New membrane systems for desalination and water reuse (MD, MCr, Membrane condensers) and their integration

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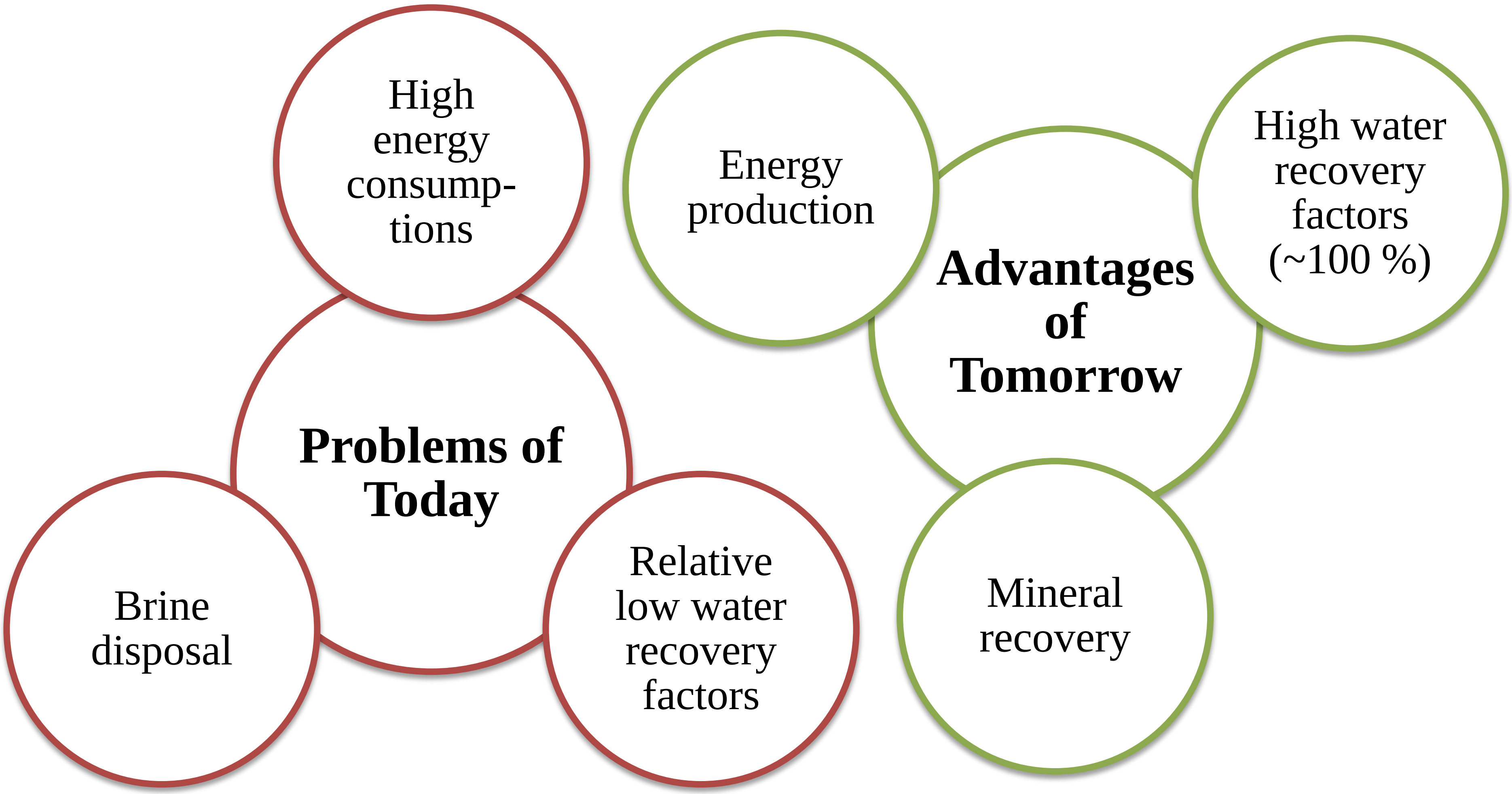
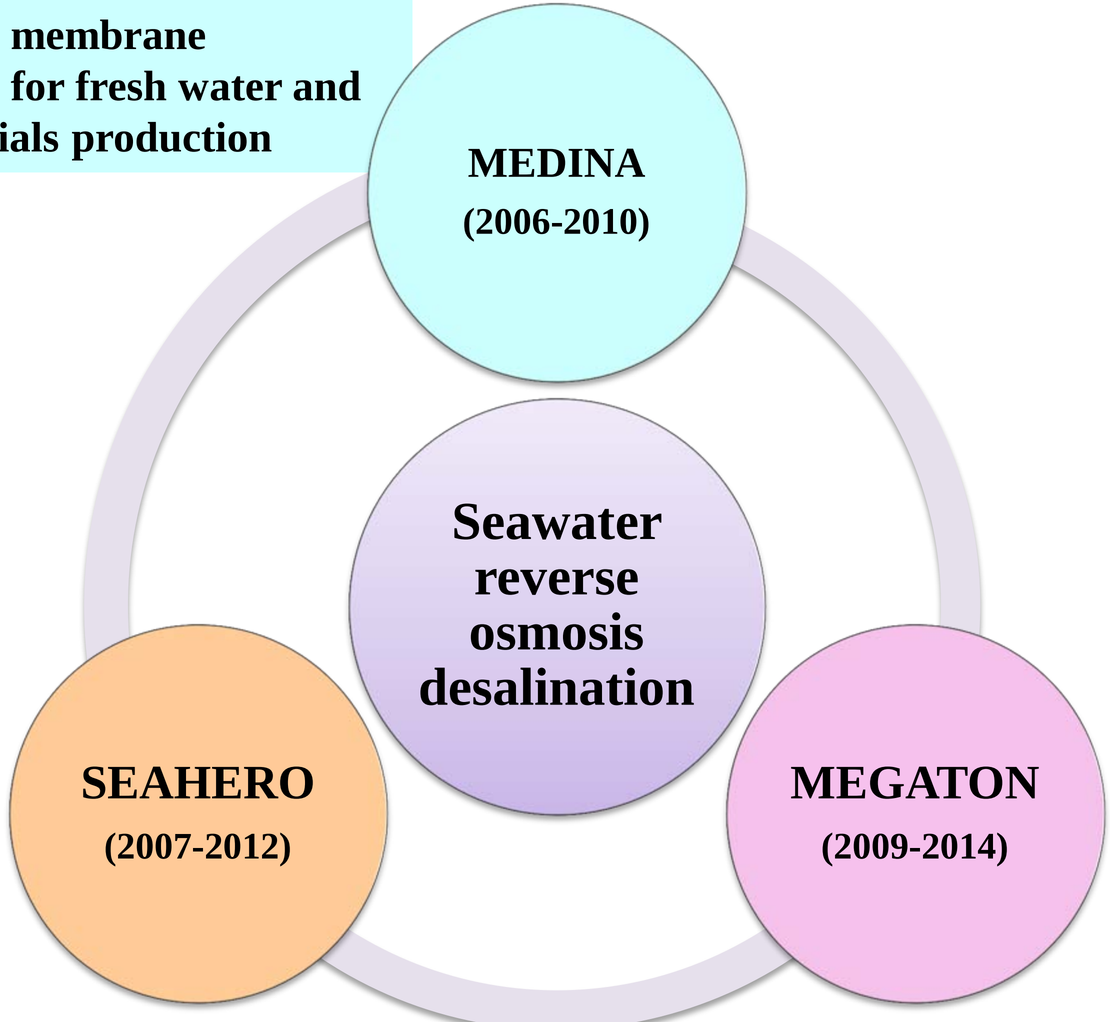
KACST, February 2014

Membrane Operations in Desalination



Membrane based Desalination Projects

Integrated membrane operations for fresh water and raw materials production



Large scale: **largest SWRO unit** (27,000 m^3/d)
Low energy: reduction by 4 kWh/m^3.
Low fouling: reduction of 50 %

Efficient design to obtain capacity of **1,000,000 m^3/d.** Large size element and module, intake technology, **pressure retartted osmosis, energy recovery,** pipe design

http://medina.unical.it
M. Kurihara, M. Hanakawa / Desalination 308 (2013) 131–137.
S. Kim et al. / Desalination 238 (2009) 1–9

Membrane-Based Desalination: An Integrated Approach (acronym MEDINA)

SIXTH FRAMEWORK PROGRAMME - PRIORITY 1.1.6.3 - Global Change and Ecosystems

Aim: **to improve the overall performance of membrane-based water desalination processes through the integration of different membrane operations in RO pre-treatment and RO post-treatment stages.**

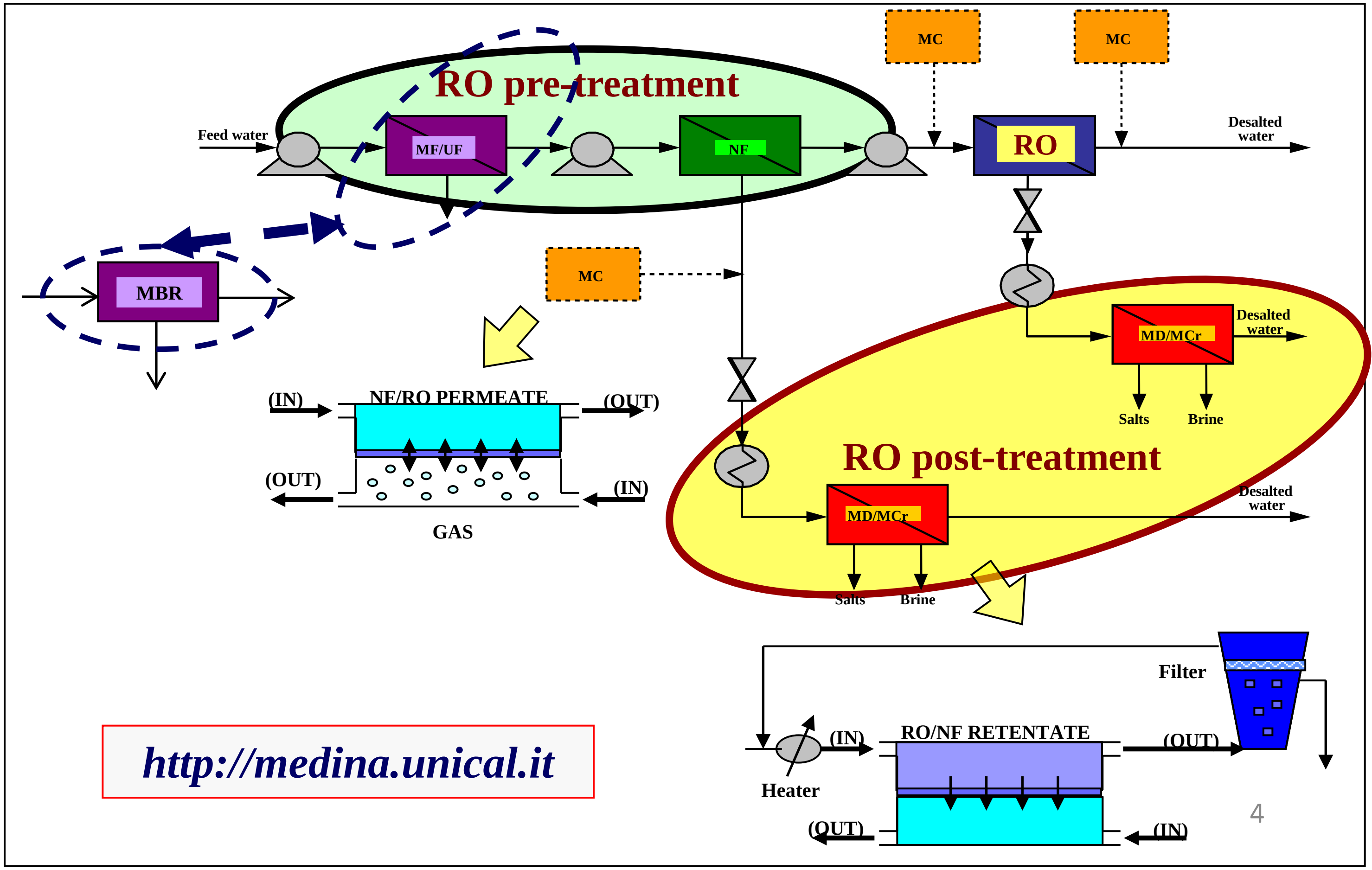
Objectives:

1. to minimise environmental impacts

2. to optimise energy sources and consumption

3. to increase fresh water production

4. to optimize sea-brackish water desalination by understanding, controlling and minimizing fouling phenomena.



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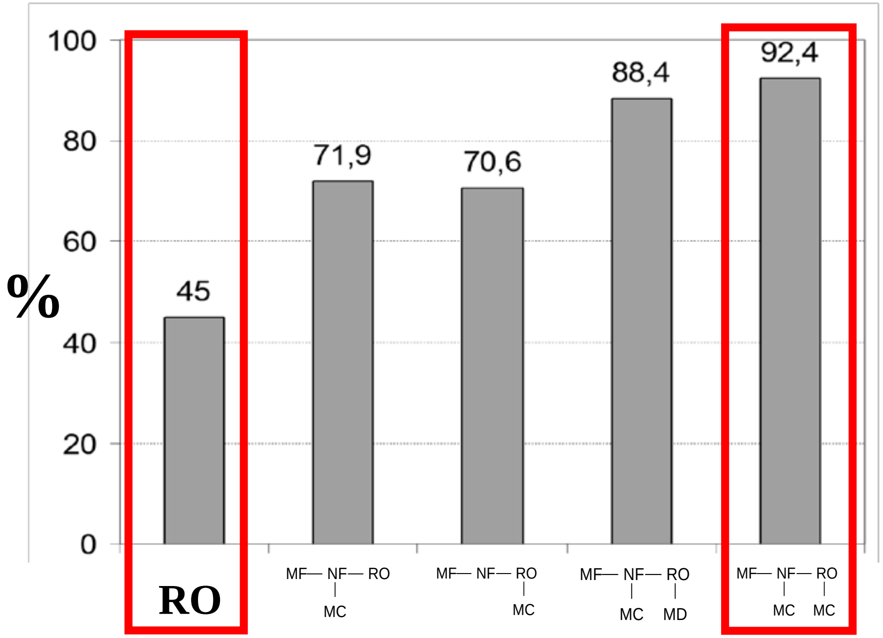
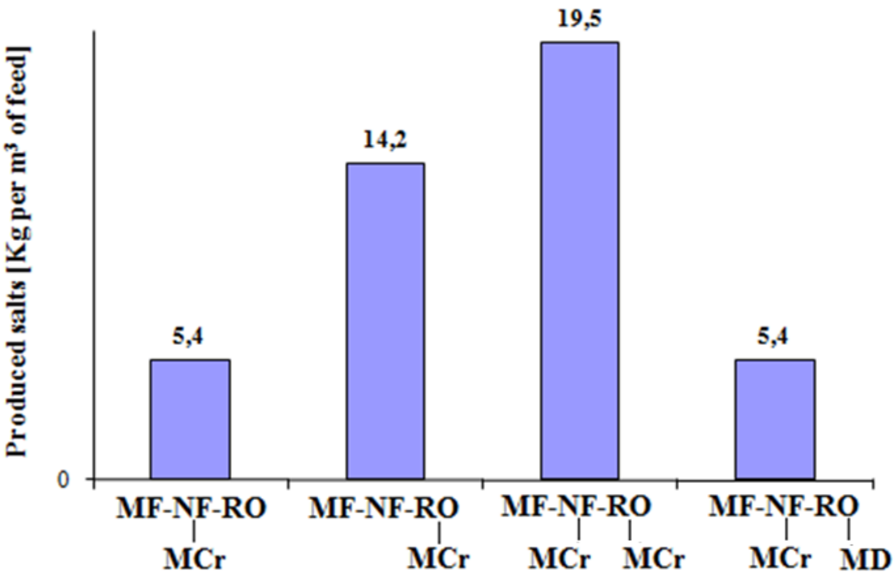
Integrated membrane operations for desalination

Recovery factors > 90% for the integrated desalination systems have been obtained.

Amount of salts recovered from different integrated membrane desalination systems.





E. Drioli et al., Chemical Engineering Research and Design, 84 (A3) (2006) 209–220. - E. Drioli et al., Desalination and Water Treatment, 18 (2010) 224-234.

Mega-Ton Water System project

Research Organization

Research Supervise

Pursuiting Extremely-High Technology

Pursuiting Basic Technology for the future

JSPS※1 — Fund

Chief Scientific Director

Research Support Organization (NEDO)※2

Contract

Elemental Technology

- High-Efficiency/Large Scale Membrane Element Modules
- Seawater Intake Technology
- Osmotic Power Generation
- Highly Efficient Energy Recovery
- Low-Cost/Highly Durable Piping

System Technology

- Optimization of 1 million m3 class plants
- Resource Producing Innovative Sewage integration Membrane System
- No Chemical Seawater Desalination System

University The University of Tokyo, Tokyo Institute of Technology, Hokkaido University, Kobe University etc… 10 Universities in total

Company TORAY, HITACHI, TOSHIBA, MITSUBISHI HEAVY INDUSTRIES, etc… 17 companies in total

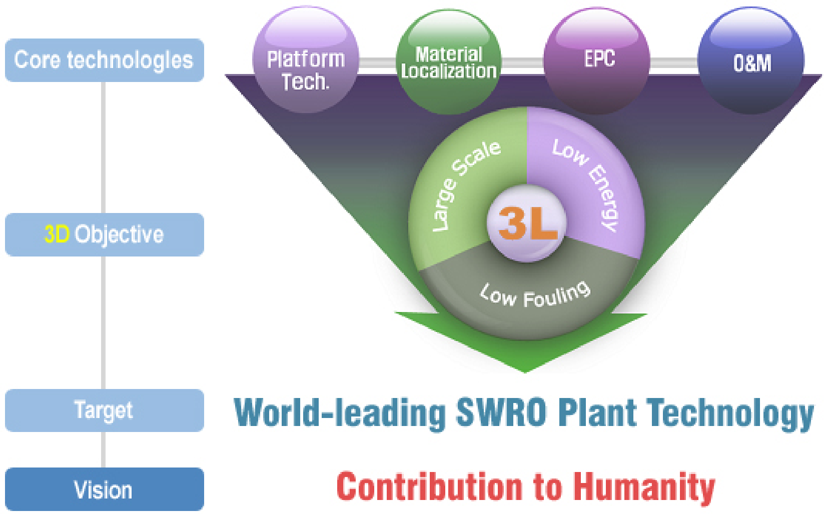
Others Tokyo Bureau of Sewage, Japan Sewage Works Agency

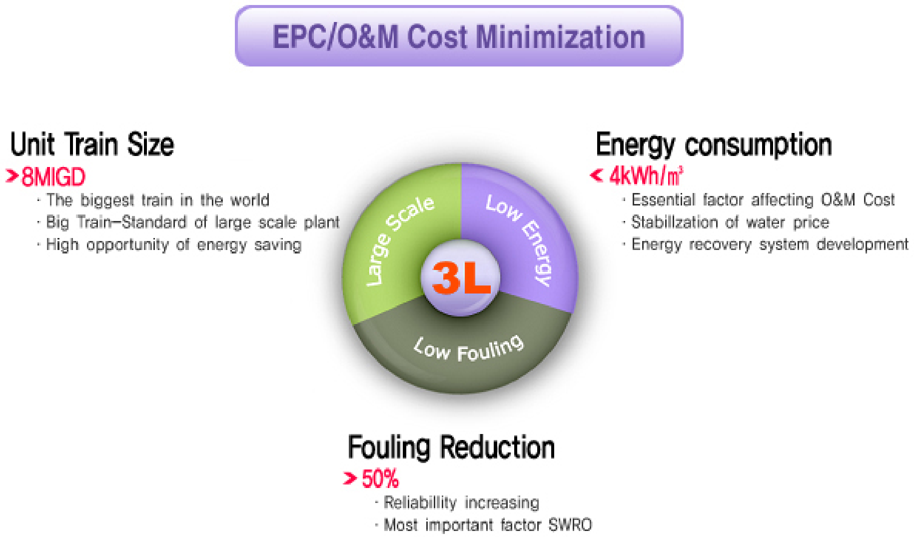
Registered Researcher 140 people total. （20 from University, 120 from company）

※1 JSPS・・・Japan Society for the Promotion of Science
※2 NEDO・・・New Energy and Industrial Technology Development Organization

Seawater Engineering & Architecture of High Efficiency Reverse Osmosis (SeaHERO) project is targeting to get the top SWRO technologies in the world

Center for Seawater Desalination Plant pursues the RO membrane technique which meets 3L skills. *3L* means the three main technical objectives including *large scale, low energy, and low fouling* for SWRO plants. At first, large scale is to design and construct the largest unit SWRO train [8MIGD = 36,368㎥/d] in the world.



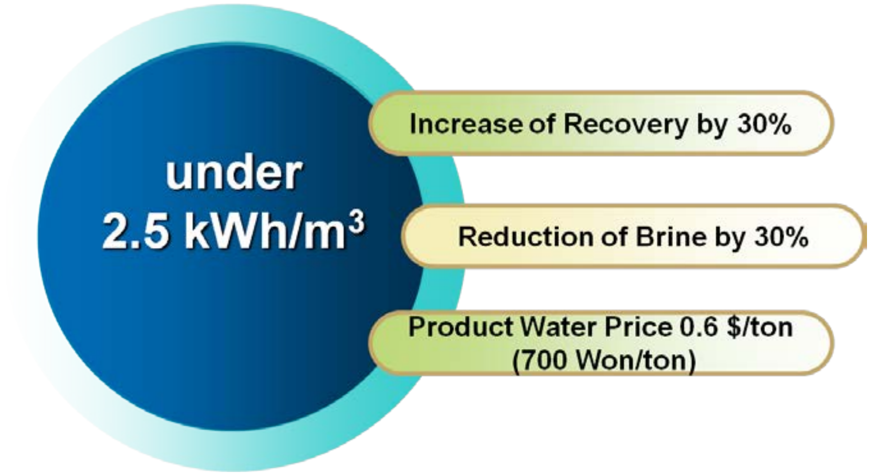


Second, low energy means to lower energy consumption of whole SWRO plant including intake, pretreatment, SWRO systems, and so on by 4kWh/㎥. At last, low fouling is to reduce fouling effect by 50% in terms of silt density index [SDI] and a new fouling parameter developed.

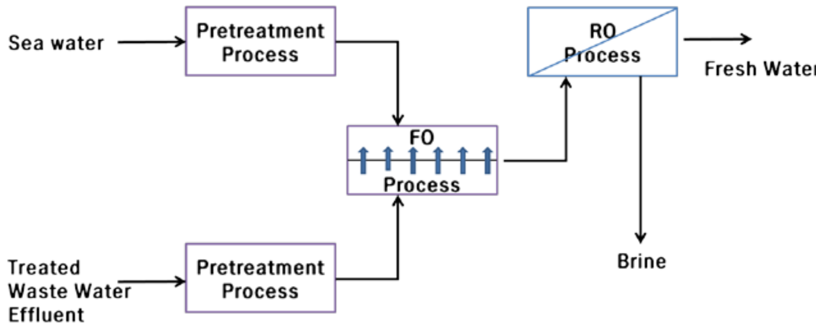
http://www.seahero.org/eng/

FO-RO Hybrid Desalination Process

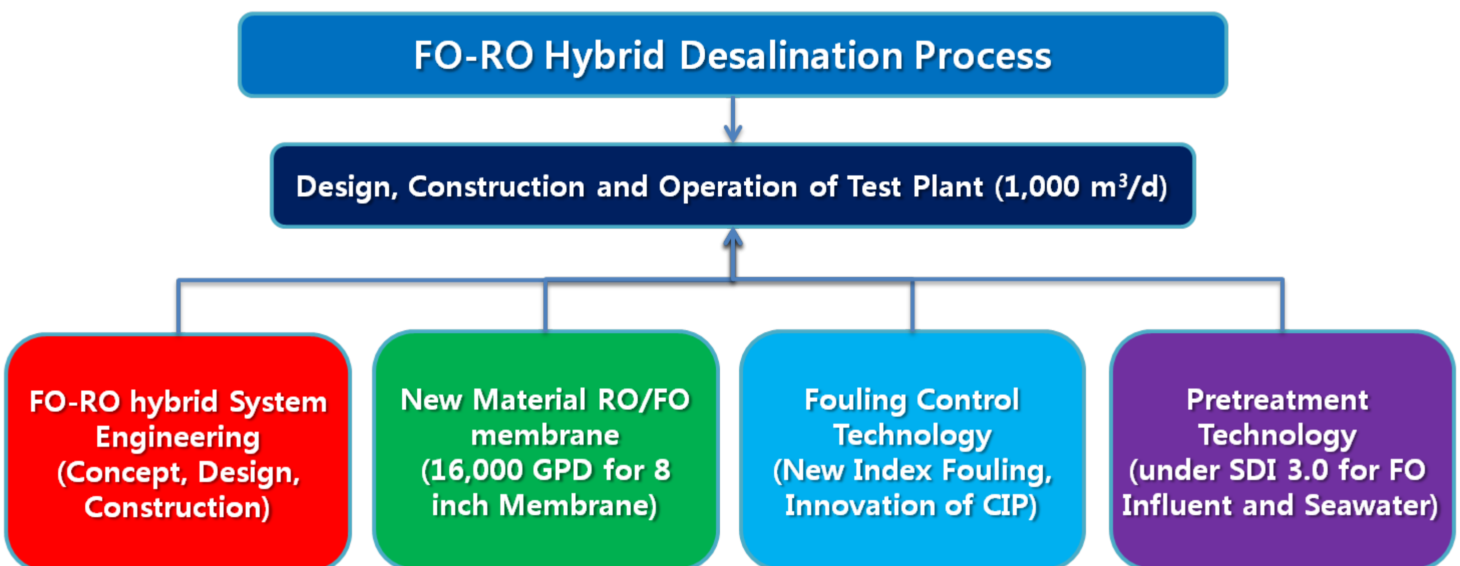
Technical Target : under 2.5 kWh/m³



FO-RO Process Concept

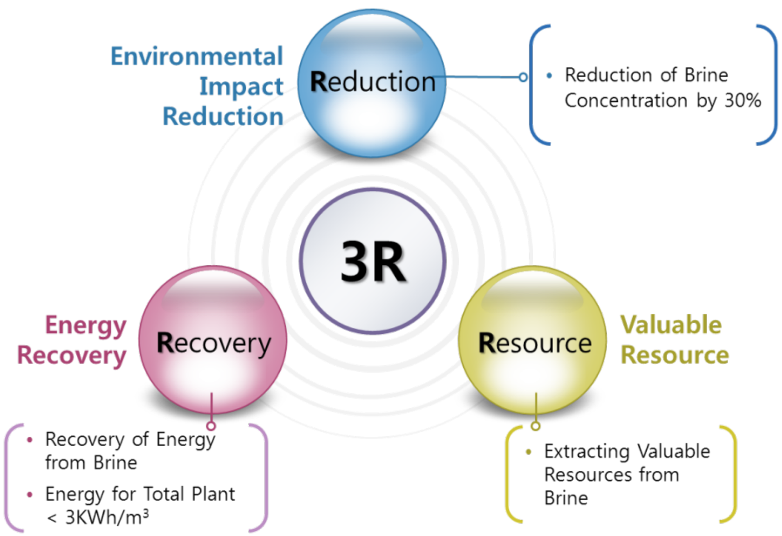


Research Center Structure

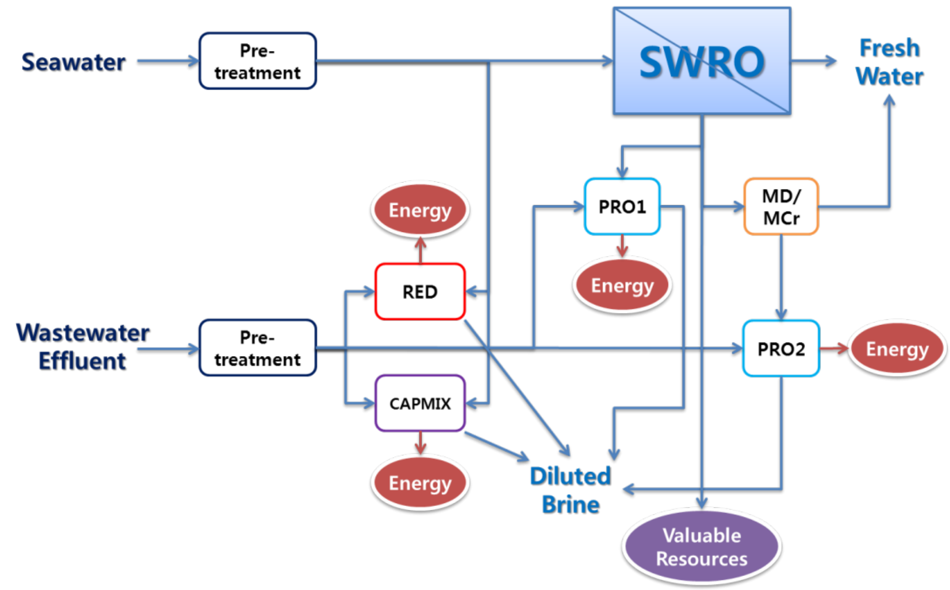


Hybrid Desalination Process for Energy/Resources Recovery

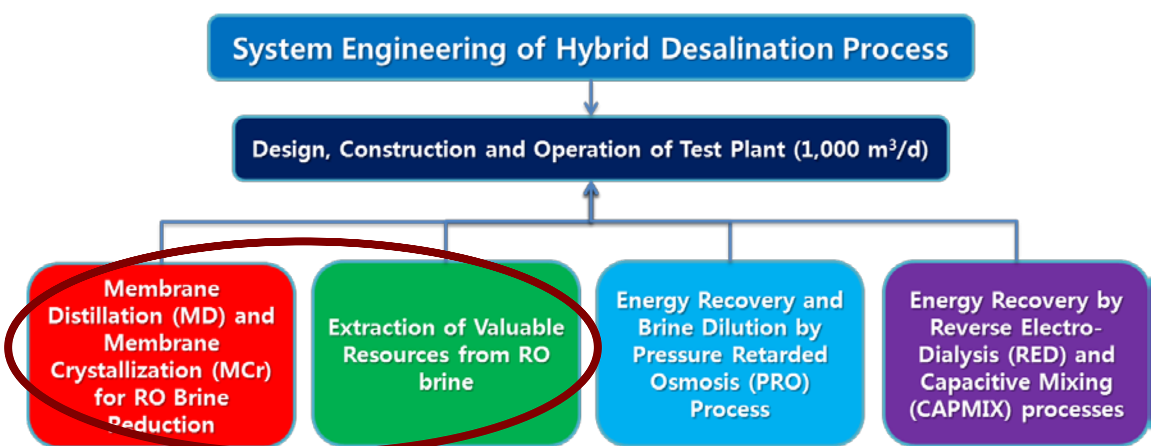
Vision: 3R



Concept



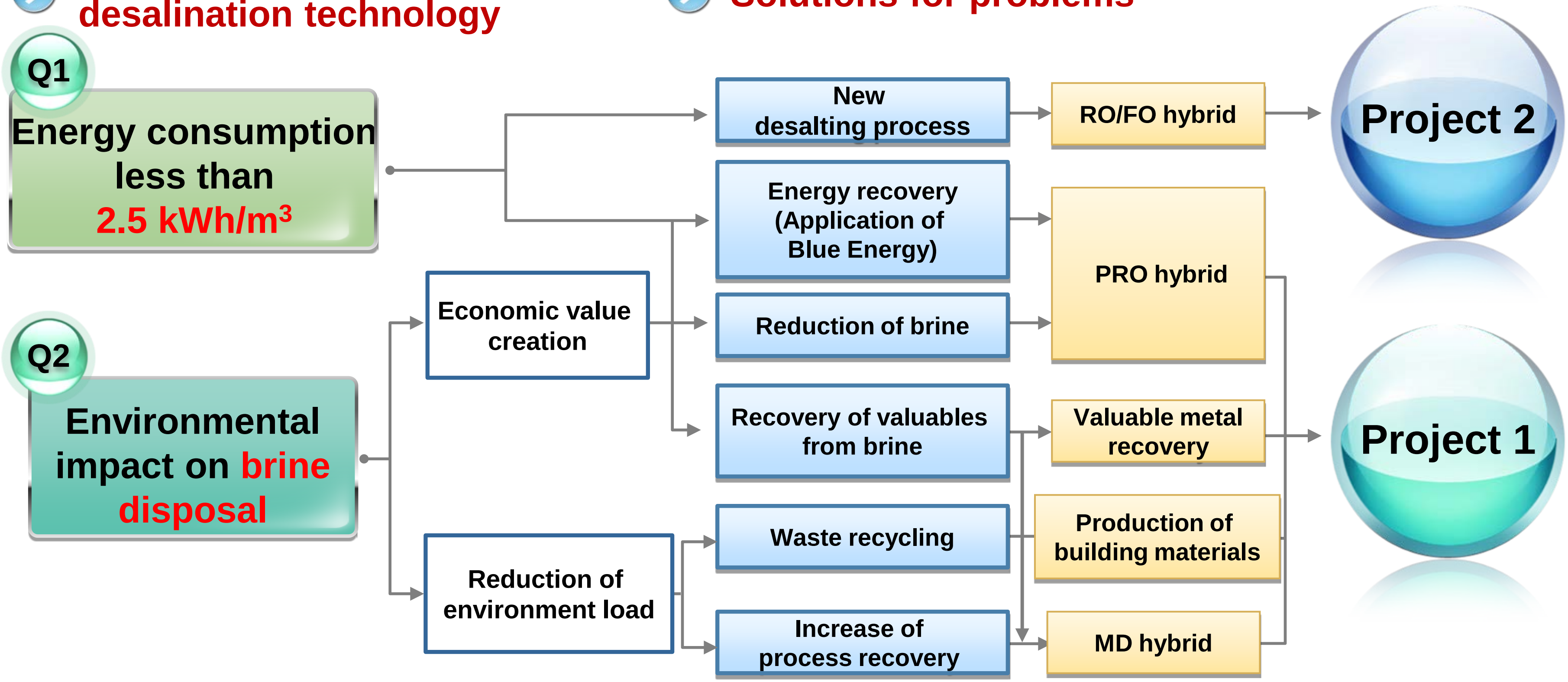
Research Center Structure



2nd SeaHERO R&D Project

Problems of current desalination technology

Solutions for problems

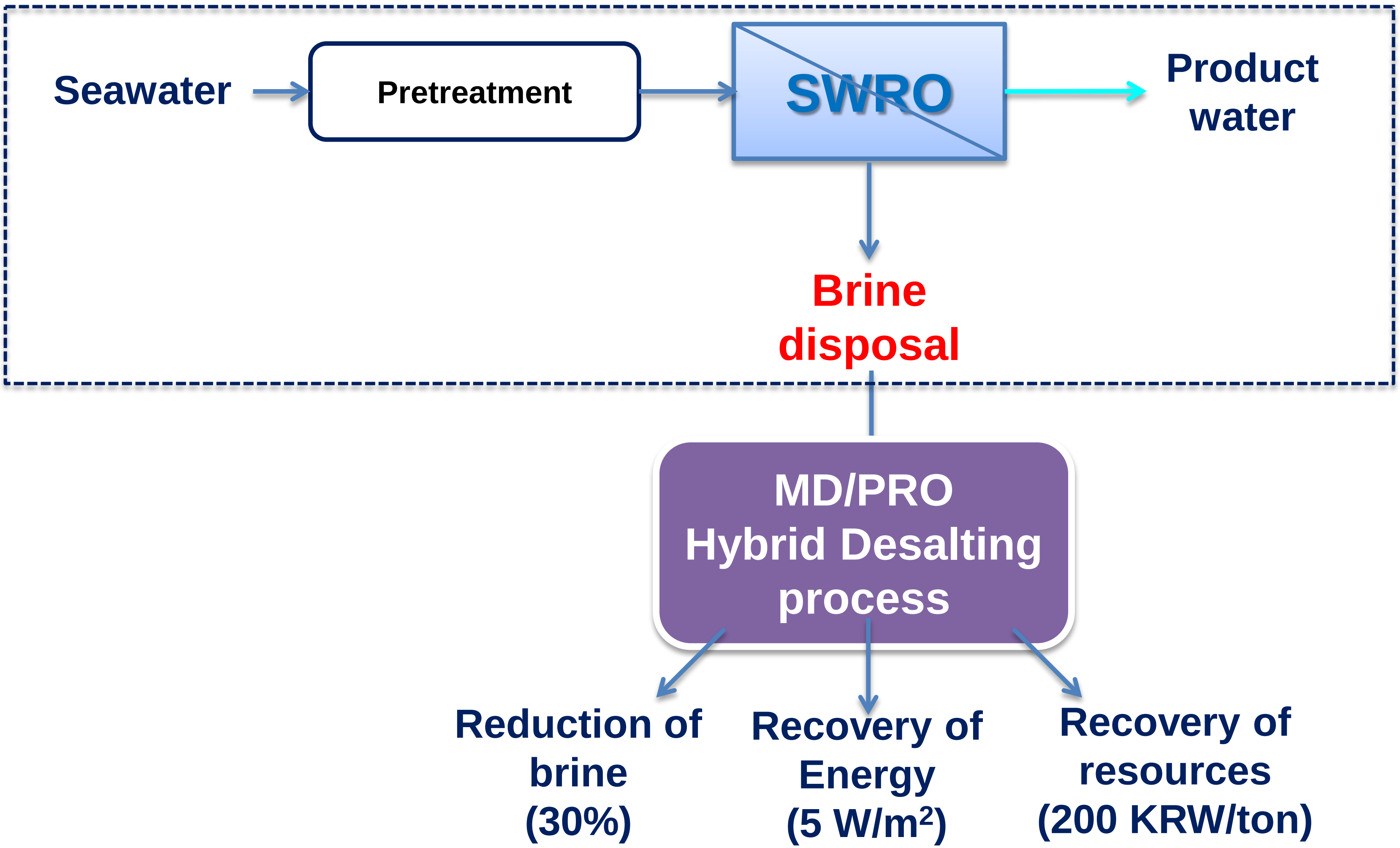


Hybrid project 1	Hybrid project 2
MD/PRO hybrid desalting technology	FO/RO hybrid desalination process

Acronyms: Forward Osmosis (FO), Membrane Distillation (MD), Pressure Retarded Osmosis (PRO)

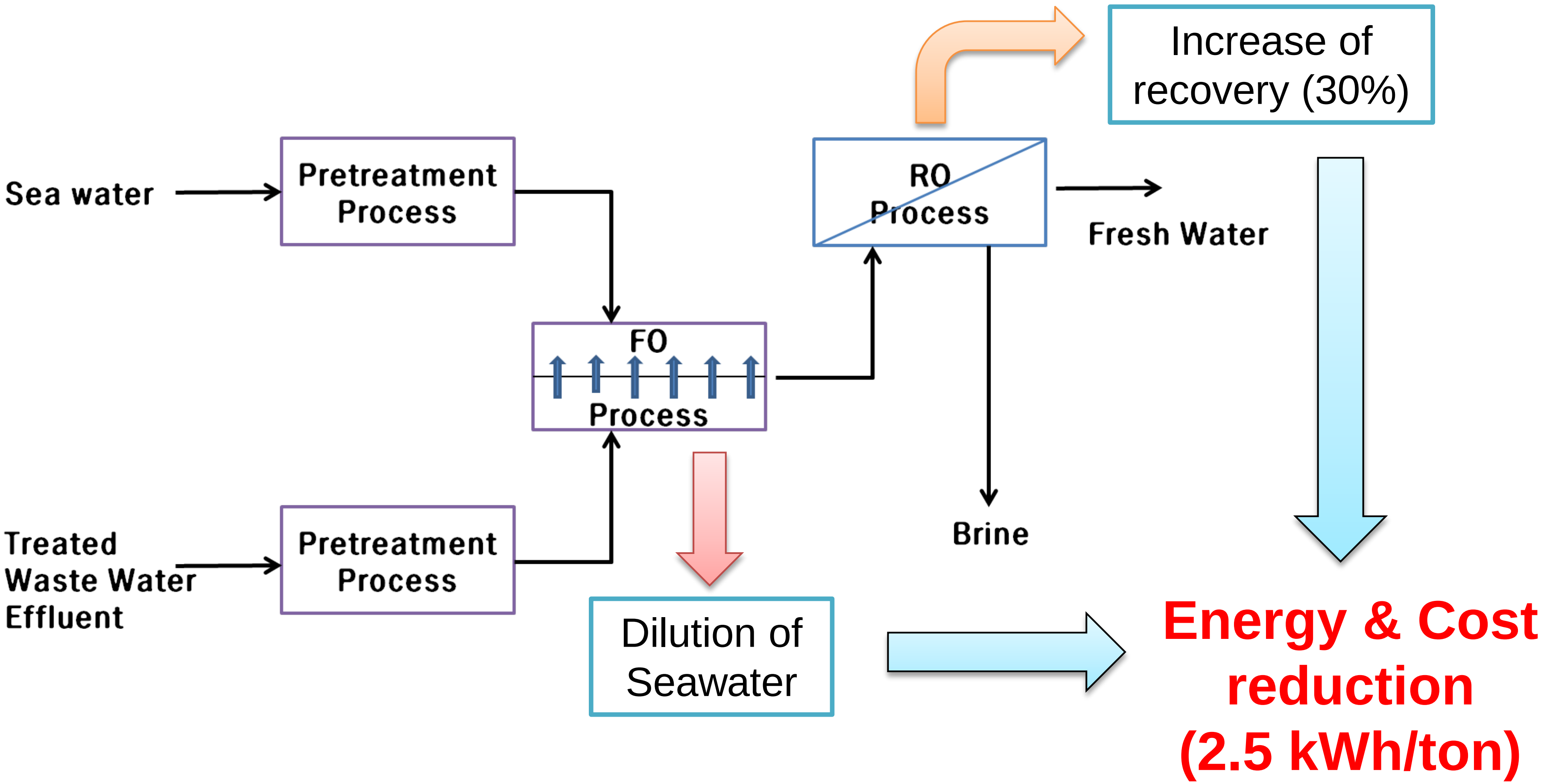
MD/PRO Hybrid process

Conventional desalination plant (Recovery < 40-50%)



FO/RO Hybrid process

Osmotic dilution of seawater using FO process



Plans for 2nd SeaHERO projects

1. MD/PRO Hybrid (Launched)

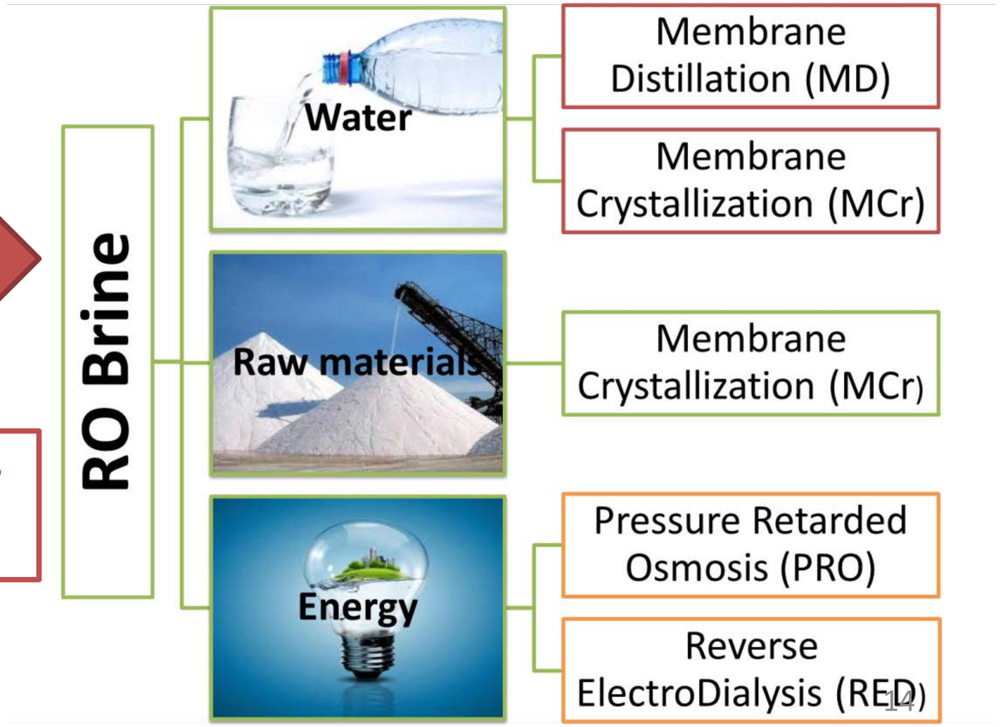
- Duration : **2013. 05 ~ 2018. 04 (5 yr)**
- Budget : 26 Billion KRW + α

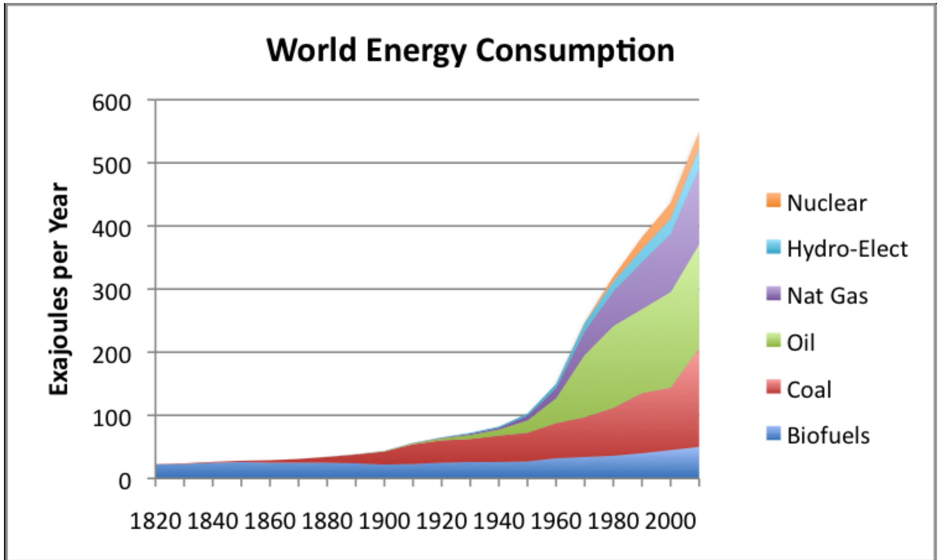
2. FO/RO Hybrid (To be)

- Duration : **2014. 05 ~ 2019. 04 (5 yr)**
- Budget : 32 Billion KRW + α

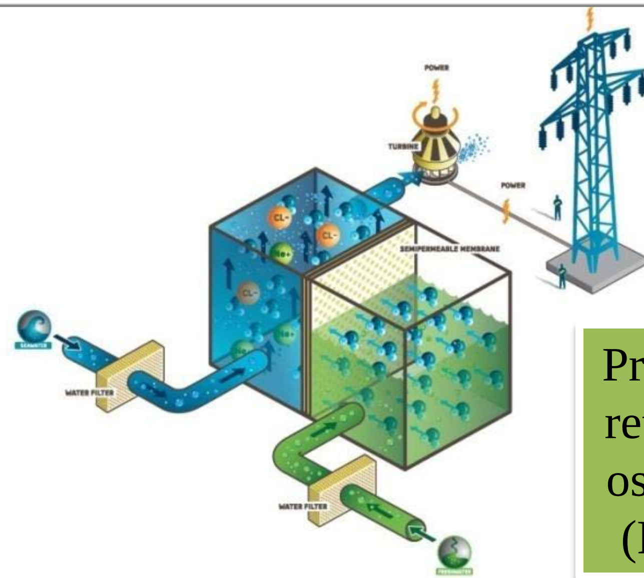
- ✓ *65.2 million m^3/d:* **the total capacity of all completed desalination plants (2010)**
- ✓ *71.7 million m^3/d:* **the cumulative contracted capacity of desalination plants around the world (2010)**
- ✓ *over 15000:* **the number of desalination facilities around the world (2010)**
- ✓ *34.8:* **the percentage of desalination plants using** *MSF or MED technology*
- ✓ *23:* **the percentage of RO water price cheaper with respect to thermal water price**
- ✓ *60:* **the percentage of desalination plants using** *reverse osmosis technology in 2011*
- ✓ *80:* **the percentage of technological change to Membrane-based Desalination (reverse osmosis)** *in 2016*

The current 37.6 million m3/d of brine can be used as a source for...

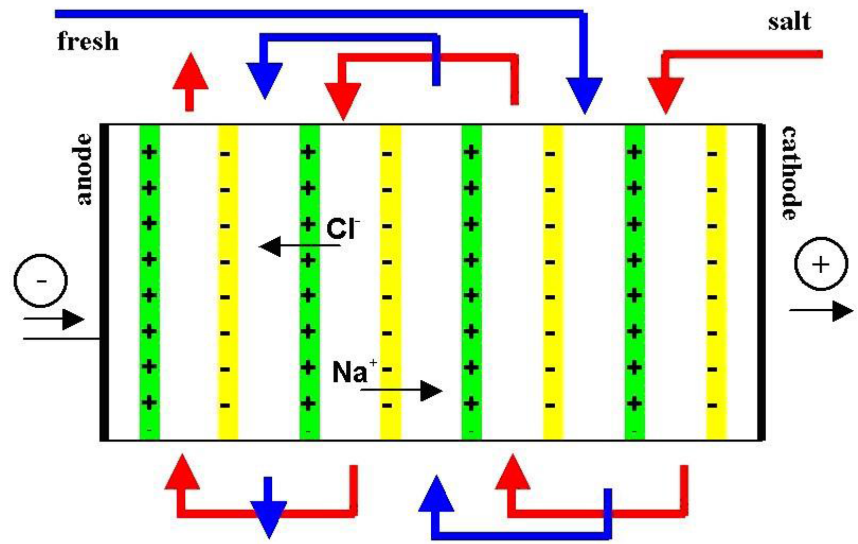




BLUE ENERGY: the possibility to generate power from salinity gradient



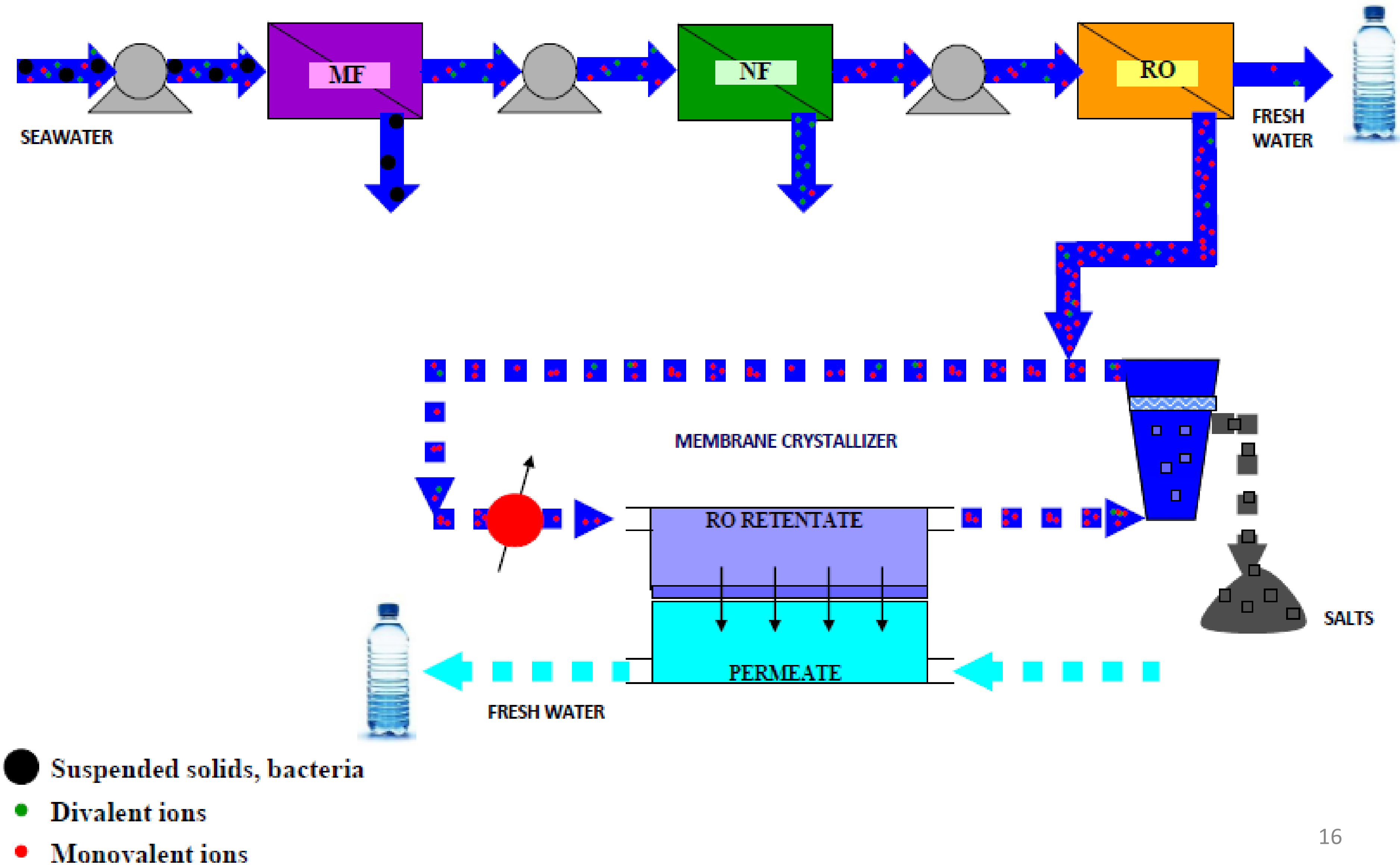
Pressure retarded osmosis (PRO)



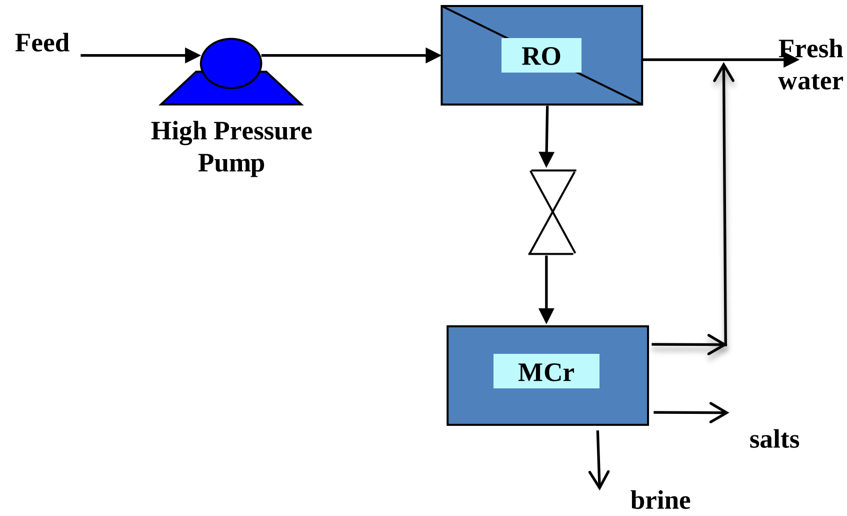
Reverse electrodialysis (RED)

PRO involves the flow of water from low salinity water to high salinity water through a semipermeable membrane to produce pressurized water that generates electricity through mechanical turbines. RED is based on the transport of ions and electrical current is generated directly from the flow of ions.

Integrated Mebrane Desalination System for Water and Raw Material



How much salts can be recovered from the current desalinated seawater?



