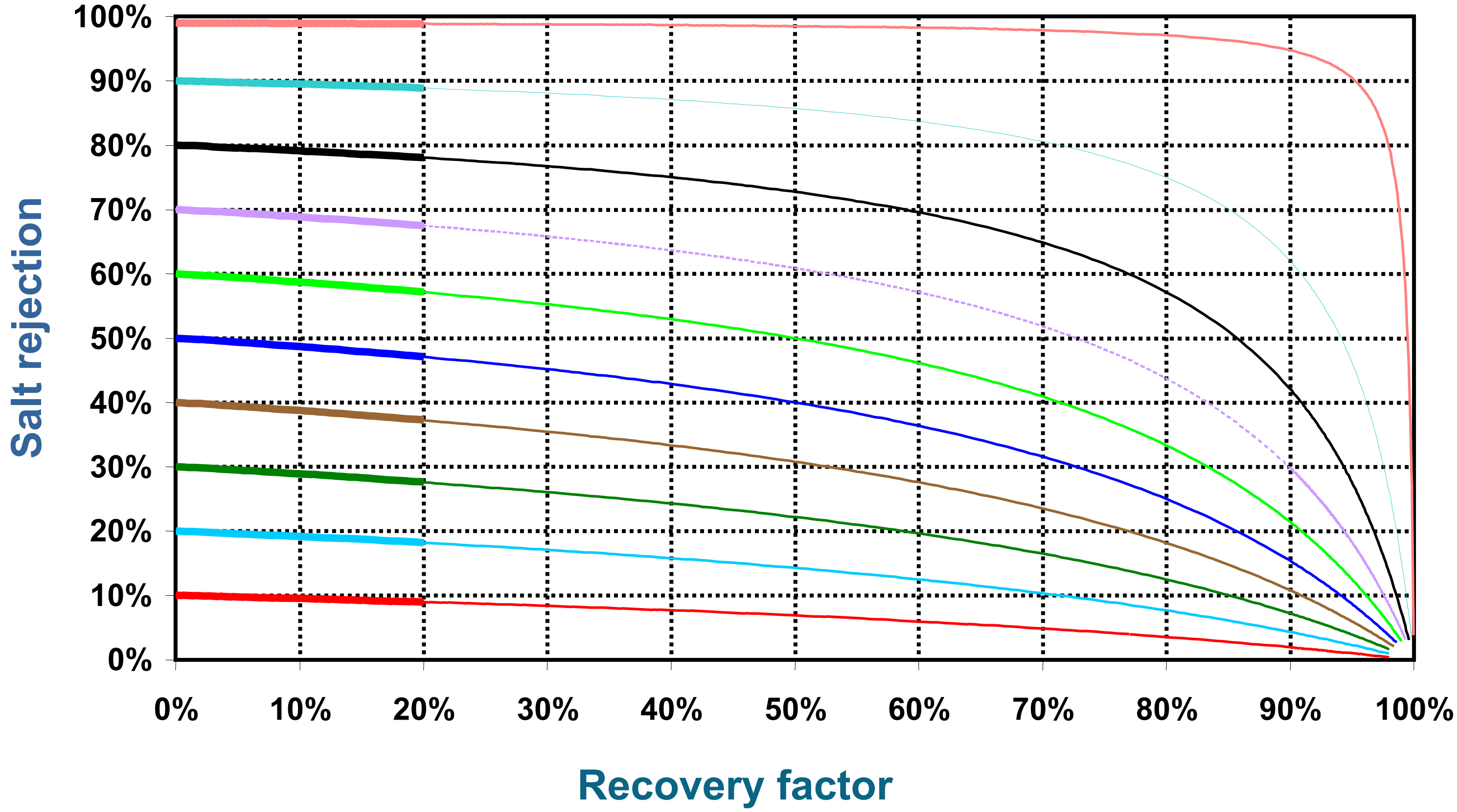
- **Conc flowrate = 81 m3/h**
- **TDS = 116 ppm**

- **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

HYDRANAUTICS
High Performance Membrane Products
A Nitto Denko Corporation

Membrane Element SWC3

Performance:	Permeate Flow:	5,900 gpd (22.3 m^3/d)
	Salt Rejection: nominal:	99.6 %
Type	Configuration:	Spiral Wound
	Membrane Polymer:	Composite Polyamide
	Nominal Membrane Area:	370 ft^2
Application Data	Maximum Applied Pressure:	1200 psig (8.27 MPa)
	Maximum Chlorine Concentration:	< 0.1 PPM
	Maximum Operating Temperature:	113 °F (45 °C)
	Feedwater pH Range:	3.0 - 10.0
	Maximum Feedwater Turbidity:	1.0 NTU
	Maximum Feedwater SDI (15 mins):	5.0
	Maximum Feed Flow:	75 GPM (17.0 m^3/h)
	Minimum Ratio of Concentrate to Permeate Flow for any Element:	5:1
	Maximum Pressure Drop for Each Element:	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)
40.0 (1016)	7.95 (201.9)	1.50 (38.1)	36 (16.4)

Notice: Permeate flow for individual elements may vary + or - 15 percent. All membrane elements are supplied with a brine seal, interconnector, and o-rings. Elements are vacuum sealed in a polyethylene bag containing a 1.0% sodium bisulfite solution, and then packaged in a cardboard 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

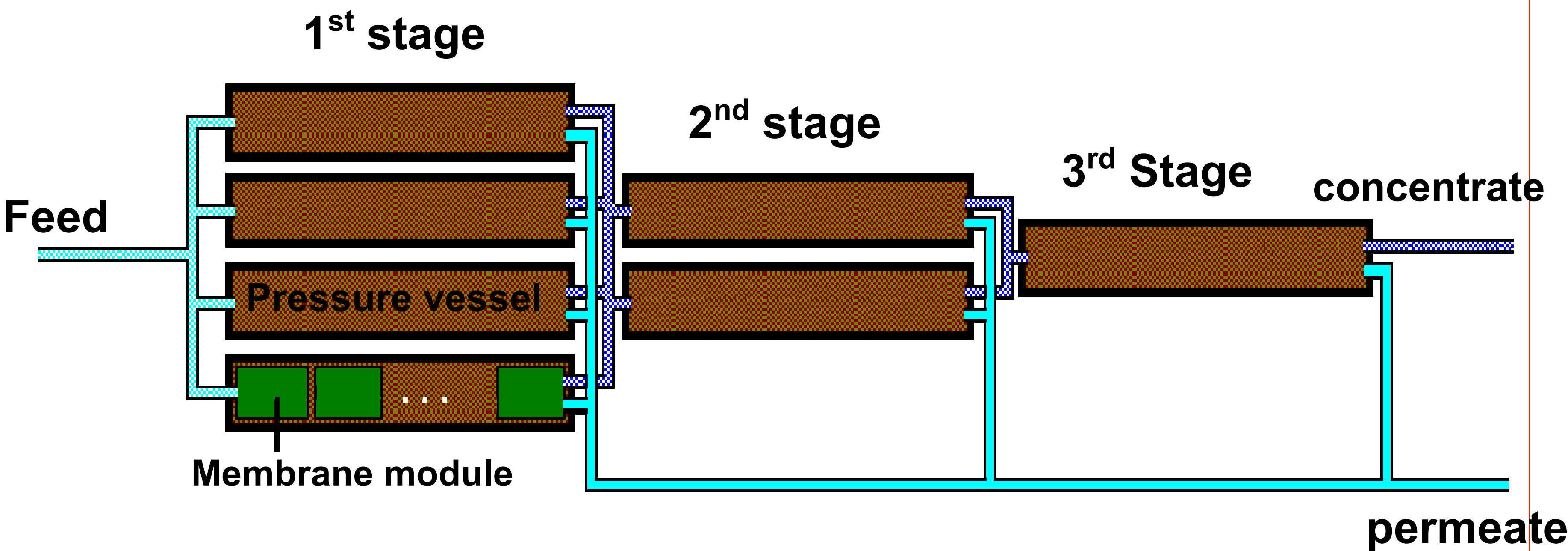
Basic principle of NF and RO systems

- **Design Flux**

Membrane Application	Design flux (l/h/m2)
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**

