New Trends and Technologies for Membrane Desalination

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- ✓ ***62.8 million m^3/d:*** **the cumulative contracted capacity of desalination plants around the world …**

- ✓ ***13869:*** **the number of contracted desalination plants worldwide as of June 30, 2008 (6% more compared with the prior year) …**

- ✓ ***80:*** **the percentage of desalination plants using membrane technology for sea-brackish water desalination (90% of which use RO technology) …**

… the rising use of membrane desalination around the world is the piece of evidence of how much membrane-based sea/brackish water desalination is emerged in the last decades as the most promising contributor to solve water shortage problem.

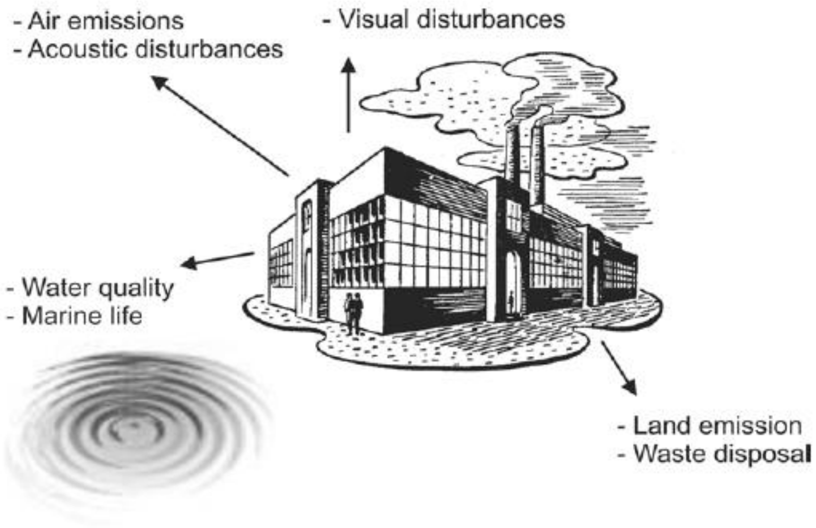
Despite the great success and the potentialities of membrane technology, the following critical problems still remain open:

increasing

- ✓ **water quality**
- ✓ **recovery factor of the desalination processes**

reducing and minimizing

- ✓ **fouling**
- ✓ **energy consumption**
- ✓ **costs**
- ✓ **brine disposal**
- ✓ **environmental impact**



Environmental impact of water treatment processes **- C. Fritzmann et al., Desalination 216 (2007) 1–76.**

Process Intensification Strategy **offers a possible solution to the problem of satisfying the increasing demand for water, energy, raw materials and products under the constrains imposed by the concept of sustainable development.**

E. Drioli and D. R. Paul, *Ind. Eng. Chem. Res.* 2007, *46*, 2235.

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

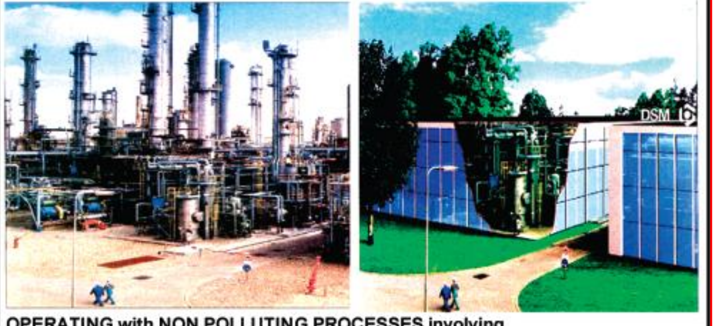
by replacing processes and equipments

- ✓ **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

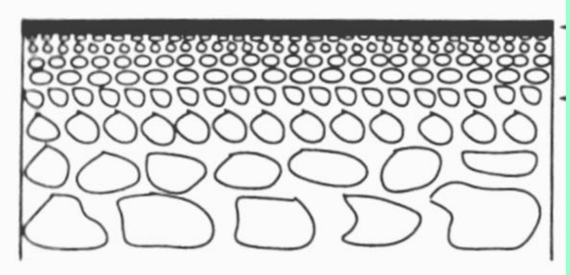
SAVINGS ABOUT 30 % (RAW MATERIALS + ENERGY + OPERATING COSTS)

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

Membrane Technology and Process Intensification principles/approaches: contact points

Optimize the Driving Forces and Maximize the Specific Surface Area to Which These Forces Apply.

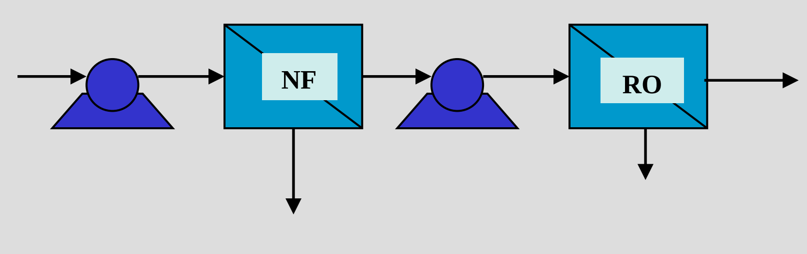
The nanostructured structure of the membranes allows to have large mass transfer surface area enclosed in a small volume.



Energy *consumption in membrane operations is order of magnitude lower than that of conventional processes.*

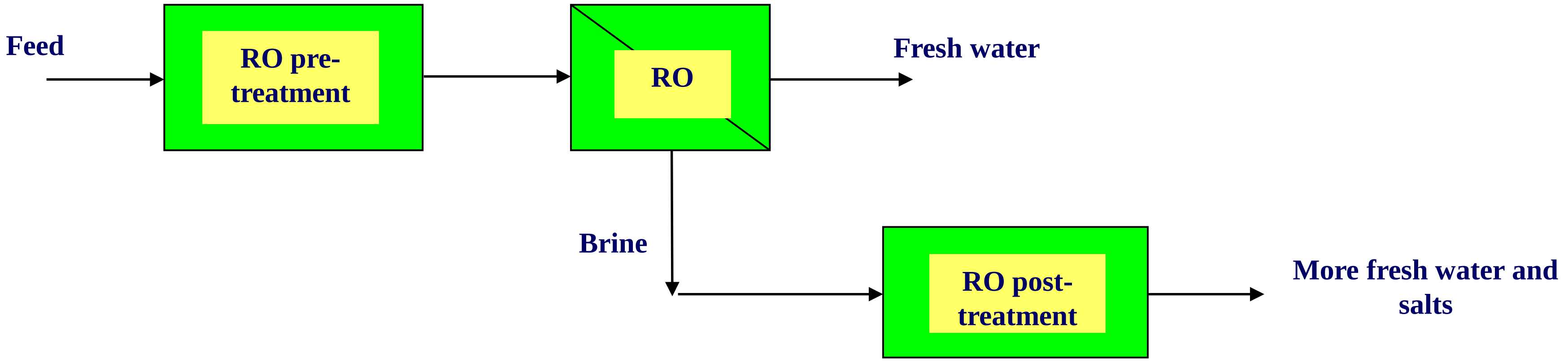
Maximize the Synergistic Effects from Partial Processes at all possible scales.

The operational simplicity of membrane operations gives the possibility to integrate different membrane techniques



The specific area with a fiber of 10^{-3} mm inner diameter can be about 10^4 m^2/m^3, at least 1 order of magnitude higher than those of traditional shell-and tube units.

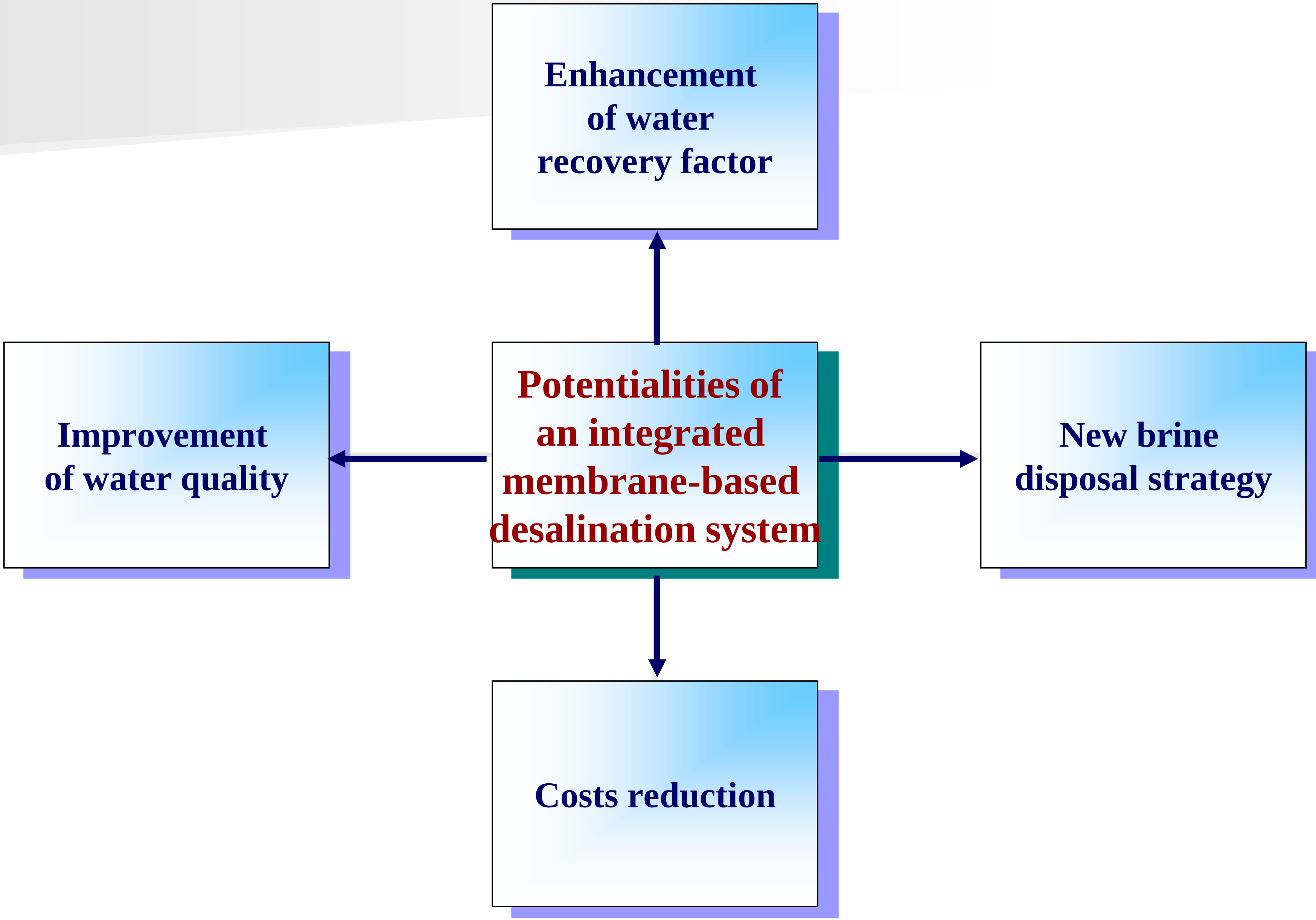
Integration of membrane technologies according to the philosophy of Process Intensification: *key-factor 1* for the improvement of RO desalination systems



The integration of different but complementary membrane operations in RO pre-treatment (MF/UF/MBR/NF/Membrane Contactor) and post-treatment stages (Membrane contactor/Membrane Distillation/Membrane Crystallizer) allows to control and minimize fouling phenomena and has the potentialities to approach the concept of "zero-liquid-discharge" and "total raw materials utilization".

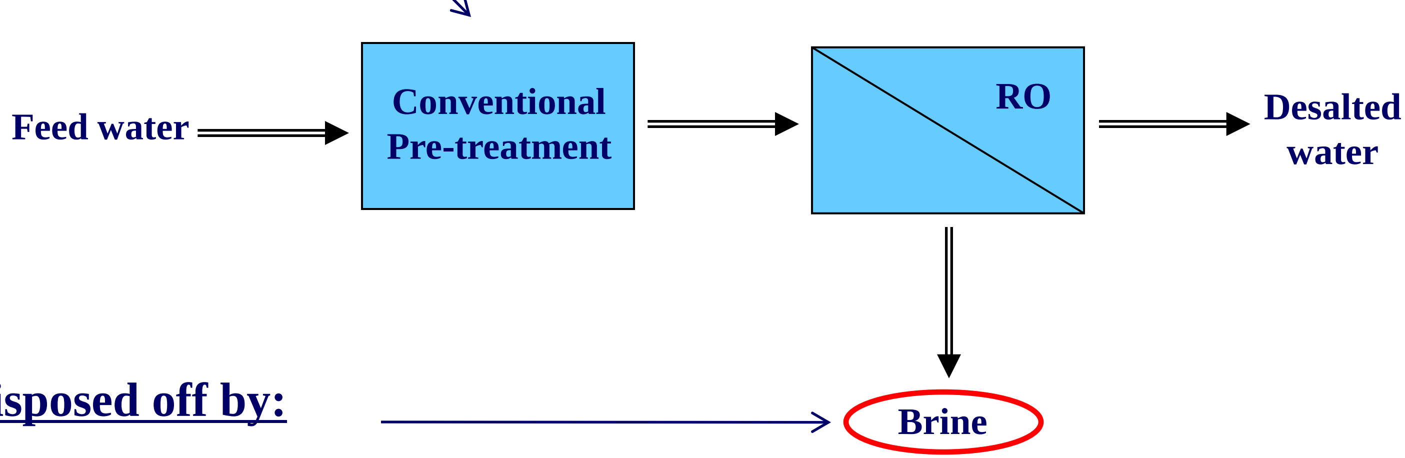
Key-factors for further improvements of desalination systems				
(Key-factor 2) Novel concentrate treatment options (such as membrane crystallization)	(Key-factor 3) New membrane modules and materials particularly adapt to water treatment with enhanced transport mechanisms, selectivity, flux and highly resistant to chlorine attack	(Key-factor 4) Optimization of system design for achieving the most increasingly stringent water quality standards with respect to new contaminants	(Key-factor 5) Development of water treatment systems coupled with renewable energy sources for a significant reduction in energy consumption and in the dependence on fossil fuel	(Key-factor 6) Reconsideratio n of pressure-retarded osmosis and reverse electrodialysis as membrane techniques to generate power from salinity gradients