RESULTS:

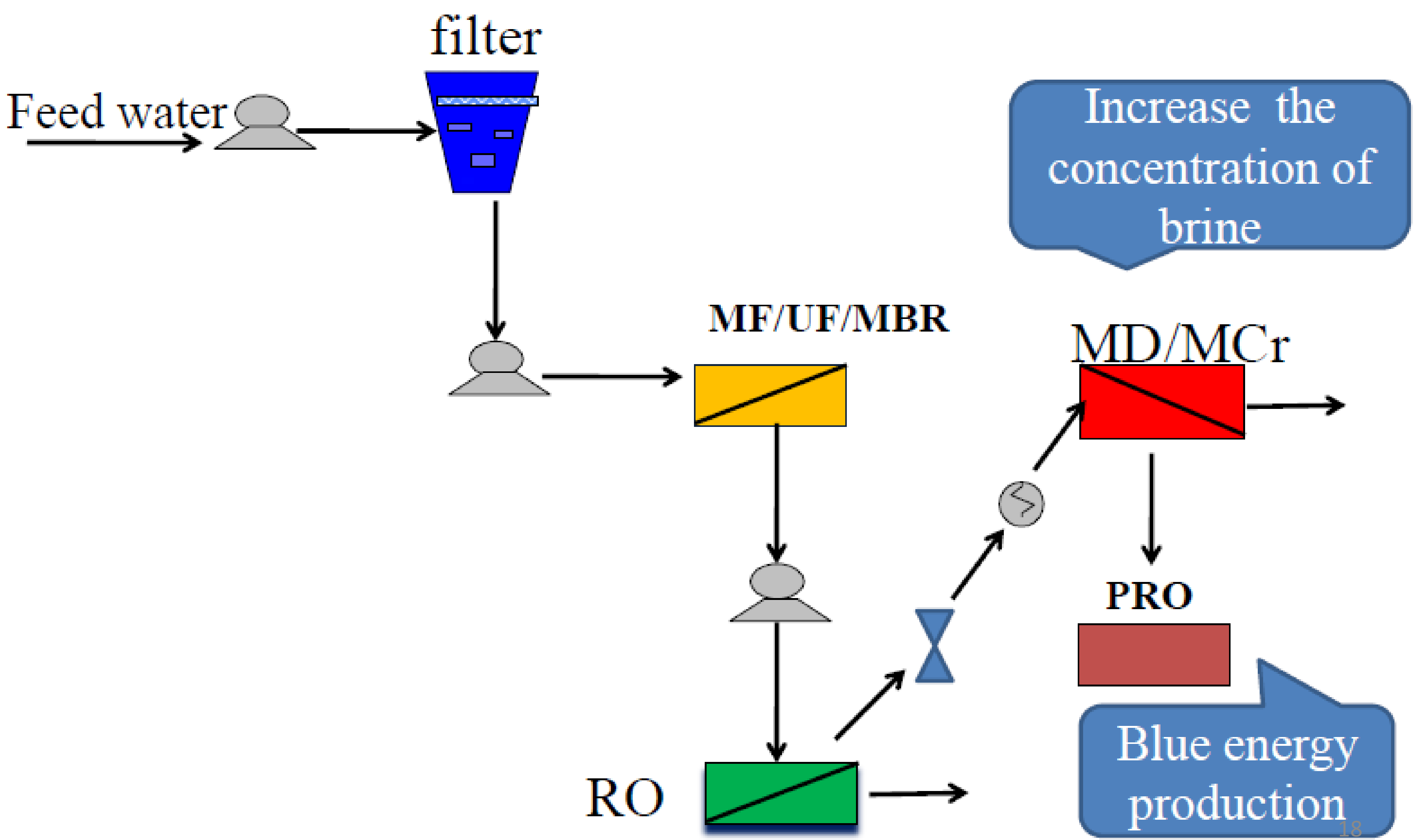
- **Brine flow rate = $4.82 \cdot 10^6$ m^3/d**
- **Brine concentration = 460.3 g/l**
- **Fresh water flow rate = $65.2 \cdot 10^6$ m^3/d**
- **Fresh water concentration = 0.074 g/l**
- **Plant recovery factor = 93%**
- **Salts:**
  - NaCl= 150 ton/day
  - CaCO3 = 68.3 ton/day

Ion	Seawater [ton/day]	Brine [ton/day]
Cl	1.332.043	1.234.555
Na	736.129	685.862
SO4	189.290	188.350
Mg	94.645	94.175
Ca	28.043	558
HCO3	9955	9906
K	26.640	244
CO3	245	1639
Br	4557	4534
Li	11,9	*11,9*
U	0,231	0,230

Mg: higher than the annual worldwide magnesium demand

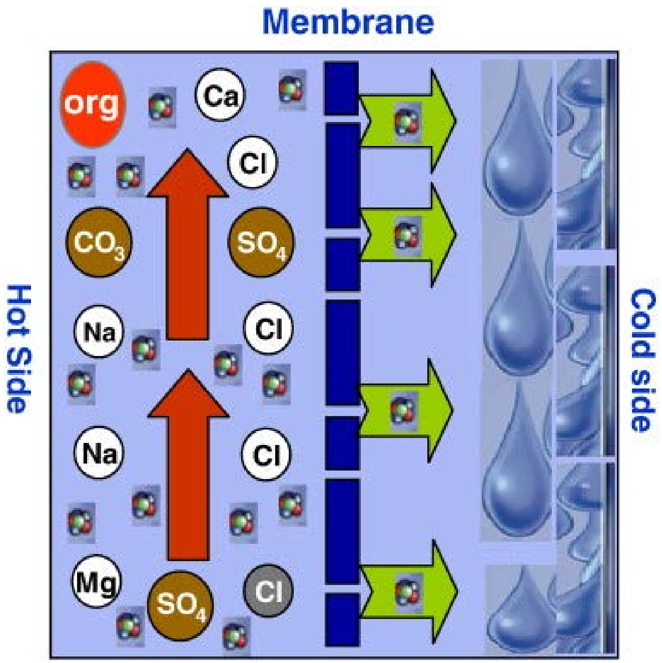
Li: 27% of the annual worldwide lithium demand

Integrated Membrane System for Energy Production



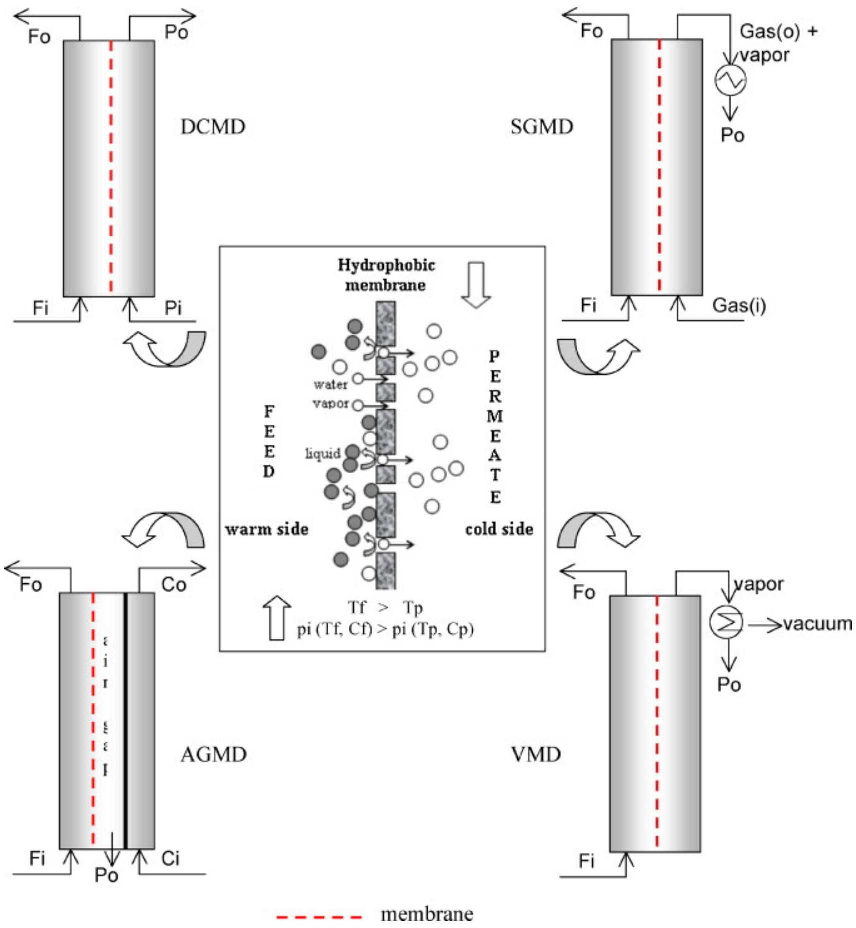
Membrane Distillation

Conceptual illustration



- Theoretically complete rejection of all non-volatiles
- Potential to use waste grade energy
- Ability to treat highly concentrated streams

Basic configurations



Materials for MD-membranes

Material	Abbreviation
Poly(vinylidenefluoride)	PVDF
Polypropylene	PP
Polyethylene	PE
Polytetra-fluoroethylene	PTFE
2,2,4-trifluoro-5-tri-fluorometoxy-1,3-dioxole	**HYFLON**
Ethylene-Chlorotrifluoroethlyene copolymer	**ECTFE**
Poly(vinylidenefluoride-co-tetra fluoroethylene)	F2.4
Polyetherimidie*	PEI
Polysulfone*	PS
Polyethersulfone*	PES
Cellulose acetate*	CA
cellulose nitrate*	CN
Various ceramic materials	
CNT bucky paper	

* Some materials have been modified to change/improve their wetting behavior.

M. Khayet, Advances in Colloid and Interface Science 164 (2011) 56–88

Membrane Characteristics

1) The membrane must be hydrophobic and porous;
2) Appropriate pore size and pore size distribution is required.
   (Large pore size → high mass transfer, however higher probability for wetting);

$$LEP = -\frac{2B\gamma_L \cos\theta}{r_{\max}}$$

B : Geometric factor
γ_L : Surface tension
θ : Contact angle
r : Pore radius

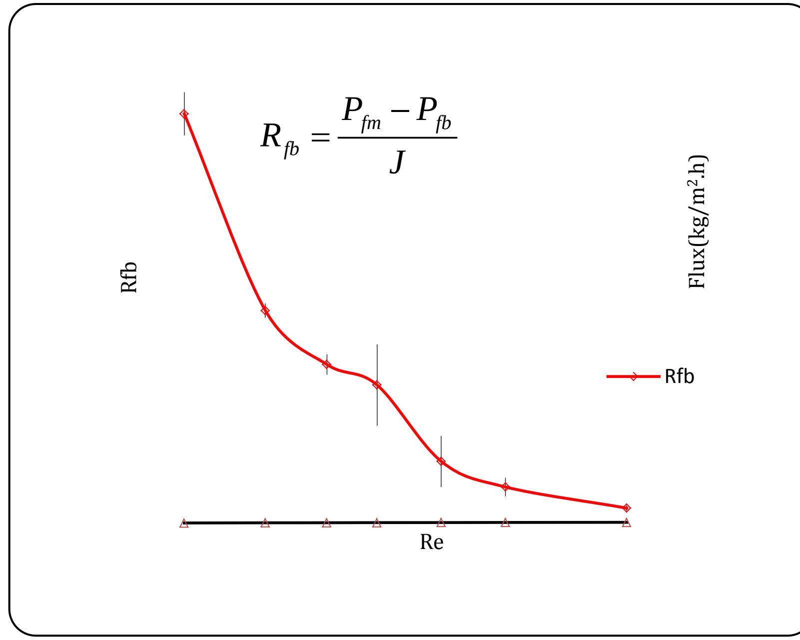
3) High overall porosity;
4) The tortuosity factor should be small;
5) Low thermal conductivity of the membrane material is necessary to prevent heat losses
6) High thermal stability;
7) High chemical resistance and
8) Long-term stability in terms of mechanical, chemical and thermal resistance is required to ensure the steady performance.

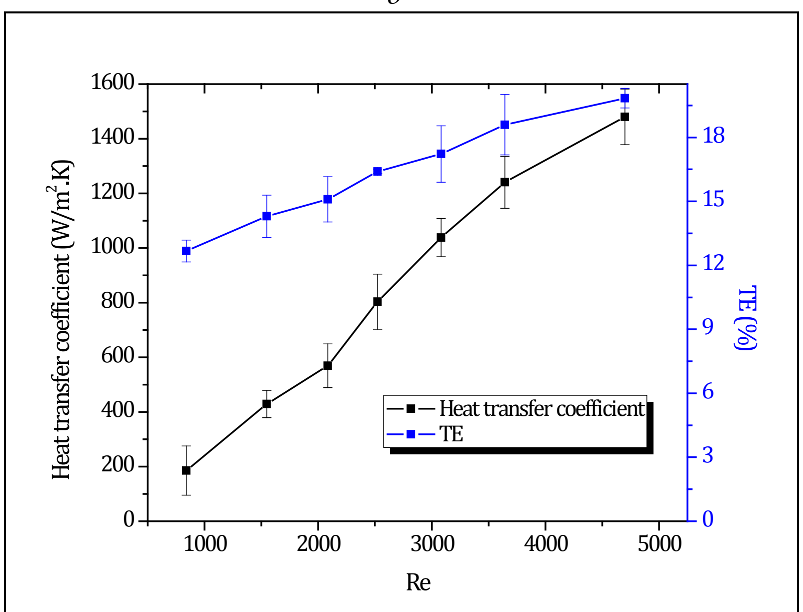
M. Khayet, Advances in Colloid and Interface Science 164 (2011) 56–88

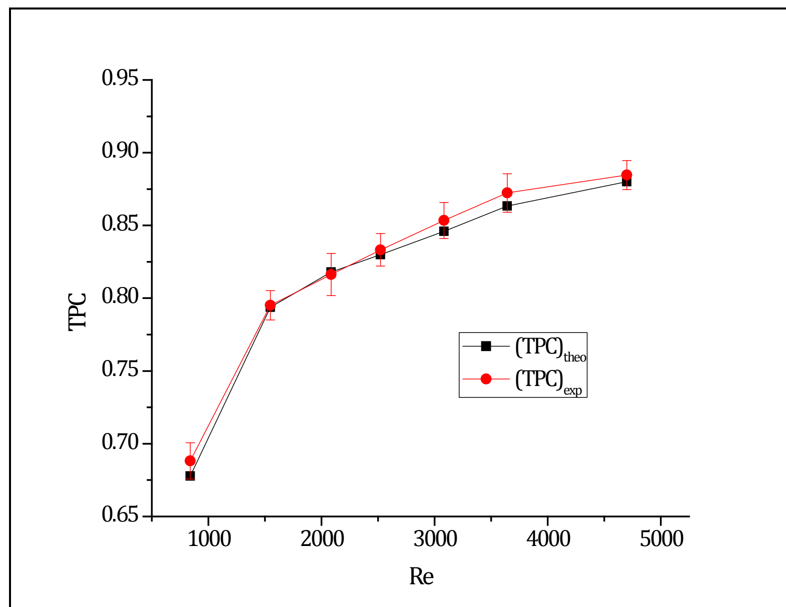
Effect of feed hydrodynamic

Rfb Feed side boundary layer resistance
Pfm Vapor pressure at membrane surface on feed side
Pfb Vapor pressure in bulk on feed side
Re Reynolds number
TPC Temperature polarization coefficnet
TE Thermal efficiency

$$TE(\%) = \frac{JH_v\{T\}}{JH_v\{T\} + \frac{K_m}{\delta}\left(T_{fm} - T_{pm}\right)} \times 100$$





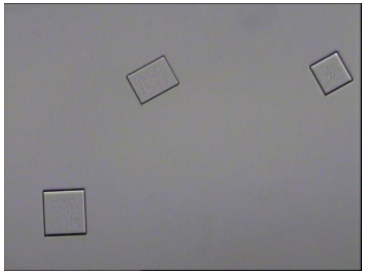


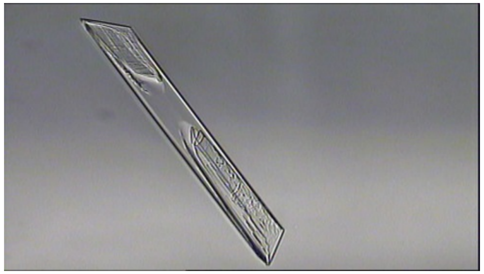
A. Ali, F. Macedonio, E. Drioli, Accepted in ChERD

Membrane Crystallization

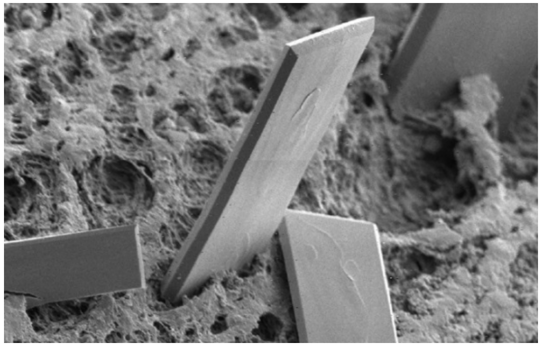
... Extension of the Membrane Distillation concept.

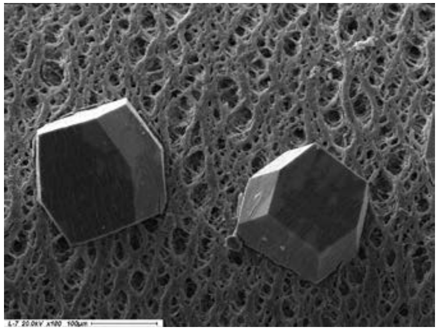
Applications:





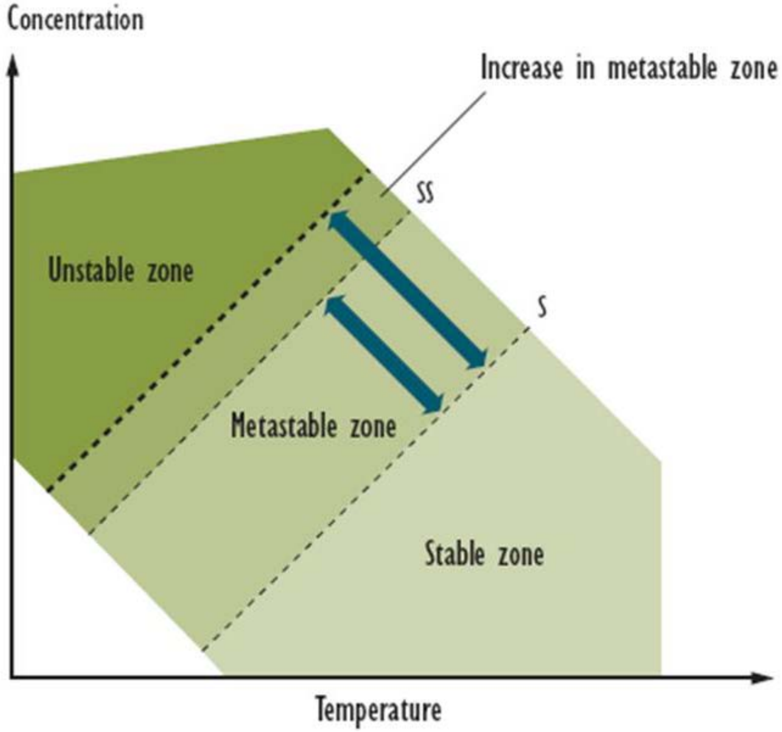
- ✓ **Inorganic salts**
- ✓ **Small organic molecules**
- ✓ **Biological macrmolecules**



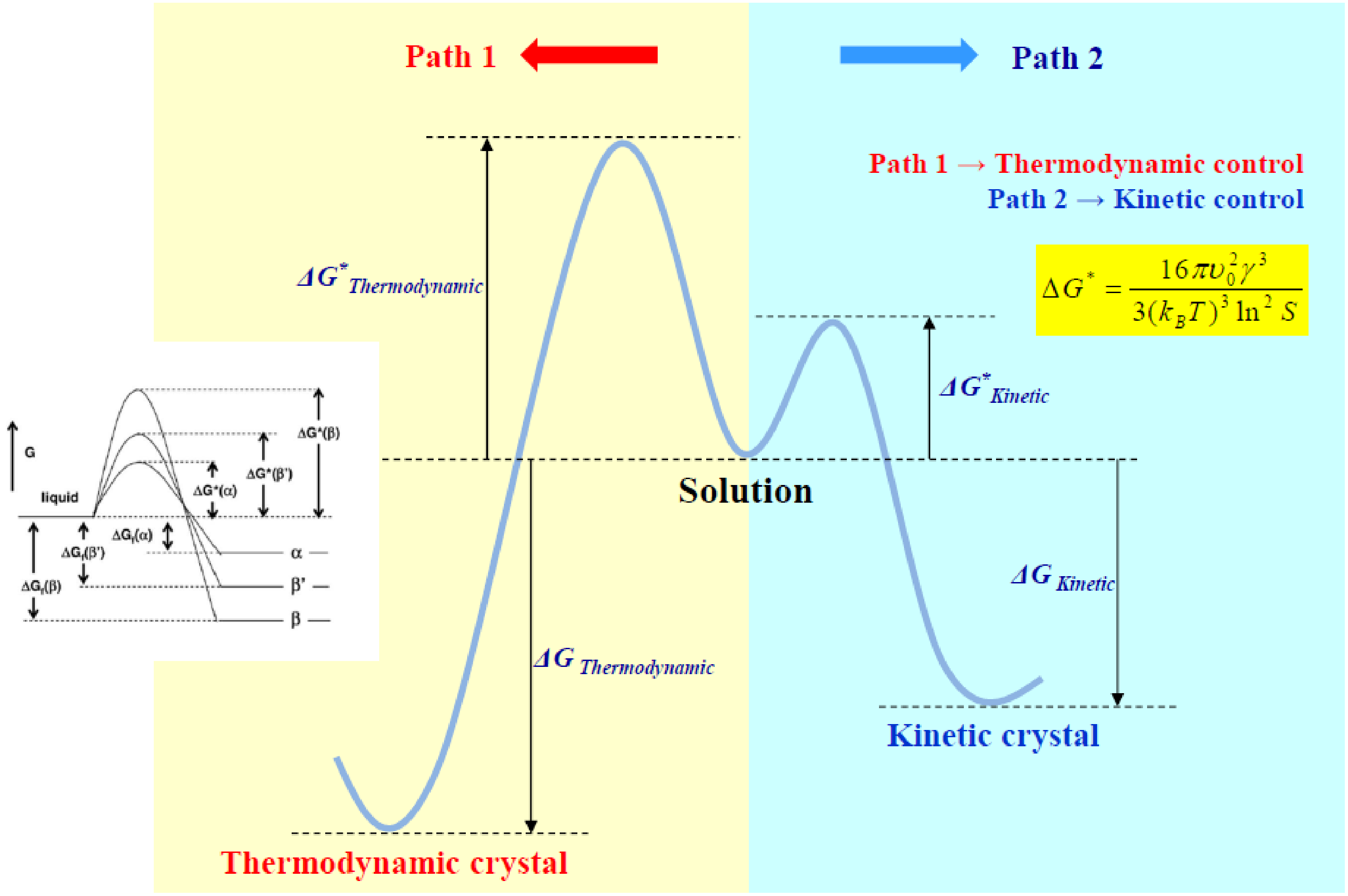


Membrane Crystallization

- ✓ **Application on large and small scale for different uses.**
- ✓ **Control of supersaturation.**
- ✓ **Avoid scaling by control of trans-membrane flux, flow rate and temperature i.e. in crystallization of SWRO brine.**
- ✓ **Enhancement of crystallization kinetics by heterogeneous nucleation on the membrane surface i.e. in crystallization of organic molecules and proteins.**



Kinetic and thermodynamic balance in the crystallization



Chen et al. Cryst. Growth Des. 2011, 11, 887

Which salts can be recovered from desalinated seawater?

Integration of MD and MCr with RO can:

- **Increase water recovery factor.**
- **Recovery of rare or valuable componets from SW.**
- **Enhance the recovered product quality.**
- **Etc.**

Component	Seawater [ppm]	Rejection RO [%]	Brine [ppm]	Brine after Ca removal [ppm]	Mass [ton/day]
Na	10,800	98	21,168	21,927	1.184E+04
Cl	19,400	98	38,024	38,024	2.053E+04
Mg	1,290	98	2,528	2,528	1.365E+03
SO4	2,708	98	5,308	5,308	2.867E+03
K	392	96	753	753	406.4
Ca	411	98	806	16.1	8.70
Br	67.3	96	129	129	69.8
B	4.45	70	6.23	6.23	3.364
HCO_3	142	98.4	279	85.8	46.36
Li	0.17	98.9	0.34	0.34	**0.1816**
Ba	0.021	96	0.040	0.040	**0.02177**
Sr	8.1	99.9	16	16	**8.74**
U	0.0033	99	0.01	0.0065	**0.003528**
Rb	0.12	98	0.24	0.24	**0.1270**
Cs	0.0003	99.7	0.00	0.0006	**0.0003230**

Recovery of LiCl from seawater

Solubility LiCl: 14 M				
	Seawater	RO	MD	MCr
Li concentration [ppm]	0.17	0.34	1.3	$9.8 \cdot 10^{4}$
Li concentration [M]	$2.5 \cdot 10^{-5}$	$4.8 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$	14
Rejection		98.9	99	99
Water recovery [%]		50	75	99.999
Volume [m^3]	1080,000	540,000	135,000	1.815
Concentration factor		2	8	594,940

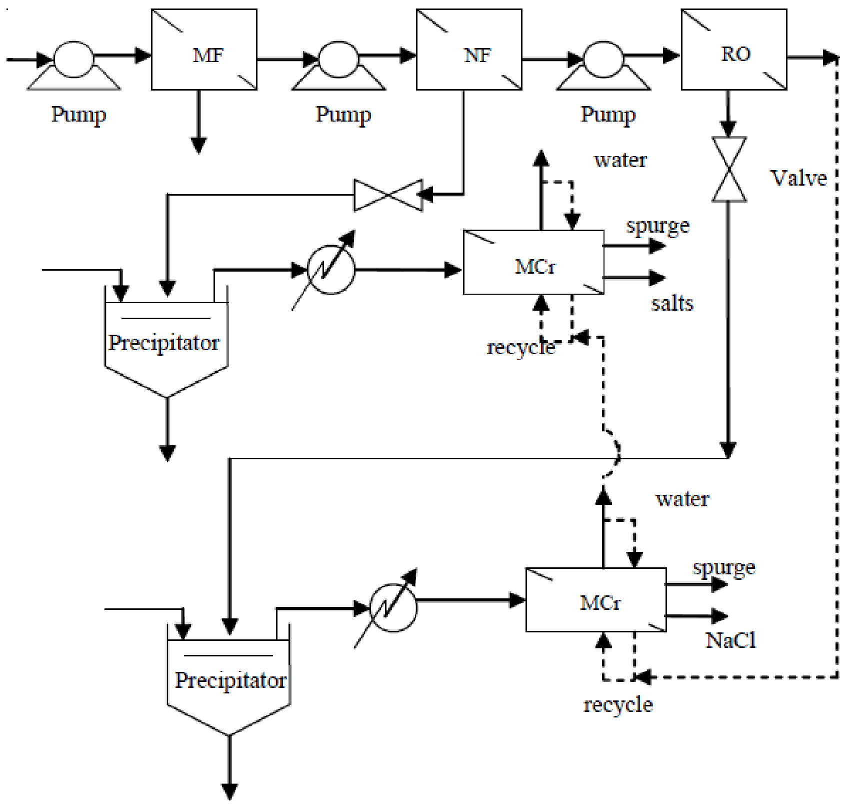
Initial volume of seawater (1080,000 m^3) has to be decreased to less than 2 m^3 for LiCl precipitation.

Recovery of Magnesium Sulphate

Brine flow rate, m^3/h	74.60
Brine concentration, g/l	214.4
Fresh water flow rate, m^3/h	974.9
Fresh water concentration, g/l	0.1433
Fresh water recovery, %	92.80
$CaCO_3$ flow rate, kg/h	979.3
NaCl flow rate, kg/h	19,840
$MgSO_4 \cdot 7H_2O$ flow rate, kg/h	**938.6**

$CaCO_3$, \$/y	478,700
NaCl, \$/y	4,693,000
$MgSO_4 \cdot 7H_2O$, \$/y	**4,218,000**
Total annual profit, \$/y	9,389,000
Total annual cost, \$/y	5,593,000
Total annual cost per m^3 of fresh water produced, \$/m^3	**–0.49/–0.68 (a**

(a) If thermal energy is available in the plant or the stream is already at the operating temperature of the MCr unit.



If the salts do not contribute to the economic of the process, the water production cost is ranging from 0.51 - 0.73 \$/m^3 depending on the availability of thermal energy and ERD.

F. Macedonio. E. Curcio, E. Drioli, Desalination 203 (2007) 260-276.

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

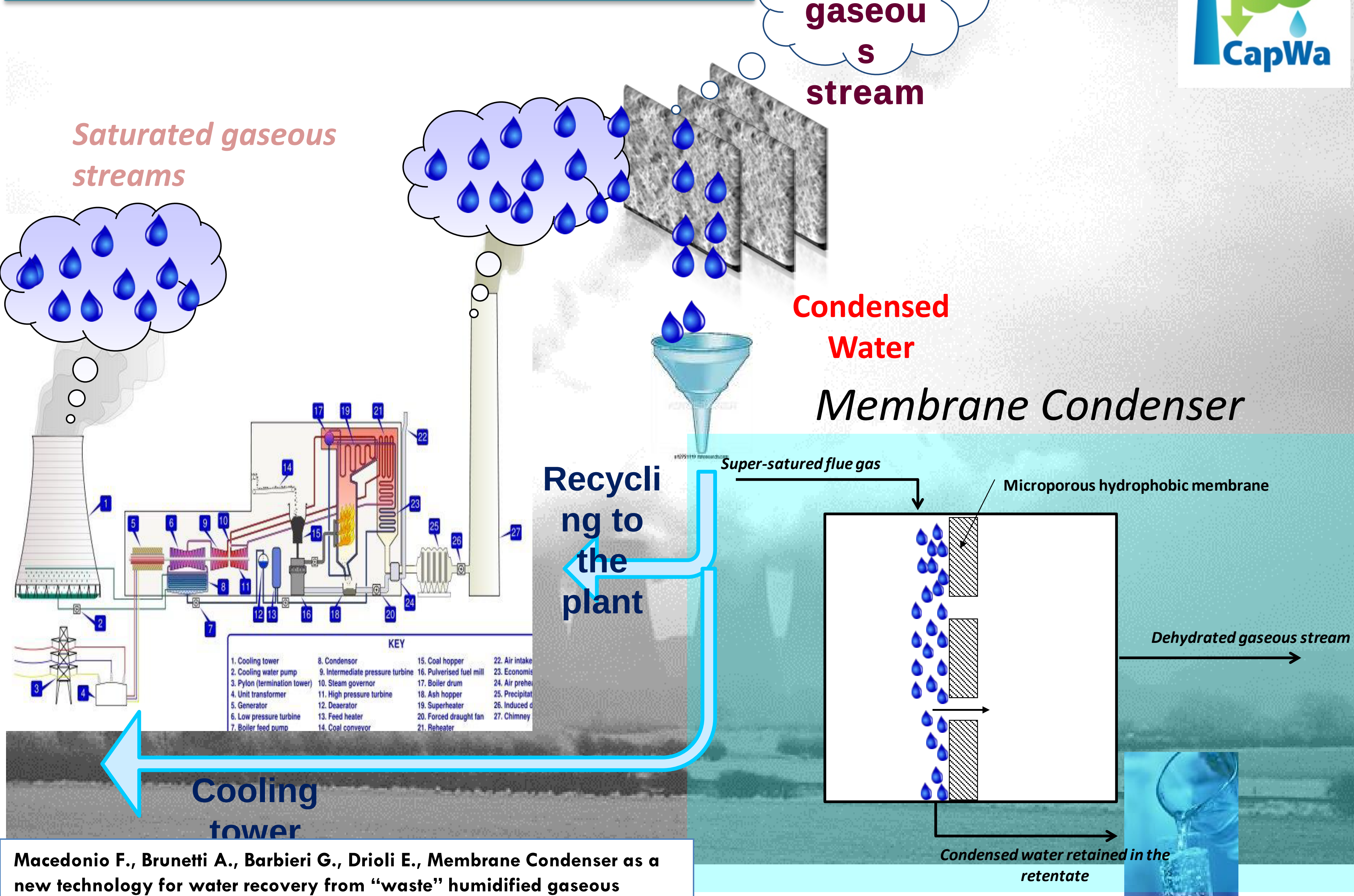
	Only RO	NF-RO	MF/NF/RO	MF-NF-RO | MCr	MF-NF-RO | MCr	MF - NF - RO | | MCr MCr	MF - NF - RO | | MCr MD
Total annual profit for salts sale[$/yr]	-	-	-	*6,398,000*	2,991,000	*9,389,000*	*6,398,000*
Total annual cost [$/yr]	2,040,000	2,005,000	1,871,000	*4,024,000*	3,440,000	*5,593,000*	*5,445,000*
Unit 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.

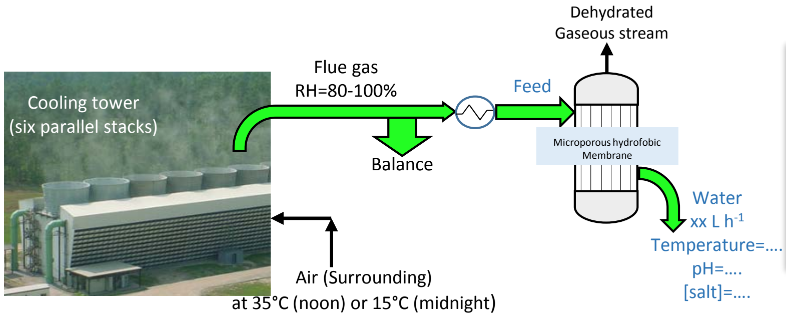
E. Drioli, F. Macedonio et Al., Chemical Engineering Research & Design, 84 (A3) (2006) 209–220.

Membrane Condenser



Macedonio F., Brunetti A., Barbieri G., Drioli E., Membrane Condenser as a new technology for water recovery from "waste" humidified gaseous streams, *Industrial Engineering & Chemistry Research*, 2013, 52 (3), pp 1160–1167.

Configuration 1: cooling of the membrane condenser by external sources



The membrane module can be placed at a certain distance from the chimney of the tower and its cooling can occur exploiting the temperature difference between the feed gas and the environment.

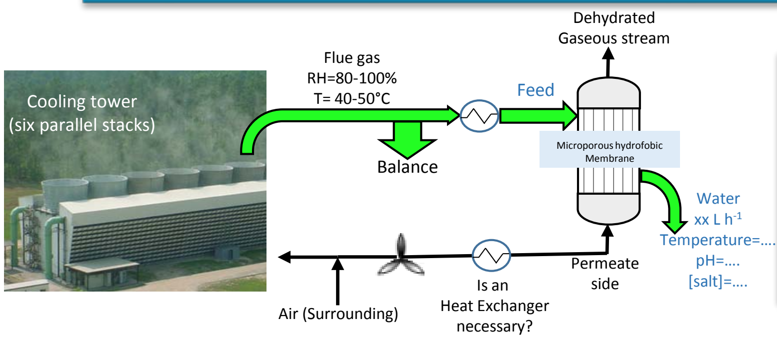
Advantages

- Low energy consumption in particular if low ΔT are required

Disadvantages

- Difficult removal of water from the fiber.
- Difficult to control the temperature of the module.

Configuration 2: cooling of fibers with coldsweep gas



The membrane surface can be cooled with a sweep gas fed on the permeate side of the membrane module.
The sweep can consist of air coming out from the surrounding that can be cooled in an heat exchanger if necessary.

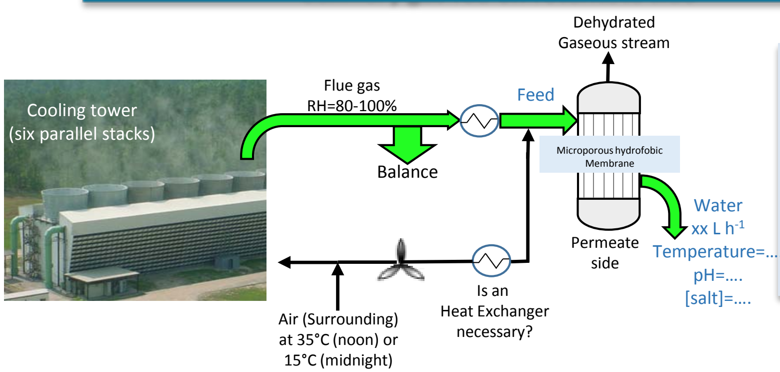
Advantages

- Easy removal of water

Disadvantages

- Possible condensation inside membrane pores

Configuration 3: Cooling of the membrane condenser by cold auxiliary gas fed on retentate side



The membrane surface can be cooled with a cold gas fed on the retentate side of the membrane module.
The cooling gas can consist of air coming out from the surrounding that can be cooled in an heat exchanger if necessary.

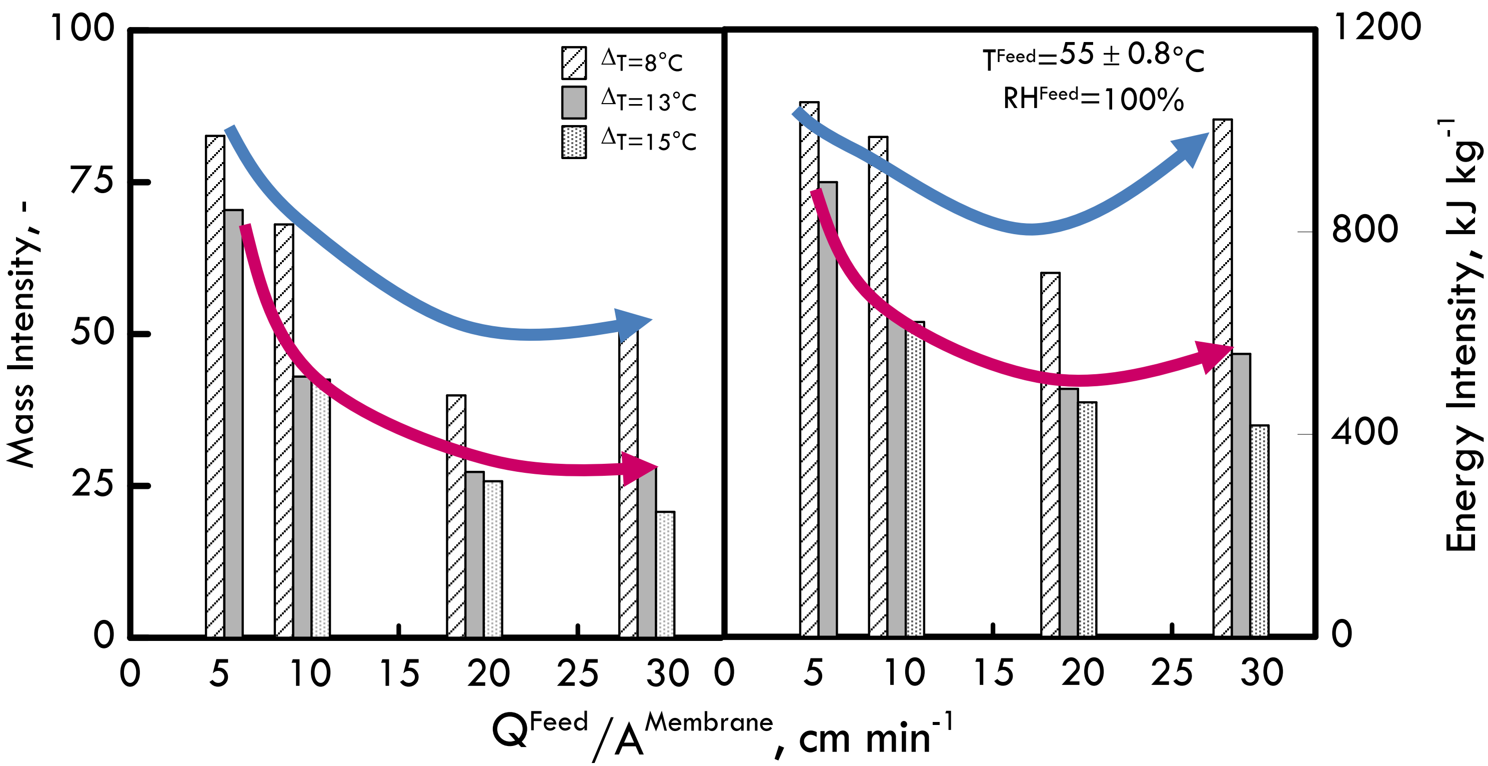
Advantages

- Easy removal of water

Disadvantages

- Dilution of the feed and consequent reduction of the relative humidity and therefore of the water recovered.

Indexes for PI strategy



The indexes tend to a minimum. The lower the ΔT the lower the $Q^{feed}/A^{membrane}$ value corresponding to the minimumhe minimum. A high ΔT favours the water condensation compensating the low effect on condensation due to a low contact time. On the contrary, when the ΔT is low, the contact time is a fundamental parameter and the temperature becomes the rate determining step

Brunetti A., Santoro S., Macedonio F., Figoli A., Drioli E., Barbieri G., Membrane condenser for the recovery of water from humidified "waste" gaseous streams: an experimental study, Clean 2013 (Accepted)

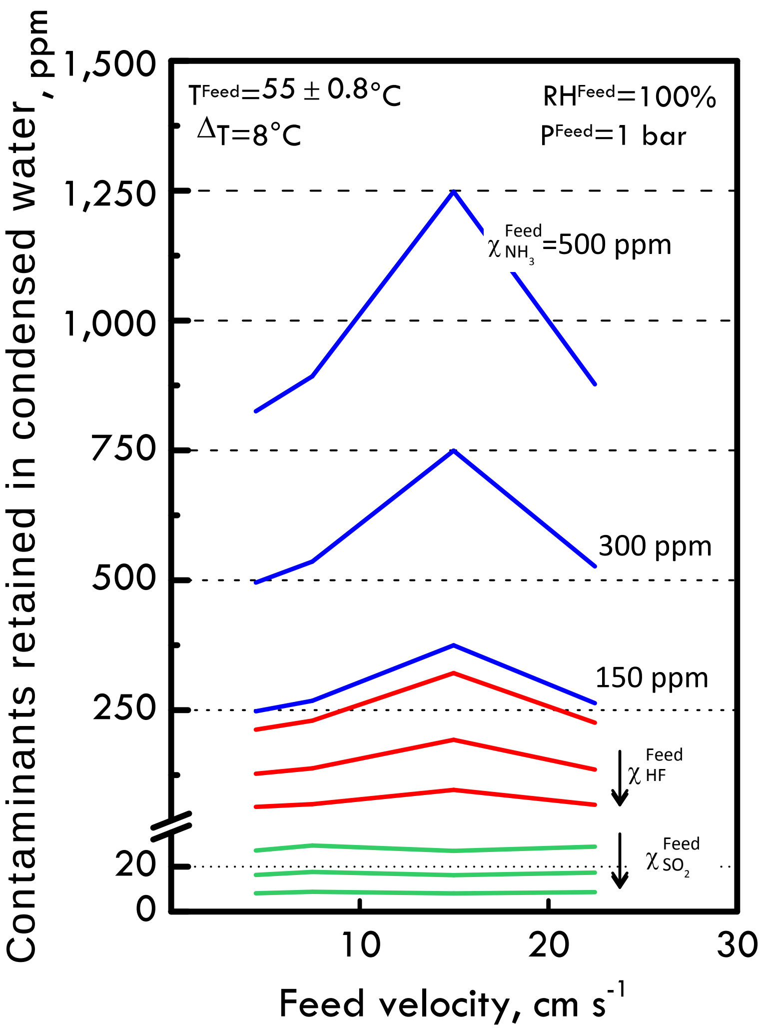
	Liquid sorption [1]	Cooling with condensation [2]	Dense Membranes [3]	Membrane condensers
Water recovery	22-62%	< 70%	20-40%	> 70%
Water purity	>95%	Sufficient for cooling tower make up Contaminants	>95%	Sufficient for cooling tower make up Contaminants
Maintanance and durability	Corrosion and salt crystals formation due to salt dessicants presence and O_2 in the flue gas	Corrosion due to the formation of a thin liquid layer of diluted acids and fly ashes forming deposits	Ashes removal and FGD necessary to avoid membrane damaging	Ashes removal to avoid membrane damaging
Environmental aspects	Increase of CO_2 emissions Reduction of SO_x emission $CaCl_2$ losses	Co-capture of SOx and NOx could results in a environmental profit reducing the DENOx and FGD systems	Clean operation	Clean operation
Investments costs	5.8 mln $ (2006) +200.000 $/year (2006) as operational costs	6.4 mln EURO (2011)	To be determined	To be determined
Economic viability	4.4 $/m^3	1.5-2 EURO/m^3	1.5 Euro/m^3 (WET regions) 10 EURO/m^3 (DRY regions)	**1.5- 2.5 Euro/m^3 (*)**

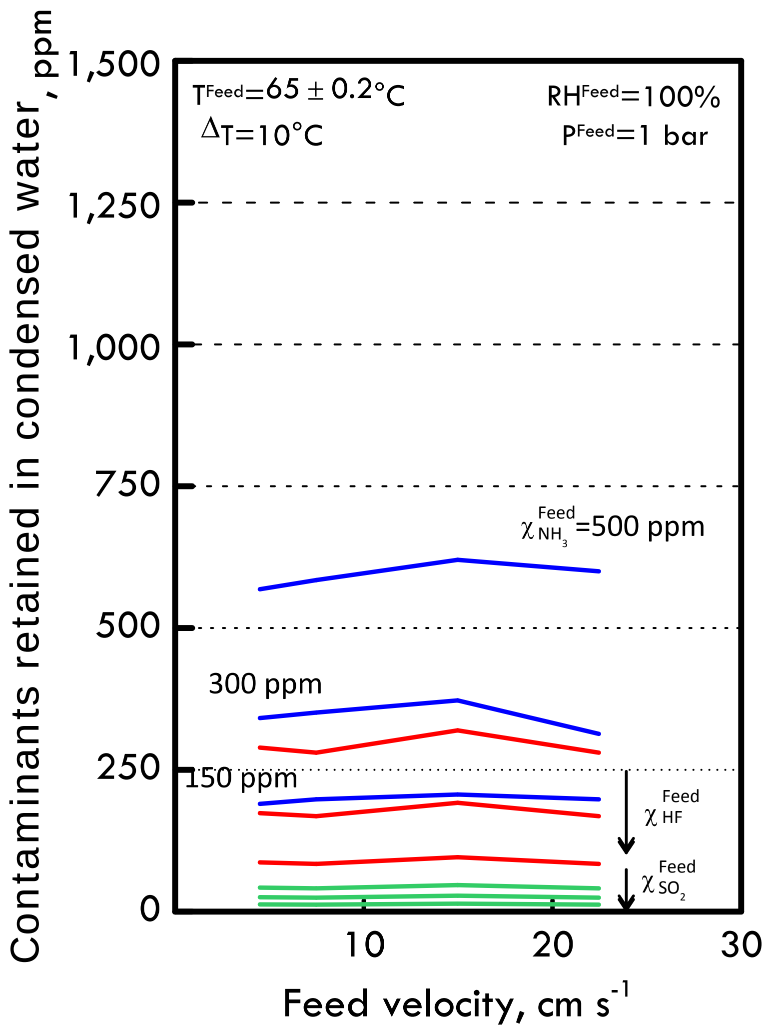
[1]Folkedahl, B., Weber, G.F., Collings, M.E. Water extraction from coal-fired power plant flue gas. Final report. DOE Cooperative Agreement No. DE-FC26-03NT41907. December 2006 . http://www.netl.doe.gov/technologies/coalpower/ewr/water/pp-mgmt/pubs/41907/41907%20Final.pdf

[2] Michels, B., Adamczyk, F., Koch, J. Retrofit of a flue gas heat recovery system at the Mehrum power plant. An example of power plant lifetime evaluation in practice. VGB PowerTech, Nr. 10, 2004.

[3] http://www.watercapture.eu/downloads/paper-powergen-europe.pdf

PRELIMINARY CALCULATIONS ON CONTAMINANTS





Macedonio, Brunetti, Drioli et al, *IN PREPARATION*

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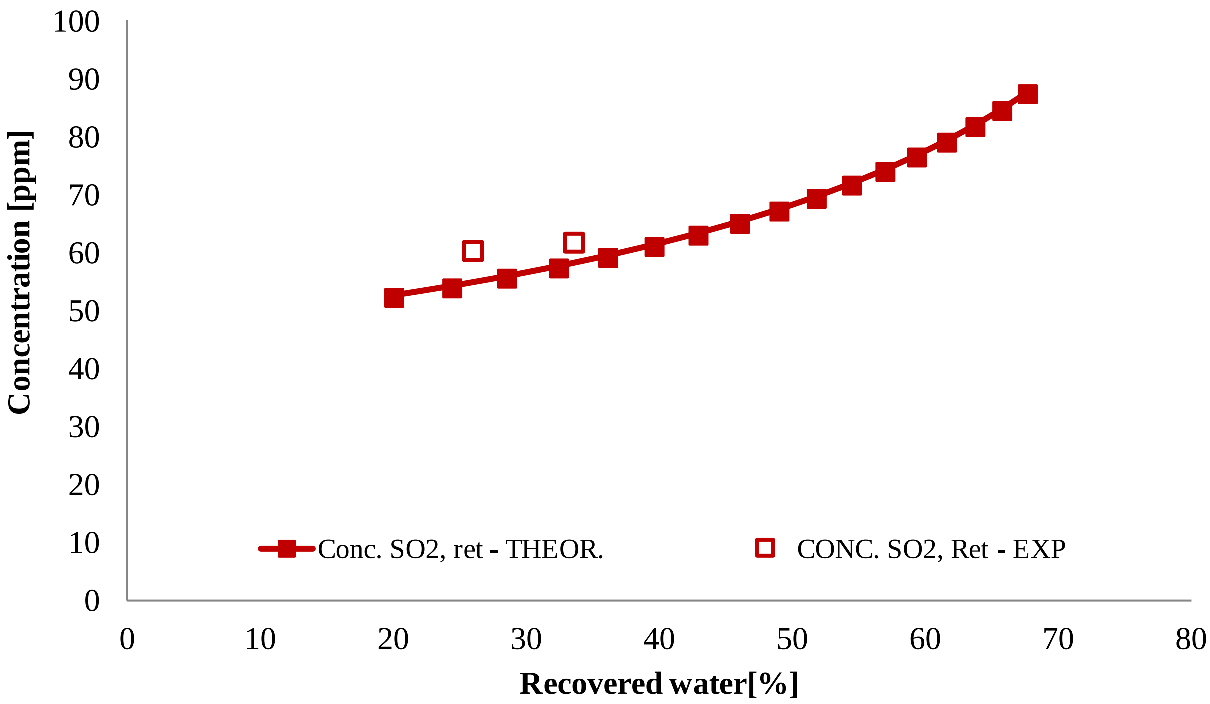
Configuration 1 - COMPARISON BETWEEN EXPERIMENTAL TESTS AND MODEL



SO_2 concentration vs recovered water. Flue gas with RH_{Feed}=100%, T_{feed} = 55.73°C, feed flow rate=659 SCCM.

Macedonio, Brunetti, Drioli et al, *IN PREPARATION*

Consiglio Nazionale delle Ricerche

ISTITUTO PER LA TECNOLOGIA DELLE MEMBRANE

c/o Università della Calabria, Rende (CS), Italy

مدينة الملك عبدالعزيز
للعلوم والتقنية KACST

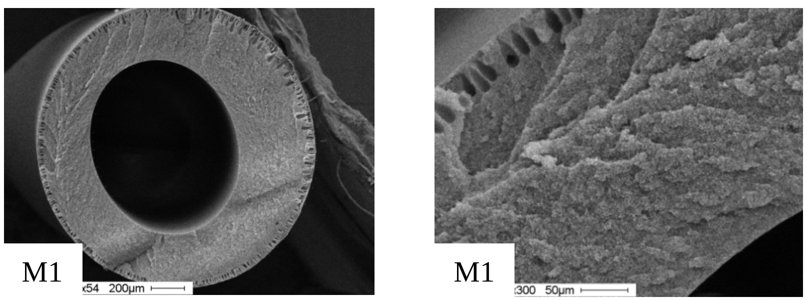
Direct-Contact Membrane Distillation, Osmotic Distillation and Membrane Crystallization

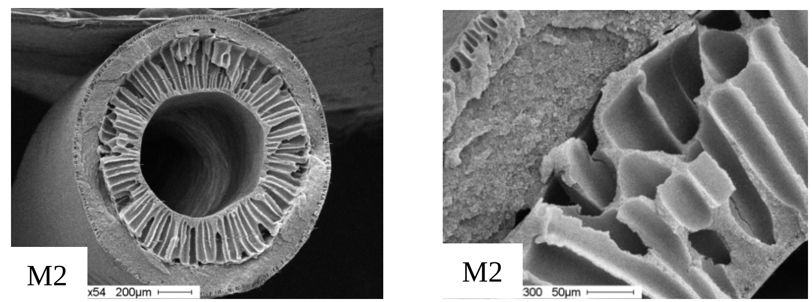
Objectives:

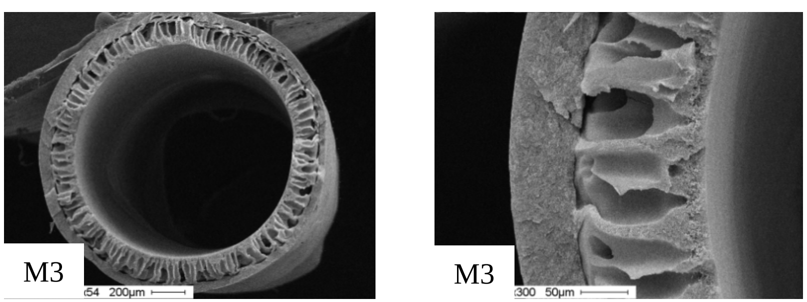
- **Test of various fabricated PVDF membranes**
- **Evaluation of the performance of the membranes with concentrated solutions on the feed side,**
- **Analyze the correlation between the membrane properties and the DCMD/MCr performance,**
- **Investigate the long term stability of the membranes together with the cleaning methods.**

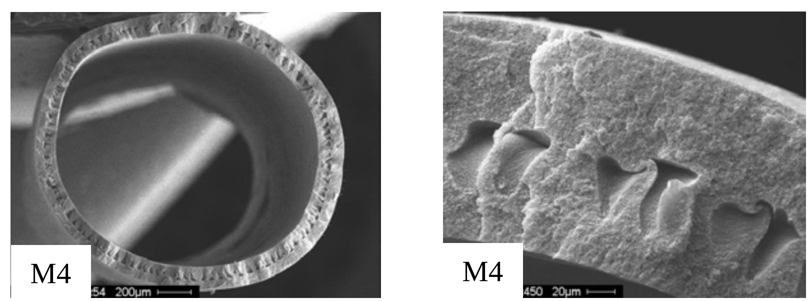
Membrane Properties

Fiber type	O.D. [mm]	I.D. [mm]	Thickness [mm]	Emod [N/mm²]	Rm [N/mm²]	Break [%]	W [Nm]	Bubble Point [bar]	Pore size [µm]	Porosity
M1	1.75	0.94	0.40	65.76	3.86	259.95	0.71	0.40	0.47	80.77
M2	1.59	0.70	0.45	57.15	2.84	192.88	0.30	0.37	0.43	79.11
M3	1.60	1.15	0.23	63.71	2.62	163.82	0.19	031	0.52	83.39
M4	1.78	1.40	0.19	150.53	4.49	223.30	0.34	0.93	0.29	65.44

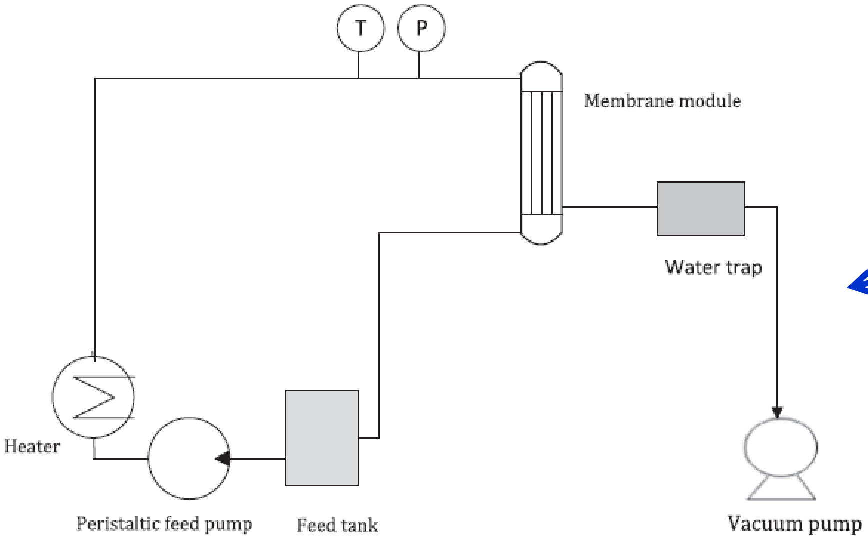






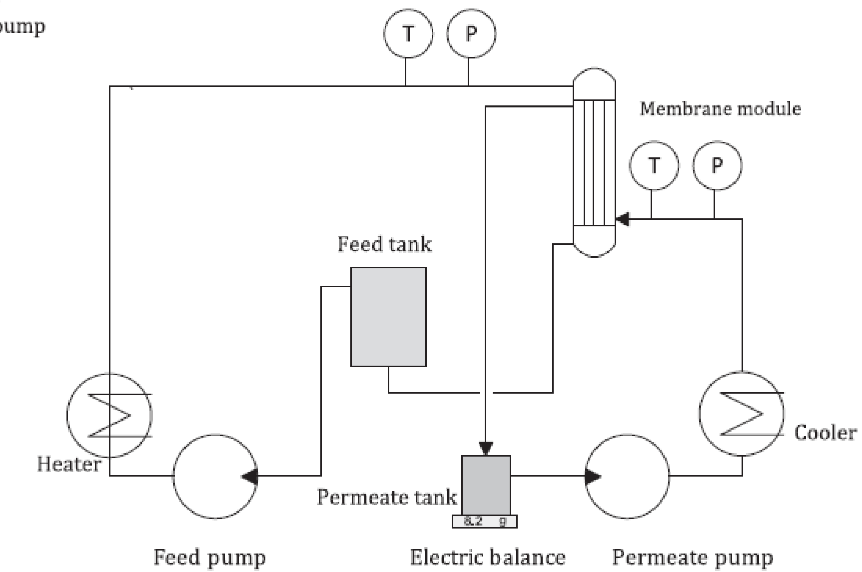


PVDF Membrane performance in VDM and DCMD



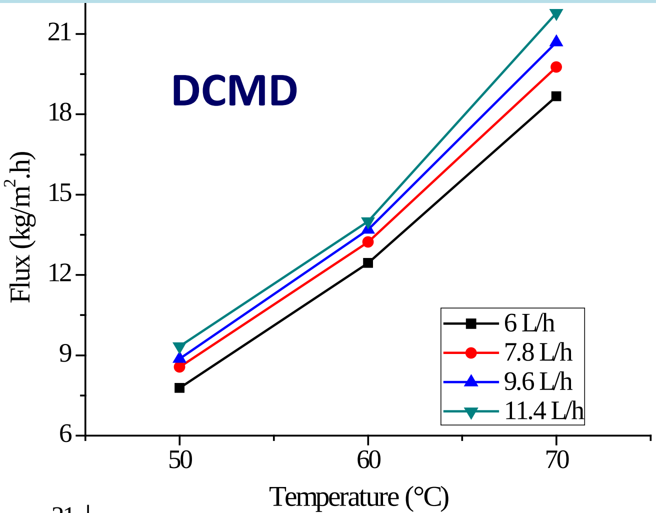
Vaccum membrane distillation (VMD) plant

Direct contact membrane distillation (DCMD) plant



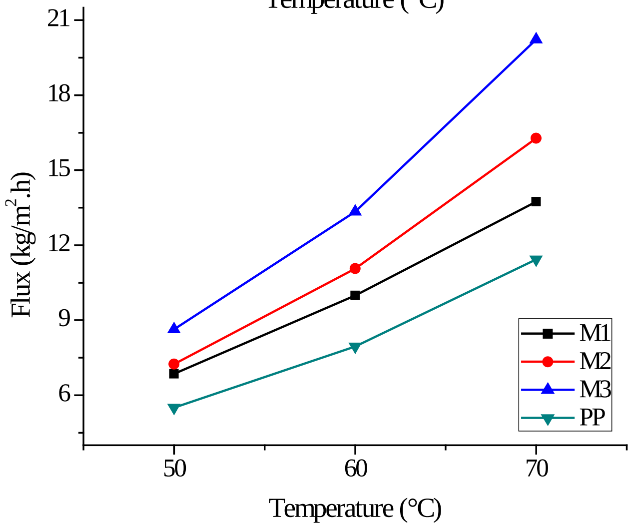
E. Drioli et al. / Separation and Purification Technology 115 (2013) 27–38