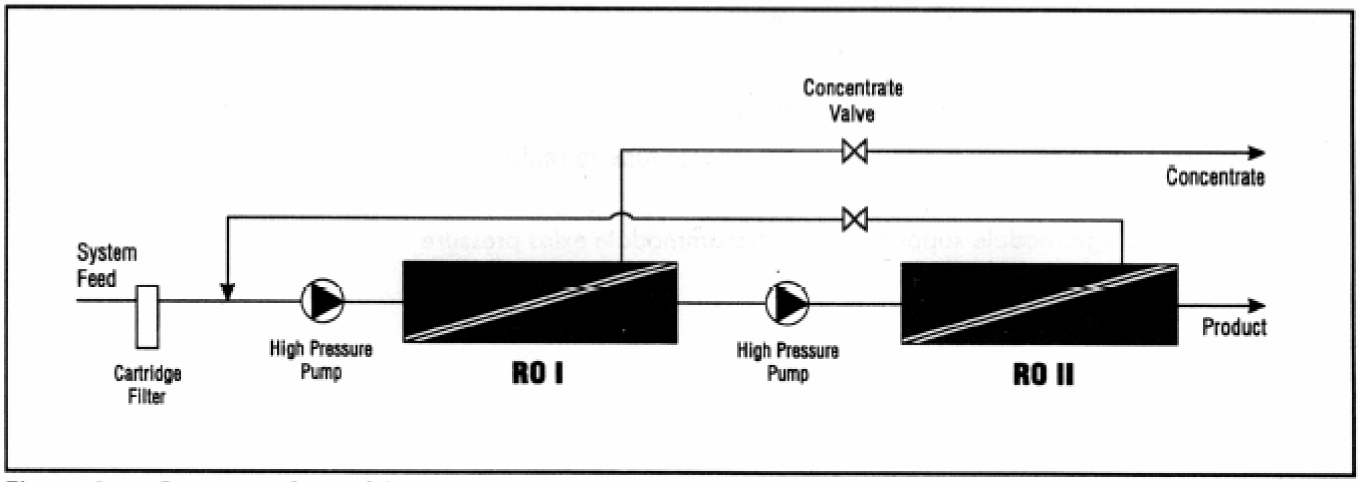


Figure 1: Permeate Staged System

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

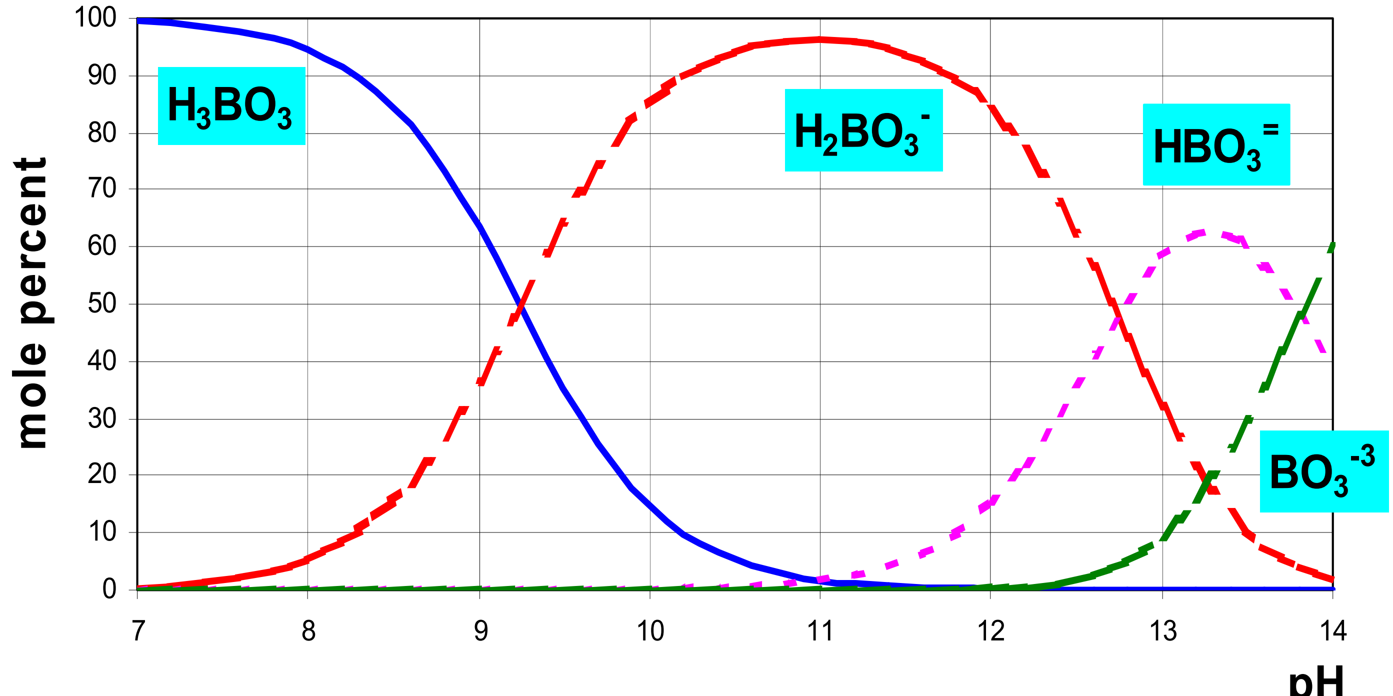


Figure 1 Ortho Boric acid dissociation

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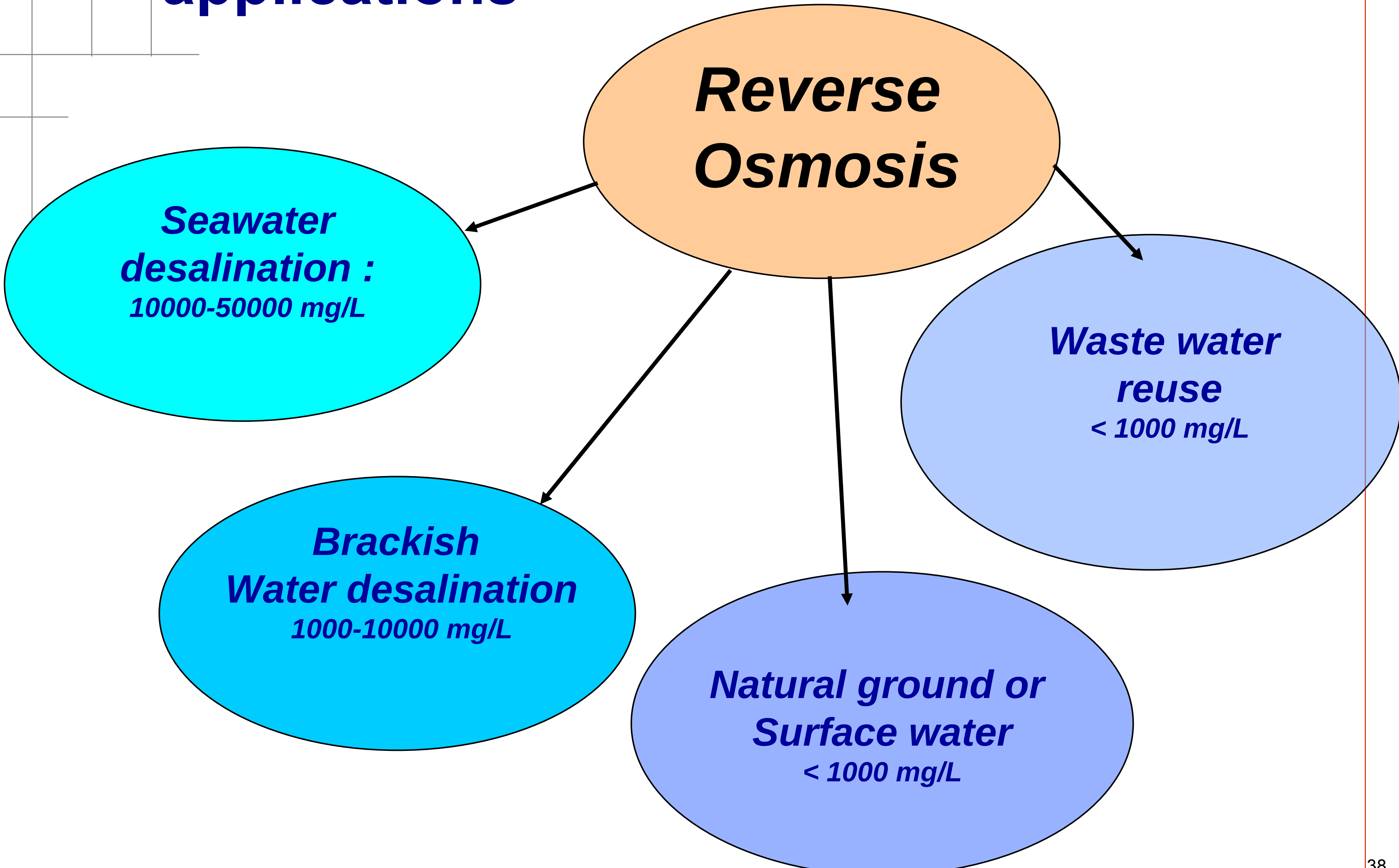
NF and RO efficiency