Key-factor 1: Integrated Membrane Systems for Desalination



Conventional Pre-treatment to Sea Water Reverse Osmosis (SWRO) Desalination

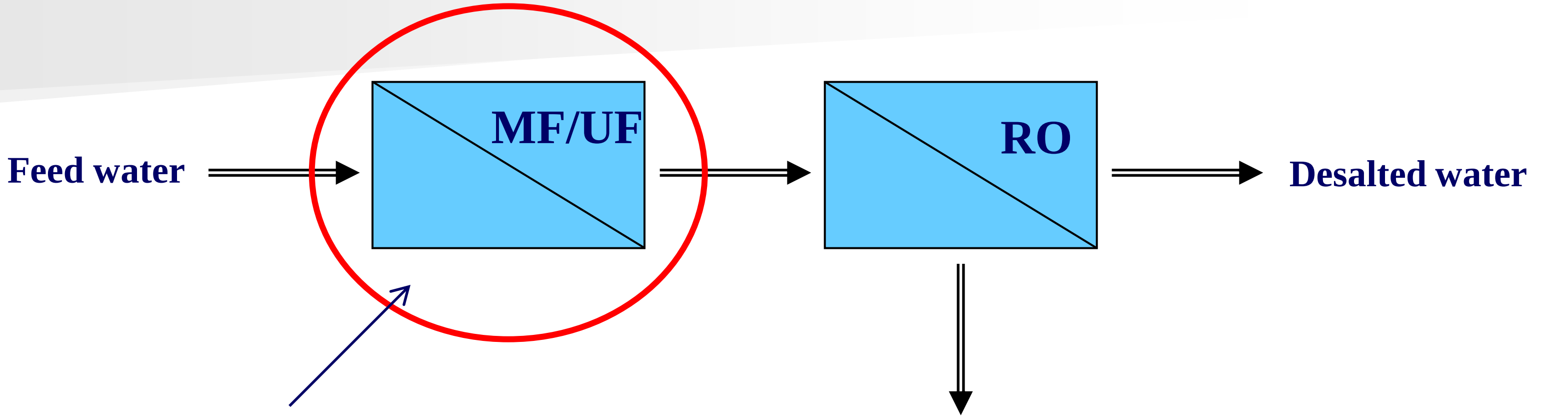
Extensive use of chemicals (disinfection, flocculant, anti-scaling agent) and mechanical filtration units (sand filtration, media filtration, cartridge filtration)



<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**

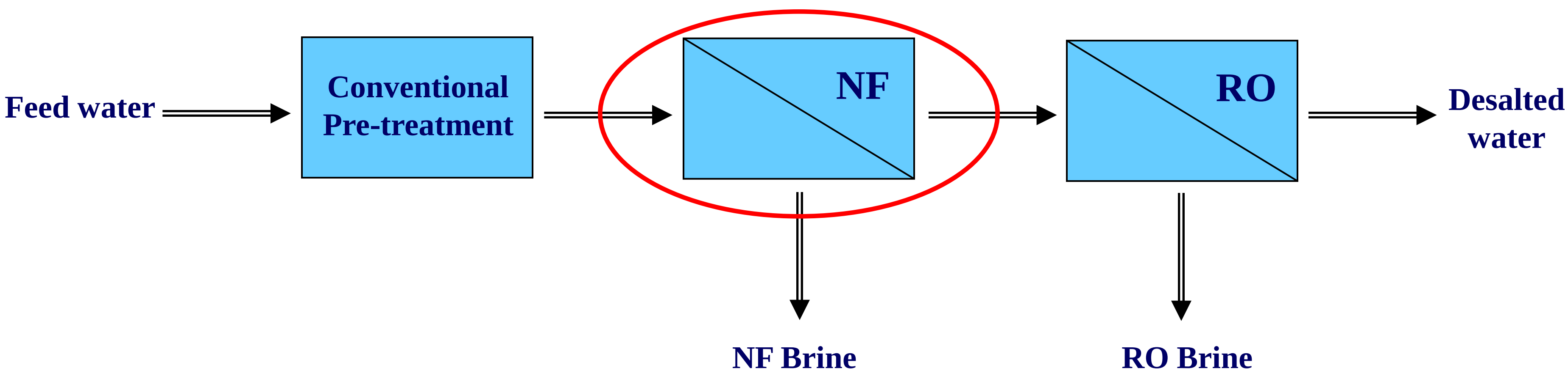
✓ **Less maintenance cost for the high pressure pump and the measuring instruments**

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

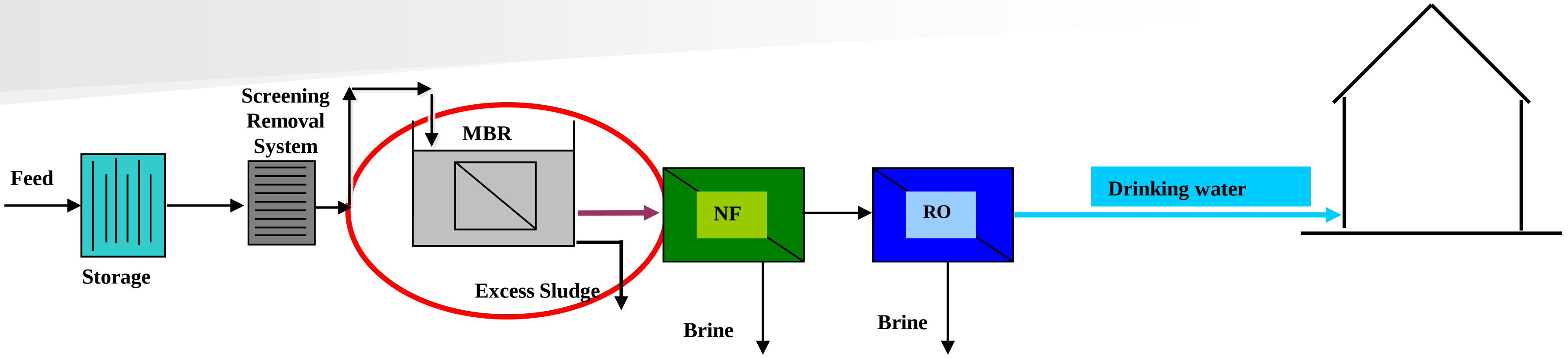
Nanofiltration (NF) as "Softening" Step for RO

- 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)

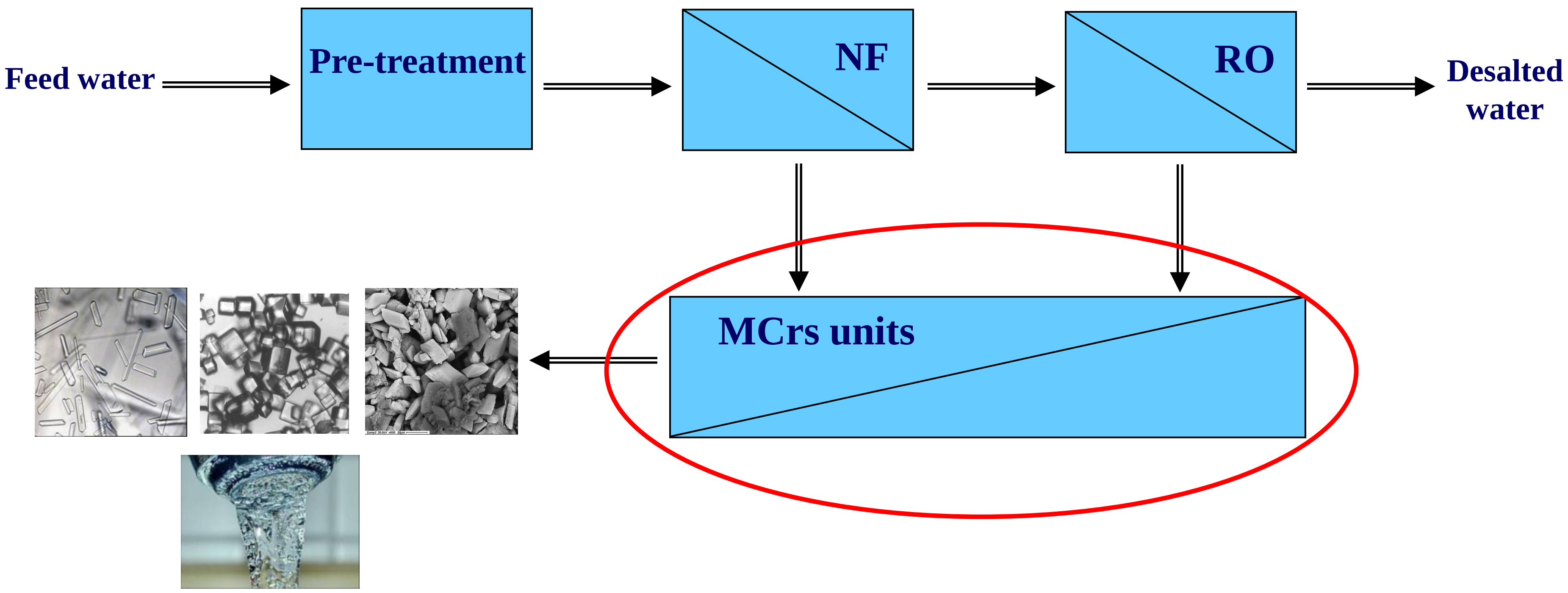


Membrane Bioreactor as SWRO pre-treatment and not only for municipal and industrial wastewater treatment

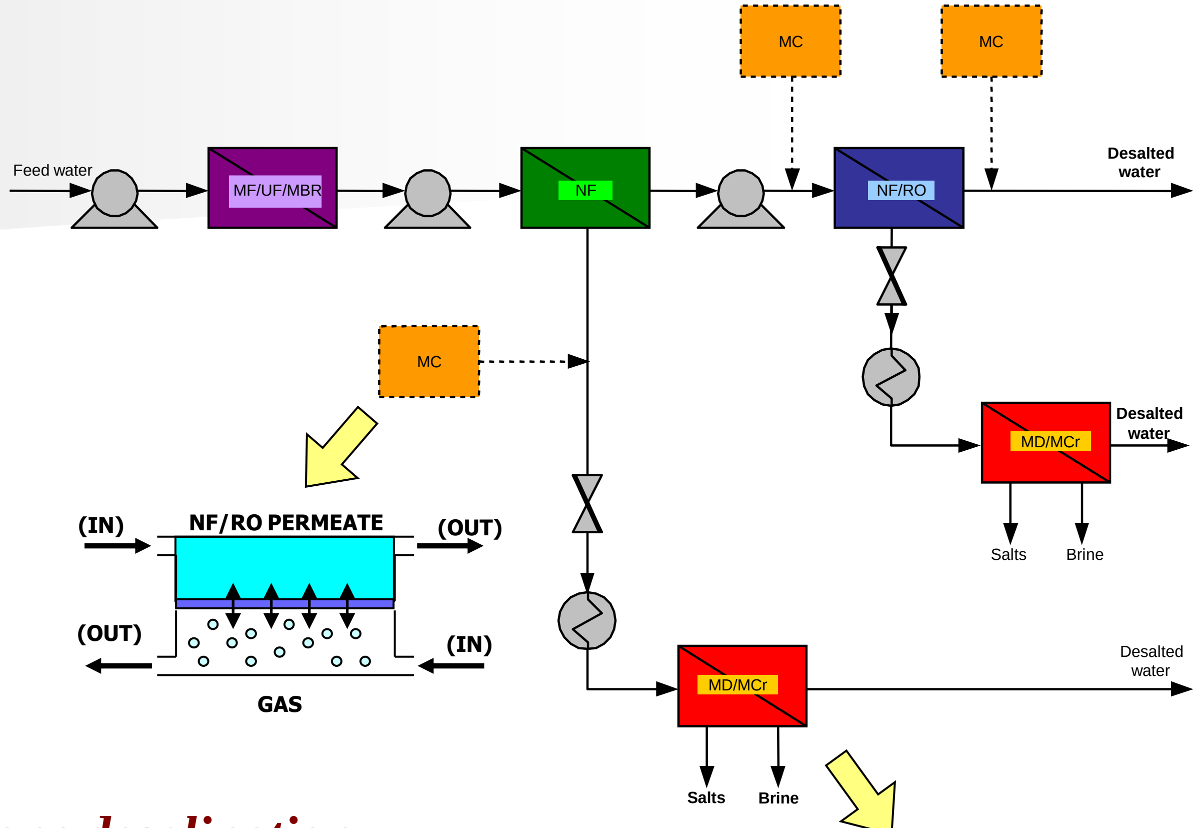


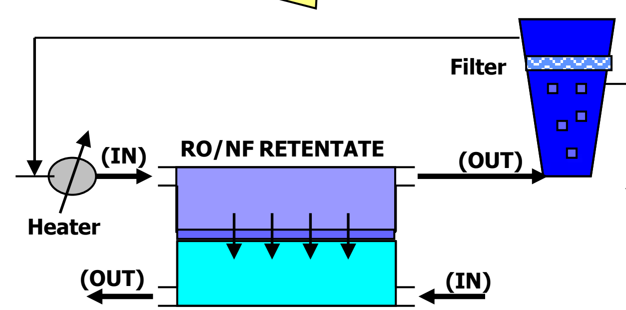
The possibility to use Membrane Bioreactor as SWRO pre-treatment could be of interest for the removal of a variety of anthropogenic organic pollutants and fouling agents that are increasingly present in sea/brackish-water. With respect to costs, MBR is considered a high tech process with high initial investment costs when applied to wastewater treatment. This should not be the case when MBR was used to treat seawater, with a typical total organic carbon concentration in the range of 1.0-3.0 mg/L. Under such conditions the use of MBR technology could be a very cost-effective process.

Membrane Crystallization (MCr) Operating on the Brines of NF and/or RO



Drioli et al. Chem. Eng. Res. Des. 2006, 84, 209.



