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Integrated Membrane Systems

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Integrated Membrane Systems

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Sustainable development: definition

"Sustainable development is a process of change in which the exploitation of resources, the direction of investments, the orientation of technical development, and institutional change are all in harmony and enhance both current and future potential to meet human needs and aspirations"

Common Future (World Commission on Environment and Development, 1987)

Membrane science **has led to significant innovation in processes and products over the past few decades offering new opportunities in the design, rationalisation and optimisation of innovative productions, for the sustainable industrial growth and environmental protection. At present, one of the most interesting developments for industrial membrane technologies are related to the possibility of** ***integrating different membrane operations*** **with overall important benefits in the logic of** ***Process Intensification.***

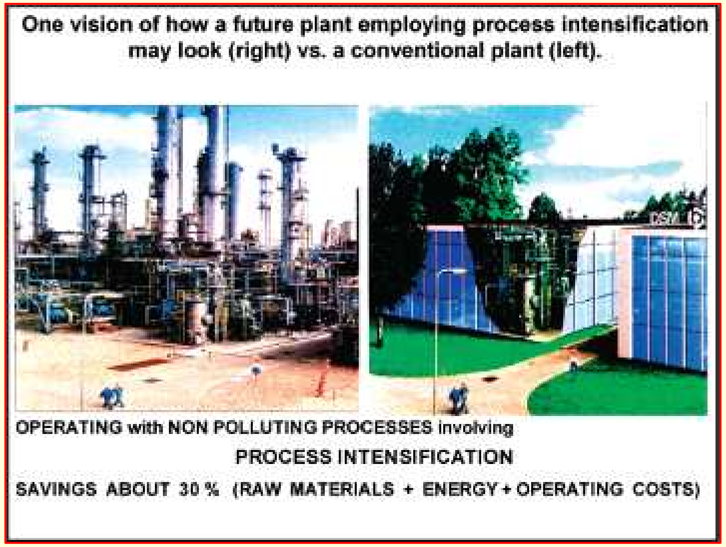
Process Intensification: strategy aiming to *produce much more with much less**

by replacing processes and equipments

- ✓ large
- ✓ expensive
- ✓ energy intensive
- ✓ polluting

with avant-garde versions

- ✓ smaller
- ✓ less costly
- ✓ more efficient
- ✓ less polluting
- ✓ highly safe
- ✓ automatized
- ✓ compact



One vision of how a future plant employing process intensification may look (right) vs. a conventional plant (left).

OPERATING with NON POLLUTING PROCESSES involving

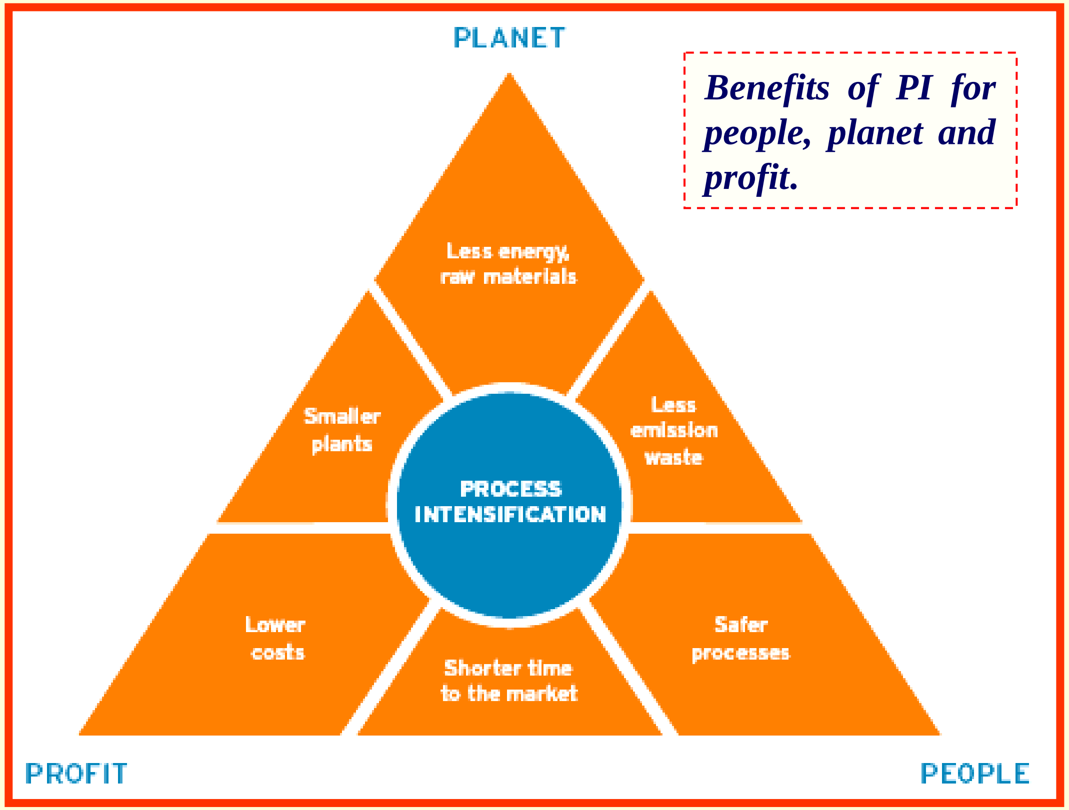
PROCESS INTENSIFICATION

SAVINGS ABOUT 30 % (RAW MATERIALS + ENERGY + OPERATING COSTS)

* Jean-Claude Charpentier, *Ind. Eng. Chem. Res.* 2007, *46*, 3465-3485.

Process Intensification (PI) **addresses several needs of the process industry: energy savings, CO_2 emission reduction and enhanced cost competitiveness.** ***The potential benefits of PI that have been identified are significant.***

The needs vary somewhat between sectors but the benefits promised by PI impact each sector in one way or another.



Benefits of PI for people, planet and profit.

Process Intensification provides radically innovative principles (“paradigm shift”) in process and equipment design which can benefit (often with more than a factor of two) process and chain efficiency, capital and operating expenses, quality, wastes, process safety and more.

Action Plan Process Intensification, **www.creative-energy.org.**

Nanostructured artificial membranes: technologies addressed towards the *Process Intensification Strategy*.

Membrane technologies respond efficiently to the requirements of the "Process Intensification Strategy", because they permit improvements in manufacturing and processing, substantially decreasing the equipment-size/production-capacity ratio, energy consumption, and/or waste production and resulting in cheaper, sustainable technical solutions.

Some examples:

Process	Problem	Advantages
Separation processes	Around 40-50% of the energy use in industries is consumed in separation processes	In membrane operations over *an order* of magnitude reduction in energy use can be obtained in comparison with thermal driven separation
Seawater desalination	An optimized thermal distillation plant producing 100 million gallons per day requires 73 kw hr/m^3	A seawater RO system (with an energy consumption of only 2.2 (kw hr)/m^3) is over *10 fold more efficient* than the thermal approach.
Power	Electrochemical oxidation of a fuel to extract power can be performed in a fuel cell or via a heat cycle. Current fuel cells have efficiencies in the range of 50-60% (higher than the 33% efficiency for optimized thermal systems).	Using a 50% efficiency limit, a fuel cell coupled to a RO unit would show an improvement of *16 fold* better than the thermal alternative!

W.J. Koros, Journal of Membrane Science, 300 (2007) 1.

Advantages of membrane technology

✓ **efficiency and operational simplicity…**

✓ **high selectivity and permeability for the transport of specific components…**

✓ **low energetic requirement…**

✓ **good stability and compatibility between different membrane operations…**

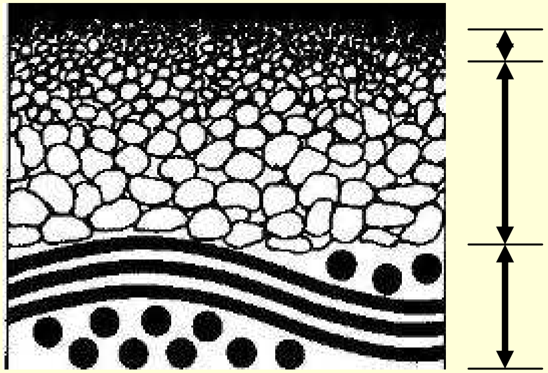
✓ **environment-compatibility…**

✓**large flexibility and easy scale-up…**

✓**advanced levels of automatisation and remote control …**

… the driving forces of a technology addressed towards the *Process Intensification Strategy*

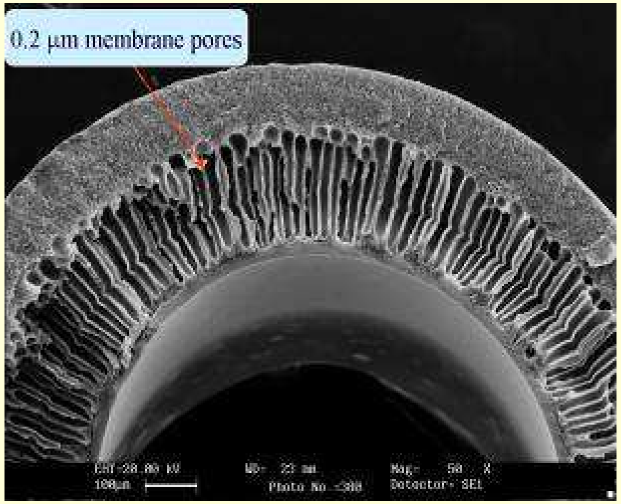
Nanostructured asymmetric membranes



Dense Layer

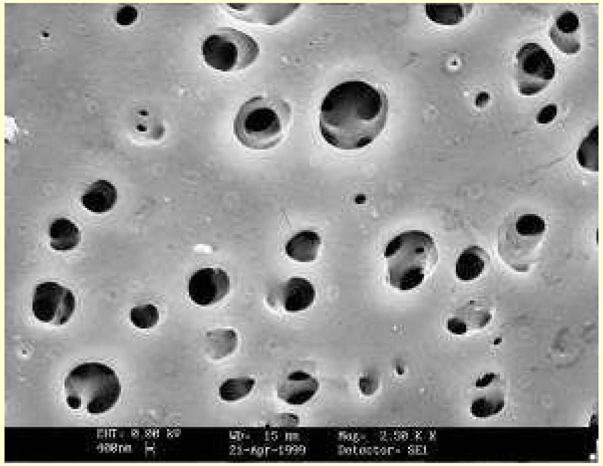
Porous support

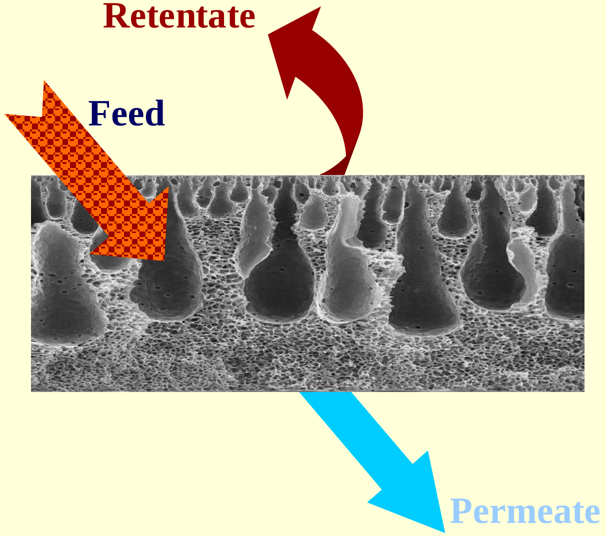
Fiber Support



SEM cross section of ultrathin TiO2 nanofiber membrane (http://www3.ntu.edu.sg/home/DDSun/research.html)

Appearance of clean *UF Membrane surface* (http://www3.ntu.edu.sg/home/DDSun/research.html)





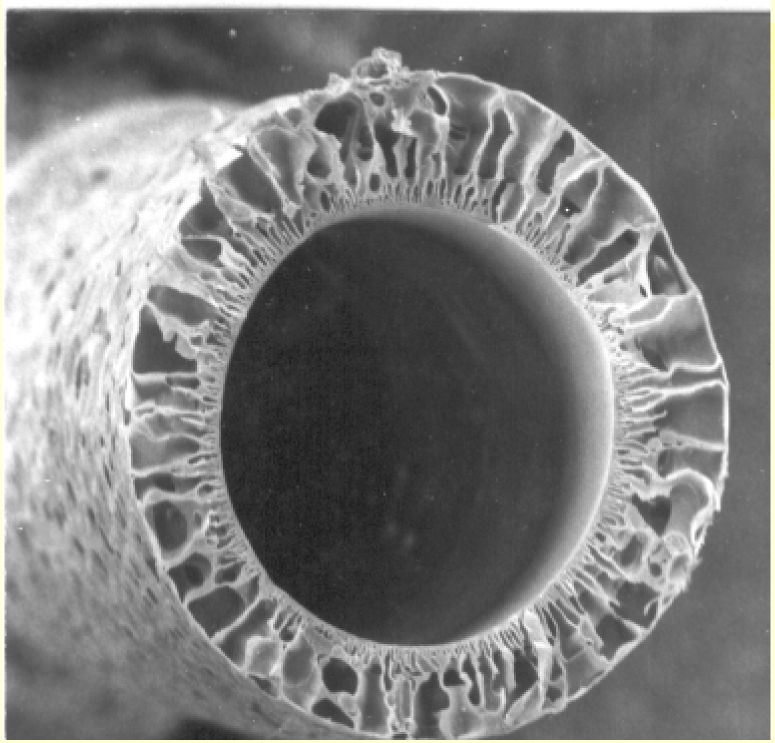
Retentate

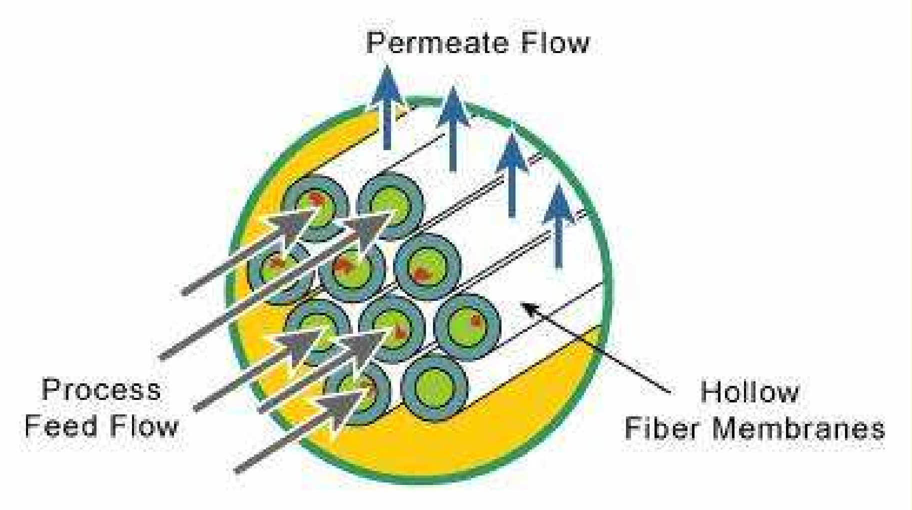
Feed

Transport mechanism

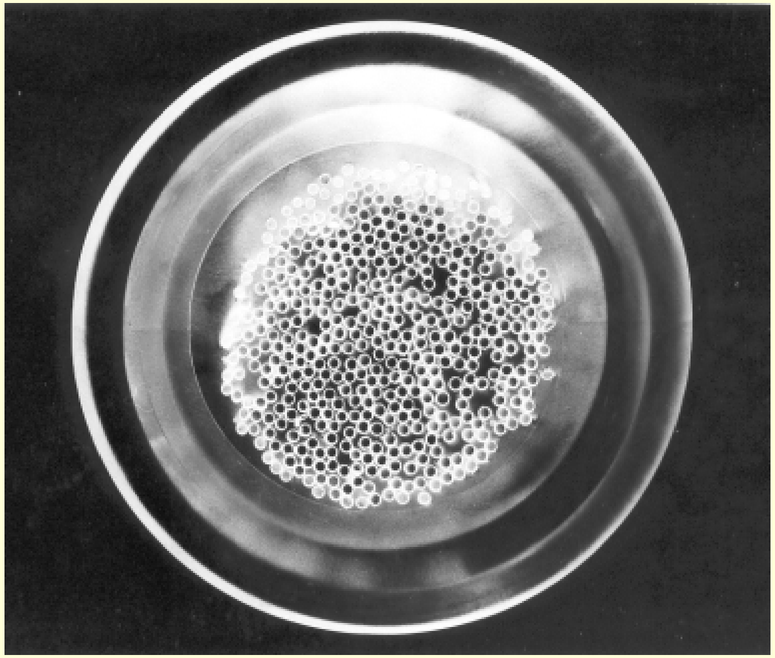
Permeate

Hollow Fibres Membrane and Module

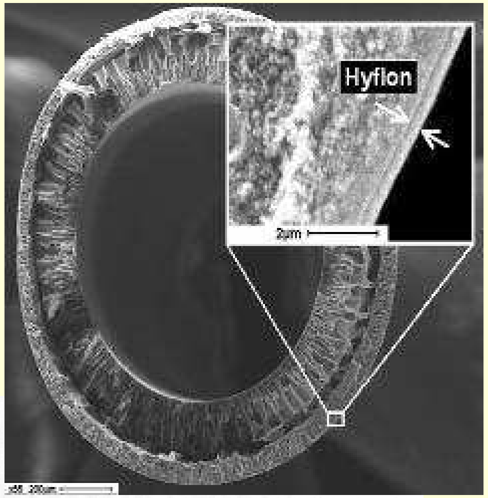


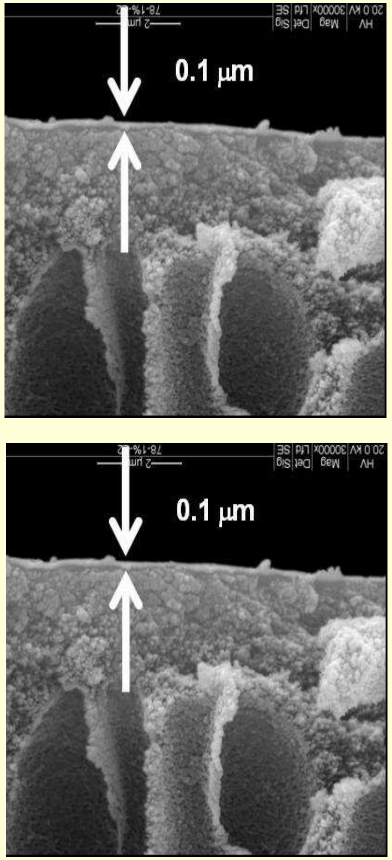


H. Strathmann, L. Giorno, E. Drioli, *An Introduction to Membrane Science and Technology*, CNR-Servizio Pubblicazioni, 2006.

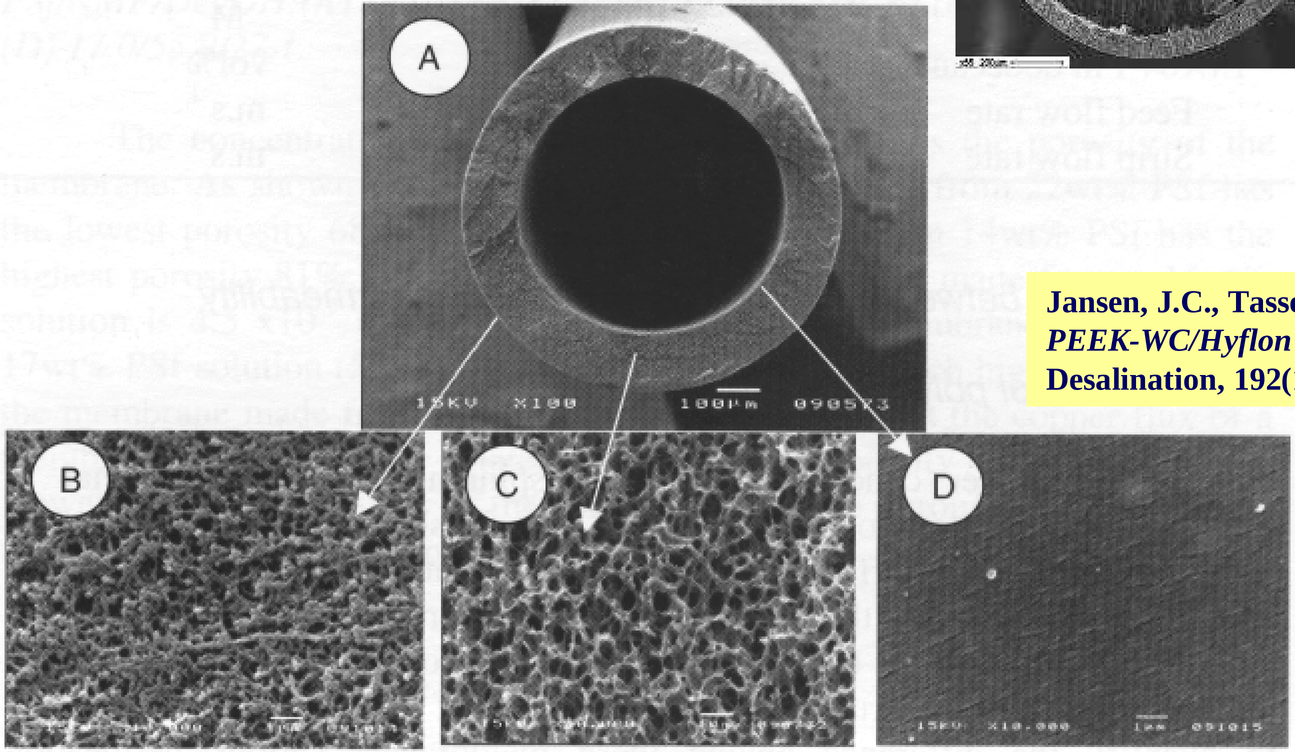


Structures of Hollow Fiber Membranes





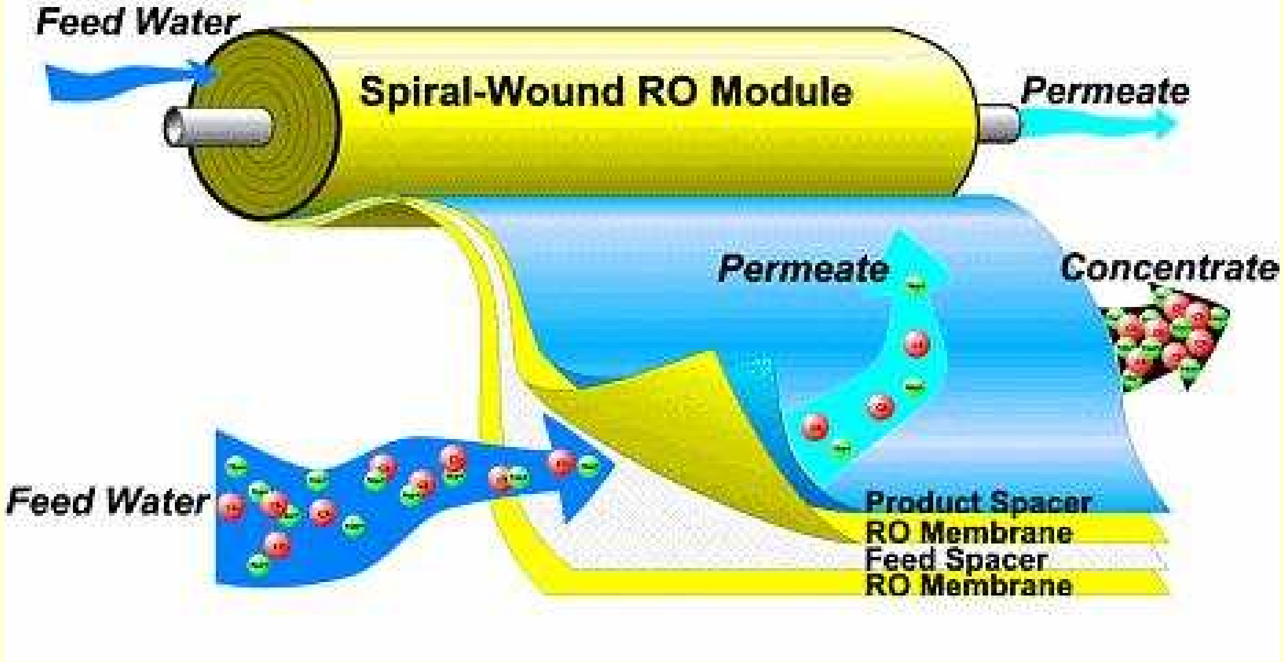
Jansen, J.C., Tasselli, F., Tocci, E., Drioli, E., *Composite PEEK-WC/Hyflon hollow fiber membranes*, Desalination, 192(1-3), (2006) 207-213.

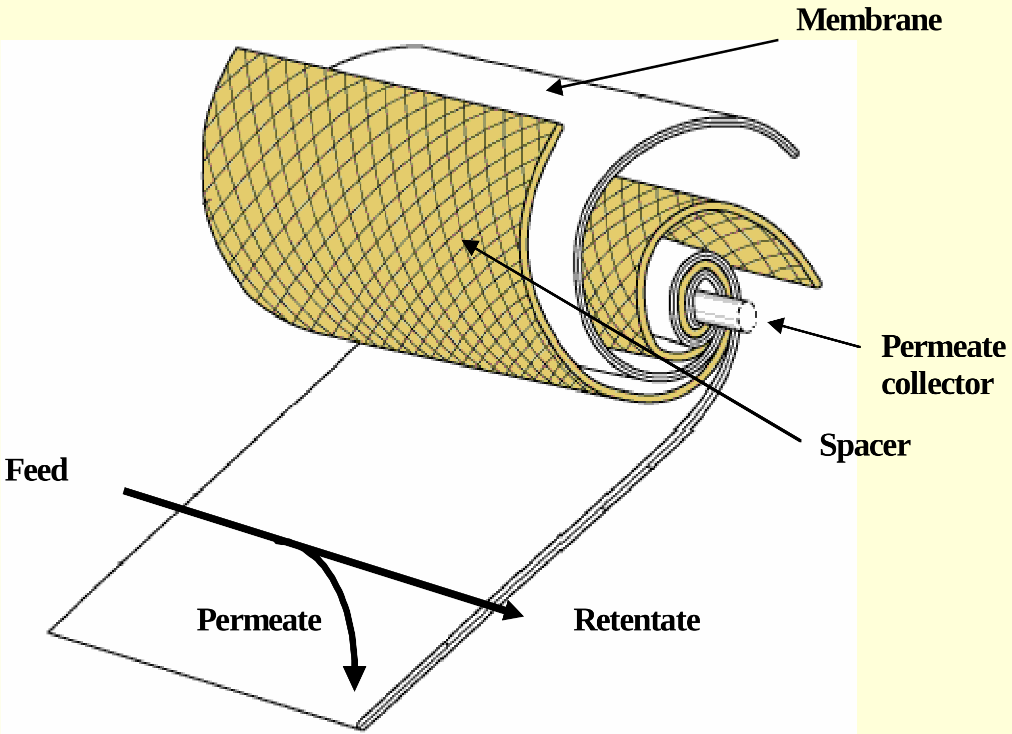


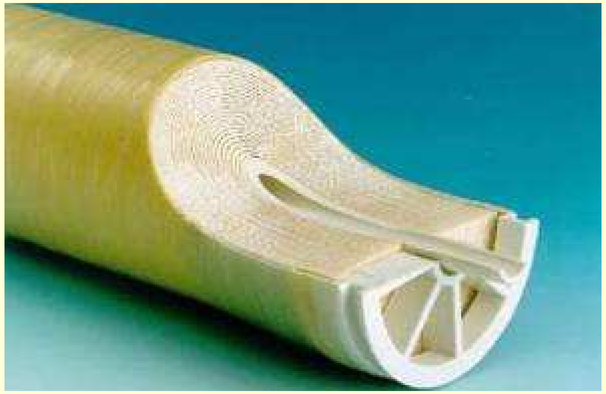
Source: H. Strathmann

Industrial Hollow Fiber Production

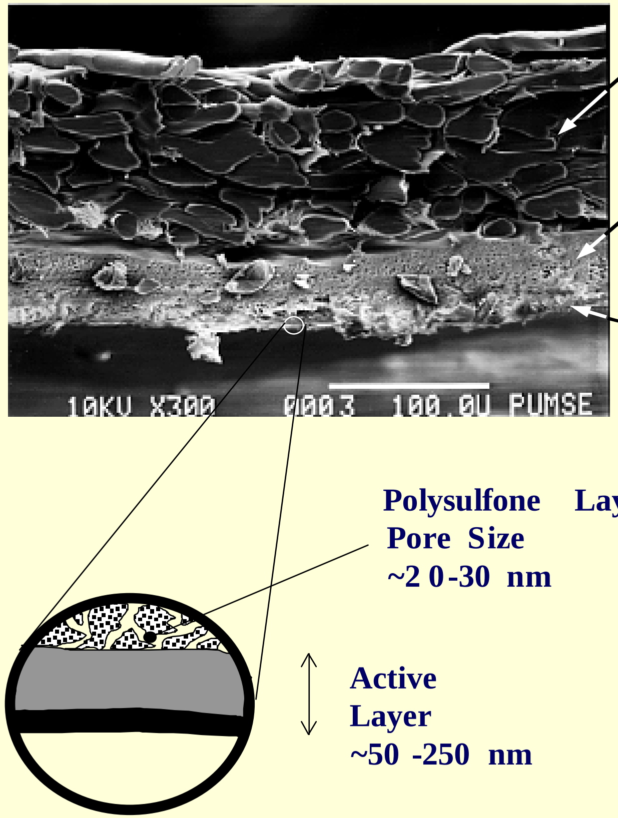
Spiral-Wound Membranes







Membrane used in RO elements



Polyester Fiber Backing ~120 µm

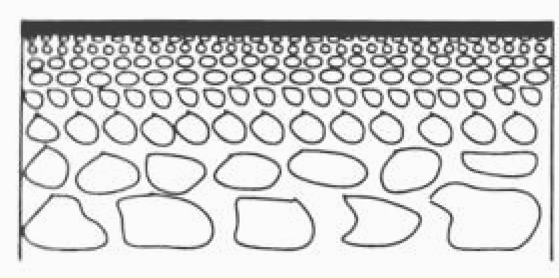
Polysulfone Support ~50 µm

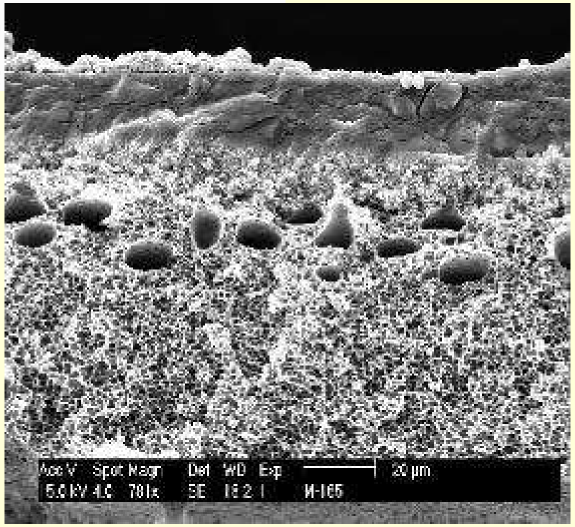
Active NF/RO Layer

Polysulfone Layer Pore Size ~20-30 nm

Active Layer ~50 -250 nm

RO spiral wound element with thin film composite membrane are used in 98% of all RO systems. These elements are made of polyamide, polysulfone, polyurethane, noryl, polypropylene, polyester, polyethilene





SEM picture of a membrane synthesized by incorporating amino groups in polymeric network with its thin-film composite structure of a thin selective layer (<20 µm) on a nanoporous support (http://engineering.osu.edu/nie/article.php?e=792&s=6&a=1).

Transport through the membranes takes place when a driven force is applied to the components in one phase. In most of the membrane processes the driving force is a pressure difference or a concentration (or activity) difference across the membrane.

Parameters such as pressure, concentration (or activity) and even temperature may be included in one parameter, the chemical potential μ.