Membrane performance in VDM and DCMD



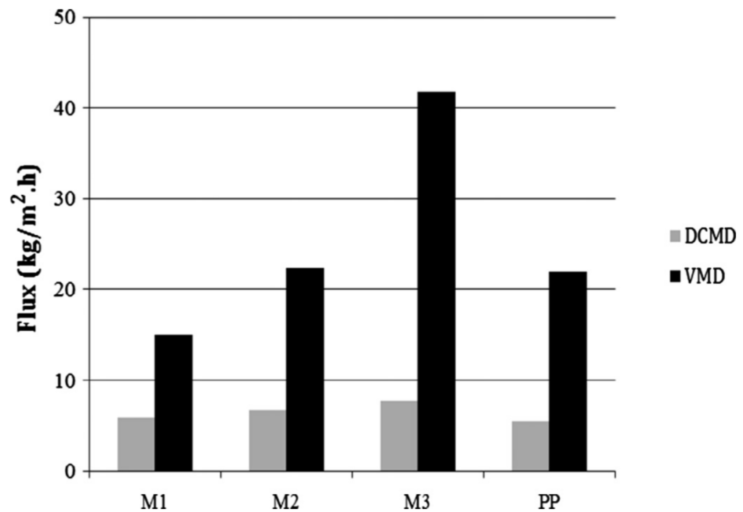
VMD

Fiber	VMD flux (H2O) (kg/h m2)
M1	15.06
M2	22.37
M3	41.78



Permeate temperature: 25 C
Permeate flow-rate: 6 l/h

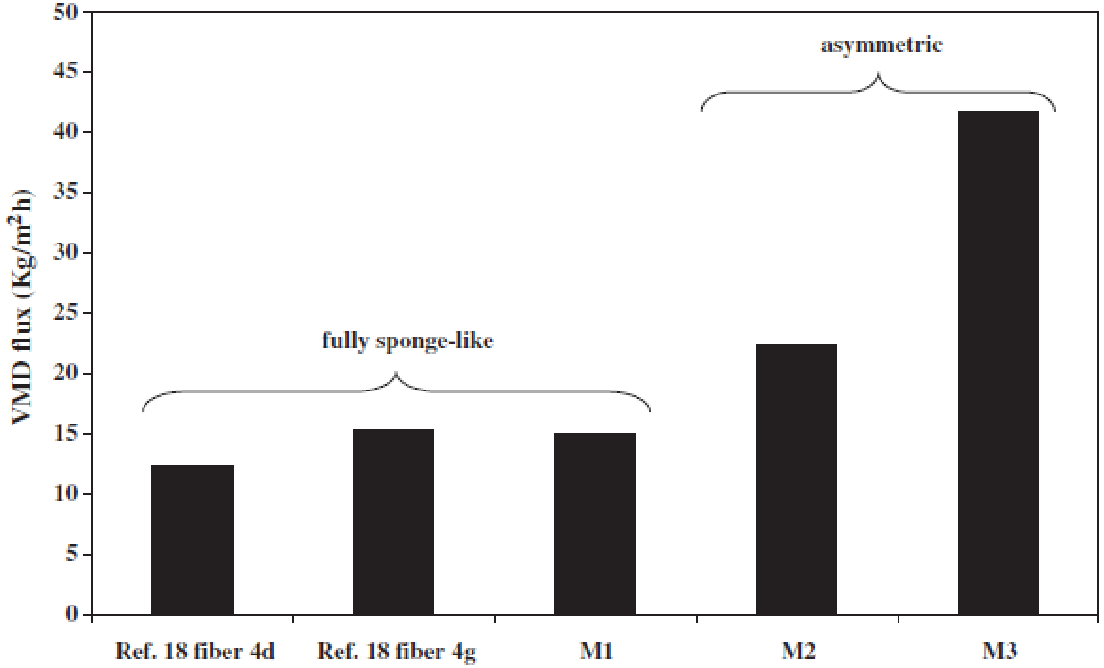
Pvacuum 40 mbar, Tfin 50 °C, Qfeed 6 l/h



E. Drioli et al., Separation and Purification Technology 115 (2013) 27–38

Morphology vs performance

Fiber	Morphology	Thickness (mm)	Porosity (%)
Ref. 18 fiber 4b	Spongy with some fingers at outer surface	0.174	81.23
Ref. 18 fiber 4d	Spongy with some fingers at outer surface	0.202	78.09
Ref. 18 fiber 4g	Spongy with some fingers at outer surface	0.139	78.45
M1	Spongy with some fingers at outer surface	0.38	80.9
M2	Asymmetric with fingers at inner and outer surface	0.45	79.11
M3	Asymmetric with fingers towards inner surface	0.23	83.39



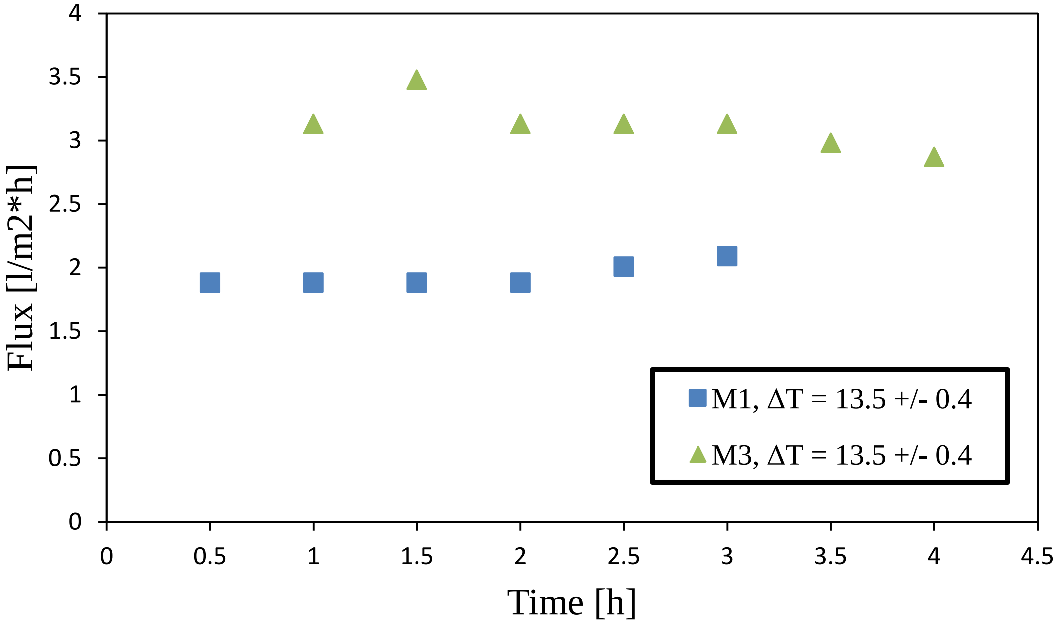
E. Drioli et al., Separation and Purification Technology 115 (2013) 27–38,
S. Simone et al. / Journal of Membrane Science 364 (2010) 219–232

Comparison with literature data

Membrane type	*DCMD Flux (kg/m^2.h)*	*VMD flux (kg/m^2.h)*	*Operating parameters*		*Reference*
			VMD	*DCMD*	
PVDF	*18.9*	*22.4*	*Tfin=73 °C,P=315mbar ,35g/L NaCl solution*	*DCMD Feed=35g/L NaCl, solution Tfin=73 °C Tpin=25°C*	*[1]*
PVDF	*~16.5*	*~23.5*	*65±0.2 °C, P=900 mbar, 9.09% NaCl*	*DCMD Feed=9.09% NaCl, Tfin=65-65.2 °C Tpin=25°C*	*[2]*
PVDF	*83.4±3.66*	*-*	*-*	*DCMD Feed=3.5% NaCl solution, Tfin=80 °C, Tpin=17±0.5°C*	*[3]*
PVDF–PTFEPVDF–PTFE	*40.4*	*-*	*-*	*DCMD, 3.5% NaCl solution, Tfin=80±0.5 °C, Tpin=17.5±0.5°C*	*[4]*
PVDF-Clay nanocomposite	*~5.7*	*-*	*-*	*DCMD, 3.5% NaCl solution, Tfin=80 °C Tpin=17±2 °C*	*[5]*
PVDF-FS		*1.39*	*Tfin=25 °C, P=9.33-30 mbar*		*[6]*
PVDF-HF		*0.5*	*Tfin=50 °C, P=16.7mbar*		*[7]*
PVDF-HF		*18.5*	*Tfin=50 °C, P=20mbar*		*[8]*
PVDF	*21.9*	*50*	*50 °C, P=40 mbar*	*Distilled water, Tfin=70°C, TPin=25 °C*	*Current study*

[1] Fan et al, Chem. Eng. Sc., 79 (2012) 94–102
[2] Tang et al, Desalination 287 (2012) 326–339
[3] Edwie et al, Chemical Engineering Science 68 (2012) 567–57
[4] Chung et al, Separation and Purification Technology 66 (2009) 229–236
[5] Prince et al, Journal of Membrane Science 397–398 (2012) 80–86
[6] Khayet and Matsuura, Industrial & Engineering Chem-istry Research 40 (2001) 5710–5718.
[7] Khayet et al, Journal of Membrane Science 238 (2004) 199–211
[8] Simone et al, Journal of Membrane Science 364 (2010) 219-232, doi:10.1016/j.memsci.2010.08.013

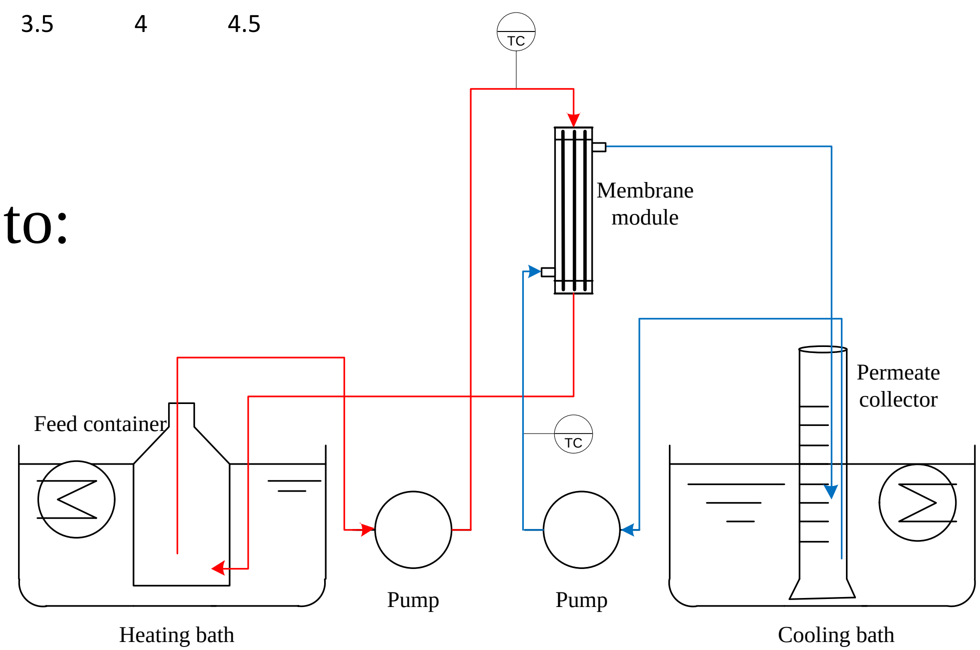
Comparison of M1 and M3



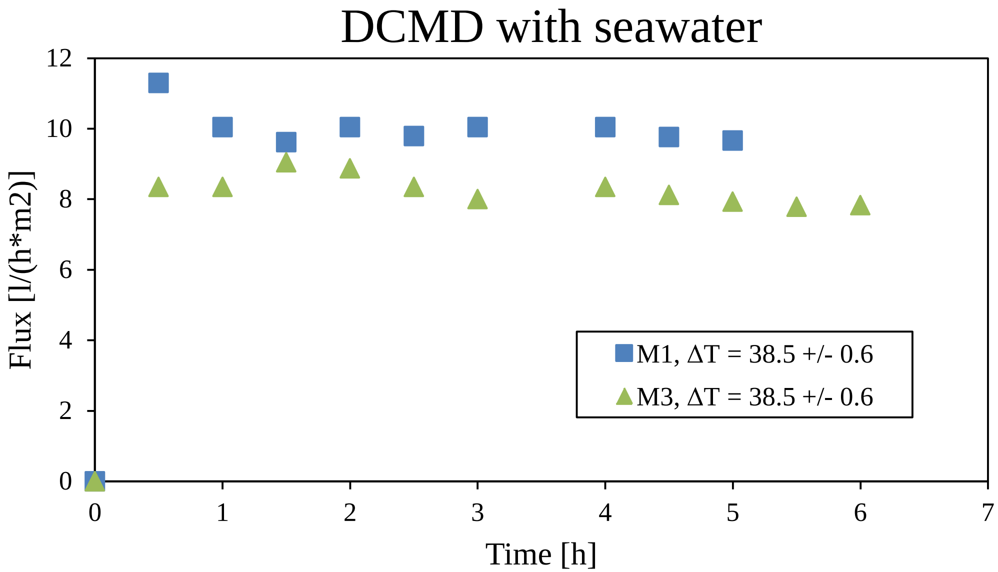
DCMD performance with distilled water as feed.

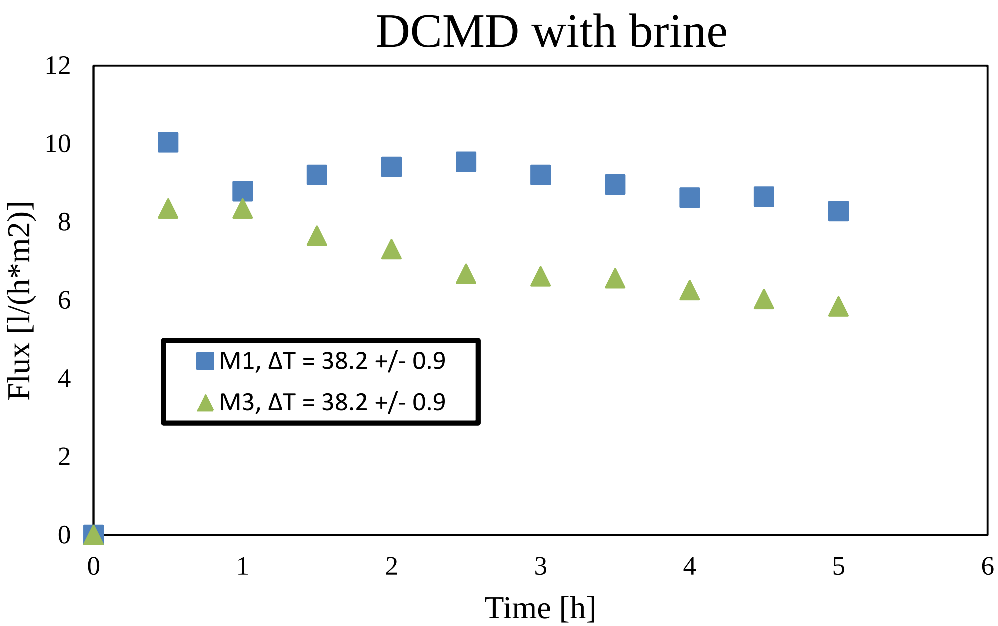
M3 shows the higher flux due to:

- Lower thickness
- Larger pore size
- Higher porosity

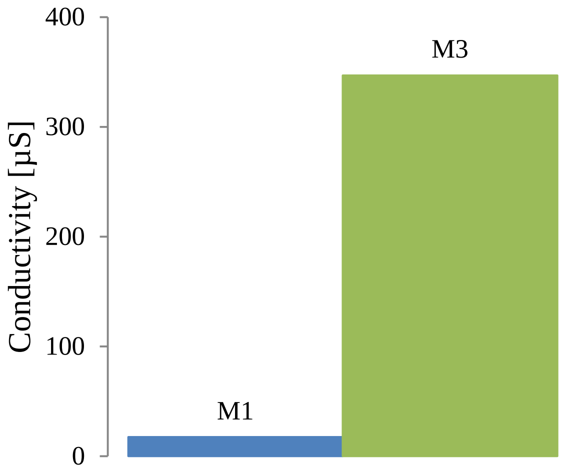


Comparison of M1 and M3





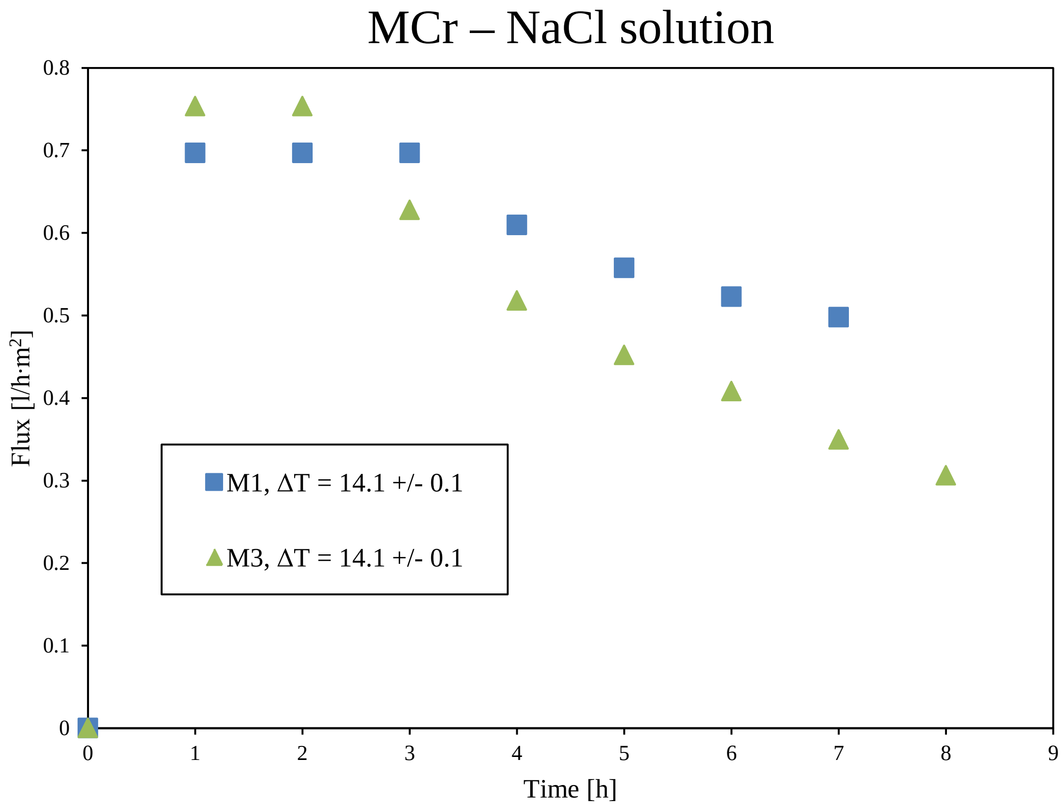
Composition	Seawater [ppm]	Brine [ppm]
Na^+	12500	26478
Mg^{2+}	1520	3101
Ca^{2+}	490	20
Cl^-	22300	45500
SO^{4-}	3189	6507
HCO_3^-	150	107

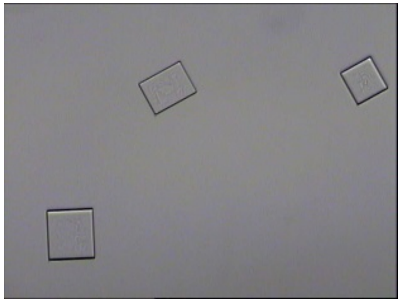


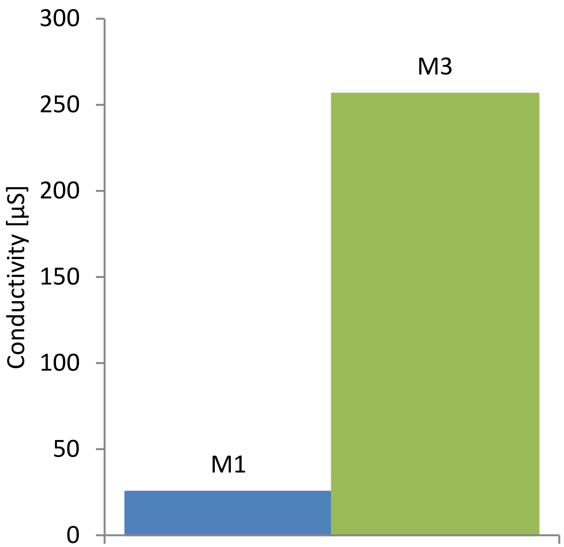
Comparison of M1 and M3

Opposite flux behavior of the membrane performance is observed when seawater and concentrated solutions are used.

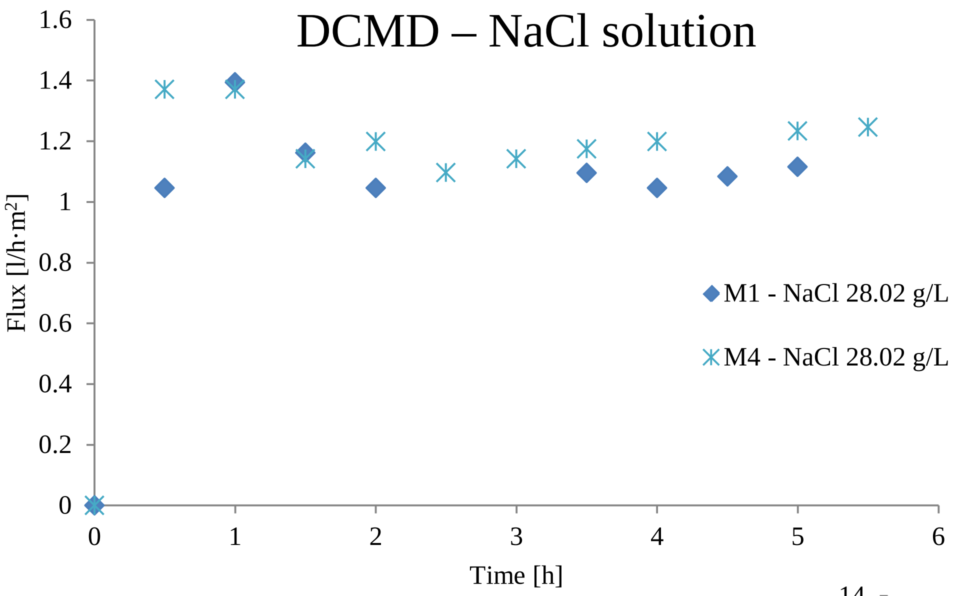
Wetting probability of M3 is higher than M1





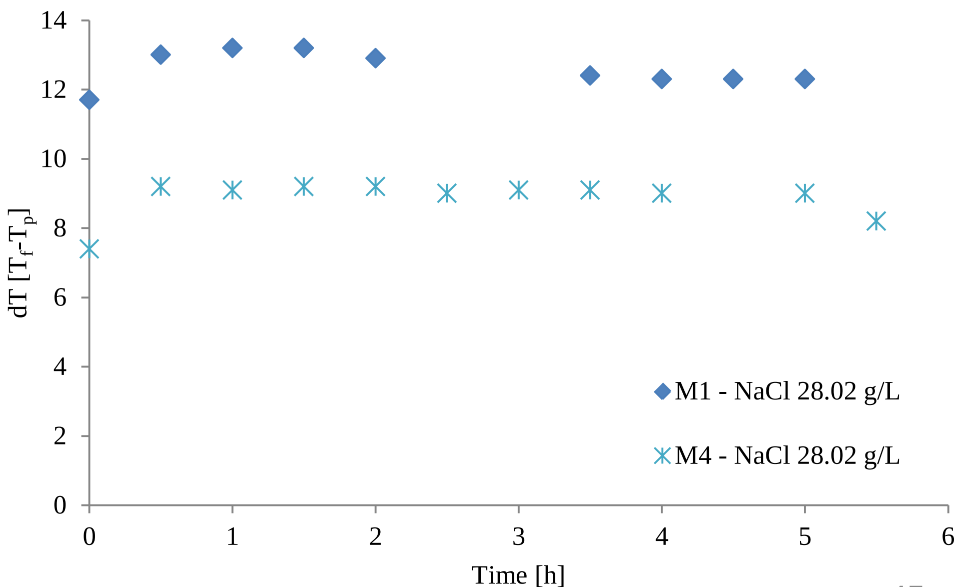


Comparison of M1 and M4 – NaCl (28.02 g/L)

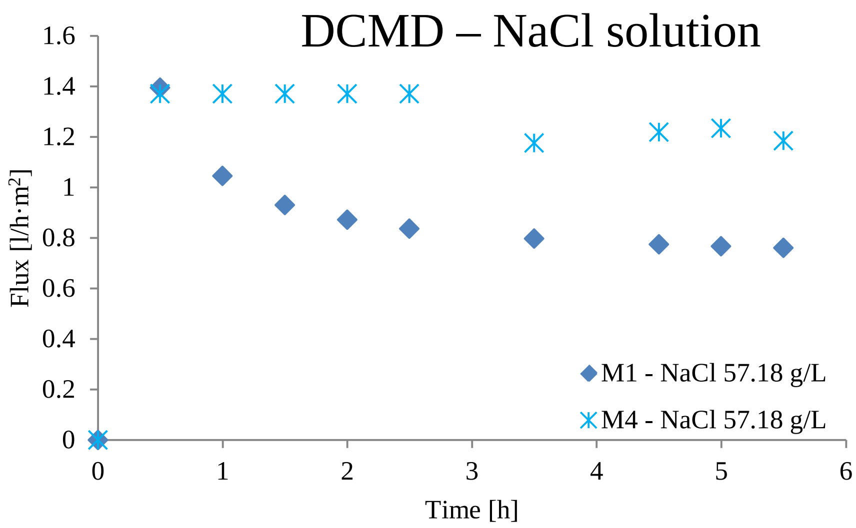


	Feed in shell side	
	Flow rate [ml/min]	Temperature [°C]
Retentate	100	36.1 +/- 1.4
Permeate	20	24.7 +/- 2.0

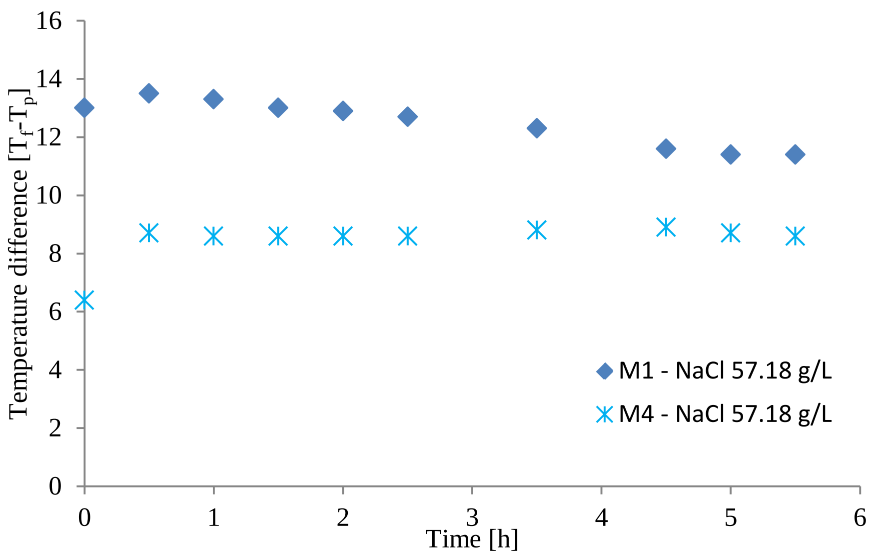
Despite the higher driving force for M1 a tendency towards **higher trans-membrane flux of M4** is observed.



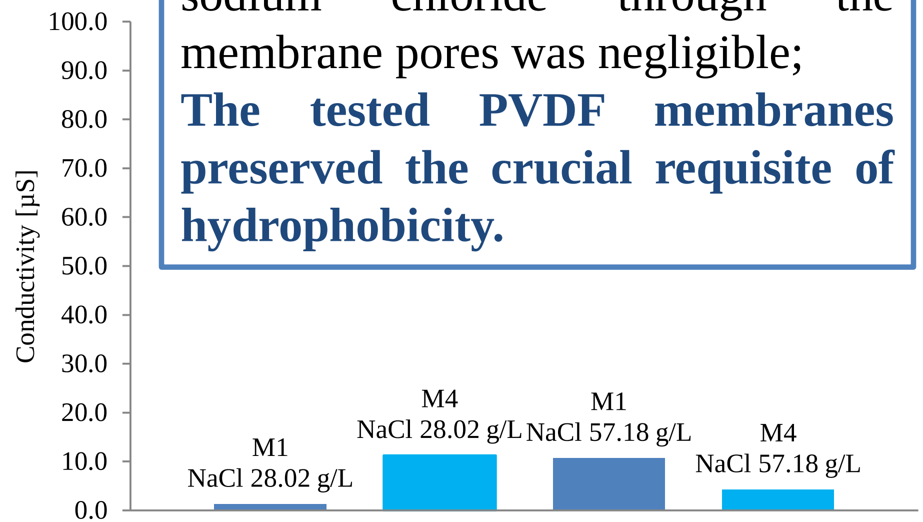
Comparison of M1 and M4 – NaCl (57.18 g/L)



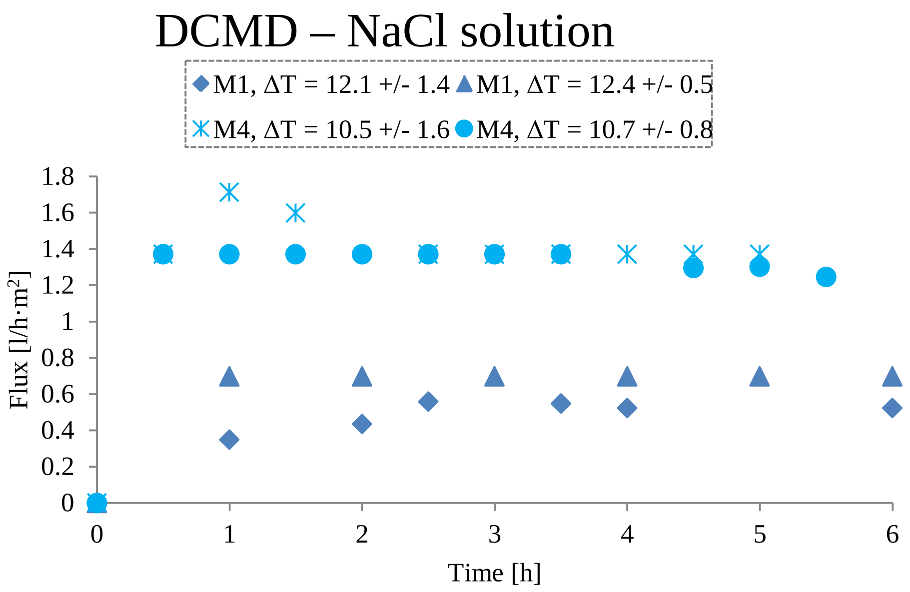
Both at low and high NaCl concentration, the higher flux is achieved with membrane M4 despite the lower driving force.

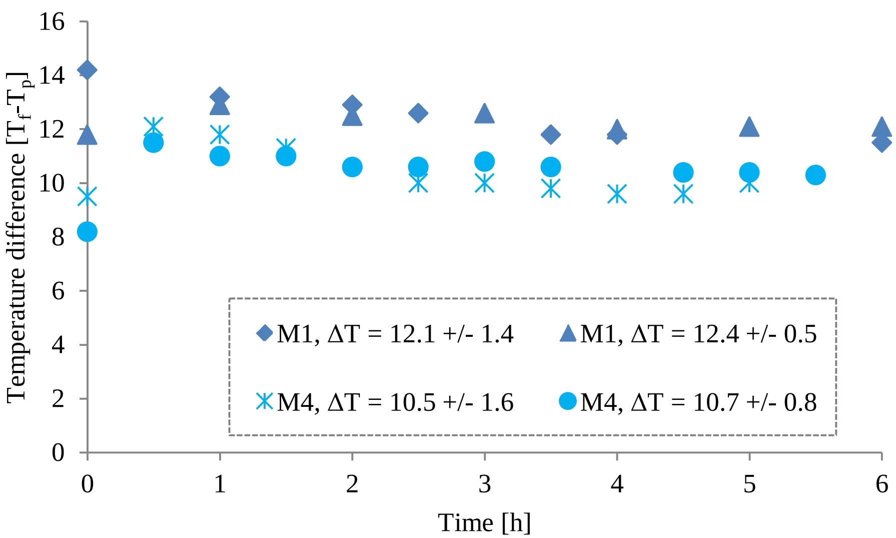


Conductivity measurements carried out on samples of solutions taken out from the distillate tank demonstrated that the infiltration of sodium chloride through the membrane pores was negligible; **The tested PVDF membranes preserved the crucial requisite of hydrophobicity.**

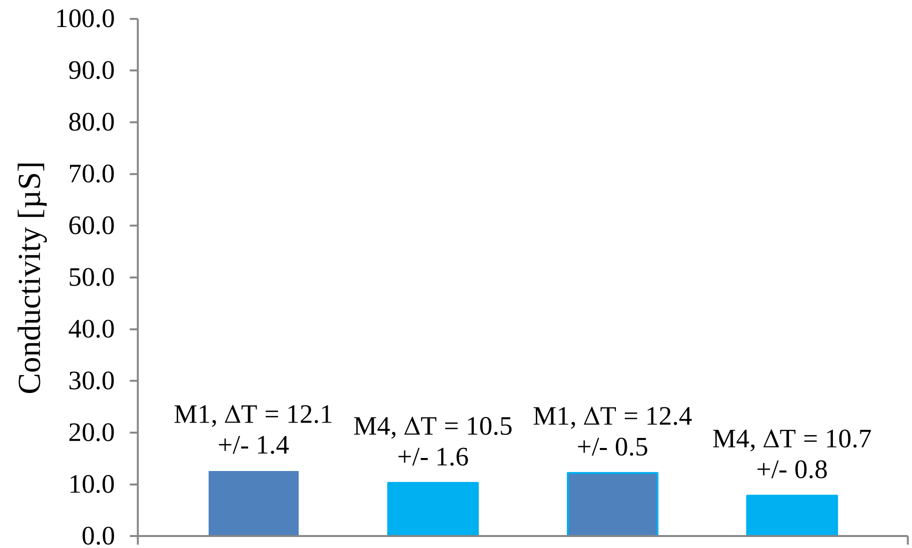


Comparison of M1 and M4 – Seawater and Brine



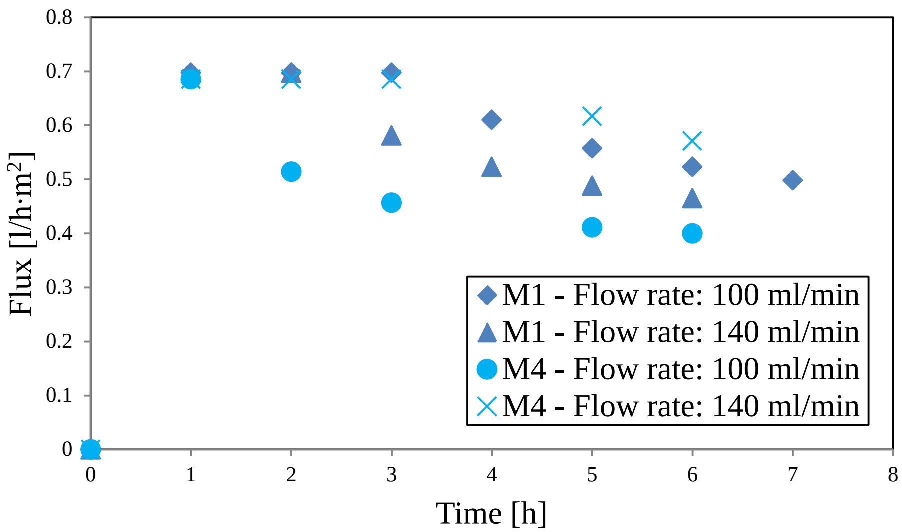


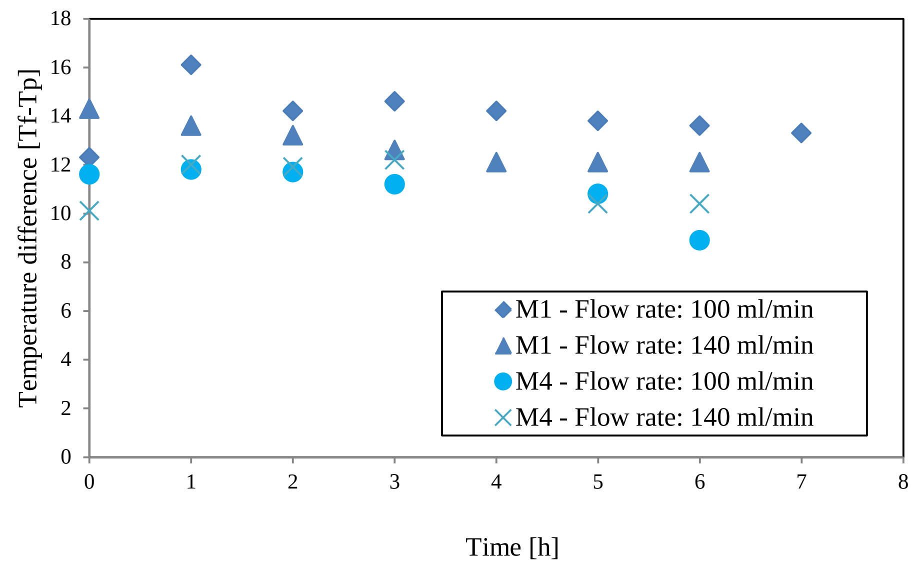
Membrane M4 showed an higher flux with respect to M1 also in the case in which seawater and/or brine are used as feed solutions despite the lower driving force.



Conductivity measurements of the permeates demonstrated that membrane hydrophobicity is preserved in these tests too.

Comparison of M1 and M4 - Crystallization of NaCl



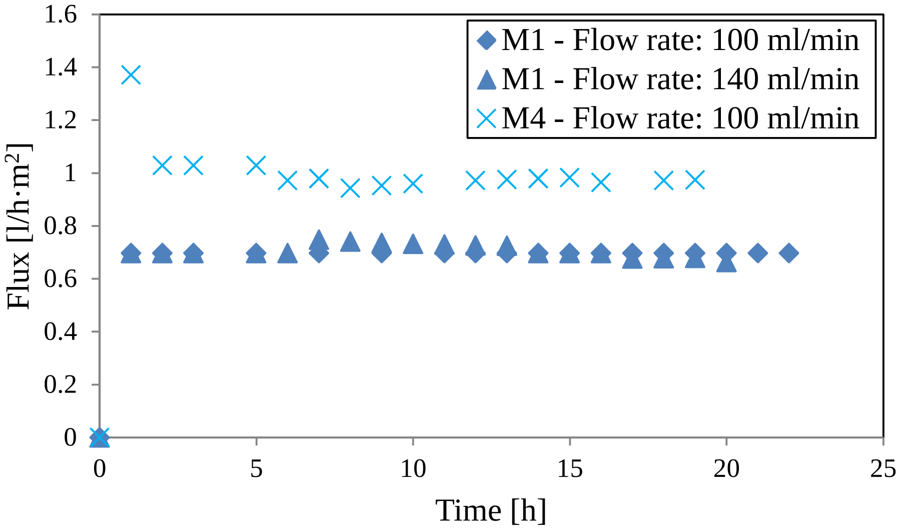


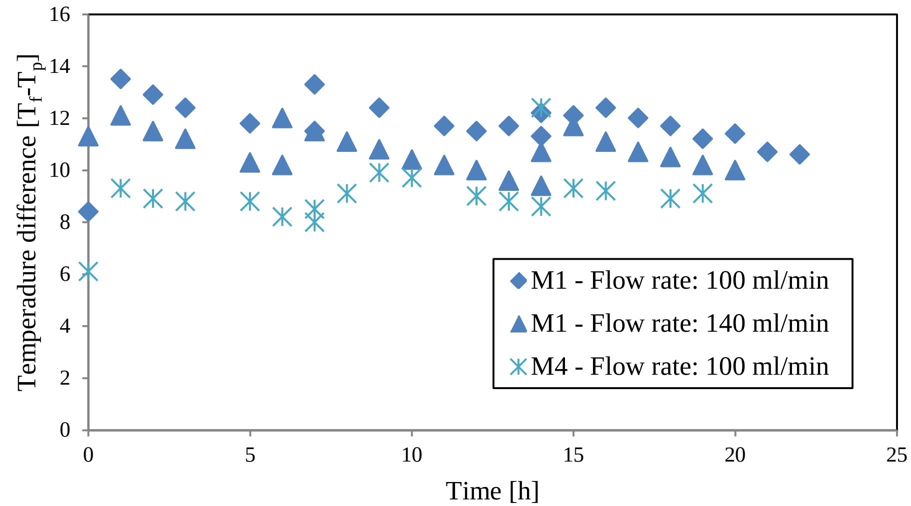
Characteristics of the obtained NaCl crystals by utilizing membrane M4

Retentate flow rate	Time for crystals sample taking [min]		
	Sample 1	Sample 2	Sample 3
100 ml/min	300	330	360
140 ml/min	300	330	360

Retentate flow rate	Mean diameter [µm]			Growth rate [µm/min]		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
100 ml/min	39.40	34.38	24.46	0.1056	0.1270	0.05065
140 ml/min	23.24	25.23	35.41	0.04118	0.04892	0.08062

Comparison of M1 and M4 - Crystallization of Epsomite





Characteristics of the obtained Epsomite crystals by utilizing membrane M1

Retentate flow rate	Time for crystals sample taking [h]		
	Sample 1	Sample 2	Sample 3
100 ml/min	21	21.5	22
140 ml/min	19	19,5	20

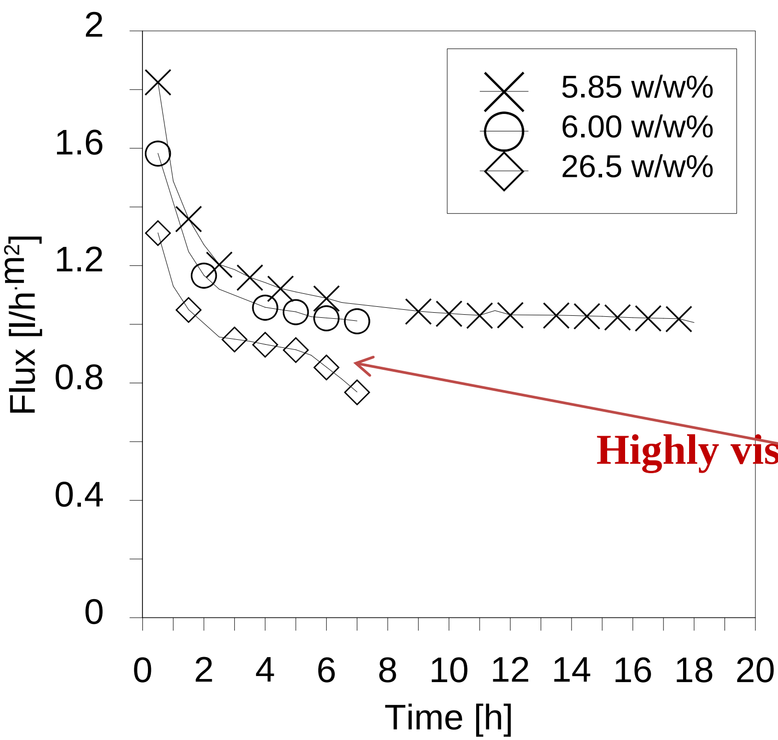
Retentate flow rate	Mean diameter [µm]			Coefficient of Variation [%]			Growth rate [µm/min]		
	Sample 1	2	3	Sample 1	2	3	Sample 1	2	3
100 ml/min	367.2	330.8	361.5	33.58	69.70	41.44	0.1111	0.1109	0.09752
140 ml/min	589.2	541.1	598.4	40.95	48.66	30.52	0.3576	0.4086	0.4478

Na_2SO_4 experiments (Single Salt)

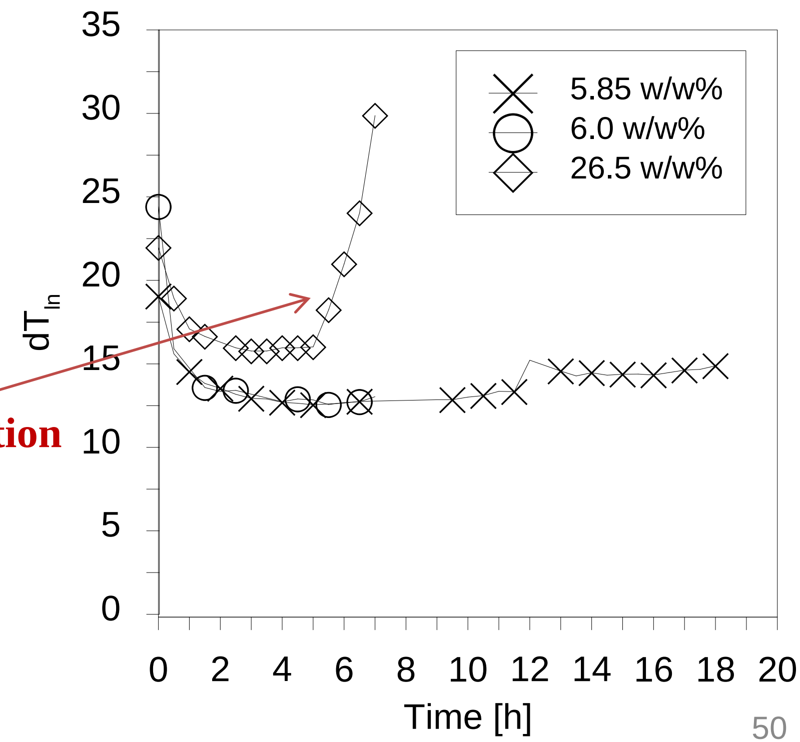
Initial concentration [w/w%]	Initial volume [L]	Nucleation time [h]
5.85	12	88
6.00	11	80.5
26.5	2.5	9.5

Sodium sulfate precipitation occurs at a weight percent of 37.9 w/w%.

$$\Delta T_{\ln} = \frac{(T_{feed,in} - T_{distillate,out}) - (T_{feed,out} - T_{distillate,in})}{\ln\left(\frac{T_{feed,in} - T_{distillate,out}}{T_{feed,out} - T_{distillate,in}}\right)}$$

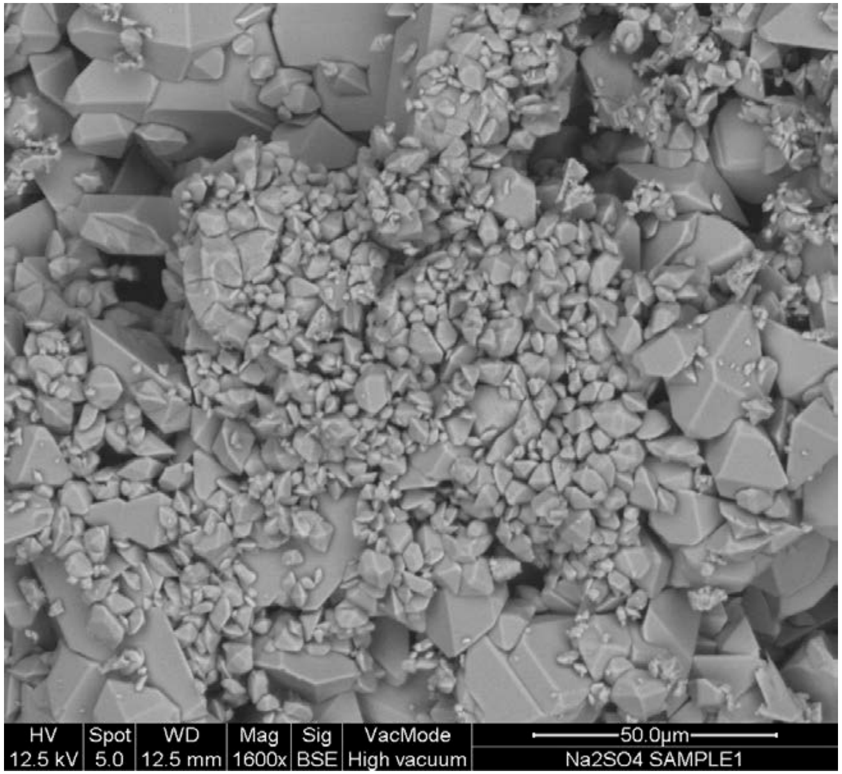


Highly viscous solution

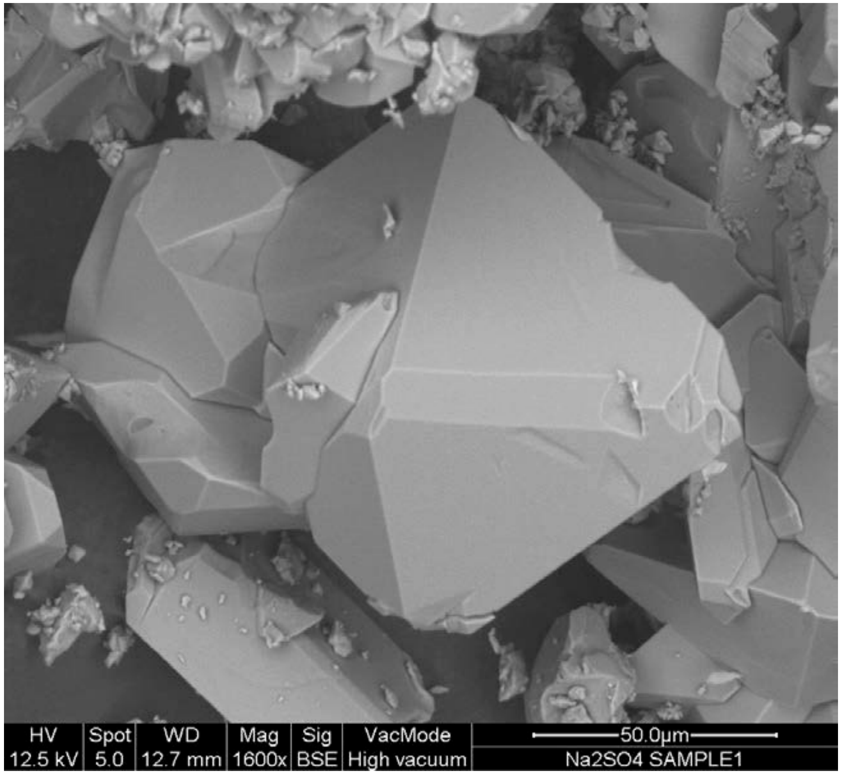


SEM images of Na_2SO_4

Crystals obtained by Membrane Crystallization.



Example of area.

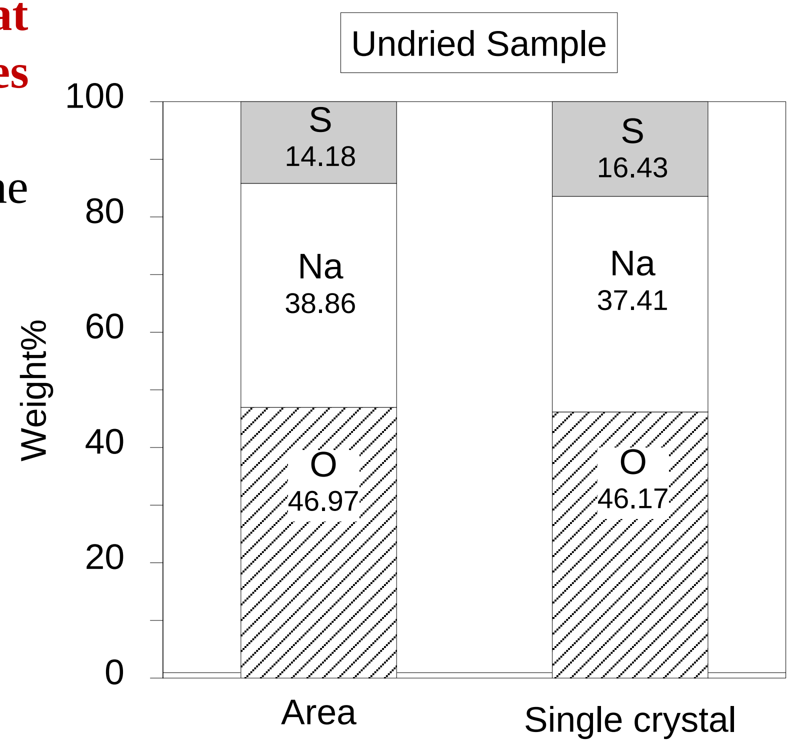


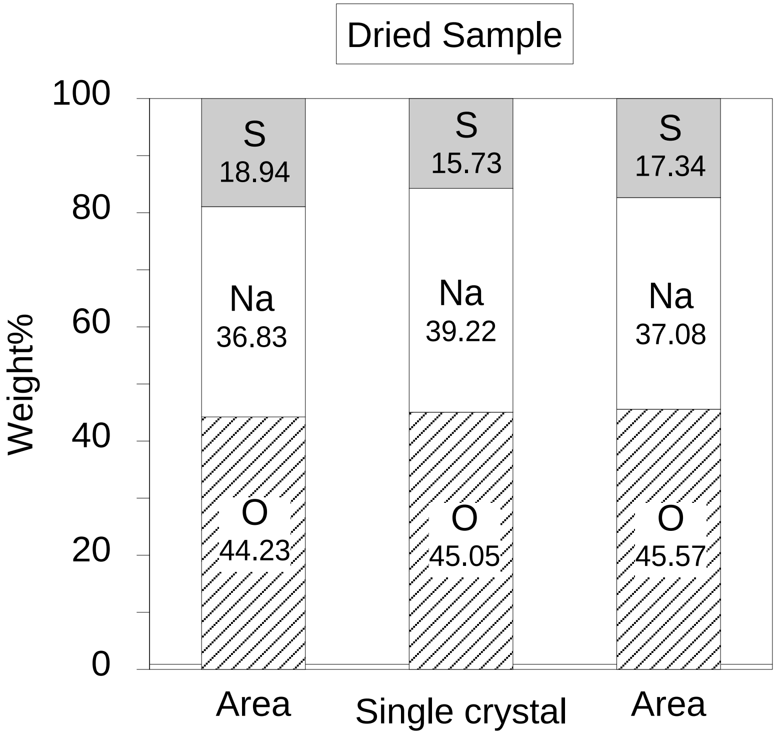
Example of single crystal.

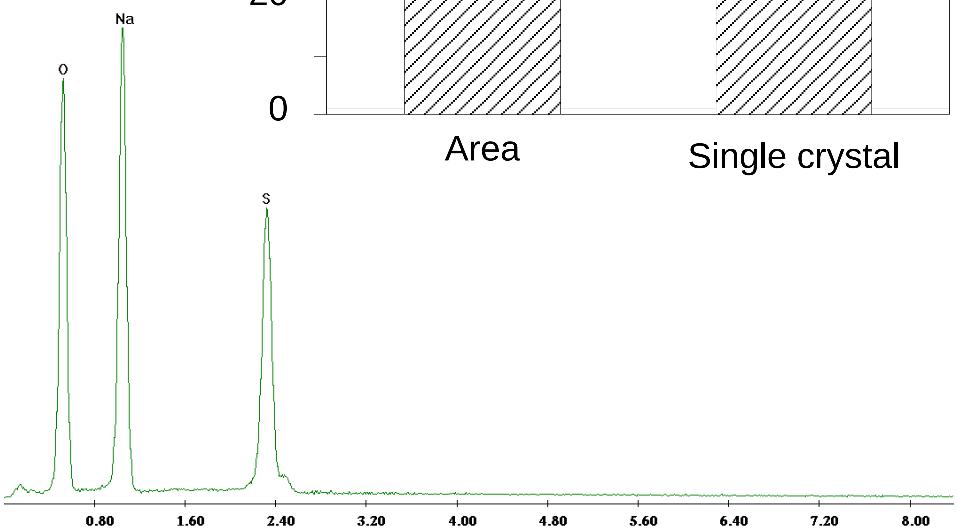
EDX analysis of Na_2SO_4

The weight % of the different ions indicates that anhydrous Na_2SO_4 (Thenardite) precipitates both from the dried and undried samples.

The EDX spectra are all looking similar due to the single salt solution.



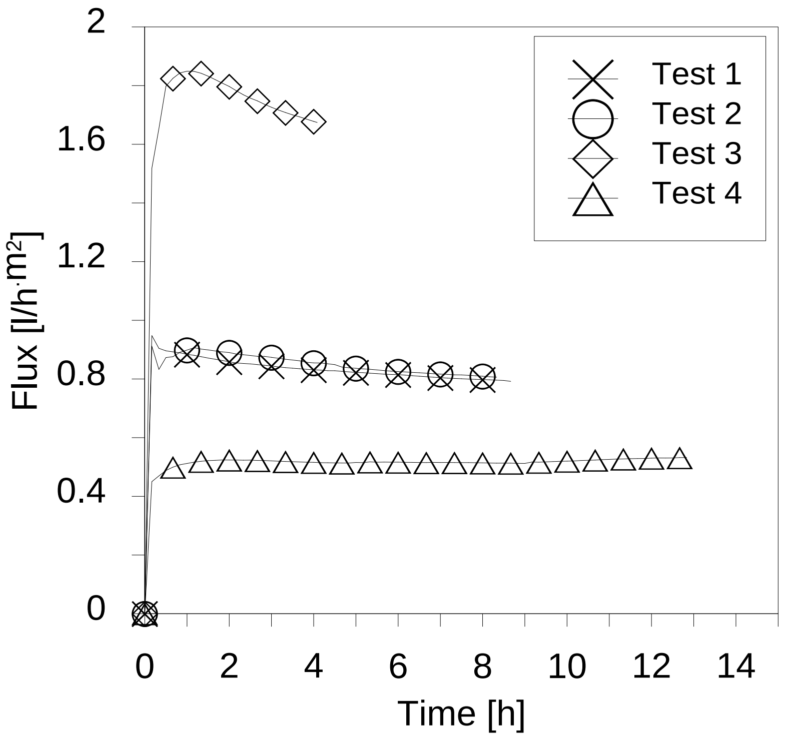


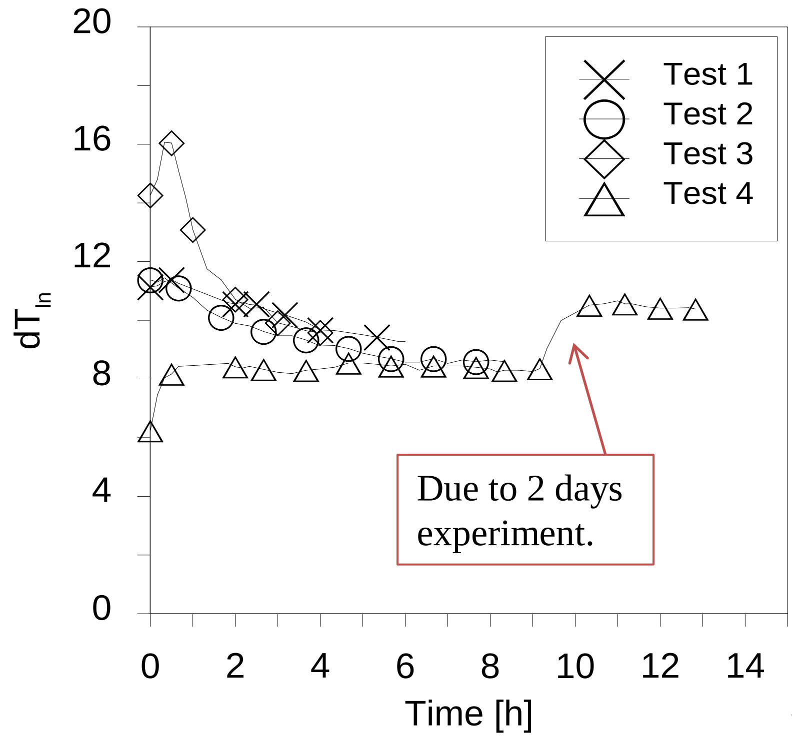


DCMD performance

Experiment	Flow rate [l/h]		Temperature inlet [°C]	
	Feed	Distillate	Feed	Distillate
Test 1	100	100	37.8 +/- 0.3	24.1 +/- 1.8
Test 2	200	100	38.3 +/- 0.5	27 +/- 2.9
Test 3	200	100	50.9 +/- 0.6	35.8 +/- 6.3
Test 4	200	100	31.3 +/- 0.1	19.9 +/- 1.6

$$\Delta T_{\ln} = \frac{(T_{feed,in} - T_{distillate,out}) - (T_{feed,out} - T_{distillate,in})}{\ln\left(\frac{T_{feed,in} - T_{distillate,out}}{T_{feed,out} - T_{distillate,in}}\right)}$$





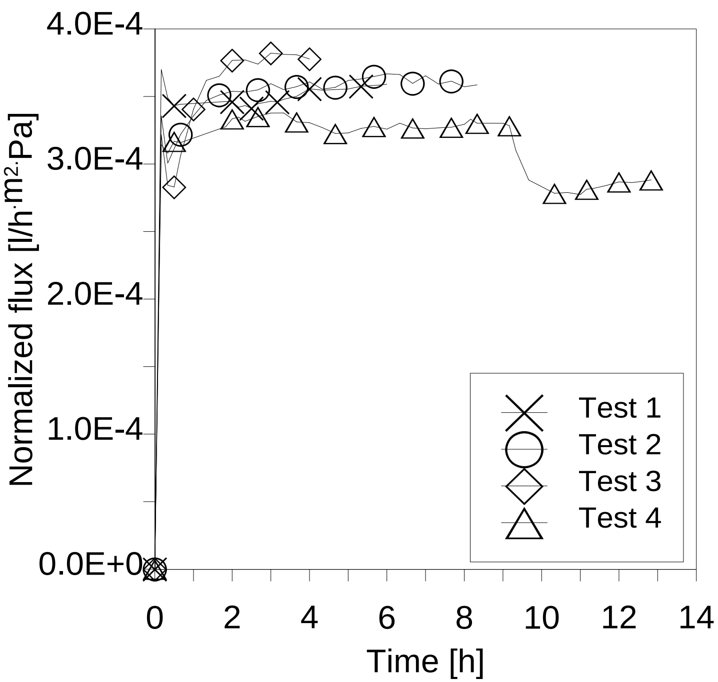
DCMD performance

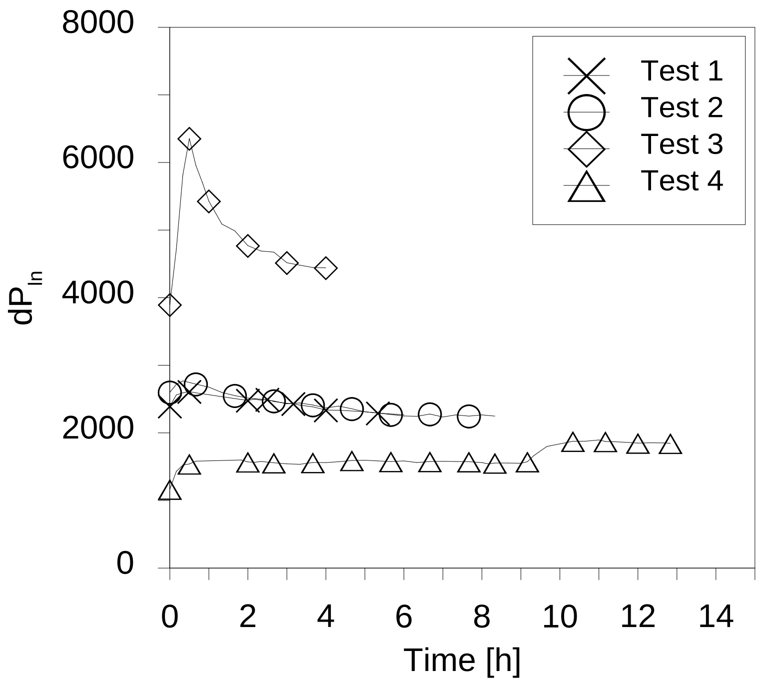
The trans-membrane flux has been normalized in order to neglet the difference in driving force (vapor pressure difference).