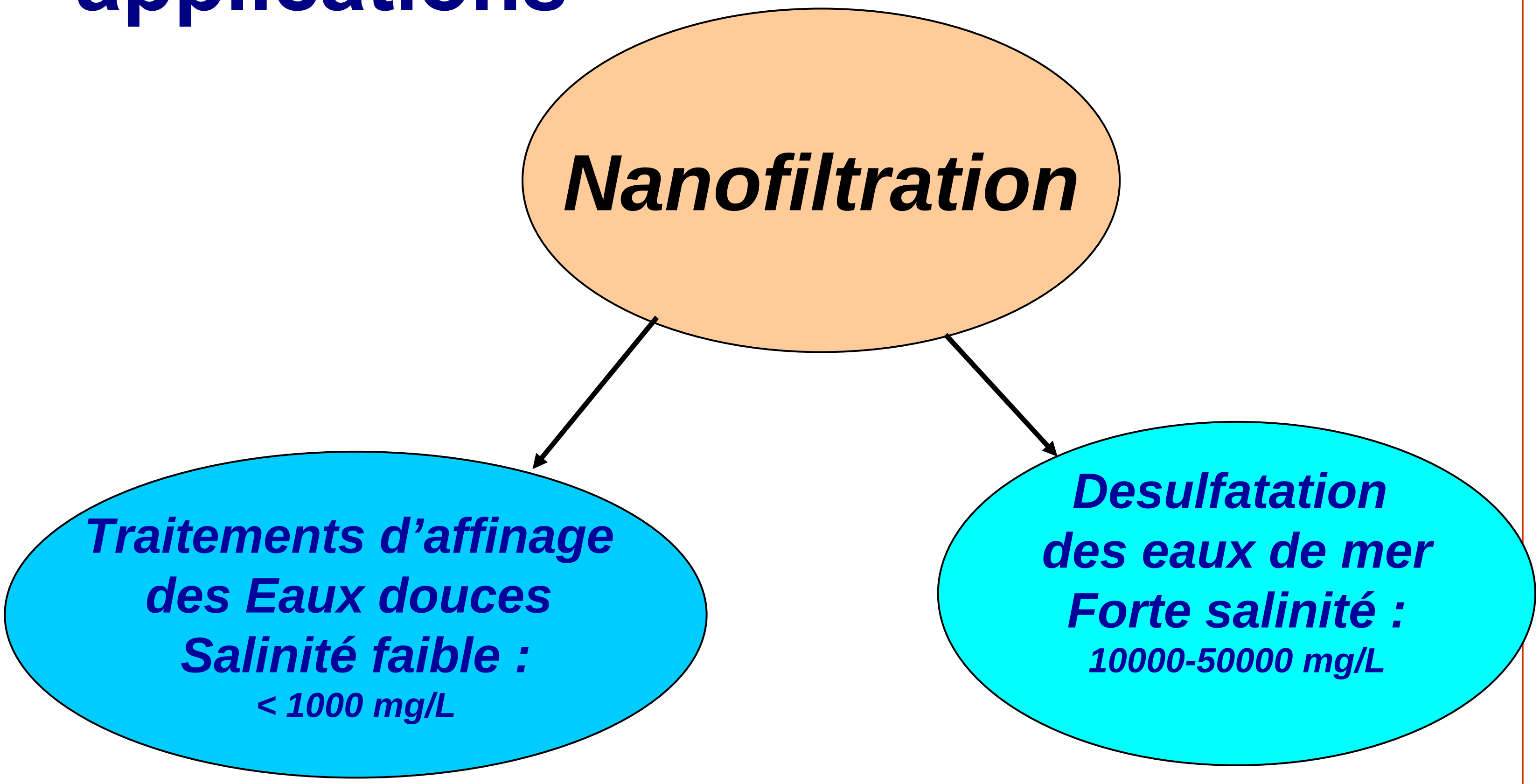
➲ Removal of :

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

applications



applications



NF/RO products

- 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$/m^2 to 9$/m^2

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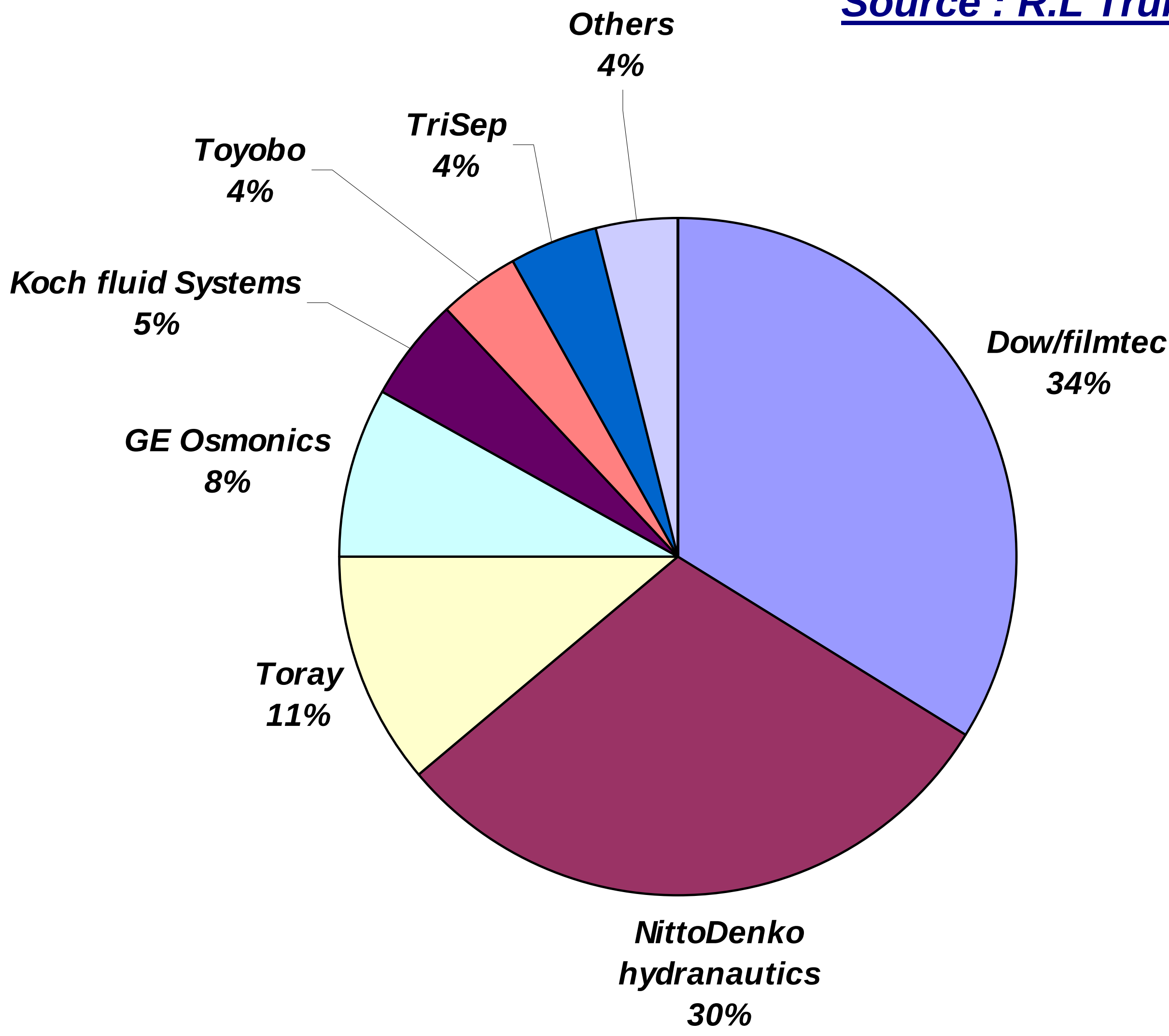
2003 RO/NF Membrane Sales by Competitors

Source : R.L Truby & Associates (2004)