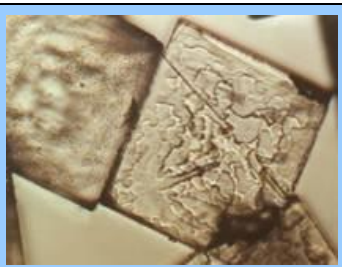


Possible integrated membrane desalination system at the basis of MEDINA project (one of the European funded projects in the Sixth Framework Programme)

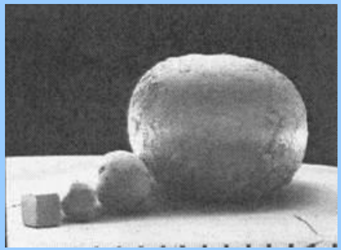
MEDINA web-site: http://medina.unical.it

Advantages in the use of Membrane Crystallization as novel concentrate treatment option compared to traditional techniques (*Key-factor 2)*

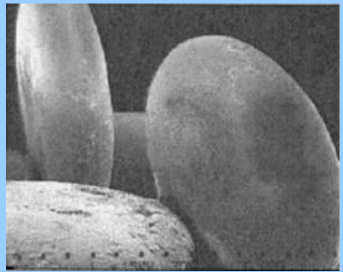
- ✓ High specific area for mass transfer
- ✓ Optimal control of the supersaturation level
- ✓ Shorten induction periods
- ✓ High values of the crystal growth rate at low supersaturation
- ✓ Possibility to act on the heterogeneous nucleation choosing appropriate polymeric membrane
- ✓ Well ordered organization of the molecules, finally resulting in the formation of crystals with better structural properties, when working under forced solution flow regime



NaCl from a membrane crystallizer

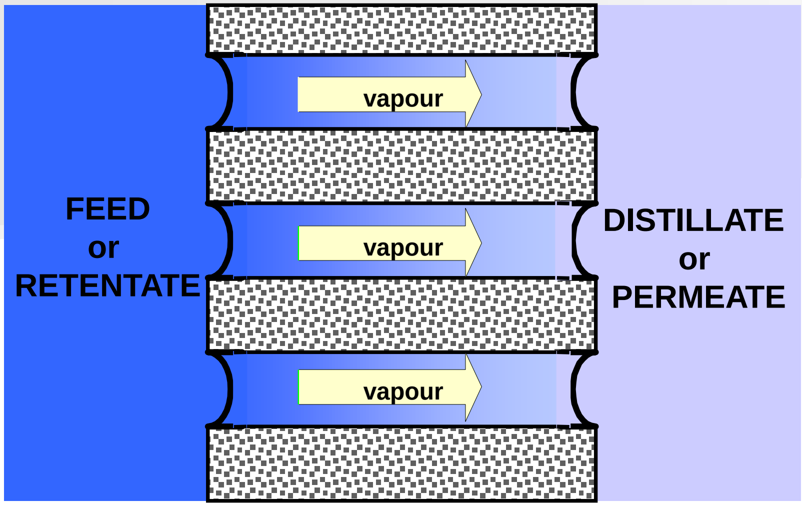


NaCl from a Draft Tube Buffled crystallizer

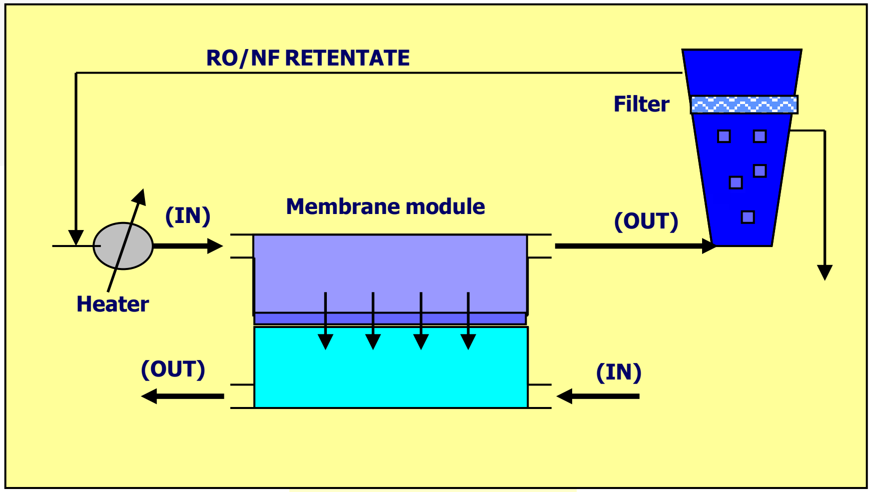


NaCl crystals grown in a rotating flow

Advantages of Membrane Crystallization Technique



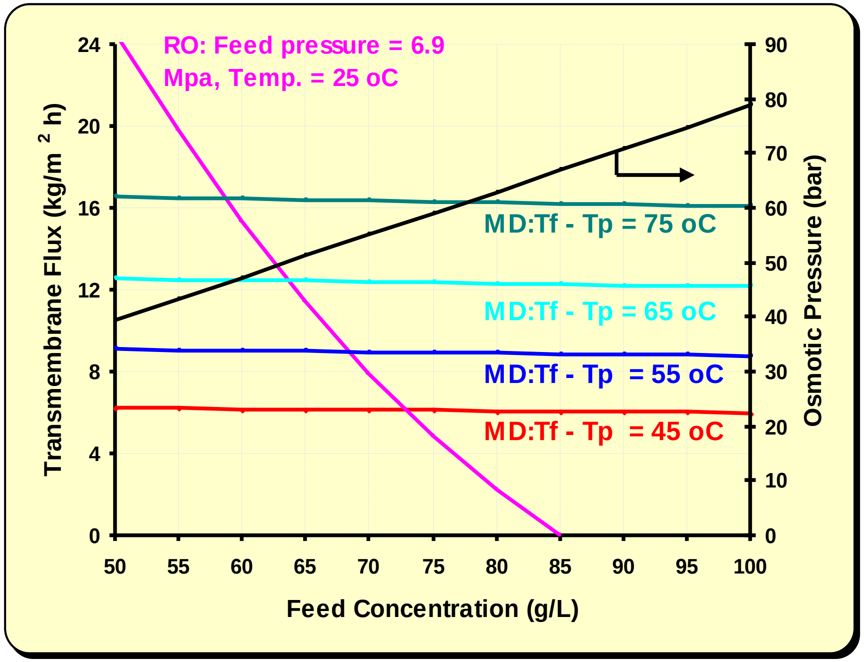
Mcr principle



MCr process

✓ **The process is not limited by concentration polarization phenomena → pure water can also be obtained from highly concentrated feeds with which RO cannot operate.**

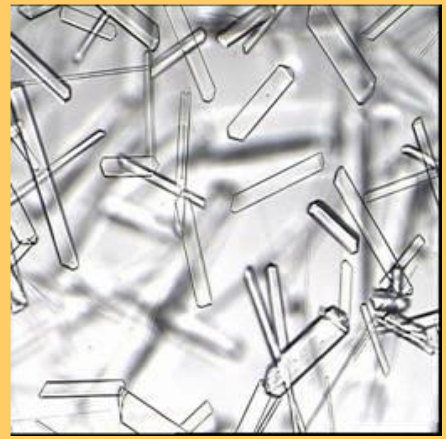
✓**MCr is characterized by the separation of the two crucial steps of a crystallization process: the solvent evaporation and the crystallization.**



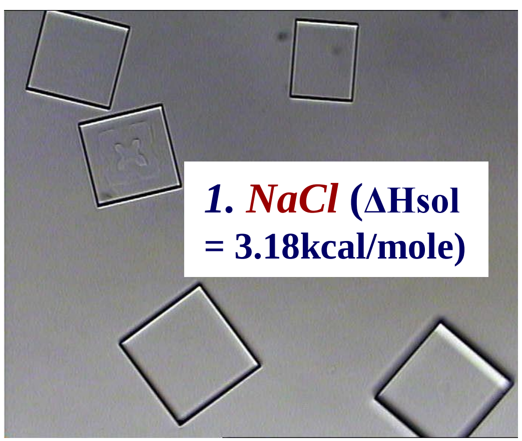
Salts that can be recovered as high quality crystals from NF/RO brine

Detailed composition of NF/RO brines [g/L]

Ion [g/L]	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

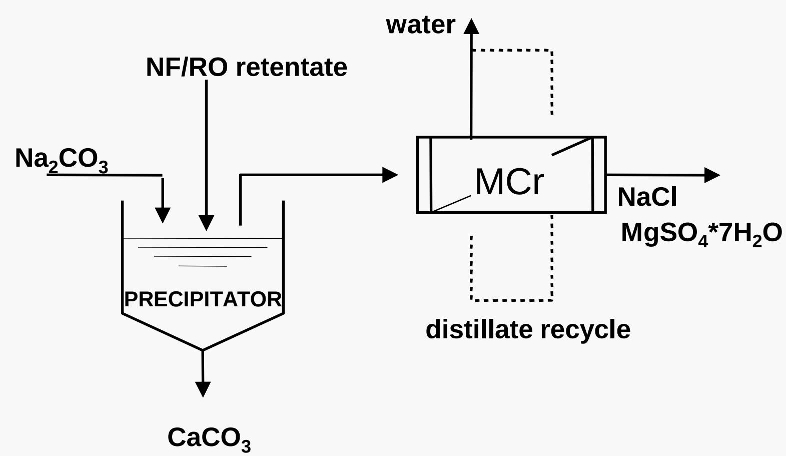


2. *Magnesium sulphate* which, at 25°C, precipitates in the form of epsomite (ΔH_{sol} = 3.18 kcal/mole)



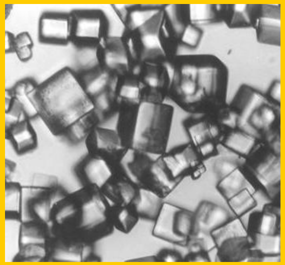
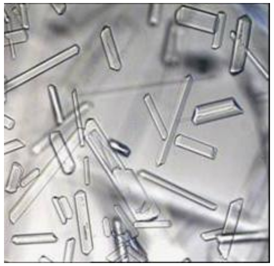
1. *NaCl* (ΔHsol = 3.18kcal/mole)

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



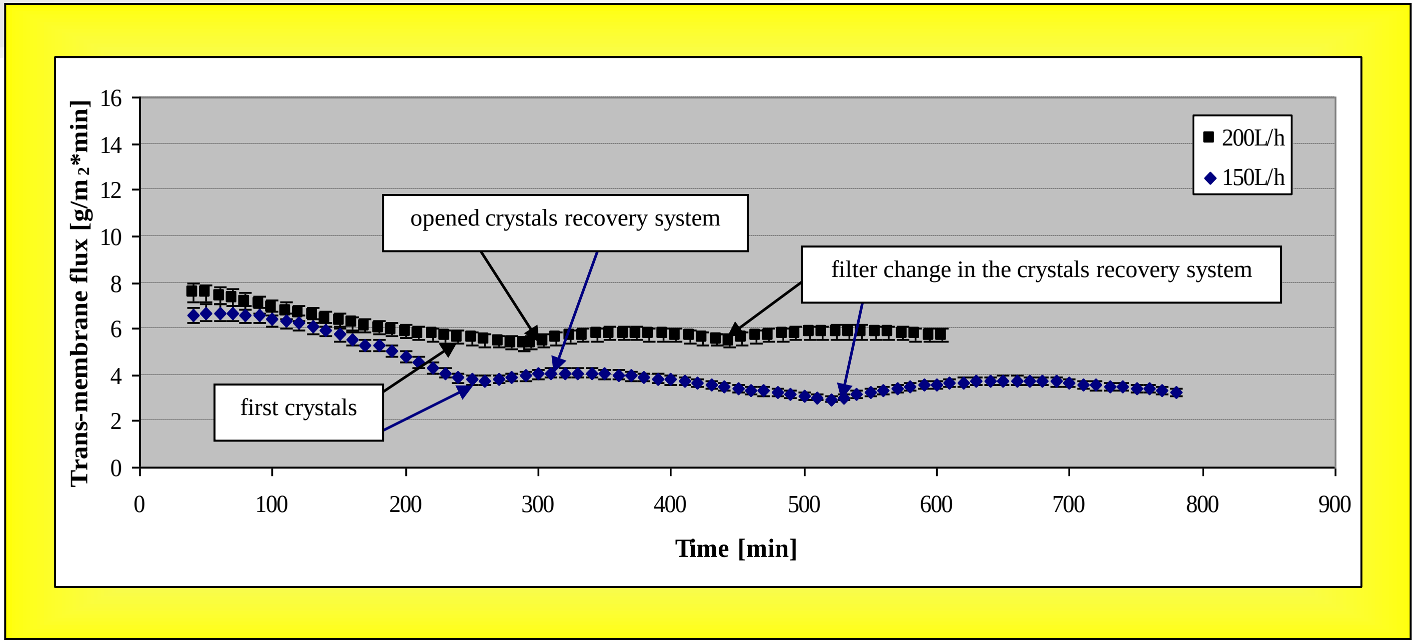
* By considering: Standard seawater inorganic composition; EC SW30HR LE-400 in RO and Osmonics NF300 PA in NF.