Test 3 shows a better normalized flux possible due to lower effect of temperature polarization compared to the other tests.

$$Normalized\ flux = \frac{Trans-membrane\ flux}{Driving\ force\ (\Delta P_{\ln})}$$

$$\Delta P_{\ln} = \frac{(P_{feed,in} - P_{distillate,out}) - (P_{feed,out} - P_{distillate,in})}{\ln\left(\frac{P_{feed,in} - P_{distillate,out}}{P_{feed,out} - P_{distillate,in}}\right)}$$

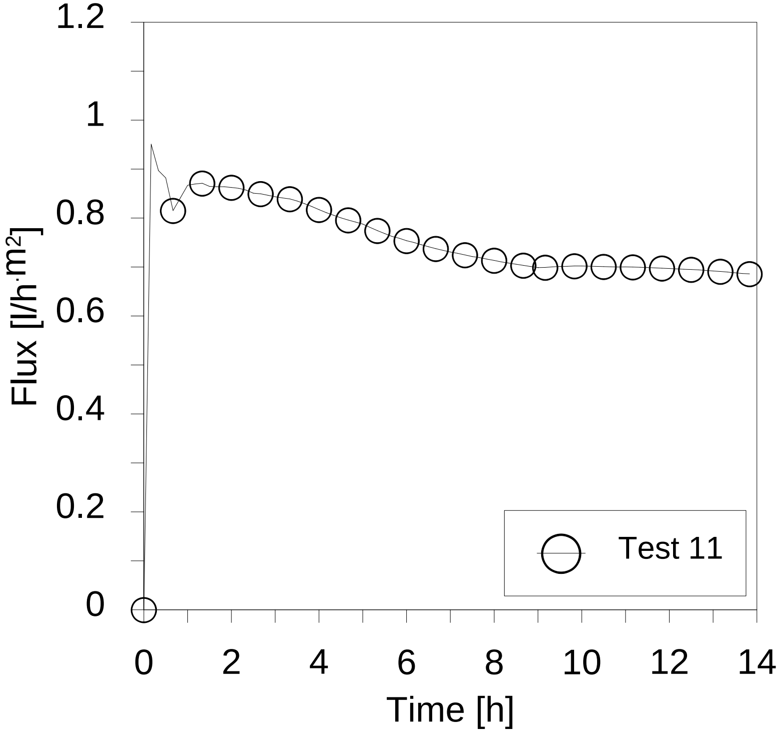




MCr performance

During the crystallization test a temperature equal to 35°C has been maintained in the crystallization tank in order to control:

1. the crystallization process,
2. the Na_2SO_4 solubility and
3. the formation of anhydrous Na_2SO_4.

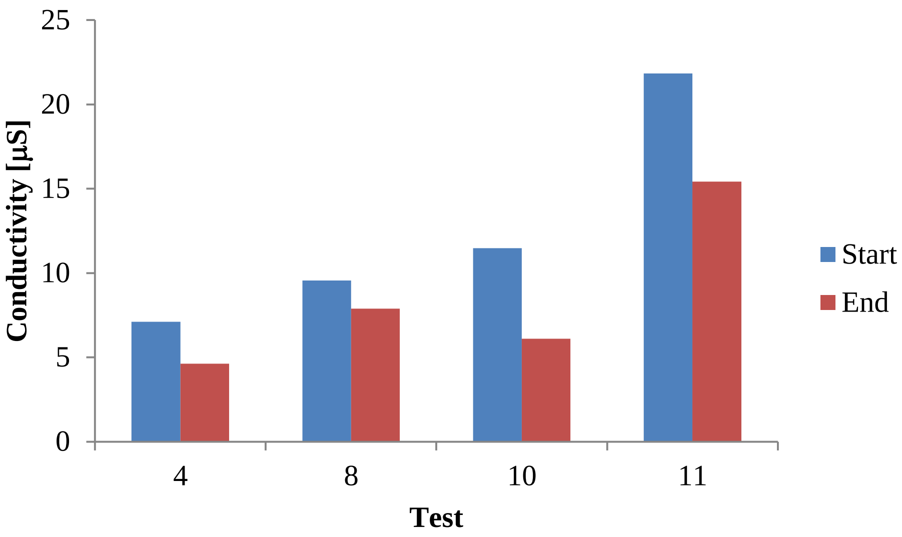


Experiment	Flow rate [l/h]		Temperature inlet [°C]	
	Feed	Distillate	Feed	Distillate
Test 11	200	100	36.8 +/- 1.8	22.5 +/- 2.0

The trans-membrane flux is slightly decreasing during the experiment due to the increase in concentration and, as a consequence, to the decrease of vapor pressure and driving force.

Permeate Conductivity

The conductivity of permeate has been measured frequently during the tests in order to detect eventually wetting of the membrane. In all the carried out tests permeate conductivity at the end of each test was lower with respect to its value at the start of the experiment.



This demonstrated that the infiltration of feed solution through the membrane pores was negligible;

The polypropylene membranes preserved the crucial requisite of hydrophobicity, at least during the operative time of these experiments.

Concluding remarks

- The membranes produced are very interesting and competitive for applications in MD and MCr compared to commercial membranes.

- Attention towards the problems of membrane wetting and fouling and to the necessary preventive measures for avoiding these dangerous phenomena.

- The overall results show that MD is a promising methodology for separation, purification and crystallization and therefor for the continued crystallization of salts.

- Due to the advance of low convective flux and small concentration profile in MD it is more difficult to accumulate materials on the membrane surface compared to e.g. NF.

Thank You

SEAWATER AND BRACKISH WATER DESALINATION TODAY: STATE OF THE ART

Enrico Drioli[1,2,3,4]

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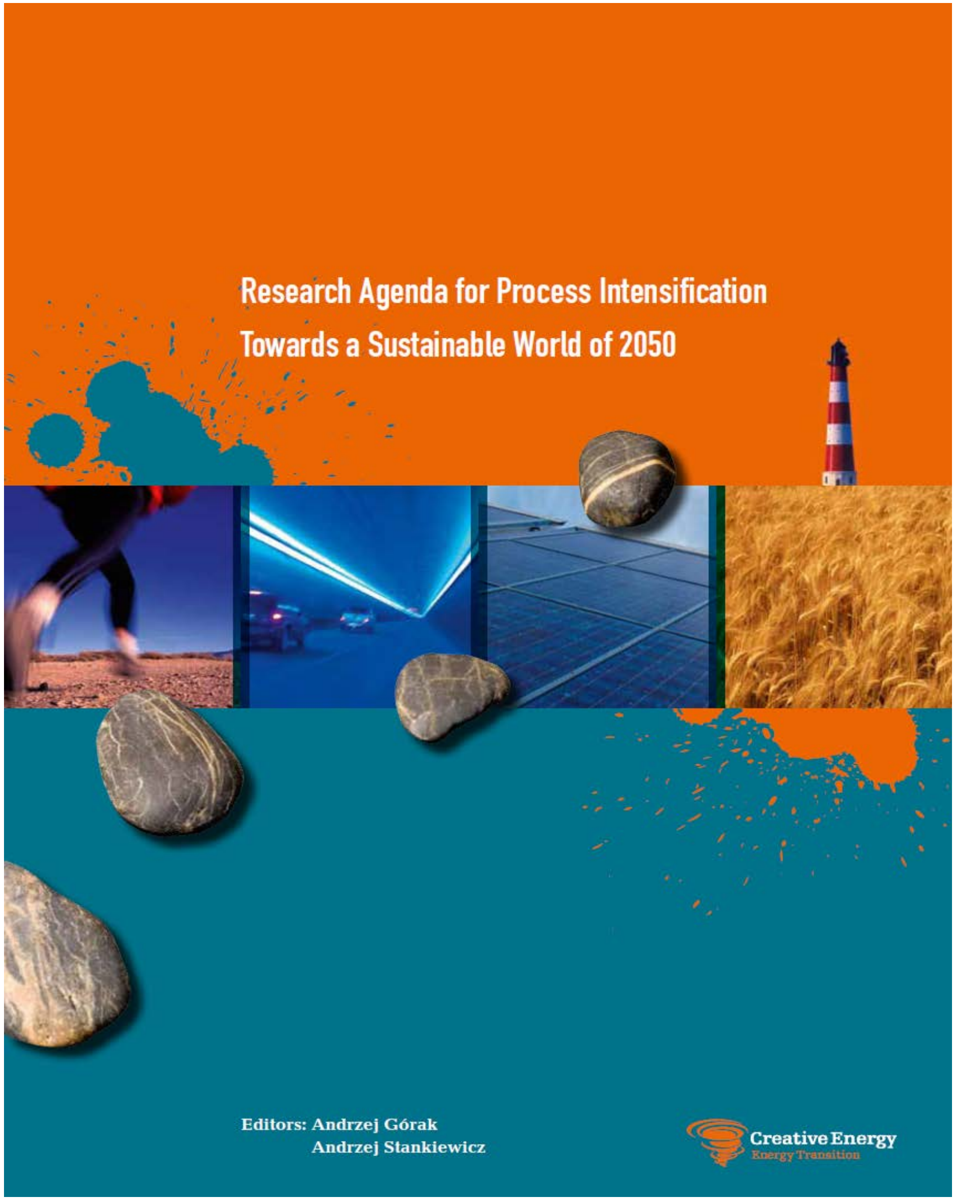
[2]Department of Chemical Engineering and Materials, University of Calabria, via P. Bucci, Rende (CS)

[3]WCU Energy Department, Hanyang University, Seoul 133-791 S. Korea

[4] Distinguished Adjunct Professor, Center of Excellence in Desalination Technology, King Abdulaziz University, Jeddah Saudi Arabia

KACST, February 2014

Sustainable growth - how to answer?



Process Intensification Strategy

- Less Energy and Raw Materials
- Increase Effciency
- Low Cost
- Small Footprints
- High Safety
- Low Emission
- Short way to the market
- Automatization

PRINCIPLES/OBJECTIVES OF PROCESS INTENSIFICATION

Principle (objective)	Focus issues related to the principle
Maximize the effectiveness of intra- and intermolecular events	Control of spatial orientation and energy in molecular collisions
Give each molecule the same processing experience	Spatial uniformity, no unwanted (e.g. temperature) gradients
Optimize the driving forces at every scale and maximize the specific surface area to which these forces apply	Transport across interfaces
Maximize the synergistic effects from partial processes	Combining functions

PROCESS INTENSIFICATION: STRATEGY AIMING TO PRODUCE NOT THE BIGGEST PLANTS BUT THE MOST EFFICIENT PLANTS !

- E. Drioli et al., *Journal of Membrane Science, 380 (2011) 1-8.*
- T. Van Gerven, A. Stankiewicz, *Ind. Eng. Chem. Res*., 48 (2009) 2464-2474.

Redesign of process engineering via:

1) **new molecular separation units**
2) **new catalyst design and chemical reactor**
3) **new unit operations for mass and energy transfer between different phases**

↔

Impact on strategic sectors:

1) **energy/electricity (fuel cells, battery, salinity gradients);**
2) **water and mineral resources (optimization via desalination and water reuse);**
3) **razionalization of industrial productions via integrated industrial production.**

- ✓ **Membrane technologies are providing unprecedented opportunities to develop more cost effective and environmentally acceptable processes.**

- ✓ **Membrane technologies cover all operations, from molecular separations to chemical conversions, energy and mass transfer, energy conversion and in advanced biomedical applications**

- ✓ **Traditional areas like seawater and brackish water desalination, wastewater treatments, fruit juice concentration, biochemical engineering, regenerative medicine, petrochemical industry, pharmaceutical production and gas separation have been substantially modified and innovated with the transfer of membrane engineering principles in these sectors. Practically any industrial sectors can benefit from these operations.**

PIS and membrane technology

Membrane technology interestingly matches with the requirements of PIS.

- **Significant reduction in energy consumption when applied in processes.**
- **Better interactions at molecular level to increase the yield of the process**
- **Reduced equipment size**
- **Enhancement of the process efficiency**
- **Better use of raw material**
- **Recovery and reuse of the useful/harmful components from the effluent streams**
- **Environmental friendly**
- **Safe processes with small foot print**

Membrane Operations

RO desalination system over *10 fold more efficient* than the thermal approach.

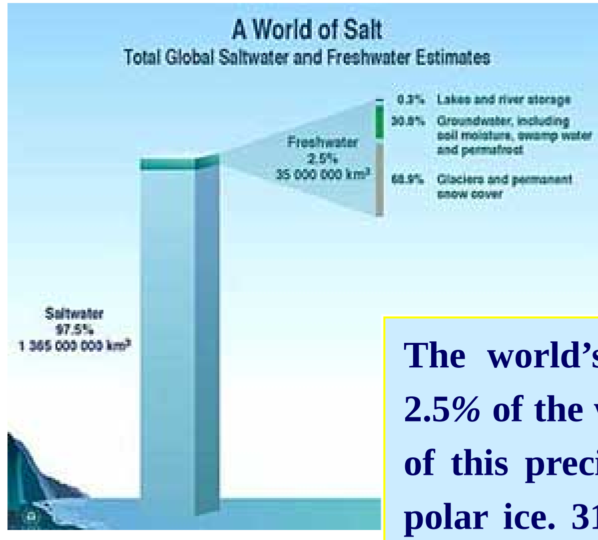
MBR is up to *5 times more compact* than a conventional activated sludge plant.

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!

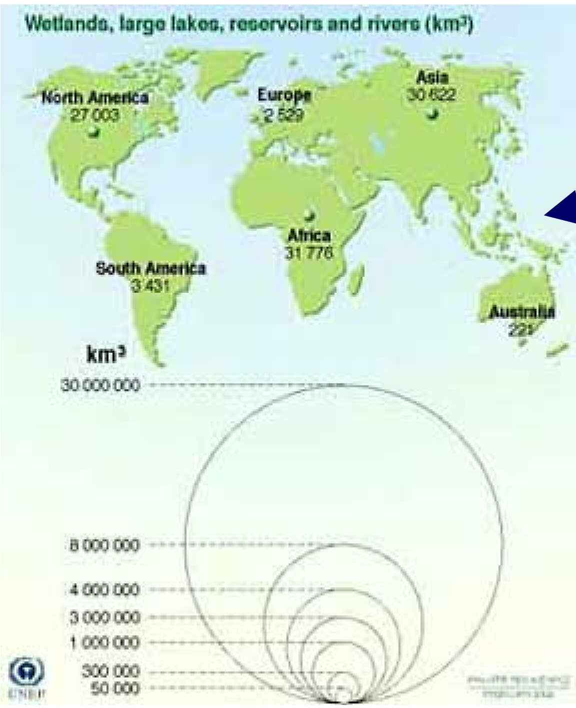
MR conversion much *higher (5 times)* than TR

Membrane processes address the goals of Process Intensification because they have the potential to replace conventional energy-intensive techniques, to accomplish the selective and efficient transport of specific components, and to improve the performance of reactive processes.

Water usage is globally increased by *six* times in the past 100 years and will *double* again by 2050.

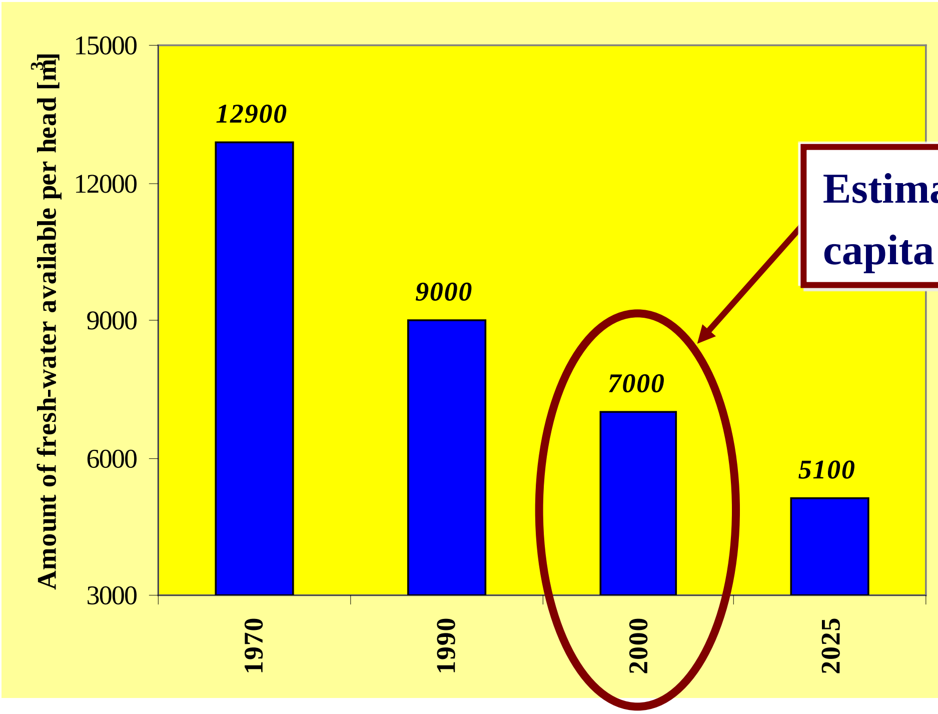


The world's potable water reserve represents 2.5% of the world's total water resources. 68.9% of this precious limited supply is locked in the polar ice. 31.1% can be found as groundwater, lakes, natural reservoirs and rivers.

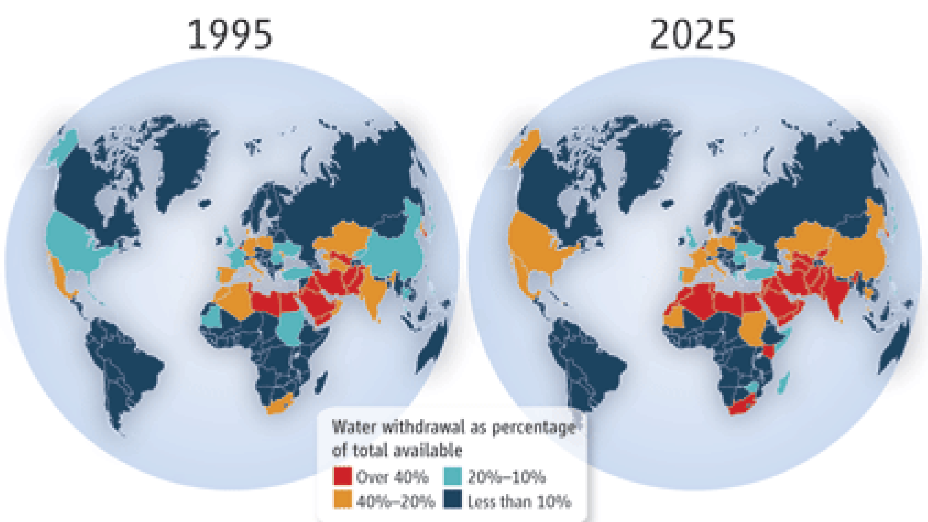


Only 1% of global freshwater (≈0.01% of global waters≈200.000Km³) is available for people and ecosystems.

Source: http://www.greencrossitalia.it



Estimated, but not effective, average per capita water availability.

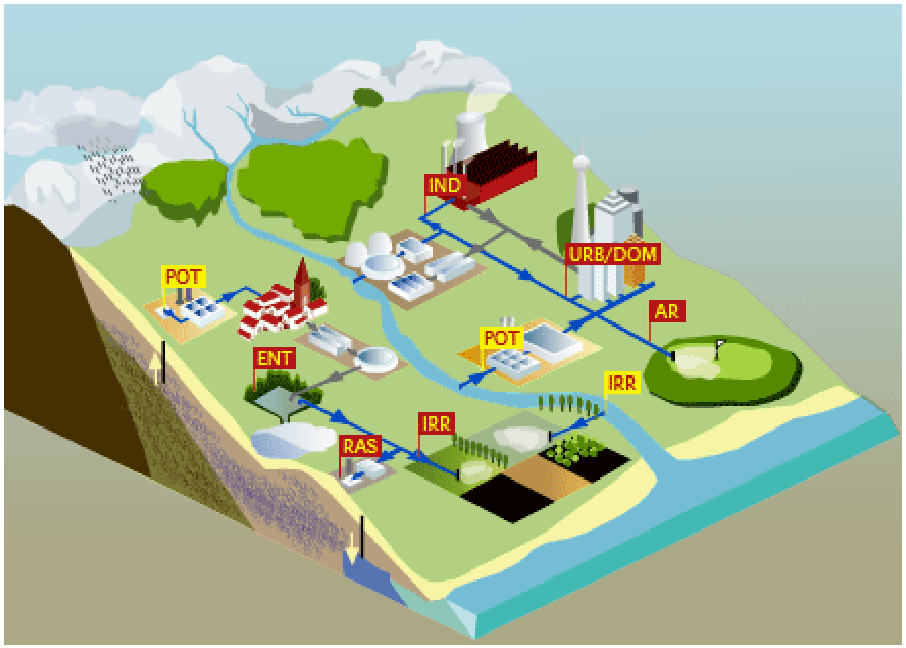


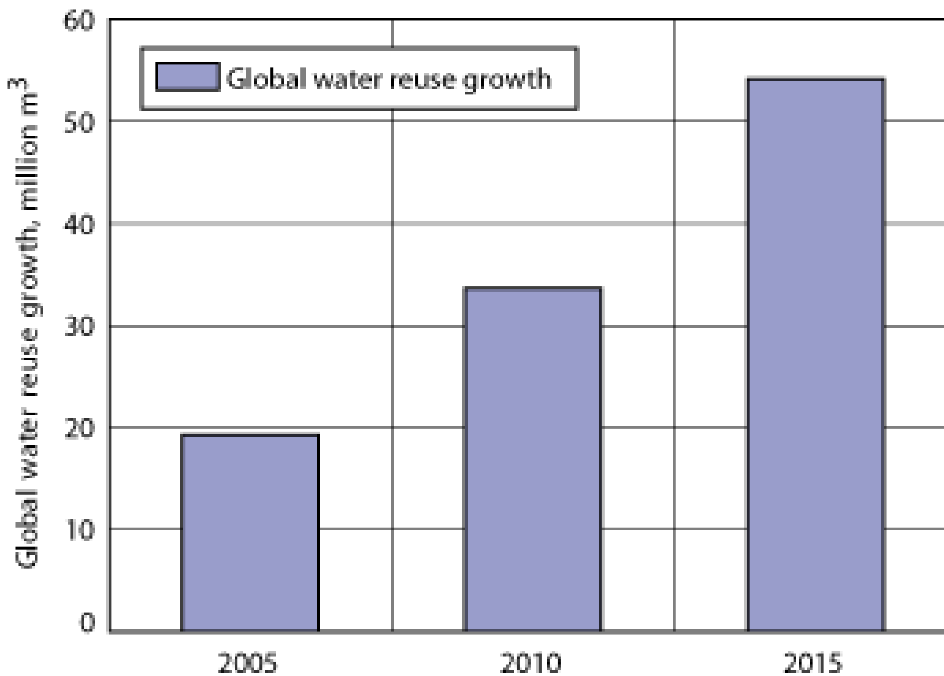
The availability of water might be sufficient for the overall world-wide population.

Nevertheless, the geographic distribution of water sources is not proportional to the resident population. ***Nowadays, 1/3 of the world-wide population live in "Water Stress Countries" and will double by 2025.***

Water reuse trend around the globe

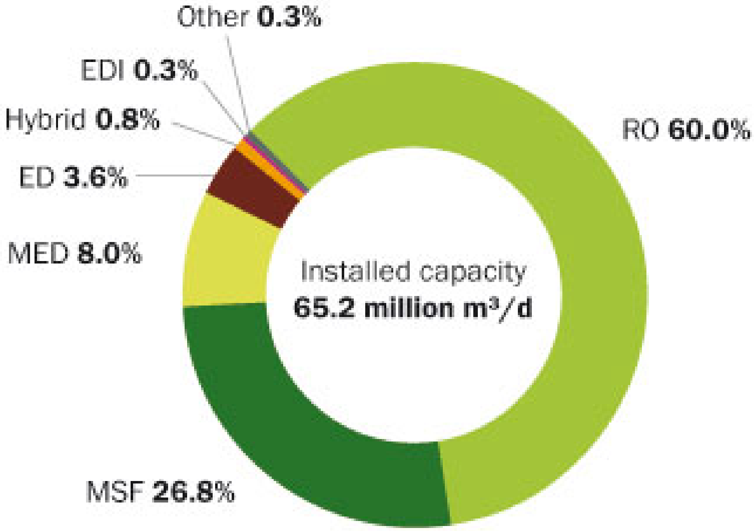
Many parts of the world are facing the problem of water scarcity. The shortage of water can be attributed to various factors including rapidly growing population, contamination of surface and ground, natural uneven distribution of water resources and periodic drought.



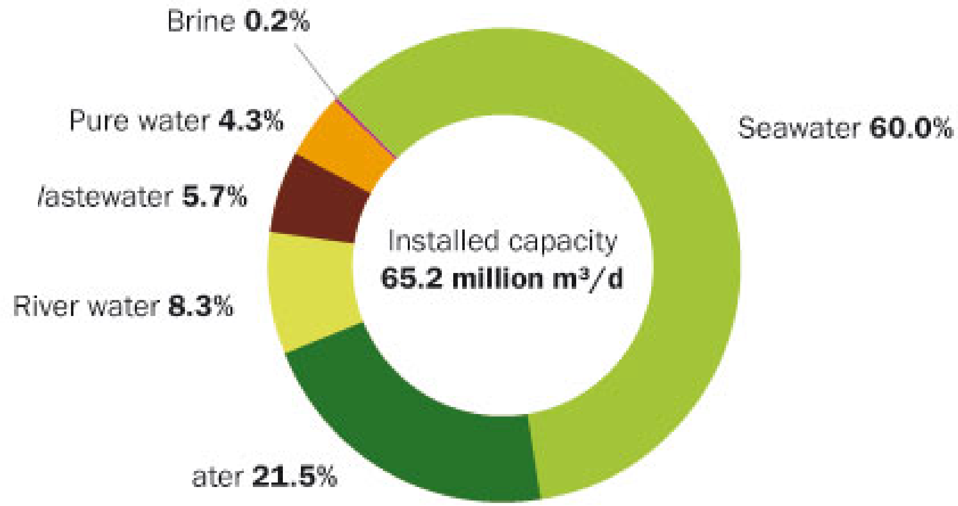


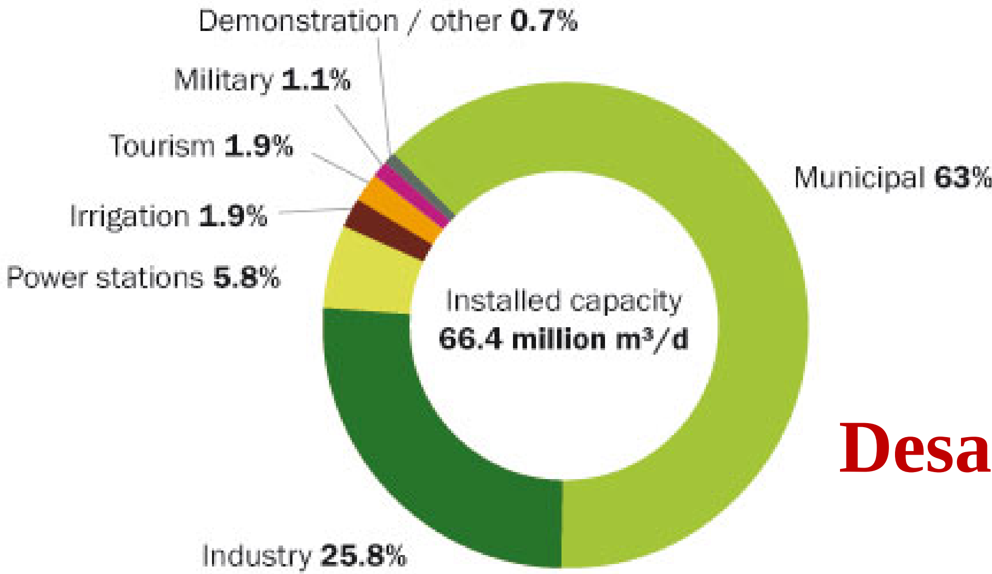
Current estimates clearly indicate the need to reuse the water, not only to save the existing clean water resources but also to keep them safe and clean.

Desalination Technologies



Desalination Sources





Desalination End-products

Desalination plants in Saudi Arabia

Ras al-khair Phase 1

World's largest desalination plant

(Planned to be in operation in 2013)

Multi stage flash (MSF) and Reverse osmosis (RO)

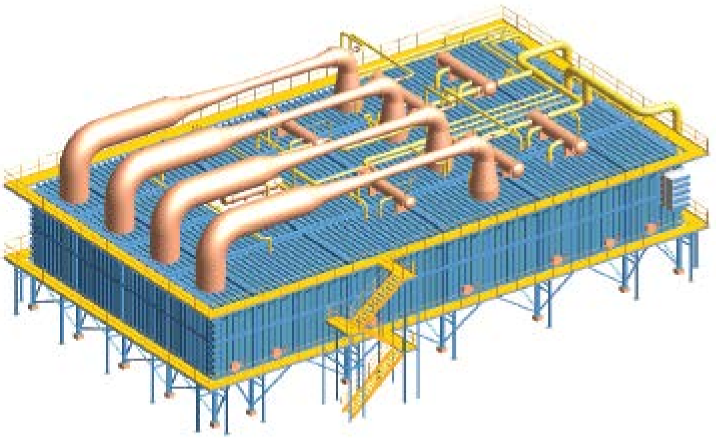
MSF 160 MIGD + RO 68 MIGD

1 MIGD = 4,546 m3/day

http://www.doosan.com/doosanheavybiz/attach_files/services/water/wte_water%20Plants.pdf

Desalination plants in Saudi Arabia

Yanbu Phase 2 Expansion
& **Marafiq Yanbu**



Multi-Effect Distillation (MED)

World's largest MED distiller with capacity of 15 MIGD (Yanbu Ph. 2)

Yanbu phase 3: ~121 MIGD (completion by March 2016)

http://www.doosan.com/doosanheavybiz/attach_files/services/water/wte_water%20Plants.pdf
http://www.desalination.biz/news/news_story.asp?id=6838&title=Doosan+takes+Yanbu+3+MSF+plant+in+Saudi

Desalination plants in Saudi Arabia

Jeddah Phase 3

Reverse osmosis desalination plant

With capacity of 52.8 MIGD

The biggest RO project in Middle East

http://www05.abb.com/global/scot/scot281.nsf/veritydisplay/dd8d615aabeea76ac1257899004c009f /$file/2009_jeddah%20phase%202%20ro%20desal_deabb%201640%2010%20en.pdf

http://www.doosan.com/en/pressRelease.do?cmd=viewPressRelease&no=20081204112043393503
http://www.doosan.com/doosanheavybiz/attach_files/services/water/wte_water%20Plants.pdf

Recent desalination plants in Saudi Arabia

	Method	Capacity [m^3/d]	Year Awarded
Yanbu Ph.2 Expansion	MED	68,190	2011
Marafiq Yanbu	MED	54,550	2011
Ras Al Khair Ph.1	MSF & RO	1,036,490	2010
Rabigh Power No.2	MSF	9,820	2010
Jeddah Ph.3	RO	240,030	2009
Qurayyah Add-on	MSF	6,000	2009
Shuaibah Ph.3 Expansion	RO	150,020	2007
Shuaibah Ph.3	MSF	881,920	2006

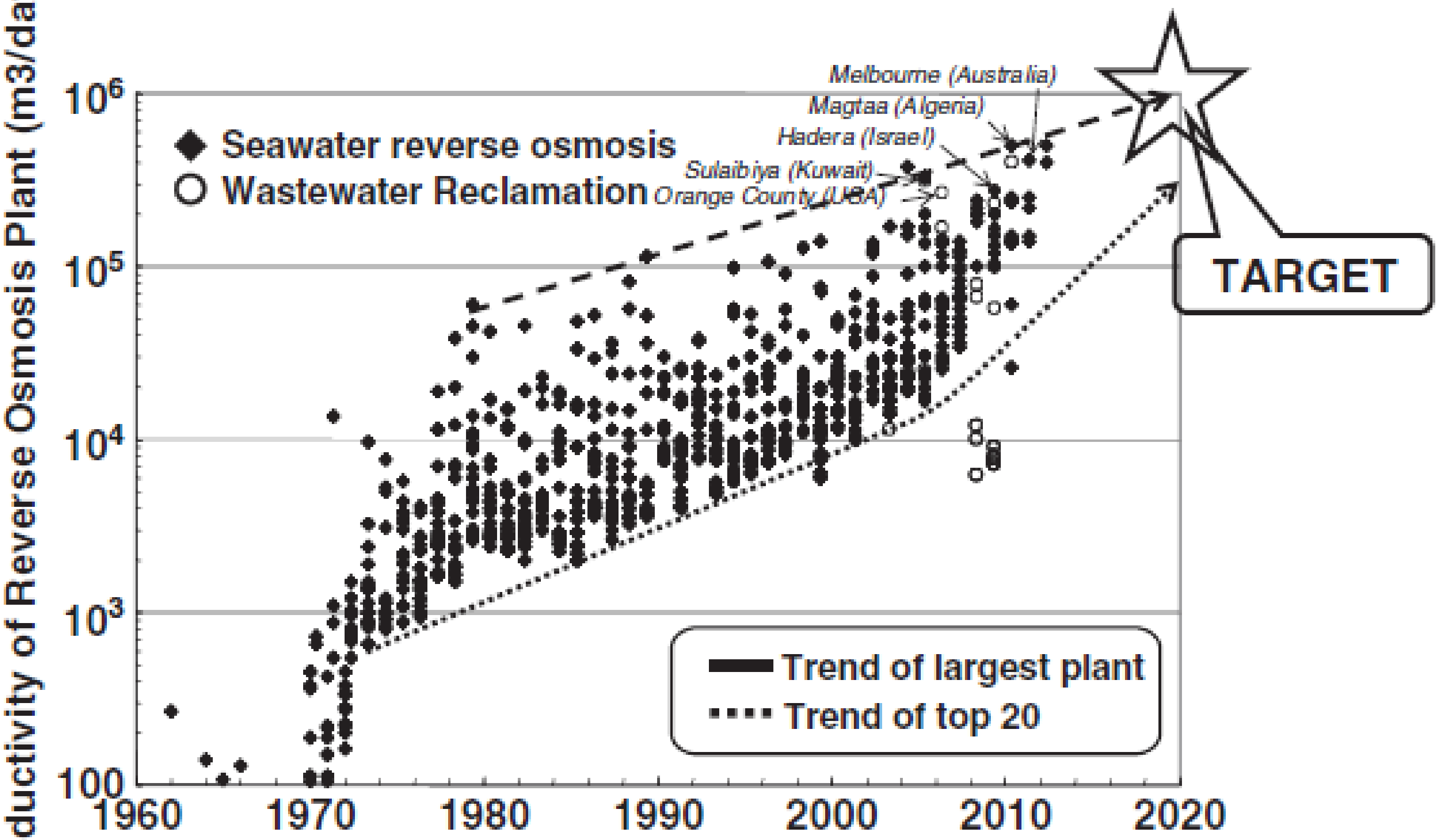
World's largest Desalination plants

Fully operational now

Worlds largest desalinations plants		
	Capacity [m^3/d]	Online date
Sorek, Israel	540,000	3Q 2013
Magtaa, Algeria	500,000	3Q 2013
Hadera, Israel	456,000	2010

www.ide-tech.com
Water Desalination Report – 3 june 2013

Desalination capacity



RO is today the leading desalination technology.
It has overtaken conventional thermal technology such as multi-stage flash (MSF) and it is expected to further consolidate its leadership in the future

M. Kurihara, M. Hanakawa, Desalination 308 (2013), 131-137

✓ ***65.2 million m^3/d:*** **the total capacity of all completed desalination plants (2010)**

✓ ***71.7 million m^3/d:*** **the cumulative contracted capacity of desalination plants around the world (2010)**

✓ ***over 15000:*** **the number of desalination facilities around the world (2010)**

✓ ***60:*** **the percentage of desalination plants using** ***reverse osmosis technology***

✓ ***34.8:*** **the percentage of desalination plants using** ***MSF or MED technology***

✓ ***23:*** **the percentage of RO water price cheaper with respect to thermal water price**

Source: IDA Desalination Yearbook 2010-2011.

Applications of RO membranes in China

- **Drinking water**
- **Pure water industry**
- **Desalination of seawater**
  - **Equipments (>100 m^3/d) No.: 40**
  - **Total capacity: 4.3×10^5 m^3/d**
  - **Under construction: > 9×10^5 m^3/d**

Production of RO membranes: 1,200,000 m^2/y

First desalination of seawater plants in China with capacity of 10,000 t/d

Desalination of seawater plants in Guangdong Jiulong (100,000 t/d)

Pure water production in Nongfu Spring (2112 t/d)

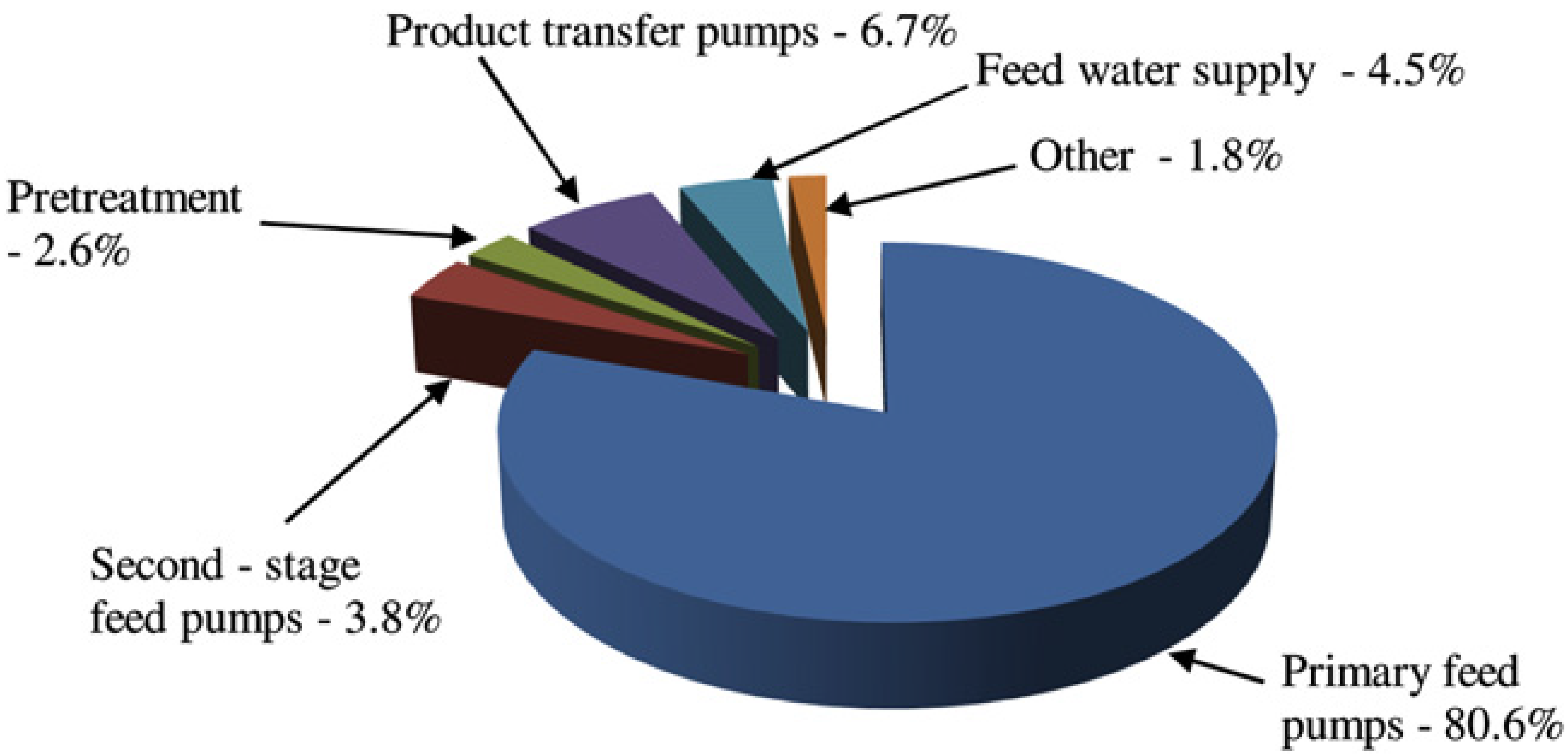
From Development Center of Water Treatment Technology
Changchun Institute of Applied Chemistry
Vontron company

Why RO is the leader in current desalination installations?

Because …

Thermal desalination processes (MSF, MED, VC)	Membrane desalination processes (RO)
Energy consumption (MSF) = 17 ÷ 18 kWh/m³	Energy consumption =2.2 ÷ 6.7 kWh/m³
Recovery factor ≈ 10÷ 20%	Recovery factor ≈ 40 ÷ 60%
High capital costs High operating costs	Low capital costs Low operating costs
Desalted water cost ≈ 0.9÷1.4 $/m³ (MSF) ÷ 0.7-1.0 (MED, TVC)	Desalted water cost ≈ 0.50 ÷ 0.70$/m³ (in the most part of SWRO plants) and 0.36$/m³ (from brackish water sources)

Distribution of power usage in a two-stage seawater RO system



Subramani et al. water research 45 (2011) 1907 -1920

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.

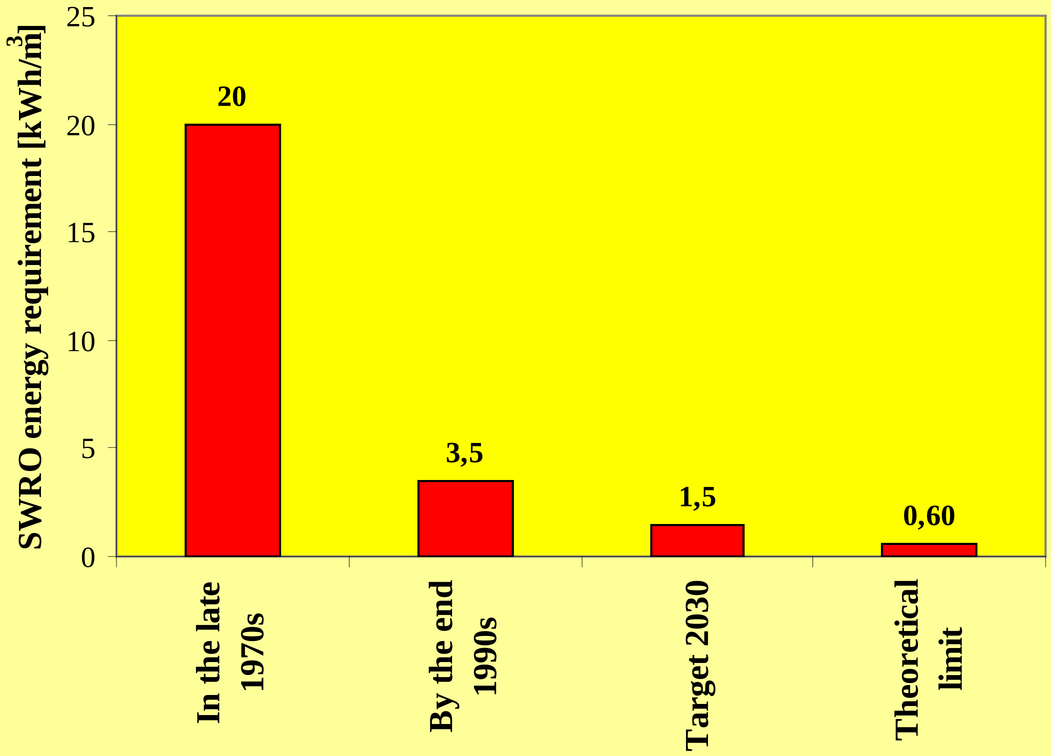
By 2000, the membrane-based desalination plants conquered the market.

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.

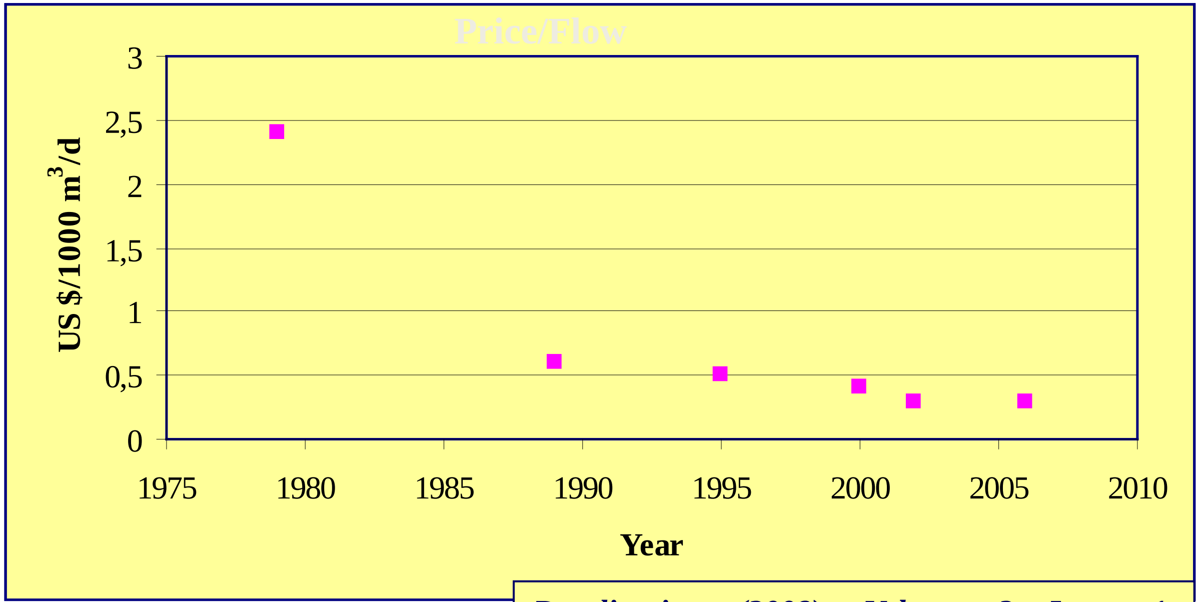
SWRO energy requirement



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

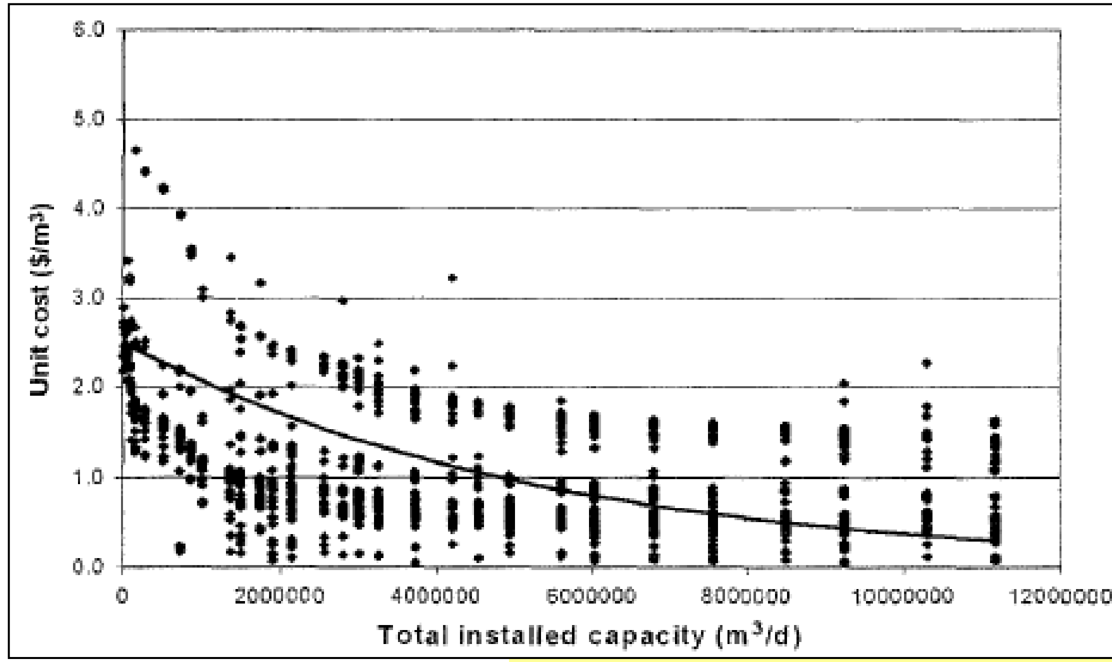


Desalination (2008). Volume 3 Issue 1, Pages: 12-14.

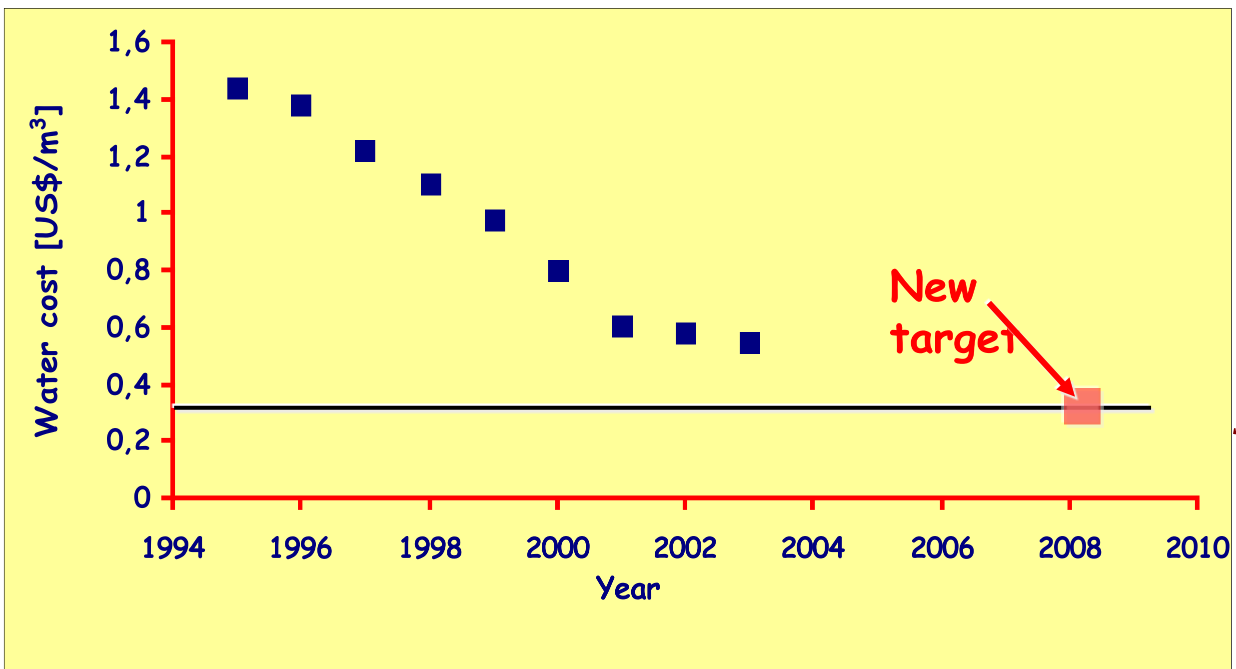
In the 1980s and 1990s the cost of the RO membranes dropped of about 50%. An example is in some SWRO elements developed by the Dow Chemical Company: the market price of a SW30HR-380 element in 1996 was about 50% that of a SW30HR-8040 element in 1985 (another SWRO membrane of nine years older, with a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

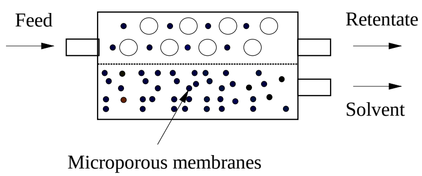
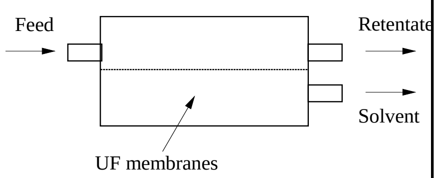
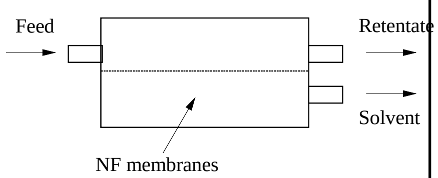
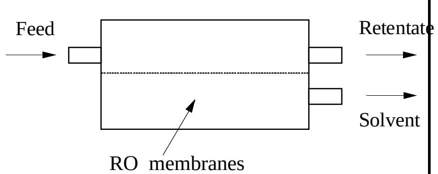


Y. Zhou, R. S.J. Tol, Desalination 164 (2004) 225-240.



Unit water cost by RO over years and new target

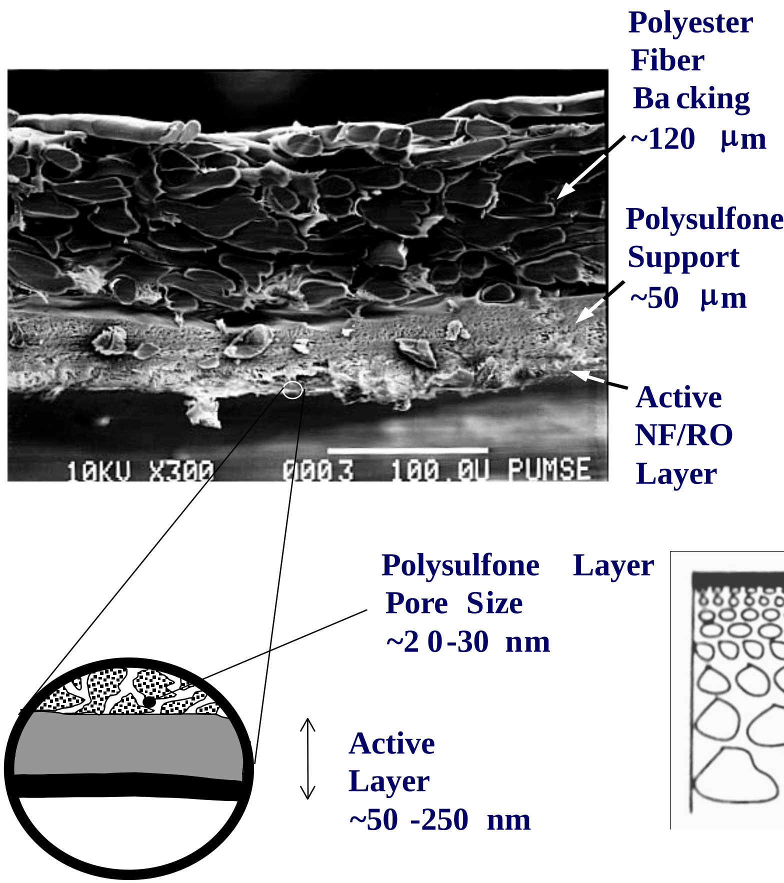
Technically relevant pressure-driven membrane separation processes used in desalination

Process	Concept	Driving Force	Mode of transport	Species Passed	Species Retained
Microfiltration (MF)		< 2 bar	size exclusion convection	solvent (water) and dissolved solutes	suspended solids, fine particulars, some colloids
Ultrafitlration (UF)		1-10 bar	size exclusion convection	solvent (water) and Low molecular weight solutes (<1000 Da)	macrosolutes and colloids
Nanofiltration (NF)		10 - 25 bar	size exclusion solution diffusion Donnan exclusion	solvent (water), low molecular, weight solutes, monovalent ions	molecular weight compounds > 200 Da multivalent ions
Reverse Osmosis (RO)		20 - 80 bar	solution diffution mechanism	solvent (water)	dissolved and suspended solids

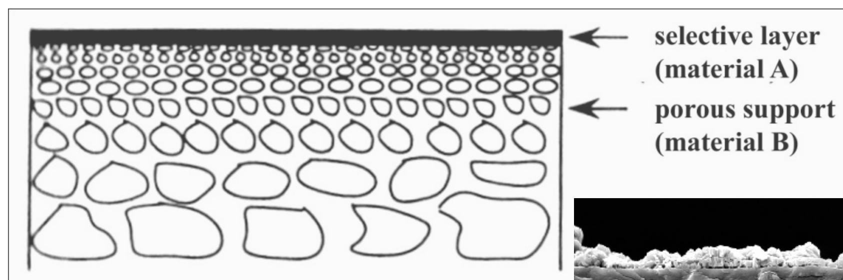
Membrane type and applications

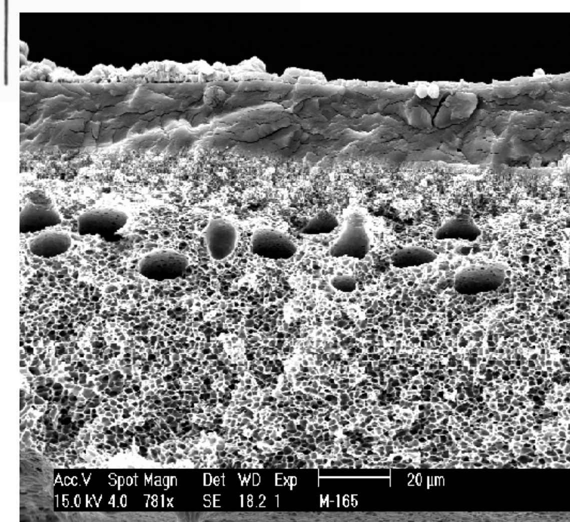
Separation process	Membrane type used	Applications
Microfiltration (MF)	symmetric macroporous, pore radius 0.1-10 mm	water purification, sterilization
Ultrafiltration (UF)	asymmetric macroporous, pore radius 2-10 nm	separation of molecular mixtures
Nanofiltration (NF)	asymmetric mesoporous, pore radius 0.5-2 nm	separation of molecular mixtures and ions
Reverse osmosis (RO)	asymmetric skin-type, dense or microporous	sea & brackish water desalination

Membrane used in RO elements

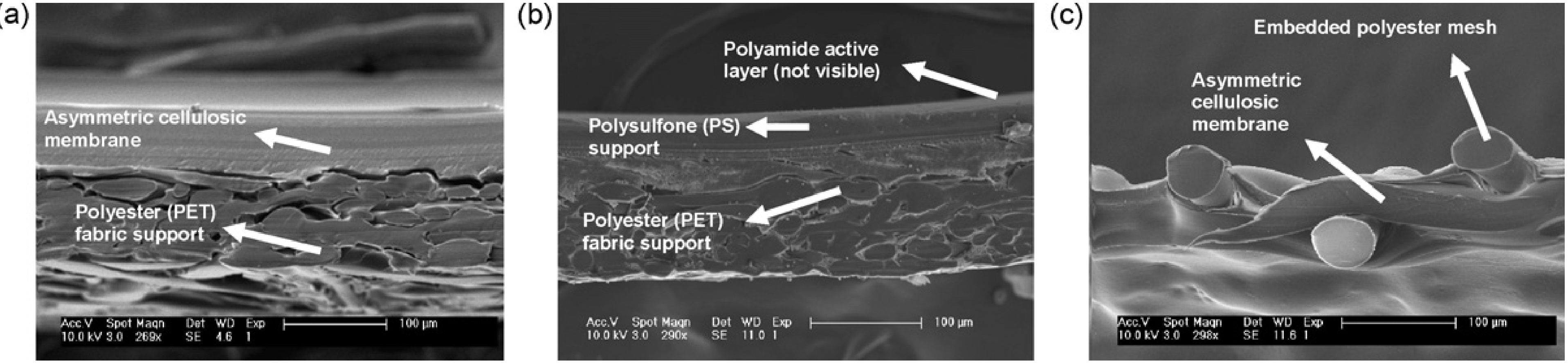


RO spiral wound element with thin film composite membrane are used in 98% of all RO systems. These elements are made of polyamide, polysulfone, polyurethane, noryl, polypropylene, polyester, polyethilene





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).