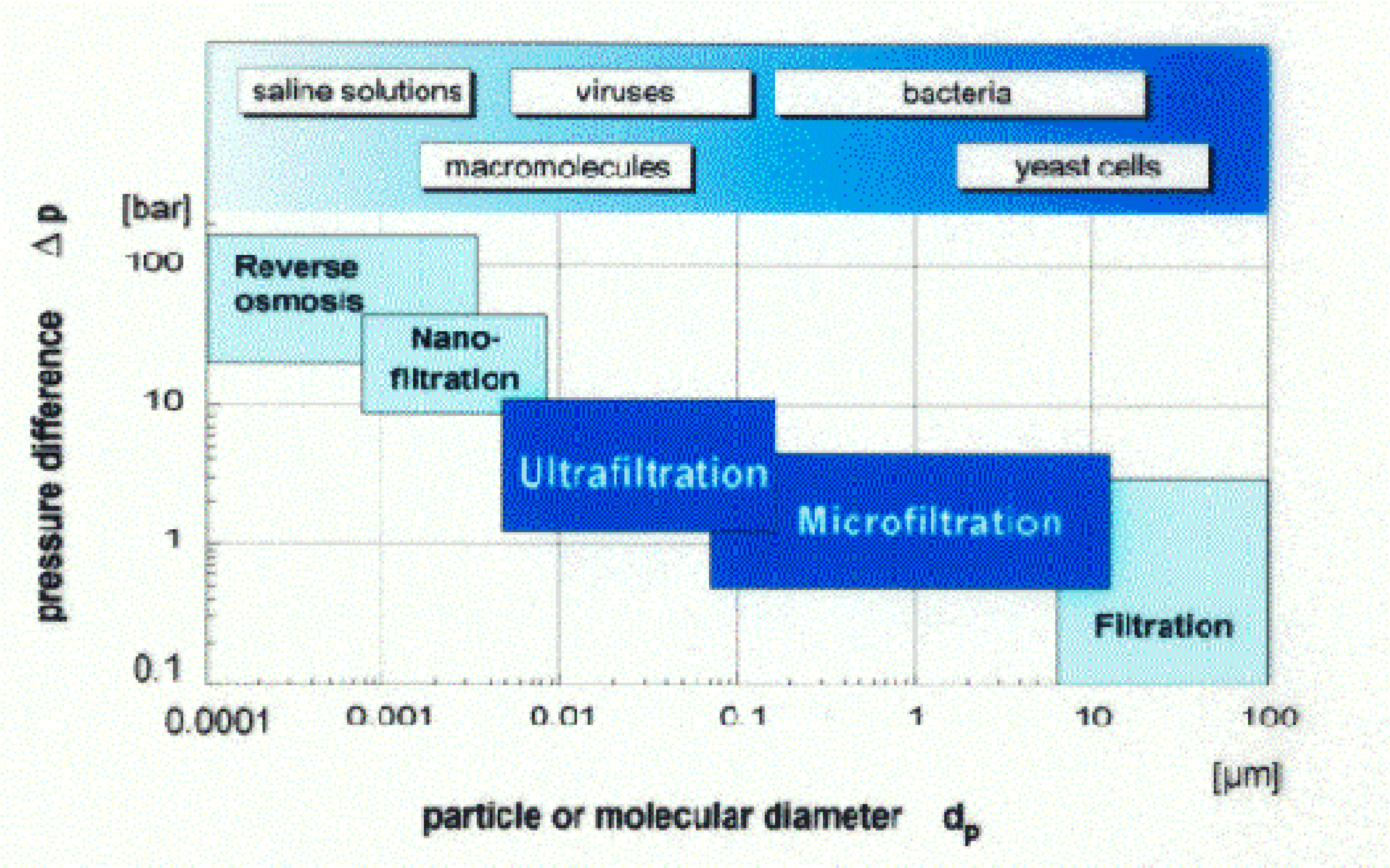
$$\mu = f\ (T, P, a \text{ or } c)$$

$$Ji = -Li \frac{d\mu i}{dx}$$

J_i **flux of a component *i***

L_i **coefficient of proportionality**

$\frac{d\mu_i}{dx}$ **gradient of chemical potential**

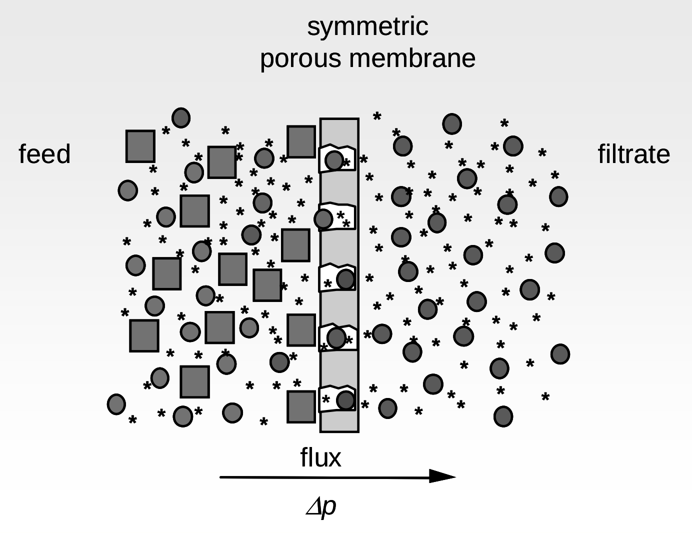


Removal threshold for various membrane processes

Comparison of various pressure driven membrane processes

Microfiltration	Ultrafiltration	Reverse Osmosis
Separation of particles (bacteria, yeasts)	Separation of macromolecules (proteins)	Separation of low MW solutes (salt, glucose, lactose)
Osmotic pressure negligible	Osmotic pressure negligible	Osmotic pressure high
Applied pressure low (< 2 bar)	Applied pressure low (1-10 bar)	Applied pressure high (10-60 bar)
Symmetric structure (not always)	Asymmetric structure	Asymmetric structure
Thickness of separating layer ≈ 10-150 µm	Thickness of actual separating layer ≈ 0.1-1.0 µm	Thickness of actual separating layer ≈ 0.1-1.0 µm
Separation based on particle size	Separation based on particle size	Separation based on differences in solubility and diffusivity

The Principle of Microfiltration



Darcy's law:

$$J = K\Delta P$$

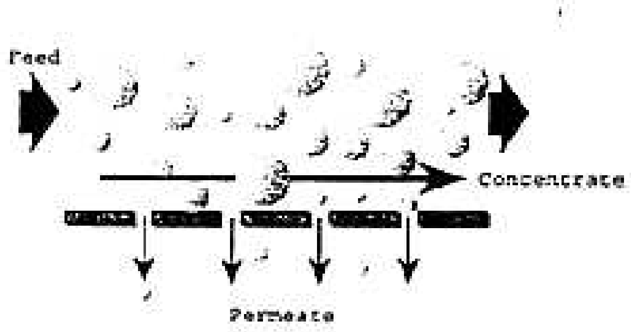
For straight capillaries membranes → Hagen-Poiseuille relationship:

$$J = \frac{\varepsilon\, r^2}{8\,\eta\,\tau}\,\frac{\Delta P}{\Delta x}$$

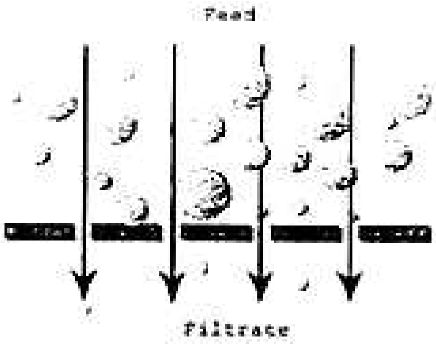
For nodular structure → Kozeny-Carman equation:

$$J = \frac{\varepsilon^3}{K\,\eta\,S^2\,(1-\varepsilon)^2}\,\frac{\Delta P}{\Delta x}$$

Process Mode

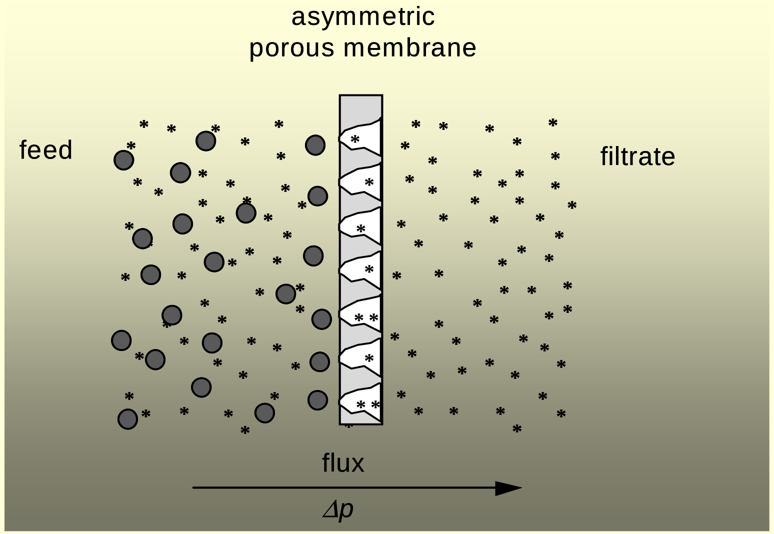


CROSS FLOW



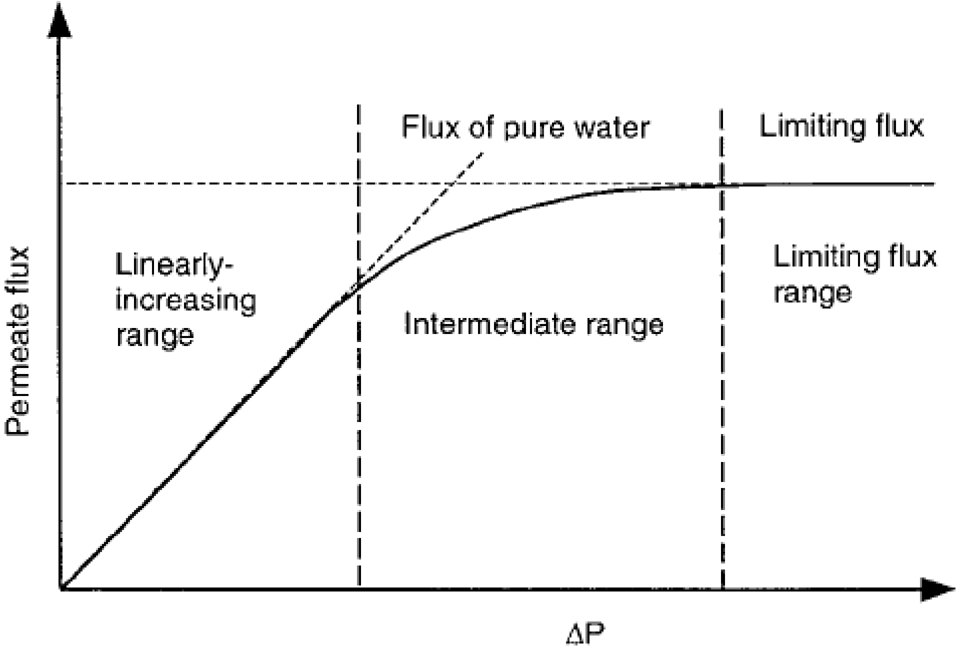
DEAD-END

The Principle of Ultrafiltration



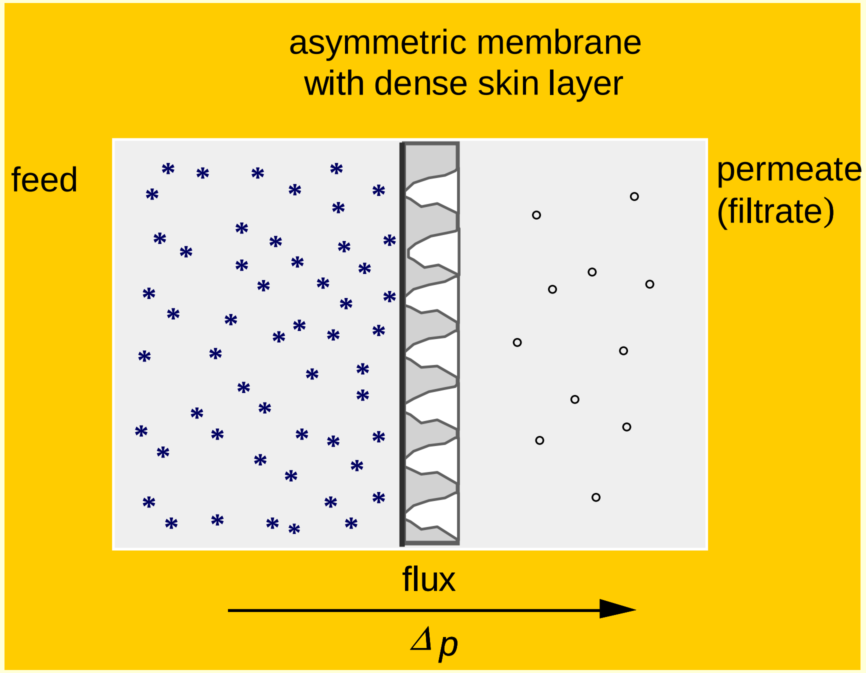
Darcy's law:

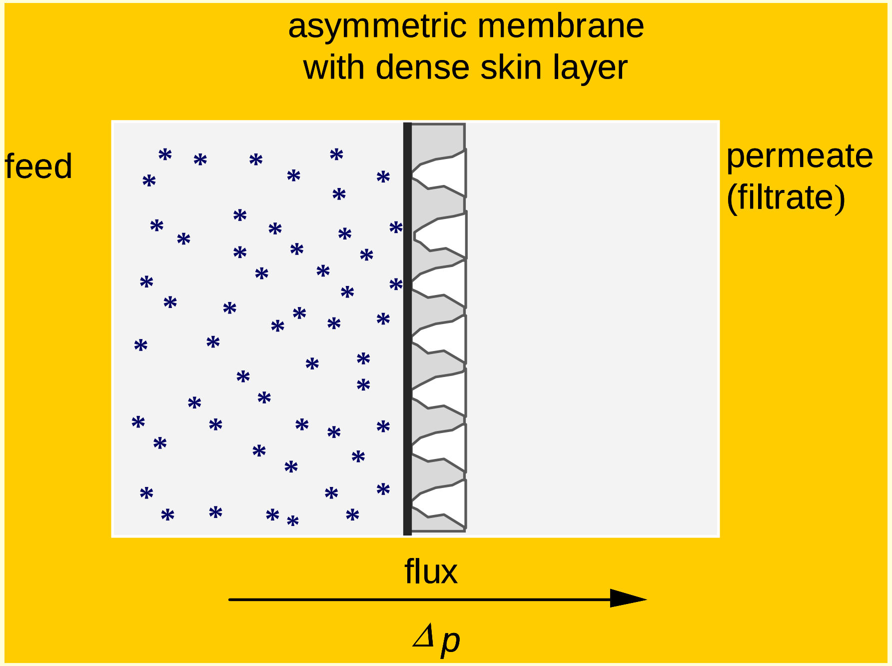
$$J = K\Delta P$$



Schematic drawing of the relationship between flux and applied pressure in UF

The Principle of Nanofiltration and Reverse Osmosis

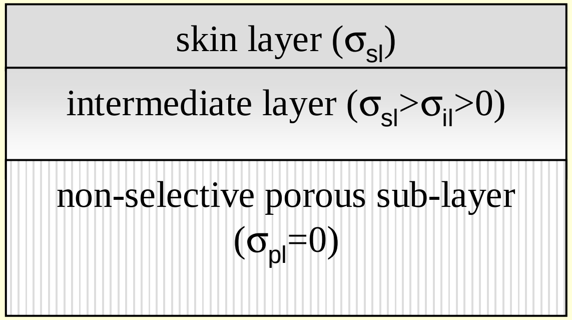




Nanofiltration

Reverse Osmosis

NF/RO membranes have in general an asymmetric or a thin-film composite structure where a porous and thin top layer acts as selective layer and determines the resistance to transport. Macroscopically these membranes are homogeneous. However, on the microscopic level, they are systems with two phases in which the transport of water and solutes takes place.



skin layer (σ_{sl})

intermediate layer ($\sigma_{sl}>\sigma_{il}>0$)

non-selective porous sub-layer
($\sigma_{pl}=0$)

Schematic presentation of a thin-film composite membrane structure with (i) the highly selective skin layer which acts as a barrier, (ii) the intermediate porous layer where the selectivity decreases to zero and (iii) the non-selective porous sub-layer.

When theories are proposed to describe membrane transport, either the membrane can be treated as a ”black box” or a physical model of the membrane can be introduced. The general description obtained in the first case gives no information on flow- and separation-mechanisms. On the other hand, the correctness of data on flow- and separation-mechanisms obtained in the second case depend on the chosen model.

The transport models can be divided into three categories:

- ***phenomenological transport models*** **which are independent of the mechanism of transport and are based on the theory of irreversible thermodynamics (irreversible thermodynamics-phenomenological transport and irreversible thermodynamics-Kedem-Spigler models),**
- ***nonporous transport models*****, in which the membrane is supposed to be nonporous or homogeneous (solution-diffusion, extended solution-diffusion and solution-diffusion-imperfection models),**
- ***porous transport models*****, in which the membrane is supposed to be porous (preferential sorption-capillary flow, Kimura-Sourirajan analysis, finely porous and surface force-pore flow and friction models).**

Phenomenological Transport Models

Irreversible Thermodynamics-Phenomenological Transport Model : **fluxes Ji are related to the forces Fj through the phenomenological coefficient Lij**

$$J_i = L_{ii}F_i + \sum_{i \neq j} L_{ij}F_j \quad \text{for} \quad i = 1, \dots, n$$

Kedem and Katchalsky's phenomenological transport equations:

$$J_v = l_p(\Delta P - \sigma\Delta\pi) \qquad J_s = \omega\Delta\pi + (1-\sigma)J_v(\overline{c}_s)_{ln}$$

Phenomenological transport equations have been rarely applied for describing RO membrane transport both because the often large concentration difference across the membranes invalidate the linear laws and because this analysis doesn't give many information regarding the transport mechanism.

Irreversible Thermodynamics-Kedem-Spigler Model

$$J_v = \frac{p_v}{\Delta x}(\Delta P - \sigma\Delta\pi)$$

$$R = \frac{\sigma\{1 - \exp[-J_v(1-\sigma)\Delta x/p_s]\}}{1 - \sigma\exp[-J_v(1-\sigma)\Delta x/p_s]}$$

As well as phenomenological transport equations also Spiegler and Kedem relationships do not give information on the membrane transport mechanism.

p_v water permeability, x coordinate direction perpendicular to the membrane, p_s solute permeability, J_v solvent flux, R retention, Δx membrane thickness, lp-ω-σ simple functions of the original phenomenological coefficient Lij.

Nonporous Transport Models

Solution-Diffusion Model:

$$J_v = A(\Delta P - \Delta\pi) \qquad J_s = B\left(c_s''' - c_s''\right)$$

with $$A = \frac{\bar{D}_v \bar{c}_v V_v}{\Re T \Delta x}$$

The solution-diffusion model assumes that (i) membrane surface layer is homogenous and nonporous and (ii) both solute and solvent dissolve in the surface layer and then they diffuse across it independently. Water and solute fluxes are proportional to their chemical potential gradient. The latter it is expressed as the pressure and concentration different across the membrane for the solvent, whereas it is equal to the solute concentration difference across the membrane for the solute.

Solution-Diffusion-Imperfection Model:

$$J_v = \underbrace{k_1(\Delta P - \Delta\pi)}_{\text{diffusion}} + \underbrace{K_3 \Delta P}_{\text{pore flow contribution to water flux}}$$

$$J_s = k_2 \Delta\pi + \underbrace{K_3 \Delta P c_s'}_{\text{pore flow of solute through the membrane}}$$

The solution-diffusion-imperfection model (SDIM) considers that small imperfections exist on the membrane surface, and solvent and solute can flow through them without any change in concentration. SDIM include pore flow as well as diffusion of solute and solvent through the membrane and it can be considered a compromise between solution-diffusion and porous models.

Porous Transport Models

Friction model considers that the transport through porous membrane occurs both by viscous and diffusion flow. The pore sizes are considered so small than the solutes cannot pass freely through the pores but friction between solute-pore wall and solvent-pore wall and solvent-solute occurs.

$$F_{ij} = -X_{ij}\left(u_i - u_j\right)$$

The frictional force F is linearly proportional to the velocity difference through a proportionally factor X called “friction coefficient” indicating the interaction between solute and pore wall. From the model, the ratio between the solute concentration in the bulk at feed (c’) and permeate (c’’) side is:

$$\frac{c_2'}{c_2''} = \frac{1+\frac{b}{K}\left[\exp\left(u\varepsilon\frac{\tau\cdot\lambda}{\varepsilon}\frac{X_{21}}{RT}\right)-1\right]}{\exp\left(u\varepsilon\frac{\tau\cdot\lambda}{\varepsilon}\frac{X_{21}}{RT}\right)}$$

Finely-porous model is a combination between viscous flow and frictional model. Its premise is to describe the transport in the intermediate region between solution-diffusion model and Poiseuille flow:

$$\frac{c_2'}{c_2''} = \frac{b}{K} + \left(1-\frac{b}{K}\right)\exp\left(-\frac{\tau\cdot\lambda}{\varepsilon}\cdot\frac{J_v}{D_2}\right)$$

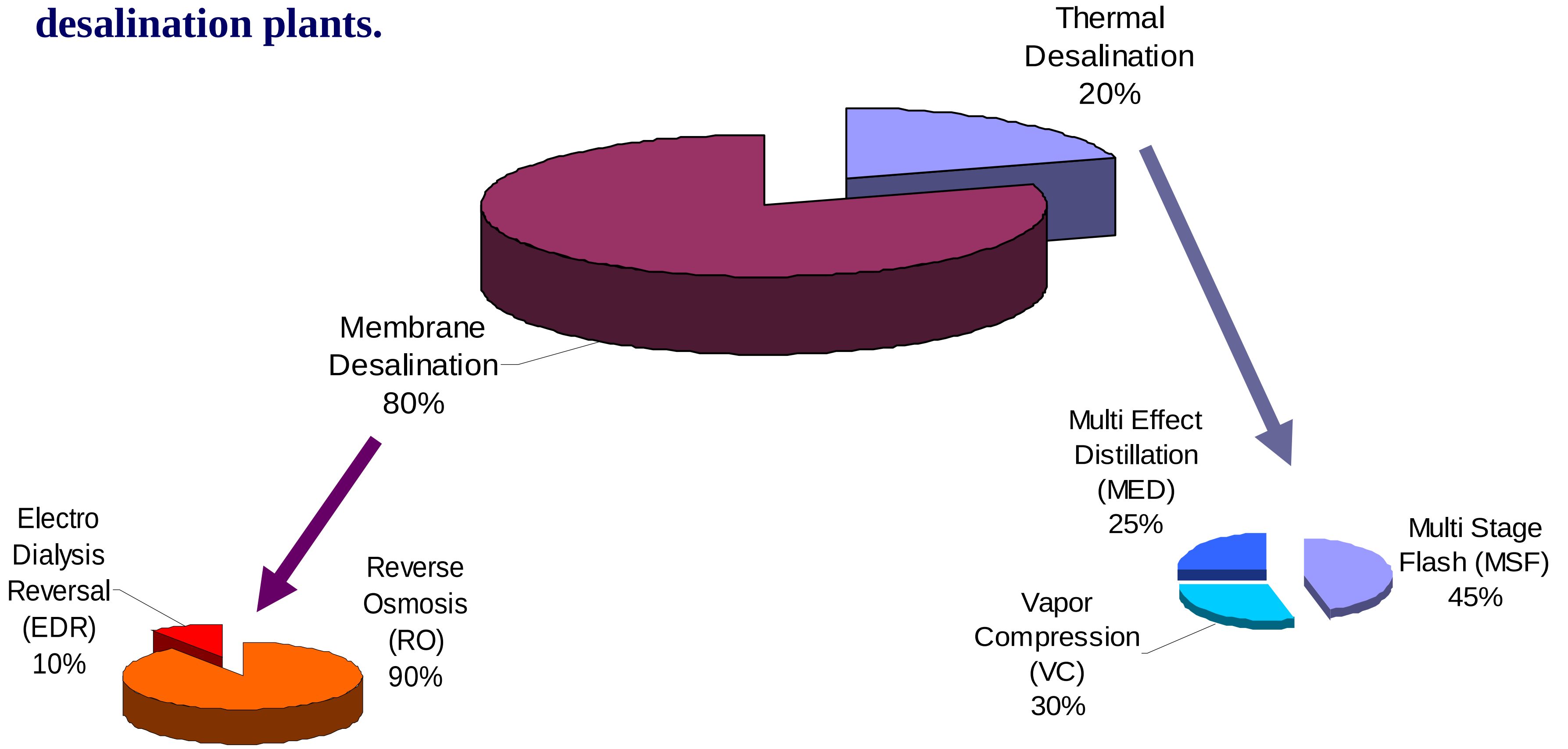
- Solution-diffusion model is reasonable when applied to very dense membranes and solutes which are almost totally rejected,
- Poiseuille flow can be used to describe the transport through porous membranes consisting of parallel pores.

Main applications of various pressure driven membrane processes

Microfiltration	Ultrafiltration	Reverse Osmosis
- Analytical applications - Sterilization (food, pharmaceutical) - Ultrapure water (semiconductors) - Clarification (beverages) - Cell harvesting and membrane bioreactor (biotechnology) - Plasmapheresis (medical)	- Dairy (milk, whey, cheese making) -- Food (potato starch and proteins) -- Metallurgy (oil-water emulsions) -- Textile - Pharmaceutical (enzymes, antibiotics)	- Desalination of brackish water and seawater -- Production of ultrapure water (electronic industry) -- Concentration of food juice and sugars (food industry), and the concentration of milk (dairy industry)

Membrane Technology and Integrated Membrane Processes for Seawater Desalination

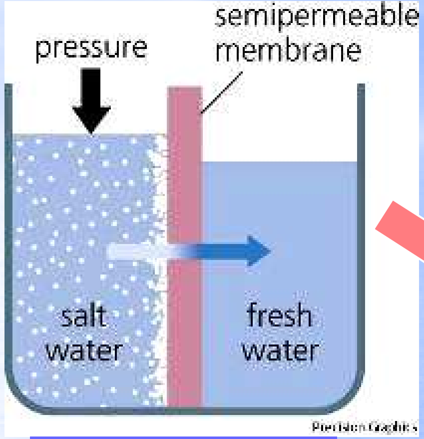
The current global installed desalination capacity is 52 million m^3/d. In the current and future sea-brackish water desalination plants, membrane based systems are the most widely used processes, whose installations account for close to 80% of all desalination facilities (around 15,000) and provide about 50% of the total capacity of desalination plants.



V. Frenkel, Desalination & Water Reuse 17 (2008) 47-50

The success of membrane desalination operations is due, in particular, to their lower energy consumption and higher recovery factor with respect to thermal processes.

Reverse Osmosis (RO): "The most economical way to desalinate water" - SIDNEY LOEB Co-Inventor of Practical Reverse Osmosis



RO phenomenon

Prof. Sidney Loeb and engineer Ed Selover remove newly manufactured RO membrane from plate-and-frame production unit *1960* **(Source: http://www.engineer.ucla.edu/history/osmosis.html).**

***RO membrane units* from El Paso Desalination Plant, Texas: the site of the world's largest *inland* desalination plant *(104,000 m^3/d)*. Production costs for the water: *less than 0.36$/m^3*.** **(*Source:* http://www.epwu.org/167080115.html)**

At the start-up of the first desalination plant at Freeport (Texas), 1961, boiling or evaporating water was used to separate water from salt. Desalination by RO entered the commercial market only in the late 1960s when the membrane manufacturing process became efficient enough to produce desalted water that was competitive with thermal processes. However, though more efficient than vaporization or distillation and requiring far less physical space for the same operation, the first plants demanded a high energy input.

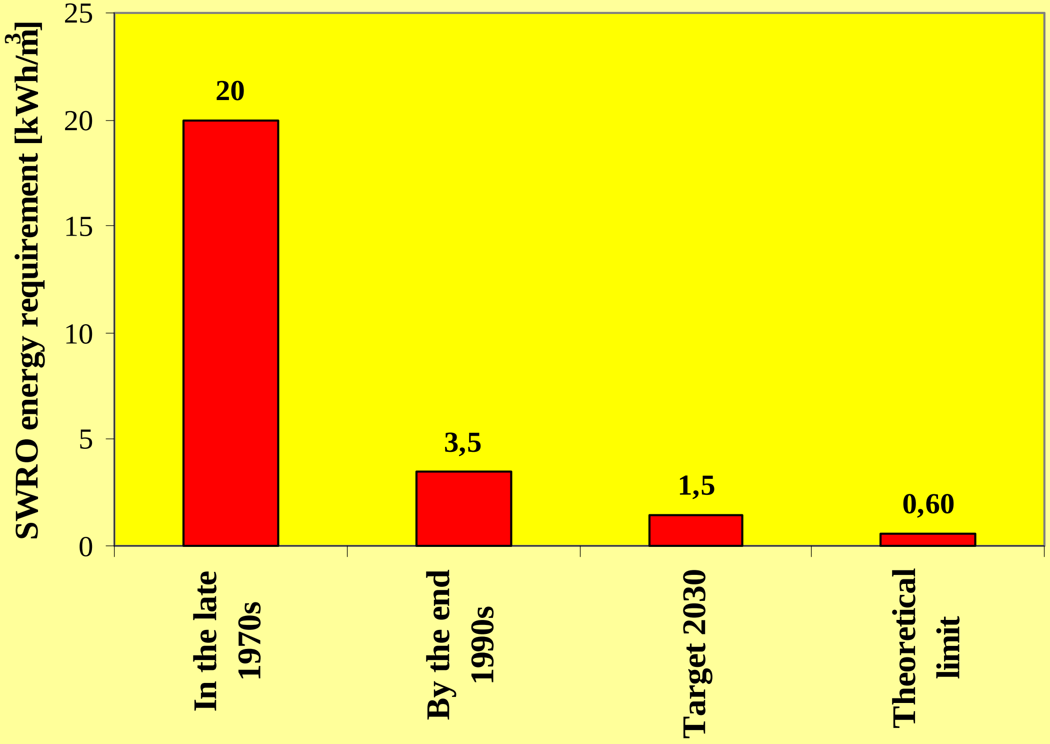
By 2000, the membrane-based desalination plants conquered the market.

This was in large part due to several advances in technology which include:

- **new low energy RO membranes with improved salt rejection and lower price,**
- **high efficiency pumps and motors**
- **more efficient Energy Recovery Systems (like Pelton turbine, Pressure Exchanger System, etc.).**

This led to sheer drops in the energy consumption and, as a consequence, in the desalted water cost.