Amount of salts produced per cubic meter of NF brine

MCr recovery factor		90.2%	95.2%	97%
Recovered salts per m³ of NF brine				
		kg/m^3	kg/m^3	kg/m^3
$CaCO_3$		3.39	3.39	3.39
NaCl		17.0	35.3	41.8
$MgSO_4*7H_2O$		0.00	0.04	10.1
Total amount of recovered salts per m^3 of NF brine		20.4	38.7	55.2

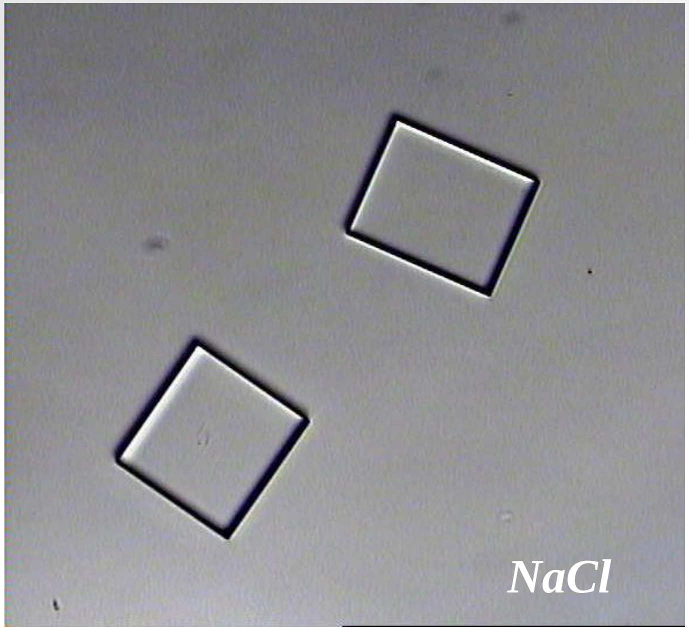
Fluid-dynamic effect on MCr operation - no crystals deposition on membrane surface - "crystals recovery system"

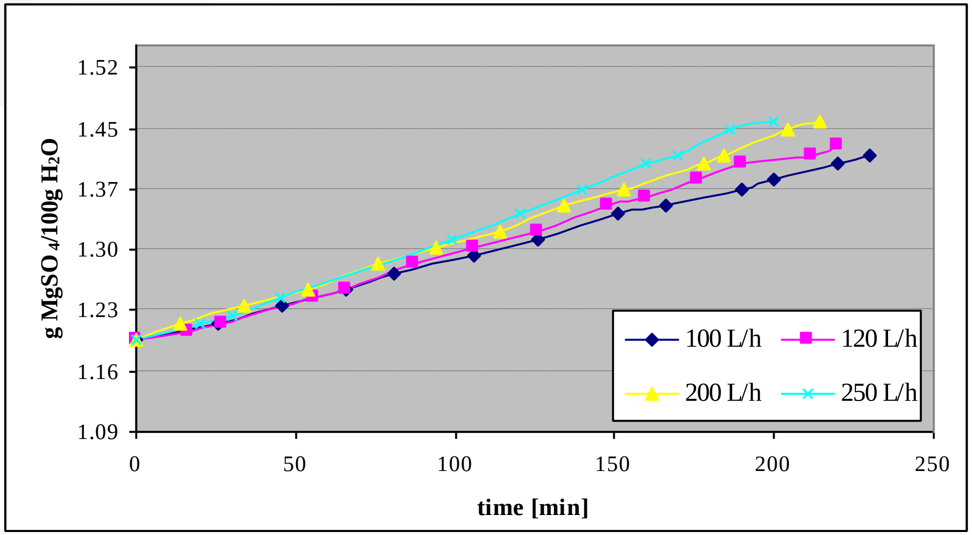
NF brine crystallization



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

RO brine crystallization: type of produced salts



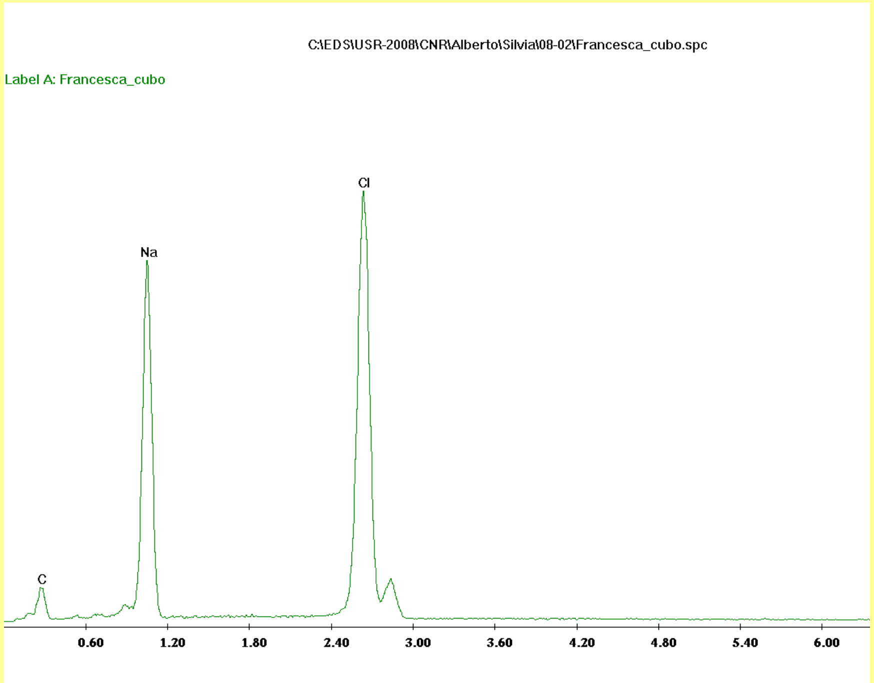


Magnesium sulphate concentration vs time at different feed flow rates for the lab tests of aqueous solution of NaCl.

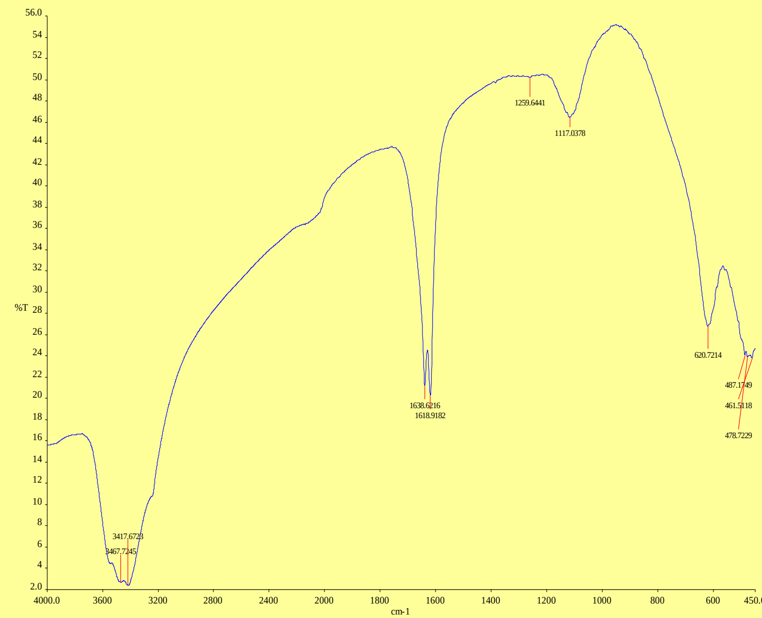
✓ **Only NaCl can be produced from the RO retentate crystallization.**

✓ **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.

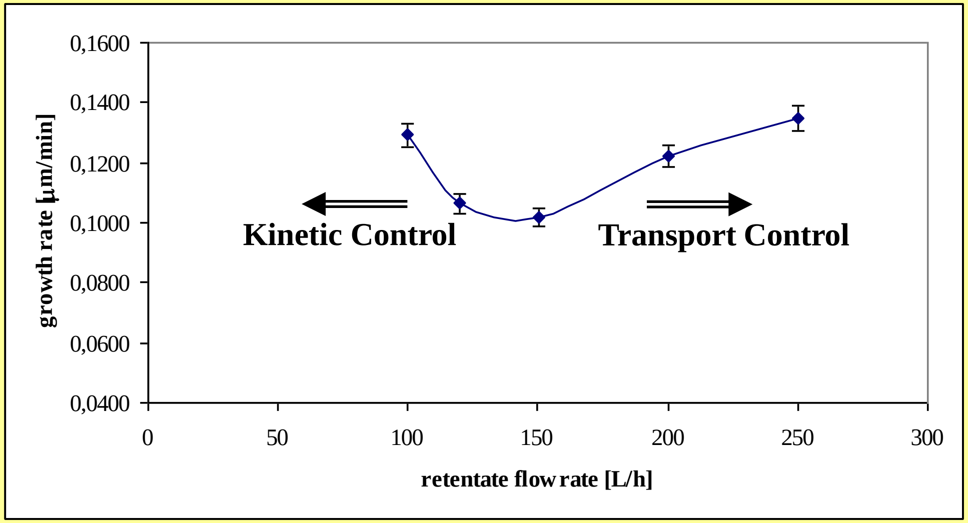
Methods:

- 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 $MgCl_2*6H_2O$

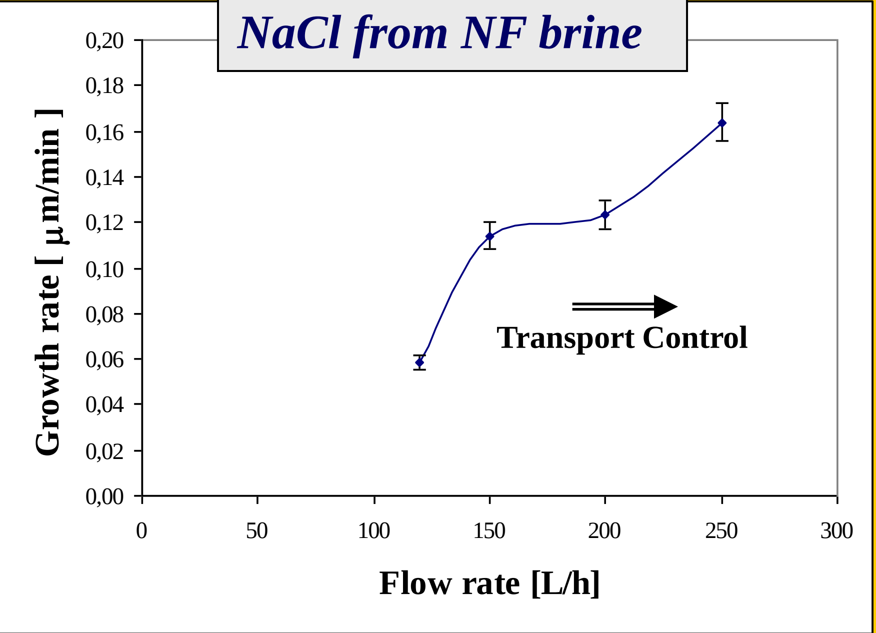
Crystallization kinetics of produced salts: Nucleation and Growth



NaCl from RO brine

Retentate flow rate [L/h]	G [mm/min]	B° [no/L*min]
100	**0.0001294**	87,831
120	**0.0001063**	127,590
150	**0.0001017**	115,511
250	**0.0001349**	103,031

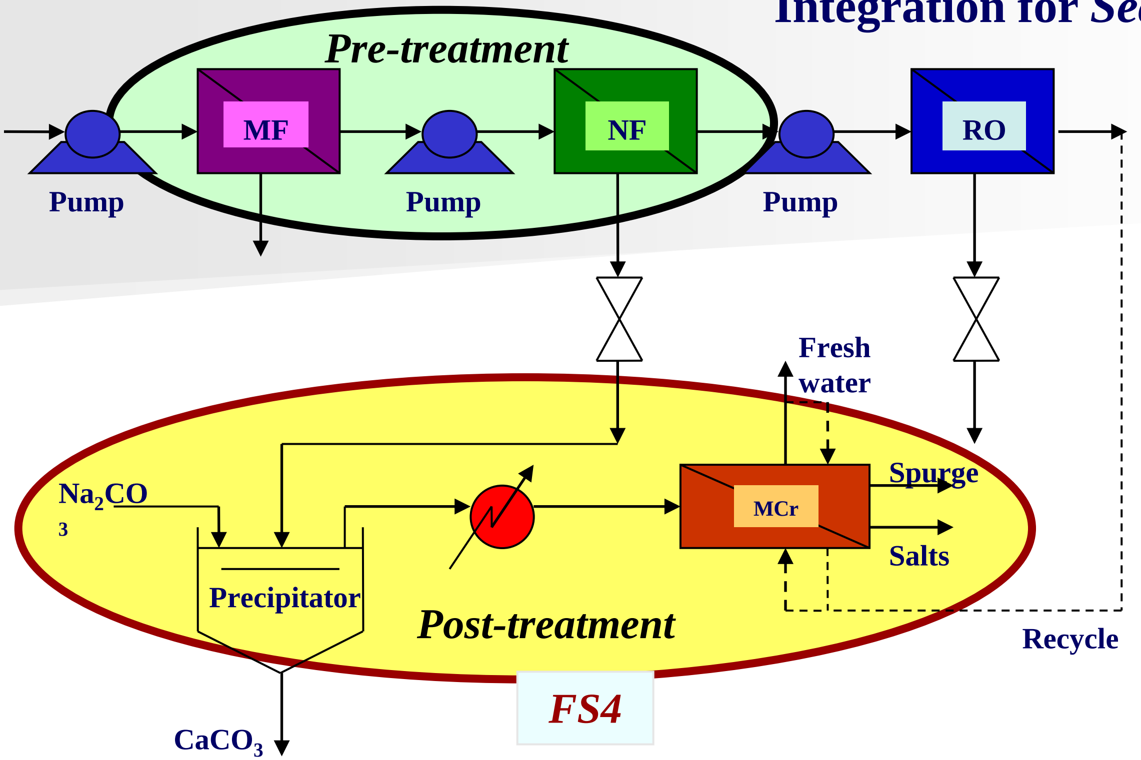
NaCl from NF brine



Retentate flow rate [L/h]	G [mm/min]	B° [no/L*min]
120	**0.0000585**	200,200
150	**0.0001142**	194,110
200	**0.0001235**	168,714
250	**0.0001639**	199,914

Lab tests have proved that growth rate increases with feed flow rate: the crystal growth is limited by the diffusional resistance to the movement of molecules to the growing crystal face.