J.R. McCutcheon, M. Elimelech, Journal of Membrane Science 318 (2008) 458–466

(a) RO asymmetric cellulosic membrane from GE Osmonics (Fairfield, CT)

(b) RO thin film composite (TFC) membrane from Dow Filmtec (Midland, MI)

(c) FO asymmetric cellulosic membrane from Hydration Technologies, Inc. (Albany, OR)

http://www.kochmembrane.com

The MegaMagnum® spiral wound RO Element by Koch Membrane Systems, Inc.:

World's Largest Reverse Osmosis Element (45.72 cm x 154.9 cm) designed for advanced:

- **Brackish Water Treatment**
- **Municipal Water Reuse**
- **Seawater Desalination**

Some of the state-of-the-art SWRO membrane modules in application.

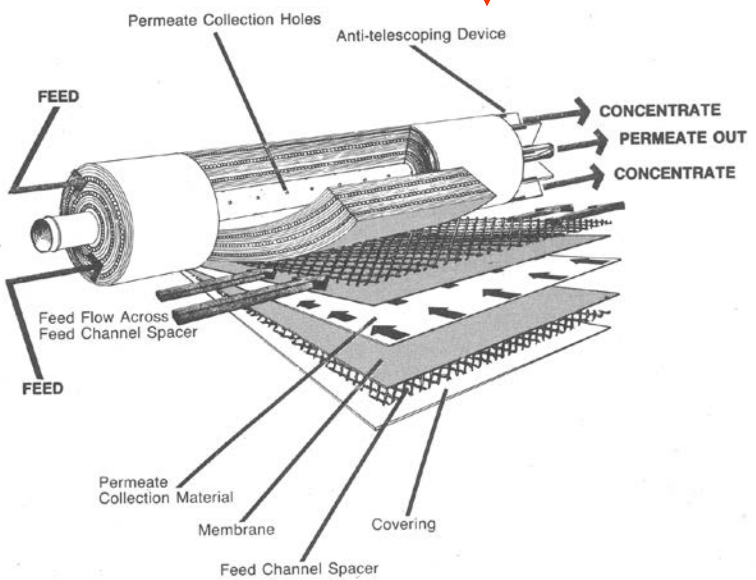
Membrane module brand name	Material and module	Permeate flux (m^3 day^{-1})	Salt rejection (%)	Energy consumption ($kWh\ m^{-3}$) [d]
DOW FILMTEC™ 8-in. SW30HRLE	TFC cross linked fully aromatic polyamide spiral wound	28.0 [a]	99.60-99.75 [a]	3.40 at Perth SWRO Plant Australia
Hydranautics 8-in. SWC4+	TFC cross linked fully aromatic polyamide spiral wound	24.6 [b]	99.70-99.80 [b]	4.17 at Llobregat SWRO Plant, Spain
Toray 8-in. TM820C	TFC cross linked fully aromatic polyamide spiral wound	19.7-24.6 [a]	99.50-99.75 [a]	4.35 at Tuas SWRO Plant, Singapore
Toyobo 16-in. HB10255	Asymmetric cellulose tri-acetate hollow fibre	60.0-67.0 [c]	99.40-99.60 [c]	5.00 at Fukuoka SWRO Plant, Japan

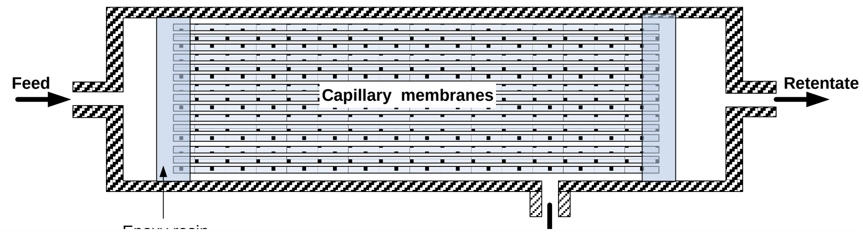
Test conditions: [a] 32 g/L NaCl solution, 55 bar 25°C, pH 8 and 8% recovery; [b] 32 g/L NaCl solution, 55 bar 25°C, pH 7 and 10% recovery; [c] 35 g/L NaCl solution, 54 bar 25°C and 30% recovery
[d] These number should not be compared directly because of the different operating parameters at the different desalination plants

K.P. Lee et al. Journal of Membrane Science *370 (2011) 1*

Membrane configuration

flat-sheet | spiral wound | tubular | capillary | Hollow fiber

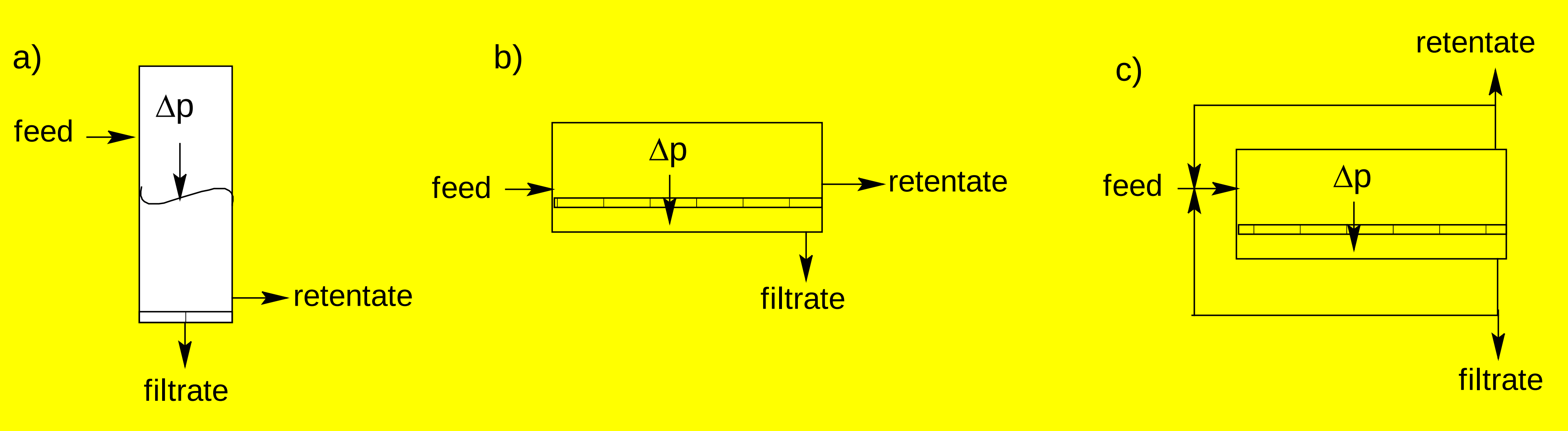




Comparison between different typologies of membrane modules

	Tubular	Plate-and-frame	Spiral-wound	Capillary	Hollow fibre
Packing density	Low	→	→	→	High
Investment cost	High	←	←	←	Low
Fouling tendency	Low	→	→	→	High
Cleaning	Good	←	←	←	Poor

OPERATION MODES IN FILTRATION PROCESSES



BATCH PROCESS

Under a hydrostatic pressure certain components, i.e. mainly a solvent, permeate the membrane and are collected as filtrate. When a certain concentration in the retentate is achieved the process is terminated.

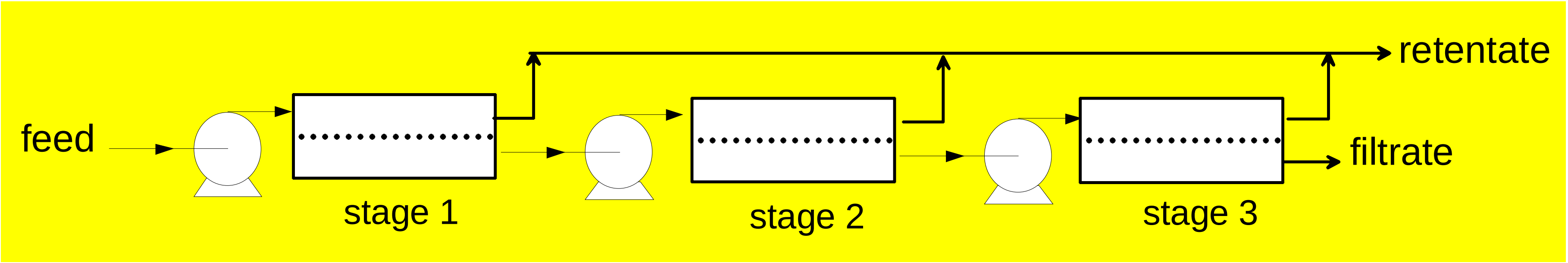
CONTINUOS PROCESS

Solution is continuously fed into the filtration device. The retained components are concentrated during the path-way through the device leaving at the end of the process path as the retentate.

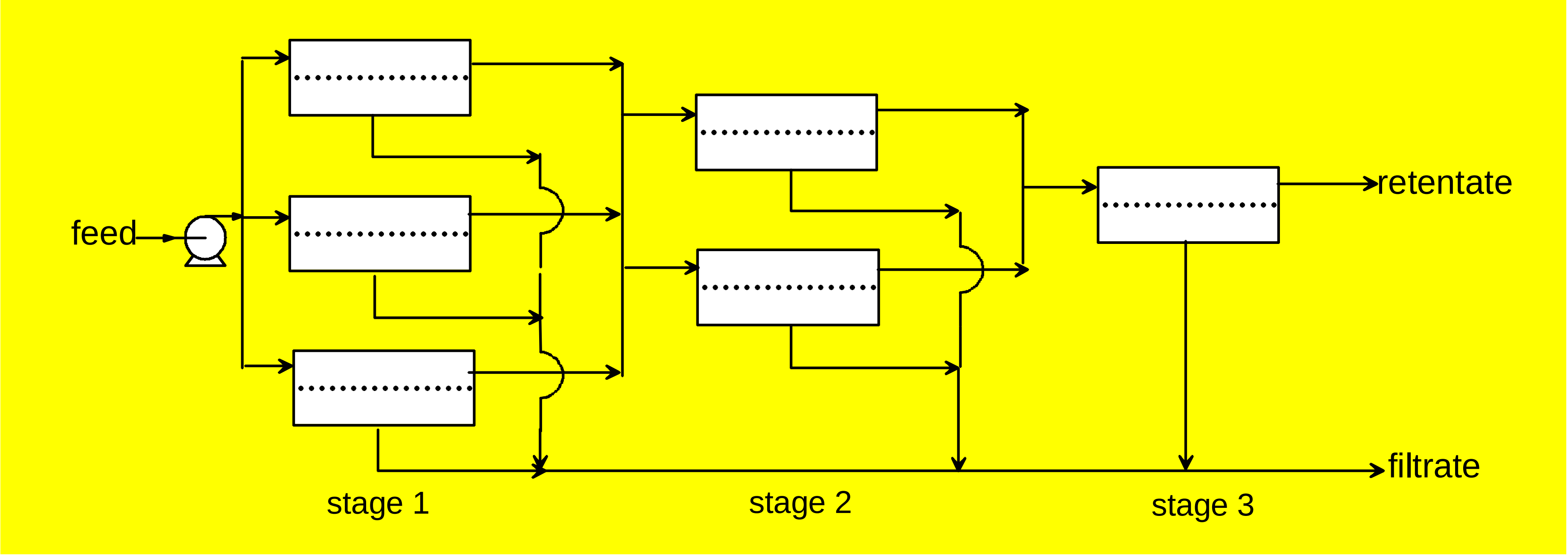
FEED & BLEED PROCESS

Part of the retentate is recycled to the device inlet and mixed with the feed solution.

Three stage filtration cascade



Three stage retentate cascade



PROBLEMS IN MEMBRANE DESALINATION: BRINE DISPOSAL, RECOVERY FACTOR, FOULING AND BIO-FOULING

Enrico Drioli[1,2,3,4]

[1]Institute on membrane Technology, National Research Council of Italy, ITM-CNR, c/o University of Calabria, via P. Bucci cubo 17/C, Rende (CS) Italy

[2]Department of Chemical Engineering and Materials, University of Calabria, via P. Bucci, Rende (CS)

[3]WCU Energy Department, Hanyang University, Seoul 133-791 S. Korea

[4] Distinguished Adjunct Professor, Center of Excellence in Desalination Technology, King Abdulaziz University, Jeddah Saudi Arabia

KACST, February 2014

Problems in Desalination today

- Energy consumptions
- Brine disposal

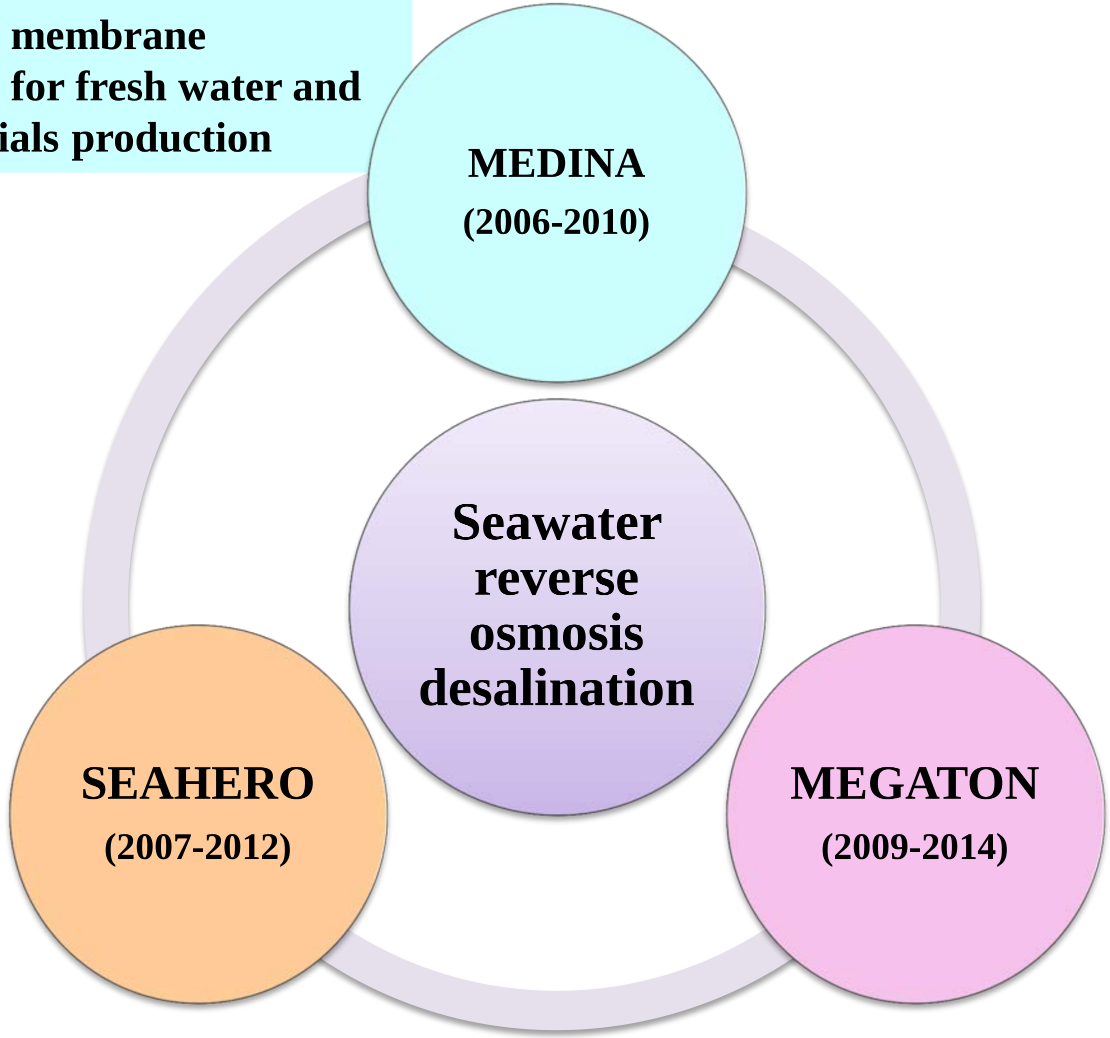
Problems of tomorrow

- No Energy consumptions
  Energy Production
- No Brine disposal
  Mineral production

Water prices at the production costs as requested by the public

Membrane based desalination projects

Integrated membrane operations for fresh water and raw materials production



Large scale: **largest SWRO unit** (27,000 m^3/d)
Low energy: reduction by 4 kWh/m^3.
Low fouling: reduction of 50 %

Efficient design to obtain capacity of **1,000,000 m^3/d.**
Large size element and module,
intake technology,
pressure retarted osmosis,
energy recovery,
pipe design

http://medina.unical.it
M. Kurihara, M. Hanakawa / Desalination 308 (2013) 131–137.
S. Kim et al. / Desalination 238 (2009) 1–9

Membrane-Based Desalination: An Integrated Approach (acronym MEDINA)

SIXTH FRAMEWORK PROGRAMME - PRIORITY 1.1.6.3 - Global Change and Ecosystems

Aim: **to improve the overall performance of membrane-based water desalination processes through the integration of different membrane operations in RO pre-treatment and RO post-treatment stages.**

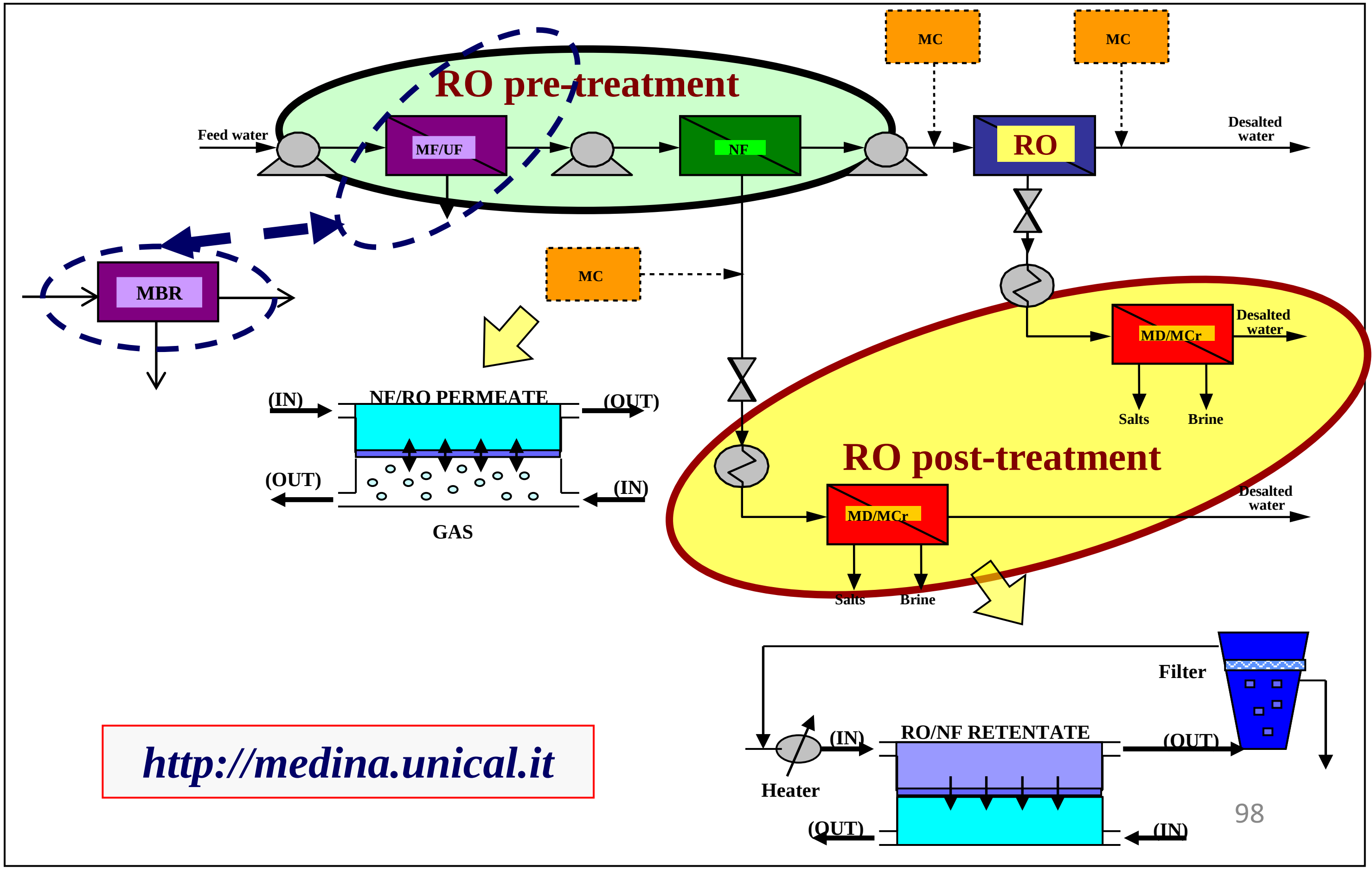
Objectives:

1. to minimise environmental impacts

2. to optimise energy sources and consumption

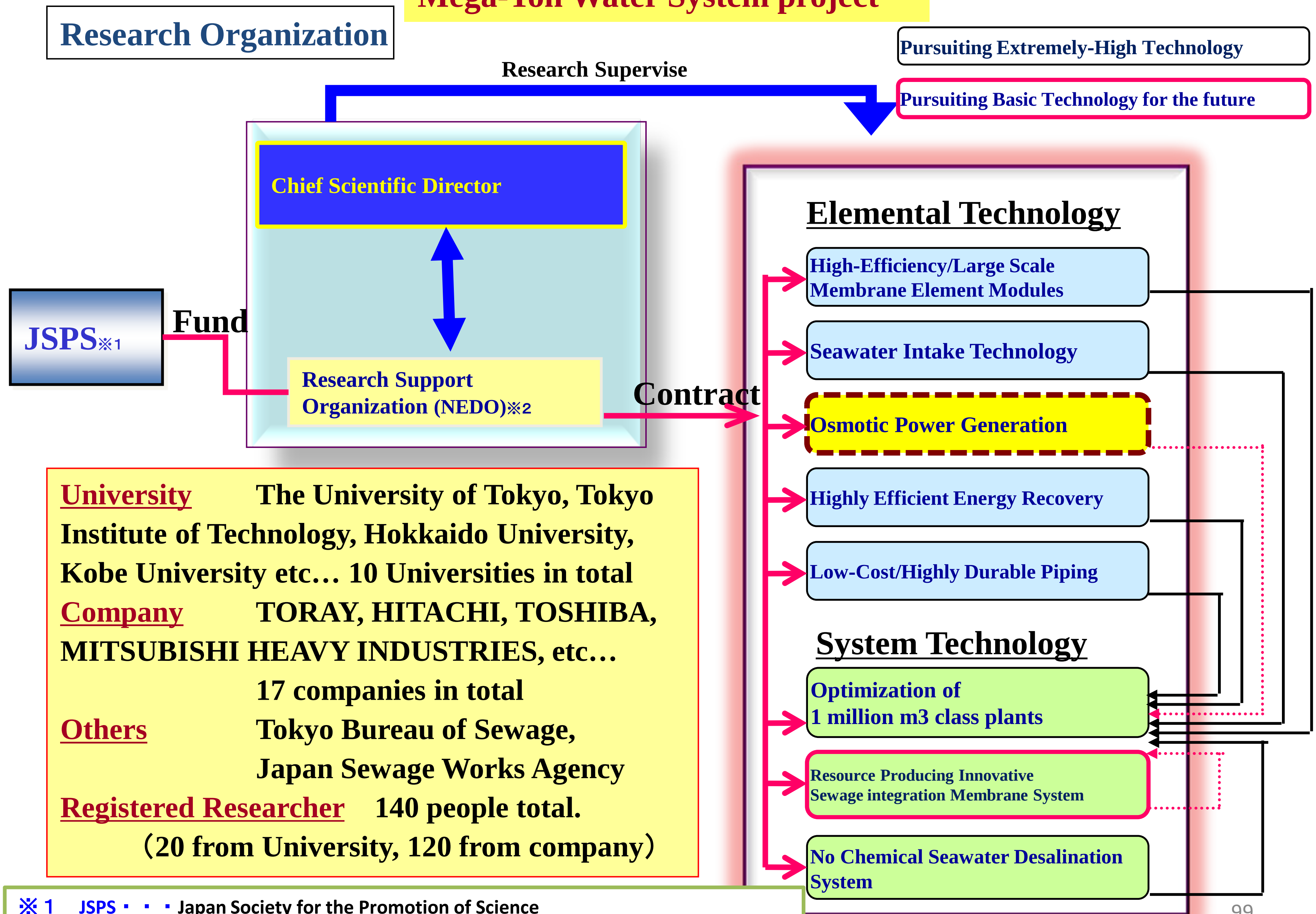
3. to increase fresh water production

4. to optimize sea-brackish water desalination by understanding, controlling and minimizing fouling phenomena.



http://medina.unical.it

Mega-Ton Water System project



University The University of Tokyo, Tokyo Institute of Technology, Hokkaido University, Kobe University etc… 10 Universities in total

Company TORAY, HITACHI, TOSHIBA, MITSUBISHI HEAVY INDUSTRIES, etc… 17 companies in total

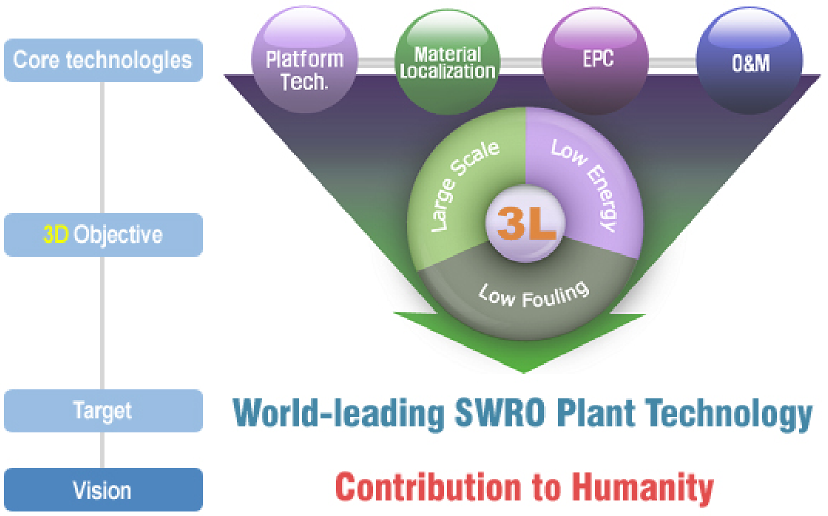
Others Tokyo Bureau of Sewage, Japan Sewage Works Agency

Registered Researcher 140 people total.
（20 from University, 120 from company）

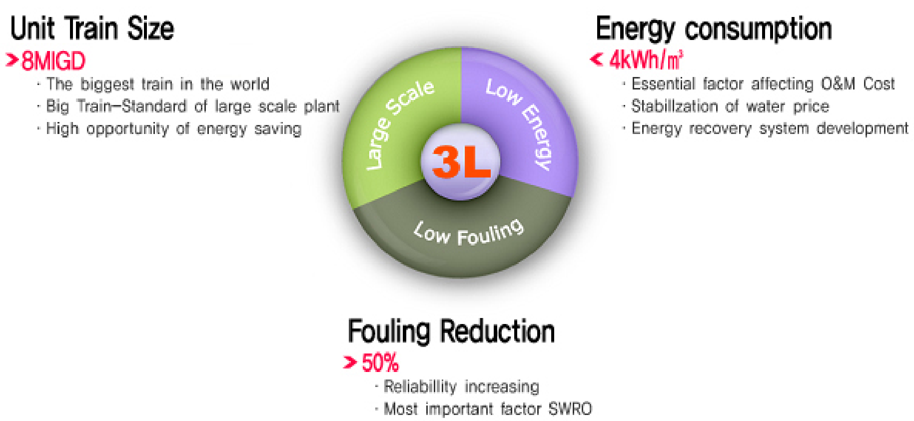
※1 JSPS・・・Japan Society for the Promotion of Science
※2 NEDO・・・New Energy and Industrial Technology Development Organization

Seawater Engineering & Architecture of High Efficiency Reverse Osmosis (SeaHERO) project is targeting to get the top SWRO technologies in the world

Center for Seawater Desalination Plant pursues the RO membrane technique which meets 3L skills. *3L* means the three main technical objectives including *large scale, low energy, and low fouling* for SWRO plants. At first, large scale is to design and construct the largest unit SWRO train [8MIGD = 36,368㎥/d] in the world.



EPC/O&M Cost Minimization



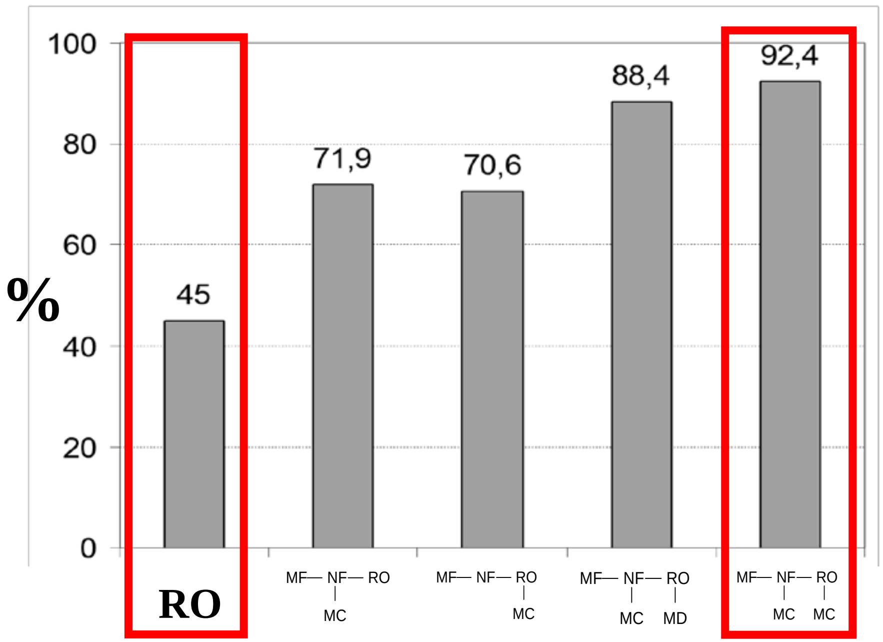
Second, low energy means to lower energy consumption of whole SWRO plant including intake, pretreatment, SWRO systems, and so on by 4kWh/㎥. At last, low fouling is to reduce fouling effect by 50% in terms of silt density index [SDI] and a new fouling parameter developed.

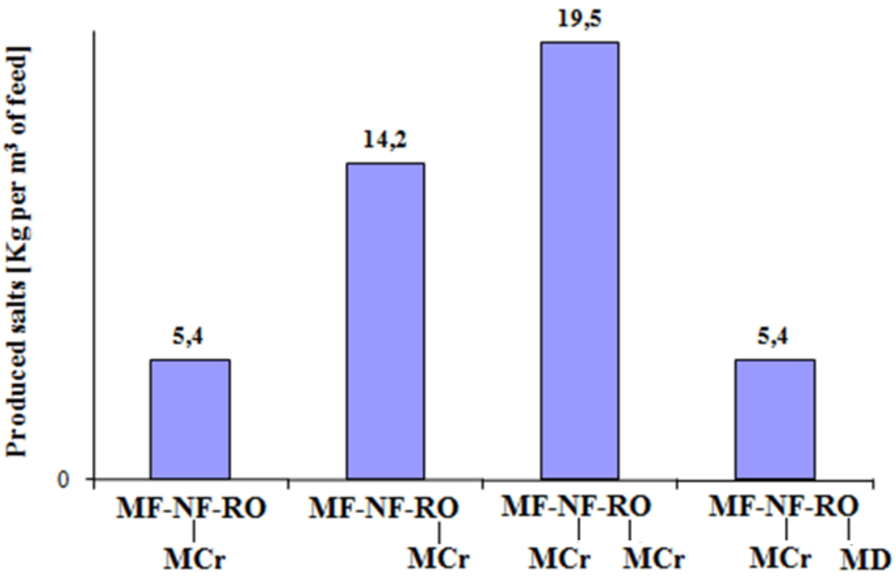
http://www.seahero.org/eng/

Integrated membrane operations for desalination

Recovery factors > 90% for the integrated desalination systems have been obtained.

Amount of salts recovered from different integrated membrane desalination systems.





E. Drioli et al., Chemical Engineering Research and Design, 84 (A3) (2006) 209–220. - E. Drioli et al., Desalination and Water Treatment, 18 (2010) 224-234.

Commercial membrane brands

- Dow-Filmtec
- Hydranautics
- Toray
- GE-Osmonics (Desal)
- Koch Membrane Systems (Fluid Systems™)
- CSM / Saehan
- Inge
- Parker
- Ropur
- TriSep
- Axeon

Some material usually used for thin-film composite (TFC) membrane

FT-30 (Dow-Filmtec based)
Cross linked Fully Aromatic Polyamide
Flux: 1.0m3 m-2 day−1
Salt Rejection: 99%
Test: > 15 bar, 0.2% NaCl solution

UTC series (Toray based)
Cross linked Fully Aromatic Polyamide
Flux: 0.8m3 m−2 day−1
Salt Rejection: 98.5%
Test: > 15 bar, 0.5% NaCl solution

NS-200
Polyfurane
Flux: 0.8m3 m−2 day−1
Salt Rejection: 99.8%
Test: > 100 bar, 3.5% NaCl solution

PEC-1000
Polyether-Polyfurane
Flux: 0.5m3 m−2 day−1
Salt Rejection: 99.9%
Test: > 69 bar, 3.5% NaCl solution
-Excellent organic rejection

Hi-Flux CP
Sulfonated Polysulfone
Flux: 0.06m3 m−2 day−1
Salt Rejection: 98%
Test: > 69 bar, 3.5% NaCl solution
-Excellent chlorine resistance

NS-100
Polyamide via polyethylenimine
Flux: 0.7m3 m−2 day−1
Salt Rejection: 99%
Test: > 100 bar, 3.5% NaCl solution

Some material usually used for thin-film composite (TFC) membrane

PA-300 or RC-100
Polyamide via polyepiamine
Flux: 1.0m3 m−2 day−1
Salt Rejection: 99.4%
Test: > 69 bar, 3.5% NaCl solution

WFX-X006
Polyvinylamine
Flux: 2.0m3 m−2 day−1
Salt Rejection: 98.7%
Test: > 40 bar, Conductivity = 5000Scm−1

Polypyrrolidine
Flux: 0.8m3 m−2 day−1
Salt Rejection: 99.7%
Test: > 40 bar, 0.5% NaCl solution

NS-300
Polypiperazine-amide
Flux: 3.3m3 m−2 day−1
Salt Rejection: 68%
Test: > 100 bar, 3.5% NaCl solution

A-15
Cross linked Aralkyl Polyamide
Flux: 0.26m3 m−2 day−1
Salt Rejection: > 98%
Test: > 55 bar, 3.2% NaCl solution

X-20 (Trisep based)
Cross linked Fully Aromatic Polyamide – 3
Flux: 1m3 m−2 day−1
Salt Rejection: 99.3%
Test: > 15 bar, 0.2% NaCl solution

Commercial RO membranes: Some examples

DOW FILMTECTM 8-in. SW30HRLE

TFC cross linked fully aromatic polyamide
Spiral wound
Permeate flux: 28.0 m3/d
Salt rejection: 99.60-99.75 %

Hydranautics 8-in. SWC4+

TFC cross linked fully aromatic polyamide
Spiral wound
Permeate flux: 24.6 m3/d
Salt rejection: 99.70-99.80 %

Toray 8-in. TM820C

TFC cross linked fully aromatic polyamide
Spiral wound
Permeate flux: 19.7-24.6 m3/d
Salt rejection: 99.50-99.75 %

Toyobo 16-in. HB10255

Asymmetric cellulose tri-acetate
Hollow fiber
Permeate flux: 60.0-67.0 m3/d
Salt rejection: 99.40-99.60 %

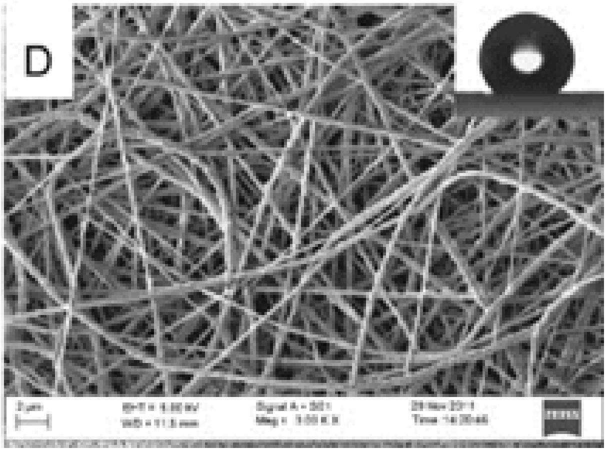
New materials for membranes

The development of new and better membranes specially adapted to water treatment helps to improve the overall efficiency of the desalination plant and reduce the production costs.

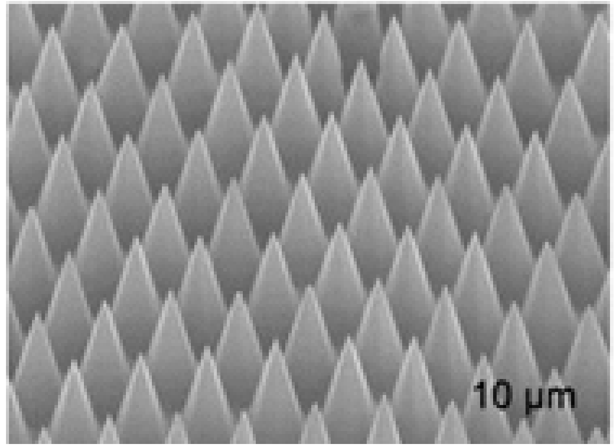
Key-factors for the membrane properties:

- Enhanced transport mechanisms
- Improved selectivity and flux
- Superior resistance to chlorine attack

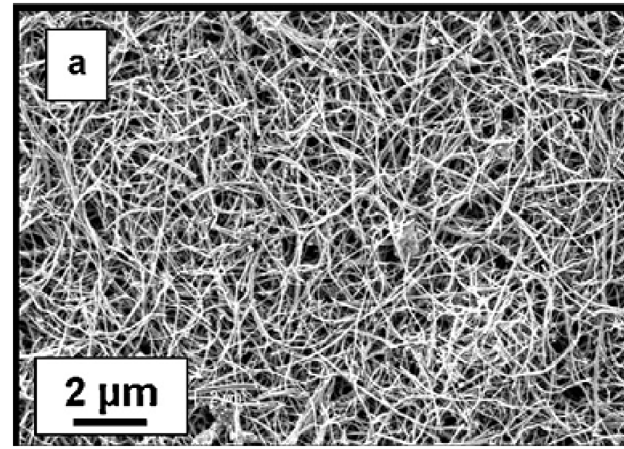
Membrane type	Principle	Energy consumption	Advantages	Drawbacks
Nanocomposite	Zeolite nanoparticles incorporated in polyamide matrix creating enhanced transport of water molecules.	20% lower energy consumption than conventional seawater RO (NanoH2O, 2010).	More than double the flux of currently available seawater RO membranes (NanoH2O, 2010).	Chemical compatibility and structural stability is not known. Rejection of specific contaminants is not known. Long-term operational data not available.
Nanotube	Transport of water molecules through structured carbon and boron nitride nanotubes.	30–50% lower energy consumption than conventional seawater RO (Hilder et al., 2009).	Ten – fold higher flux than currently available seawater RO membranes (Hilder et al., 2009).	Only modeling results available. Rejection of specific contaminants is not known.
Biomimetic	Aquaporins used to regulate transport of water molecules.	Energy consumption is not known.	Hundred times permeable than currently available seawater RO membranes (AquaZ, 2010).	Inability to withstand high operating pressures. Rejection of specific contaminants is not known. Long-term operational data not available.



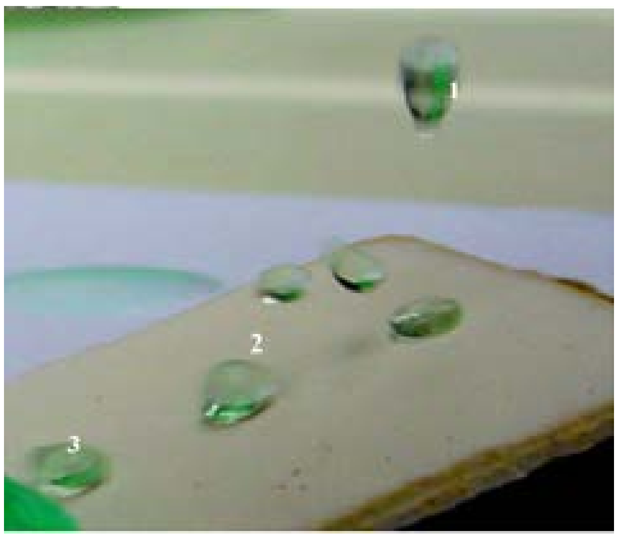
Surface morphology and contact angle of electro-spun PVDF membrane
Liao et al, Journal of Membrane Science 425–426 (2013) 30–39



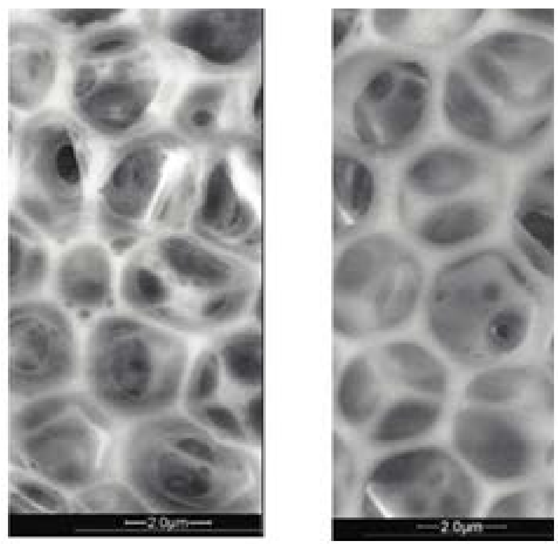
Surface of supehydrophobic nanospike glass membranes
MA et al, Langmuir Lett, 25 (2009), pp. 5446–5450



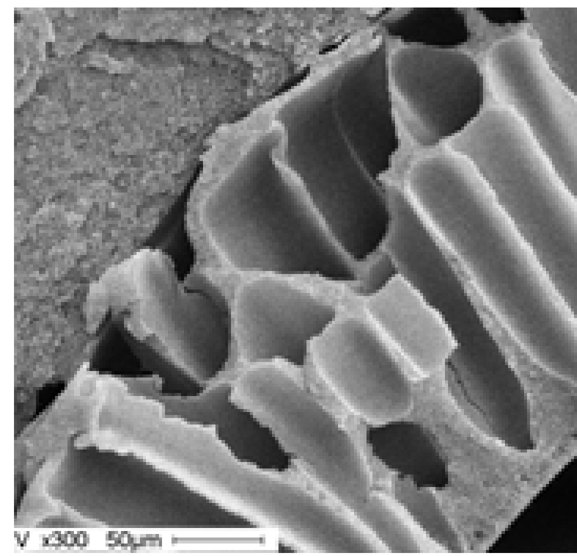
Surface of CNT bucky paper membrane
Dumée et al, Journal of Membrane Science 376 (2011) 241–246



Surface of zirconia for ceramic membranes
Cerneaux et al, Journal of Membrane Science 337 (2009) 55–60



Surface of membranes prepared thorough self-assembly technique
Gugliuzza et al, J. Phys. Chem. B2008, 112, 10483–1049

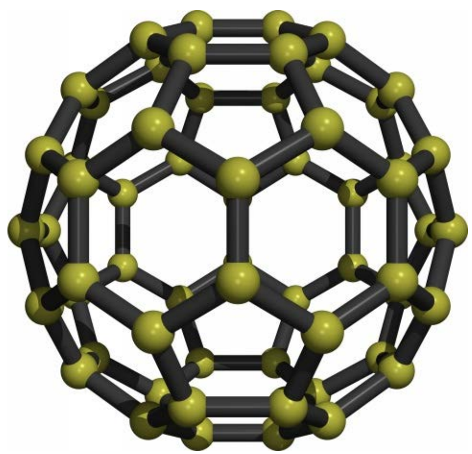


New concept of Dual layer membranes
Current work, Manuscript in progress

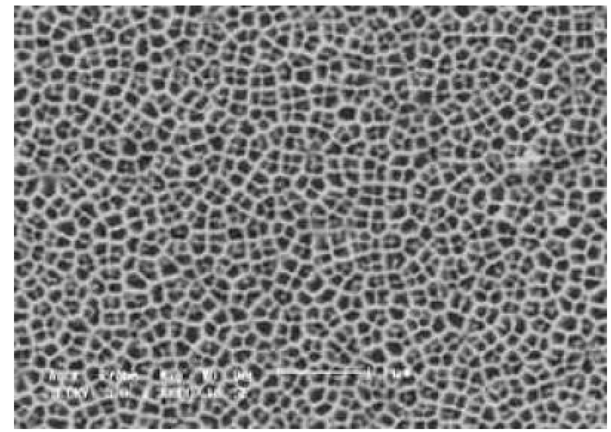
Fullerene

Fullerene treated membranes hinder the ability of bacteria and other microorganisms to accumulate on the membrane surface.

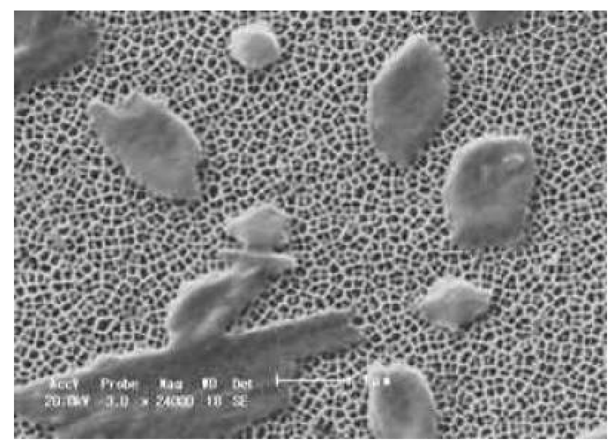
Moreover fullerene inhibited respiration or the ability of the bacteria to use oxygen to fuel its activities.



Fullerene treated membrane



Non treated membrane



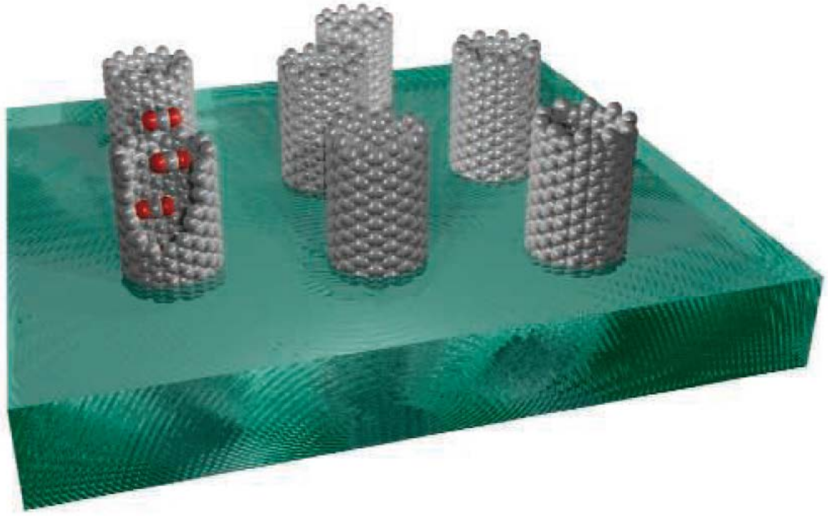
R. Merritt, Buckyballs could keep water systems flowing - http://www.eurekalert.org/pub_releases/2009-03/du-bck030209.php

Nanotube membranes

Billions of tubes acts as the pores in membranes.

Smooth surface inside the tube makes rapidly flow of gas and liquids, while the small pore size causes that larger molecules cannot flow through.

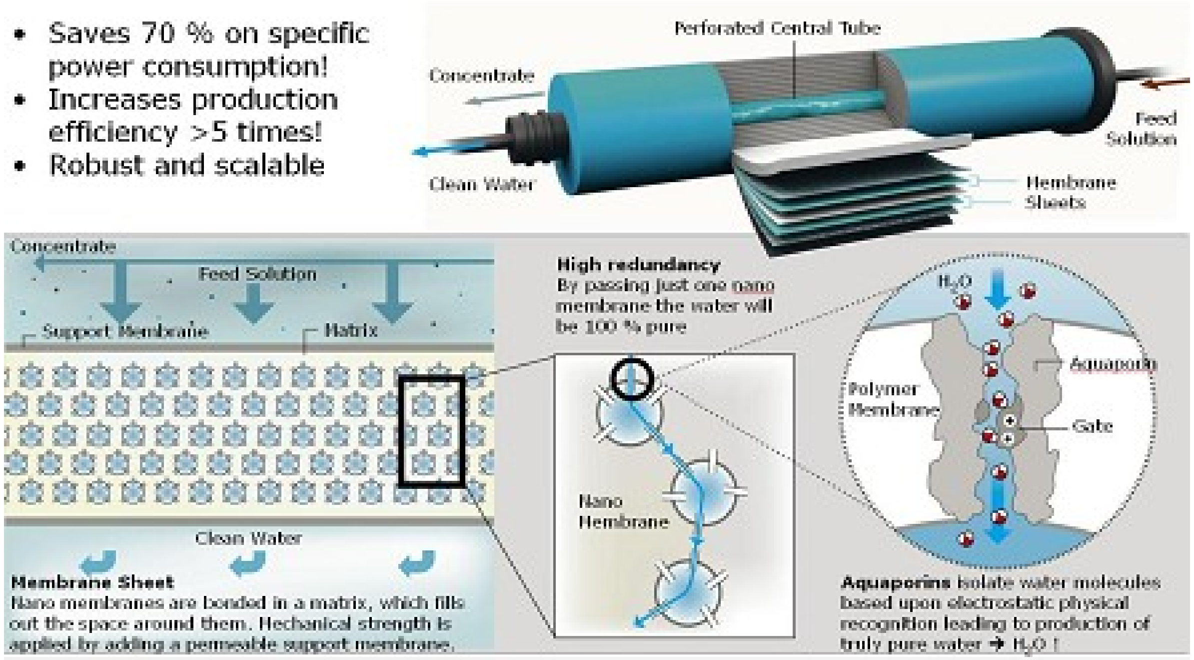
The water flux is 100 to 10,000 times faster than what classical models predict.



F. Macedonio et al. / Chemical Engineering and Processing 51 (2012) 2– 17
Sholl and Johnson, Making High-Flux Membranes with Carbon Nanotubes Science 312, 1003 (2006)

Aquaporin channels

Aguaporins are water conducting channels found in biological membranes and have a unique hourglass architecture with a “pore opening” of 2.8Å; the narrow pore size prevents the passage of large molecules. Synthetic nanotubes with hydrophobic walls use a similar transport mechanism.

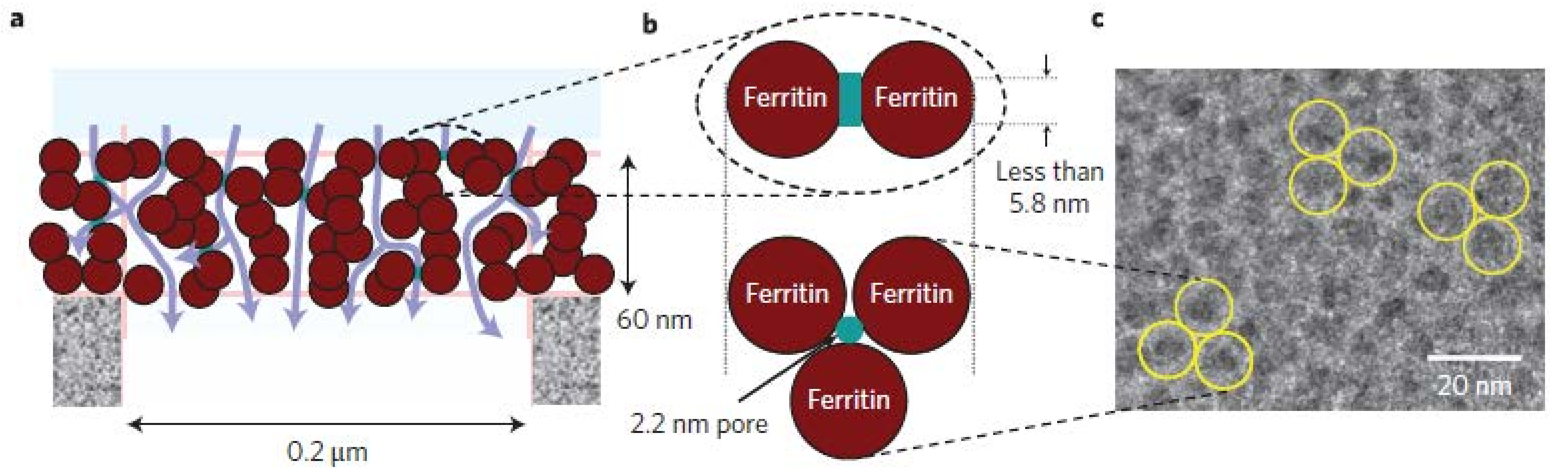


http://aquaz.dk/

Protein-based membranes

Protein-based membranes are made by crosslinked proteins.

The membranes are mechanically robust, with channels with diameter less than 2.2 nm.



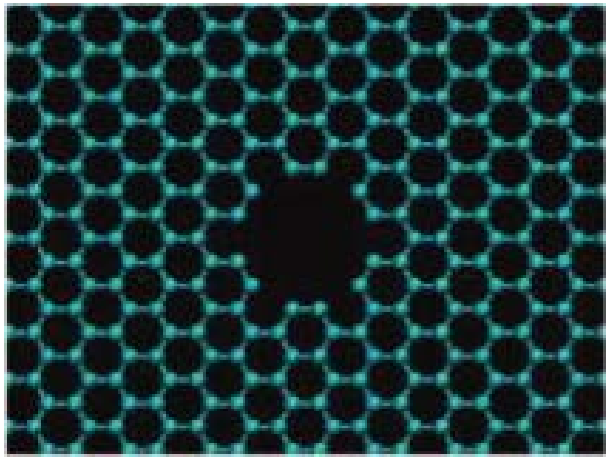
A 60-nm-thick membrane can concentrate aqueous dyes with fluxes up to 9000 L/h/m2/bar, which is ~1000 times higher than the fluxes that can be withstood by commercial filtration membranes with similar rejection properties.