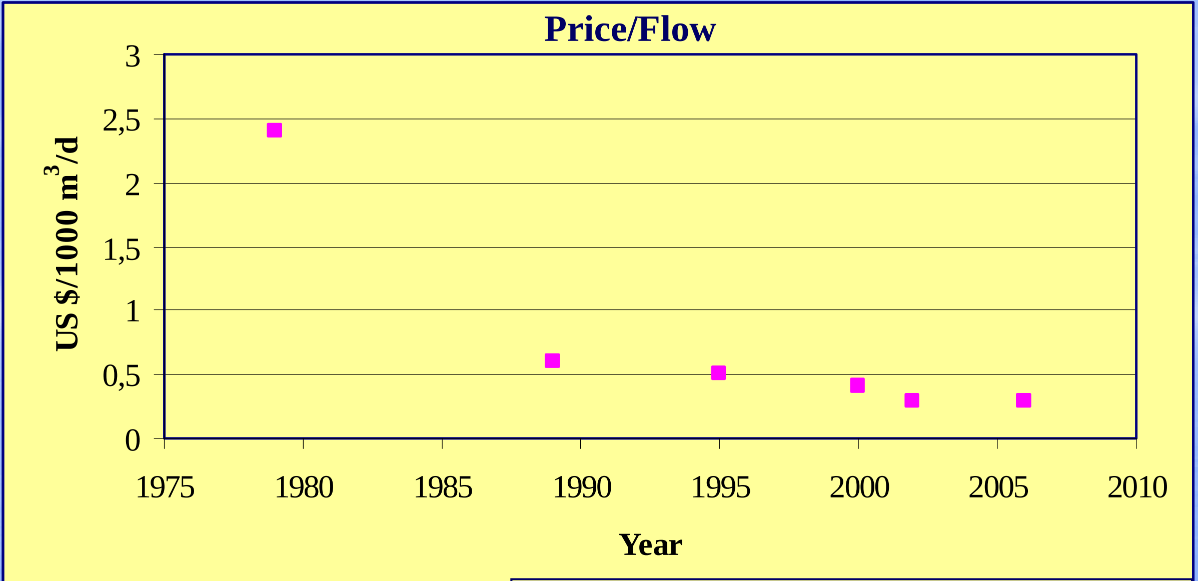
SWRO energy requirement



Today the total energy requirement (pretreatment + RO) ranges between 3 and 4 kWh/m^3. Recent studies performed in the USA by the Affordable Desalination Consortium (ADC) demonstrated that energy requirements for the RO desalination process alone can be lowered to 1.7÷1.58 kWh/m^3 through optimization of conventional RO membrane and use of highly-efficient energy recovery device. A recent Request for Research Proposal issued by the US Defense Advanced Research Projects Agency has set an objective of 1.3 kWh/m^3, while the ADC project is aiming for a consumption of 1.5 kWh/m^3, not far from the theoretical inferior limit of 0.6 kWh/m^3.

Plant/Technology/Energy consumption [kWh/m^3]	Reference
Lanzarote IV / SWRO = 3.65÷3.85	J.A.Redondo, Desalination, 138 (2001) 231-236
MSF (producing both electric power and desalted water) = 22.26 MSF (driven by steam throttled directly from boiler) = 40 SWRO = 5.09 SWRO in the Caribbean (Curacao) = 3.15 MEB (Multi Effect Boiling) = 8.14 MEB with TVC = 12.44	M.A. Darwish et al., Desalination, 152(2002) 83-92
Bodrum plant/SWRO on beach well feed and with pressure exchanger = 2.04	M. Busch, W.E. Mickols, Desalination, 165 (2004) 299-312
MED-MVC plant (Boujdour-Marocco) = 10 SWRO plants Laayoune and Boujdour-Marocco) = 5	K. Tahri, Desalination, 136 (2001) 43-48
MSF (single purpose desalination plant and power generation=0) = 47.5 SWRO = 4.5	O.A.Hamed, Desalination, 186 (2005) 207-214
MSF (Multi Stage Flash) = 20 MVC (Mechanical Vapor Compression) and LT-MEB (Low Temperature Multi Effect Boiling) = 10 SWRO plant in Yanbu, Saudi Arabia = 5.2	M.A. Darwish et al., Desalination, 220 (2008) 483-495

Trend of the price of membranes per unit capacity over the past 20 years

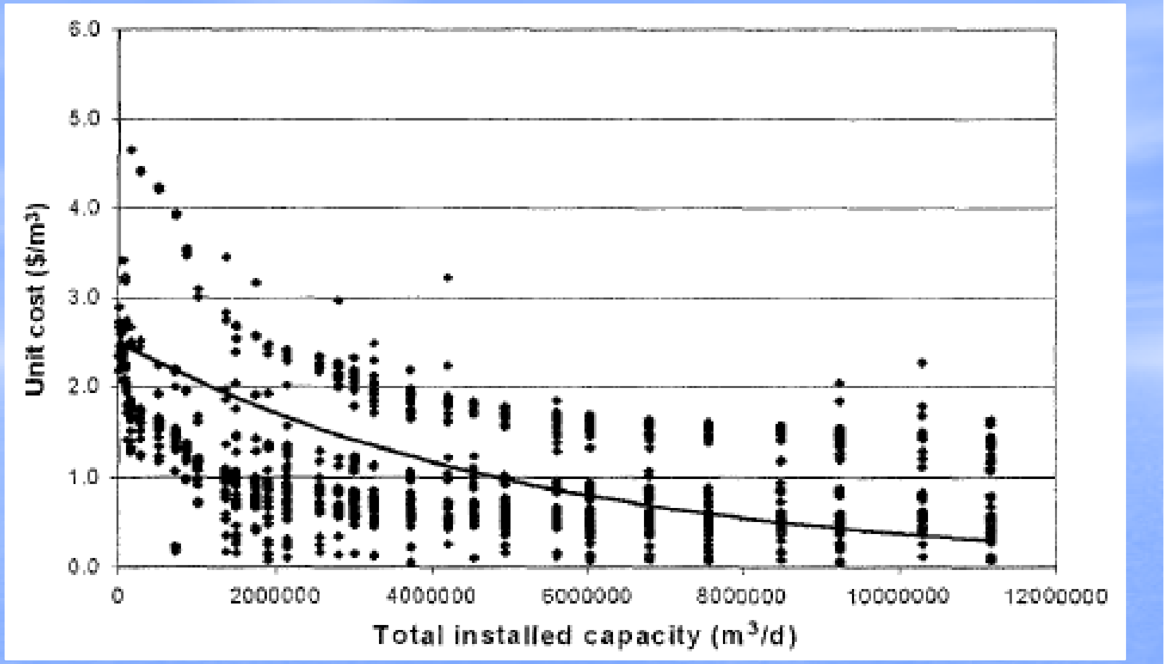


Desalination (2008). Volume 3 Issue 1, Pages: 12-14.

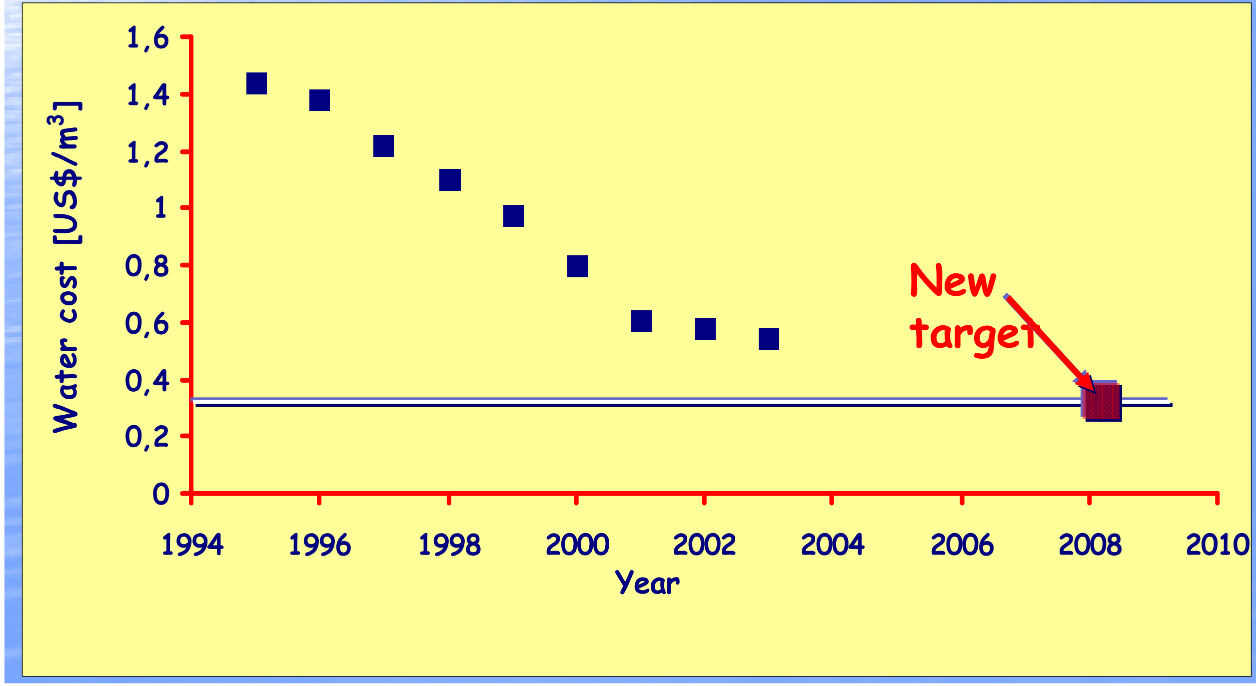
In the 1980s and 1990s the cost of the RO membranes dropped of about 50%. An example is in some SWRO elements developed by the Dow Chemical Company: the market price of a SW30HR-380 element in 1996 was about 50% that of a SW30HR-8040 element in 1985 (another SWRO membrane of nine years older, with a nominal flux lower than 25% and a salt passage lower than 33%).

Distribution of the unit costs with total installed capacity by the RO process.

Unit costs have declined with the cumulative installed capacity as a result of technological developments and experience.



Y. Zhou, R. S.J. Tol, Desalination 164 (2004) 225-240.



Unit water cost by RO over years and new target

KEY-FACTORS FOR FURTHER IMPROVEMENT OF RO DESALINATION SYSTEMS

Enhancement of water recovery factor

Costs reduction

Improvement of water quality

New brine disposal strategy

Reduction of fouling problems

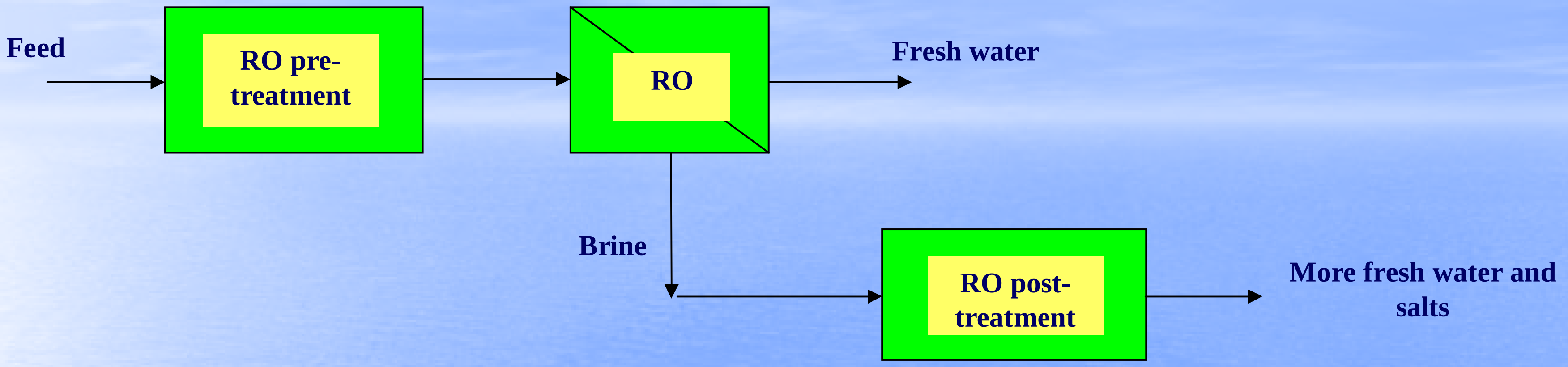
1) Integrated Membrane Systems

2) New Membrane Modules and Materials

The possibility to redesign important industrial production cycles by combining various membrane operations available in the separation and conversion units by realising *integrated membrane processes* is an attractive opportunity because of:

- **the synergic effects that can be reached;**
- **the simplicity of these units;**
- **the possibility of advanced levels of automatization.**

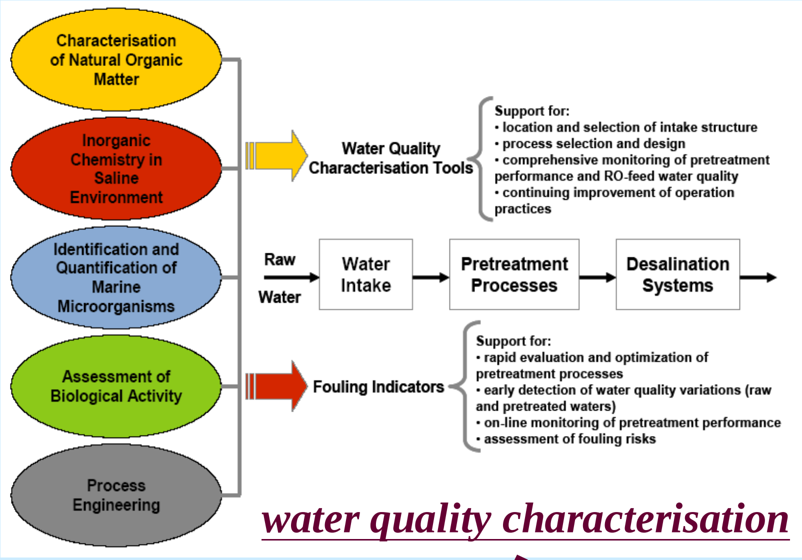
CASE 1: Integrated Membrane System for Desalination



The integration of different membrane operations for controlling and minimizing fouling phenomena and offering a reliable solution to the water shortage problem well approaching the concept of "zero-liquid-discharge" and "total raw materials utilization".

The proposed approach is based on the integration of different membrane operations in RO pre-treatment (MF/UF/Membrane Bioreactor/NF/Membrane Contactor) and post-treatment stages (MC/MD/Membrane Crystallizer/working on the concentrates) according to the philosophy of Process Intensification.

In the RO pre-treatment steps,
the integration of



Characterisation of Natural Organic Matter

Inorganic Chemistry in Saline Environment

Identification and Quantification of Marine Microorganisms

Assessment of Biological Activity

Process Engineering

Water Quality Characterisation Tools

Support for:
- location and selection of intake structure
- process selection and design
- comprehensive monitoring of pretreatment performance and RO-feed water quality
- continuing improvement of operation practices

Raw Water → Water Intake → Pretreatment Processes → Desalination Systems →

Fouling Indicators

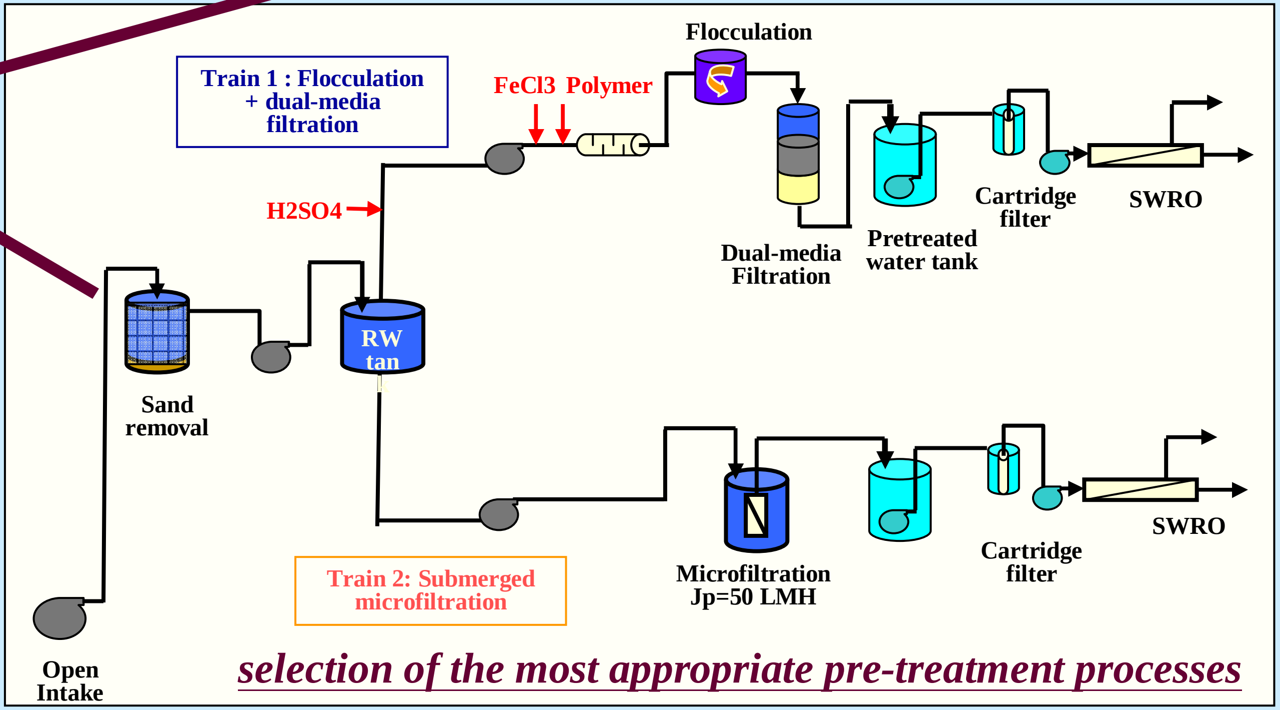
Support for:
- rapid evaluation and optimization of pretreatment processes
- early detection of water quality variations (raw and pretreated waters)
- on-line monitoring of pretreatment performance
- assessment of fouling risks

water quality characterisation

membrane cleaning strategies

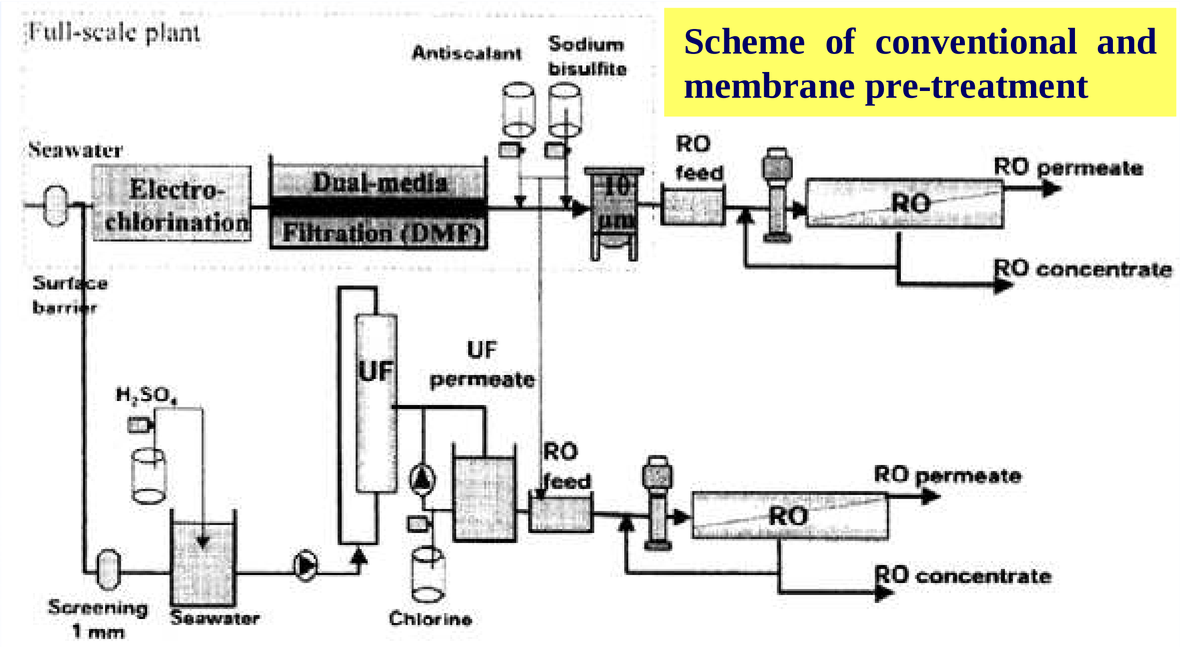
tools for RO fouling characterization and understanding

leads to the minimisation of membrane replacement needs thereby reducing the operating costs



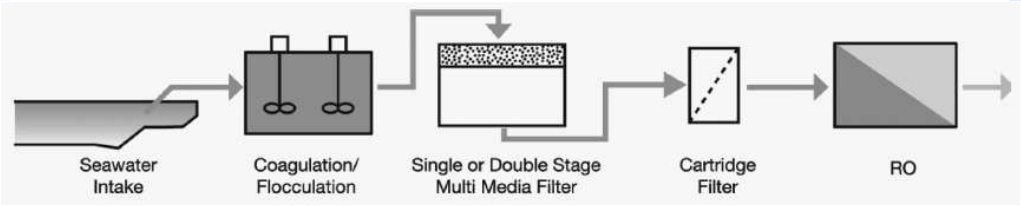
selection of the most appropriate pre-treatment processes

RO pre-treatment

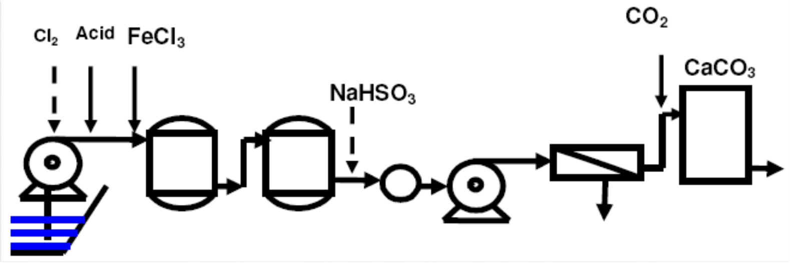


Scheme of conventional and membrane pre-treatment

Conventional pre-treatment scheme (chemical and physical)



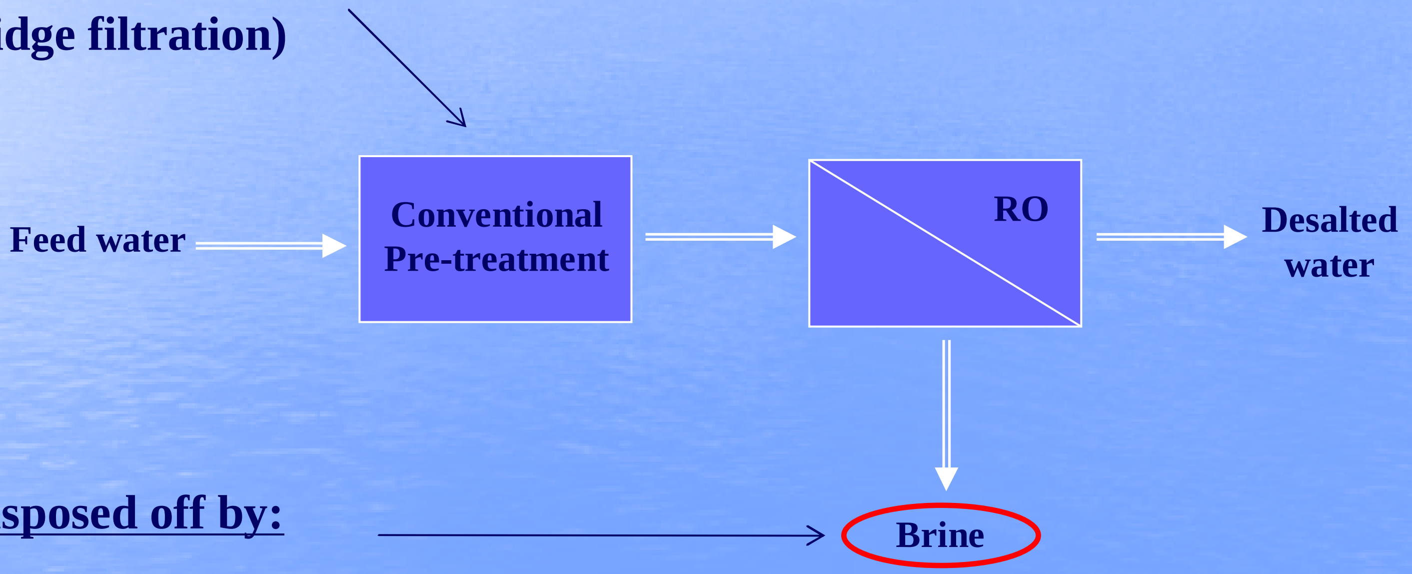
Details of a chemical-conventional pre-treatment



In the past, most RO plants used *conventional pre-treatment, which is defined as chemical* (the treatment of feed water with coagulant addition, disinfection, scale reduction, de-chlorination) *and physical pre-treatment* (sand filters followed by cartridge filters to remove and control particulate and colloidal matter) without the use of membrane technologies. However, with declining raw water quality and decreasing membrane costs, in more projects the use of *membrane pre-treatment (MF, UF, NF)* prior to RO stage is being considered as an alternative to conventional pre-treatment.

Conventional Sea Water Reverse Osmosis (SWRO) Desalination

Extensive use of chemicals (disinfection, flocculant, anti-scaling agent) and mechanical filtration units (sand filtration, media filtration, cartridge filtration)



Feed water

Conventional Pre-treatment

RO

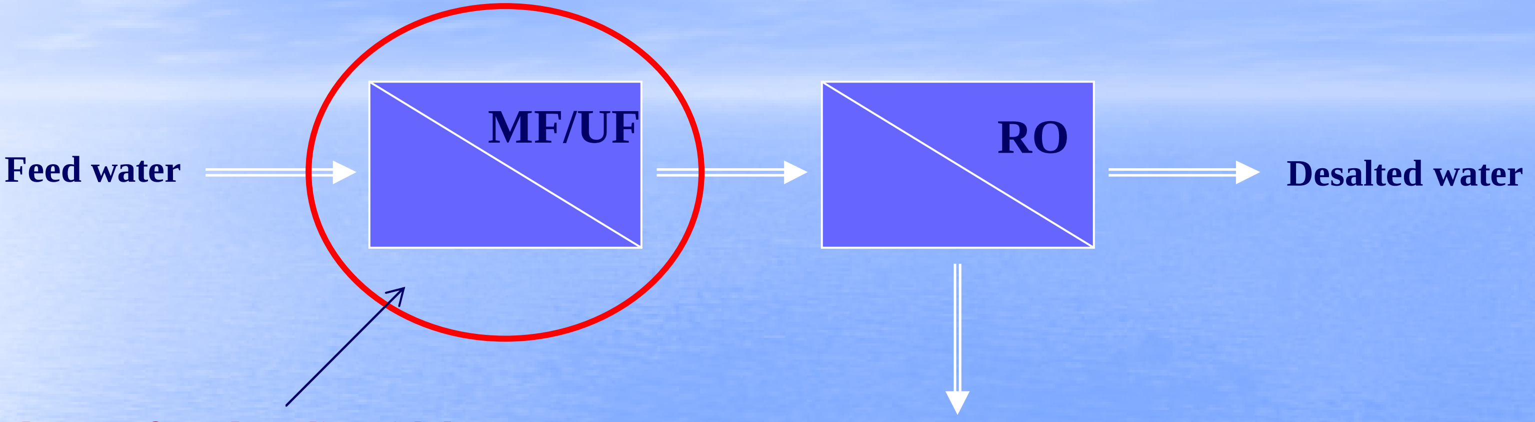
Desalted water

Brine

<u>50-60% to be disposed off by:</u>

environmental discharge (lakes, rivers, ocean and sewer)
land applications
deep well injection
evaporation pond
blending with wastewaters and power plant cooling water
thermal crystallization for landfill disposal

Membrane (MF or UF) as RO pre-treatment



- *RO feedwater of good quality* with lower COD/BOD a SDI

- *Reduction in capital and operating cost*:

✓ Elimination of fine filters in the RO systems

✓ Less membrane replacement cost (due to the lengthened membrane useful life)

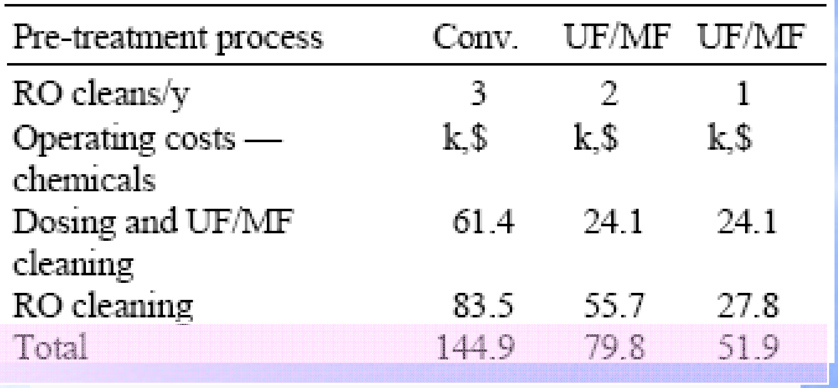
✓ Less chemical consumption cost (less chemicals are needed for disinfection, coagulation and dechlorination)

✓ Elimination of cartridge filters cost

✓ Less maintenance cost for the high pressure pump and the measuring instruments

✓ Less labor cost (less manpower is needed to operate the conventional pretreatment system and to clean the membrane and maintain the system)

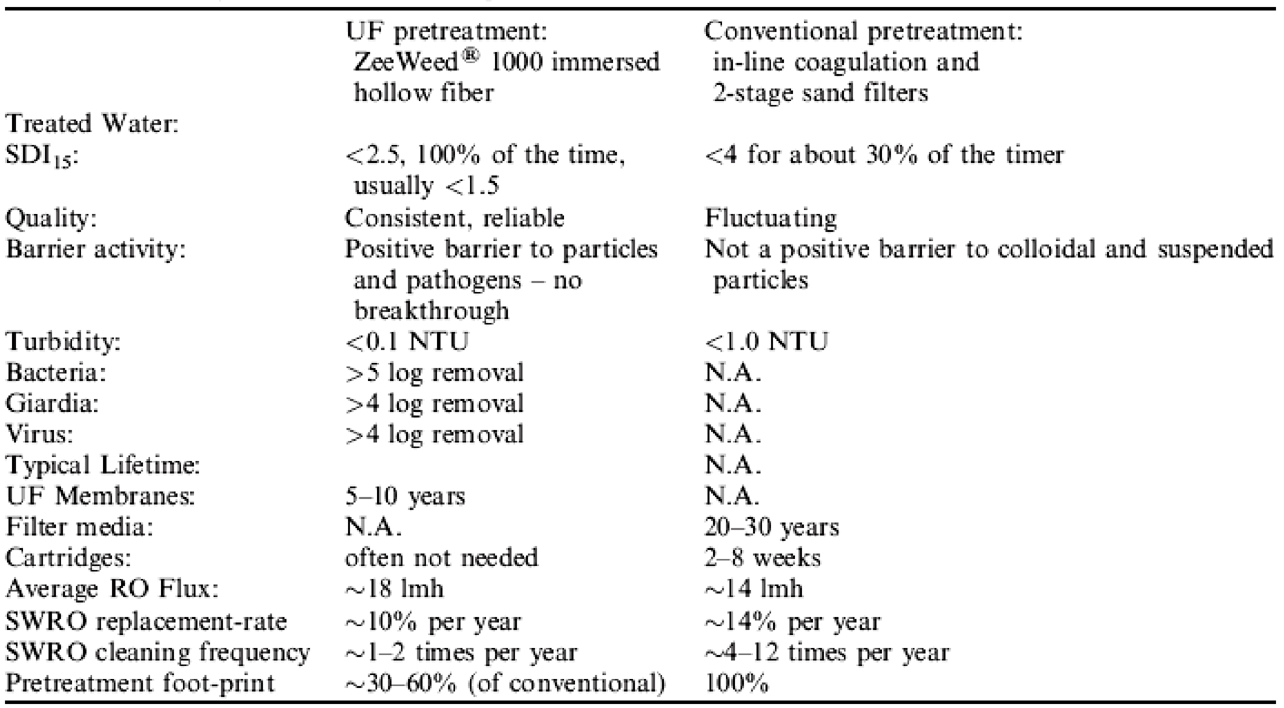
Advantages in the use of MF/UF as RO pre-treatment: some examples



Pre-treatment process	Conv.	UF/MF	UF/MF
RO cleans/y	3	2	1
Operating costs — chemicals	k,$	k,$	k,$
Dosing and UF/MF cleaning	61.4	24.1	24.1
RO cleaning	83.5	55.7	27.8
Total	144.9	79.8	51.9

G.K. Pearce, Desalination 203 (2007) 286–295.