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



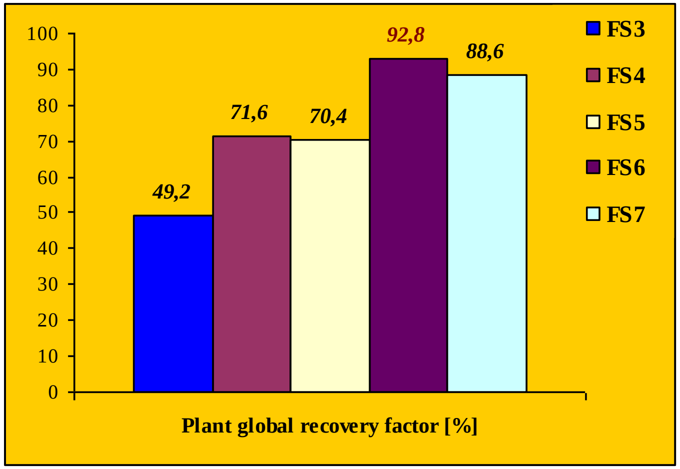
FS4: MF-NF-RO, MCr on NF brine

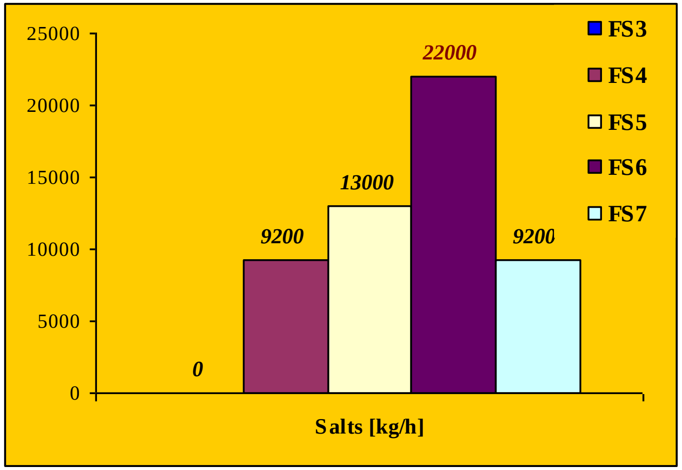
FS5: MF-NF-RO, *MCr on RO brine*

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 et al., Chemical Engineering Research and Design, 84 (A3) (2006) 209–220. - E. Drioli et al., Desalination and Water Treatment, in press.

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* [$/m^3]	0.61/0.40[a]	0.47/0.40[a]	0.46/0.39[a]	0.68/0.63[a]	0.59/0.54[a]	0.73/0.69[a]	0.74/0.71[a]
Unit cost*, b [$/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.

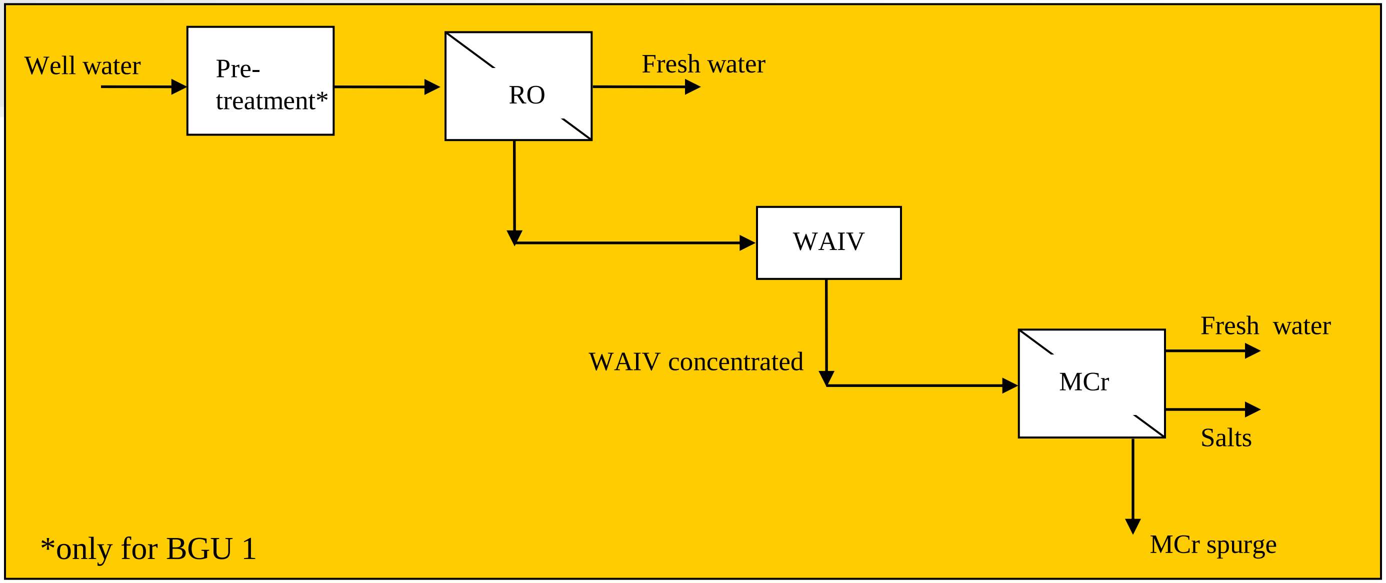
Advantages in the use of integrated membrane systems: 1) increase in plant recovery factor; 2) production of solid materials of high quality and controlled properties (as specific polymorph of salts) with important added values, transforming the traditional brine disposal cost in a potential new profitable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

Due to the increasing of water shortage problems, in future the need for brackish water desalination will continue to increase and the primary limitations to further application of RO inland are the cost and technical feasibility of concentrate disposal. Also the optimization of antiscalant dosing, chemical addition, and pH control are essential parameters to monitor for improving the concentrate treatment.

The application of novel concentrate treatment options (such as membrane crystallization) can help also in developing inland brackish water RO, minimizing the impact of concentrates on the environment towards zero discharge *(Key-factor 2)*.

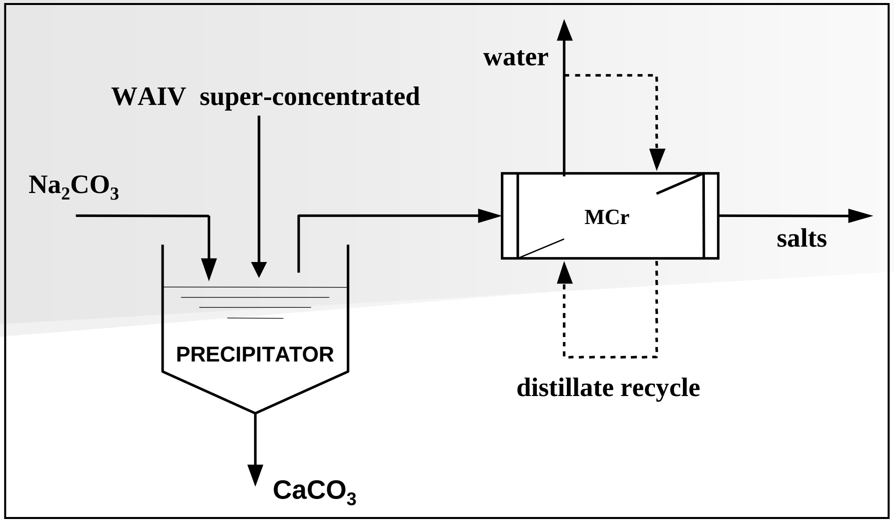
MCr tests on super-concentrated real brackish water RO brine: some examples



Two different types of WAIV (Wind-Aided Intensified eVaporation) super-concentrated were further concentrated through the MCr process:

a) a first sample named BGU 1 without antiscalant and organics,

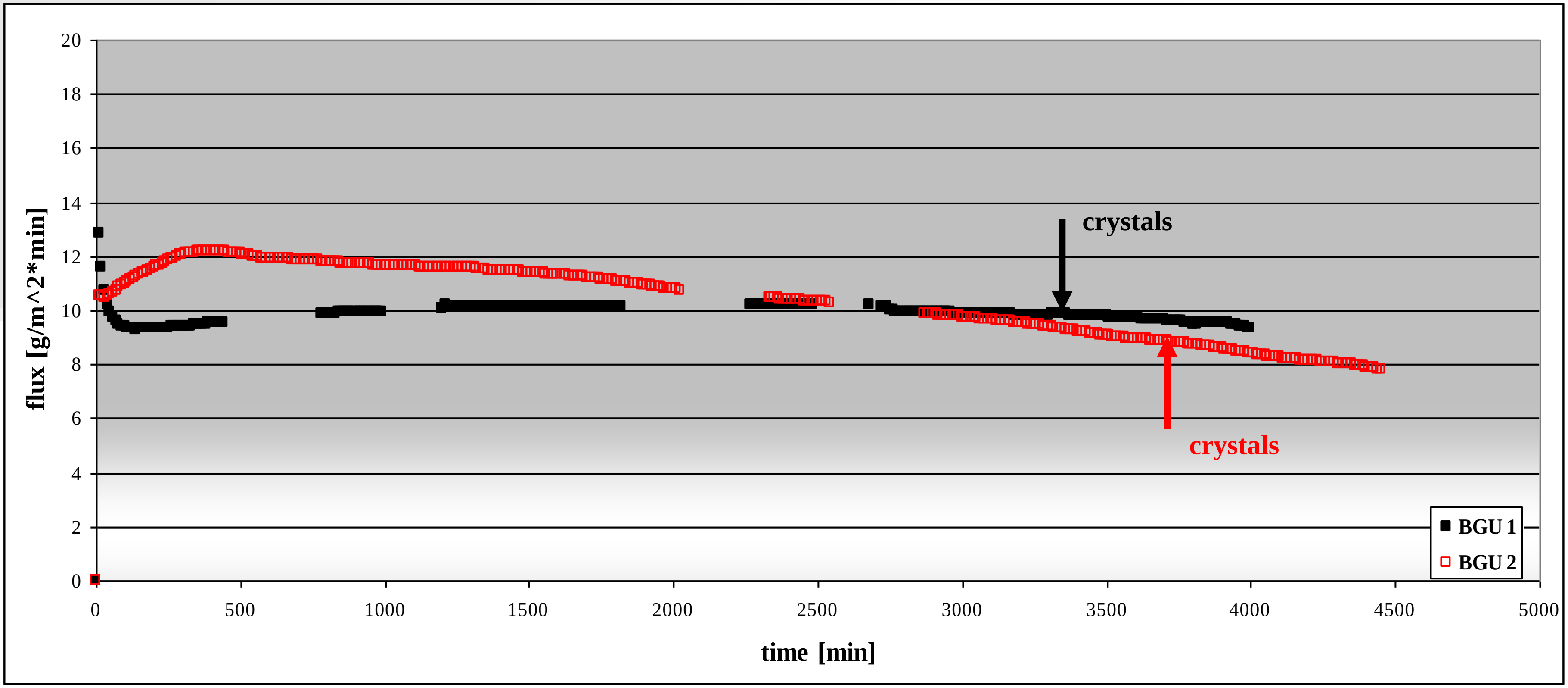
b) a second sample named BGU 2 with antiscalant and organics.



Na_2CO_3 was added in 1:1.05 molar ratio of Ca^{2+}/CO_3^{2-} (both in BGU 1 and in BGU 2).

	BGU 1	BGU 2
Ca	1426 ppm	907.2 ppm
Na_2CO_3 used	4.126 g/L	2.857 g/L
$CaCO_3$ recovered	3.56 g/L	2.04 g/L
Ca^{++} ions recovered	96.3 %	79.4 % (17.5% lower than BGU 1)

1st effect of antiscalants (sodium hexametaphosphate): decrease in the amount of recovered $CaCO_3$.



Trend of flux vs time in the MCr test carried out using as feed water the WAIV super-concentrates.
BGU 2 (with organics. First crystals after 3720 min) - BGU 1 (without organics. First crystals after 3390 min).

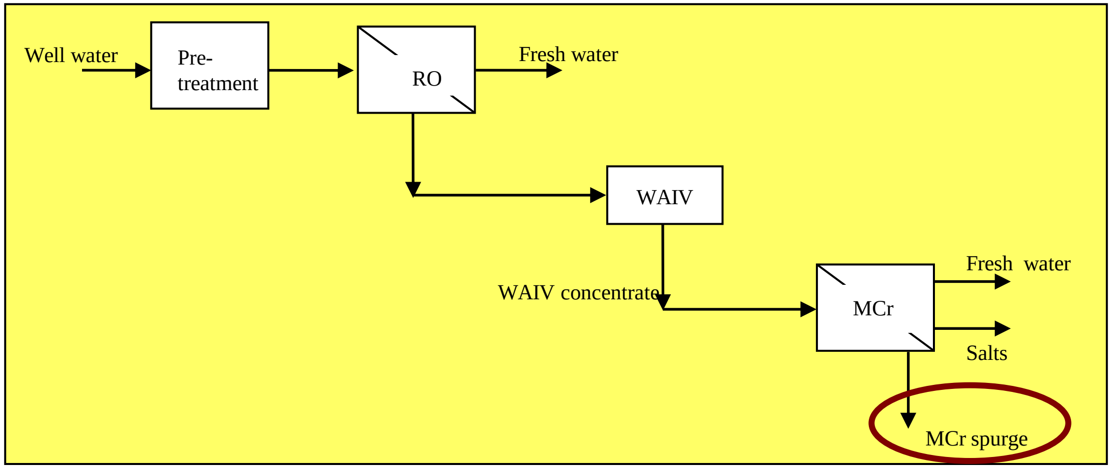
	BGU 1	BGU 2
T inlet – feed side [°C]	33±1	38±1
ΔT feed/permeate [°C]	15±1	15±1
Feed flow rate [L/h]	200	200
Permeate flow rate [L/h]	100	100

2nd effect of organics and antiscalants: decrease of flux during time due (i) to the formation of small amount of $CaSO_4$ (since only 79.4% of Ca^{2+} ions were recovered as calcite in the precipitation step)

and (ii) to the higher organic concentration which probably caused a fouling layer.

	BGU 1	BGU 2
Recovery factor of the MCr process [%]	75.0	69.9
Volume Concentration Factor of the WAIV concentrates	29.4	30.1
Recovery factor of the RO+WAIV+MCr process [%]	76.6	76.8
MCr_spurge [%]	*0.52*	*0.75*
Amount of produced salts [g/10 L of MCr feed solution]	26.53	18.73

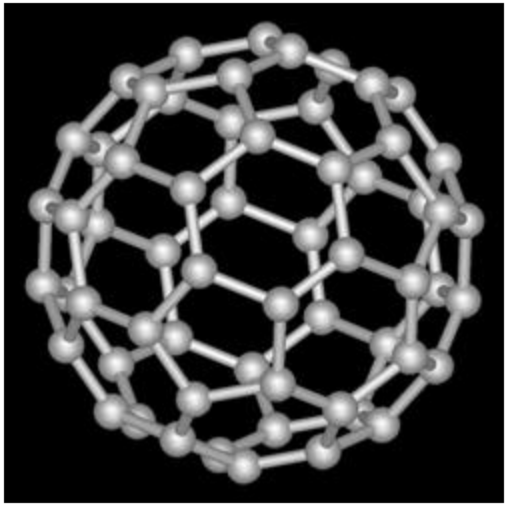
3rd effect of organics and antiscalants: slight decrease in the amount of recovered water due to the deterioration of flux.