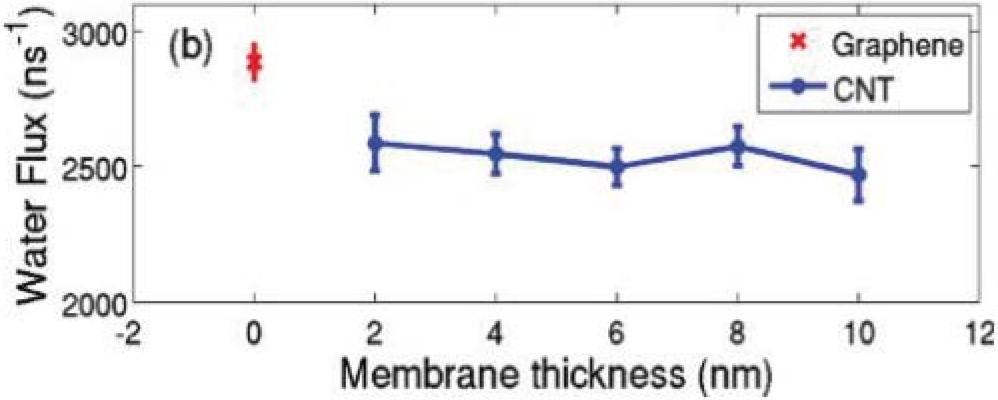
F. Macedonio et al. / Chemical Engineering and Processing *51 (2012) 2– 17*

Peng et al., Ultrafast permeation of water through protein-based membranes, Nature Nanotechnology

Graphene membranes

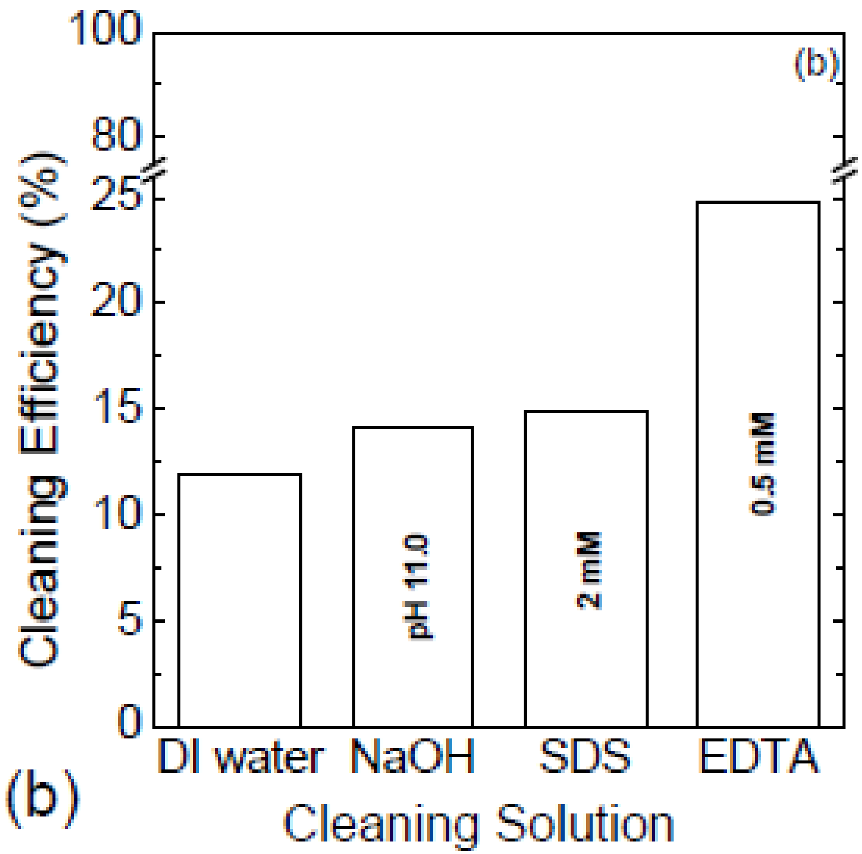
Molecular dynamics simulations showed water transport through a porous graphene membrane and compare the results with water transport through thin (less than 10 nm in thickness/length) carbon nanotube membranes. They found that for larger diameter pores, where the water structure is not single-file, graphene membranes provide higher water flux compared to carbon nanotube membranes.

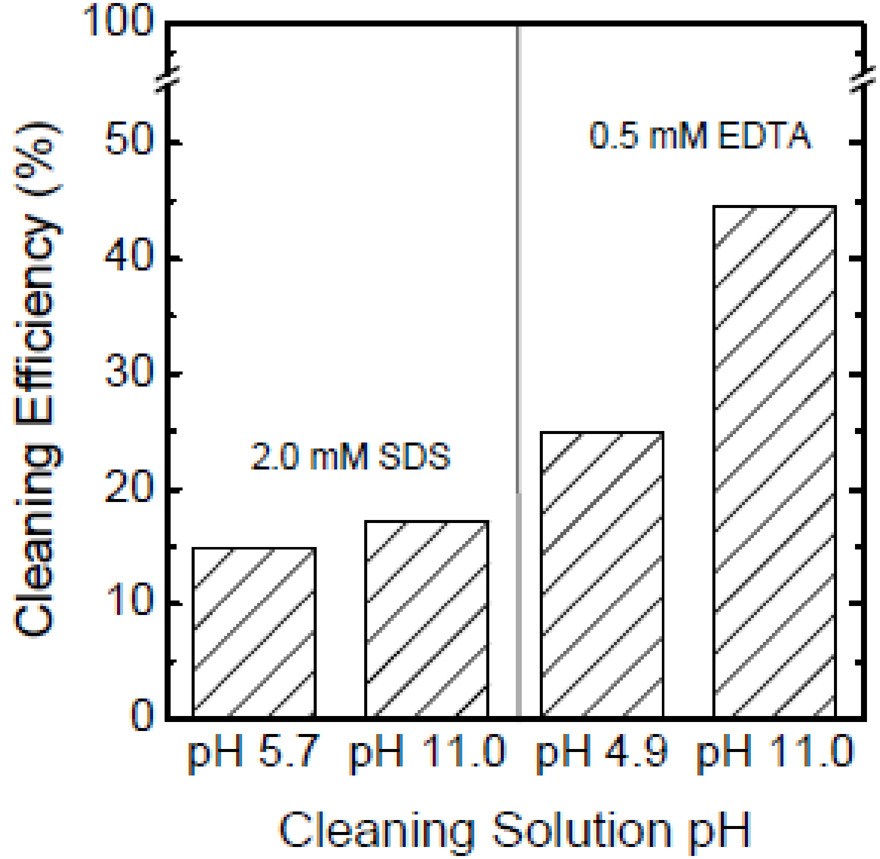




F. Macedonio et al. / Chemical Engineering and Processing *51 (2012) 2– 17*
Suk and Aluru, J. Phys. Chem. Lett. 2010, 1, 1590–1594

Efficiency of cleaning of a organic fouled RO membrane

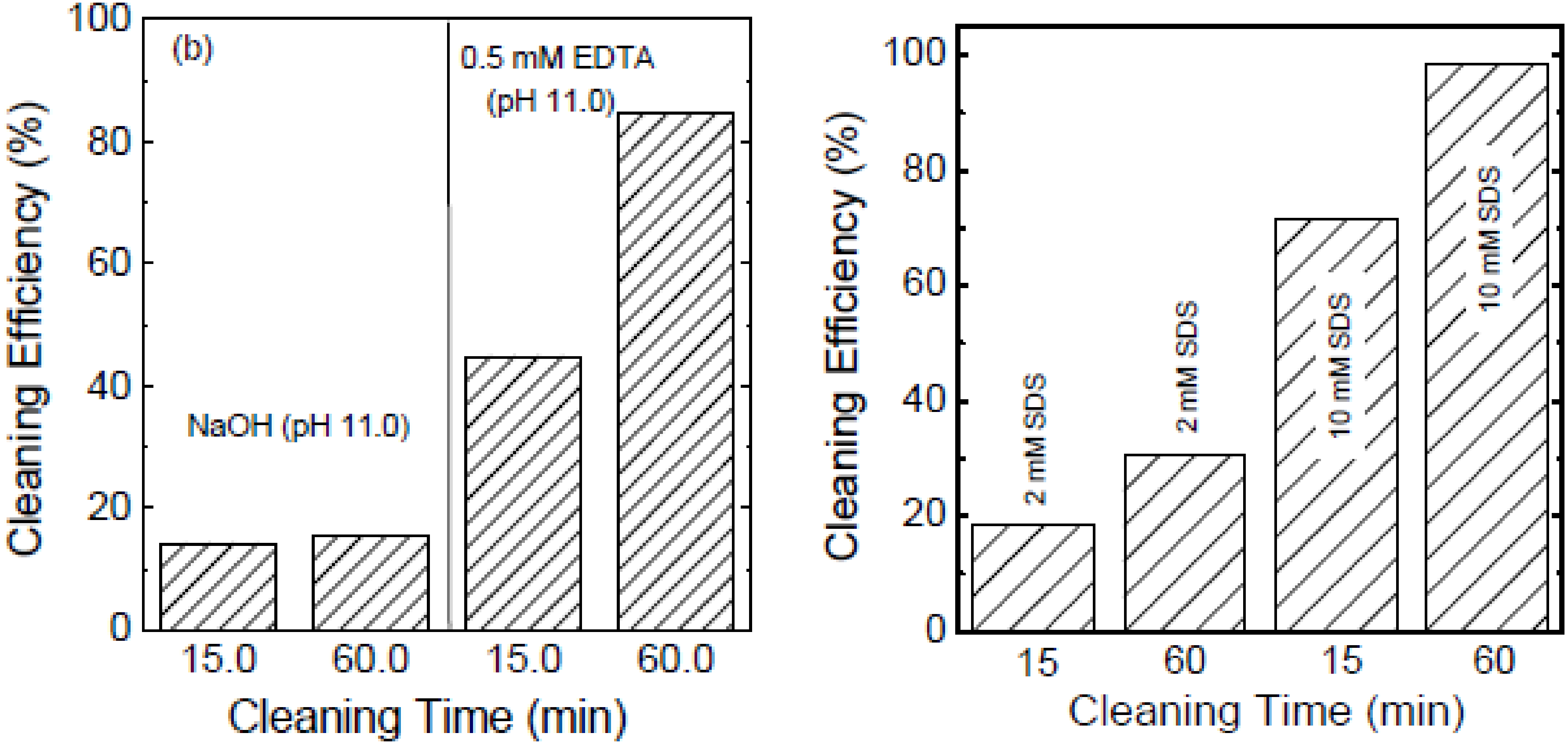




SDS: sodium dodecyl sulfate, EDTA: disodium ethylenediaminetetraacetate

Ang & Elimelech : Optimization of Chemical Cleaning of Organic-Fouled Reverse Osmosis Membranes, Report 2008.

Efficiency of cleaning of a organic fouled RO membrane

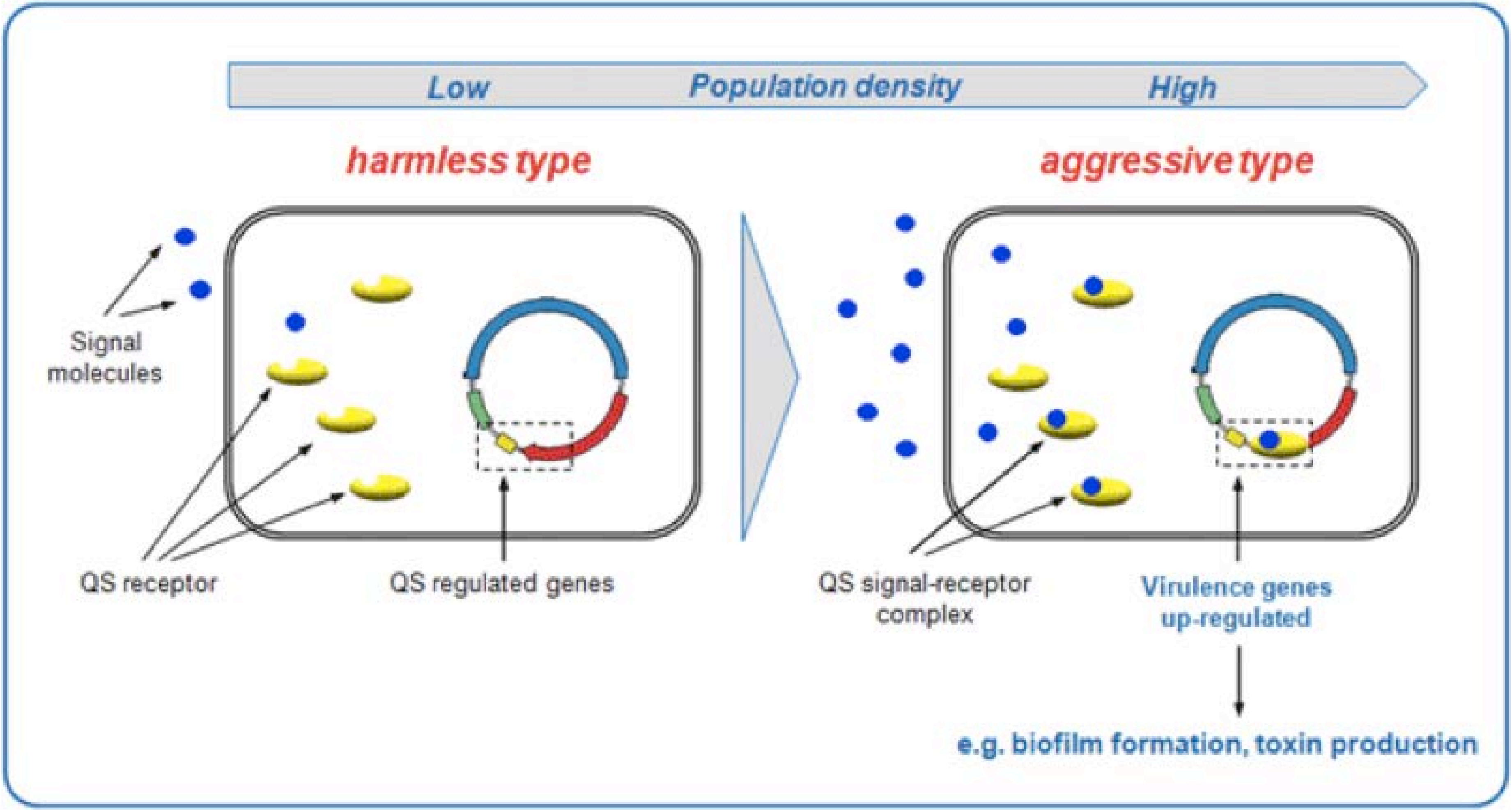


SDS: sodium dodecyl sulfate, EDTA: disodium ethylenediaminetetraacetate

Ang & Elimelech : Optimization of Chemical Cleaning of Organic-Fouled Reverse Osmosis Membranes, Report 2008.

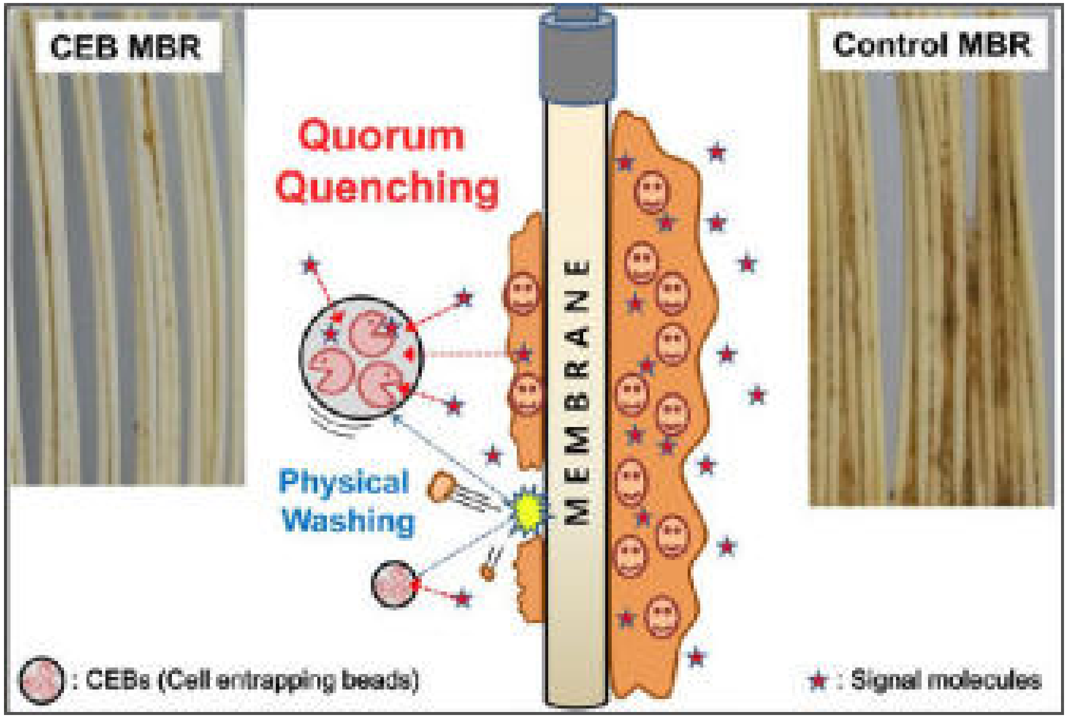
Fouling - Quorum Sensing

Describes the phenomenon whereby the accumulation of signaling molecules enable a single cell to sense the number of bacteria (cell density)



Fouling - Quorum Sensing

Free-moving beads entrapped with quorum quenching bacteria were applied to the inhibition of biofouling in a MBR.



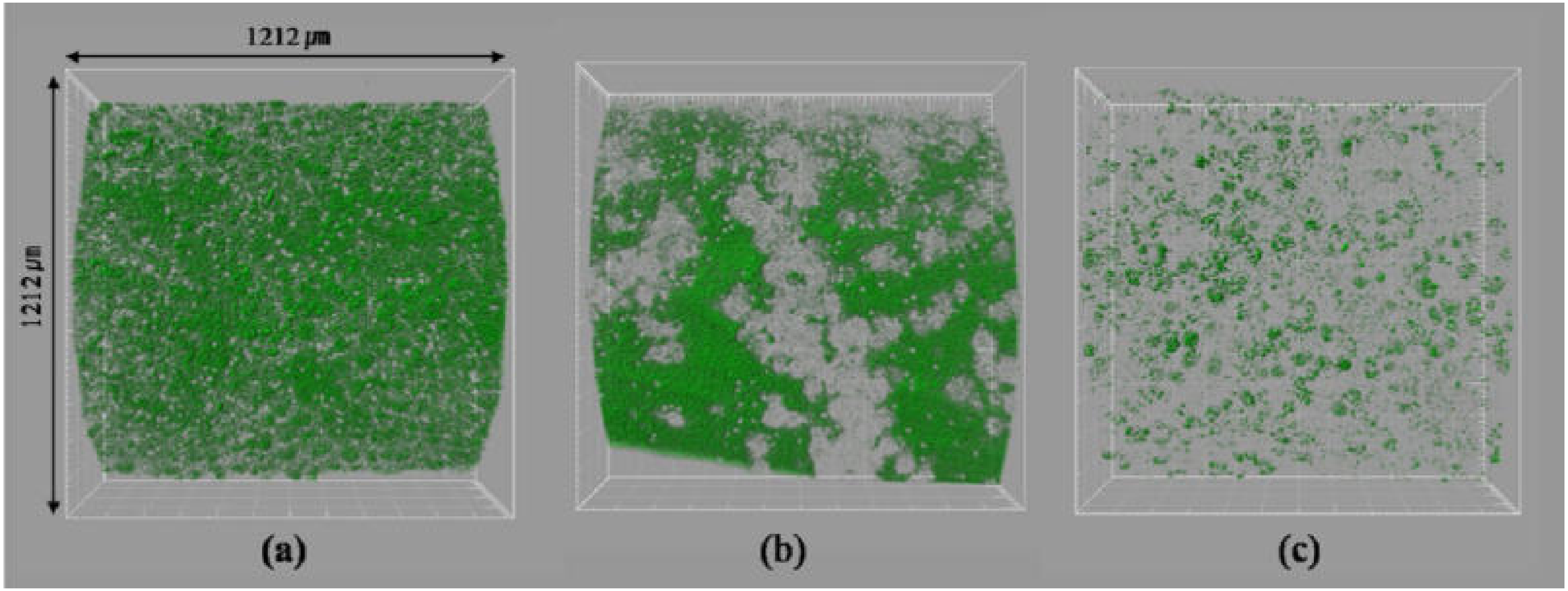
Cell entrapping beads (CEBs) with a porous microstructure were prepared by entrapping quorum quenching bacteria (Rhodococcus sp. BH4) into alginate beads.

Kim et al., Environ. Sci. Technol. 2013, 47, 836–842

Fouling - Quorum Sensing

Reconstructed images of biofilm formed on the membrane surfaces which were removed from the MBRs operated for 48 h.

Less biomass was attached to the membrane with the CEBs. In short, CEBs can inhibit biofilm formation by quorum quenching.



(a) control MBR, **(b)** MBR with vacant beads, and **(c)** MBR with CEBs

Kim et al., Environ. Sci. Technol. 2013, 47, 836−842

EMS

European Membrane Society

XXXI EMS Summer School 2014

on

Innovative Membrane Systems

organized by the Institute on Membrane Technology

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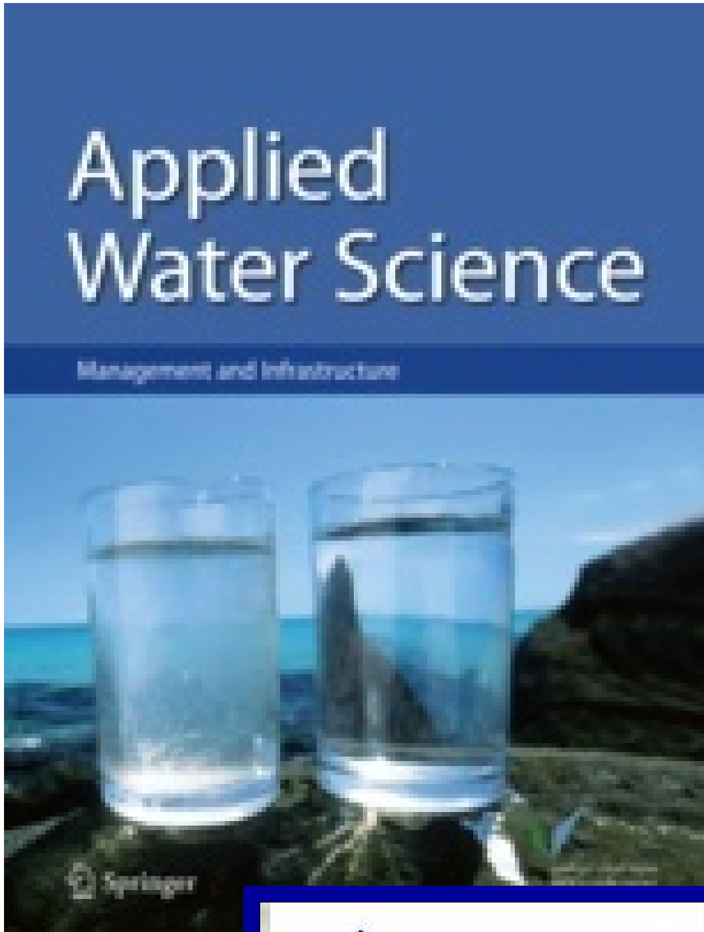

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Applied Water Science explores water scarcity solutions from a holistic system oriented viewpoint. From the sustainable management of natural water resources to the development of the technologies and infrastructure for the production of clean fresh water from natural and waste water.
The journal accepts innovative and sound theoretical research on different water issues, exploring potential alternative water sources via recycling and reuse of wastewater with a focus on arid and semiarid environments and the following topics: water desalination, drinking water treatment, wastewater treatment, water resources planning, investigation and management.

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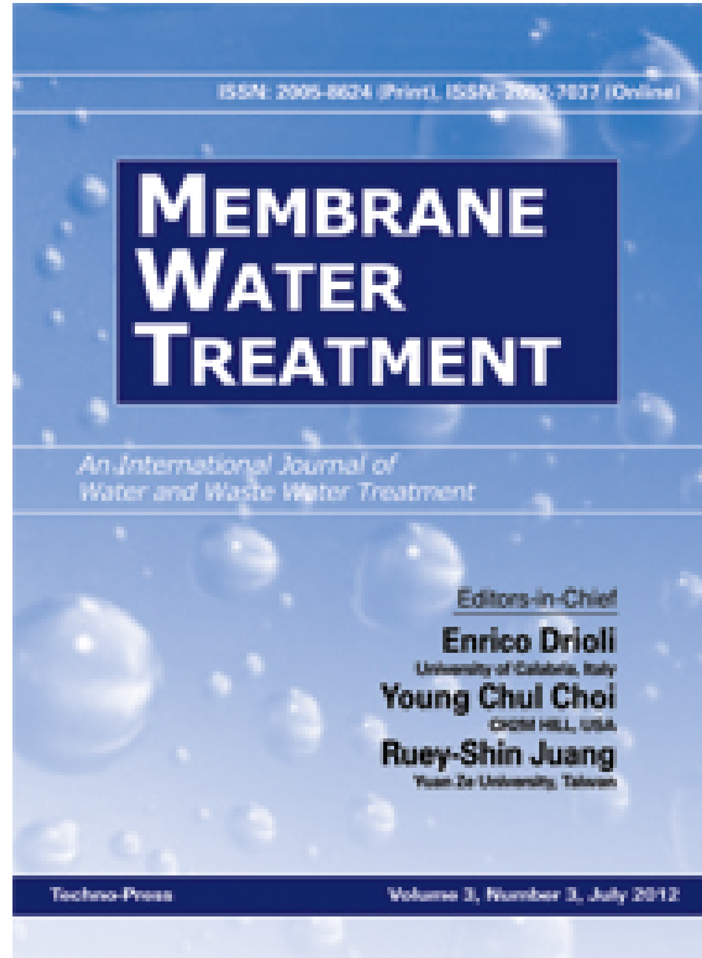

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NEW MEMBRANE DESALINATION SYSTEMS

Enrico Drioli[1,2,3,4]

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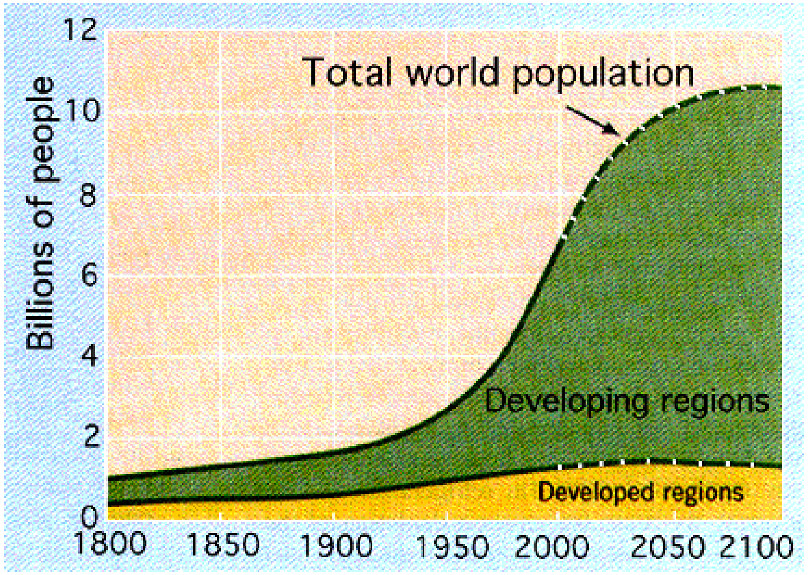
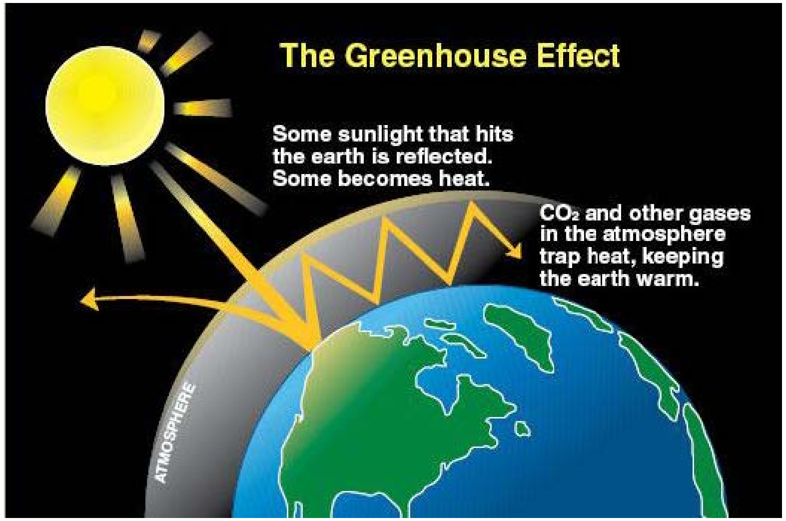
KACST, February 2014

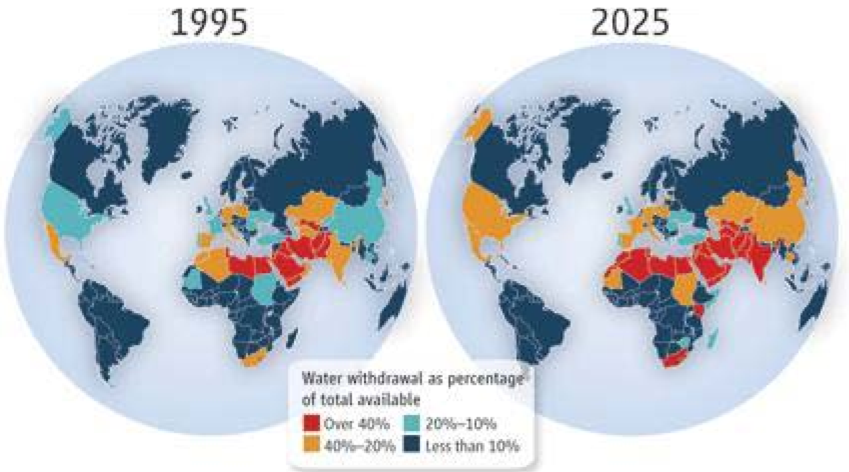
The last century has been characterized

- **by a huge <u>population growth</u> and a significant elongation of life expectancy**
- **by an intensive <u>industrial development</u>**
- **by an overall increasing of the standards of life**





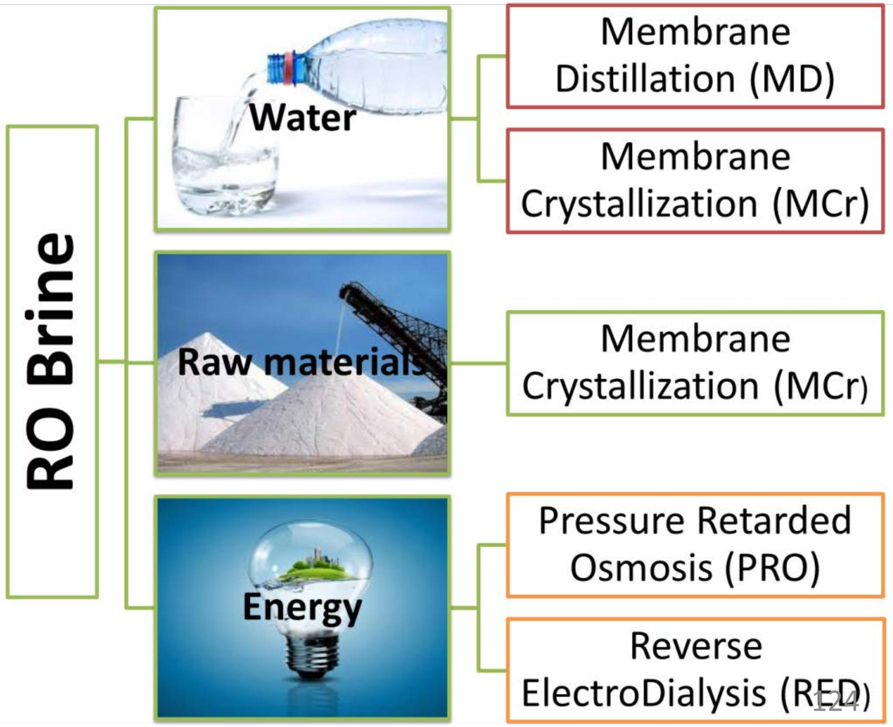
- **by <u>global worming</u>**
- **by an increasing <u>energy consumption</u>**
- **by a <u>depletion of raw materials</u>**



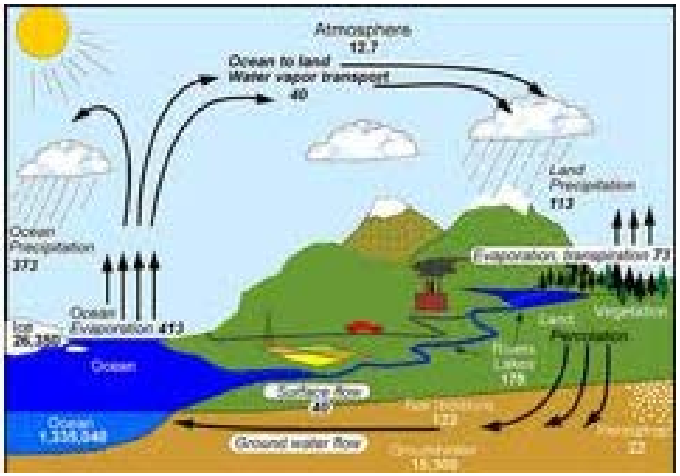
- **by <u>WATER STRESS</u>**

- ✓ *65.2 million m³/d:* **the total capacity of all completed desalination plants (2010)**
- ✓ *71.7 million m³/d:* **the cumulative contracted capacity of desalination plants around the world (2010)**
- ✓ *over 15000:* **the number of desalination facilities around the world (2010)**
- ✓ *34.8:* **the percentage of desalination plants using** *MSF or MED technology*
- ✓ *23:* **the percentage of RO water price cheaper with respect to thermal water price**
- ✓ *60:* **the percentage of desalination plants using** *reverse osmosis technology in 2011*
- ✓ *80:* **the percentage of technological change to Membrane-based Desalination (reverse osmosis)** *in 2016*

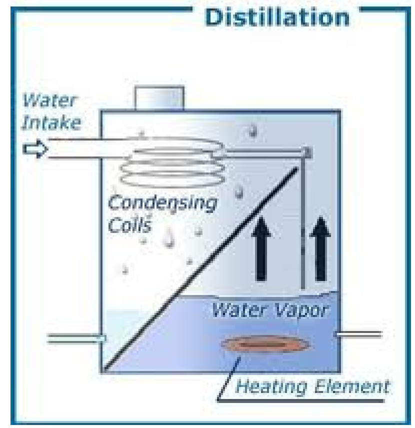
The current 37.6 million m3/d of brine can be used as a source for...



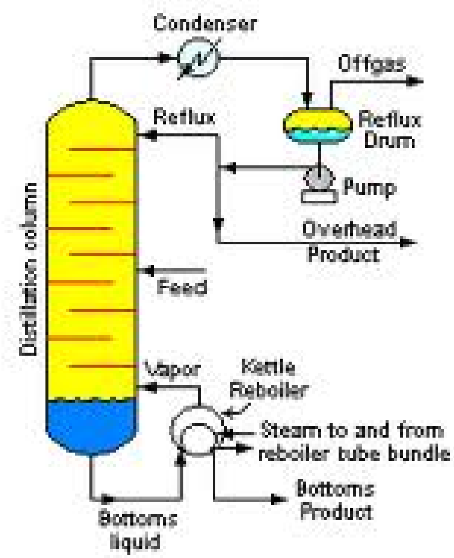
Natural vs thermal vs membrane distillation for fresh water production



Natural hydrological cycle

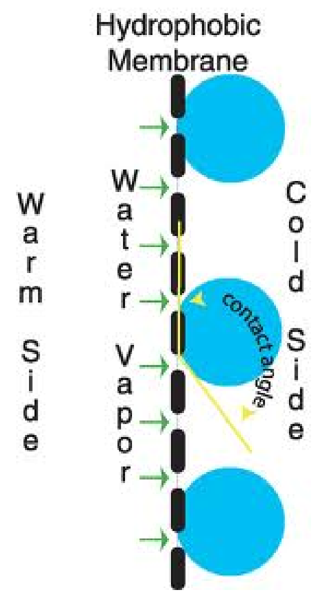


Thermal distillation



Distillation column

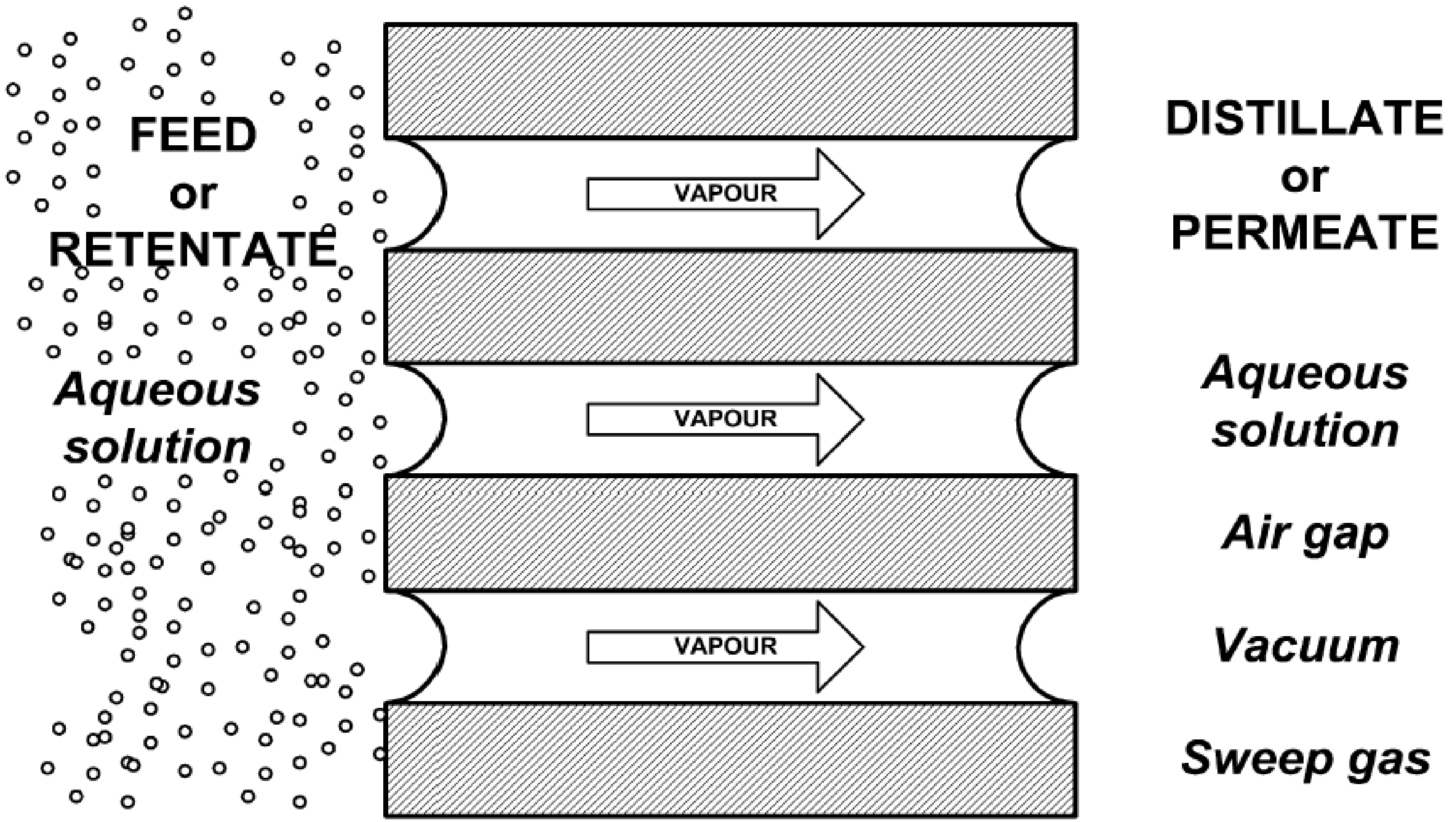
Membrane Distillation



MEMBRANE DISTILLATION APPLICATIONS

Desalination and pure water production from seawater and/or brackish water
Treatment of water for the semiconductor industry or power plants
Nuclear industry (concentration of radioactive solutions and wastewater treatments; pure water production)
Textile industry (removal of dyes and wastewater treatment)
Industrial and municipal used waters (removal of small size and persistent contaminants)
Chemical industry (concentration of acids, removal of VOCs from water, separation of azeotropic aqueous mixtures such as alcohol/water mixtures and crystallization)
Pharmaceutical and biomedical industries (removal of water from blood and protein solutions, wastewater treatment)
Food industry (concentration of juices and milk processing) and in areas where high temperature applications lead to degradation of process fluids

MD 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 TO MASS TRANSFER

The flux J_i is proportional to the partial pressure difference Δp_i across the membrane:

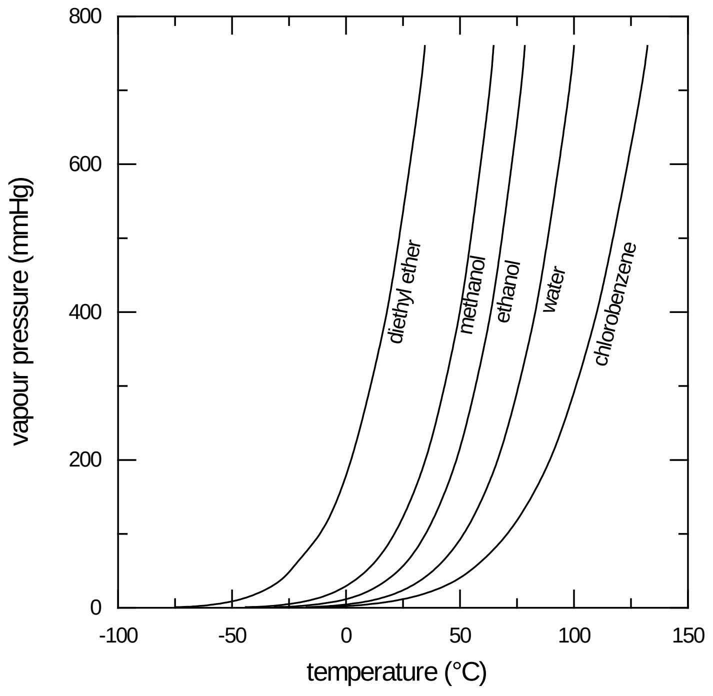
$$J_i = K \Delta p_i$$

K is a function of TEMPERATURE, PRESSURE, COMPOSITION and MEMBRANE STRUCTURE.

For non-ideal mixtures:

$$p_i = P\, y_i = p_i^0 a_i = p_i^0\, \xi_i x_i$$

P: total pressure, a_i: activity of i-th component, x_i: liquid mole fraction; y_i: vapour mole fraction; ξ_i: activity coefficient



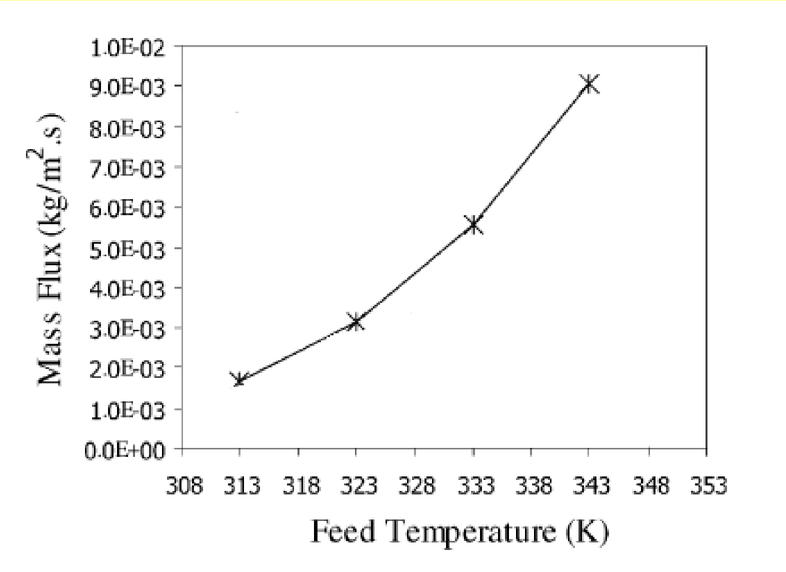
The vapour pressure of a pure substance varies with temperature according to the Clausius-Clapeyron equation:

$$\frac{dp^0}{dT} = \frac{p^0 \lambda}{RT^2}$$

λ: latent heat of vaporization (=9.7 cal/mole for water at 100°C);

R: gas constant; T: absolute temperature

The increase of flux with temperature



Adapted from J. Phattaranawik et al., Journal of Membrane Science, 212 (2003) 177–193.

MASS TRANSFER

According to an electrical analogy, mass transport can be conveniently described in terms of serial resistances upon the transfer between the bulks of two phases contacting the membrane:

$$K = \frac{1}{1/k_f + 1/k_M + 1/k_d}$$

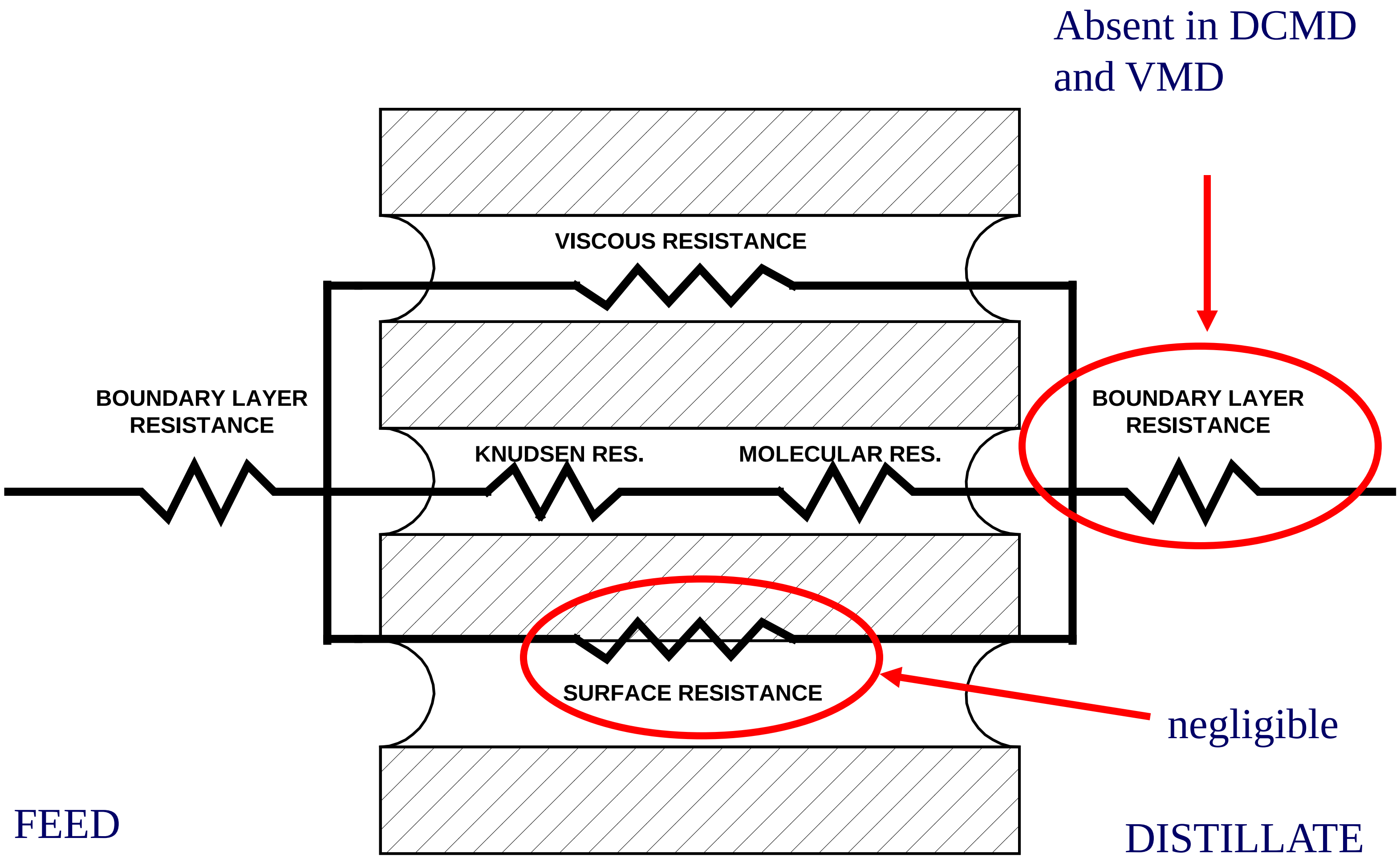
OVERALL MASS TRANSFER COEFFICIENT

feed

membrane

distillate

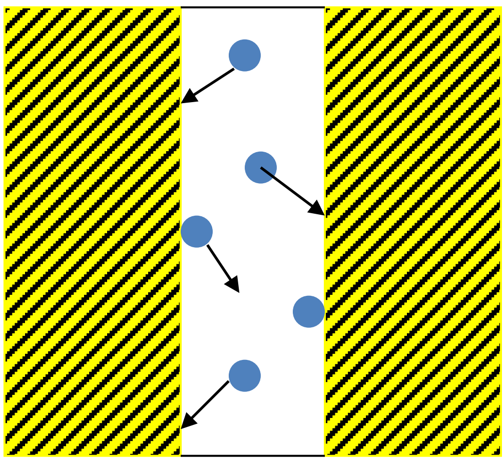
MASS TRANSFER



Serial and parallel arrangement of resistances to mass transport.

$$\text{KNUDSEN NUMBER (Kn)} = \frac{\text{mean free path } \lambda \text{ of diffusing molecules}}{\text{mean pore size of the membrane}}$$

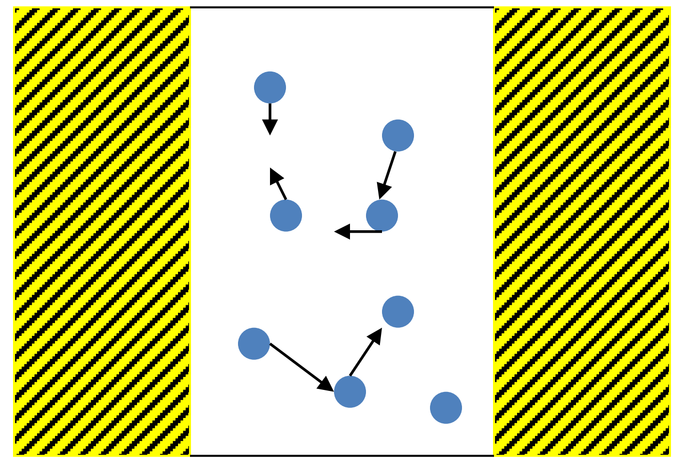
Kn>1



KNUDSEN DIFFUSION

Predominance of collisions between molecules and membrane walls

Kn<1



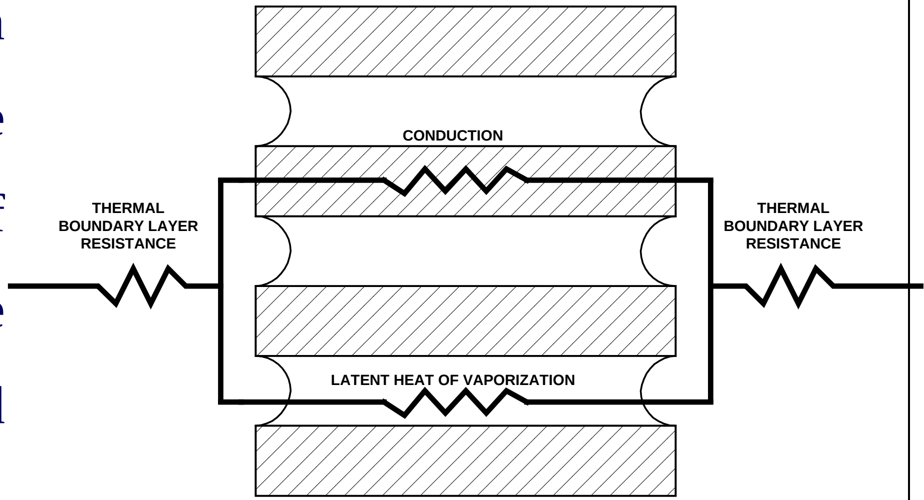
MOLECULAR DIFFUSION

Predominance of collisions between molecules

For saturated water at 60°C and 20 kPa, λ=0.7 mm. In many practical cases, λ is comparable to the typical pore size of MD membranes.

HEAT TRANSFER

The complex relations between simultaneous heat and mass transfer are generally described in terms of a set of serial and parallel resistances through the boundary layers of the membrane and through the membrane itself.



$$Q = \left[\frac{1}{h_f} + \frac{1}{h_m + J_i \Delta H_v / \Delta T_m} + \frac{1}{h_p} \right]^{-1} \Delta T$$

Total heat flux

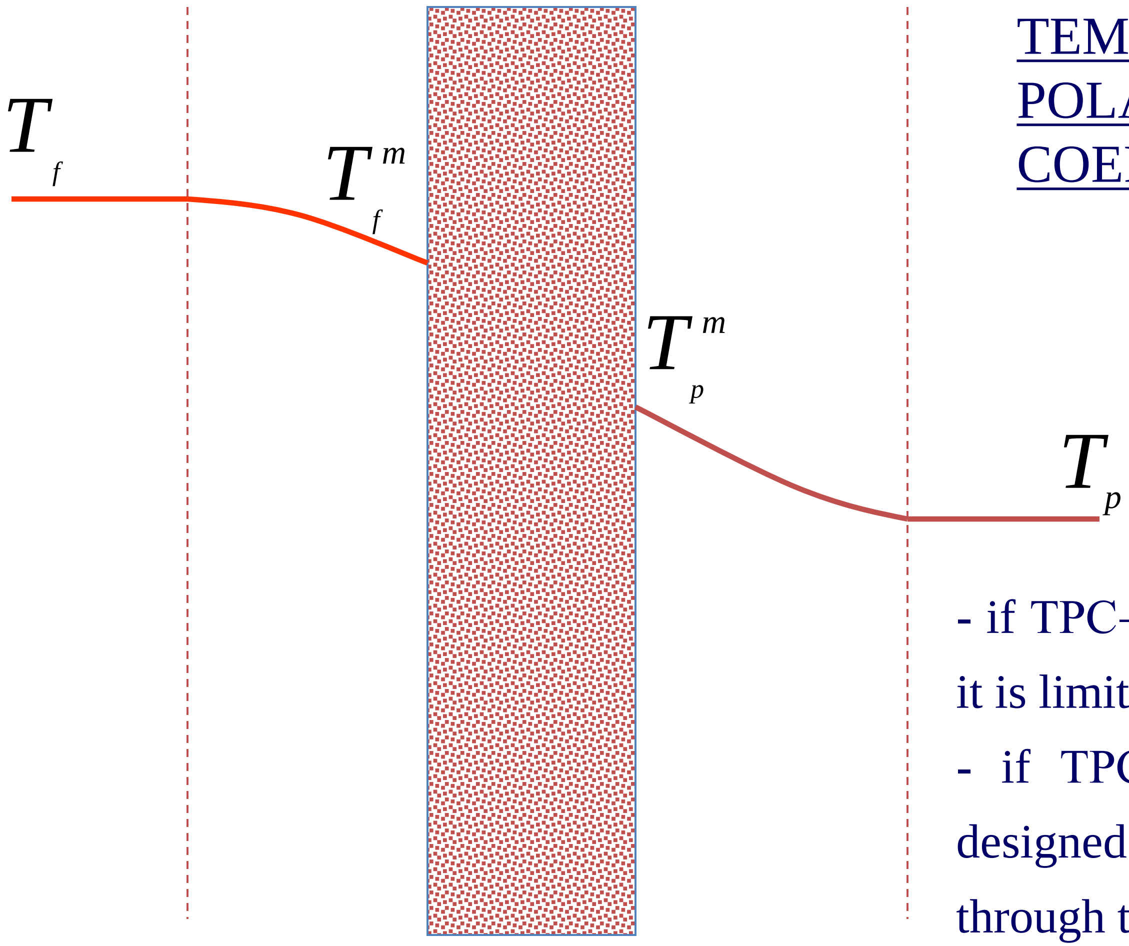
Heat transfer coefficients (feed/permeate)

conduction vaporization

MEMBRANE

HEAT TRANSFER BOUNDARY LAYERS (TEMPERATURE POLARIZATION)

The most unfavourable effect due to boundary layer resistances is the creation of a temperature difference between the bulk and the membrane surface where vapour-liquid transition occurs.



<u>TEMPERATURE POLARIZATION COEFFICIENT:</u>

$$TPC = \frac{T_f^m - T_p^m}{T_f - T_p}$$

- if TPC→1, the system is well designed and it is limited by mass transfer;
- if TPC→0 , the MD system is poorly designed and it is limited by heat transfer through the boundary layers.