Chemical cost comparison for different pre-treatment options



	UF pretreatment: ZeeWeed® 1000 immersed hollow fiber	Conventional pretreatment: in-line coagulation and 2-stage sand filters
Treated Water:		
SDI_{15}:	<2.5, 100% of the time, usually <1.5	<4 for about 30% of the timer
Quality:	Consistent, reliable	Fluctuating
Barrier activity:	Positive barrier to particles and pathogens – no breakthrough	Not a positive barrier to colloidal and suspended particles
Turbidity:	<0.1 NTU	<1.0 NTU
Bacteria:	>5 log removal	N.A.
Giardia:	>4 log removal	N.A.
Virus:	>4 log removal	N.A.
Typical Lifetime:		N.A.
UF Membranes:	5–10 years	N.A.
Filter media:	N.A.	20–30 years
Cartridges:	often not needed	2–8 weeks
Average RO Flux:	~18 lmh	~14 lmh
SWRO replacement-rate	~10% per year	~14% per year
SWRO cleaning frequency	~1–2 times per year	~4–12 times per year
Pretreatment foot-print	~30–60% (of conventional)	100%

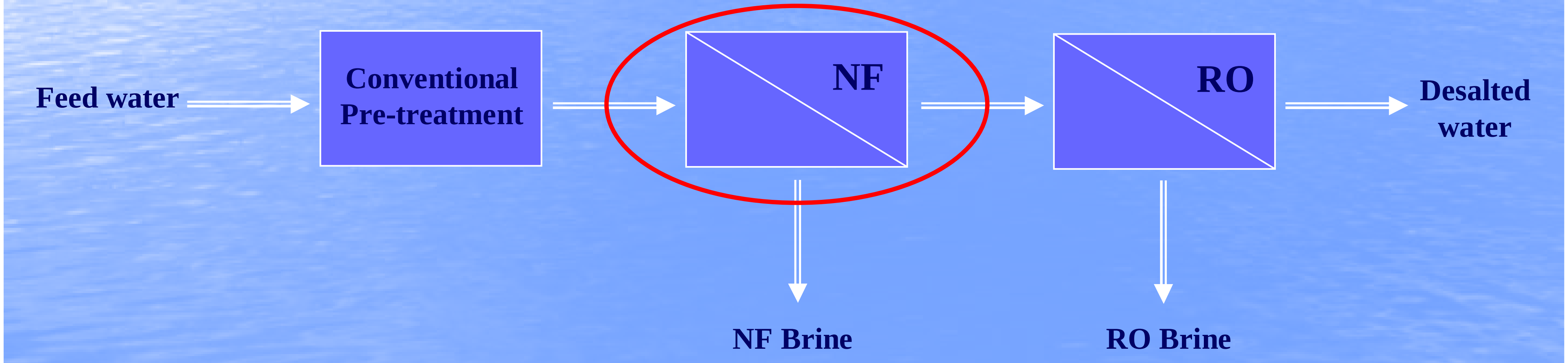
P. H. Wolf et al.,Desalination, 182 (2005) 293–300.

Comparison of the impact of UF vs conventional pre-treatment on a RO based seawater desalination plant

Nanofiltration (NF) as "Softening" Step for RO

- To reduce hardness, TDS, micro organisms, and turbidity
- Multivalent ions rejection: ~ 90%
- Monovalent ions rejection: 10-50%

- Lower osmotic pressure, so that the RO unit can operate at lower pressure
- Higher recovery factor than conventional RO
- Lower desalted water cost than conventional RO
- Process more environmentally friendly (because less additives are needed)



Feed water

Conventional Pre-treatment

NF

RO

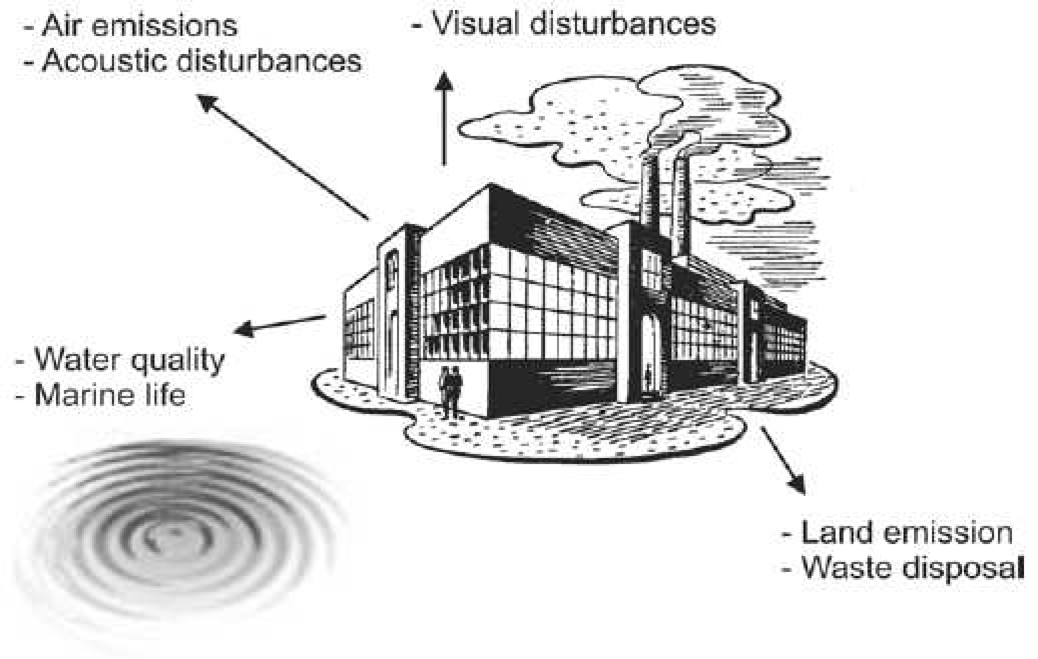
Desalted water

NF Brine

RO Brine

RO post-treatment

Environmental impact of water treatment processes



C. Fritzmann et al., Desalination 216 (2007) 1–76.

Water treatment processes are positively contributing to solve the problem of water quality and shortage but, at the same time, they cause locally some negative impacts on the environment that need to be minimized: noise is emitted, energy is consumed and highly concentrated brine as well as waste membranes have to be discharged. Special attention has to be paid to the way brine is discharged to make a desalination project environmentally sound.

RO
post-treatment

Brine composition

- backwash water from physical pre-treatment (high loads of solids, containing biological, mineral and organic matter),

- saline concentrate from the reverse osmosis separation unit, often containing anti scalants

- membrane cleaning solutions

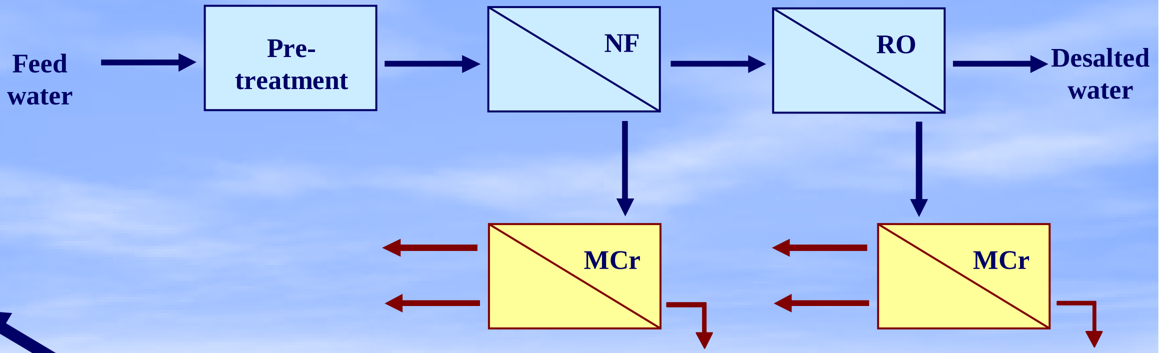
Options for brine disposal

For desalination plant located close to the shore discharge into the open sea is considered to be the least expensive option.

For desalination plants not located close to the shore several al options are available:

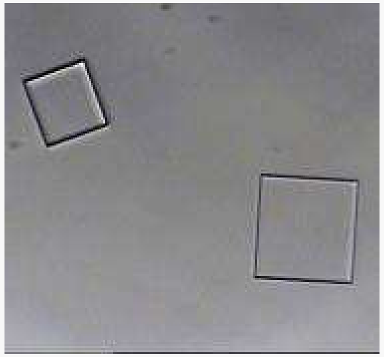
- **discharge into solar evaporation ponds,**
- **disposal to wastewater systems,**
- **land application (spray irrigation, percolation ponds),**
- **injection into deep saline aquifer (non drinking water aquifer),**
- **disposal onto land surface,**
- **disposal into the sea through long pipeline systems.**

Membrane Contactors for NF/RO post-treatment

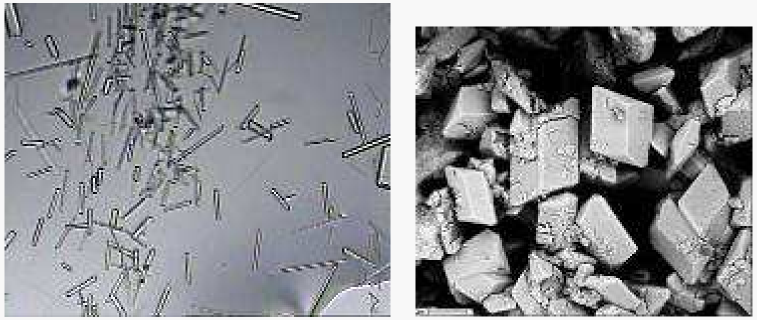


In the post-treatment stages, MD/MCr working on the concentrates for

increasing recovery factor

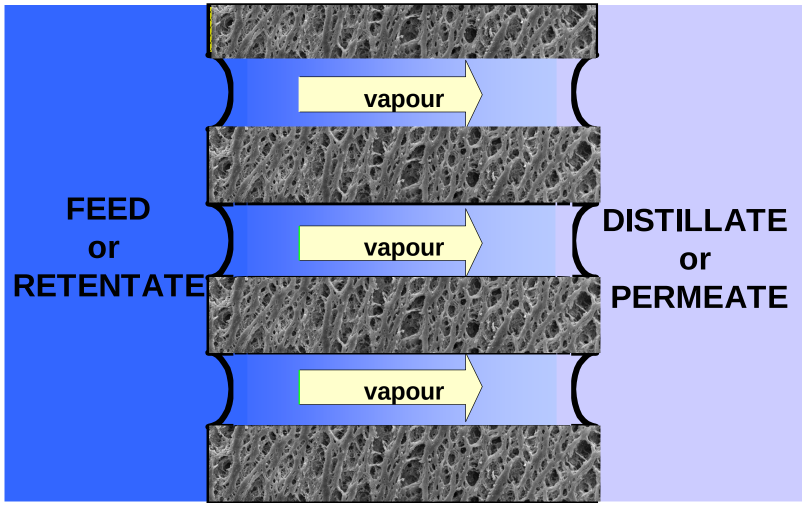


recovering the crystals **dissolved in the highly streams of the desalination plants (NaCl, $CaCO_3$, epsomite, etc.)**



reducing brine disposal problem

Membrane Contactor Technology



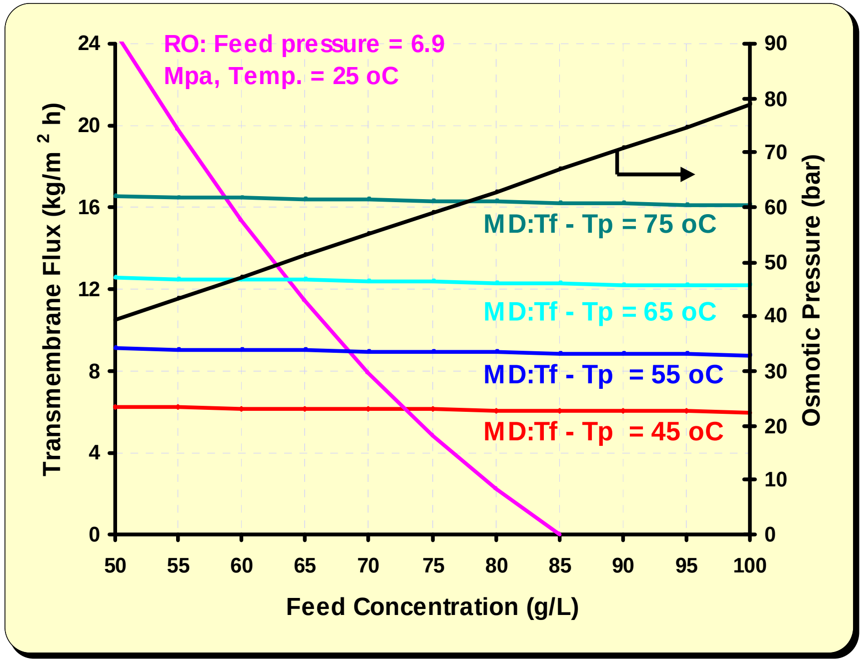
MC principle

➢ **Volatile compounds evaporate at the interface of a microporous hydrophobic membrane, diffuse and/or convect across the membrane, and are condensed and/or removed on the opposite side (permeate or distillate) of the system.**

Driving force: ***partial pressure difference***

$$J = \Phi\,\Delta p(T,c)$$

✓ **The process is not limited by concentration polarization phenomena as it is the case in pressure driven operations → pure water can also be obtained from highly concentrated feeds with which RO cannot operate.**

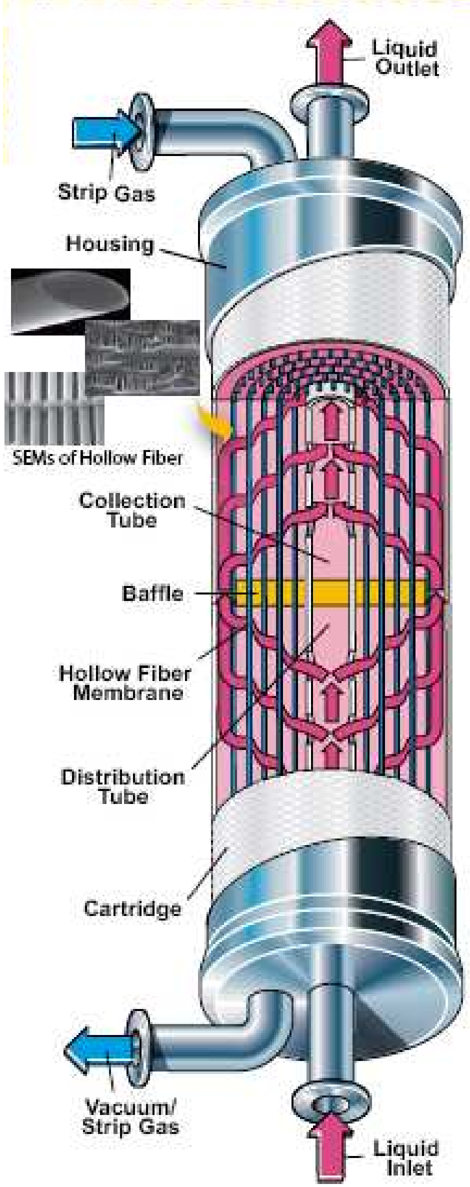


Membrane Contactors: techniques that well fit in *Process Intensification Strategy*

ADVANTAGES	
- High interfacial area per volume unit ***- Reduced size of modules*** **- No dispersion between phases** **- No flooding, loading, foaming** **- Wide range of operating flowrates**	***- Low operating temperatures*** **- Possibility to carry out simultaneously reaction and separation** **- Flexibility, easy scale up, control and automatization** **- Modular design, no moving parts** **- Plastic modules, no corrosion**

MEMBRANE CONTACTORS	CONVENTIONAL UNIT OPERATIONS
Membrane distillation and osmotic distillation	**Distillation columns, evaporators**
Membrane crystallizers	**Crystallizers**
Membrane strippers/scrubbers	**Packed and bubble columns**
Membrane extractors	**Packed columns, mixer-settler, centrifugal devices**
Supported liquid membranes	**Packed columns, mixer-settler, centrifugal devices**
Membrane emulsifiers	**High pressure homogenizers**
Phase transfer catalysis	**Chemical reactors**

MC MODULES



Source: http://www.liqui-cel.com

MD Serie (Microdyn)

Liqui-Cel Membrane Contactors

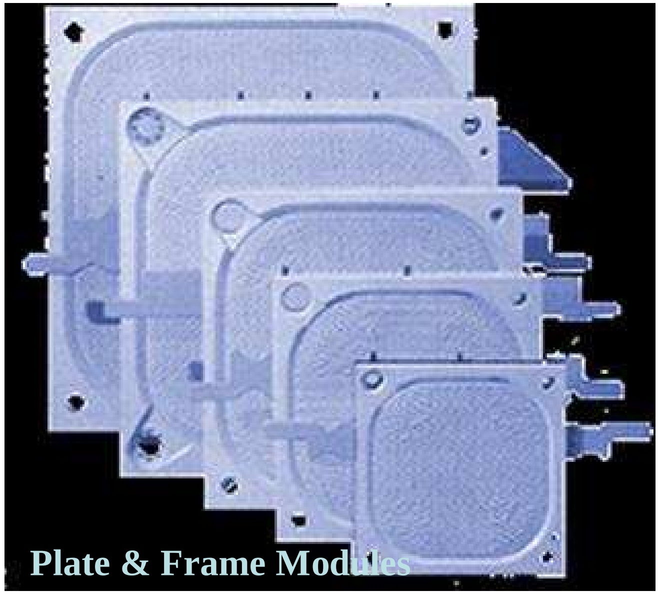


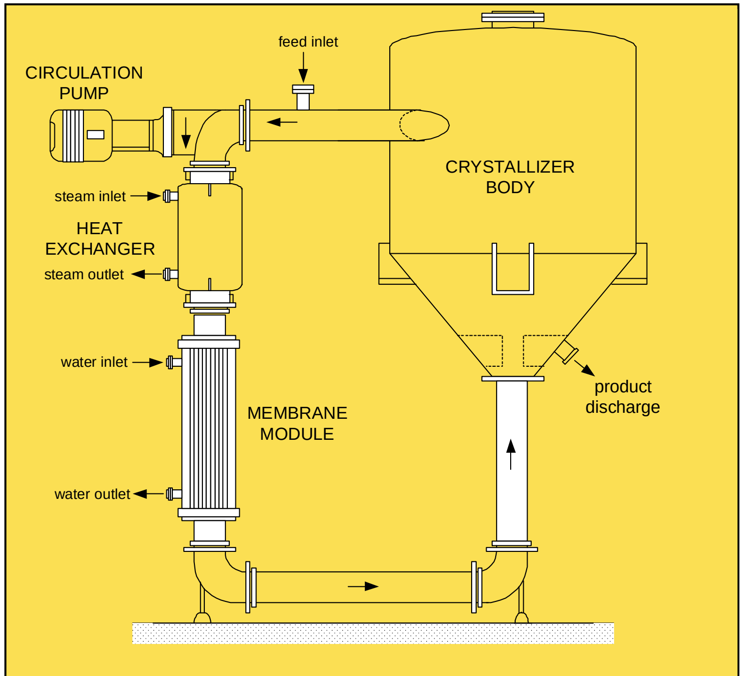
Plate & Frame Modules

Membrane contactor technology can be used in water treatment processes for…

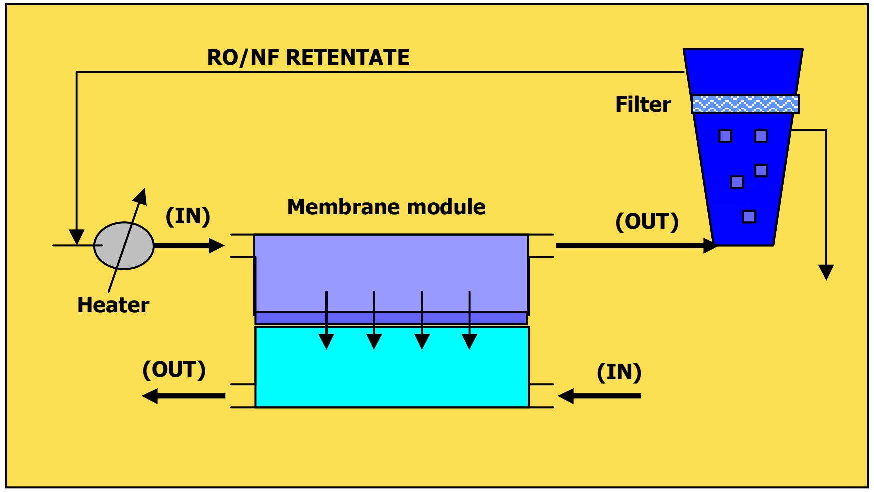
- reducing O_2 and CO_2 dissolved avoiding the final use of chemicals. In particular it can be used for decreasing the amount of dissolved CO_2 which affects the pH and the conductivity of the water
- achieving a bubble-free efficient water ozonation as well as an efficient oxidation for converting As(III) in As(V)
- treatment of polluted water (by using Membrane Distillation (MD))
- increasing water recovery factor and for reducing brine disposal problem (by using Membrane Distillation (MD) and Membrane Crystallization (MCr) techniques).

E. Drioli et. al., *Membrane Contactors: Fundamentals, Applications and Potentialities*, Membrane science and technology, Elsevier, 2006.
F. Macedonio, E. Drioli, *Pressure-driven membrane operations and MD technology integration for water purification*, Des., 2007.

Membrane Crystallization Technology



Membrane Crystallizer (MCr)



MCr process

- MCr is characterized by the separation of the two crucial steps of a crystallization process: the solvent evaporation and the crystallization. The evaporation occurs inside the membrane module while the crystallization occurs inside a separate tank on the retentate line.

Salts precipitation

The salts precipitation occurs when the solution is supersaturated. Unless a solution is supersaturated, crystals can neither form nor grow.

Supersaturation refers to the quantity of solute present in solution compared with the quantity which would be present if the solution were kept for a very long period of time with solid phase in contact with the solution. The latter value is the equilibrium solubility at the temperature and pressure under consideration. Therefore, the potential salts precipitation can be predicted by the comparison between the solubility product (Ksp) and the ionic product (IP):

- if $K_{sp} > (IP)$ the solution is not saturated and the precipitation doesn't occur;
- if $K_{sp} = (IP)$ the solution is saturated;
- if $K_{sp} < (IP)$ solid will precipitate until the saturation concentration is reached.

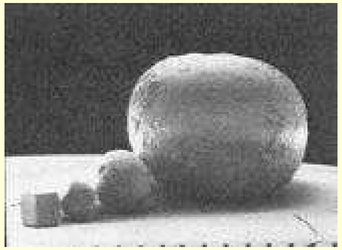
Advantages of Membrane Crystallization compared to traditional techniques (1)

- ✓ **High specific area for mass transfer**
- ✓ **Optimal control of the supersaturation level**
- ✓ **Shorten induction periods**
- ✓ **High values of the crystal growth rate at low supersaturation**
- ✓ **Possibility to act on the heterogeneous nucleation choosing appropriate polymeric membrane**

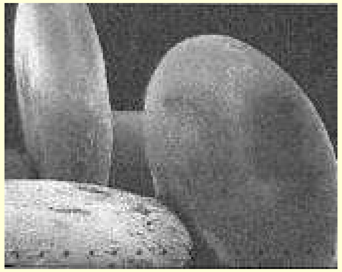
Advantages of Membrane Crystallization compared to traditional techniques (2)

NaCl from a membrane crystallizer

NaCl from a Forced Circulation crystallizer



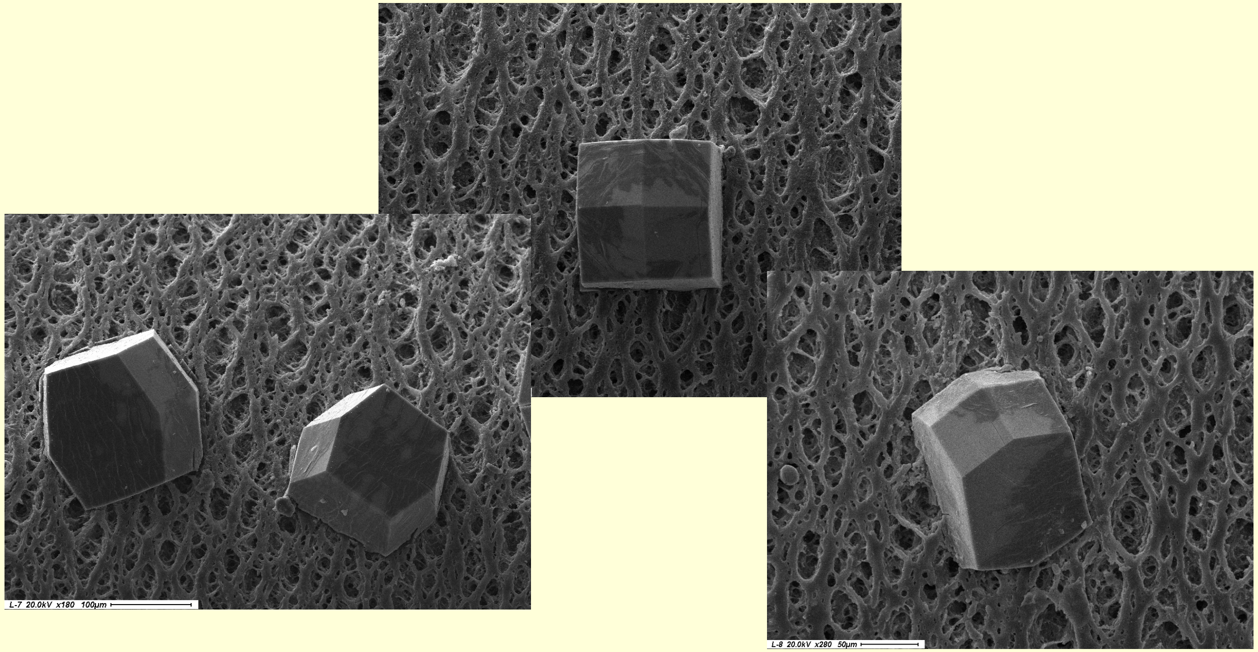
NaCl from a Draft Tube Buffled crystallizer



NaCl crystals grown in a rotating flow

✓ **Well ordered organization of the molecules, finally resulting in the formation of crystals with better structural properties, when working under forced solution flow regime**

Advantages of Membrane Crystallization Technique (3)



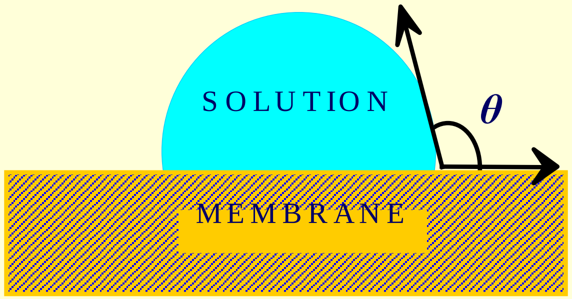
Lysozyme crystals grown on PP microporous hydrophobic membrane

✓ **The presence of the polymeric membrane increases the probability of nucleation with respect to other locations in the system (heterogeneous nucleation)**

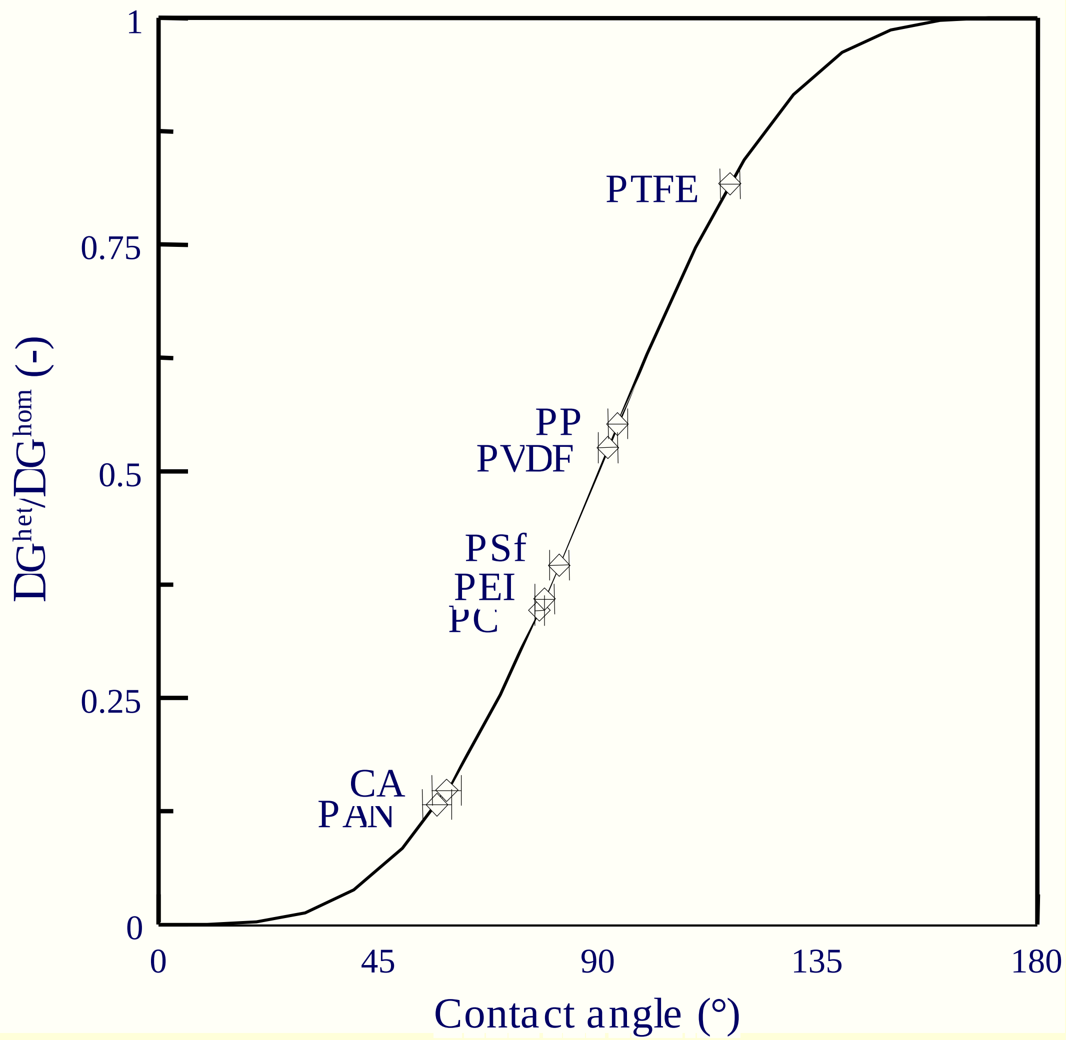
G. Di Profio, E. Curcio, E. Drioli, Journal of Crystal Growth, 257 (2003) 359-369

Reduction in the free energy of nucleation as a function of the contact angle with the polymeric surface

The <u>hydrophobic character</u> of the material is strictly associated with the activation energy of the nucleation, which is the primer of the crystallization processes



CA: cellulose acetate;
PAN: polyacrylonitrile;
PC: polycarbonate;
PET: polyetherimide;
PES: polyethersulfone;
PP: polypropylene;
PSf: polysulfone;
PTFE: polytetrafluoroethylene;
PVDF: polyvinylidenefluoride