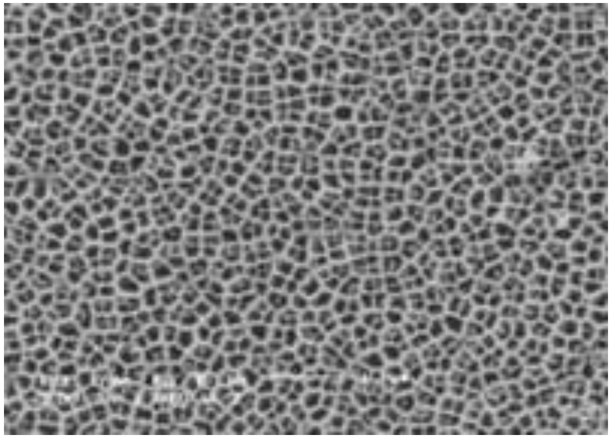


If the amount of brine discharged from the system is considered, it represents only *0.52* and *0.75%* of the RO feed in the tests named BGU 1 and BGU 2 respectively!

Key factor 3 for further improvements of water treatment systems: New Membrane Modules and Materials

Example 1: Fullerenes prevent biofouling of water MF membrane





Buckyball-treated membrane

A research study finds that C60 carbon fullerenes or "buckyballs" hinder the ability of bacteria and other microorganisms to accumulate on the membranes used to filter water in treatment plants. This attribute leads the researchers to believe that coating pipes and membranes with these nanoparticles may prove to be an effective strategy for addressing one of the major problems and costs of treating water. The addition of "buckyballs" to treatment membranes had a two-fold effect. First, treated membranes showed less bacterial attachment than non-treated membranes. Second, the presence of the fullerenes inhibited respiration, or the ability of the bacteria to use oxygen to fuel its activities.

Source: Richard Merritt, Buckyballs could keep water systems flowing, 5-Mar-2009 (http://www.eurekalert.org/pub_releases/2009-03/du-bck030209.php)

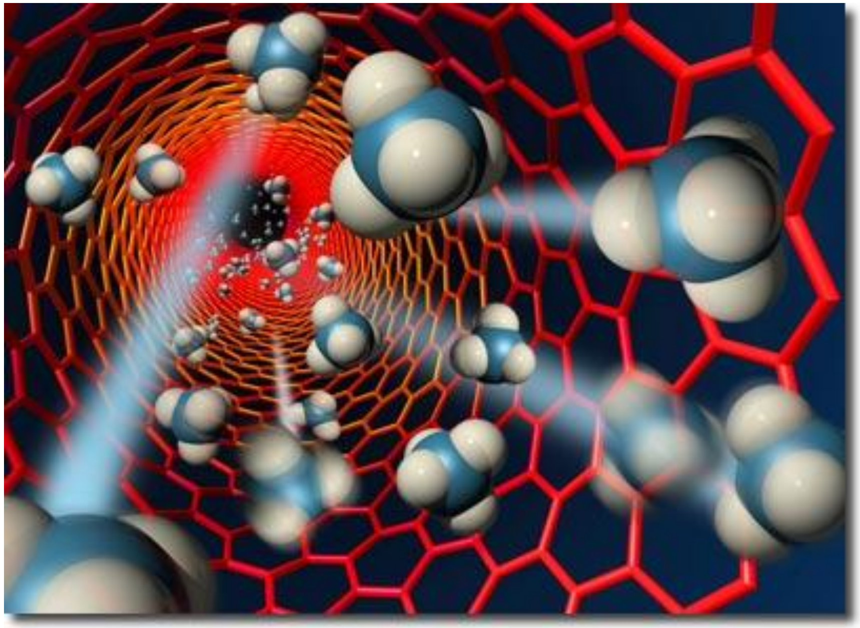
Key factor 3 for further improvements of water treatment systems: New Membrane Modules and Materials

Example 2: Nanotube membranes offer possibility of cheaper desalination

The nanotubes are hollow and more than 50,000 times thinner than a human hair. Billions of these tubes act as the pores in the membrane. The super smooth inside of the nanotubes allow liquids and gases to rapidly flow through, while the tiny pore size can block larger molecules.

The membrane is created by filling the gaps between aligned carbon nanotubes with a ceramic matrix material. The pores are so small that only 6 water molecules could fit across their diameter.

The measured water flux is from 100 to 10,000 times faster than what classical models predict.



Molecules flowing through a carbon nanotube less than two nanometers in diameter

Source:

https://publicaffairs.llnl.gov/news/news_releases/2006/NR-06-05-06.html

***Science*, *May 19, 2006* Making High-Flux Membranes with Carbon Nanotubes”**

Optimization of system design for achieving the most increasingly stringent water quality standards with respect to new contaminants individuated in water streams: key factor 4 **for further improvement of water treatment systems**

Not only *scarcity* is becoming a problem but also *quality* due to:

1. **The occurrence of *trace pharmaceuticals and organics***
2. **Some specific components that become detrimental for human health if their concentrations are higher than the maximum recommended values (i.e., boron)**
3. **Many components originated from discarded electronics products, known as *"e-waste"*, which often ends up in landfills or incinerators instead of being recycled.**

E-WASTE

It's often cheaper and more convenient to buy a new PC than to upgrade an old one!

The fruits of our high-tech revolution are pure poison if these products are improperly disposed of at the end of their useful life. More than 4.6 million tons of it entered U.S. landfills in 2000, and that amount is projected to grow fourfold in the next few years.*

It is easy for toxic substances (like arsenic, lead, cadmium and mercury) to get into the environment. This means that toxic substances commonly used in these products can contaminate the land, water and air. Careful surveillance may be needed to prevent future disease.

***Ted Smith, founder of the Silicon Valley Toxics Coalition (web site http://www.surplusexchange.org/)**

Old and new feed water contaminants - E-waste. Possible solutions *(Key-factor 4)*

1. **Recent experiments with a membrane bioreactor (MBR) suggest that some of these drugs can be efficiently removed with MBR.**

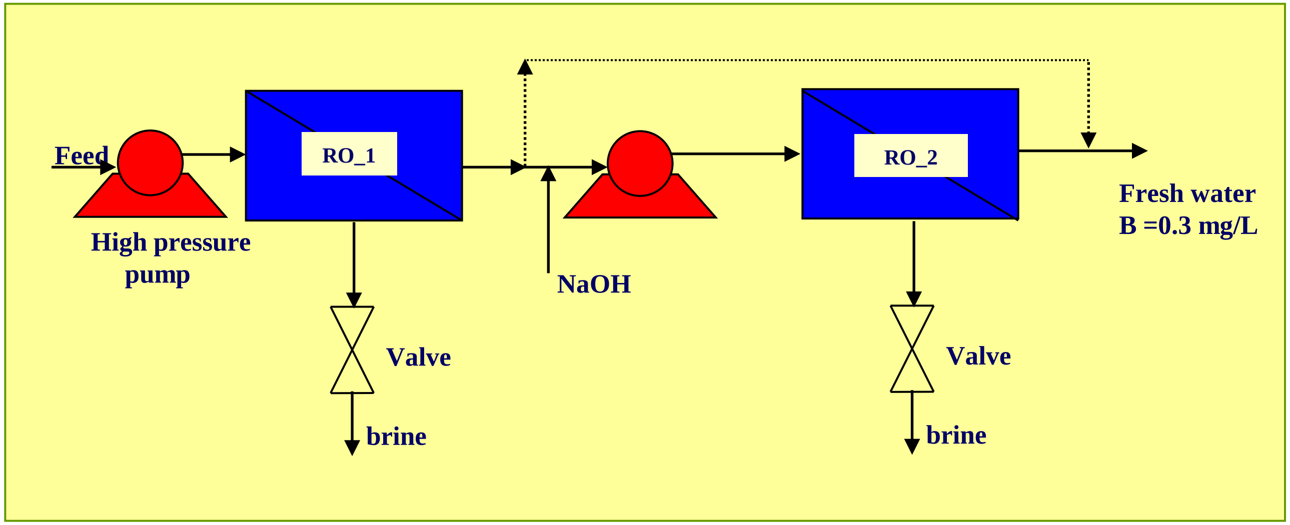
2. **Also RO operation is a potential treatment candidate for the removal of hydrophilic organic compounds.**

Old and new water contaminants - E-waste. Possible solutions

(Key-factor 4)

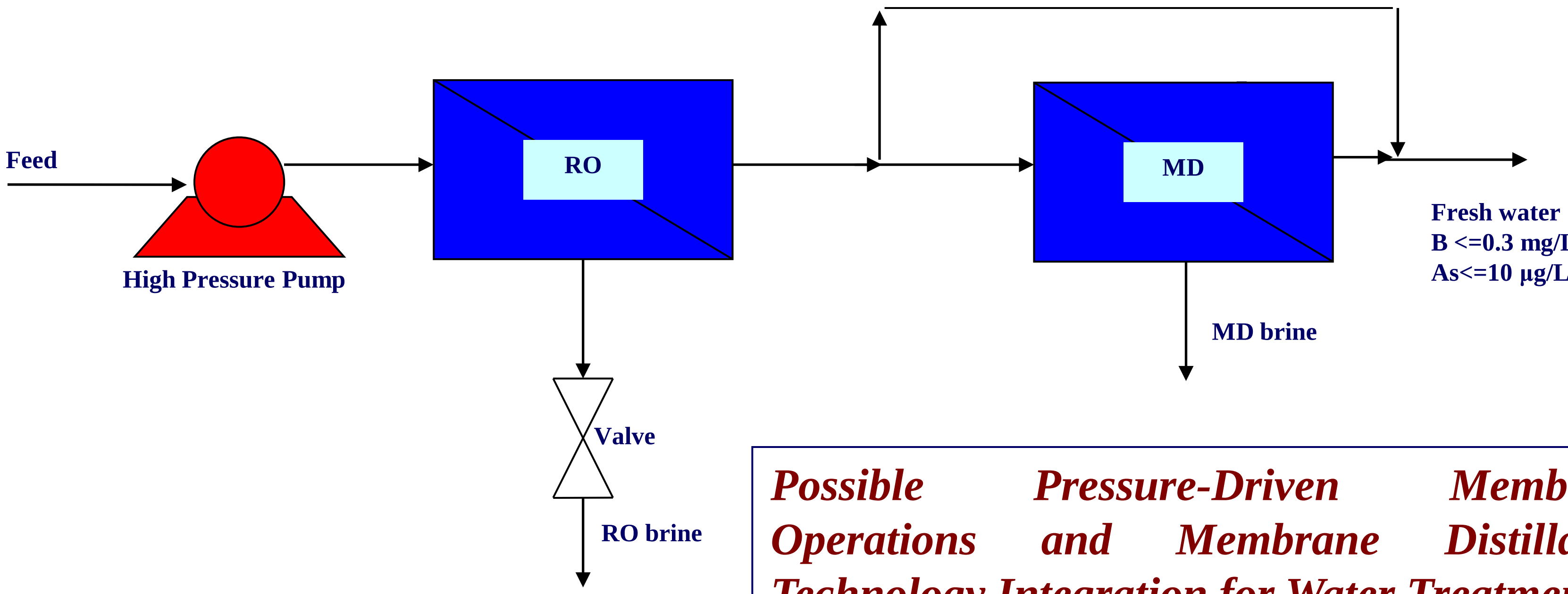
3. **Development of (i) new RO membranes with high rejections and (ii) RO systems with several pass-stages, for improving the removal of those components that become detrimental when their concentration are higher than the maximum recommended values (i.e., boron).**

SOCIETY	Membrane Type	B Rejection [%]
Hydranautics	SWC3	89
	SWC3+	91
	SWC4	92
	SWC4+	93
Toray	TM820A	94-96
FILMTEC	SW30HR LE-400	91



Old and new feed water contaminants - E-waste. Possible solutions *(Key-factor 4)*

4. **MD and/or an integrated membrane desalination system RO-MD can be a promising technology for the removal of non-volatile contaminants from water.**



Possible Pressure-Driven Membrane Operations and Membrane Distillation Technology Integration for Water Treatment

Possible Pressure-Driven Membrane Operations and Membrane Distillation Technology Integration for Water Treatment: an example

Ion	Feed water concentration [mg/L]
Chloride	19,350
Sodium	10,750
Sulphate	2,701
Magnesium	1,295
Calcium	416
Bicarbonate	145
Boron	*4.5*
Arsenic	*0.4*
Ratio As(V) to As(III) = 4 : 1	

Membranes properties		
Membrane Type	RO	MD
Recovery factor	40%	77%
Rejection Values [%]		
Cl^-	98.95	≈100%
Na^+	98.92	
SO_4^{2-}	99.63	
Mg^{2+}	99.56	
Ca^{2+}	99.69	
HCO_3^-	98.46	
As (III)	92.50	
As (V)	97.50	
Boron	90.00	

Ion	Permeate water concentration [g/L]
Cl	1.354 E-01
Na	7.741 E-02
SO4	6.662 E-03
Mg	3.799 E-03
Ca	8.597 E-04
HCO3	1.489 E-03
As(III)	4.000 E-06
As(V)	5.333 E-06
As (total)	*9,333 E-06*
B	*3.000 E-04*
Total	0.23

To achieve the desired B and As content in the fresh water produced, only a fraction (≈36%) of the RO permeate has to be sent to the MD module.