HEAT TRANSPORT ACROSS THE MEMBRANE

The two important mechanisms of heat transfer across the membrane are:

1. the transfer of the latent heat (ΔH_v) of vaporization associated with the mass flux J: $Q_v = J \cdot \Delta H_v$
2. conduction through the membrane material and the vapor within the membrane pores: $Q_m = k_m \cdot \frac{\Delta T_m}{d}$ (d=membrane thickness)

$$k_m = (1-\varepsilon)k_s + \varepsilon k_g$$

ε =porosity

k_s=thermal conductivity of the solid membrane material

k_g=thermal conductivity of the vapor within the membrane

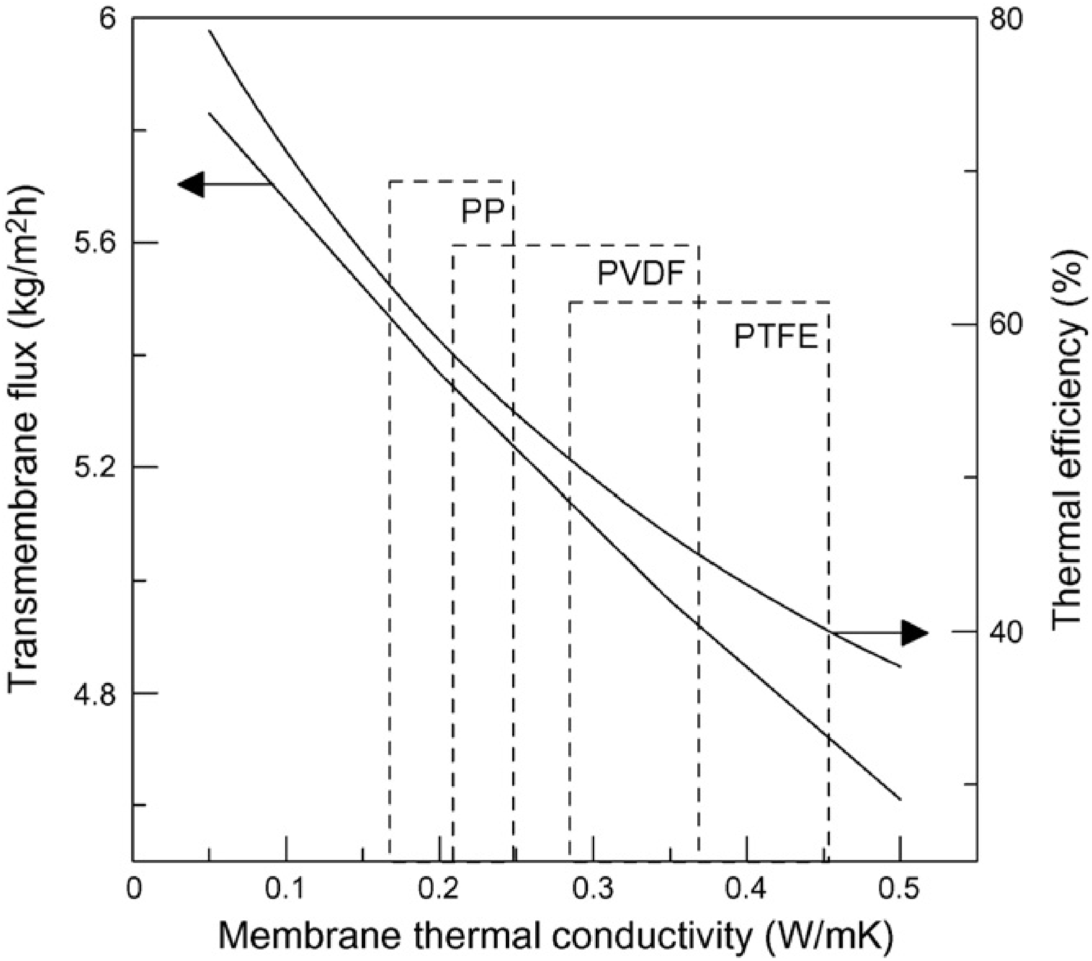
Polymer	Thermal conductivity ($W\ m^{-1}K^{-1}$)
Polypropylene	**0.11-0.16**
Polyvinylidenedifluoride	**0.17-0.19**
Polytetrafluoroethylene	**0.25-0.27**

$$k_{air} = 2.72 \cdot 10^{-3} + 7.77 \cdot 10^{-5} T$$

$$k_{H_2O} = 2.72 \cdot 10^{-3} + 5.71 \cdot 10^{-5} T$$

$$k_{H_2O}(60°C) = 0.022 W / m \cdot k$$

Since k_g is generally an order of magnitude smaller than k_s, heat lost by conduction through the membrane can be reduced by increasing the membrane porosity ε.



$$J \ \alpha \ \frac{\langle r^{\alpha} \rangle \varepsilon}{\tau \cdot \delta}$$

$\langle r^{\alpha} \rangle$ is the everage pore size

(for Knudsen diffusion : $\alpha = 1$,

for viscous flux : $\alpha = 2$)

$$\text{Thermal efficiency} = \frac{J \cdot \Delta H_v}{U \cdot \Delta T}$$

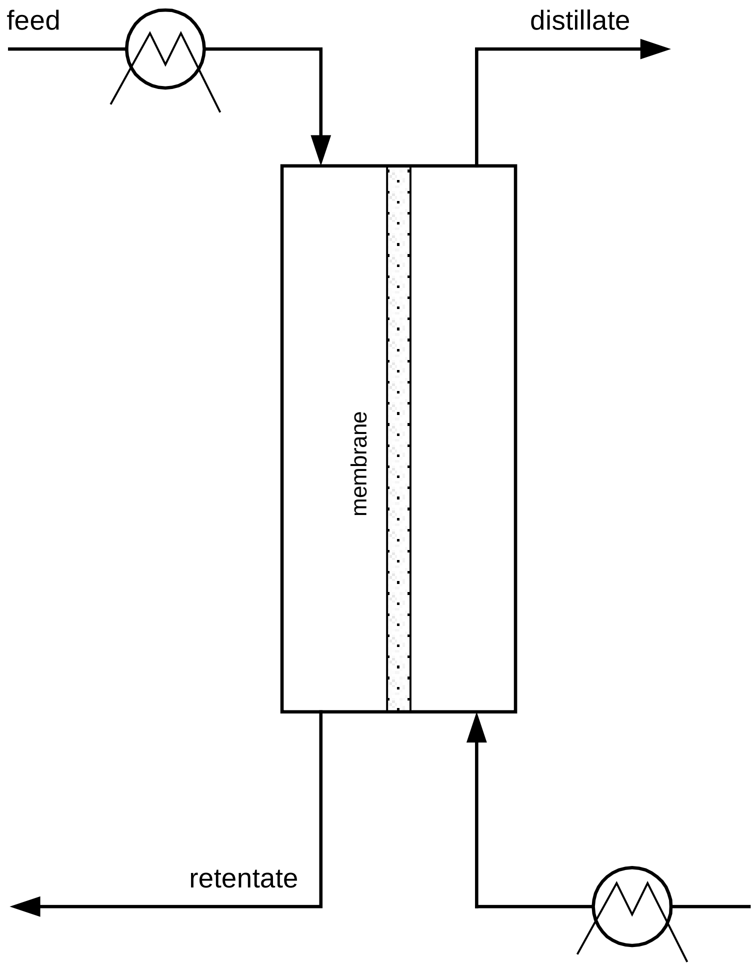
Effects of membrane thermal conductivity on simulated DCMD permeate flux and thermal efficiency (feed concentration: 35 g/L, inlet feed temperature: 55 °C, temperature d

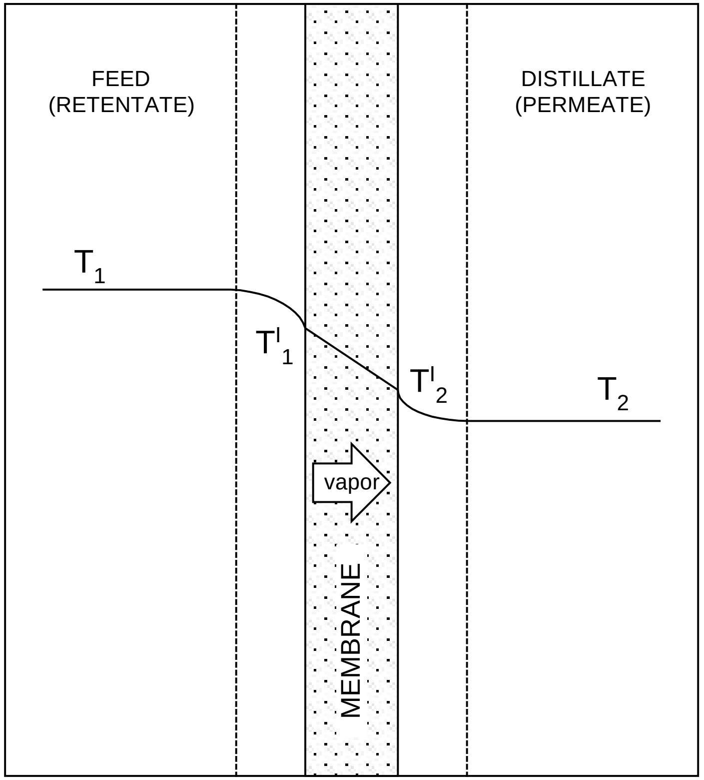
S. Al-Obaidani, E. Curcio, F. Macedonio, G. Di Profio, H.Al-Hinaid, E. Drioli, Journal of Membrane Science 323 (2008) 85–98.

The low to moderate flow rates and high heat transfer coefficients reduce the impact of concentration polarization, which is lower than that of the temperature polarization effect. In fact, boundary layers next to the membrane can contribute substantially to the overall transfer resistance: heat transfer across the boundary layers is often the rate limiting step for mass transfer because a large quantity of heat must be supplied to the membrane surface to vaporize the liquid, and because the membrane fabrication technology has improved in the last decades so much that the process has shifted away from being limited by mass transfer across the membrane to being limited by heat transfer through the boundary layers on either side of the membrane.

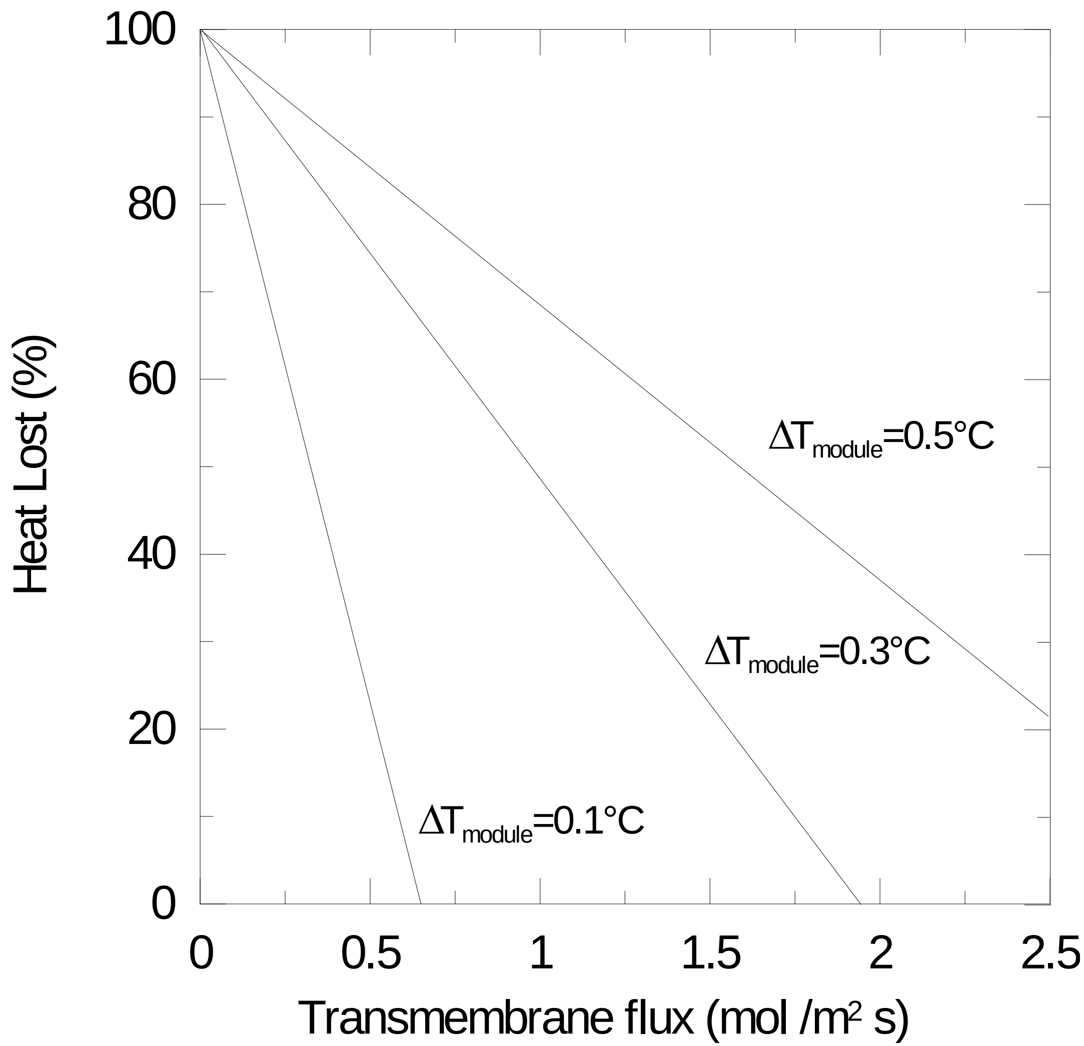
DIRECT CONTACT MEMBRANE DISTILLATION

DCMD represents the oldest and simplest configuration of membrane distillation. The liquid feed and the liquid distillate (or permeate) are kept in contact with the membrane and maintained at different temperatures.



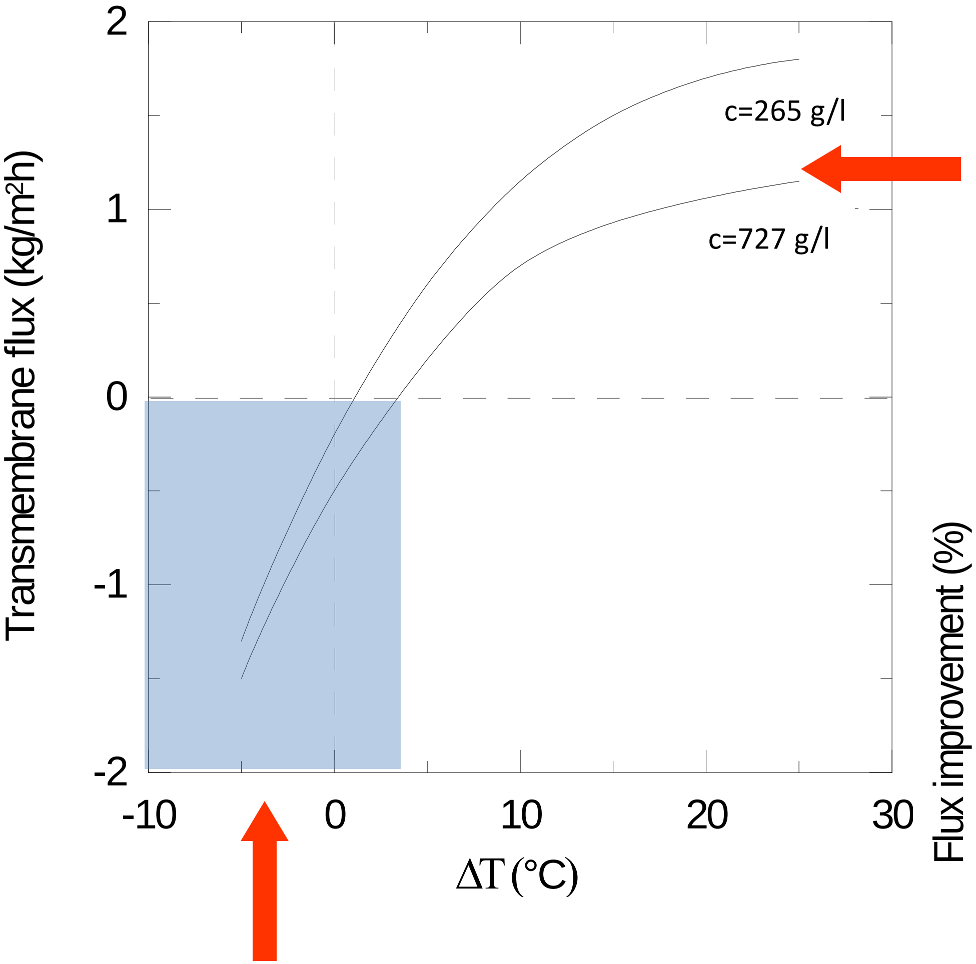


Temperature profile in DCMD



Percentage of heat lost by conduction in DCMD experiments with pure water (membrane module: 3M Corporation, feed flowrate: 1 gpm)

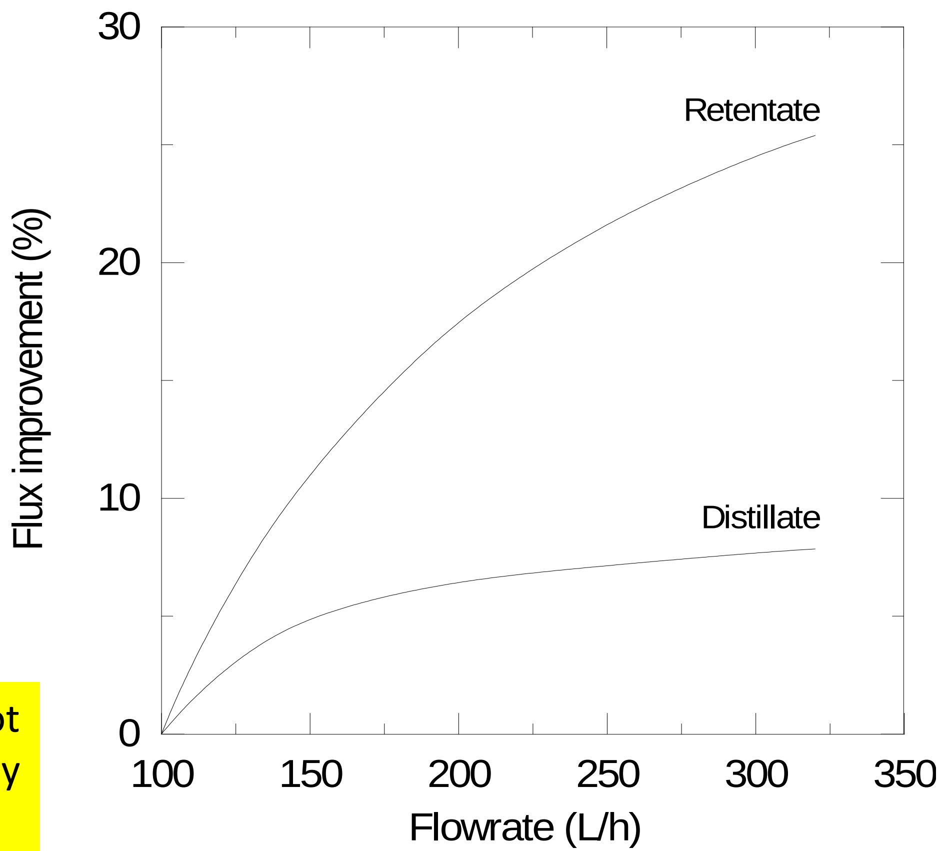
K.W. Lawson and D.R. Lloyd. Membrane distillation. II. Direct contact MD. J. Membrane Sci., 120 (1996) 123-133



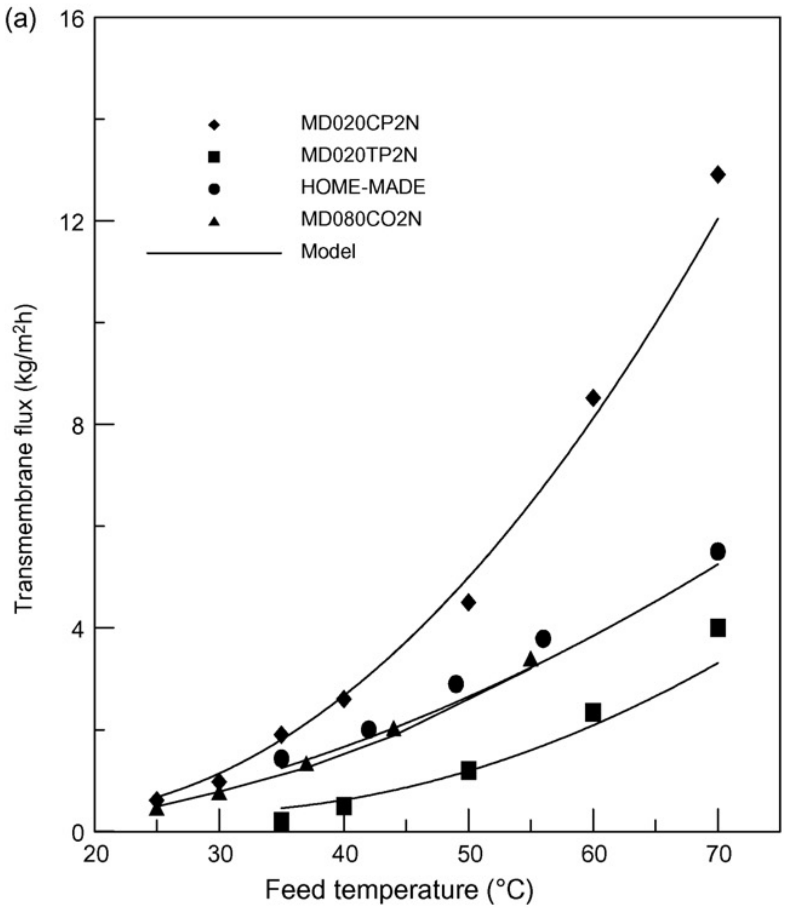
The shape of the curves depends on the way to set ΔT; in this case, the retentate temperature is keep constant and the distillate temperature is progressively decreased.

The net flux inverts its direction whenever ΔT is not sufficient to compensate the reduction of activity on the retentate side.

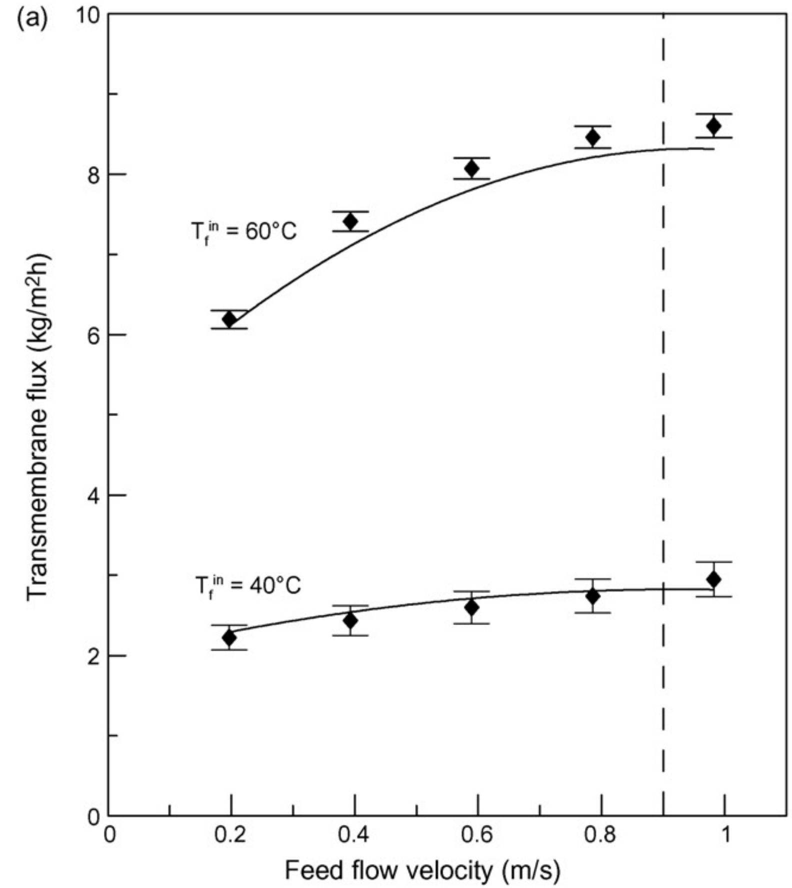
Effect of the feed apple juice concentration on the transmembrane flux versus ΔT (feed temperature: 32°C).



Variation of the transmembrane flux as function of feed and distillate flowrates (feed temperature: 29°C, ΔT =20°C).

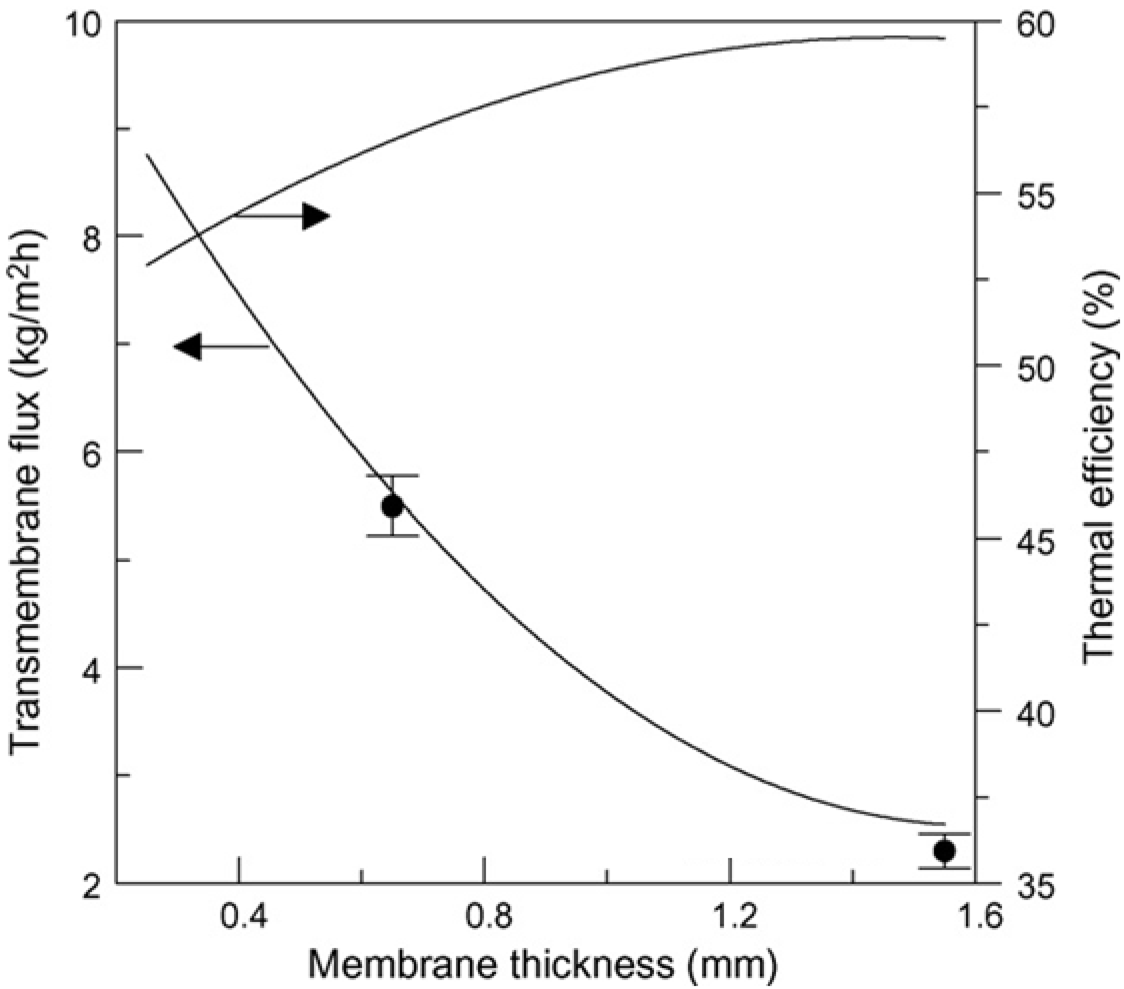


Thermal efficiency significantly enhances at higher feed temperatures.



Flux increases significantly with feed temperature and flow velocity.

S. Al-Obaidani, E. Curcio, F. Macedonio, G. Di Profio, H.Al-Hinai, E. Drioli, Journal of Membrane Science 323 (2008) 85–98.



Effects of themembrane thickness on the MD performance .

The transmembrane flux declines rapidly when the membrane thickness increases, as expected from the inverse proportional relationship between *J* and *δ*.

However, a conflict exists between the requirements of high mass transfer associated with thinner membranes and low conductive heat losses achieved by using thicker membranes. In fact, the thermal efficiency increases gradually as the membrane thickness increases.

MEMBRANE CHARACTERISTICS

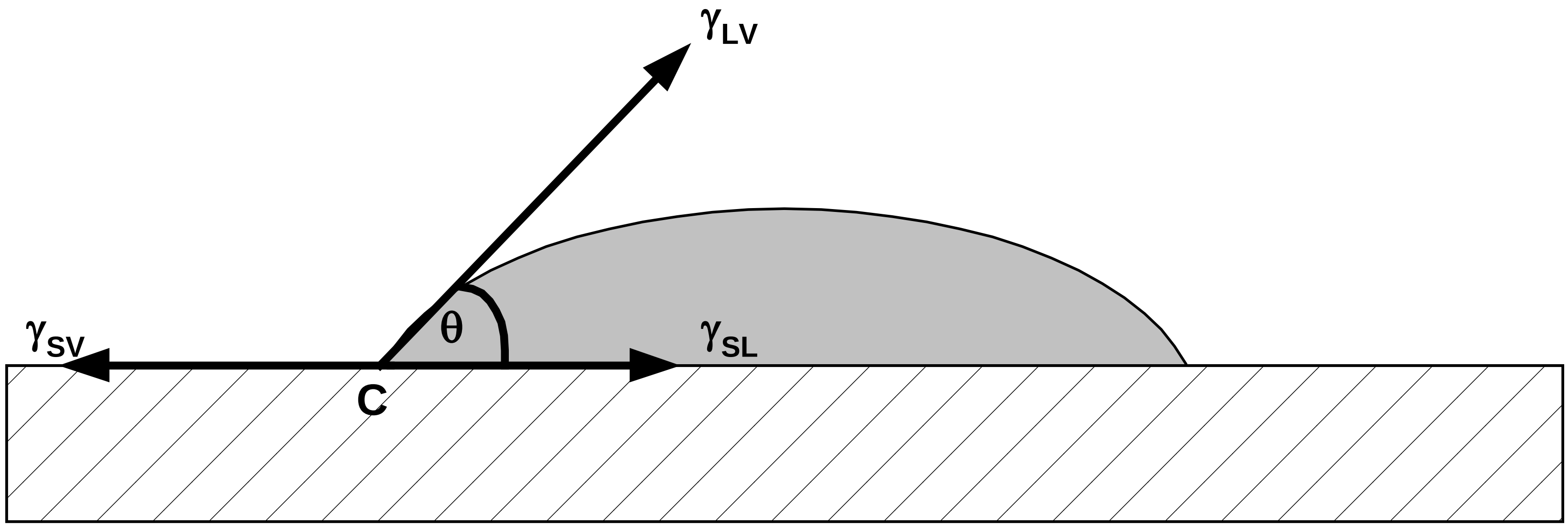
- **Morphology: symmetric or asymmetric porous**
- **Thickness: 20-100 mm**
- **Pore size: 0.1 – 1.0 mm (even if 0.2-0.3 mm is better)**
- **Membrane material:**

  - hydrophobic, hydrophobic/hydrophilic

  - resistant to alchools and surfactants
- **Membrane porosity: 70-80%**

HYDROPHOBIC PROPERTIES

Contact angle measurement is a traditional method to describe the hydrophobic or hydrophilic behaviour of a material. The value of the contact angle made by a liquid droplet deposited on a smooth surface is greater than 90° if the affinity between liquid and solid is low; in case of water, the material is considered hydrophobic.



Contact angle (θ) of a liquid droplet deposited on the surface of a solid. Representation of the thermodynamic equilibrium at the triple point C.

At the triple point C where solid-liquid vapour interfaces are in contact, the thermodynamic equilibrium is expressed by the Young equation:

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$$

γ_{LV}: *surface tension for liquid-vapour*

γ_{SV}: *surface energy of the polymer*

γ_{SL}: *solid-liquid surface tension*

Test liquid	γ_{LV} (mN/m)
Water	72.8
Glycerol	64
Ethylene glycol	48
Formamide	58
Dimethylsulfoxide	44
Chloroform	27.2
Diiodomethane	50.8
A-bromonaphthalene	44.4

NON IDEAL SURFACES

Young equation is rigorously applicable if the solid substrate is smooth, if the surface is homogeneous and rigid, chemically inert and insoluble to contacting liquids.

$$\cos\theta^* = f_1 \cos\theta - f_2$$

f1 and f2 are the fractions of liquid-solid and liquid-air surfaces

Franken, A.C.M., Nolten, J.A.M., Mulder, M.H.V., Bargeman, D., and Smolders, C.A. (1987) J. Membrane Sci., 33: 315–328

For PTFE membranes:

$$\cos\theta^* = y^2 \cos\theta - (1-y)^2 - 2y(1-y)\sqrt{\frac{\gamma_{SV}}{\gamma_{LV}} - \cos\theta}$$

If porosity (ε) < 0.5, 1-y = ε/τ

τ: pore tortuosity

Courel, M., Tronel-Peyroz, E., Rios, G.M., Dornier, M., and Reynes, M. (2001) 140: 15–25

MEMBRANE WETTING

LAPLACE EQUATION:

$$P_{liquid} - P_{vapor} = \Delta P_{interface} < \Delta P_{entry} = \frac{-2\,B\ \gamma \cos\theta}{r_{max}}$$

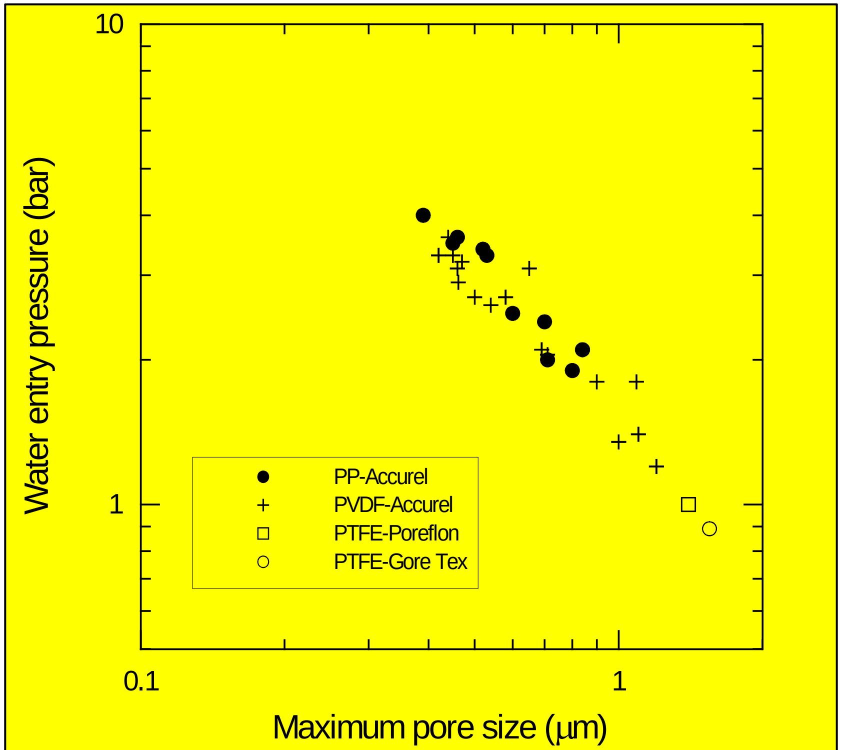
r_{max} : the largest allowable membrane pore size

g: interfacial tension

B: geometric factor related to the pore structure (= 1 for cylindrical pores)

θ: contact angle.

When the hydrostatic pressure on the feed side of a membrane exceeds Δp_{entry} (LEP_w = liquid entry pressure), liquid penetrates the pores and is able to pass through the membrane.



Water pressure entry for different membranes as a function of the maximum pore size

Modules: some examples

MD Serie (Microdyn)

COMPANY	MEMBRANE TYPE	AREA (m^2)	PORE SIZE (mm)
Microdyn	Capillary polypropylene	0.1 - 10	0.2
GVS SpA	Flat superhydrophobic	0.5 - 5	0.02-5
Celgard LLC	Hollow fiber polypropylene	0.5-220	0.03

Liqui-Cel Modules (Celgard)

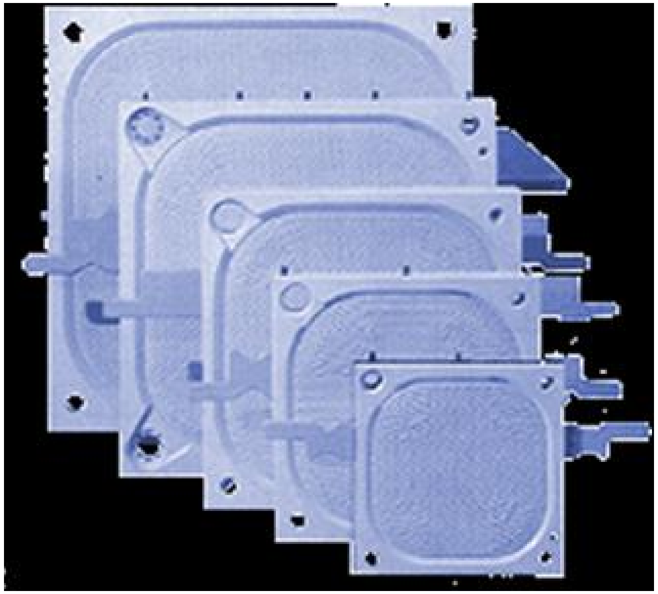
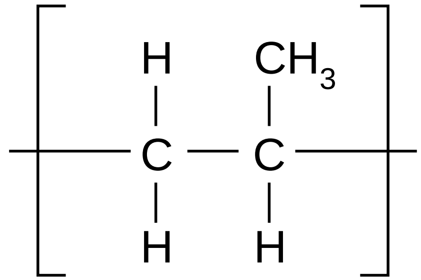
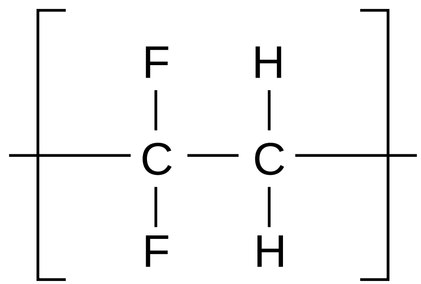
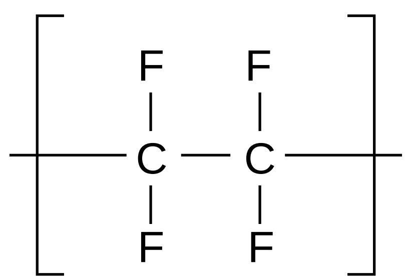


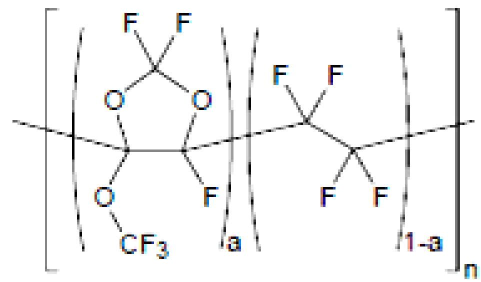
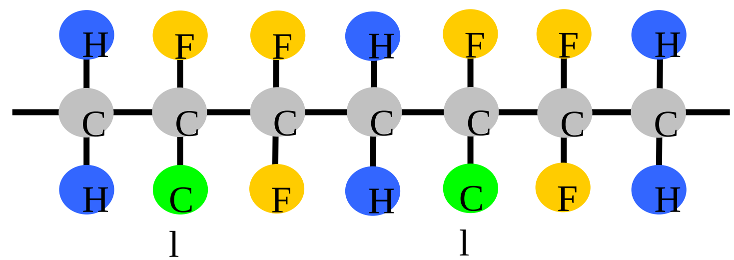
Plate & Frame Modules

MEMBRANE MATERIALS

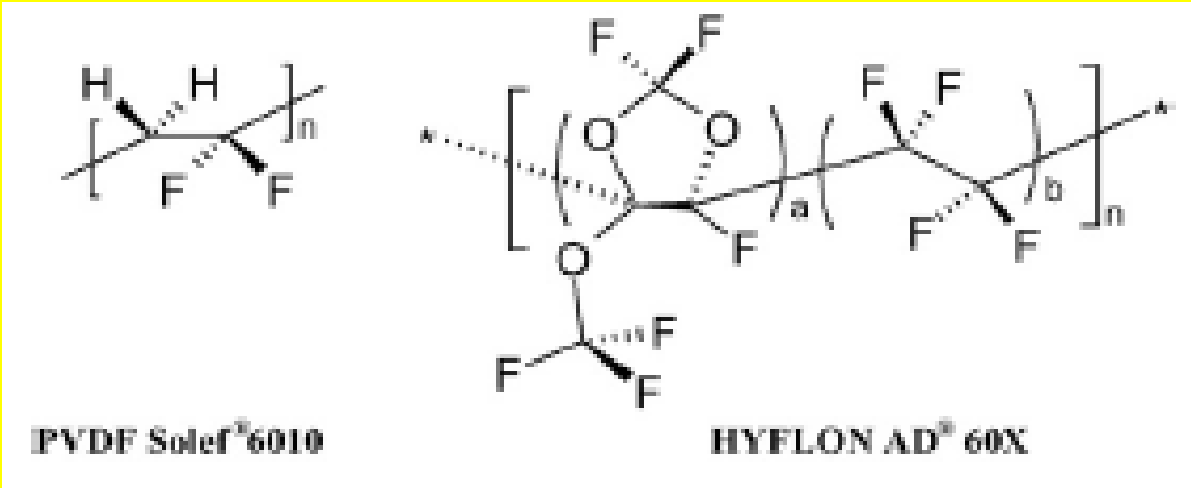
Polymers frequently used as material for microporous hydrophobic membranes.

POLYPROPYLENE		**Chemically resistant; hydrophobic**
POLY-VINYLIDENEFLUORIDE		**High temperature resistant; inherently hydrophobic**
POLY-TETRAFLUOROETHYLENE		**High temperature and chemical (acid) resistant; cannot be irradiated; inherently hydrophobic**

NEW MEMBRANE MATERIALS

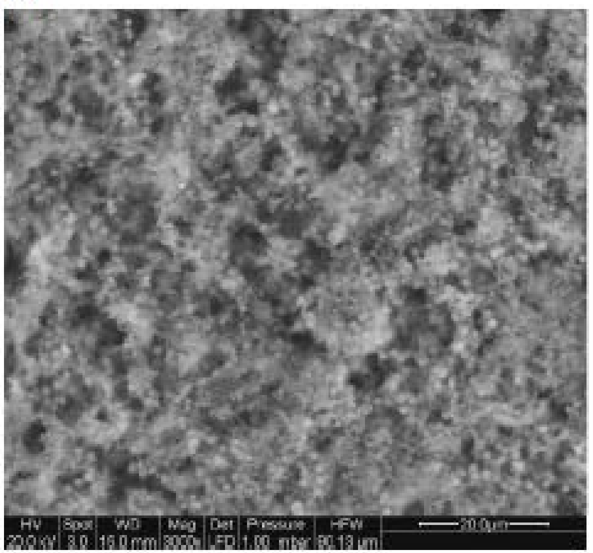
Hyflon AD		**Chemically resistant.**
ECTFE (Ethylene-Chlorotrifluoroethlyene copolymer)		**Resistant to a wide variety of corrosive chemicals and organic solvents, including strong acids, chlorine, caustic solutions and strong oxidizing agents**

PVDF and HYFLON AD composite membranes

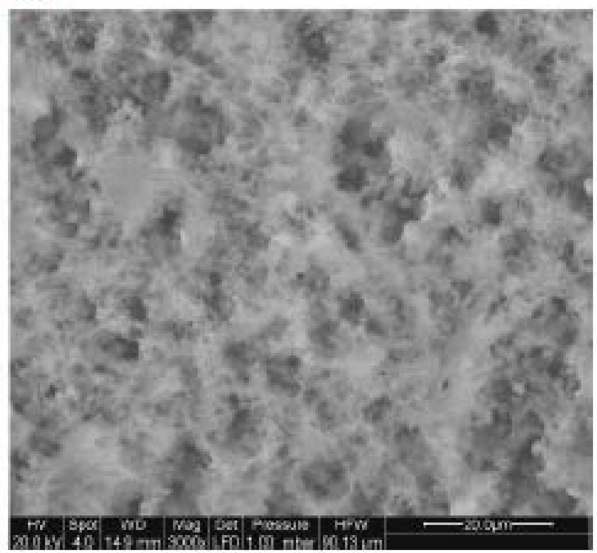


Chemical structure of PVDF and Hyflon AD 60x (a=0.6; b=0.4)

(a)

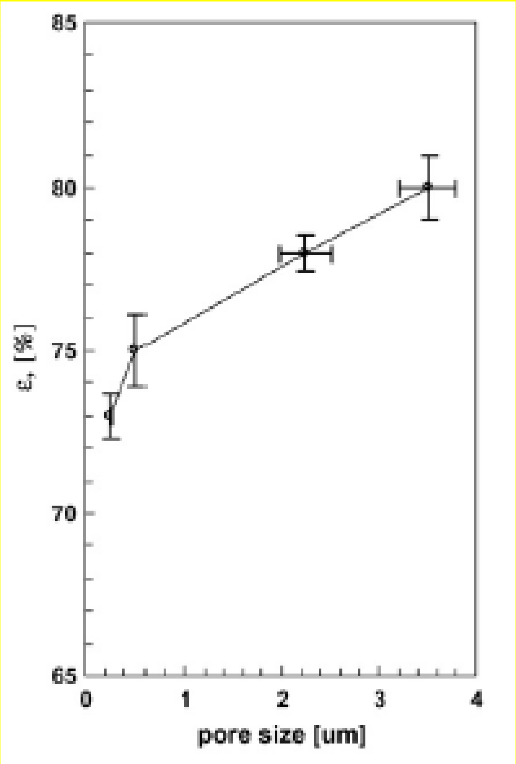


(b)

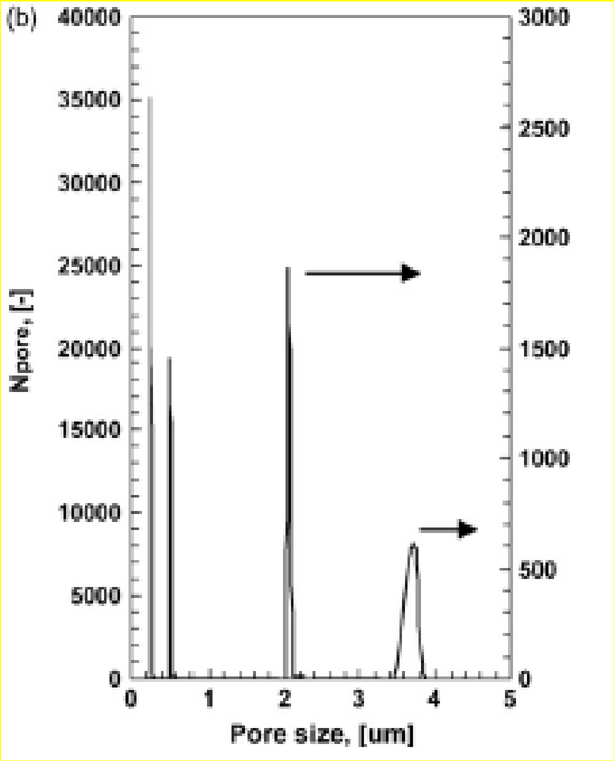


SEM images before (a) and after (b) HYFLON AD treatment (coated by HYFLON AD 60X (0.5 wt.%)).

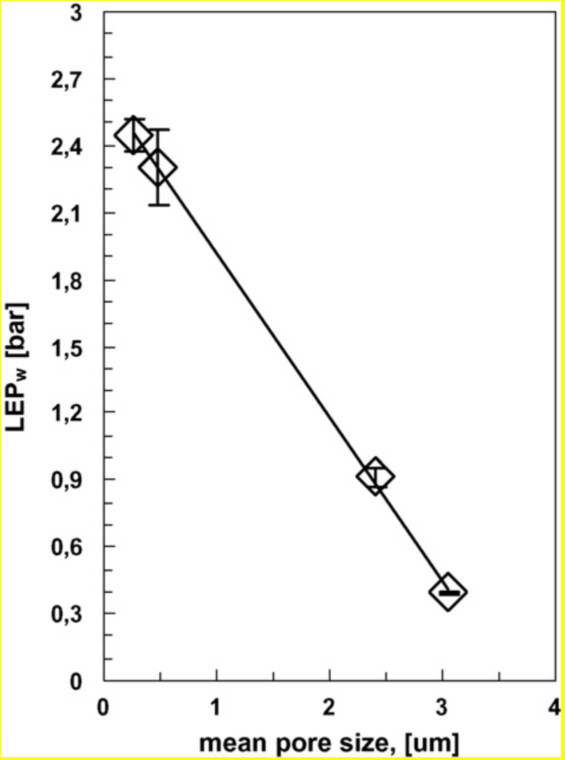
A. Gugliuzza, E. Drioli / Desalination 240 (2009) 14-20;
A. Gugliuzza, E. Drioli / J. of Membr. Science 300 (2007) 51–62.



Overall porosity vs. mean pore size for the PVDF membranes



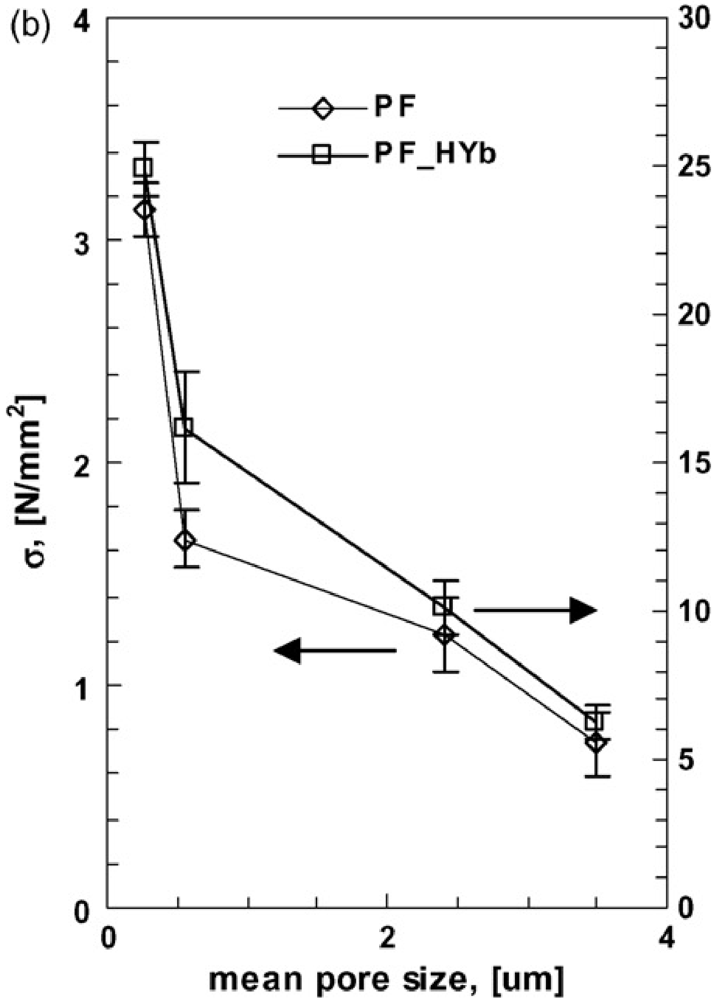
Pore distribution vs. mean pore size for the PVDF membrane



Resistance to LEP_w for the PVDF membrane

Narrow pore distribution, high overall porosity and high LEP_w for the PVDF.

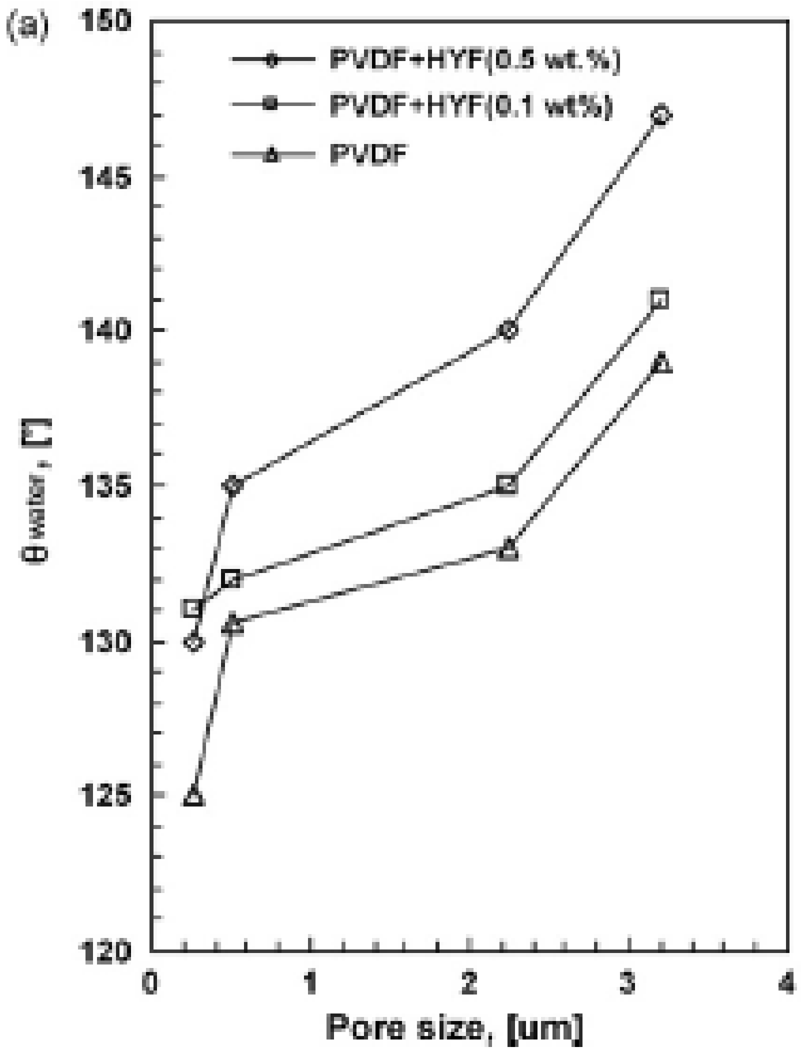
A. Gugliuzza, E. Drioli / Desalination 240 (2009) 14-20;
A. Gugliuzza, E. Drioli / J. of Membr. Science 300 (2007) 51–62.



Mechanical resistance was dramatically enhanced by coating the PVDF membranes with HYFLON AD.

Comparison of the mechanical resistance estimated for PVDF (PF) and PF-Hyb membranes: changes in tensile stress vs. mean pore size.

A. Gugliuzza, E. Drioli / Desalination 240 (2009) 14-20;
A. Gugliuzza, E. Drioli / J. of Membr. Science 300 (2007) 51–62.

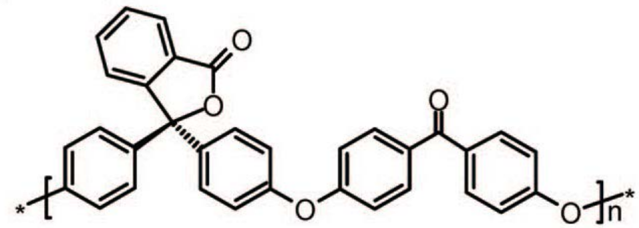


Contact angle values ranging from *126±3° to 141±4°* confirmed the super-hydrophobic character of the membranes.

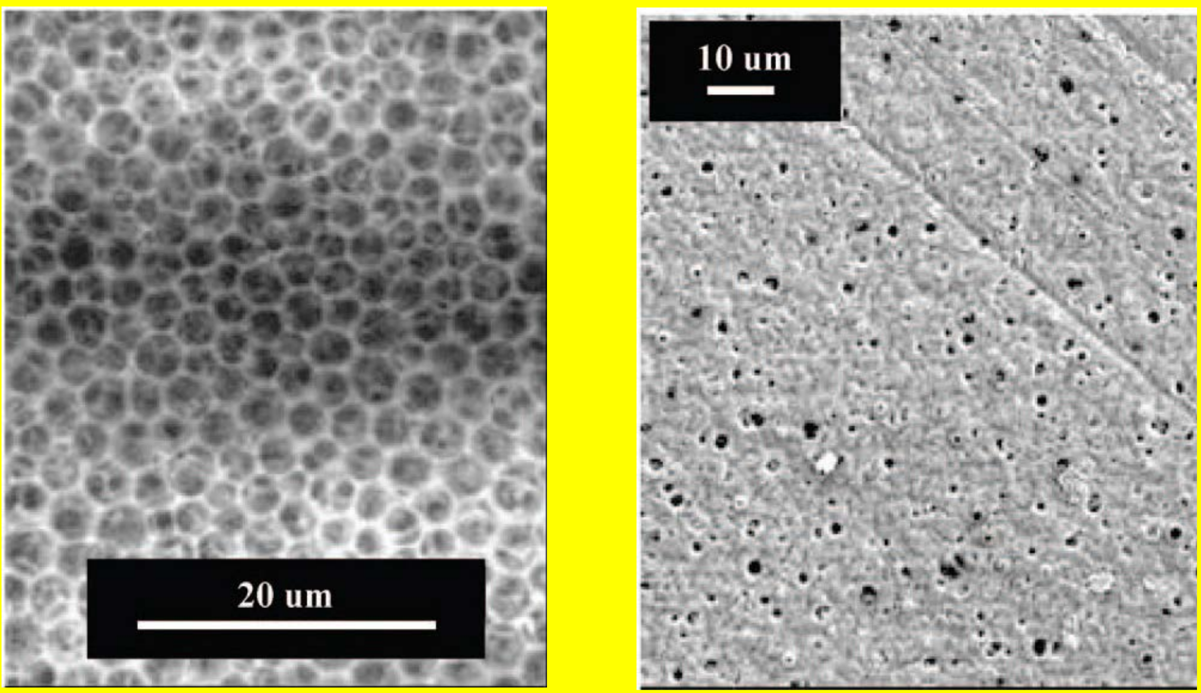
Other data from literature:

- Owens and Wendent , J. Appl. Polym. Sci. 13 (1996) 1741= *82°*
- Huang et al., J. Memb. Sci., 167 (2000) 275 = *75°*
- Nunes and Peinemann, J. Memb. Sci., 73 (1992) 25 = *80°*
-Khayet and Matsuura, Desalination, 148 (2002) 31 = *75.2° - 82.3°* (on unmodified PVDF); *112.5°* (on PVDF membranes modified)
-S. Simone et al. / J. of Memb. Science *364 (2010) 219–232* = *81° - 92°*

Self-Assembled Poly-(etheretherketone) with Cardo Membranes: *BF* PEEK-WC membranes



Chemical structure of PEEK-WC



(a) (b)

(a) SEM images showing the honeycomb packed geometry of the top surface of a PEEK-WC membrane fabricated by using the self-assembly technique; (b) SEM image showing the top surface of a PEEK-WC membrane prepared by dry-wet phase inversion.