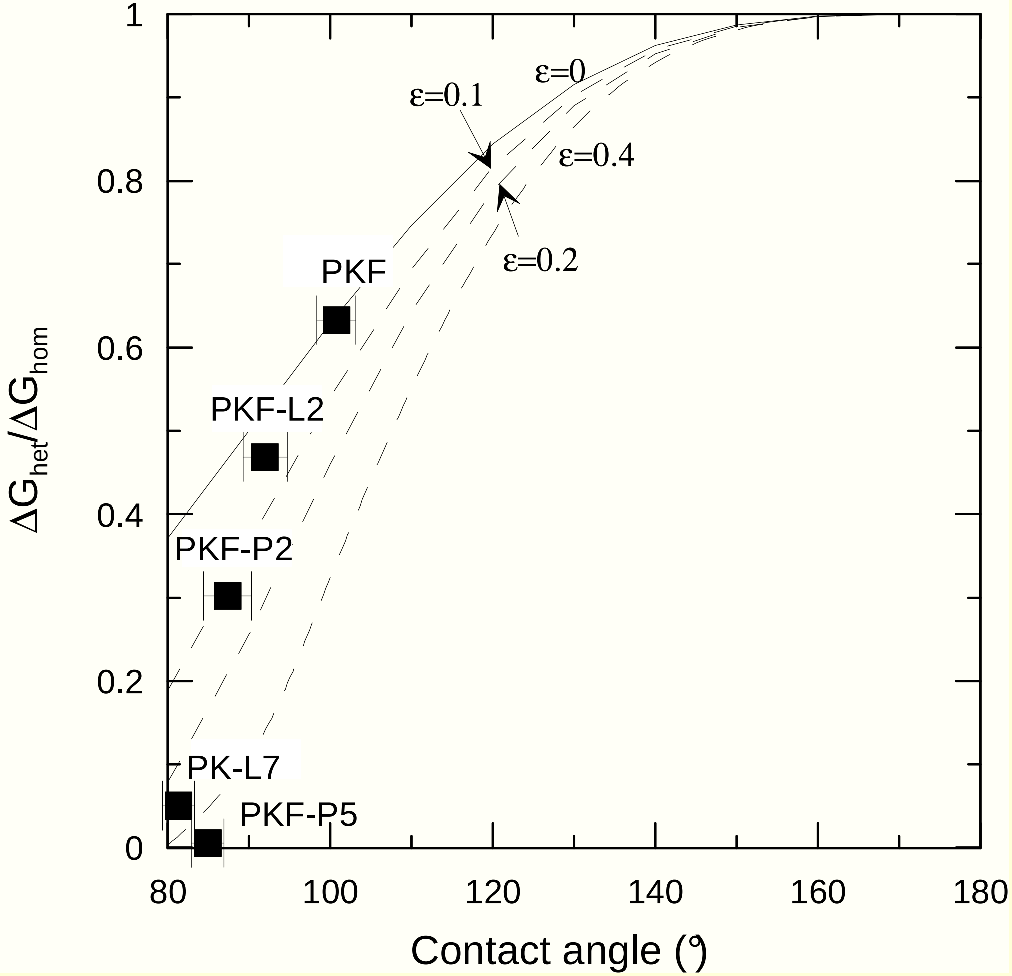


E. Curcio, E. Fontananova, G. Di Profio, E. Drioli, *Journal of Physical Chemistry* 2006, *B110*, 12438.

$\Delta G_{het}/\Delta G_{hom}$ ratio as a function of the contact angle at different porosity (ε)

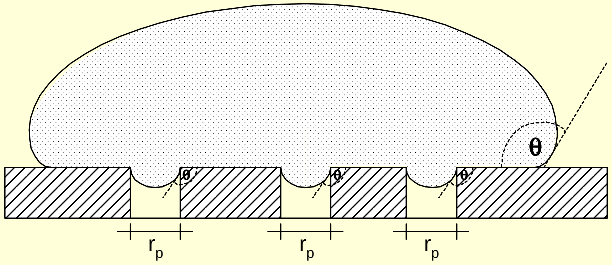
For porous surfaces …

$$\frac{\Delta G^{*}_{het}}{\Delta G^{*}_{\text{hom}}} = \frac{1}{4}(2+\cos\theta)(1-\cos\theta)^2\left[1-\varepsilon\frac{(1+\cos\theta)^2}{(1-\cos\theta)^2}\right]^3$$



Membrane	Porosity (ε)
PKF	$6.0\cdot10^{-3}$
PKF-L2	$4.3\cdot10^{-2}$
PKF-P2	$1.1\cdot10^{-1}$
PK-L7	$2.7\cdot10^{-1}$
PKF-P5	$5.4\cdot10^{-1}$

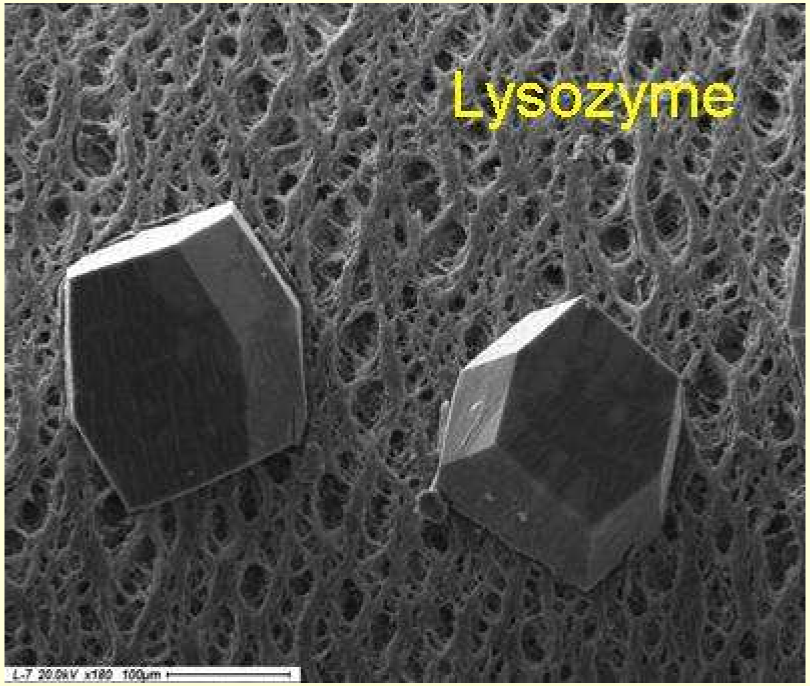
ε = pore surface/total membrane surface

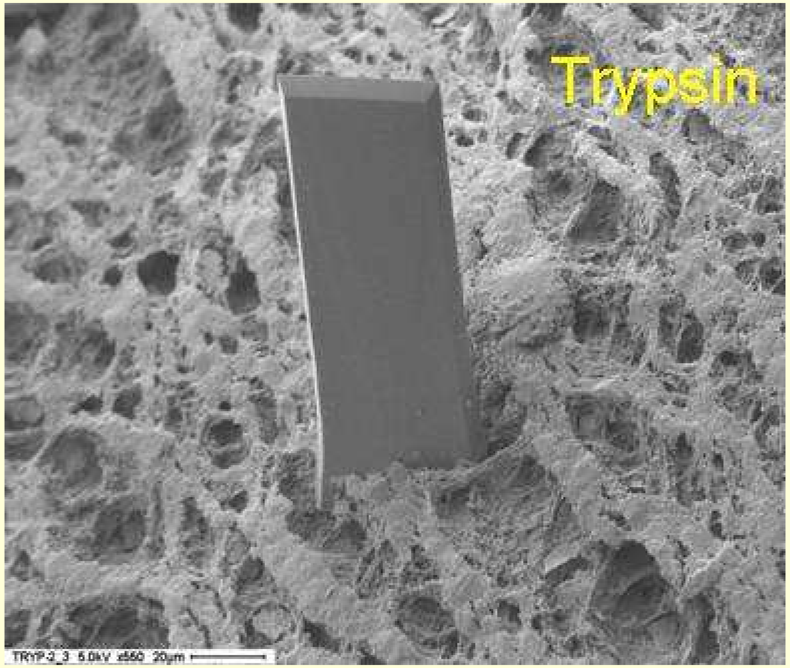


E. Curcio, E. Fontananova, G. Di Profio, E. Drioli, *Journal of Physical Chemistry* 2006, *B110*, 12438.

Advantages of Membrane Crystallization Technique (4)

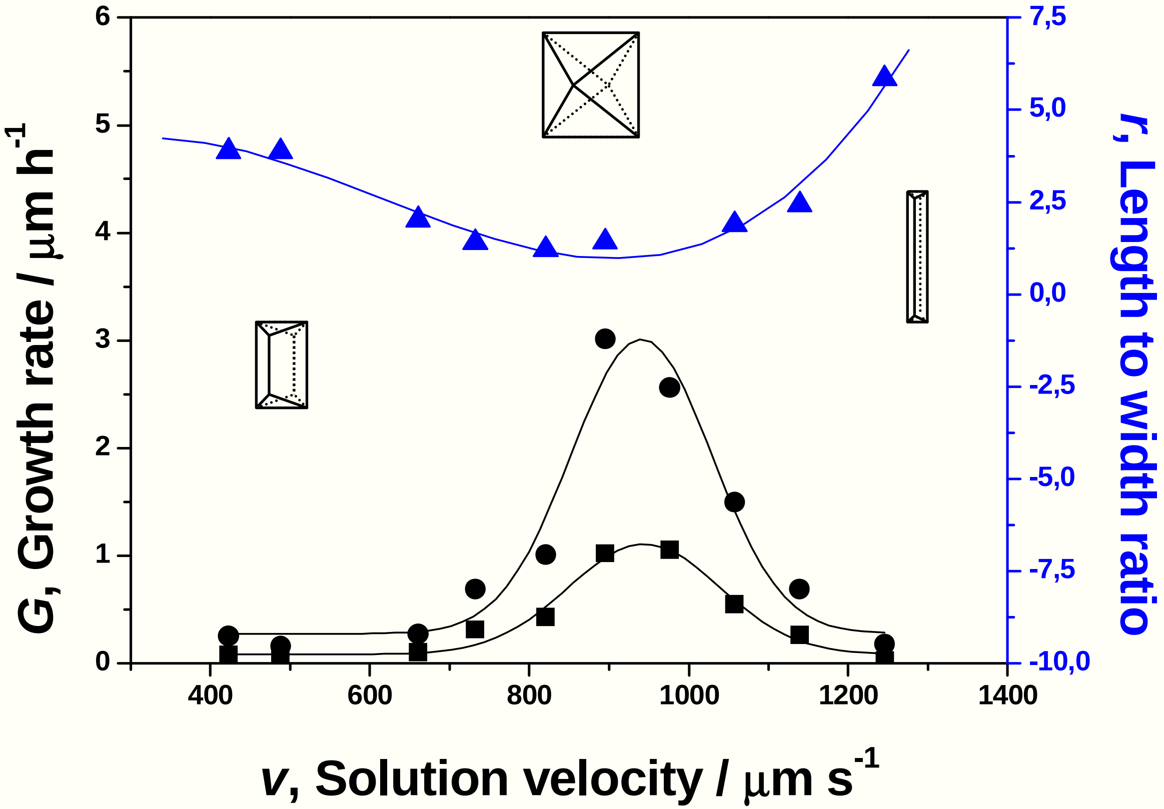
✓ **Production of catalytic crystals with a well defined size, size distribution and shape**

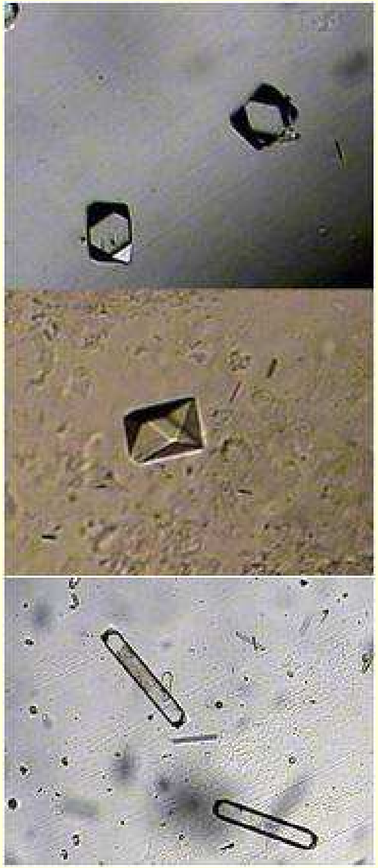




Di Profio, G. Curcio, E. Drioli E. Journal of Crystal Growth 2003; 257: 359-369.
Di Profio, G. Curcio, E. Drioli E. Journal of Structural Biology 2005; 150: 41–49.

Advantages of Membrane Crystallization Technique (5)



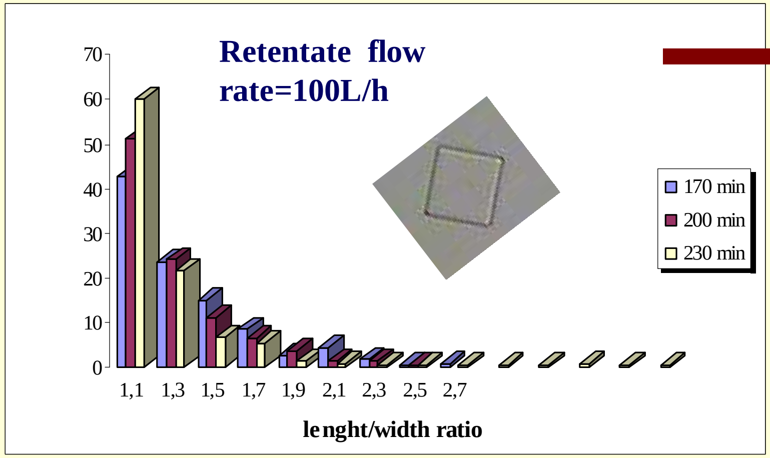


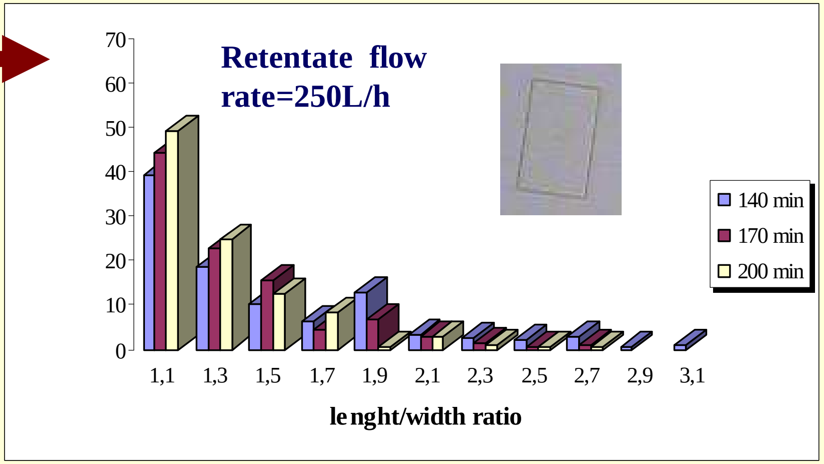
Protein: Bovine Pancreas Trypsin, M.W. = ~ 24000 Da

✓ Controlling crystals' habit of enzyme crystals

Di Profio, G.; Curcio, E.; Drioli, E. *Journal of Structural Biology* 2005, *150*, 41.

Advantages of Membrane Crystallization Technique (5)



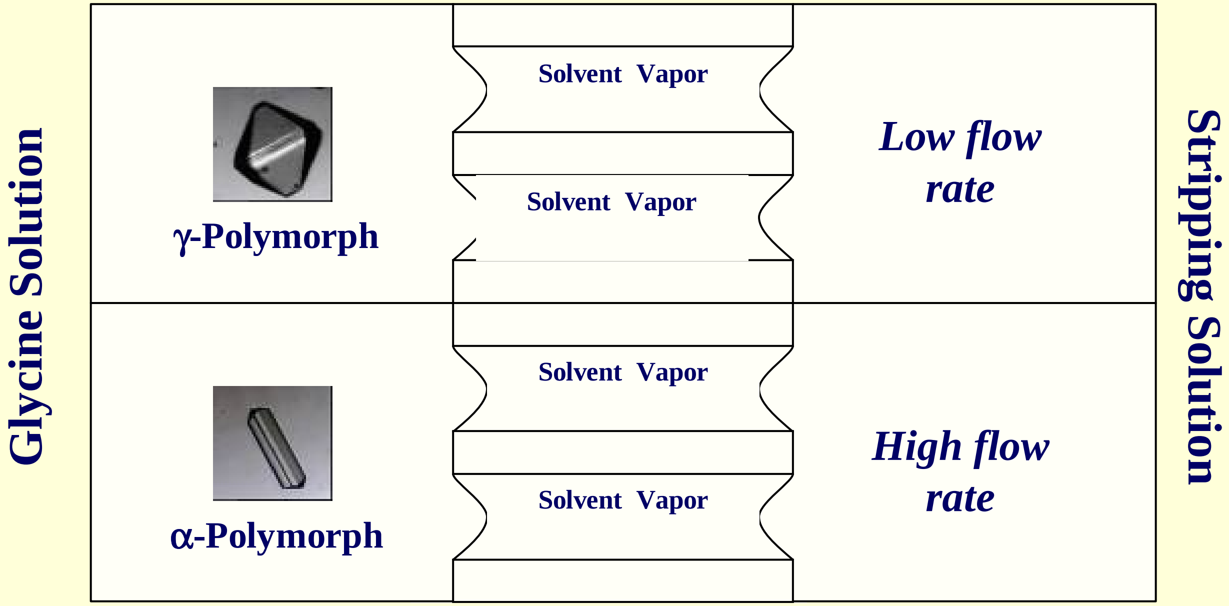


Distribution of length/with ratio for NaCl crystals obtained from the crystallization of RO brine

✓ Controlling crystals' habit of NaCl crystals acting on feed flow rate

Advantages of Membrane Crystallization Technique (6)

✓ **Selective polymorphs crystallization by controlling the rate of achievement of supersaturation**



Glycine Solution

γ-Polymorph

Solvent Vapor

Solvent Vapor

Low flow rate

α-Polymorph

Solvent Vapor

Solvent Vapor

High flow rate

Stripping Solution

The control of the rate for the achievement of supersaturation allows to switching from a kinetically to a thermodynamically controlled nucleation stage thus triggering the production of either a stable or metastable form .

Di Profio, G.; Tucci, S.; Curcio, E.; Drioli, E. *Crystal Growth & Design* 2007, *7*, 526.

The crucial requirement a the membrane crystallizer?

To prevent crystals deposition on membrane surface and inside the membrane module.

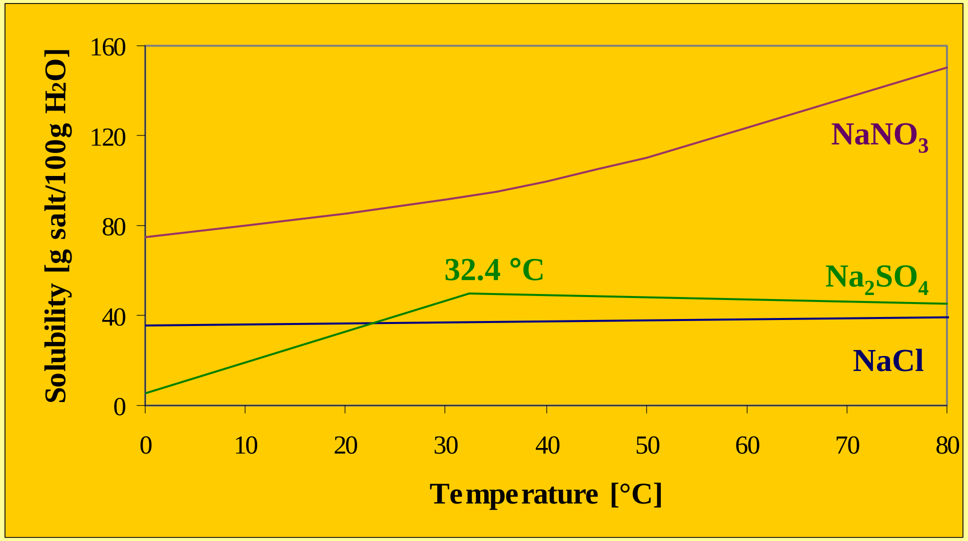
Possible solutions:

- ✓ **by re-circulating continuously the solution in order to remove particles eventually deposited on the membrane surface;**
- ✓ **by recovering the produced crystals;**
- ✓ **by controlling the temperature of the solution flowing along the membrane module.**

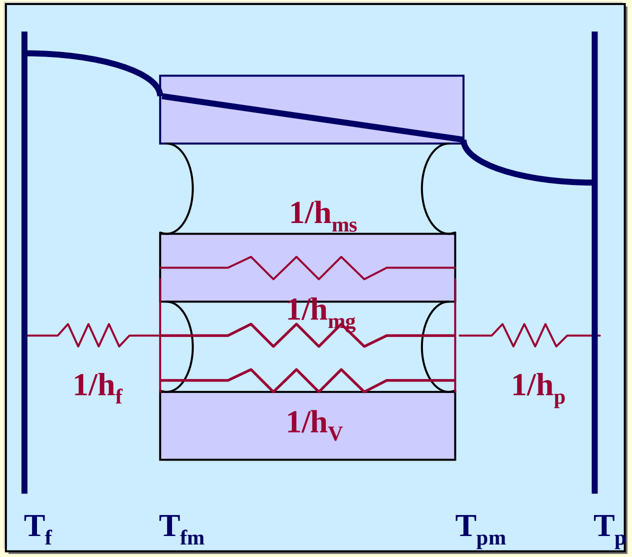
Influence of Temperature

✓ **Solubility of solids in solution depends by temperature (whose effect on salt solubility depends by its ΔH_{sol}).**

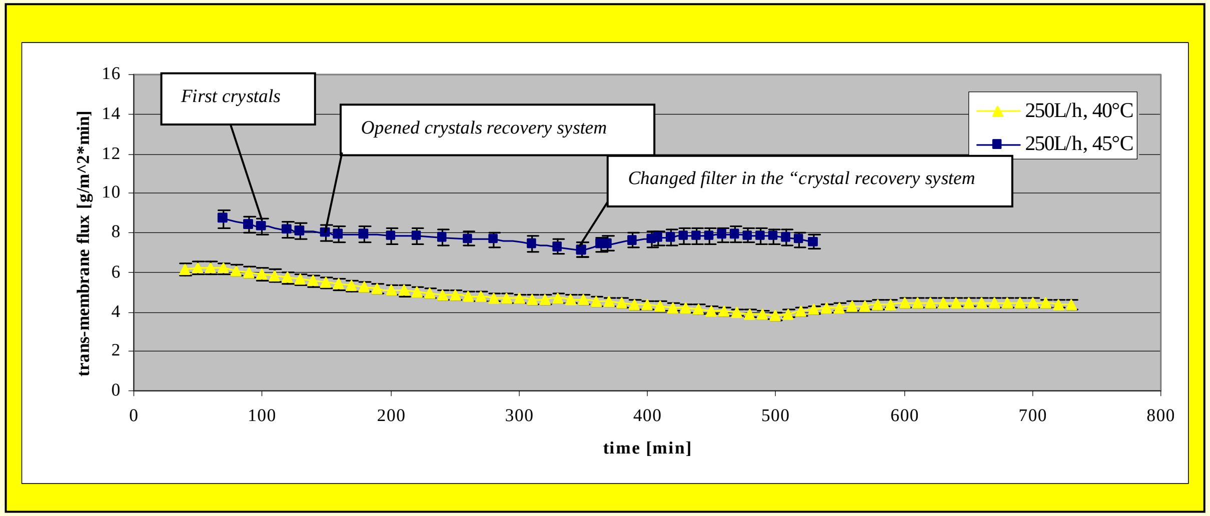
Salt	ΔH_{sol} [kcal/mole]
$NaNO_3$	5.11
NaCl	*0.93*
Na_2SO_4	-0.56
$Na_2SO_4 \cdot 10H_2O$	18.58
$CaSO_4$	-4.25
$MgSO_4$	-21.81
$MgSO_4 \cdot 7H_2O$	*3.18*



✓ **Along the capillary module, thermal exchange phenomena between cold and hot streams and the polarization cause a progressive reduction of temperature, depending on the fluid- dynamic regime.**



MCr tests on NF brine solutions: *control and effect of temperature on MCr operation*



Trend of trans-membrane flux vs time in MCr crystallization tests on NF brine solutions: apart an initial transitory stage, the almost constant trend means that there is no crystals deposition inside the membrane module.

Flux J per unit surface area of the membrane: $\mathbf{J = K\Delta P}$

Dependence of the solvent vapour pressure on temperature and concentration: P(c,T)=p0(T) a(c,T)

Trans-membrane vapour pressure difference: $\mathbf{\Delta P = p_1(c_1,T) - p_2(c_2,T) = p^0(T)\Delta a}$

where the subscripts 1 and 2 refer to the feed and permeate side, respectively.

Relation between the vapour pressure of pure water and the absolute temperature T: $\mathbf{p^0(T) \propto \exp/\left(-\frac{\lambda}{RT}\right)}$

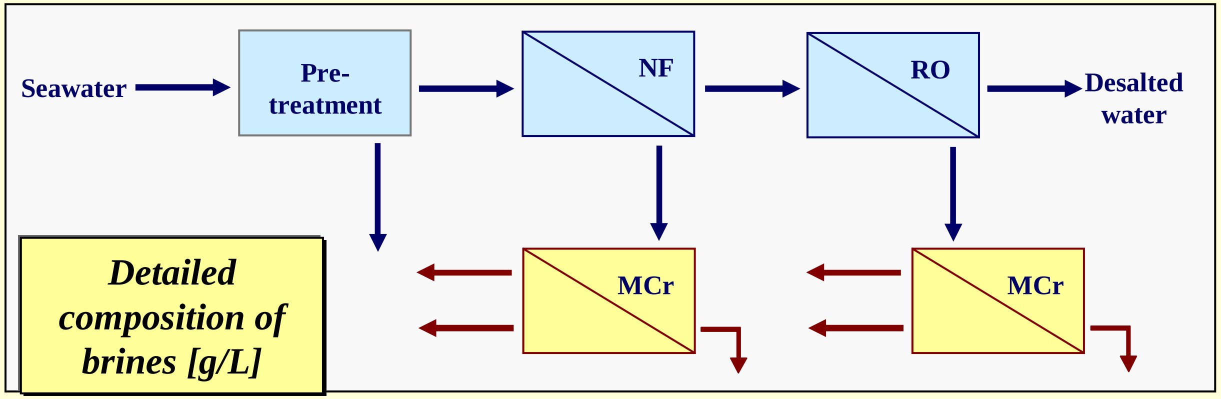
As a consequence, trans-membrane flux increases when the temperature of the feed and /or the trans-membrane temperature difference grow.

F. Macedonio et al., submitted

MCr on NF/RO brine

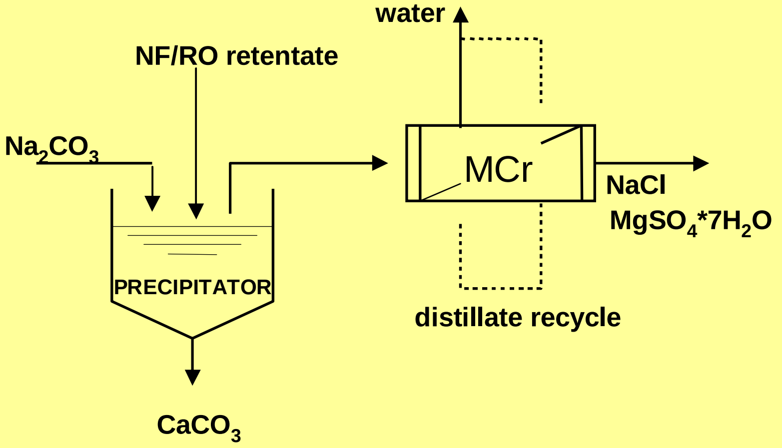
Ion	NF brine	RO brine
Cl^-	34.47	44.89
Na^+	19.05	24.81
SO_4^{2-}	10.38	0.5831
Mg^{2+}	4.959	0.5352
Ca^{2+}	1.384	0.2488
HCO_3^-	0.4160	0.1680
K^+	0.6893	0.8978
CO_3^{2-}	0.0103	0.0041
Br^-	0.0848	0.1886
Total	71.44	72.32

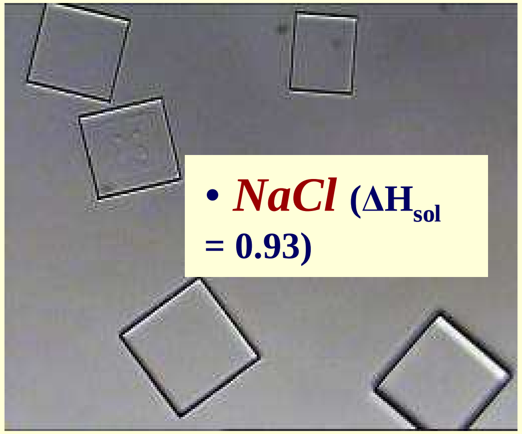
Detailed composition of brines [g/L]



- ***Magnesium sulphate*** which, at 25°C, precipitates in the form of epsomite (ΔH_{sol} = 3.18 kcal/mole)

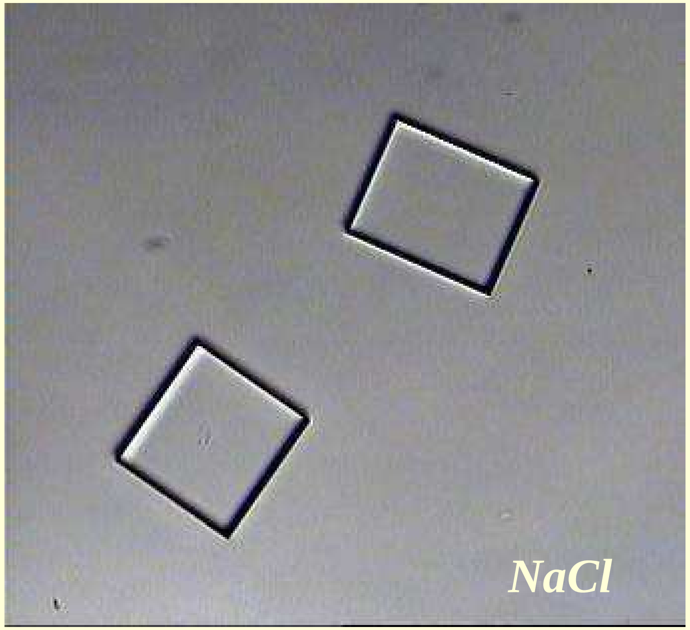
- ***Calcium sulphate:*** To limit calcium sulphate precipitation, Ca^{2+} ions are recovered as $CaCO_3$ through reactive precipitation with Na_2CO_3

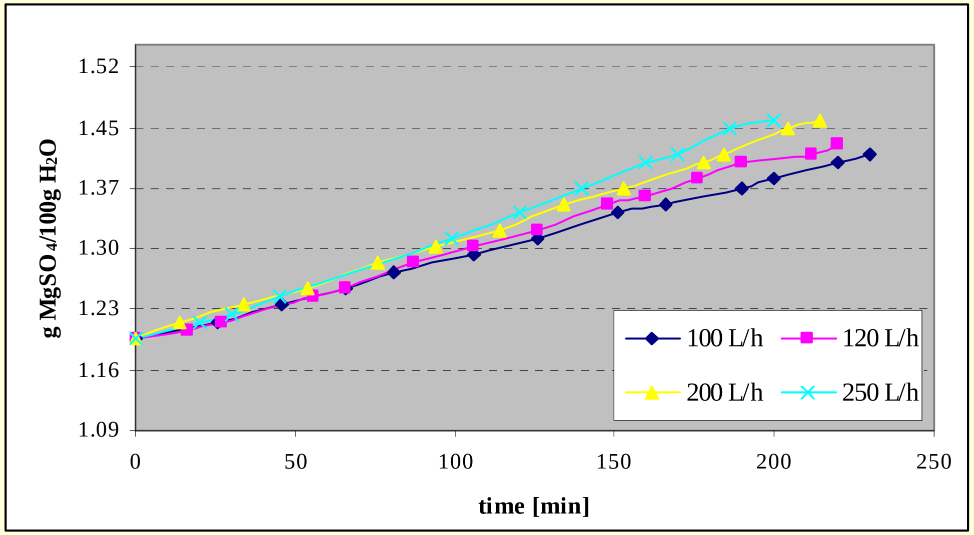




- ***NaCl*** (ΔH_{sol} = 0.93)

RO brine crystallization: type of produced salts

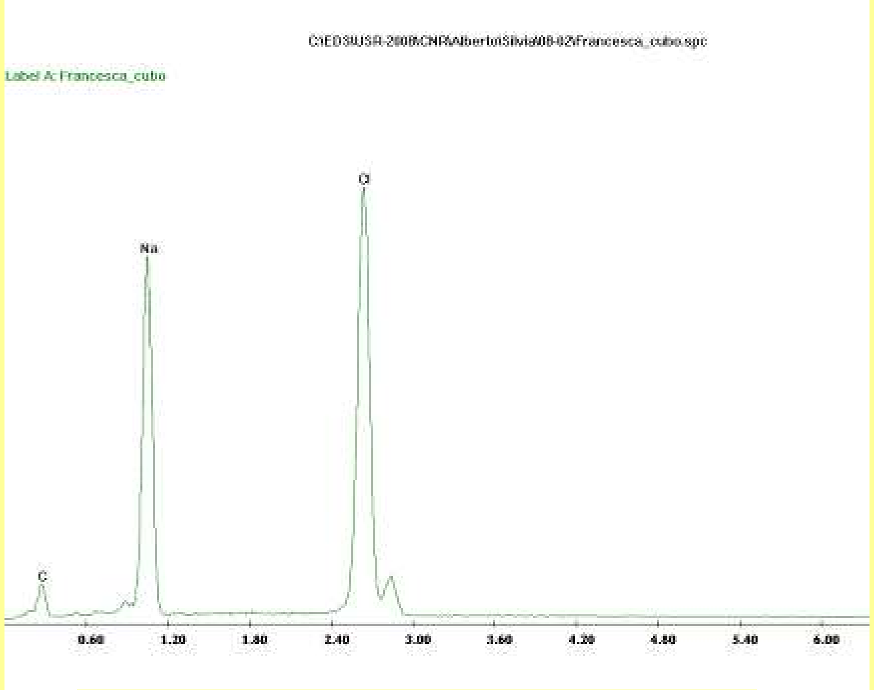




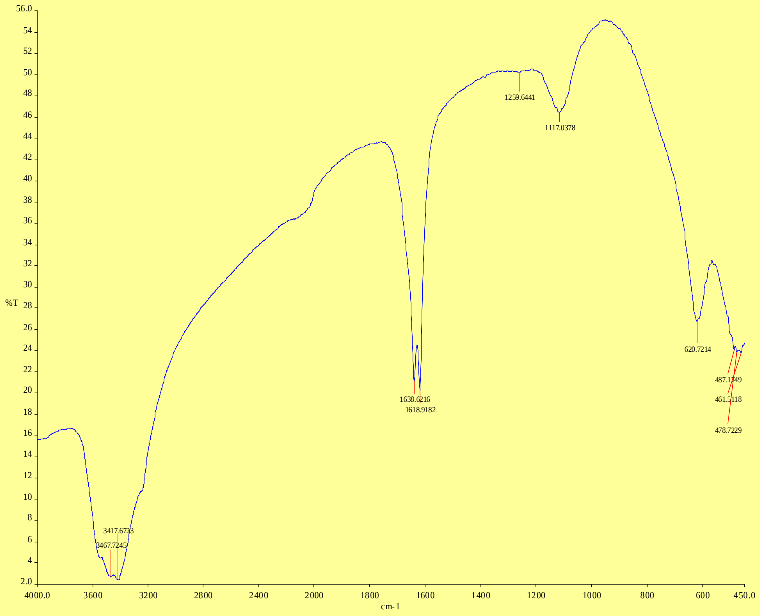
Magnesium sulphate concentration vs time at different feed flow rates for the lab tests of aqueous solution of NaCl.