Comparison of four different Integrated Membrane Systems for B and As removal from water

Flow Sheet	**RO**	**RO with pre-oxidation step**	**RO-RO**	**RO-MD**
Fresh water concentration [g/L]	0.338	0.338	0.211	0.226
Recovery rate [%]	40.1	40.1	37.6	36.4
As concentration in fresh water [g/L]	**1.400E-05**	**1.020E-05**	***6.417E-06***	***9.333E-06***
B concentration in fresh water [g/L]	**4.500E-04**	**4.500E-04**	***3.000E-04***	***3.000E-04***
Quantity of energy required per m^3 of fresh water produced [KWh/m^3]	**5.24**	**5.24**	**6.53**	***28.4 / 5.76*** [b]
Quantity of energy required per m^3 of fresh water produced [KWh/m^3][(a)]	**2.69**	**2.69**	**3.70**	***25.6 / 2.96*** [b]
Unit cost [$/$m^3$]	**0.614**	**0.616**	**0.74**	**0.967/0.797** [b]
Unit cost [a] **[$/$m^3$]**	**0.398**	**0.399**	***0.50***	**0.729/*0.559*** [b]

(a) If Pelton turbine is used as ERD.
(b) If thermal energy is available in the plant or the stream is at the operating T of MD unit.

Only the integrated systems RO-RO and RO-MD allow to obtain water with B and As concentration below the WHO and EPA maximum recommended values. If the water streams are already available at the T needed for carrying out MD operation, energy consumption and water cost of the RO-MD process decrease reaching competitive values with those of the other processes.

F. Macedonio, E. Drioli, Desalination, 223 (2008) 396-409
F. Macedonio, E. Drioli, Membrane Water Treatment, Vol. 1, No. 1 (2010) 75-81.

Development of water treatment systems coupled with renewable energy sources for a significant reduction in energy consumption and in the dependence on fossil fuel *(Key-factor 5)*

The coupling of renewable energies with RO desalination plants offers alternative solutions to decrease energy consumption and the dependence on fossil fuels.

The three main renewable energy sources available are solar (photovoltaic and thermal), wind and geothermal energy. Other renewable resources are hydroelectric, biomass and ocean energy.

Each type of renewable energy has its own advantages that make it suited to certain application. Their applicability strongly depends on the local availability of renewable energy resources, quality of water to be desalinated, plant size and availability of grid electricity.

Almost none of them releases gaseous or liquid pollutants during operation, and offer many environmental benefits compared to conventional energy sources (such as emissions of greenhouse gases, depletion of finite sources, and dependence on a few oil-exporting regions in the world).

Pressure-Retarded Osmosis and Reverse Electrodialysis: two membrane-based processes to generate power from salinity gradient *(Key-factor 6)*

The salinity-gradient energy, also called *blue energy*, is the energy that can be obtained from mixing water streams with different salt concentrations.

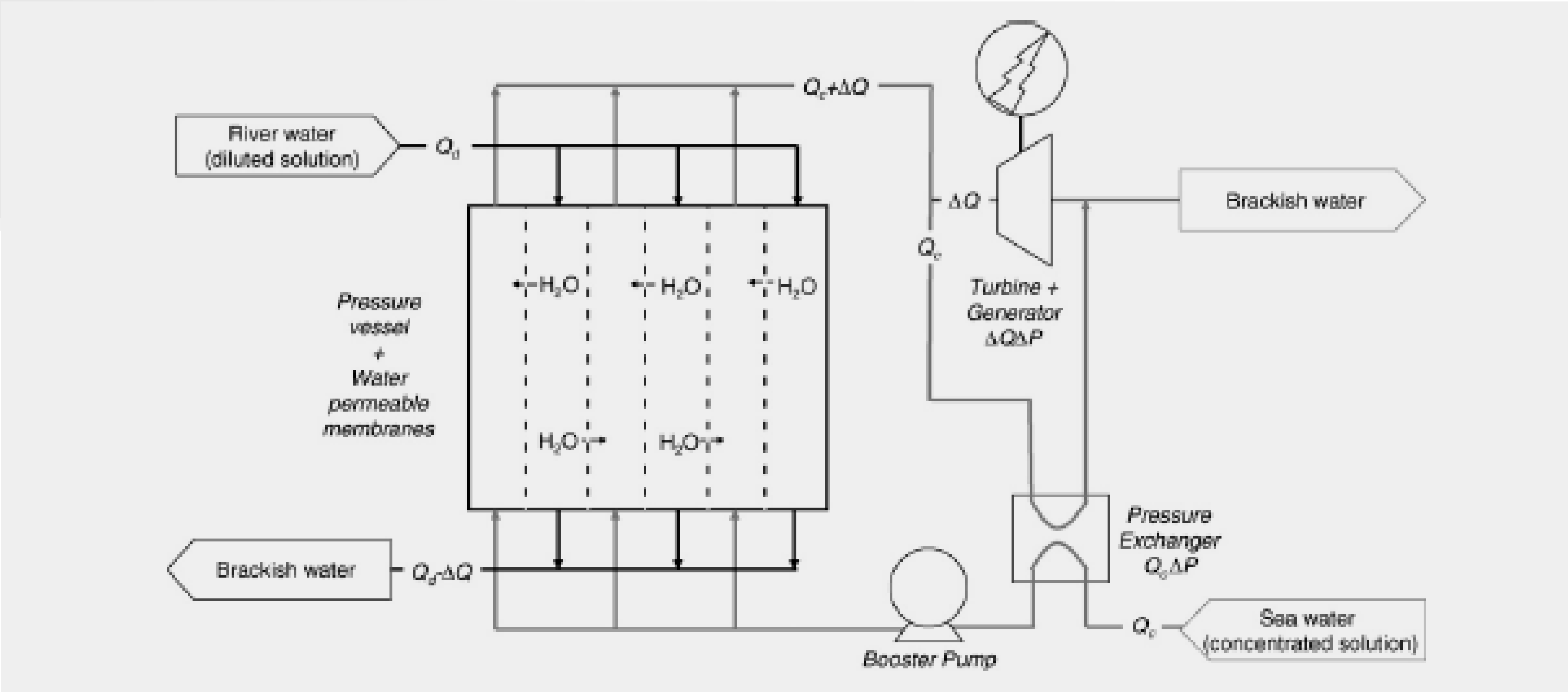
Blue energy is available where fresh water streams flow into the sea or it can be made available from natural or industrial salt brines.

J.W. Post et al. estimated that the global energy output from estuaries is $2{,}6 \cdot 10^{12}$ W, which is approximately 20% of the present worldwide energy demand.

Until now, the main drawback of these techniques was the high price of membranes. However, a reconsideration of these membrane processes is worthwhile due to the declining membrane costs and to the increasing prices of fossil fuels.

J.W. Post et al., Journal of Membrane Science 288 (2007) 218–230

Principle of pressure-retarded osmosis



In a pressure-retarded osmosis system, two solutions of different salinity are brought into contact by a semi-permeable membrane. The chemical potential difference between the solutions causes transport of water from the diluted salt solution to the more concentrated salt solution. If hydrostatic pressure is applied to the concentrated solution, the water transport will be partly retarded.

J.W. Post et al., Journal of Membrane Science 288 (2007) 218–230

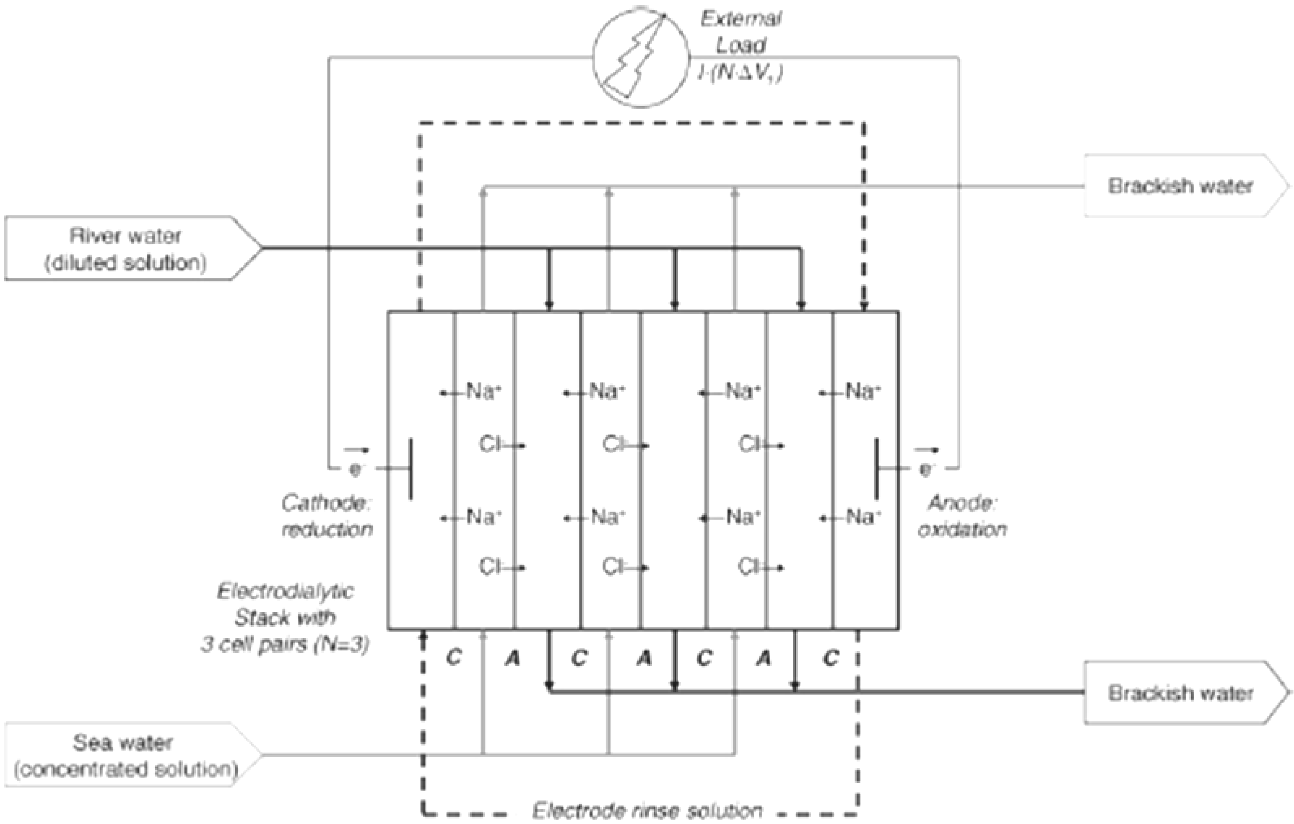
Principle and potentialities of pressure-retarded osmosis

The transport of water from the low-pressure diluted solution to the high-pressure concentrated solution results in a pressurization of the volume of transported water. This pressurized volume of transported water can be used to generate electrical power in a turbine.

Currently available RO membranes in a pressure retarded osmosis application on seawater and fresh water ($\Delta\pi$ = 20–25 bar) could yield a power density between 0.11 and 1.22 W/m^2. The higher value is obtained for mixing two solutions with $\Delta\pi$ =39 bar using cellulose acetate membranes.

Currently available RO membranes in a pressure retarded osmosis application on more concentrated brines and fresh water ($\Delta\pi$ > 75 bar) could yield a power density of 2–5 W/m^2.

Principle of reverse electrodialysis



Energy conversion scheme using reverse electrodialysis; *A* is an anion exchange membrane, *C* a cation exchange membrane, *I* the electrical current or transported charge (A), *N* the number of cell pairs (in this case *N*= 3), *N ΔV*1 the potential difference over the applied external load (V), whereas the power generated is *I* (*NΔV*) (W).

J.W. Post et al., Journal of Membrane Science 288 (2007) 218–230

Principle and potentialities of reverse electrodialysis

In a reverse electrodialysis system, the compartments between the membranes are alternately filled with a concentrated salt solution and a diluted salt solution. The salinity gradient results in a potential difference (e.g. 80mV for seawater and river water) over each membrane, *the so-called membrane potential*.

The chemical potential difference causes the transport of ions through the membranes from the concentrated solution to the diluted solution.

The electrons can be transferred from the anode to the cathode via an external electric circuit. This electrical current and the potential difference over the electrodes can be used to generate electrical power, when an external load or energy consumer is connected to the circuit.

Principle and potentialities of reverse electrodialysis

Currently available electrodialysis membranes in a RED application on seawater and fresh water (electrochemical potential difference $\Delta\varphi = 0.17$ V) could yield a power density of 0.41 W/m^2.

Currently available electrodialysis membranes in a RED application on more concentrated brines and fresh water could yield a power density of 1.2 W/m^2.