Low pressure membrane systems MF/UF

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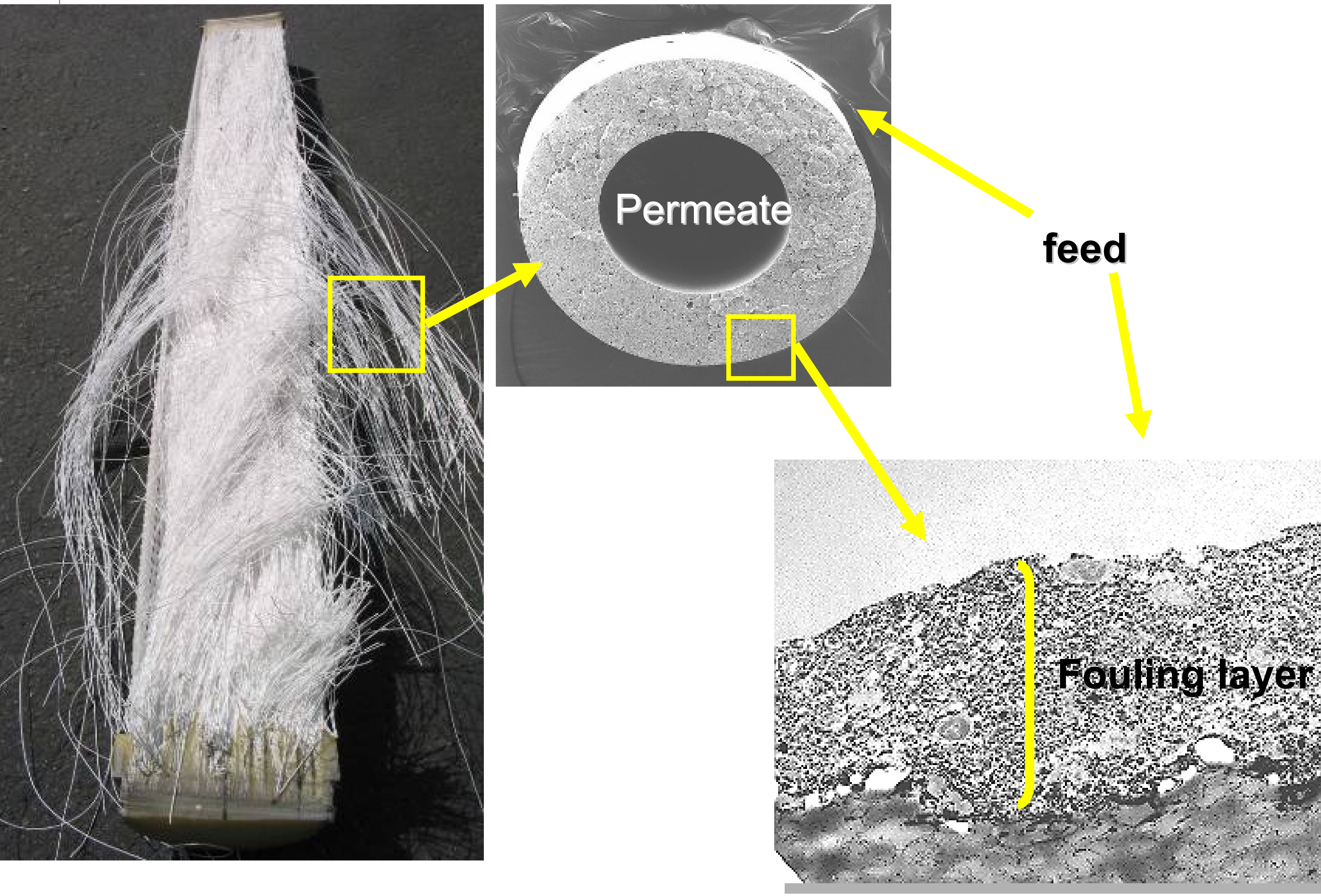
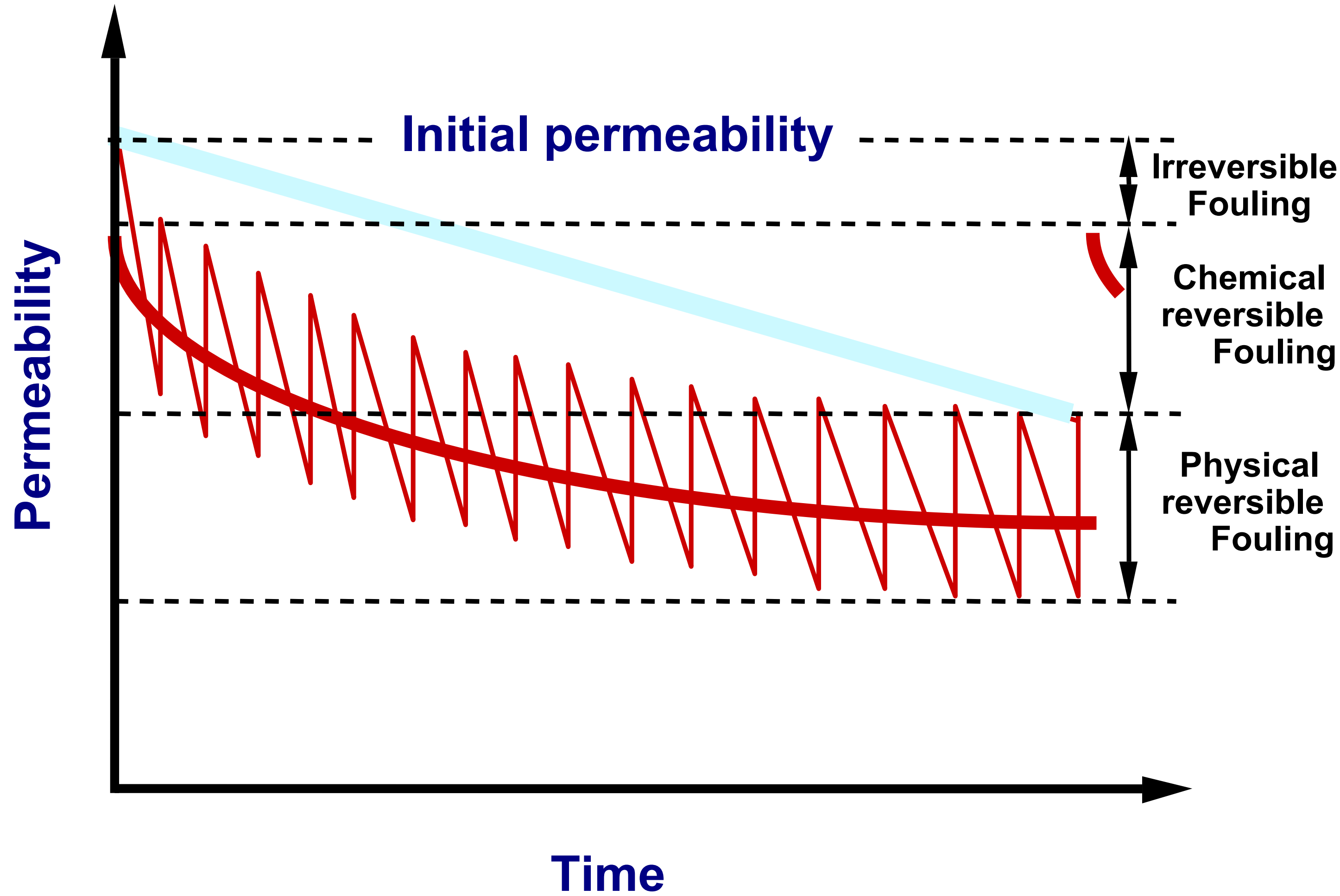
Dominating membrane : Hollow fiber configuration



Fouling affects permeability



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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