- ✓ **Only NaCl can be produced from the RO retentate crystallization.**
- ✓ **The crystallization tank work at 25°C and atmospheric pressure. At this temperature, the solubility of magnesium sulphate in water is 25.6g/100g H_2O, much higher of $MgSO_4$ concentration in the carried out tests.**

NF brine crystallization: type of produced salts



EDX spectrum of NaCl crystals formed.



FT IR spectrum of some of the achieved epsomite crystals.

Methods:

- **EDX (Energy Dispersive X-ray): NaCl**
- **FT IR (Fourier Transform Infrared Spectroscopy): $MgSO_4$*$7H_2O$, no Na_2SO_4**
- **Low temperature DSC (Differential Scanning Calorimeters - maximum temperature 250°C): no $MgCl_2$*$6H_2O$**

Integrated Membrane-Based Systems for Seawater Desalination: some examples

Conventional Integrated Membrane Systems for Seawater Desalination

FS1: *RO unit alone*

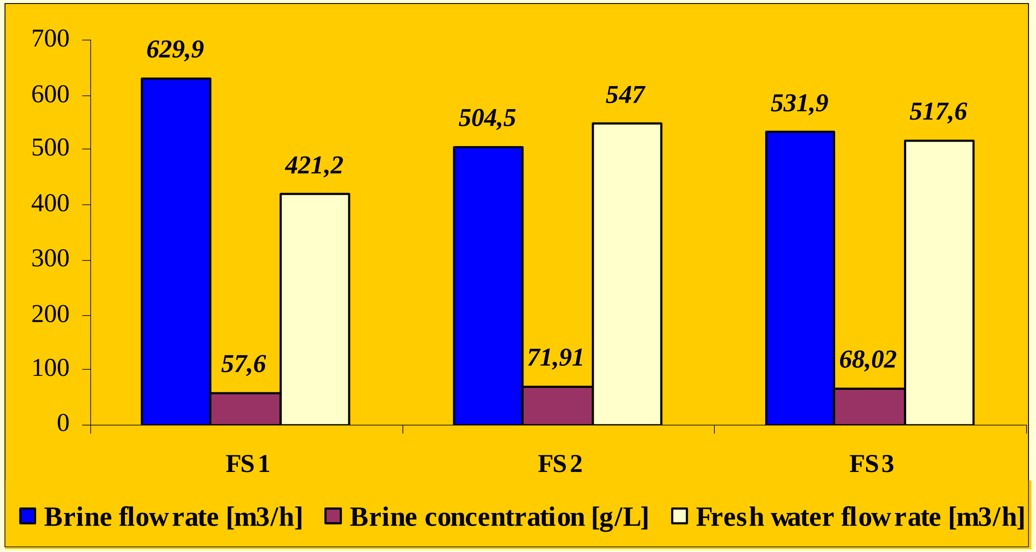
FS2: *RO operating on NF permeate*

FS3: *MF/NF/RO*

RO: Osmonic SW1 PA
Recovery factor of about 40%

NF: Osmonics NF300 PA
Recovery factor of 75.3%

MF: MEMCOR 20M10
Recovery factor = 94.7%

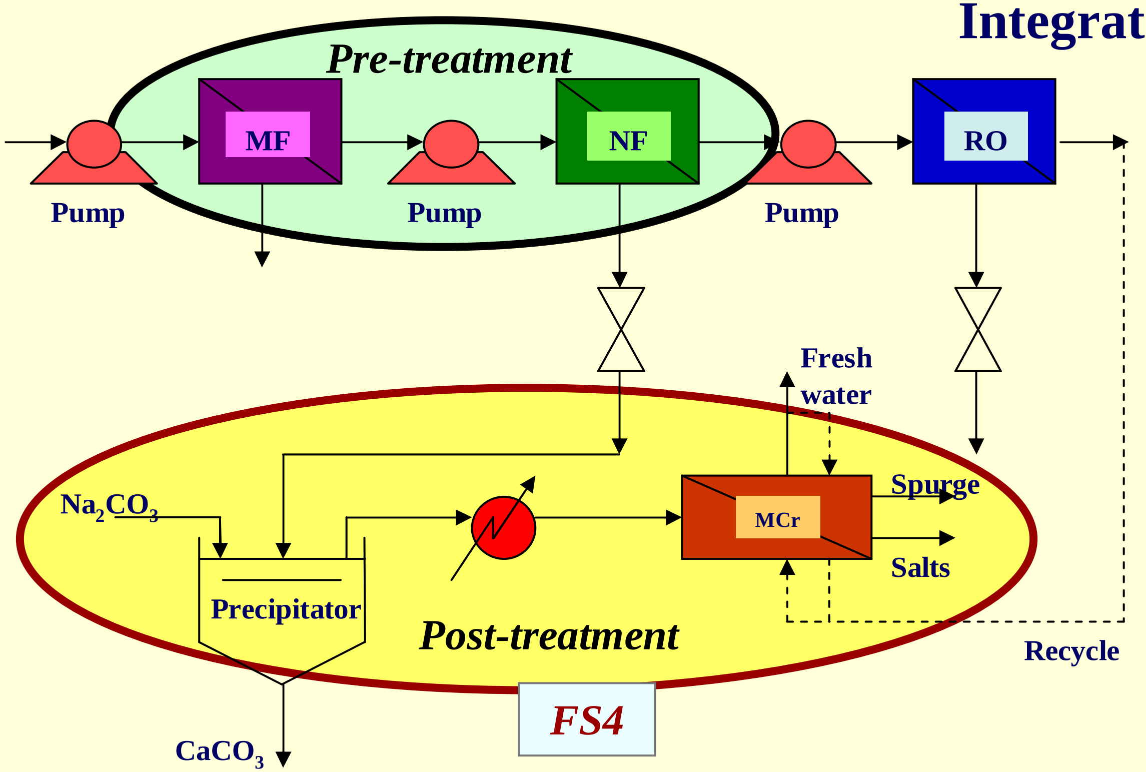


Rejection values

Ion	NF [%]	RO [%]
HCO_3^-	62.0	98.4
Na^+	22.0	98.9
Cl^-	12.8	99.0
SO_4^{2-}	90.0	99.6
Ca^{2+}	88.4	99.7
Mg^{2+}	89.0	99.6

In all the flow sheets, as feed water composition, the standard seawater composition with flow rate equal to 1050 m^3/h has been considered.

Pressure-Driven Membrane Operations and Membrane Contactor Technology Integration for *Seawater Desalination*



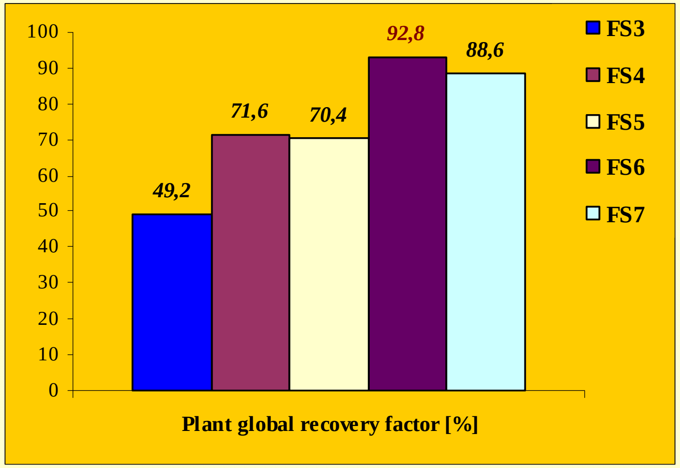
FS4: MF-NF-RO, MCr on NF brine

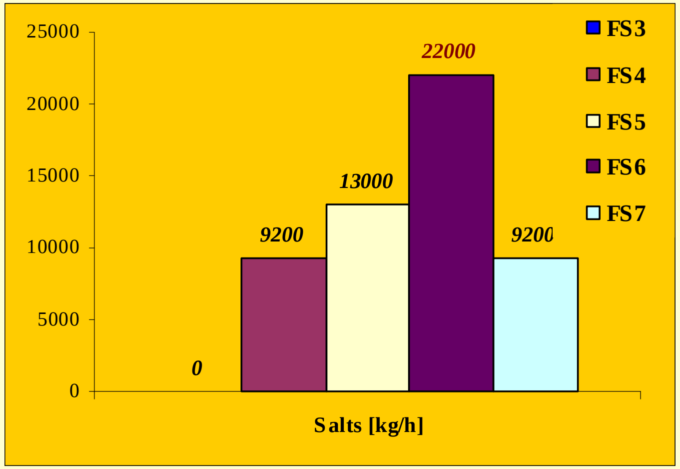
FS5: MF-NF-RO, *MCr on RO brine*

FS6: MF-NF-RO, *MCr on NF and RO brine*

FS7: MF-NF-RO, *MCr on NF brine and MD on RO brine*

Comparison for FS3, FS4, FS5, FS6 and FS7





E. Drioli, F. Macedonio et al., Chemical Engineering Research and Design, 84 (A3) (2006) 209–220.

Economic Evaluation

For each proposed flow sheet, an economic evaluation was made to determine the unit cost of fresh water produced and the gain for the salts sale.

Production cost is divided into *direct* and *indirect capital costs* and *annual operating costs*.

- ✓ ***Direct Capital Cost***
  - **Land**
  - **Process equipments**
  - **Auxiliary equipments**
  - **Building construction**
  - **Membranes**
- ✓ ***Indirect Capital Cost***
  - **Freight and Insurance**
  - **Construction overhead**
  - **Owner's costs**
  - **Contingency costs**
- ✓ ***Annual Operating Costs***
  - **Electricity**
  - **Labor.**
  - **Membrane replacement**
  - **Maintenance and spare parts**
  - **Insurance**
  - **Amortization or fixed charges**
  - **Chemicals**
  - **Brine disposal**

Desalted Water Cost Comparison for various Integrated *Membrane* System Configurations with MCr units

	Only RO	NF-RO	MF/NF/RO	MF-NF-RO | MCr	MF-NF-RO | MCr	MF - NF - RO | | MCr MCr	MF - NF - RO | | MCr MD
Total annual profit for salts sale[\$/yr]	-	-	-	*6,398,000*	2,991,000	*9,389,000*	*6,398,000*
Total annual cost [\$/yr]	2,040,000	2,005,000	1,871,000	*4,024,000*	3,440,000	*5,593,000*	*5,445,000*
Unit cost* $[\$/\text{m}^3]$	0.61/0.40^a	0.47/0.40^a	0.46/0.39^a	0.68/0.63^a	0.59/0.54^a	0.73/0.69^a	0.74/0.71^a
Unit cost$^{*, b}$ $[\$/\text{m}^3]$	0.61/0.40^a	0.47/0.40^a	0.46/0.39^a	0.55/0.51^a	0.47/0.43^a	0.54/0.51^a	0.55/0.51^a
Recovery factor [%]	*40.1*	*52.0*	*49.2*	*71.6*	*70.4*	*92.8*	*88.6*

* Desalted water unit cost without consider the gain for the salts sale. (a) If Pelton turbine is used as energy recovery device. (b) If thermal energy is available in the plant or the stream is already at the operating temperature of the MCr unit.

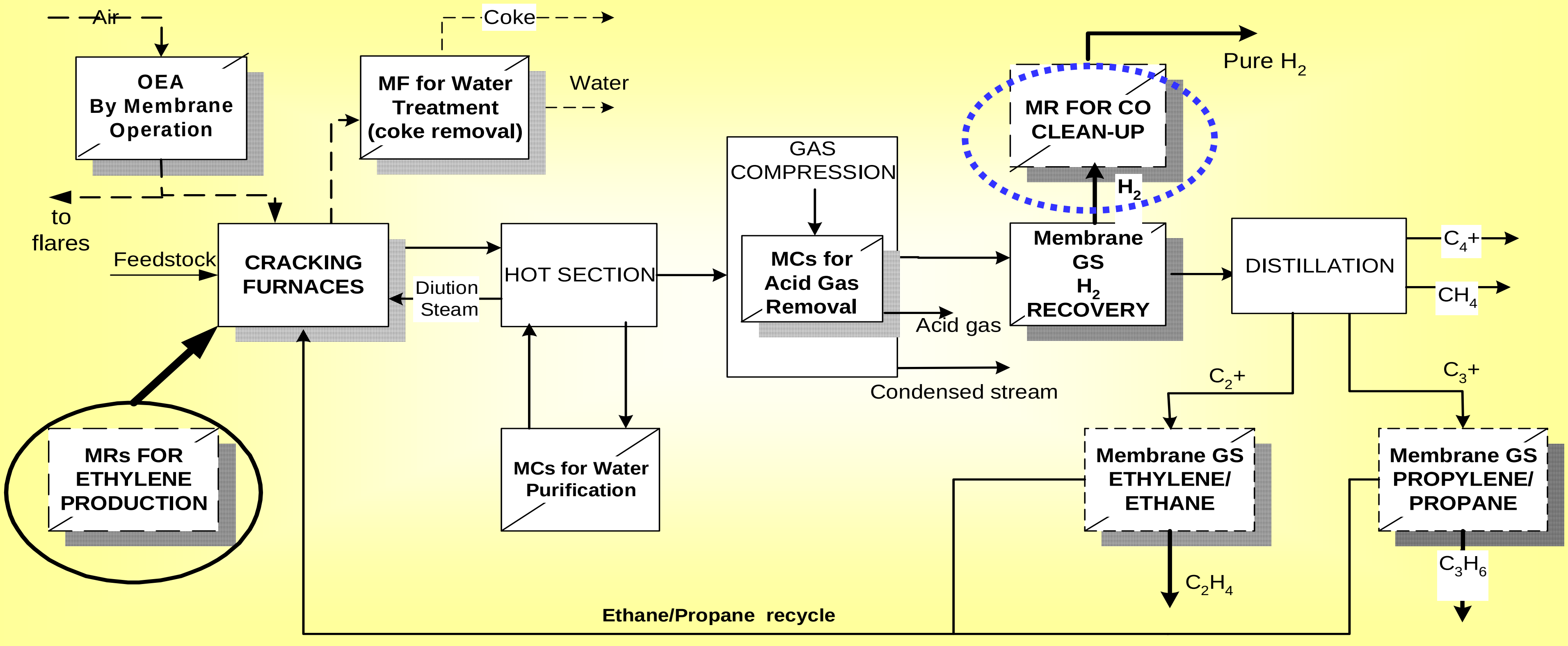
Advantages in the use of integrated membrane systems: 1) increase in plant recovery factor; 2) production of solid materials of high quality and controlled properties (as specific polymorph of salts) with important added values, transforming the traditional brine disposal cost in a potential new profitable market; 3) reduction of *environmental problems* related to the brine disposal.

E. Drioli, F. Macedonio et Al., Chemical Engineering Research & Design, 84 (A3) (2006) 209–220.

INTEGRATED MEMBRANE PROCESSES:

KEY-FACTORS FOR FURTHER IMPROVEMENT
ALSO OF OTHER INDUSTRIAL SYSTEMS

Example 1: Membrane unit operations integrated in a steam cracking ethylene plant



Air

OEA By Membrane Operation

to flares

Feedstock

CRACKING FURNACES

Coke

MF for Water Treatment (coke removal)

Water

Diution Steam

HOT SECTION

MCs for Water Purification

GAS COMPRESSION

MCs for Acid Gas Removal

Acid gas

Condensed stream

MR FOR CO CLEAN-UP

Pure H_2

H_2

Membrane GS H_2 RECOVERY

DISTILLATION

C_4+

CH_4

C_2+

C_3+

Membrane GS ETHYLENE/ ETHANE

C_2H_4

Membrane GS PROPYLENE/ PROPANE

C_3H_6

MRs FOR ETHYLENE PRODUCTION

Ethane/Propane recycle

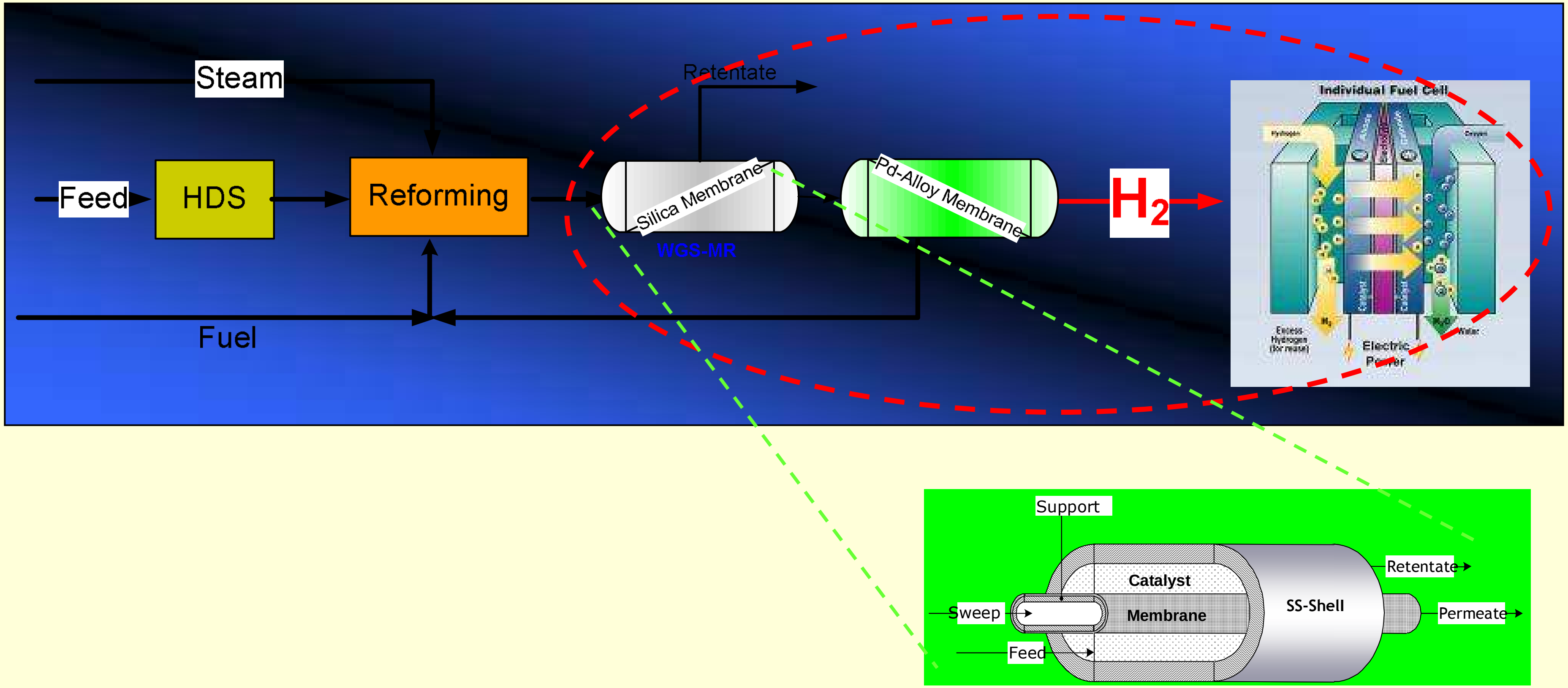
***Ethylene** is a very important product for chemical industry and there is a strong interest to study new methodologies for its production.*

Ethylene annual production is more than 110 million tons; more than 97% is produced by **steam cracking.**

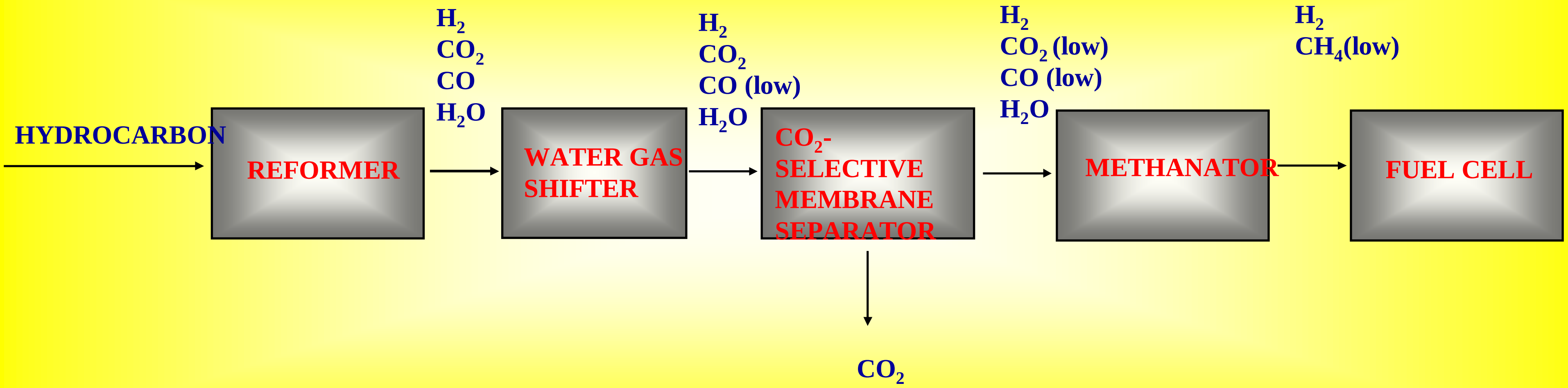
P. Bernardo, A. Criscuoli, G. Clarizia, G. Barbieri, E. Drioli G. Fleres and M. Picciotti, Applications of membrane unit operations in ethylene process, *Clean Technologies and Environmental Policy*, (2003) , 6 (2004) 78–95.

Example 2: Integrated Membrane Plant for H_2 production by Water Gas Shift Reaction

$$CO + H_2O = CO_2 + H_2 \quad \Delta H_0^{298} = -41\ kJ/mol$$



Example 3: Integrated Membrane systems in energy production



HYDROCARBON

REFORMER

H_2
CO_2
CO
H_2O

WATER GAS SHIFTER

H_2
CO_2
CO (low)
H_2O

CO_2-SELECTIVE MEMBRANE SEPARATOR

CO_2

H_2
CO_2 (low)
CO (low)
H_2O

METHANATOR

H_2
CH_4(low)

FUEL CELL

From U.S. Patent 6,579,331, ExxonMobil property

Membranes have a central role both in hydrogen production (CMRs) and purification (GS) and in the fuel cells mechanism (PEM)

Energetic and Exergetic Analyses

Analysis of the systems through the use of Energetic and Exergetic Analyses

In order to estimate the convenience in terms of environmental impact and energy savings in the use of new unit operations in chemical processes, a methodology based on energy and exergy analysis can be used for establishing, respectively, the energy requirements of the processes and their exergetic efficiency .

The exergy analysis is a technique that utilizes the Second Law of Thermodynamics for the analysis of the real systems. It has been developed to avoid the complexity and the confusion that exists in the classic approach of the Second Law .

R. Molinari, R. Gagliardi, E. Drioli, Desalination, 100 (1995) 125-137.

THE FIRST LAW OF THERMODYNAMICS, the application of the conservation of energy principle: ***The change in internal energy of a system is equal to the heat added to the system minus the work done by the system***

$$\Delta U = Q - W$$

THE SECOND LAW OF THERMODYNAMICS: ***The entropy of any totally isolated system not at thermal equilibrium will tend to increase over time, approaching a maximum value.***

The second law can be described mathematically as:

$$dS/dt \text{ tends to be } \geq 0$$

where *S* is the entropy and *t* is time.

The First Law of Thermodynamics does not consider the *quality* of the energy. The Second Law, instead, is able to do this.

Exergy and Anergy

Total *energy* is divided in two parts: *exergy and anergy*.

- ✓ ***Anergy* is the part of energy that is forced to be given to the environment as heat in conditions of complete degradation.**

- ✓ ***Exergy* is the part of energy that, by reversible transformations, can be completely converted from one form to another. Therefore, *exergy* can be defined as *the maximum amount of work obtained by the evolution of a system with reversible transformations from the initial state to the equilibrium state with the environment* – that is, the work available in the system because of its non-equilibrium with respect to the reference conditions (e.g.: *1000J of thermal energy available at 1000K has a larger quality than 1000J at 400K, when the temperature of the environment is at 300K*).**

Mathematical definition of exergy for a fluid stream:

$$Ex=G[(h-h_0)-T_0(s-s_0)]$$

where

- ✓Ex is the exergy;
- ✓G, the mass flow rate;
- ✓h, the specific enthalpy;
- ✓T_0, the reference temperature;
- ✓s, the specific entropy.

The reference state, indicated by the subscript *0*, is often taken at the surrounding conditions.

If the intensive parameters characterizing the system are temperature, pressure and concentration, the exergy can be expressed by the following equation:

$$Ex = G\left[c_p(T - T_0) - c_p T_0 \ln\left(\frac{T}{T_0}\right) + \frac{(P - P_0)}{\rho} - N_s R T_0 \ln x_1\right]$$

where:

$$Ex^T = G\left[c_p(T - T_0) - c_p T_0 \ln\left(\frac{T}{T_0}\right)\right]$$ **is the temperature exergy term,**

$$Ex^P = G\left[\frac{(P - P_0)}{\rho}\right]$$ **is the pressure exergy term,**

$$Ex^c = G(- N_s R T_0 \ln x_1)$$ **is the concentration exergy term.**

$$Ns = \frac{\left(1000 - \sum \frac{c_i}{\rho}\right)}{MW_s}$$

moles of solvent per mass unit of the solution

$$x_1 = \frac{N_s}{\left[N_s + \sum \left(\frac{\beta_i c_i}{\rho\, MW_i}\right)\right]}$$

mole fraction of the solvent under the assumption of ideal solution

c_i = mass concentration of the ith chemical component per liter of solution;

ρ = density of the liquid solution;

MW_s , MW_i = molecular weight of the solvent and of the ith chemical component, respectively;

β_i = number of particles generated from dissociation of species i;

c_p = the specific heat of the solution

P_0 = the reference pressure

During a process, depending on the transformation, there will be a change at least in one of the exergy terms changing the exergetic content. The corresponding variation may formally be written as:

$$\Delta E_x = -T_0 \cdot \dot{R}_S + \dot{W}_U + \dot{W}'_U$$

EXERGETIC BALANCE

where

$$\Delta E_x = \sum_i E_{x,i} - \sum_k E_{x,k}$$

is exergy variation between outlet and inlet streams

$$T_0 \cdot \dot{R}_S$$

is the total exergy destroyed and transformed in the production of entropy

$$\dot{W}_U = E \cdot 3600$$

is the electrical exergy

$$\dot{W}'_U = G_V \left[\left(h_v - h_c \right) - T_0 \left(s_v - s_c \right) \right]$$

is the thermal exergy supplied to the system

$$G_V = Q/\lambda_V$$ (G_V is the required steam mass flow rate)

where $$Q = G \cdot c_p \cdot (T_2 - T_1)$$

is the heat required to warm up the fluid G from temperature T_1 to temperature T_2.

Primary energy (PE) is the energy supplied by fuel combustion to produce thermal energy:

$$PE = G_V \cdot 0.8$$

where 0.8 is the primary energy (Mcal) needed in the boiler for producing 1 kg of steam.

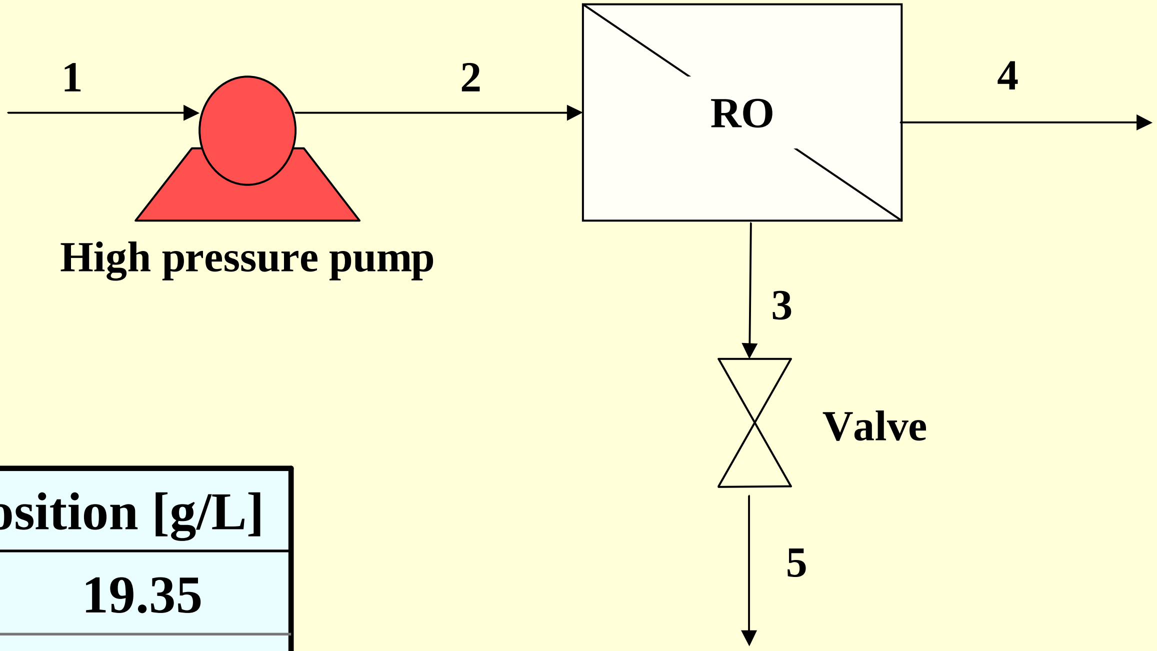
- ✓ R. Molinari, R. Gagliardi, E. Drioli, Desalination, 100 (1995) 125-137.
- ✓ A. Criscuoli, E. Drioli, Desalination, 124 (1999) 243-249.
- ✓ F. Macedonio, E. Curcio, E. Drioli, Desalination, 203 (2007) 260–276.