Forward Osmosis: another revalued

membrane process for seawater/brackish

water desalination

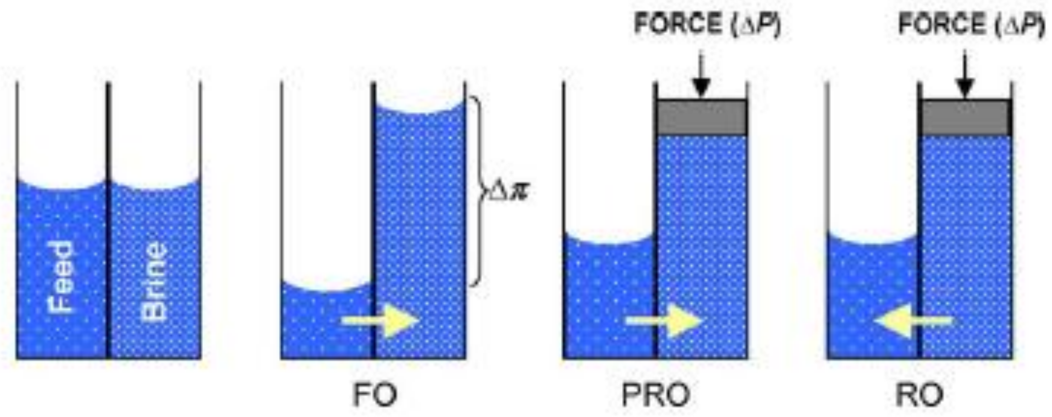
Classification of osmotic processes

- **Osmosis is the transport of water across a selectively permeable membrane from a region of higher water chemical potential to a region of lower water chemical potential.**

- **It is driven by a difference in solute concentrations across the membrane that allows passage of water, but rejects most solute molecules or ions.**

- **Osmotic pressure (π) is the pressure which, if applied to the more concentrated solution, would prevent transport of water across the membrane.**

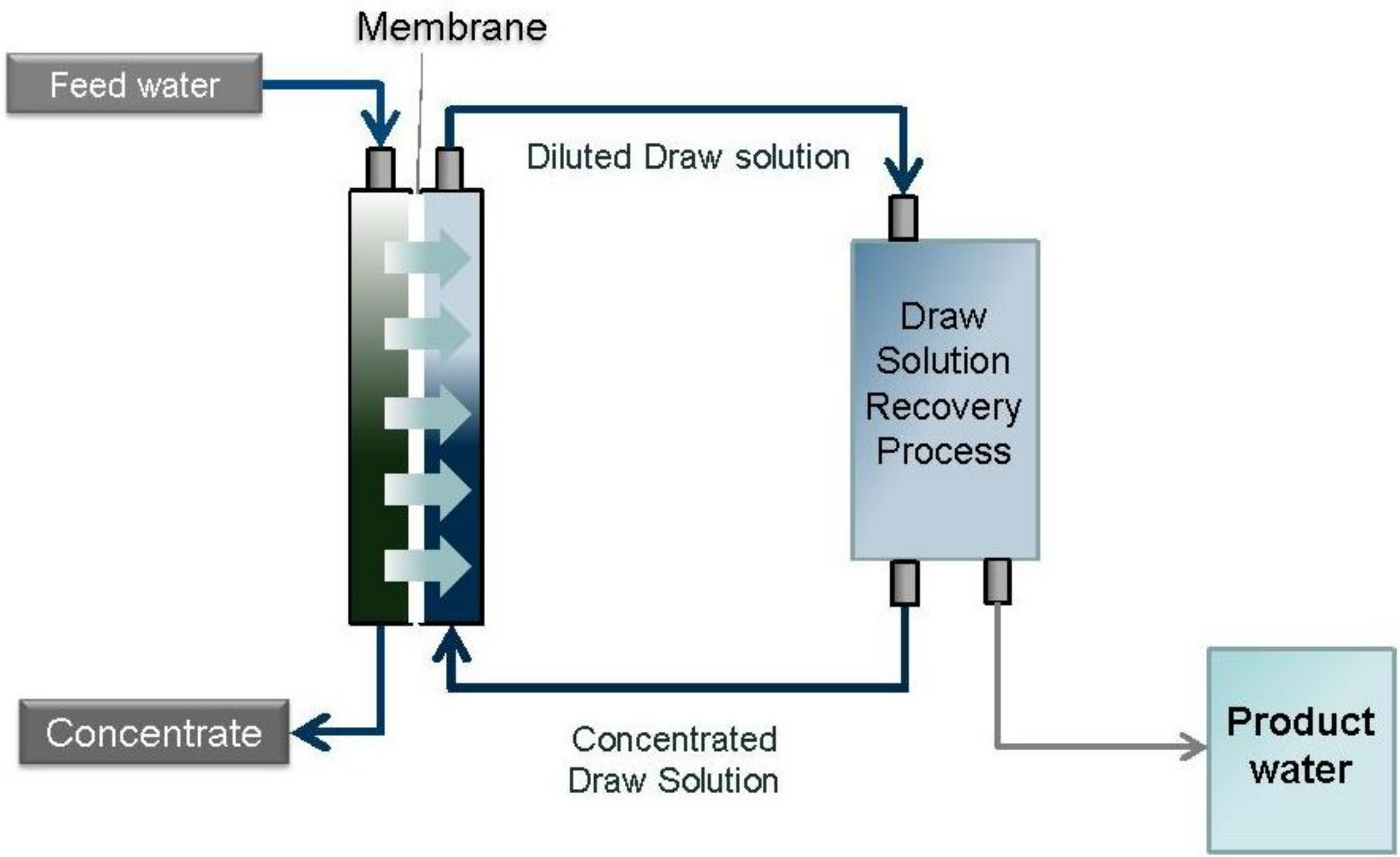
Classification of osmotic processes



- RO uses hydraulic pressure differential as the driving force for transport of water through the membrane
- FO uses π as the driving force resulting in concentration of a feed stream and dilution of a highly concentrated stream (referred to as the draw solution).
- PRO can be viewed as an intermediate process between FO and RO, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient (similar to RO). However, the net water flux is still in the direction of the concentrated draw solution (similar to FO).

T. Y. Cath et al., Jour. Of Memb. Science, 281 (2006) 70–87

Forward Osmosis Process



FO Draw Solutions

The draw solution is the concentrated solution on the permeate side of the membrane, source of the driving force in the FO process. It has to be a higher osmotic pressure than the feed solution.

Tested draw solutions in FO desalination of seawater:

- **sulfur dioxide solution;**
- **mixtures of water and another gas (e.g., sulfur dioxide) or liquid (e.g., aliphatic alcohols);**
- **aluminum sulfate solution;**
- **glucose solution;**
- **a mixed solution of glucose and fructose;**
- **solutions of potassium nitrate (KNO_3) and sulfur dioxide (SO_2);**
- **ammonia and carbon dioxide gases in specific ratios create highly concentrated draw solutions of thermally removable ammonium salts, allowing high recoveries of potable water from concentrated saline feeds and substantial reductions in brine discharges from desalination;**
- **concentrated fructose solution to create a nutritious drink during FO of seawater.**

FO Applications

FO has been used in the following fields:

- **to desalinate seawater;**
- **to treat industrial wastewaters (at bench-scale);**
- **to concentrate landfill leachate (at pilot- and full-scale);**
- **to treat liquid foods in the food industry (at bench-scale).**

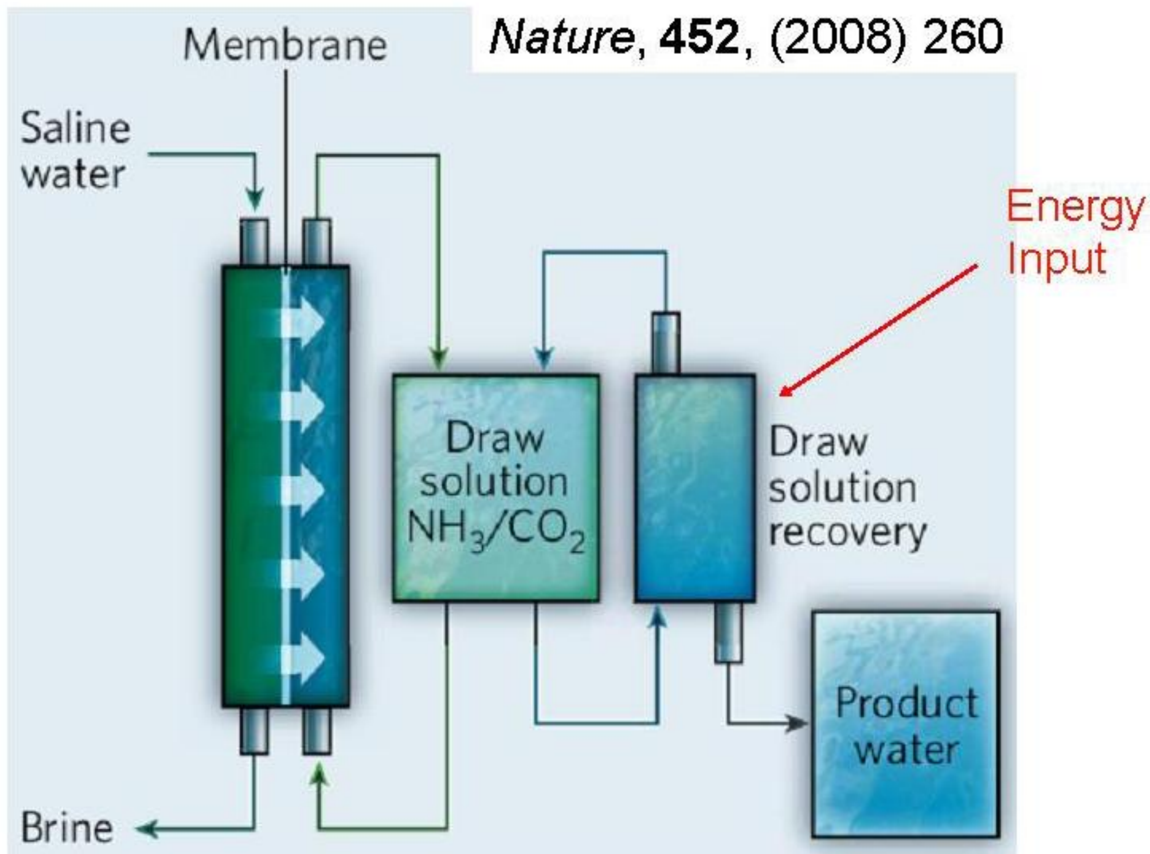
FO was evaluated:

- **for reclaiming wastewater for potable reuse in life support systems (at demonstration-scale);**
- **for purifying water in emergency relief situations;**
- **for controlling drug release in the body.**

A Forward Osmosis desalination pilot plant developed by a Yale University spinoff company called Oasys

The FO process developed at Yale uses a unique group of removable solutes to create a draw solution for desalination.

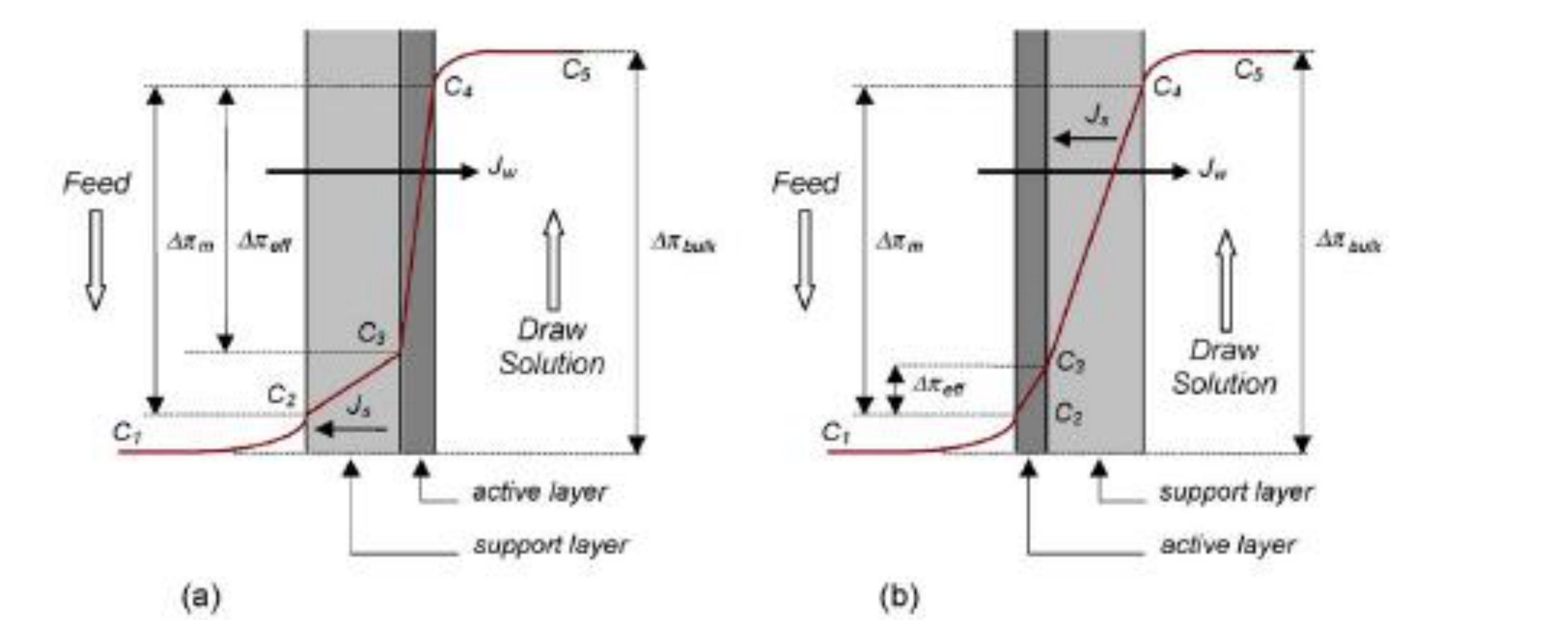
When NH_3 and CO_2 gases are dissolved in water in the correct proportion, they favour the formation of a highly concentrated solution of ammonium salts. This solution can have a very high osmotic pressure,



Desalination, **174** (2005) 1-11.

which makes it ideal for drawing water from saline feeds. These salts have the ability to decompose from solution, when heated, into ammonia and carbon dioxide gases again, thus allowing for their efficient and complete removal and reuse.

Major Challenge: Internal Concentration Polarization (CP)



(a) Concentrative internal CP and (b) dilutive internal CP across a composite or asymmetric membrane in FO

The osmotic pressure difference between the bulk feed and bulk draw solution ($\Delta\pi_{bulk}$) is higher than the osmotic pressure difference across the membrane ($\Delta\pi_m$) due to external CP. The effective osmotic pressure driving force ($\Delta\pi_{eff}$) is even lower due to internal CP. Operation of FO in a counter-current flow configuration (feed and draw solution flowing tangential to the membrane but in opposite directions) provides constant $\Delta\pi$ along the membrane module and makes the process more efficient.

FO Main Advantages

- Low or no hydraulic pressures
- High rejection of a wide range of contaminants
- Lower membrane fouling propensity than pressure-driven membrane processes
- equipment used very simple and membrane support less of a problem due to the low pressure involved

Measures for FO advancing

- Development of new membranes in order to provide
  - high water permeability,
  - high rejection of solutes,
  - substantially reduced internal concentration polarization,
  - high chemical stability,
  - high mechanical strength.
- Development of draw solutions that
  - require low energy for regeneration,
  - are easily separable from the product,
  - have low or no toxicity,
  - are chemically non-reactive with polymeric membranes.

Conclusion

Membrane operations are playing today a strategic important role in sea/brackish water desalination. The various problems still open (as increasing recovery factor, decreasing brine disposal problem, environmental impact, etc.) require:

- **development of more high-efficient membranes with enhanced transport mechanisms, selectivity, flux and highly resistant to chlorine attack;**
- **further research on concentrate treatment options (such as membrane crystallization);**
- **development of water treatment systems coupled with renewable energy sources;**
- **reconsideration of pressure-retarded osmosis, reverse electrodialysis and forward osmosis.**

Thank you for your attention