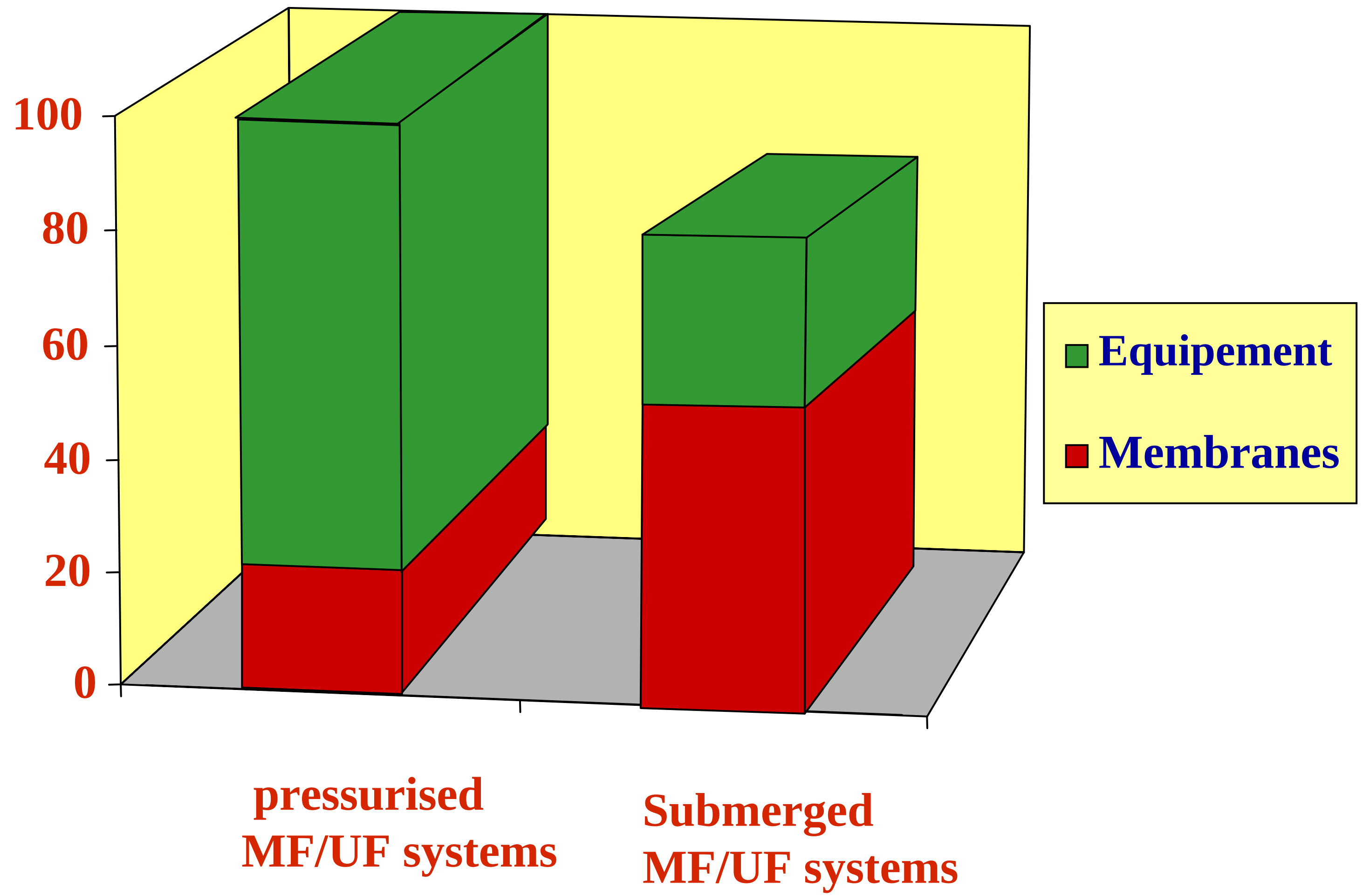
Operating conditions

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

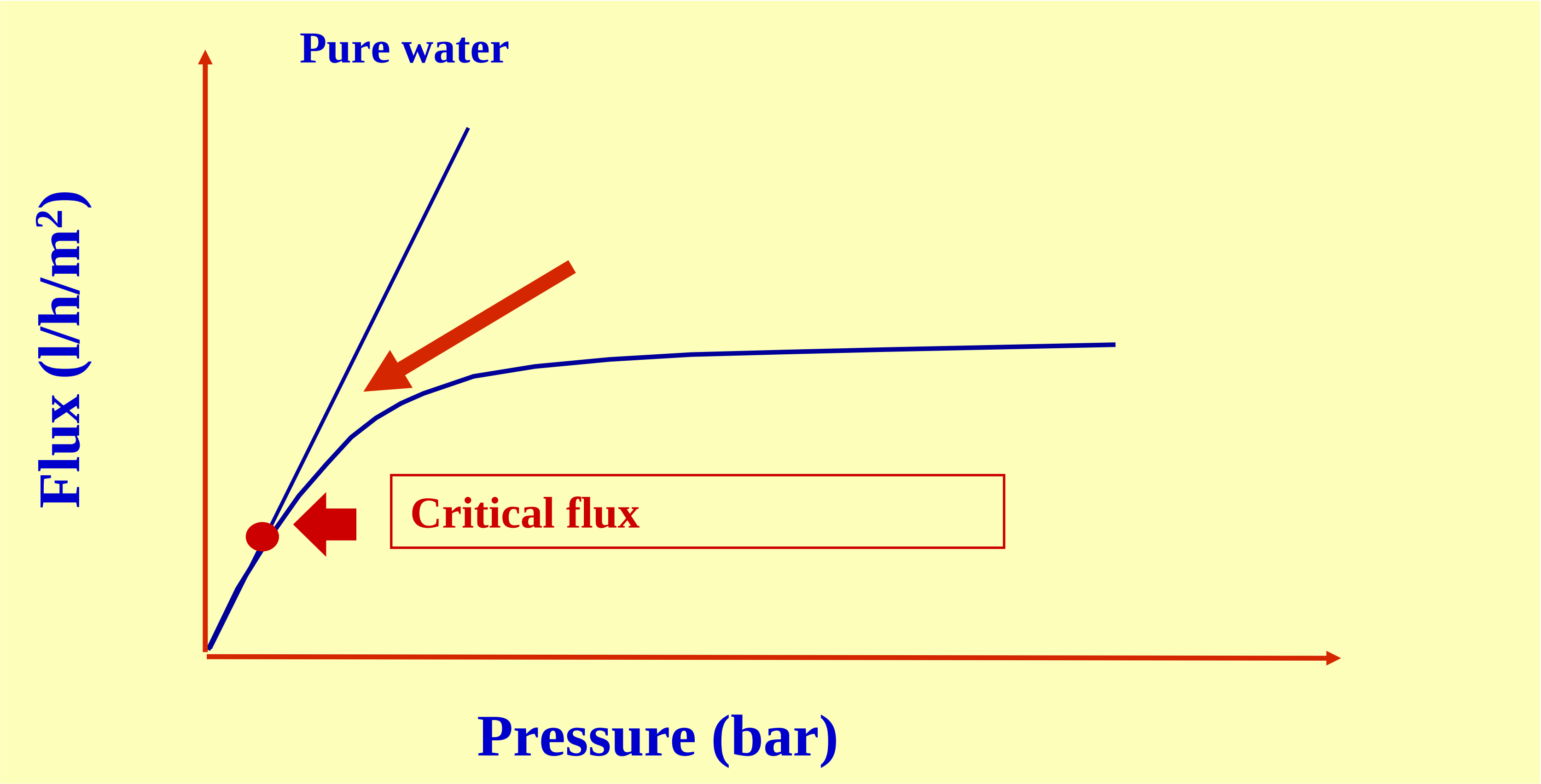
Main differences between different type of UF/MF

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



Operating conditions of submerged type



Why monitor membrane integrity?

- 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

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34 million fibres

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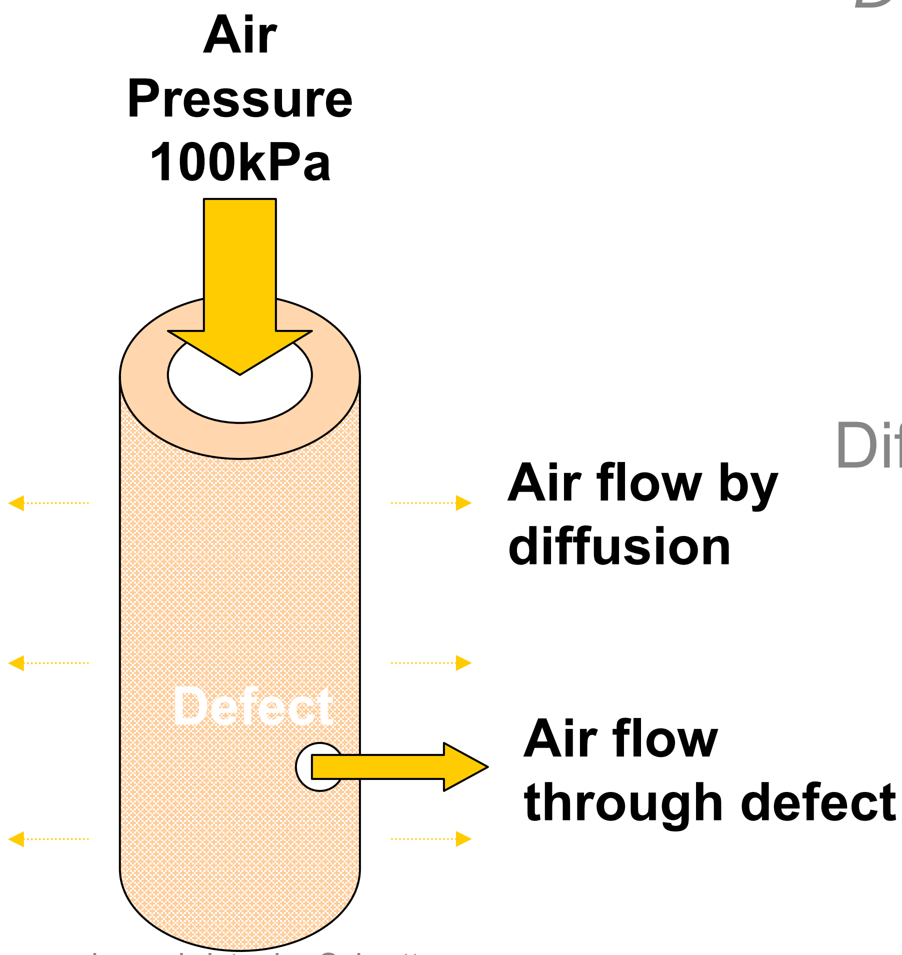