This approach is more time-consuming than an energetic analysis for the major complexity of the equations, so it is used only in those cases where the contributions that cannot be evaluated with energetic analysis are important (e.g., exergy of solutions at different concentrations but at the same temperature).

Case study:

Application of Exergy for the Analysis and Comparison of Different Integrated Membrane Systems for Seawater Desalination

Example 1: *RO unit alone (FS1)*



Feed composition [g/L]	
Cl^-	19.35
Na^+	10.75
SO_4^-	2.701
Mg^{2+}	1.295
Ca^{2+}	0.416
HCO_3^-	0.145

Since the streams considered in this system are aqueous solutions, the reference state is pure water at temperature and pressure of the feed (stream 1).

Stream	T [K]	P [MPa]	$C_{chemicals}$ [g/l]	G [kg/h]	Ex [kJ/h]
1	293.2	0.10	34.65	1,048,000	2,808,000
2	293.2	6.90	34.65	1,048,000	9,956,000
3	293.2	6.77	57.60	628,000	6,978,000
4	293.2	0.10	0.3385	420,000	11,490
5	293.2	0.10	57.60	628,000	2,777,000

Electrical energy = 2206 KWh/h

Wu = $7.942 \cdot 10^6$ KJ/h

G_V = 0 Kg/h

Wu’ = 0 KJ/h

ΔEx= $-1.972 \cdot 10^4$ KJ/h

$R_S T_0$ = $7.962 \cdot 10^6$ KJ/h

PE = 0 Mcal/h

Exergy Destruction Distribution

The use of exergy analysis allows to identify the sites of greatest losses and to improve the performance of the processes. For reaching this aim, it is necessary to calculate the exergies across the major components of the plant in an attempt to assess *the exergy destruction distribution.*

Example 1: *RO unit alone (FS1)*

Component	Stream N°	E_x [KJ/h]	ΔEx [KJ/h]
Feed	1	2,808,000	
	2	9,956,000	
High Pressure Pump			+7,148,000
	3	6,978,000	
	4	11,490	
RO unit			-2,966,000
	5	2,777,000	
Valve			-4,201,000

The positive and negative signs indicate the exergy transferred to components and the exergy destroyed by components, respectively.

The convenience of the innovative process with respect to the traditional can be evaluated in terms of exergetic efficiency of the process, as following defined:

$$\varepsilon(\%) = \frac{Ex_{output}}{Ex_{input}} \cdot 100$$

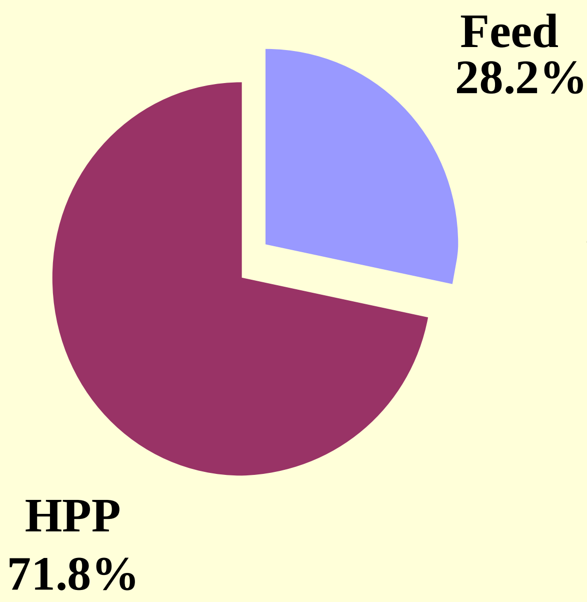
For FS1:

$Ex_{input} = 9{,}956{,}000$ kJ/h

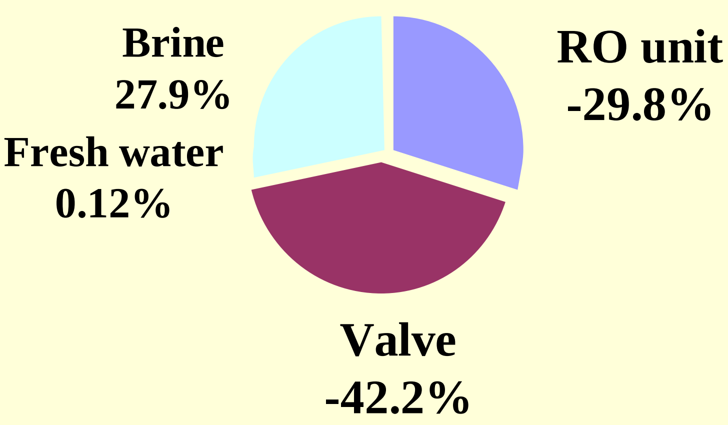
$Ex_{output} = 2{,}789{,}000$ kJ/h

$\varepsilon = 28.0\ \%$

Exergy input



Exergy output or destroyed by the components



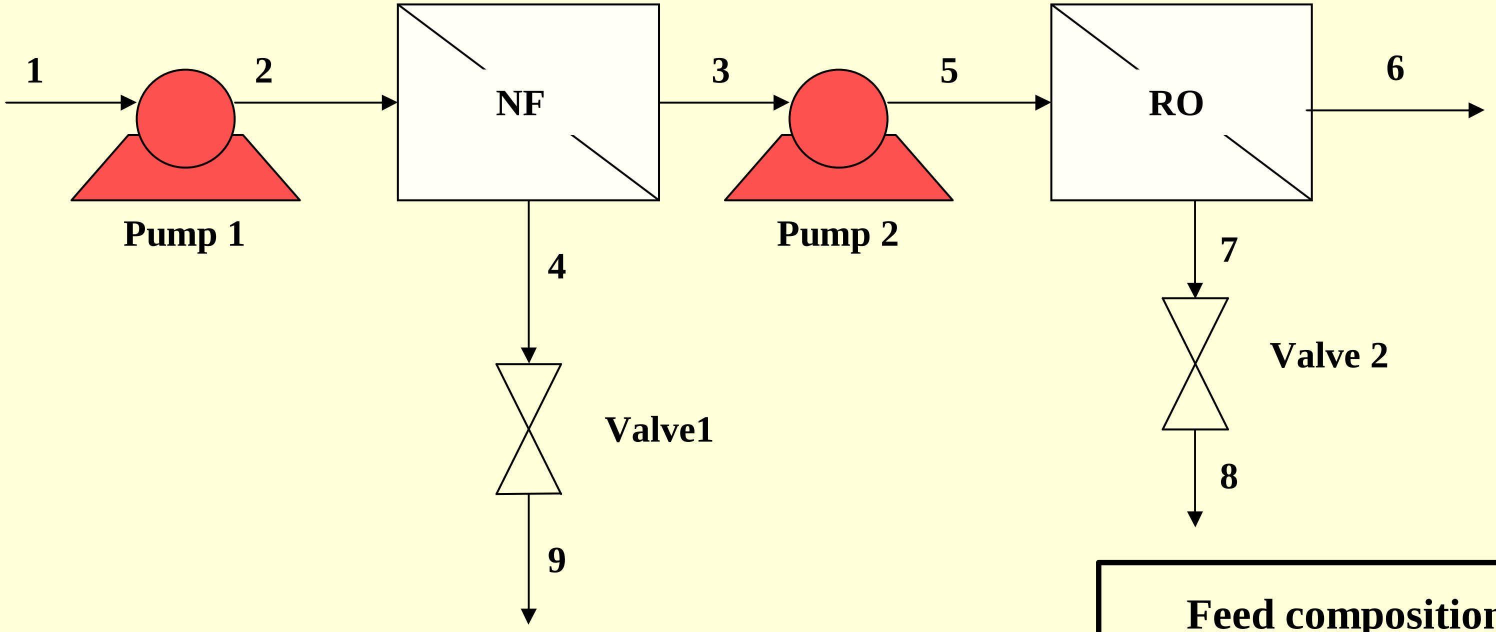
The primary locations of exergy destruction are the membrane modules in which the saline water is separated into the brine and the permeate, and the throttling valves where the pressure of the liquid is reduced. Meanwhile there is nothing that can be done to eliminate or decrease the lost of exergy in the membrane module; the most reasonable way to increase efficiency or reduce the power input of the plant is to replace the throttling valves on the brine stream by an energy recovery system.

In fact, the pressure of RO brine could be recovered by introducing a Pelton turbine which lead to a reduction of the energy consumption transferring the brine pressure to low-pressure feed water while discharging the brine at low pressure. The convenience of a process with an energy recovery device (ERD) with respect another without ERD can be evaluated in terms of exergetic efficiency of the process and, then, in its energy requirements:

- ✓ **Pelton turbine, $\varepsilon = 48.50$ %**

- ✓ **Electrical energy = 2206 kWh/h (5.24 kWh/m^3) without energy recovery system, 1132 kWh/h (2.69 kWh/m^3) with Pelton turbine.**

Example 2: *RO operating on NF permeate (FS2)*



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Ca^{2+}	0.416
HCO_3^-	0.145

	Stream	T [K]	P [MPa]	$C_{chemicals}$ [g/l]	G [kg/h]	Ex [kJ/h]	Ex supplied and/or destroyed [%]
Feed	1	293.2	0.10	34.65	1,048,000	2,808,000	30.39
	2	293.2	1.10	34.65	1,048,000	3,859,000	
Pump 1							11.37
	3	293.2	0.10	25.73	789,100	1,628,000	
	4	293.2	1.00	61.85	258,900	1,409,000	
NF unit							-8.9
	9	293.2	0.10	61.85	258,900	1,176,000	12.72
Valve 1							-2.528
	5	293.2	6.90	25.73	789,100	7,010,000	
Pump 2							58.24
	6	293.2	0.10	0.2699	545,000	11,960	0.1294
	7	293.2	6.77	82.57	244,200	3,220,000	
RO unit							-40.88
	8	293.2	0.10	82.57	244,200	1,586,000	17.16
Valve 2							-17.67

Electrical energy = 1986 KWh/h
Wu = 7.148×10^6 KJ/h
G_V = 0 Kg/h
Wu’ = 0 KJ/h
ΔEx= -3.454×10^4 KJ/h
$R_S T_0$ = 7.183×10^6 KJ/h
PE = 0 Mcal/h

For FS2:

$$Ex_{input} = 9{,}242{,}000 \text{ kJ/h}$$

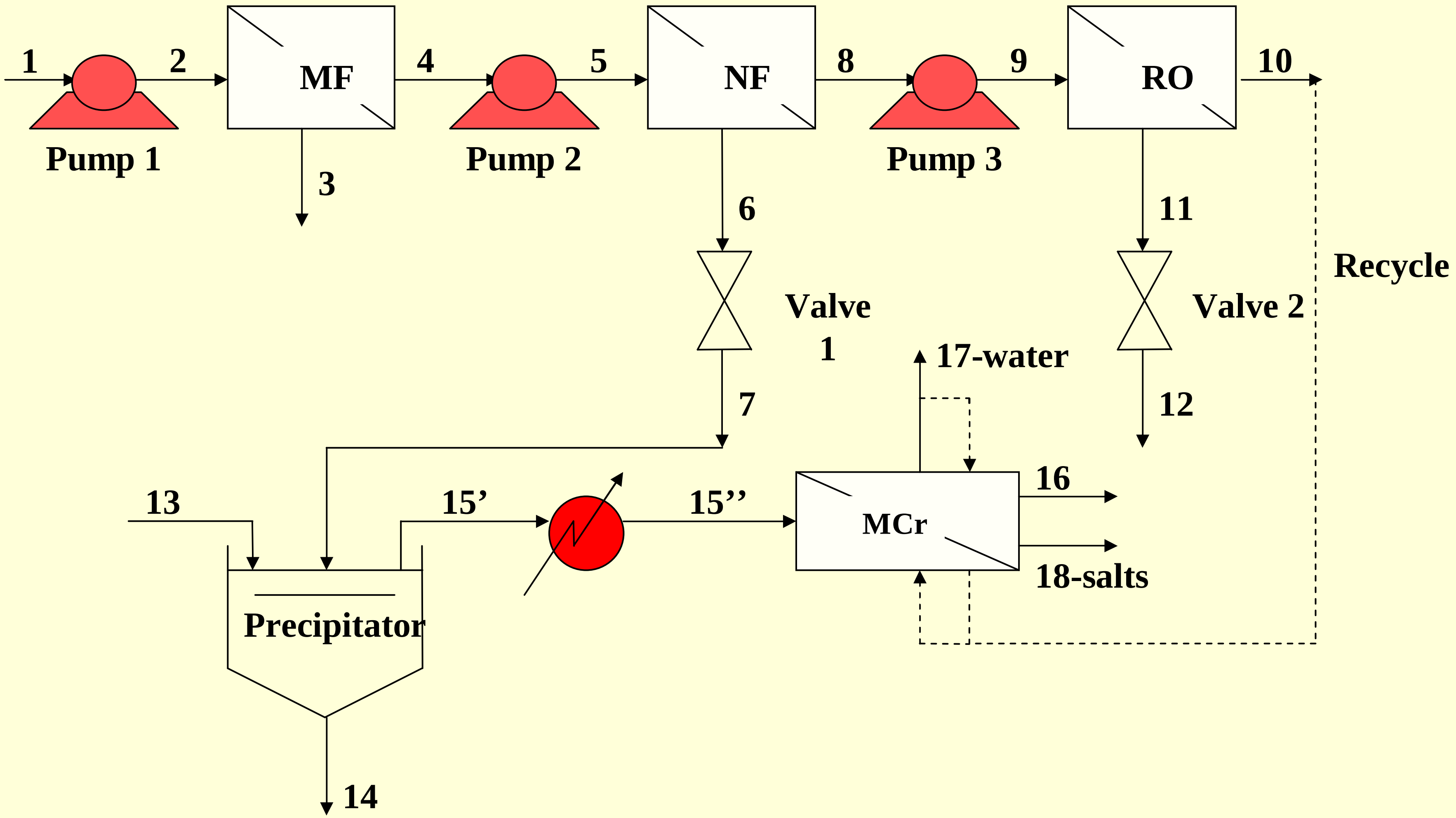
$$Ex_{output} = 2{,}774{,}000 \text{ kJ/h}$$

$$\varepsilon = 30.01\ \%$$

- ✓ **By replacing the throttling valves on the RO brine stream with a Pelton urbine, ε = 36.46 %**

- ✓ **Electrical energy = 1986 kWh/h (3.63 kWh/m^3) without energy recovery system, 1568 kWh/h (2.87 kWh/m^3) with Pelton turbine.**

Example 3: *MF-NF-RO and MCr on NF brine (FS3)*



Stream N°	$C_{chemicals}$ [g/l]	G[Kg/h]	P [MPa]	T[K]	Ex [kJ/h]
1	34.65	1.048E+06	0.10	293.2	2,808,000
2	34.65	1.048E+06	0.20	293.2	2,913,000
3	34.65	5.554E+04	0.10	293.2	148,800
4	34.65	9.925E+05	0.10	293.2	2,660,000
5	34.65	9.925E+05	1.10	293.2	3,655,000
6	61.85	2.451E+05	1.00	293.2	1,335,000
7	61.85	2.451E+05	0.10	293.2	1,118,000
8	25.73	7.473E+05	0.10	293.2	1,541,000
9	25.73	7.473E+05	6.90	293.2	6,638,000
10	0.2699	5.161E+05	0.10	293.2	11,330
11	82.57	2.312E+05	6.77	293.2	3,049,000
12	82.57	2.312E+05	0.10	293.2	1,502,000
13	0.0	996.4	0.10	293.2	0
14	0.0	893.9	0.10	293.2	0
15’	62.27	245,100	0.12	293.2	1,143,000
15’’	62.27	245,100	0.12	323,2	2,575,000
16	758.3	9,805	0.10	298.2	310,200
17	0.1856	750,700	0.10	296.2	59,210
18	0.0	8,309	0.10	298.2	360.4

Component	**Stream N°**	**E_x supplied and/or destroyed [%]**
	1	**26.90**
	2	
Pump 1		**1.007**
	3	**1.426**
	4	
MF unit		**-1.007**
	5	
Pump 2		**9.536**
	8	
	6	
NF unit		**-7.463**
	7	
Valve 1		**-2.073**
	9	
Pump 3		**48.83**
	10	
	11	
RO unit		**-34.28**

Component	**Stream N°**	**E_x supplied and/or destroyed [%]**
	12	**14.39**
Valve 2		**-14.82**
	7	
	15’	
Precipitator		**0.2335**
	15’’	
Heater		**13.72**
	18	**0.003453**
	16	**2.972**
	17	**0.5673**
MCr unit		**-21.23**

For FS3:

Ex_{input}=10,440,000 kJ/h
Ex_{output}=2,021,000 kJ/h
$\Delta Ex = -7.876 \cdot 10^5$ KJ/h

ε = 19.36 %

Electrical energy = 1913 KWh/h (19.1 kWh/m^3) without energy recovery system, Wu = $6.886 \cdot 10^6$ KJ/h

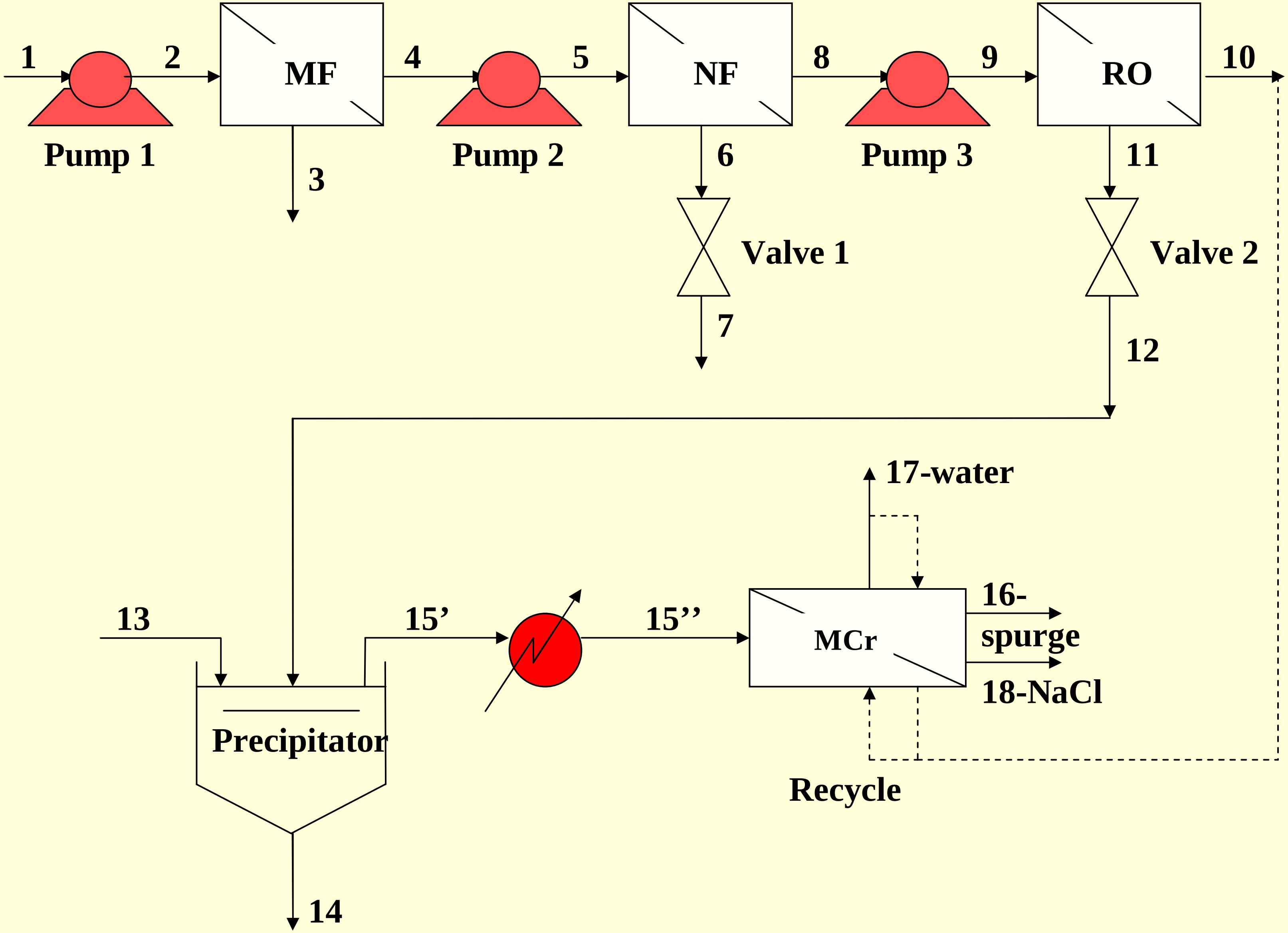
G_V = 13,430 Kg/h
Wu’ = $7.129 \cdot 10^6$ KJ/h
$R_S T_0$ = $14.80 \cdot 10^6$ KJ/h
PE = 10,750 Mcal/h

The presence of the MCr introduces a *thermal energy requirement* which increases the global energy demand. The *entropic losses* are also increased.

✓ **By replacing the throttling valves on the RO brine stream with a Pelton urbine, ε = 22.73 %**

✓ **Electrical energy = 1517 kWh/h (18.61 kWh/m3) with Pelton turbine.**

Example 4: *MF-NF-RO and MCr on RO brine (FS4)*



For FS4:

Ex_{input}=10,340,000 kJ/h
Ex_{output}=1,634,000 kJ/h
ΔEx= -11.75*10^5 KJ/h

ε = 15.80 %

Electrical energy = 1913 KWh/h (18.3 kWh/m^3) without energy recovery system, Wu = 6.886*10^6 KJ/h

G_V = 12,510 Kg/h
Wu' = 6.640*10^6 KJ/h
$R_S T_0$ = 14.70*10^6 KJ/h
PE = 10,010 Mcal/h

The *thermal energy necessary* is reduced (due to the lower flow rate which has to be heated) and the *entropic losses* are also *decreased with respect to the FS3.*

✓ **By replacing the throttling valves on the RO brine stream with a Pelton urbine, ε = 18.57 %**

✓ **Electrical energy = 1519 kWh/h (17.79 kWh/m^3) with Pelton turbine.**

The comparison between the various processes can be made also in term of *Substitution Coefficient* (SC), the ratio between the primary energy saved in the new process with respect to the conventional process and the amount of electrical energy consumed:

$$\mathbf{SC = \frac{(PE_1 - PE_2)}{(E_2 - E_1)}}$$

where PE is the consumption of thermal primary energy [MJ or Mcal], E the consumption of electrical energy [kWh], 1-2 the relative index of the conventional and innovating process, respectively.

In Italy, the primary energy required to produce 1kWh of electricity is 2.5Mcal/h.

Thus, Substitution Coefficients higher than 2.5 Mcal/kWh (or 10.5MJ/hWh) indicate a convenience from an energetic point of view.

The Substitution Coefficient calculated for FS4 with respect to FS3 is 99.3 MJ/kWh, which means that FS4 is more energetically convenient than FS3.

The calculation of the *SC* shows the same results previously obtained throughout energetic and exergetic analysis.

Conclusions- Exergy

- ✓ **The use of exergy analysis in actual processes is of growing importance from a thermodynamic point of view, because it allows to identify the sites of greatest losses and on which to act for improving the performance of the processes.**

- ✓ **The exergy method answers to the questions of *where, why and how much of the available work* is lost in the system.**

- ✓ **It allows to make this for each system, both easy and complex.**

Analysis of systems through the use of *Metrics* ...

… indicators which allow to quantify the progress of industrial processes towards sustainability, and to measure their impact on environment, economy and society.

Metrics	
Mass Intensity	$\text{MI} = \frac{\text{Total mass (seawater + reagents)}}{\text{Mass of product (fresh water + salts)}}$
Waste Intensity	$\text{WI} = \frac{\text{Total waste}}{\text{Mass of product (fresh water + salts)}}$
Energy Efficiency	$\text{EE} = \frac{\text{Total process energy (electrical + thermal)}}{\text{Mass of product (fresh water + salts)}}$
New proposed indexes*	$\text{PS (productivity/size ratio)} = \frac{\text{P/Size (membranes)}}{\text{P/Size (traditional)}}$
	$\text{PW (productivity/weight ratio)} = \frac{\text{P/Weight (membranes)}}{\text{P/Weight (traditional)}}$
	$\text{EI} = \frac{\text{P/Load of pollutant emissions (membranes)}}{\text{P/Load of pollutant emissions (traditional)}}$
	$\text{Flexibility} = \frac{\text{Variations handled. (membranes)}}{\text{Variations handled (traditional)}}$
	$\text{MI (modularity index)} = \frac{\text{Productivity}_2\text{ (scale up)}}{\text{Productivity}_1}$
	$\text{M (modularity)} = \frac{\lvert\text{Area}_2/\text{Area}_1\text{ (membranes)- MI}\rvert}{\lvert\text{Volume}_2/\text{Volume}_1\text{(traditional)-MI}\rvert}$

A. Criscuoli, E. Drioli, *New index for evaluating the performance of membrane operations in the logic of process intensification*, Engineering Conferences International, Italy, June 11-15, 2006.

- ***Mass intensity*** **takes into account yield, stochiometry, solvent, and reagents used in the reaction mixture, and expresses this on a weight/weight basis rather than a percentage. In the ideal situation, MI would approach 1. Total mass includes everything that is used in a process or process step.**

- ***Waste Intensity (or E Factor)*** **draws attention to the quantity of waste that is produced for a given mass of product. It also exposes the relative wastefulness of different parts of the chemical processing industries that includes industries as diverse as petrochemicals, specialities and pharmaceuticals. This metric may certainly be used by industry and can, if used properly, spur innovation that results in a reduction of waste.**

- **The mass indicators define both environmental impacts and raw material utilization (e.g., emissions and mass intensity), while the energy indicators evaluate energy consumption of the alternatives.**

Case study:

Application of Metrics for the Analysis and Comparison of Different Integrated Membrane Systems for Seawater Desalination

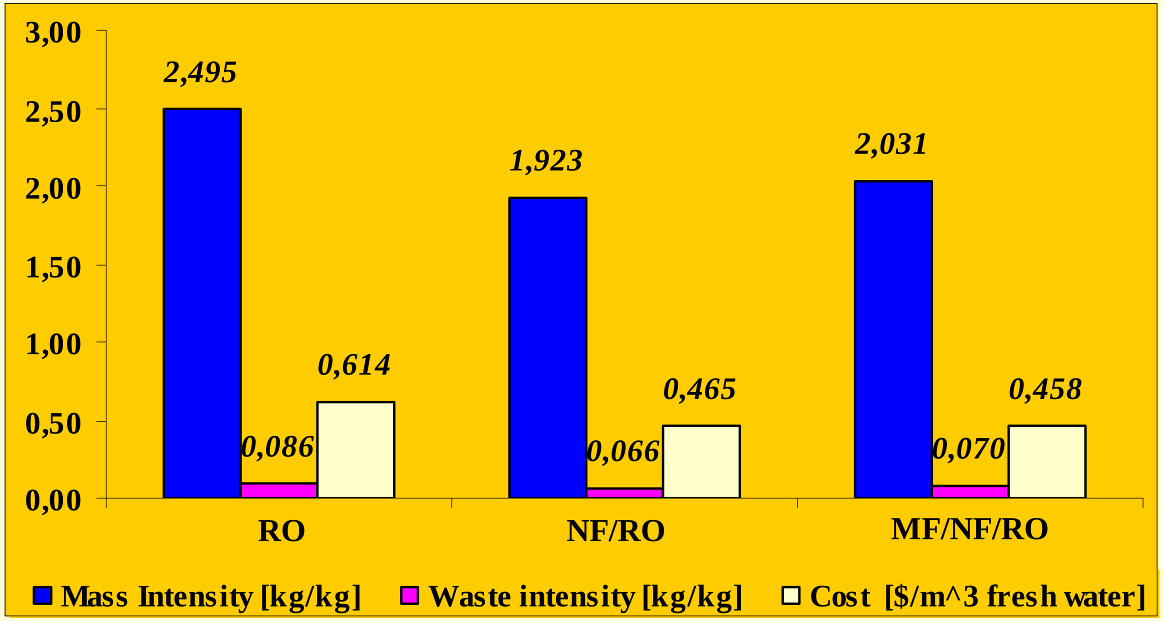
Evaluation of Mass Intensity, Waste Intensity and Energy Efficiency for the proposed Membrane Desalination Systems

$$\textbf{1) Mass intensity} = \frac{\textbf{Total mass (seawater + reagents)}}{\textbf{Mass of product (fresh water + salts)}}$$

$$\textbf{2) Waste Intensity} = \frac{\textbf{Total waste}}{\textbf{Mass of product (fresh water + salts)}}$$

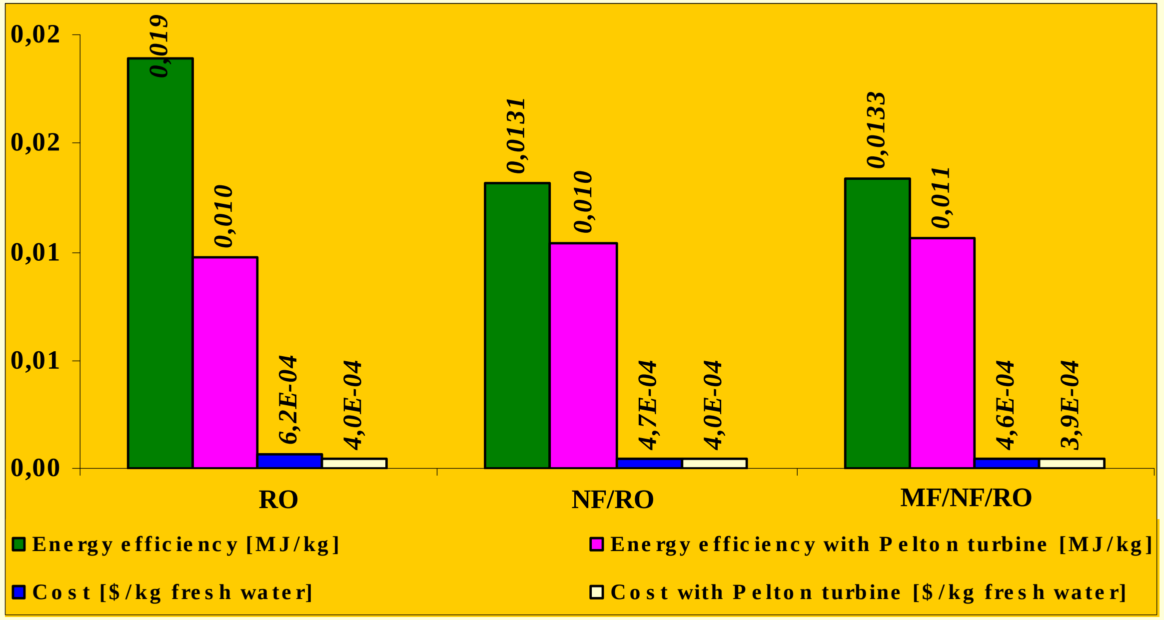
$$\textbf{3) Energy Efficiency} = \frac{\textbf{Total process energy (electrical + thermal)}}{\textbf{Mass of product (fresh water + salts)}}$$

Mass Intensity, Waste Intensity and Energy Efficiency for Conventional Integrated Membrane Systems (FS1-FS3)



Desalination processes with high Mass Intensity and, then, Waste Intensity, will have also high *environmental impact* and *cost* because their plant efficiency will be low.

Energy consumption is the term that more influences desalination cost. In fact, the presence of the Pelton wheel in the flow sheet reduces water desalination cost.

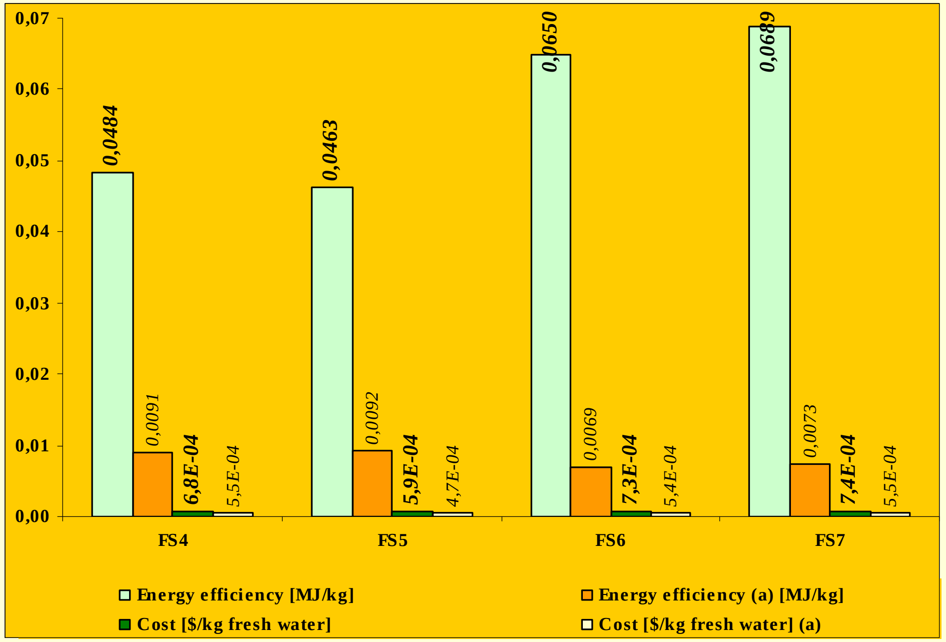


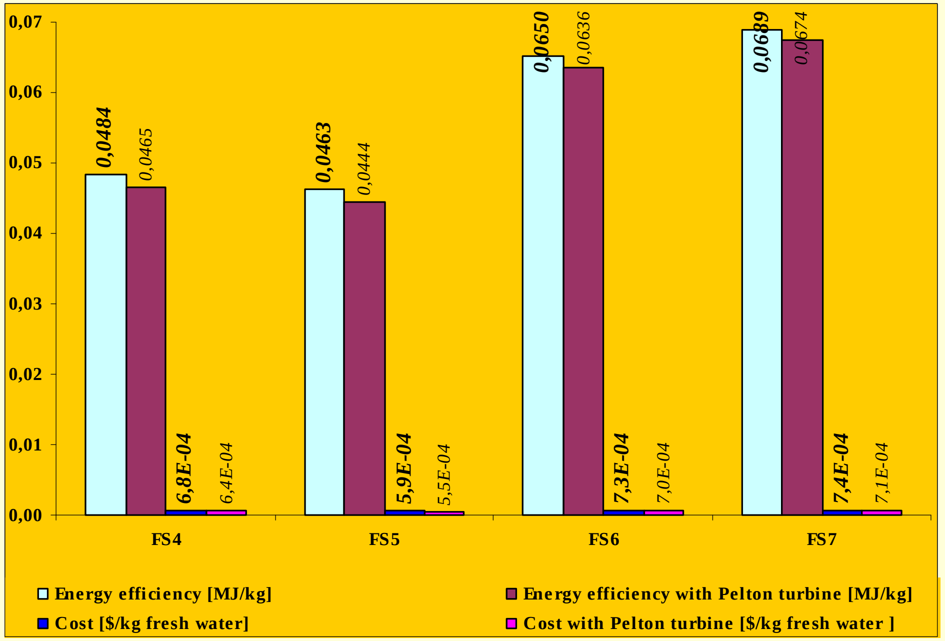
Mass Intensity and Waste Intensity Indices for Integrated Membrane Systems with MCr units (FS4-FS7)

	FS4: **MF-NF-RO** **|** **MCr**	**FS5:** **MF-NF-RO** **|** **MCr**	**FS6:** **MF - NF - RO** **| |** **MCr MCr**	**FS7:** **MF - NF - RO** **| |** **MCr MD**
Mass Intensity [kg/kg]	**1,3804**	**1,3975**	**1,0556**	**1,1184**
Waste intensity [kg/kg]	**0,0374**	**0,0316**	**0,0161**	**0,0303**

Mass Intensity much lower than that achieved in the first 3 systems (FS1, FS2, FS3) → MCr reduces brine disposal problem and its environmental impact

Energy Efficiency Indices for Integrated Membrane Systems with MCr units (FS4-FS7)





Thermal energy is the term that more influences energy consumption. Only when thermal energy is already available in the plant (a) it is possible to observe a high reduction in plant energy efficiency and water cost.

The results obtained with metrics agree with those obtained through economic analysis of the proposed integrated membrane desalination systems.

Therefore, the principles of Sustainable Development can help to the choice of the best alternative

- they allow to avoid risks from unsustainable business practices
- companies that reduce costs by decreasing Mass Intensity or Energy Intensity will be more economic profitable and will have less environmental impacts.

Comparison of the Integrated Membrane Desalination Systems through the use of PS and M metrics

PS (productivity/size ratio) = $\frac{\text{P/Size (membranes)}}{\text{P/Size (traditional)}}$

MI (modularity index) = $\frac{\text{Productivity}_2\text{ (scale up)}}{\text{Productivity}_1}$

M (modularity) = $\frac{|\text{Area}_2/\text{Area}_1\text{ (membranes)- MI}|}{|\text{Volume}_2/\text{Volume}_1\text{(traditional)-MI}|}$

With respect to the previous indicators, the new metrics take into account size and modularity of the industrial processes. Therefore, they can be coupled with the previous tools for comparing processes with respect to other aspects of the production plants, always in the logic of the Process Intensification.

PS metric

For FS4 : Productivity/Size = 12.9

For FS5: Productivity/Size = 13.3

For FS6: Productivity/Size = 10.3

For FS7: Productivity/Size = 10.5

PS for FS4, FS6 and FS7 with respect to FS5	FS4	FS5	FS6	FS7
FS5	*1,03*	*1,00*	*1,29*	*1,26*

The PS values obtained show that, between the four analyzed flow-sheets, FS5 is, among the four analyzed flow-sheet, the one that provides the better compromise among the amount of produced fresh water and salts, and the plant size. Among FS4, FS6 and FS7, the process with the highest *productivity/size* ratio is FS4 (in agreement with the results achieved with the substitution coefficient CS).

M metric

To compare the modularity of the proposed membrane process the modularity indicator was re-defined as follows:

$$M = \frac{\left|\text{area}_2 / \text{area}_1 - MI\right| (\text{process}_i)}{\left|\text{area}_2 / \text{area}_1 - MI\right| (\text{process}_j)}$$

where

$$MI\ (\text{modularity index}) = \frac{\text{Productivity}_2\ (\text{scale up})}{\text{Productivity}_1}$$

M metric compares the variations of the plant sizes for the process i with those for the process j when the plant productivity varies from the condition 2 to the condition 1. The membrane process i has a higher modularity if the modularity metric is lower than 1; modularity values higher than 1 are in favour of the process j.

For the proposed flow sheets, productivity$_1$ is the one achieved when the pressure at the inlet of the RO unit is equal to 6.9 MPa, productivity$_2$ is the one achieved when the pressure at the inlet of the RO unit is equal to 6.7 MPa.

(Process)$_i$ (Process)$_j$	**FS4**	**FS5**	**FS6**	**FS7**
FS4	1,00	0,96	1,65	1,52
FS5	1,04	1,00	1,71	1,58
FS6	*0,61*	*0,58*	1,00	0,92
FS7	*0,66*	*0,63*	1,08	1,00

The obtained results indicate that FS6 and FS7 are, between the four analyzed flow-sheet, more modular than FS4 and FS5.

Conclusions - Metrics

The comparison of the results achieved for the different flow sheets shows as follows:

- **among the desalination systems without MCr unit, FS3 is the one to prefer because of the lowest cost and better quality of the produced desalted water. The introduction of MF as pre-treatment in FS3 slightly decreases the plant recovery factor with respect to FS2 but it leads to benefits in term of reduction of membrane fouling (with consequent extension of the life time of NF/RO membranes) and chemicals dosage (because no chemicals are needed for disinfection, coagulation and dechlorination, with consequent reduction of the environmental impact of discharged NF/RO concentrated streams.**

Conclusions

- Among the desalination process with MCr unit, FS6 (which means the system with MCr operation on NF and RO retentate streams) is the one to prefer when thermal energy is available in the plant *or* the gain for the salts sale is considered because it is characterized by:

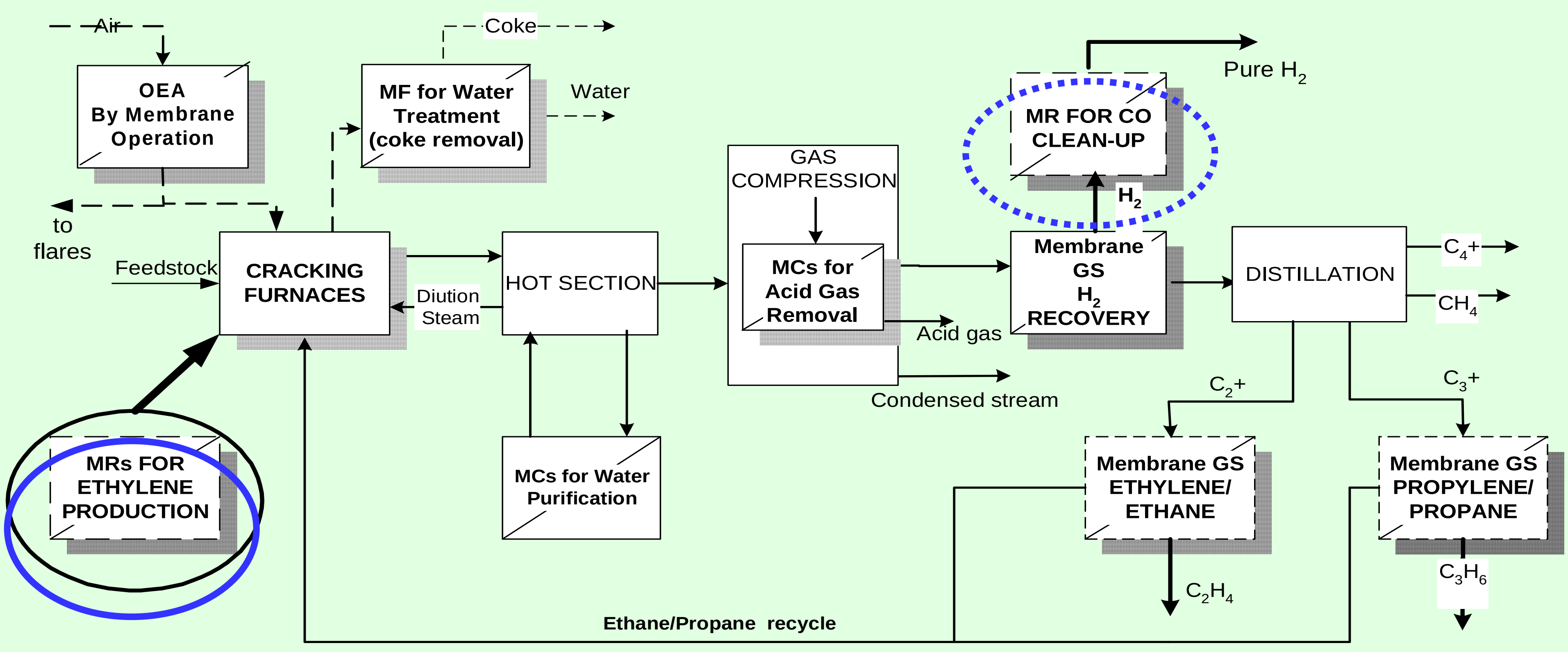
a) the highest recovery factor (92.8%),
b) the lowest amount of drained off retentate stream,
c) the lowest specific energy consumption and desalted water cost,
d) the highest modularity M,
e) *productivity/size* ratio higher than FS7 and slightly lower than FS4 and FS5.

If thermal energy is *not* available in the plant *or* if the gain for the salts sale is *not* considered, FS5 (which means MCr operates only on RO brine) is the desalination system with MCr unit to prefer for what concerns specific energy consumption, desalted water cost and *productivity/size* ratio. However, FS6 remains the best process for what concerns recovery factor, waste production and modularity.

Case study 2:

Application of Exergy and Metrics for the Analysis of Membrane operations Integrated in a Steam Cracking Ethylene Plant

Example 2: Catalytic membrane reactors (CMRs): new opportunities in the petrochemical field



Reference plant:

800,000 t/a ethylene; ethylene yield = 31%; propylene yield = 18%; H_2 yield = 1% (weight basis)

energy consumption = 30 GJ/t ethylene

P. Bernardo, A. Criscuoli, G. Clarizia, G. Barbieri, E. Drioli G. Fleres and M. Picciotti, *Clean Technologies and Environmental Policy*, (2003) , 6 (2004) 78–95.

Ethylene by catalytic processes

Cracking processes: energy and capital intensive.

Highly endothermic reactions, complex furnaces, coking.

Catalytic processes: reduced energy consumption

Ethane oxidative dehydrogenation (EOD)

Promising new way to produce ethylene

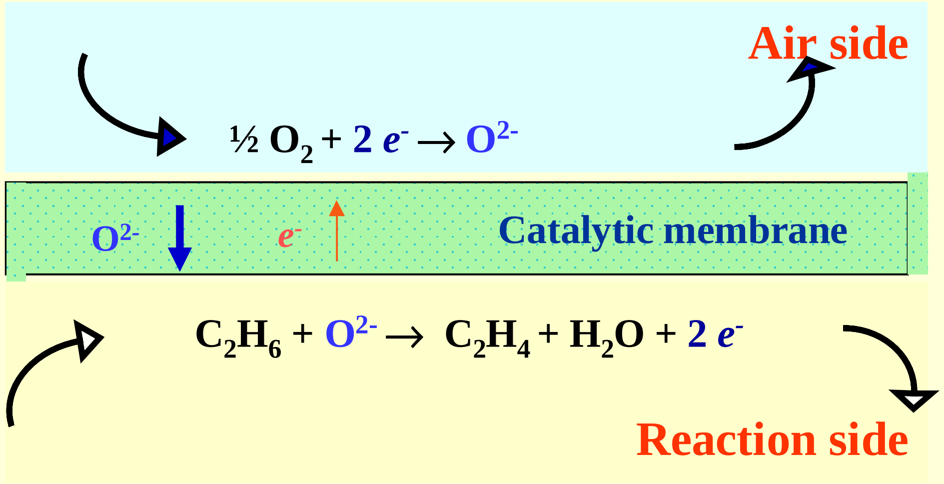
$$C_2H_6 + 1/2\ O_2 \rightarrow C_2H_4 + H_2O$$

- Exothermic and not equilibrium limited
- Coking limited by O_2; no need for steam
- Long-term stable operation

Significantly less investment expected!

Ethane oxidative dehydrogenation (EOD) with O_2 controlled addition in a CMR

$$C_2H_6 + 1/2\ O_2 \rightarrow C_2H_4 + H_2O$$



Air side

$\frac{1}{2} O_2 + 2\ e^- \rightarrow O^{2-}$

O^{2-} e^- Catalytic membrane

$C_2H_6 + O^{2-} \rightarrow C_2H_4 + H_2O + 2\ e^-$

Reaction side

O_2 separation from air

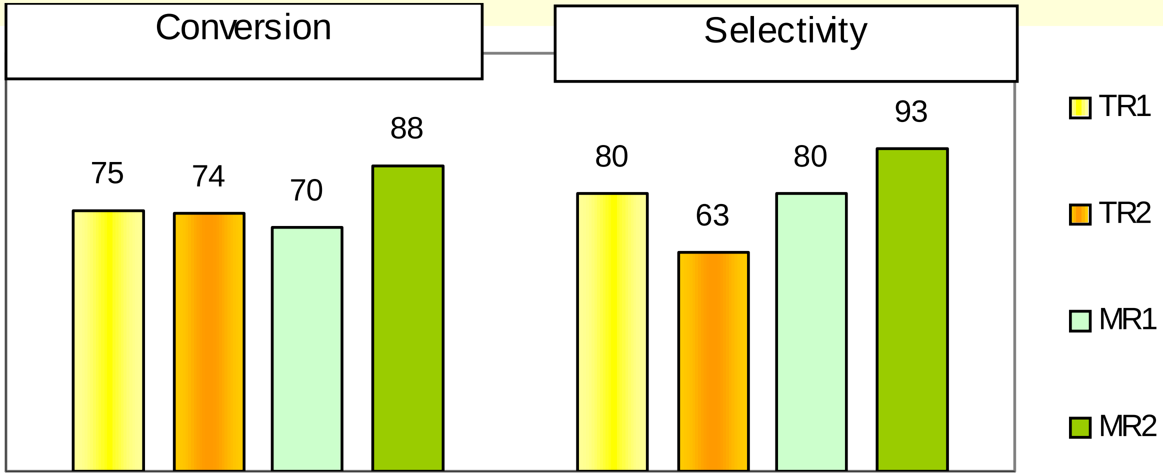
Oxygen conducting membranes*: oxygen selective transport at high *T* (>700 °C)

Activated oxygen provided to the ethane side

[*]Akin and Lin, *J Membr Sci* 209 (2002) 457.

- **Improved safety** (O_2 and C_2H_6 separated)
- **Better heat management**
- **Air can be fed to the MR**
- **Intensified process** (large amounts of inert N_2 excluded)

Ethylene by EOD: Exergetic analysis



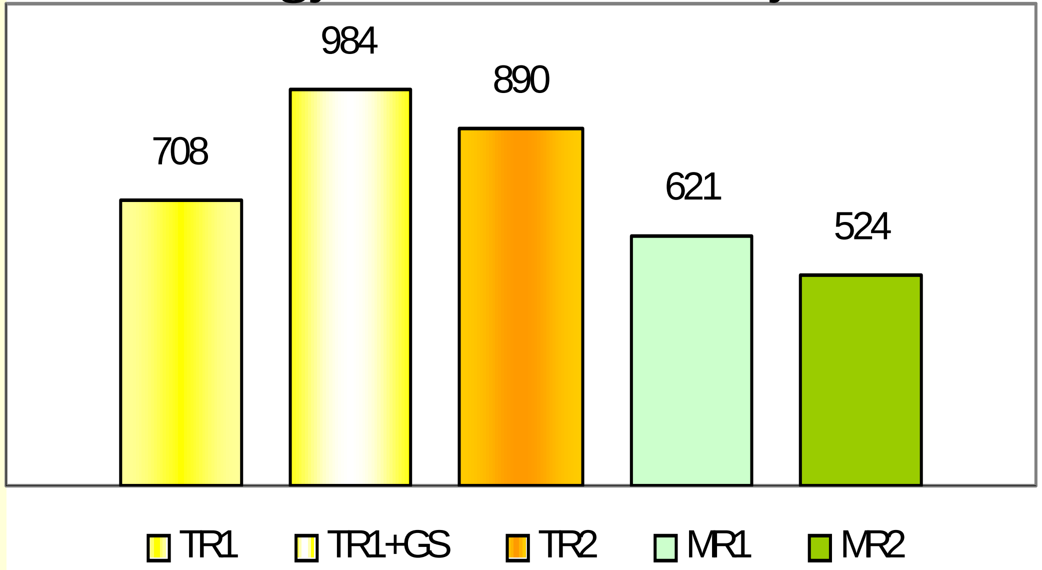
[**TR1 Monolith reactor (Pt-Cu on MgO)**] DOW: Bharadwaj *et al.*, US Patent No. 6,566,573 (2003).

[**TR2 (Perovskite catalyst)**] Donsì et al., *J Catal* 209 (2002) 51.

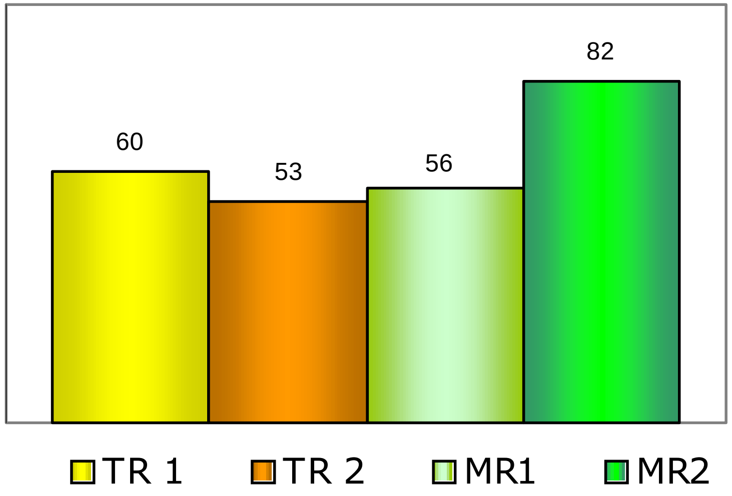
[**MR1 (catalytic membrane)**] Akin and Lin, *J Membr Sci* 209 (2002) 457.

[**MR2 (Perovskite catalytic membrane)**] Rebeilleau et al., *Catal Today* 104 (2005) 131

Exergy losses, kJ/mol ethylene



C efficiency, %



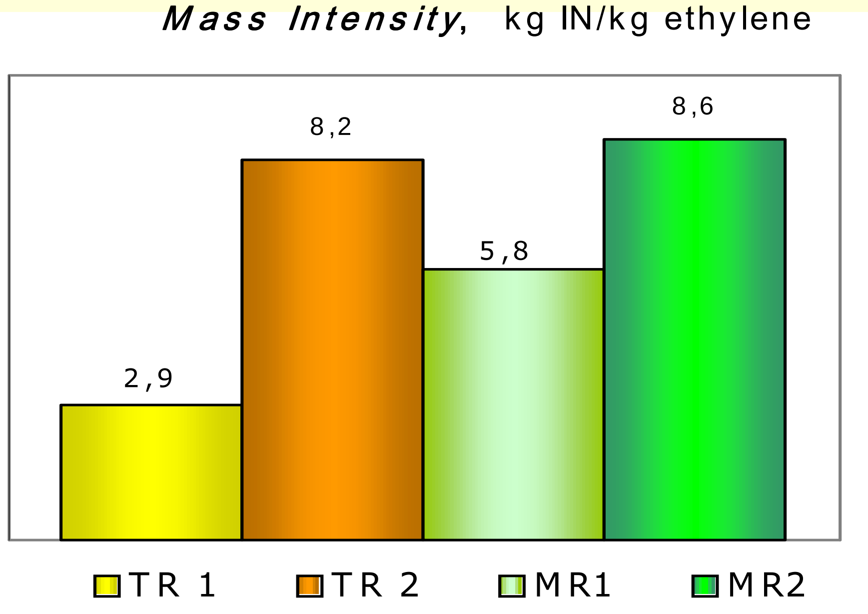
$$C \quad Efficiency = \frac{mol\ C_{C2H4}}{mol\ C_{C2H6}} \cdot 100$$

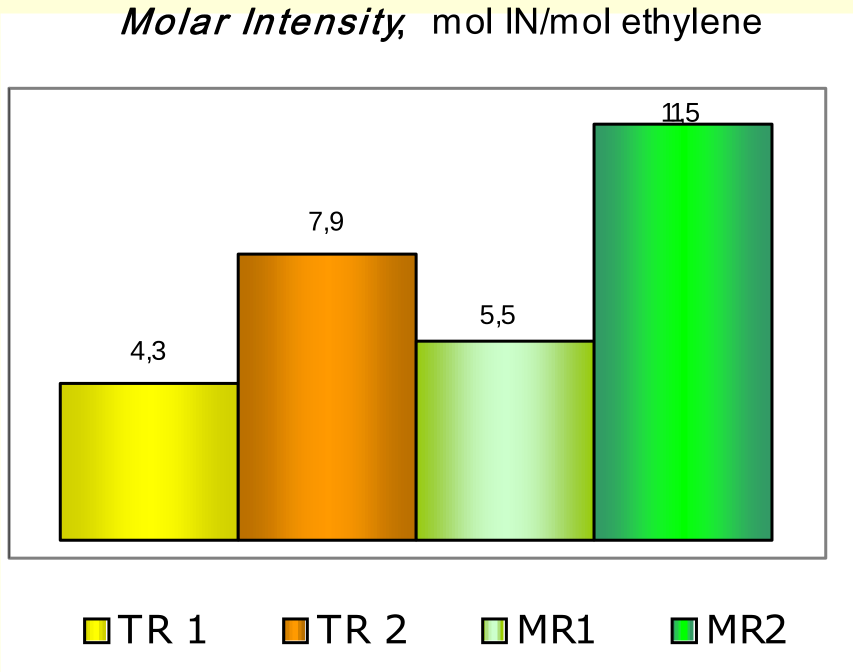
P. Bernardo, G. Barbieri, E. Drioli, An exergetic analysis of membrane unit operations integrated in the Ethyler Production cycle, *CHERD* (2006), accepted.

Reaction Metrics: Ethylene production by Ethane oxy-dehydrogenation

$C_2H_6 + O_2 \rightarrow C_2H_4 + H_2O$

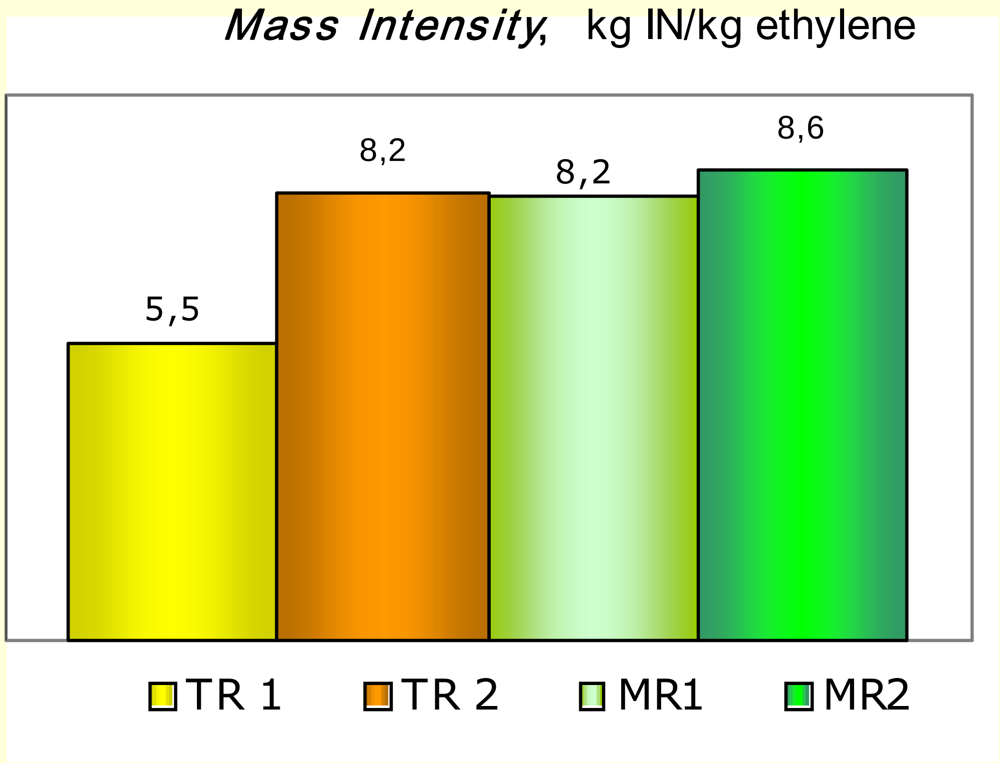
$$Mass\ Intensity = \frac{kg\ IN_{TOT}}{kg\ Ethylene}$$


Mass Intensity, kg IN/kg ethylene


Molar Intensity, mol IN/mol ethylene

Reaction Metrics: Ethylene production by Ethane oxy-dehydrogenation

Considering the air required to produce the O_2 for the reactor



Reaction Metrics: Ethylene production by Ethane oxy-dehydrogenation

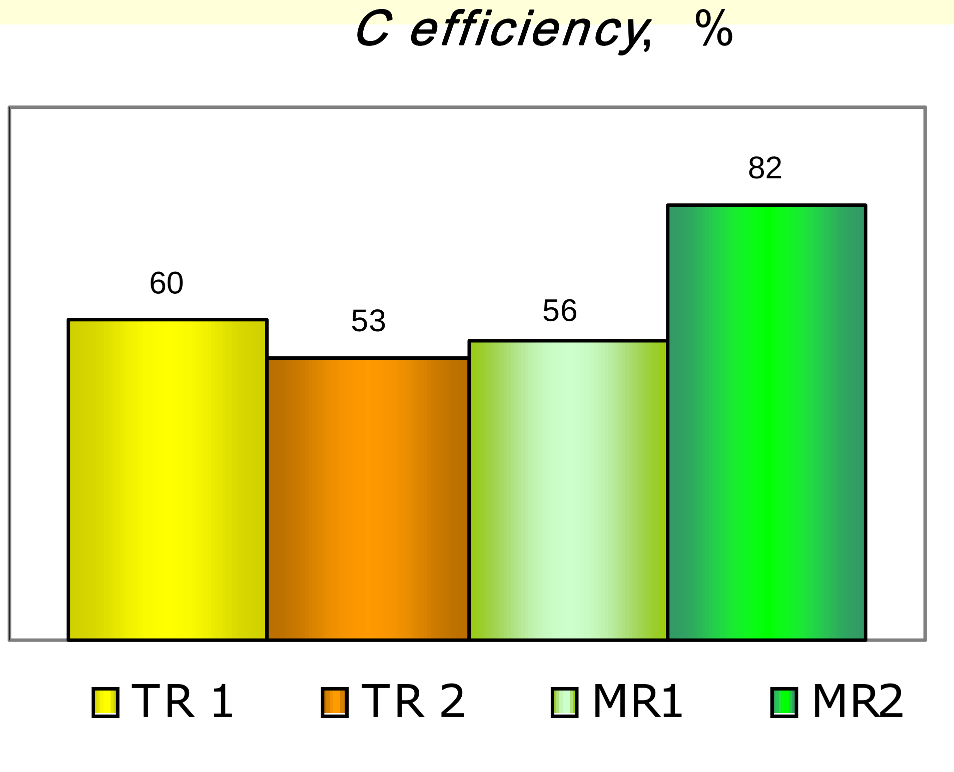
$$C_2H_6 + O_2 \rightarrow C_2H_4 + H_2O$$

$$C \quad Efficiency = \frac{mol\ C_{C2H4}}{mol\ C_{C2H6}} \cdot 100$$

$$= \frac{2\ F_{\mathrm{C2H4}}^{\mathrm{Formed}}}{2\ F_{\mathrm{C2H6}}^{\mathrm{Feed}}} \cdot 100$$

$$= \boxed{Y_{C2H6}}$$

Reaction Yield



Conclusions

It is expected that, in the next future, modern process engineering will be redesigned through all the different available membrane operations, from the more traditional pressure driven units (as RO, NF, UF and MF in various industrial processes, product formulation and extraction), to the membrane bio-reactors and catalytic membrane reactor (in chemical reaction), to the membrane contactors (Membrane Distillation, Membrane Crystallizer, Membrane Strippers and Scrubbers in energy and mass transfer processes).

Membrane technology will be considered for realizing new integrated production, purification, distribution and reuse systems in the same industrial cycle (integrated membrane processes).

Conclusions

Several indicators to quantify the progress of industrial processes towards *sustainability*, and to define and identify proper indicators to measure their impact on environment, economy and society have been presented.

mass and waste metrics are good indicators of plant efficiency and environmental impact

the new metrics (for example, PS and M) allow to compare the systems with respect to their size and the modularity

The presented indicators can be used for analyzing and comparing, in terms of Process Intensification, any process and not only membrane operations.

However, a single parameter can not univocally establish the "sustainability" and a convenience of a process. The final evaluation of a process must be always carried out by considering more and more parameters, which take into account not only the economic aspect but also its environmental and societal relapse.

Thank you for your attention