Pressure Decay Test (PDT)

Detection level : Up to Log 5.3

$$\frac{\Delta P}{time} = f\left(Q_{air\_through\_defect}\right)$$

Diffusive Air Flow Test (DAF)

Detection level : > log 7

$$Q_{water} = f\left(Q_{air\_through\_defect}\right)$$

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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 surperficial tension

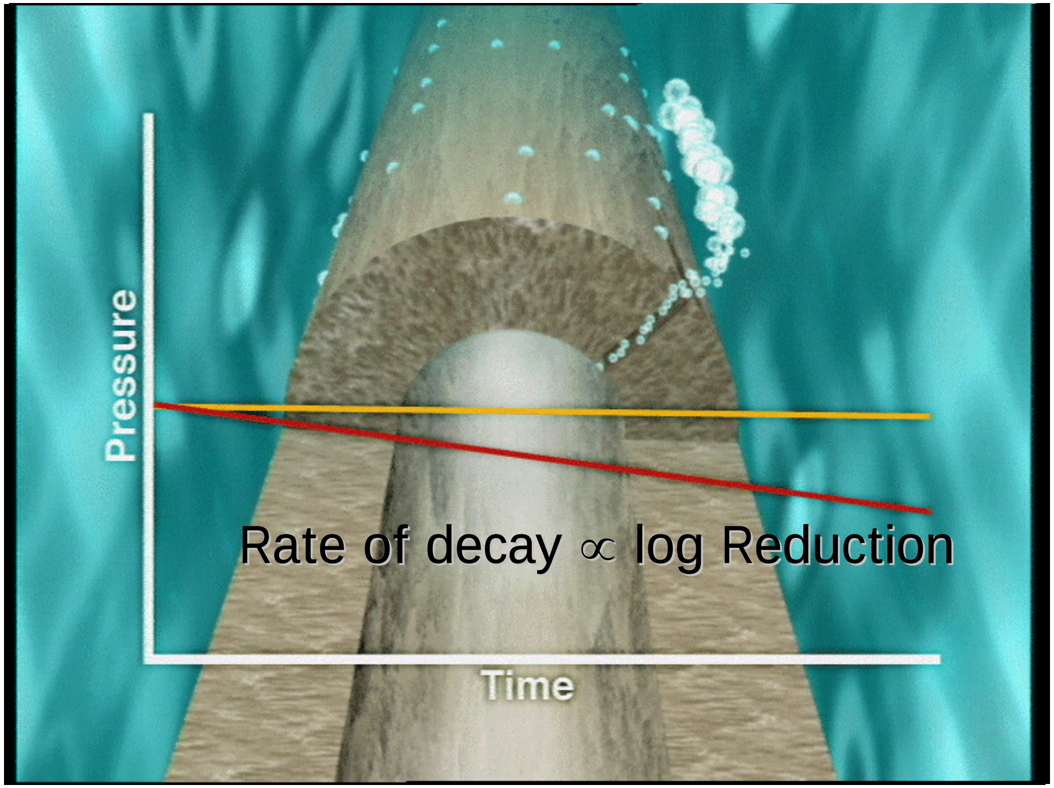
Θ = contact angle

d = pore diameter (microns)

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

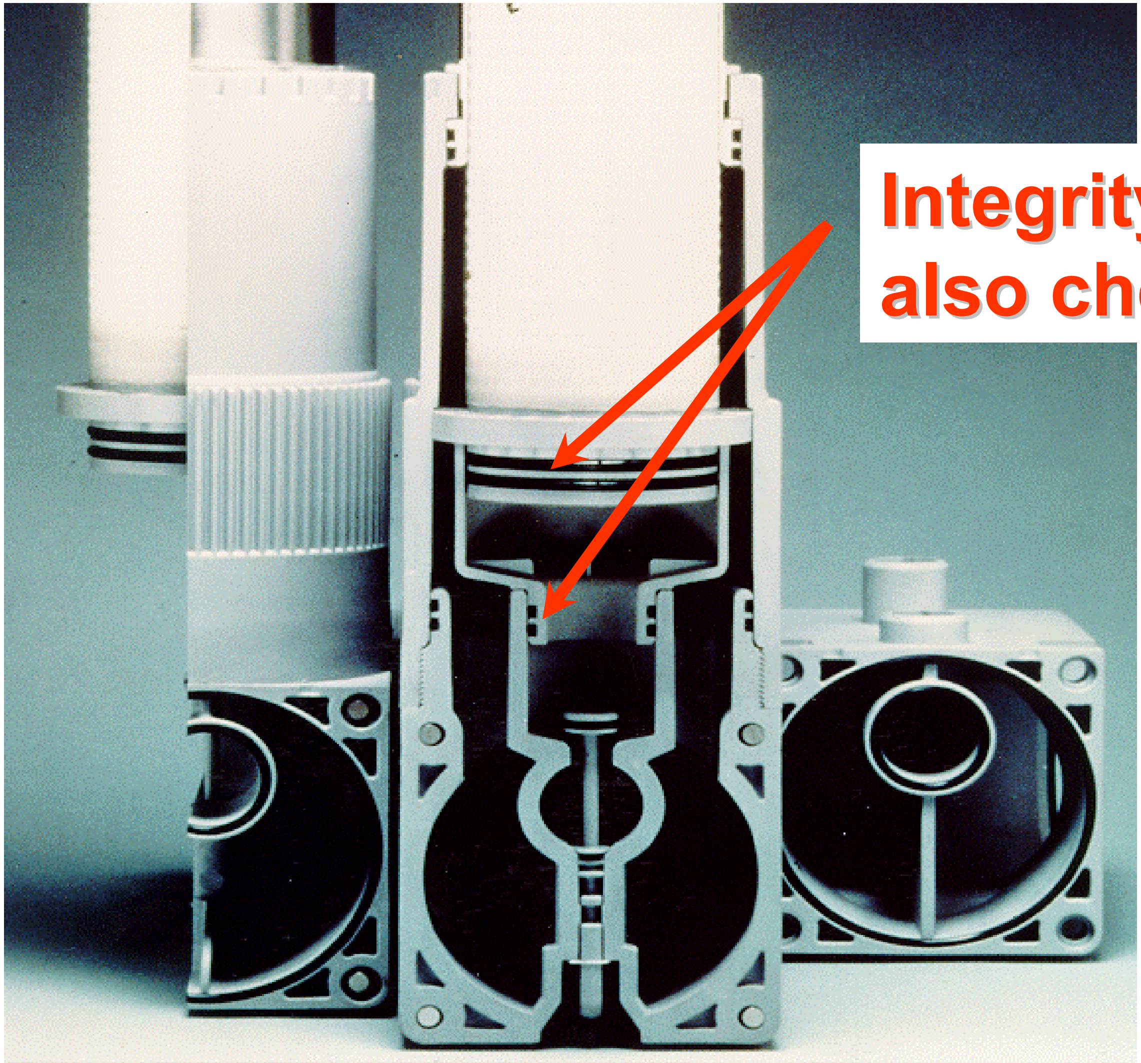
Pore diameter	APPLIED PRESSURE
0,05 µm	P = 57,6 bar
0,1 µm	P = 28,8 bar
1 µm	P = 2,88 bar
2,88 µm	**Current on site P =1 bar**

- Pressure Decay Test (PDT)



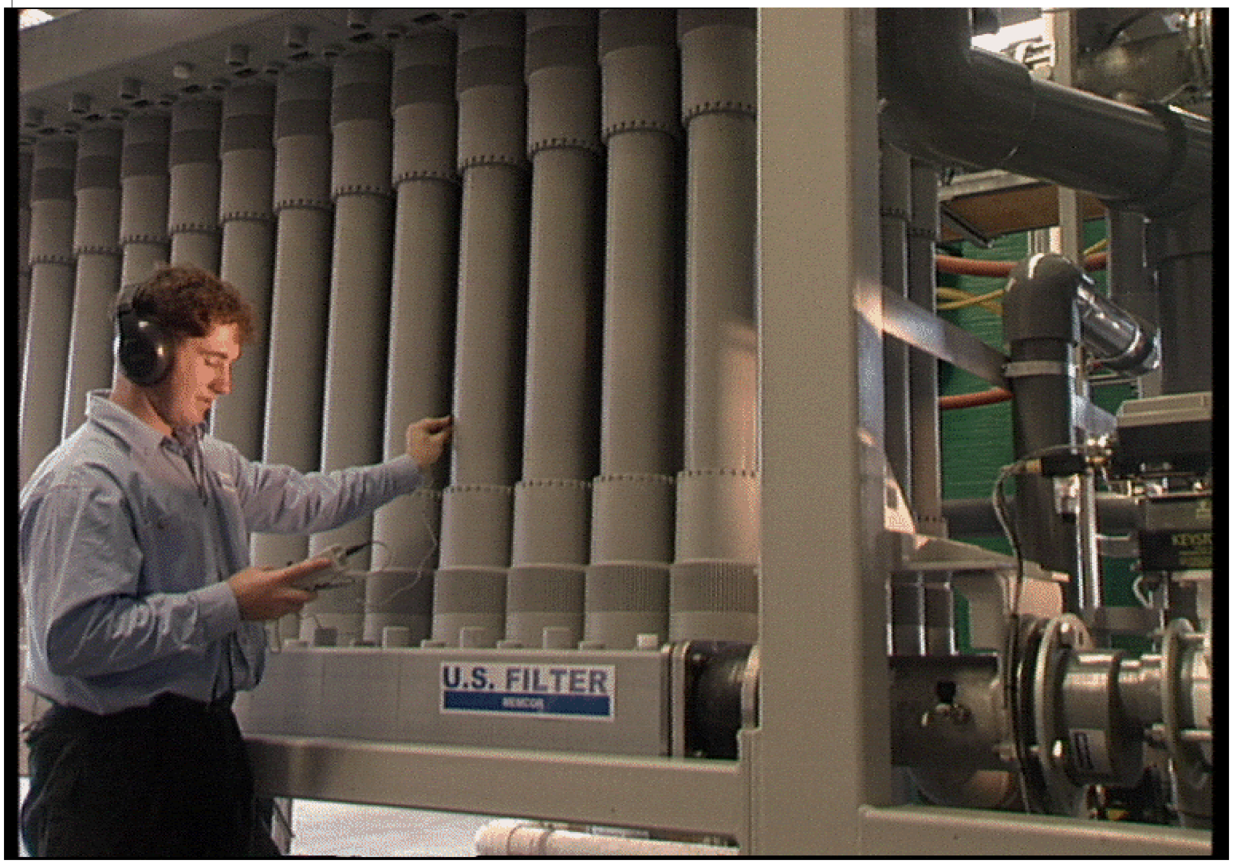
>Log 4 Crypto Sensitivity

INTEGRITY TESTING



Integrity methods also check seals

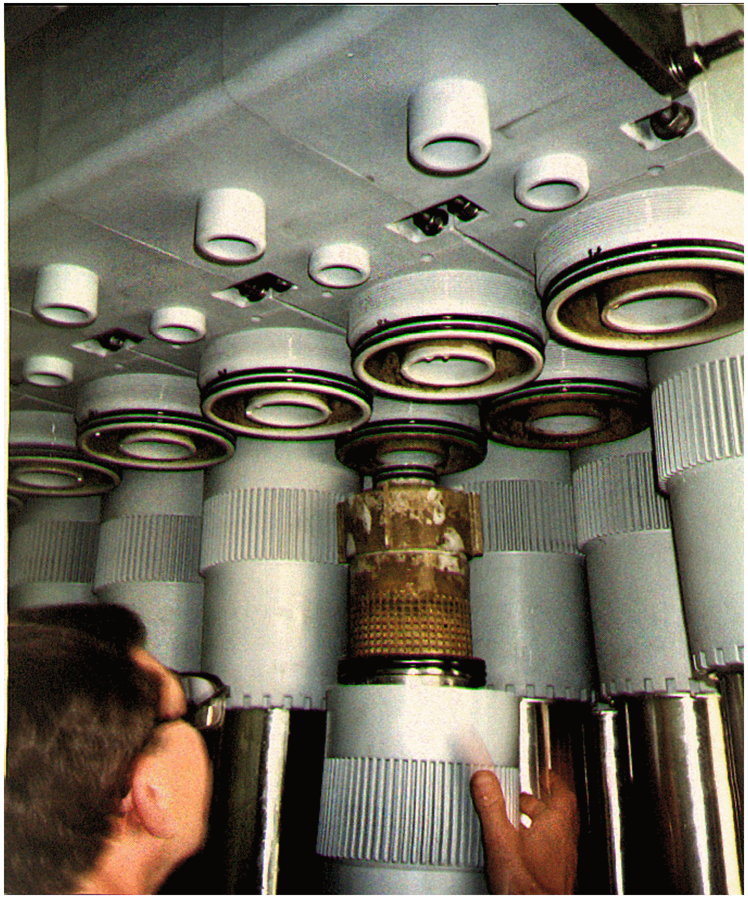
INTEGRITY TESTING : Which Module ?



Sonic Analysis

Will detect a single fibre break

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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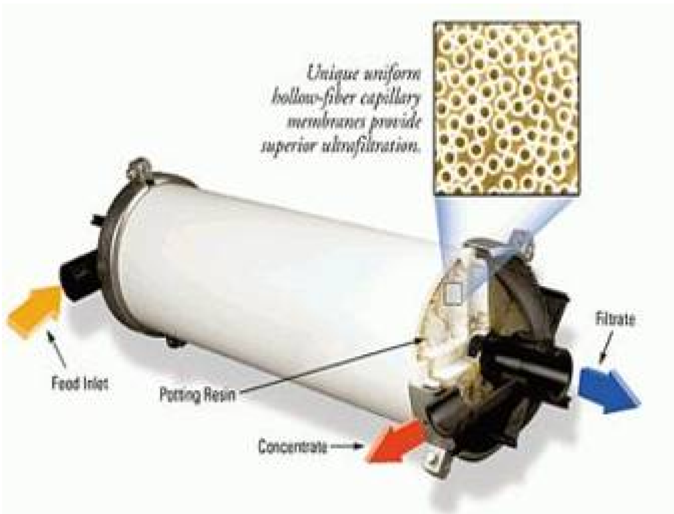
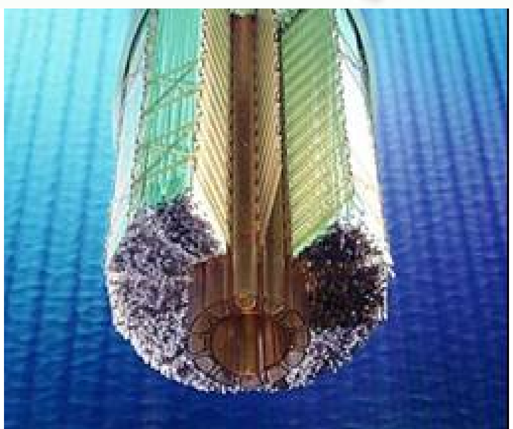
Low pressure membrane Keyplayers for Drinking water applications

Pressurized systems vs Submerged systems





Pressurized systems
(40% market share)

Submerged systems
(60% market Share)

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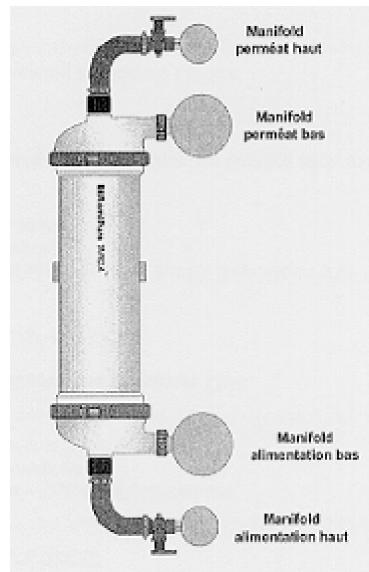
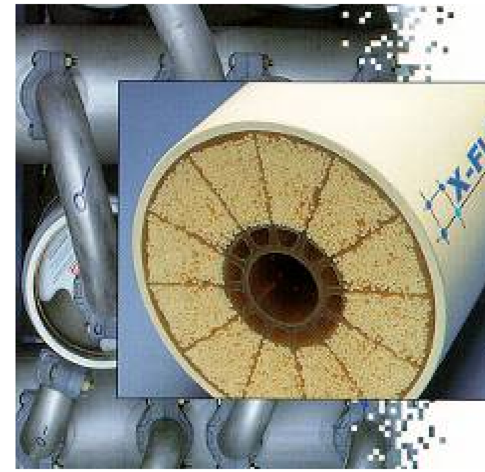




Established Players

NORIT

PALL/ASAHI

KOCH

AQUASOURCE

HYDRANAUTICS

MEMCOR (CMF)

New Entrants

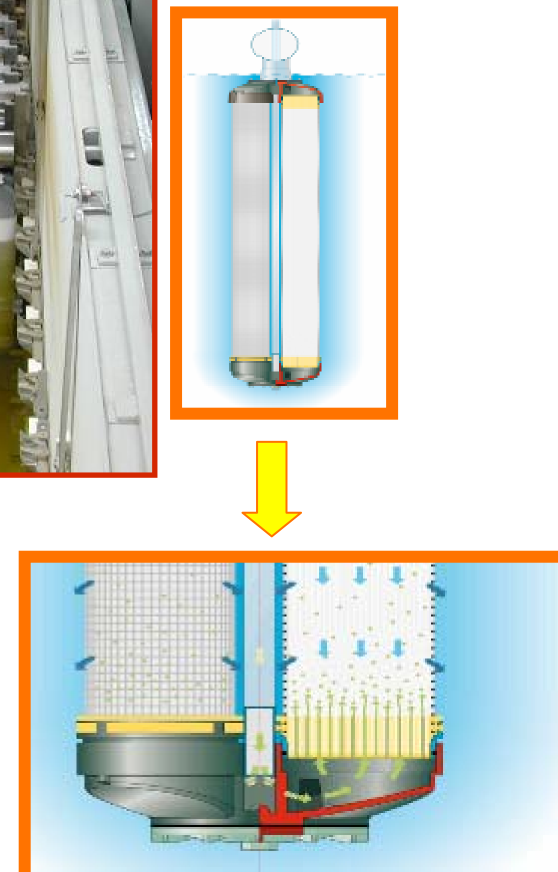
INGE

POLYMEM

DOW/OMEXELL

TORAY

Submerged Membrane systems (60% Market share)



Established Players

ZENON

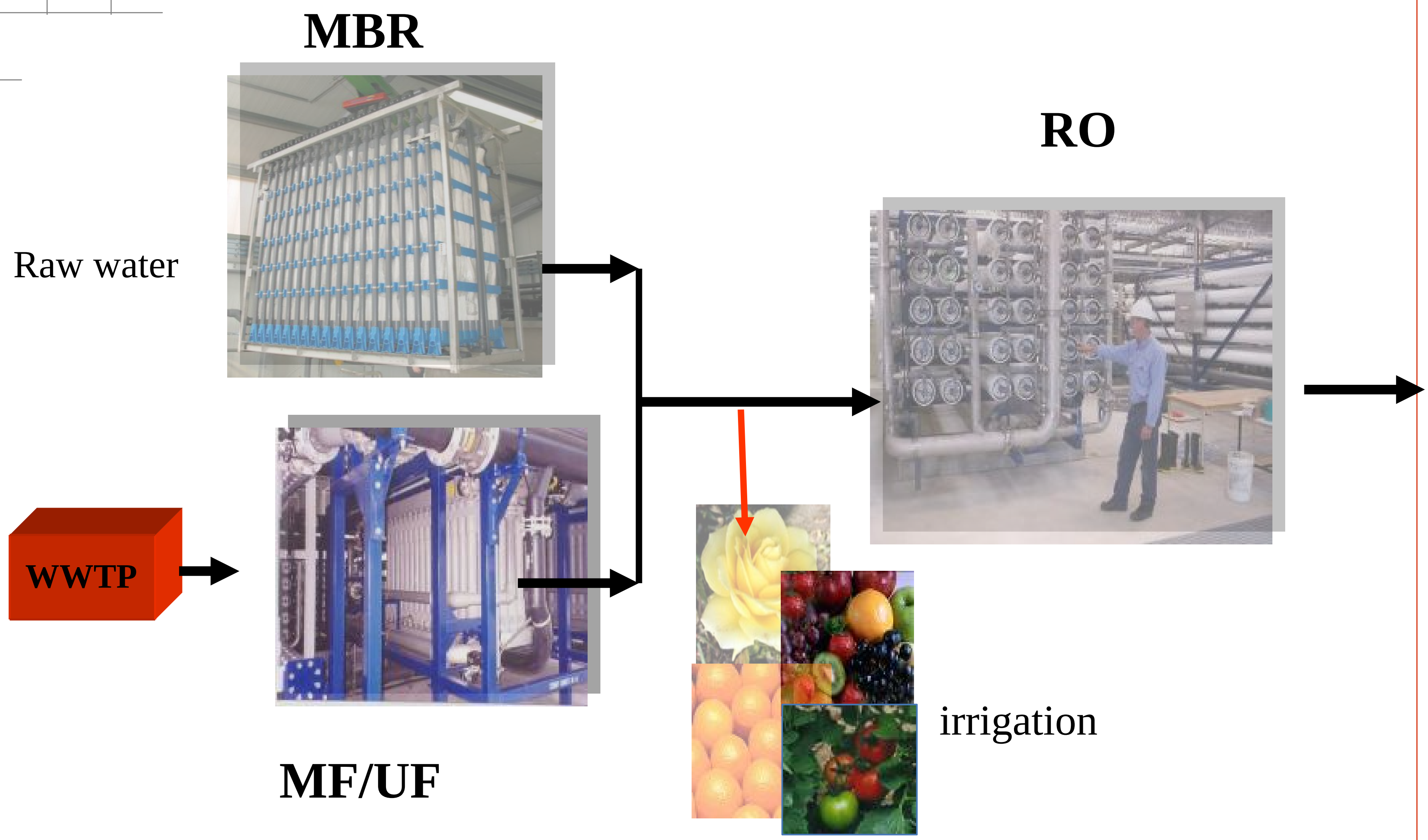
MEMCOR

Low pressure membrane Keyplayers for Municipal waste water applications

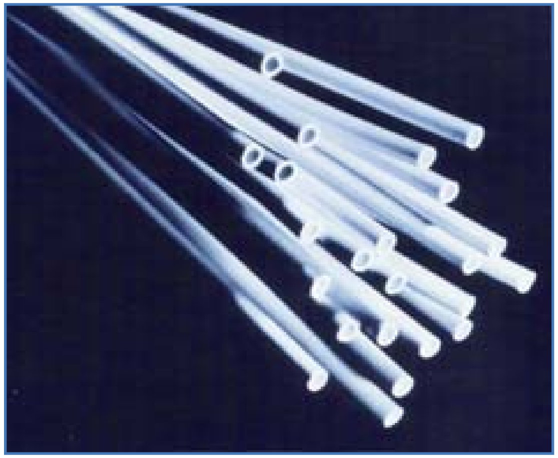
- re-use,
- tertiary treatment,
- MBR)

VEOLIA ENVIRONNEMENT

Municipal waste water applications



Tertiary treatment and reuse key players

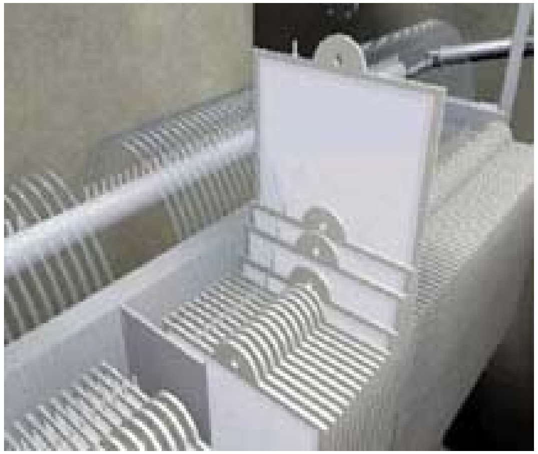


**Hollow fibers
Membranes**

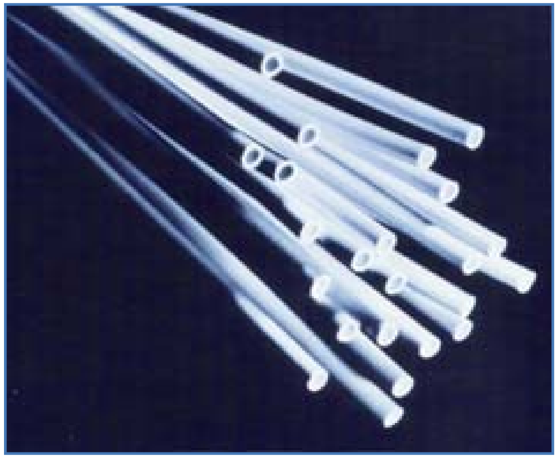
Established Players

Memcor
Norit
Zenon

MBR key players



Flat sheet membranes



Hollow fibers Membranes

Established Players

Kubota

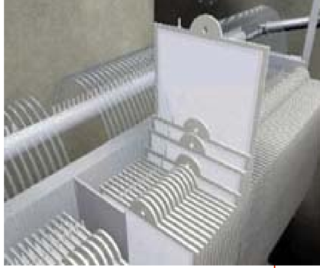
Zenon

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

an-christophe Schrotter

+ la technologie la plus adaptée