- Surface porisity: up to 85%

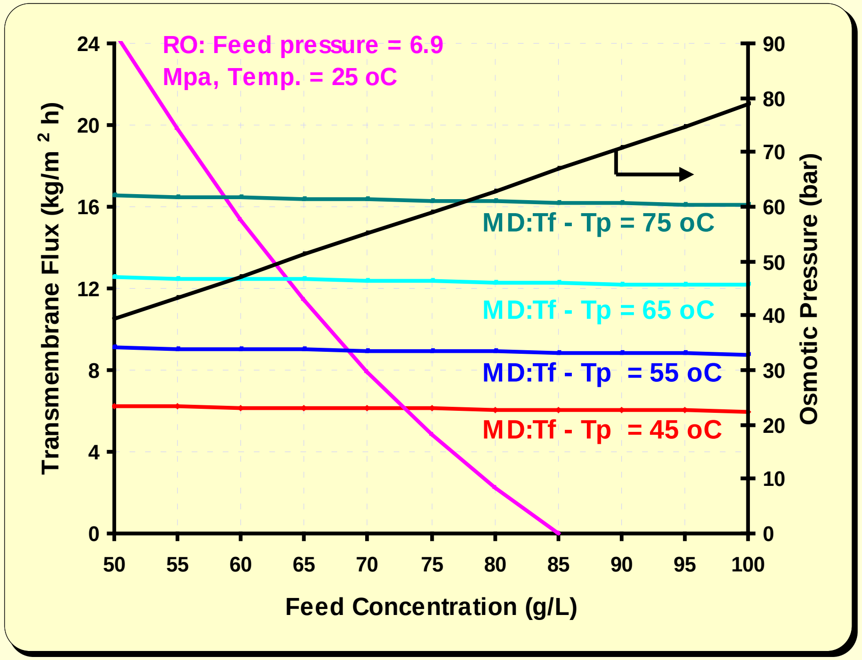
-Low wetting degree

- Contact angle = 130±3° (40° more with respect to PEEK-WC membranes (88 ± 2°) prepared by traditional techniques

A. Gugliuzza, F. Macedonio, et al., J. Phis. Chem. B, 2008, 112, 10483-10496.

Some of MD advantages with respect to conventional distillation and reverse osmosis

1. With respect to Reverse Osmosis (RO), the influence of concentration polarization on MD is limited



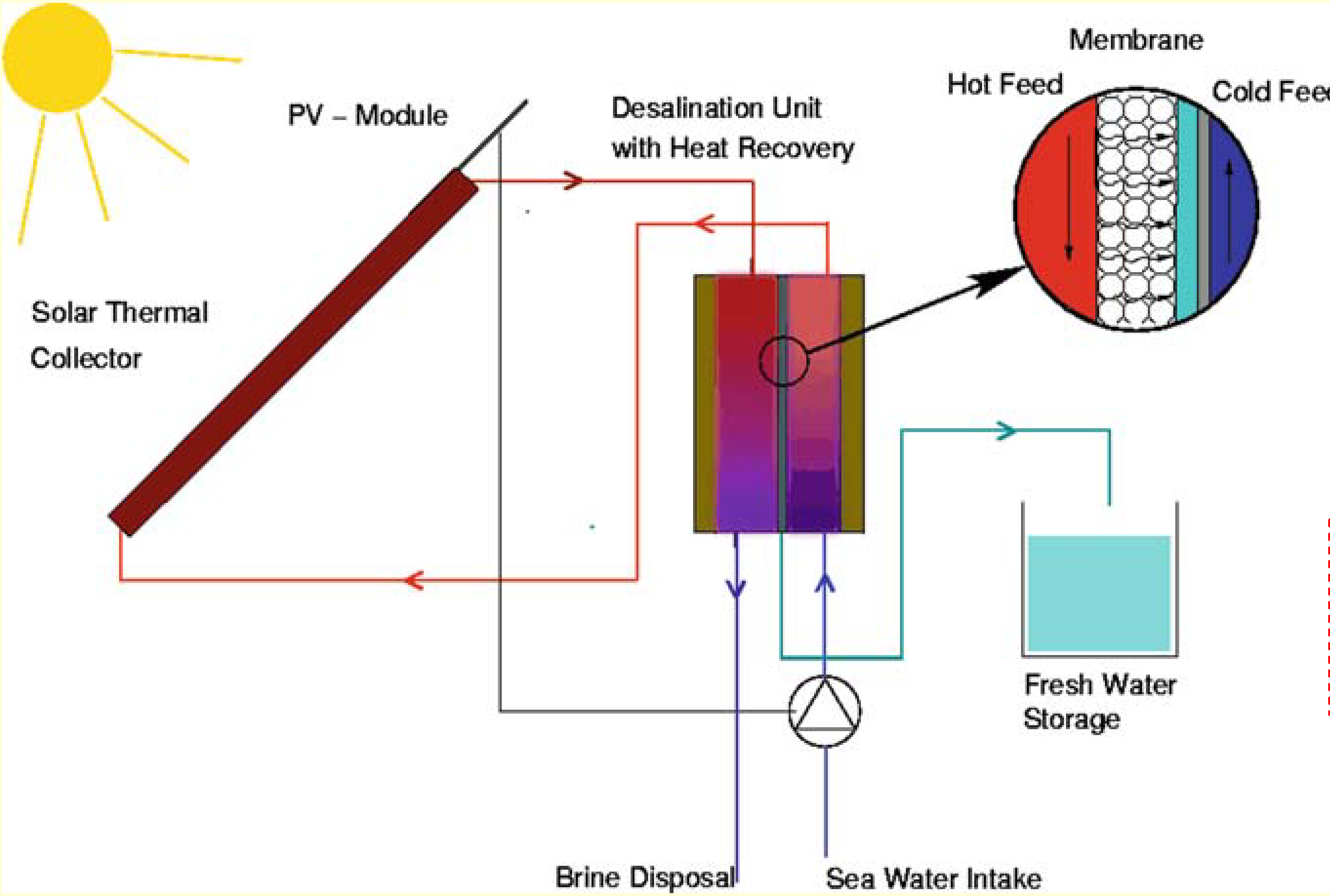
Some of MD advantages with respect to conventional distillation and reverse osmosis

2. Lower temperatures and pressures with respect to those usually used in conventional distillation columns. Possibility to reuse efficiently low-grade or waste heat streams, as well as alternative energy sources (solar, wind or geothermal)


Application in remote areas for drinking water supply of single houses or small communities.

Fraunhofer ISE - ec.europa.eu/dgs/jrc/.../jrc_aaas2011_energy_water_koschikowski.pdf.

Some of MD advantages. Solar MD Compact Systems

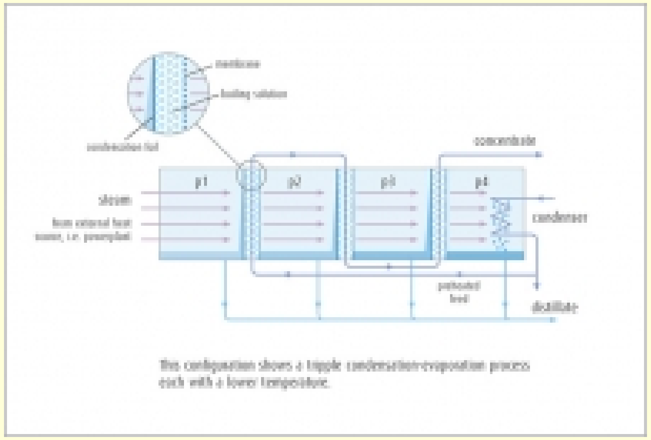


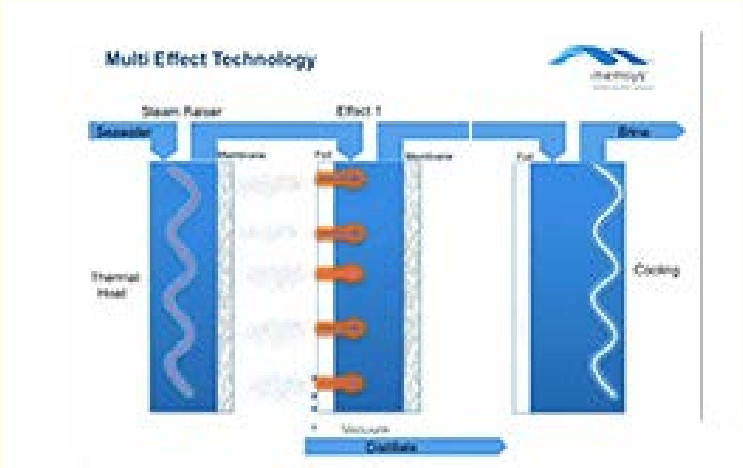
J. Koschikowski, M. Wieghaus, and M. Rommel, Membrane Distillation for Solar Desalination

In a solar MD compact System the cold feedwater is pumped by a PV powered pump into the condenser channel. The pre-heated feedwater, after leaving the condenser channel, enters the solar thermal collector, where its temperature is increased by 5–10 K. The feed water then leaves the collector to enter the evaporator channel.

memsys® - thermal Vacuum-Multi-Effect-Membran-Distillation (V-MEMD) system

Memsys clearwater distribution Pte Ltd has succeeded in combining the advantages of the most efficient thermal multi effect processes with MD into a very small modular configuration. The name of this new process is V-MEMD.

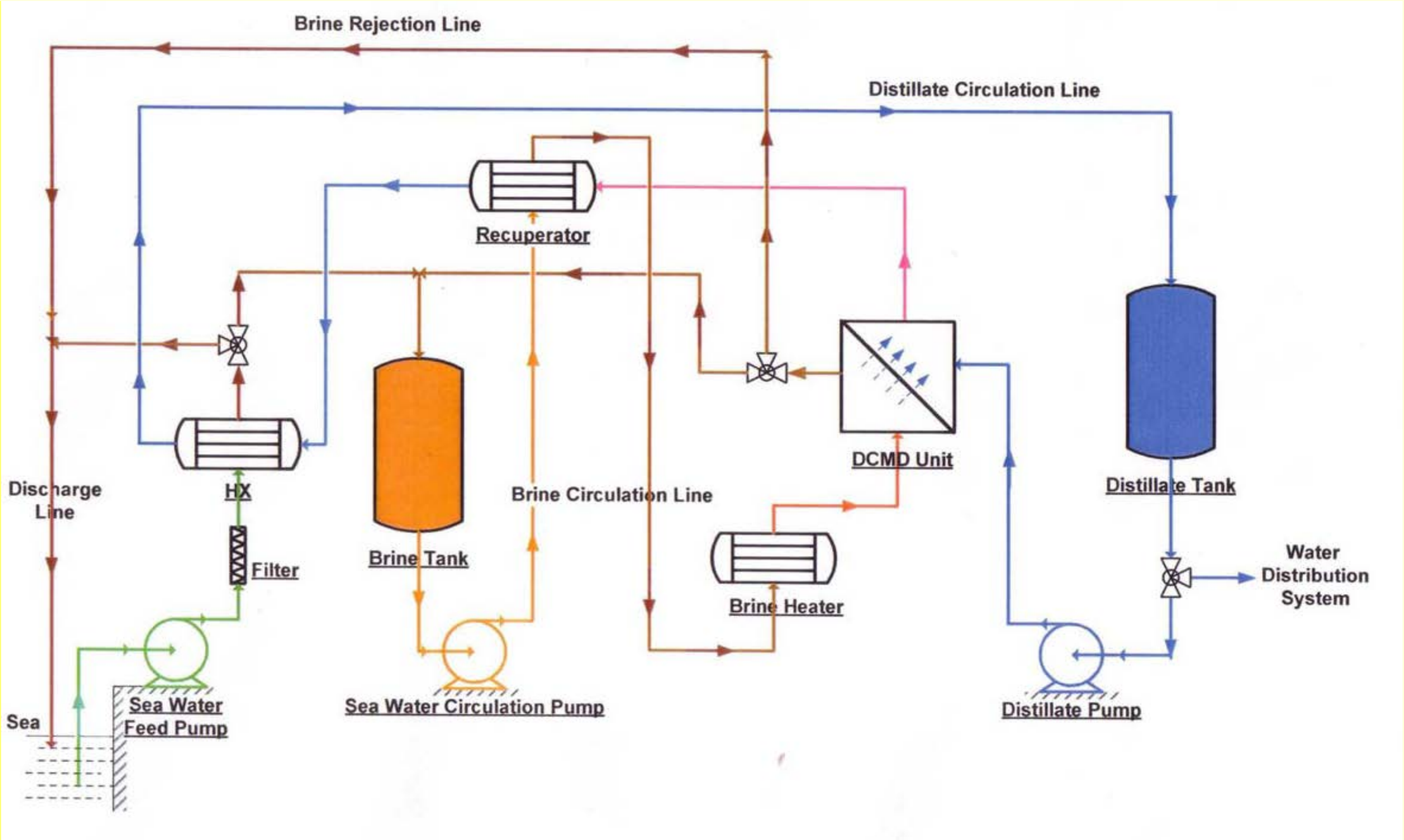




Advantages:

✓Energy advantages through the use of low level waste energy
✓Investment cost advantages though use of non steel materials
✓Operational cost advantages because of low maintenance
✓Ecological advantages because of less need of water treatment
✓Full modularity increases flexibility and scalability

Flow diagram of 1-mgd seawater DCMD desalination plant with hollow fiber heat exchangers for heat recovery



The distillate is heated up by the DCMD process, and the brine is concentrated and cooled down. Most of the concentrated brine is recirculated, and only a small part of the brine is rejected back to the sea. The heat from the distillate is recovered via a recuperator (distillate heat recovery heat exchanger) by the brine, which consisted of the recycled brine stream and fresh seawater. The distillate coming out of the recuperator (distillate heat recovery heat exchanger) needed to be cooled further before introduction into the DCMD unit. Seawater heat exchanger is used to provide this cooling.

Kamalwah K. Sirkar and Liming Song compare the cost of *RO*** and the cost of *DCMD with hollow fiber heat exchangers*:

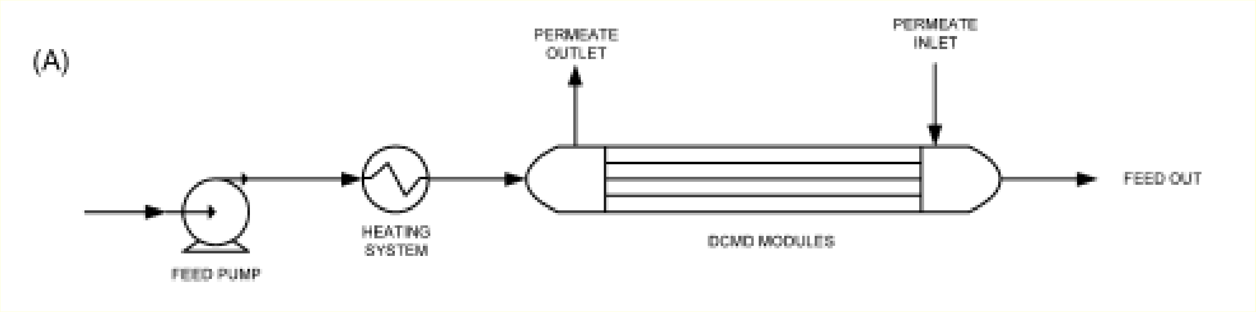
- without considering the cost of waste heat, the total production cost of water
by the DCMD process is $0.60/m^3, which is much cheaper than RO ($1.02/m^3);
-when the cost of steam is taken into account, DCMD water cost is = 0.76 – 1.04 $/m^3 (depending on the steam cost).

Moreover, DCMD can produce a water product of much lower salinity (less than 1 ppm in our pilot-scale studies) than single-pass RO (> 200 ppm). Therefore, DCMD would look even economically better compared with RO for the production of high-purity water.

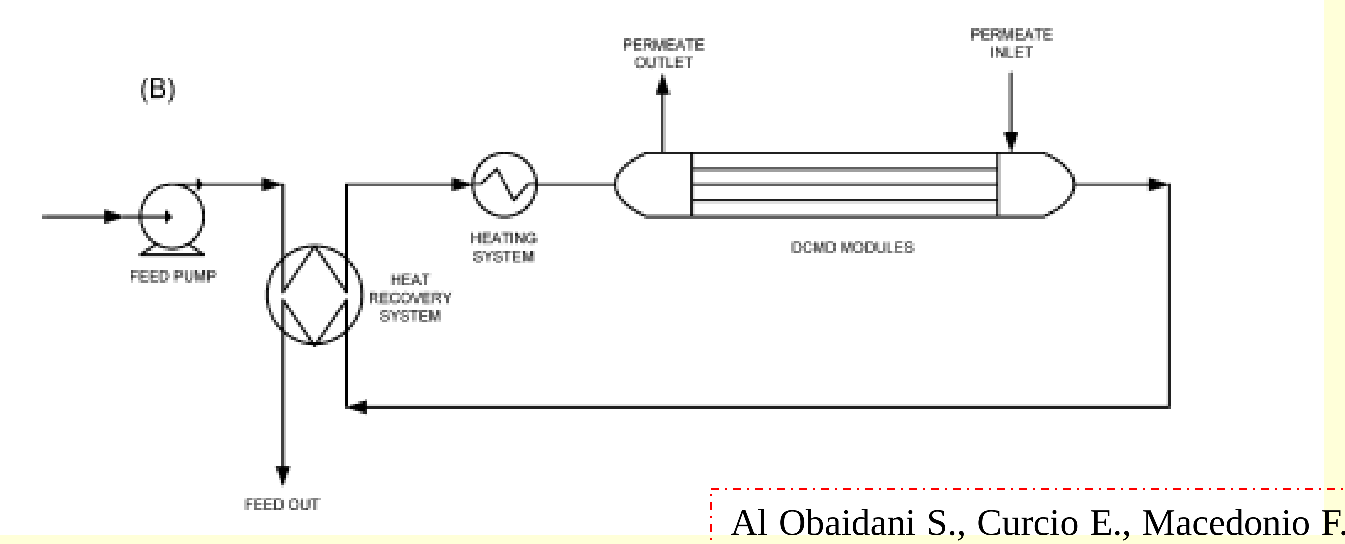
** RO operative conditions: operating pressure 1,000 psi; 30% recovery; energy recovery, 30%; lifetime 3 years)

Kamalwah K. Sirkar and Liming Song, Desalination and Water Purification Research and Development Program Report No. 134, U.S. Department of the Interior Bureau of Reclamation, September 2009

Al Obaidaini et al, compared the cost of *DCMD operated without heat recovery (HR) system* and the cost of *DCMD with HR system* (heat recovery efficiency of 80%)

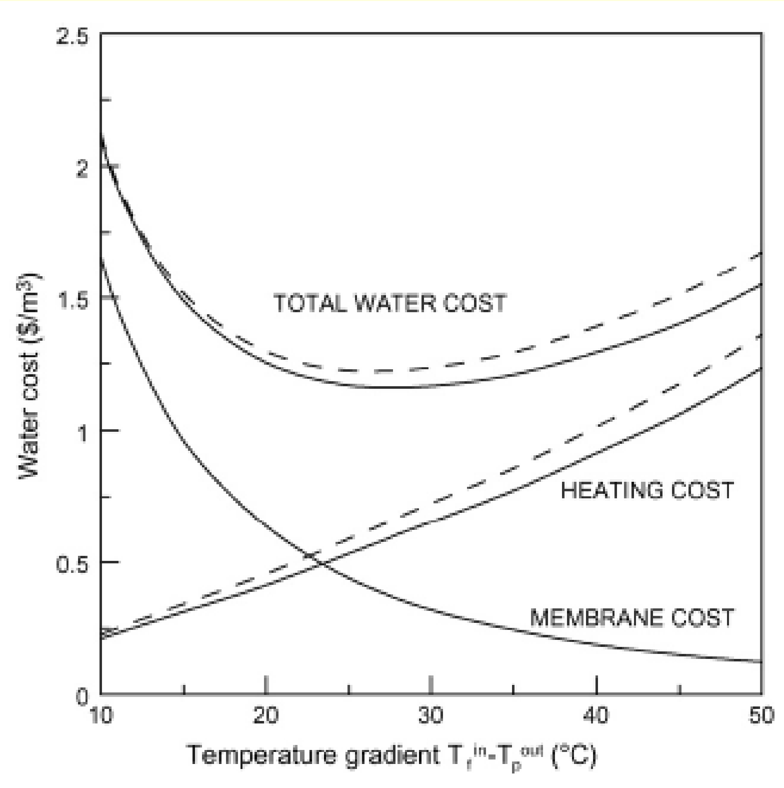


Scheme of Direct Contact Membrane Distillation (DCMD) operating: (A) without heat recovery (HR) system and (B) with HR system



Al Obaidani S., Curcio E., Macedonio F., Di Profio G., Al Hinai H., Drioli E., Journal of Membrane Science, 323 (2008) 85-98.

Al Obaidaini et al, compared the cost of *DCMD operated without heat recovery (HR) system* and the cost of *DCMD with HR system* (heat recovery efficiency of 80%)



Effects of temperature difference on the water cost for DCMD without HR system (dotted line) and for DCMD with HR system (solid line)

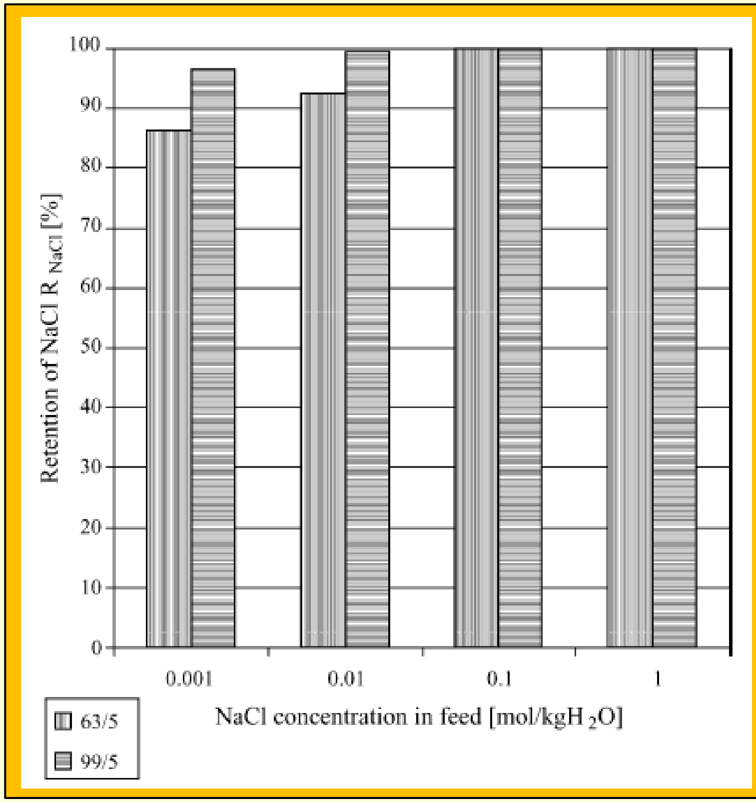
The minimum water cost is $1.23m^3 for DCMD without HR (feed temperature= 55 ◦C, DT = 25 ◦C).
The minimum water cost is $1.17m^3 for DCMD with HR (feed temperature close to 60 ◦C and DT=30).

An increase in the T difference increases permeate flux so decreasing the required membrane area and the capital cost. On the other hand, a higher T difference requires more heat energy input which increases the operational costs. Consequently, an optimization between the membrane costs and the heating costs must be considered in order to obtain the best performance with minimum unit cost of water.

Al Obaidani S., et al., Journal of Membrane Science, 323 (2008) 85-98.

3. Another MD advantage: Very high rejection *(around 100%)* of non-volatile solutes such as macromolecules, colloidal species, ions etc.

DCMD experimental results with NaCl and $CaCl_2$ aqueous solutions		
Membrane	**Solute rejection calculated from the measured total electrical conductivity**	**Solute rejection calculated from the measured Ca^{2+} concentration**
GVHP	**99.5%**	**99.7%**
TF200	**99.6%**	**99.8%**
Source: M. Khayet*, J.I. Mengual, Desalination, 168 (2004) 373-381.		



Retention coefficient for NaCl solutions at different concentration in MD process using fluoroalkylsilanes grafted zirconia membrane. Feed/permeate temperatures: 63°C/5°C and 99°C/5°C.

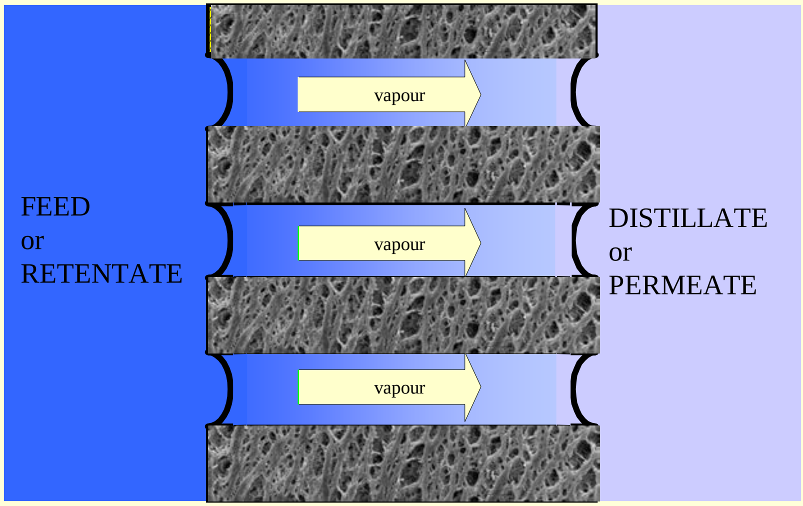
Source: S.R. Krajewski et al. / Journal of Membrane Science 281 (2006) 253–259.

MEMBRANE

CRYSTALLIZERS

MCr technology

Membrane crystallization (MCr) has been recently proposed as one of the most interesting and promising extension of the MD process



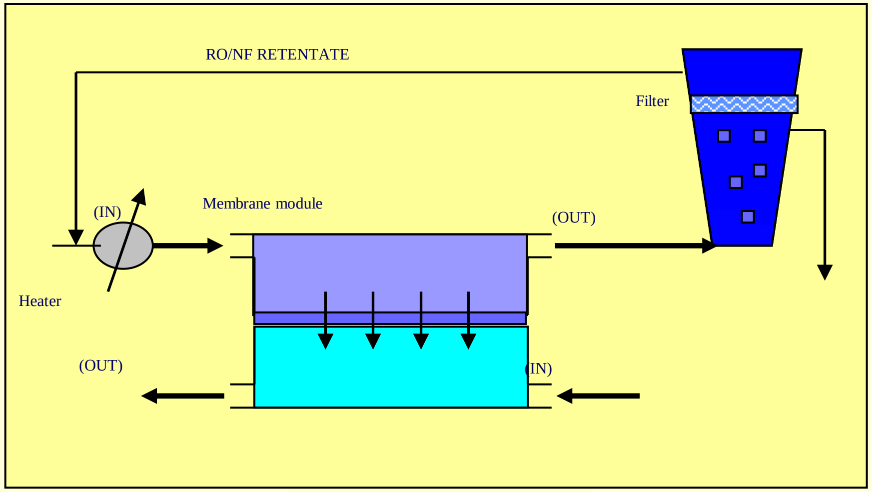
Mcr principle

Driving force: *partial pressure difference*

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

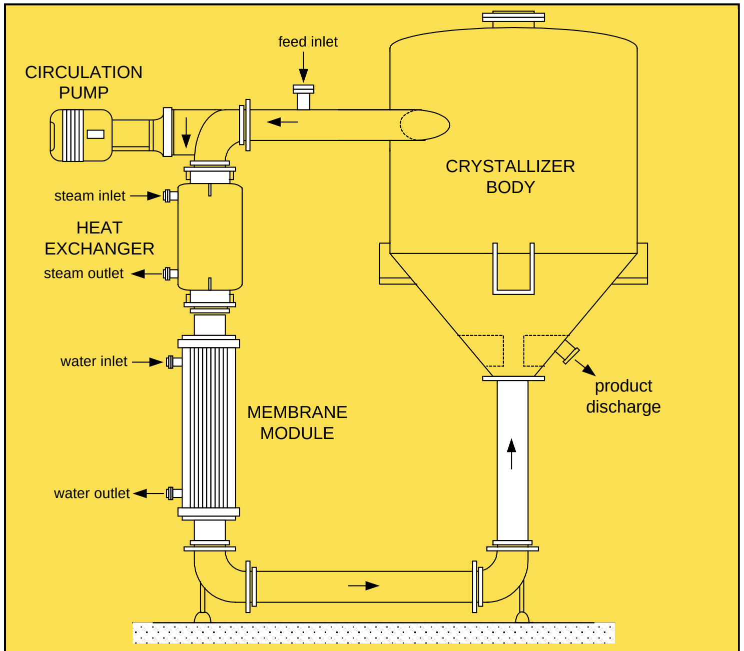
✓ The process is not limited by concentration polarization phenomena as it is the case in pressure driven operations ➡ pure water can also be obtained from highly concentrated feeds with which RO cannot operate.

✓ In MCr the membrane induces heterogeneous nucleation.

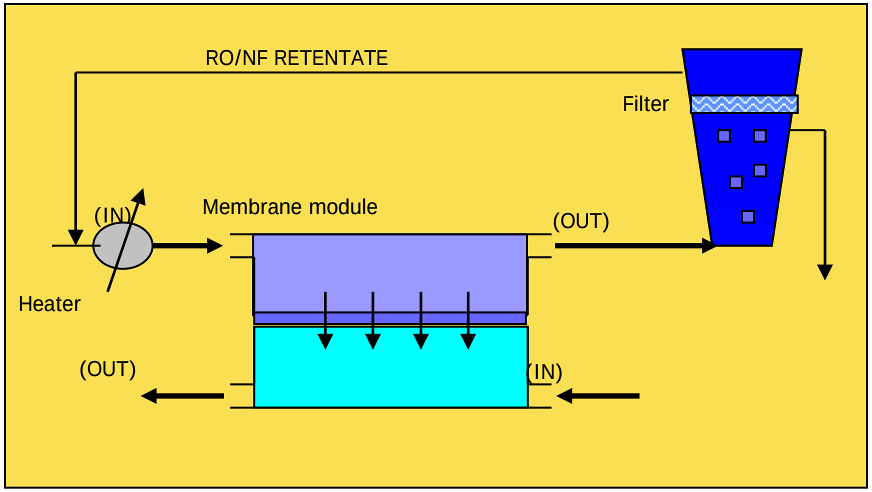


MCr process

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):

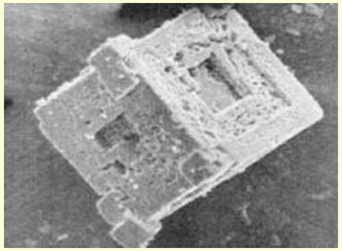
- if $\mathbf{K_{sp} > (IP)}$ the solution is not saturated and the precipitation doesn't occur;
- if $\mathbf{K_{sp} = (IP)}$ the solution is saturated;
- if $\mathbf{K_{sp} < (IP)}$ solid will precipitate until the saturation concentration is reached.

Advantages of Membrane Crystallization compared to traditional techniques (1)

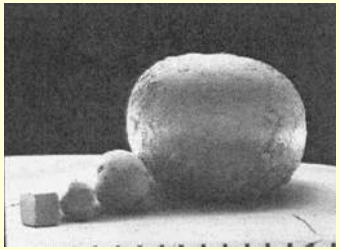
- ✓ High specific area for mass transfer
- ✓ Optimal control of the supersaturation level
- ✓ Shorten induction periods
- ✓ High values of the crystal growth rate at low supersaturation
- ✓ Possibility to act on the heterogeneous nucleation choosing appropriate polymeric membrane

Advantages of Membrane Crystallization compared to traditional techniques (2)

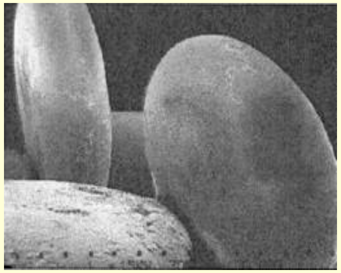
NaCl from a
membrane crystallizer



NaCl from a
Forced Circulation
crystallizer



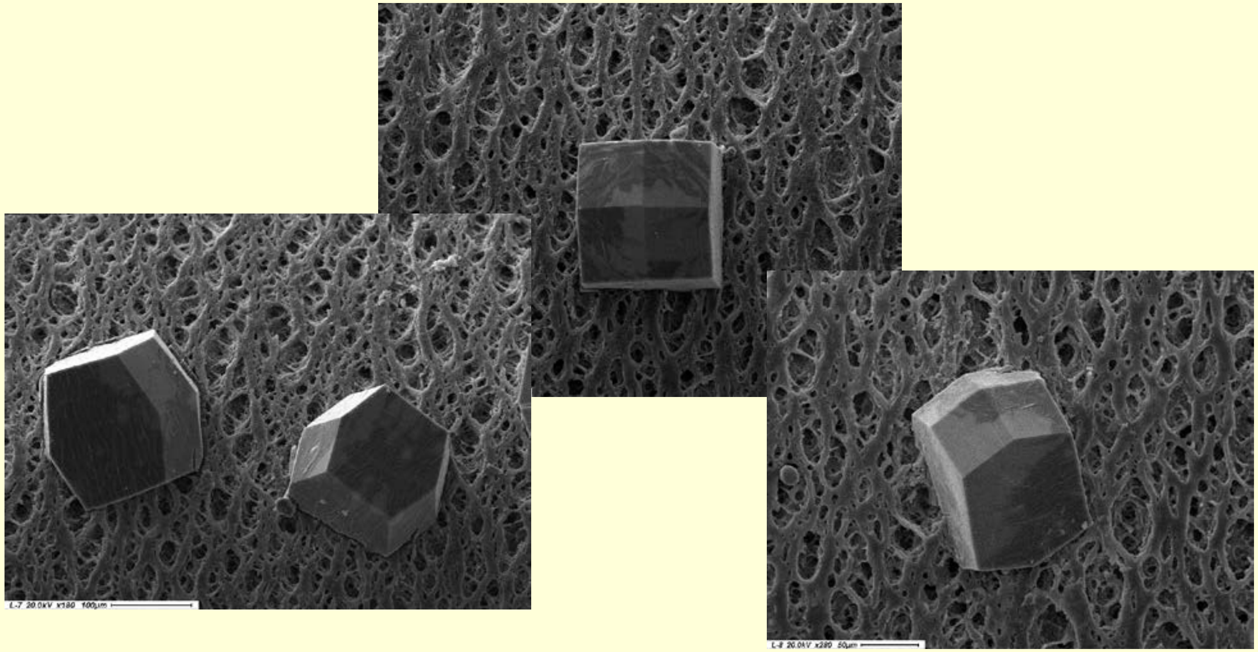
NaCl from a Draft Tube
Buffled crystallizer



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)



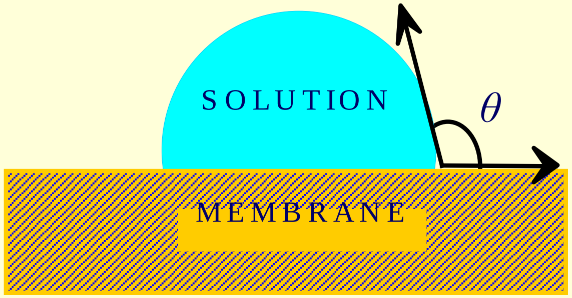
Lysozyme crystals grown on PP microporous hydrophobic membrane

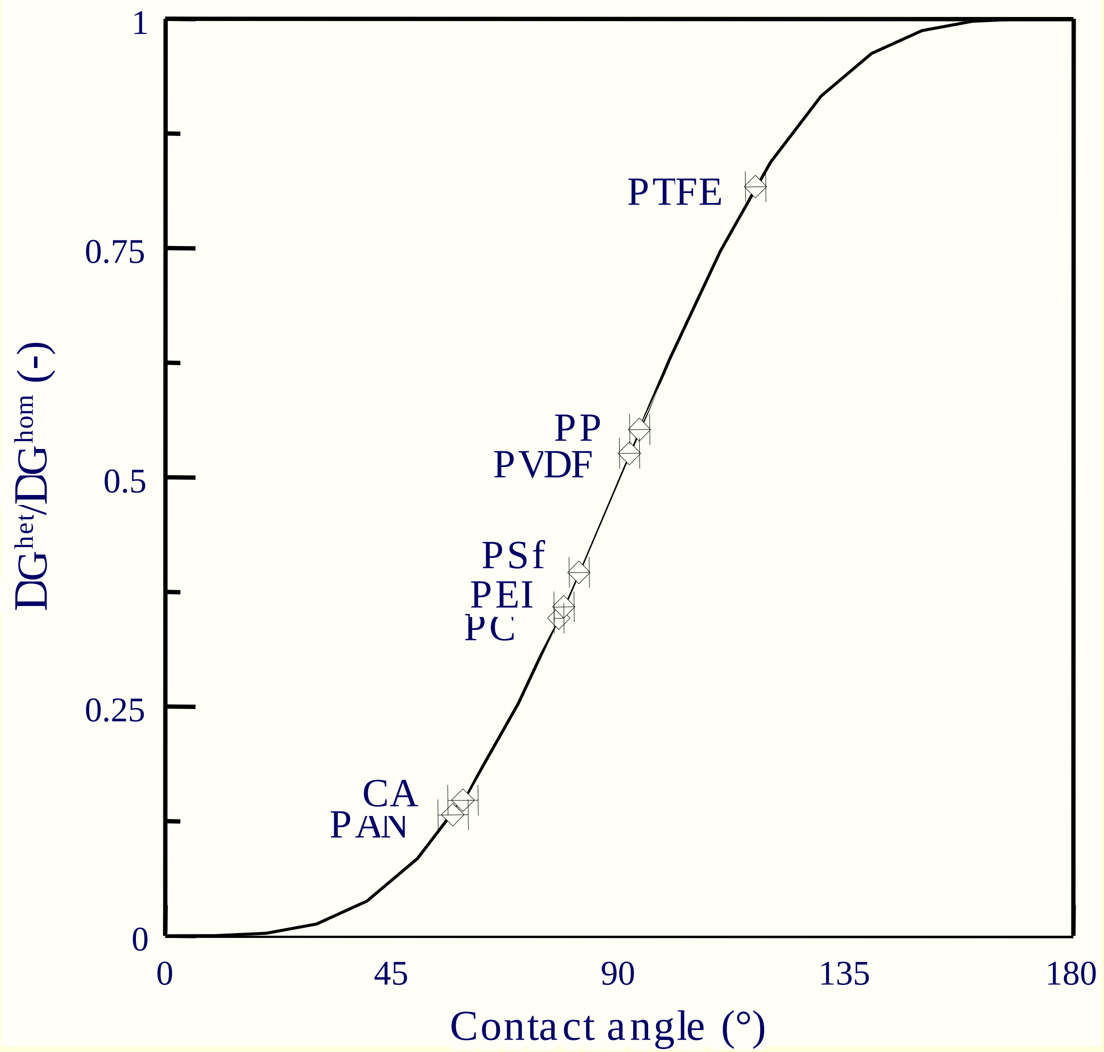
✓ The presence of the polymeric membrane increases the probability of nucleation with respect to other locations in the system (heterogeneous nucleation)

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 hydrophobic character of the material is strictly associated with the activation energy of the nucleation, which is the primer of the crystallization processes





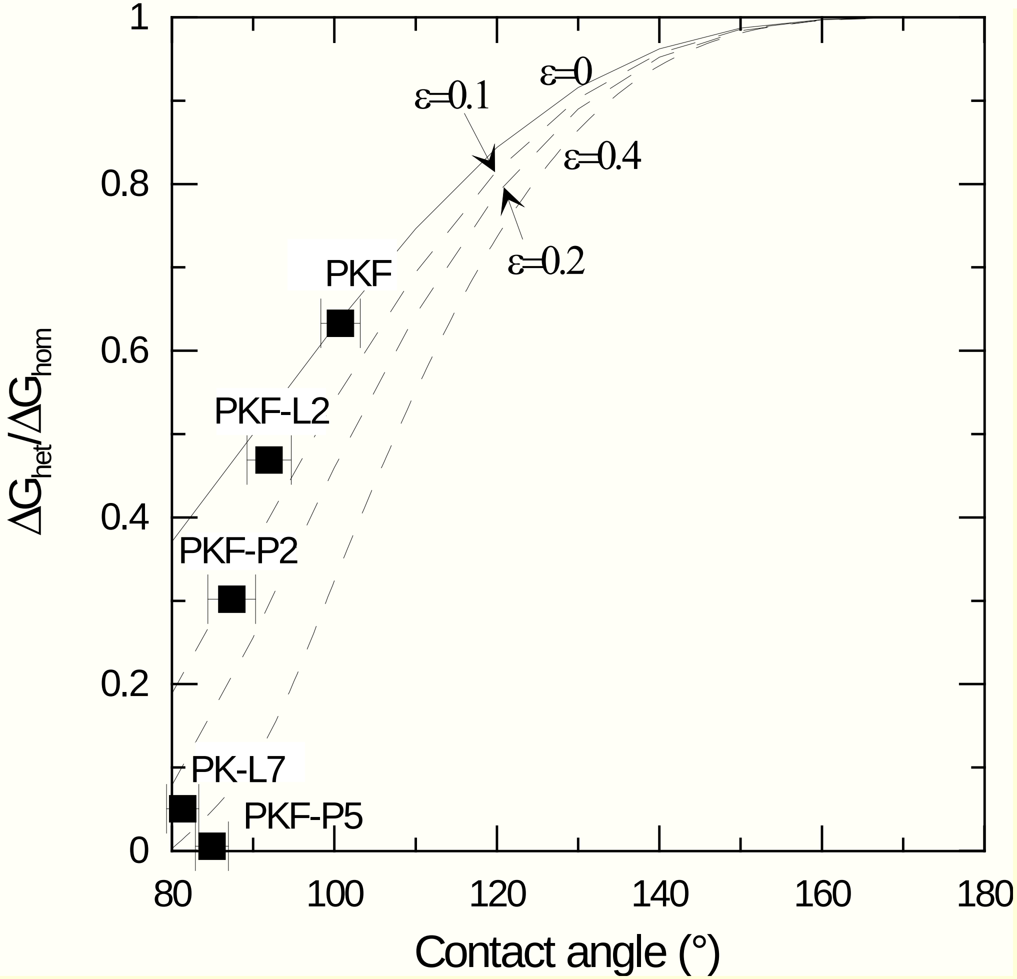
CA: cellulose acetate;
PAN: polyacrylonitrile;
PC: polycarbonate;
PET: polyetherimide;
PES: polyethersulfone;
PP: polypropylene;
PSf: polysulfone;
PTFE: polytetrafluoroethylene;
PVDF: polyvinylidenefluoride

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)

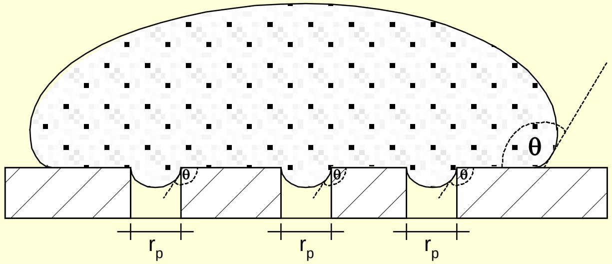
For porous surfaces …

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



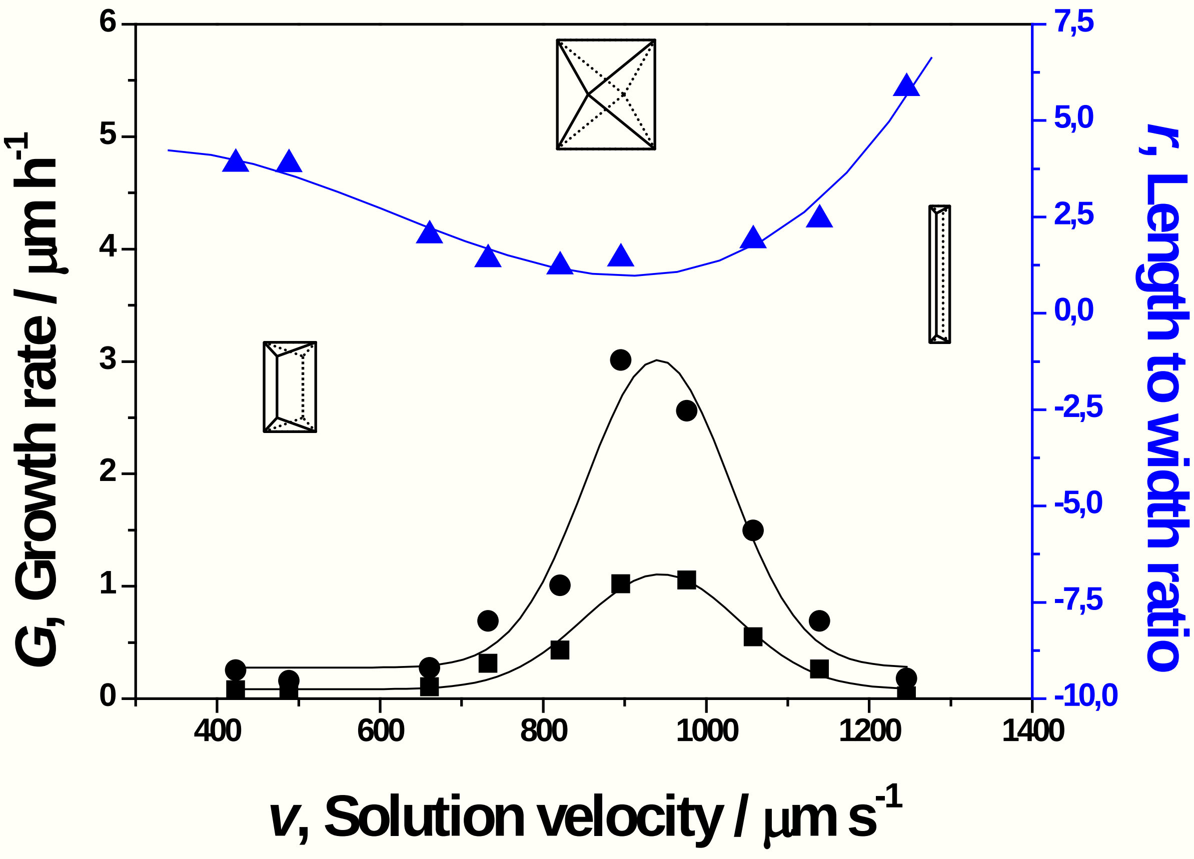
Membrane	Porosity (ε)
PKF	**$6.0\cdot10^{-3}$**
PKF-L2	**$4.3\cdot10^{-2}$**
PKF-P2	**$1.1\cdot10^{-1}$**
PK-L7	**$2.7\cdot10^{-1}$**
PKF-P5	**$5.4\cdot10^{-1}$**

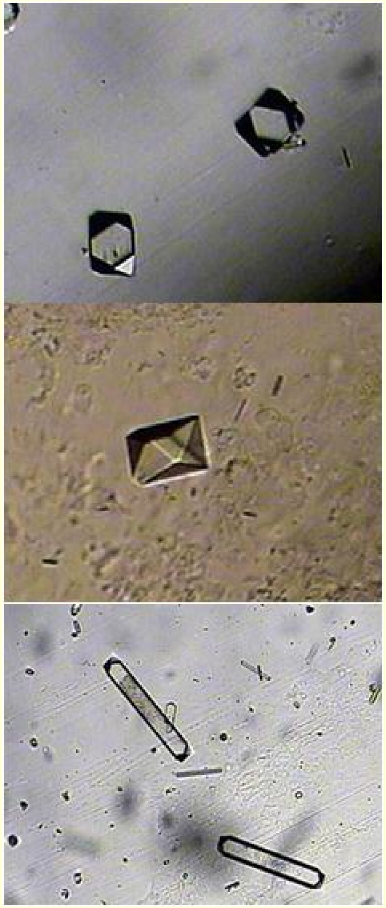
ε = pore surface/total membrane surface



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

Advantages of Membrane Crystallization Technique (5)



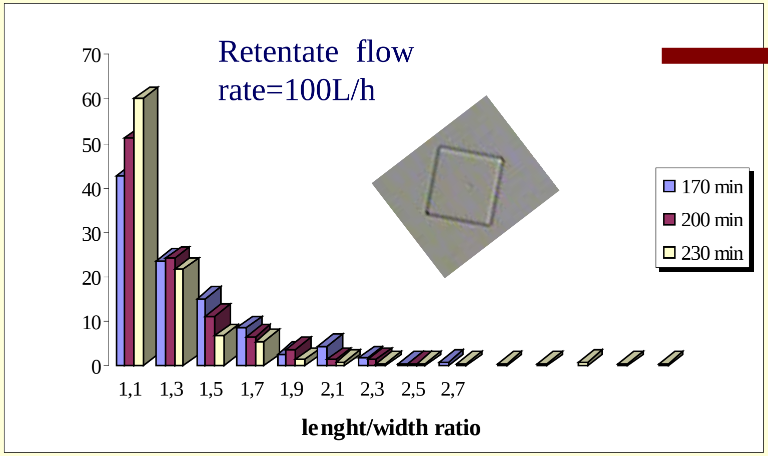


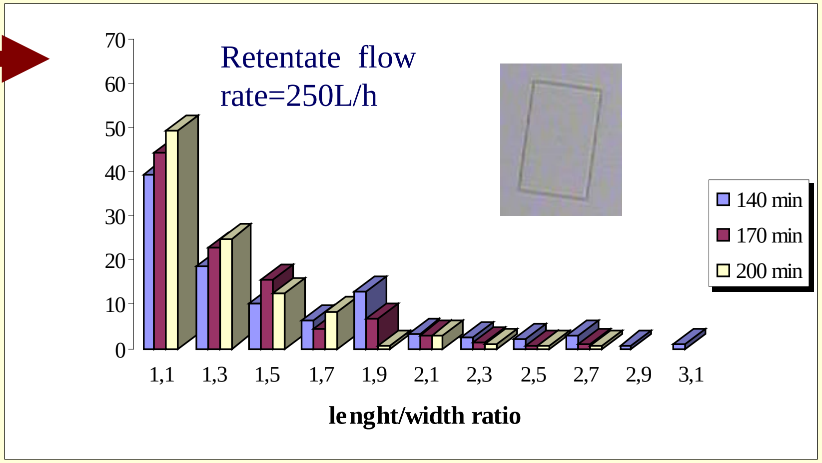
Protein: Bovine Pancreas Trypsin, M.W. = ~ 24000 Da

✓ 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)



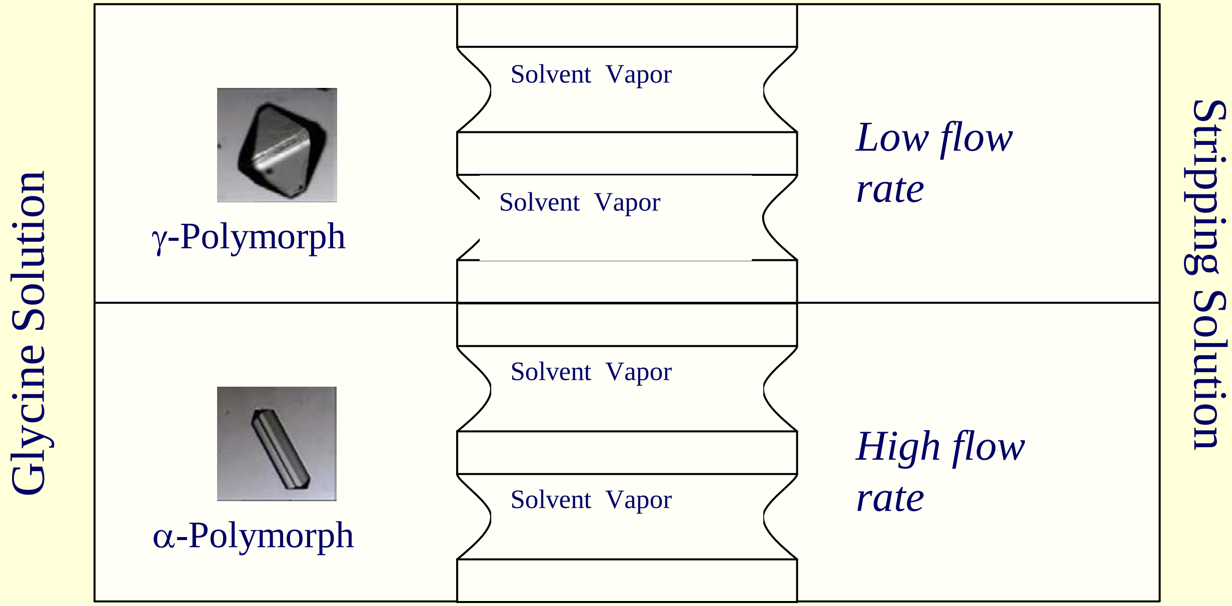


Distribution of length/with ratio for NaCl crystals obtained from the crystallization of RO brine

✓ 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



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.

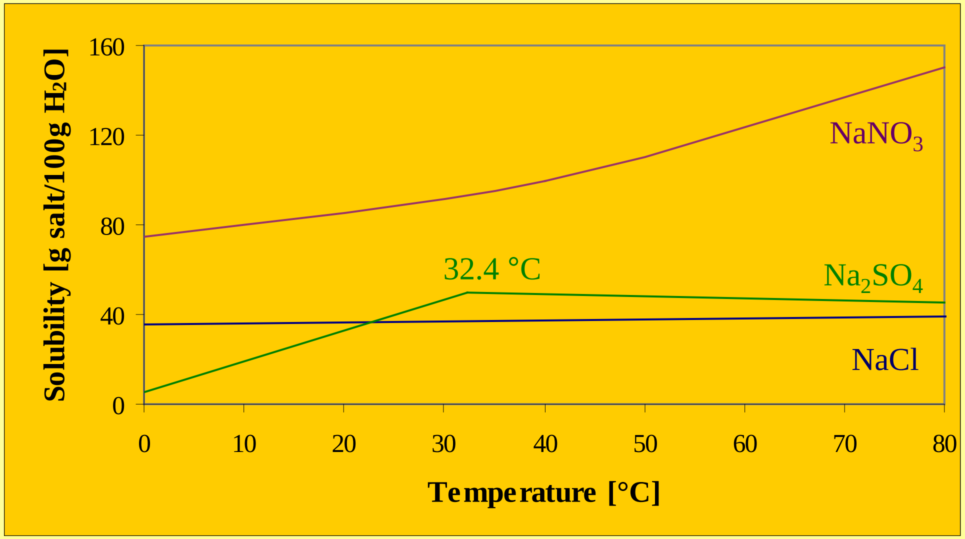
Possible solutions:

- ✓ 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.

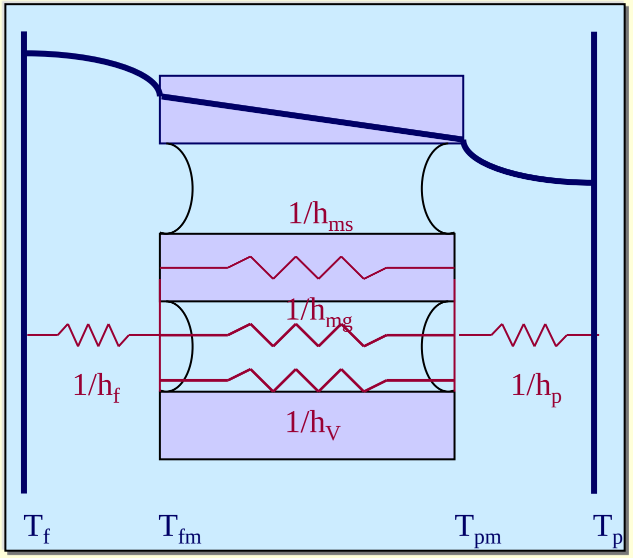
Influence of Temperature

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

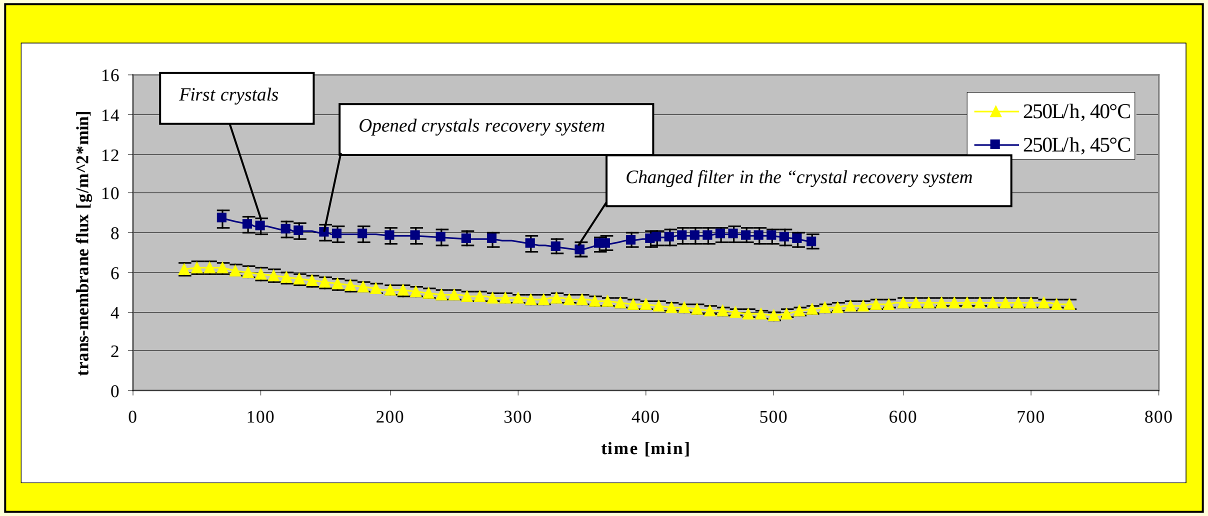
Salt	ΔH_{sol} [kcal/mole]
$NaNO_3$	5.11
NaCl	*0.93*
Na_2SO_4	-0.56
$Na_2SO_4 \cdot 10H_2O$	18.58
$CaSO_4$	-4.25
$MgSO_4$	-21.81
$MgSO_4 \cdot 7H_2O$	*3.18*



✓ 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.

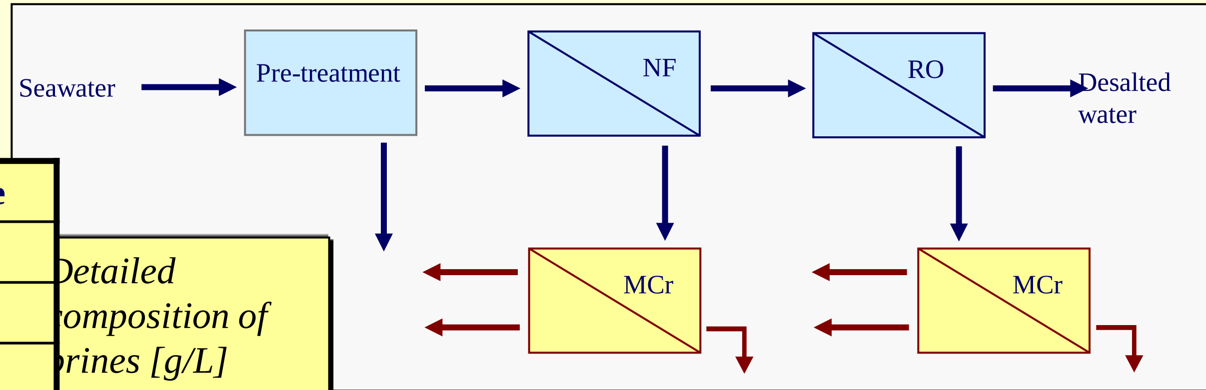
Relation between the vapour pressure of pure water and the absolute temperature T: $\mathbf{p^0(T) \propto \exp/\left(-\frac{\lambda}{RT}\right)}$

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

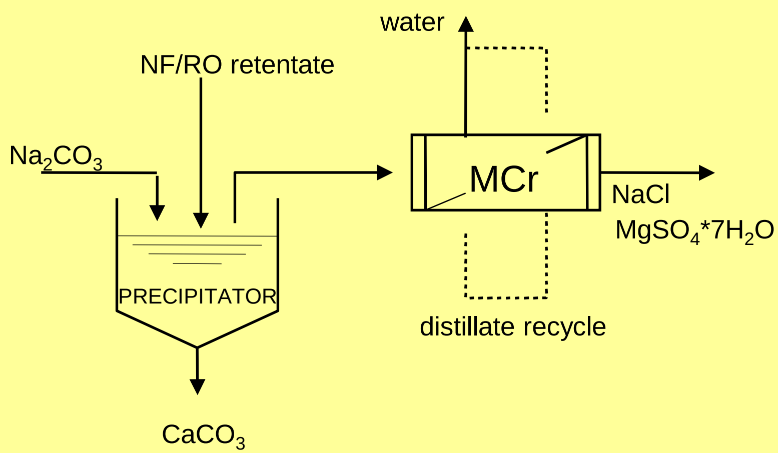
Ion	NF brine	RO brine
Cl^-	34.47	44.89
Na^+	19.05	24.81
SO_4^{2-}	10.38	0.5831
Mg^{2+}	4.959	0.5352
Ca^{2+}	1.384	0.2488
HCO_3^-	0.4160	0.1680
K^+	0.6893	0.8978
CO_3^{2-}	0.0103	0.0041
Br^-	0.0848	0.1886
Total	71.44	72.32

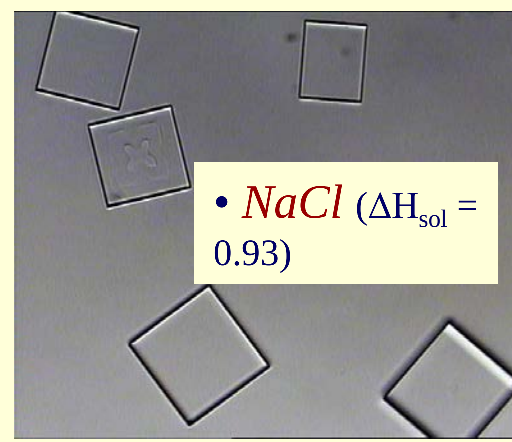


Detailed composition of brines [g/L]

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

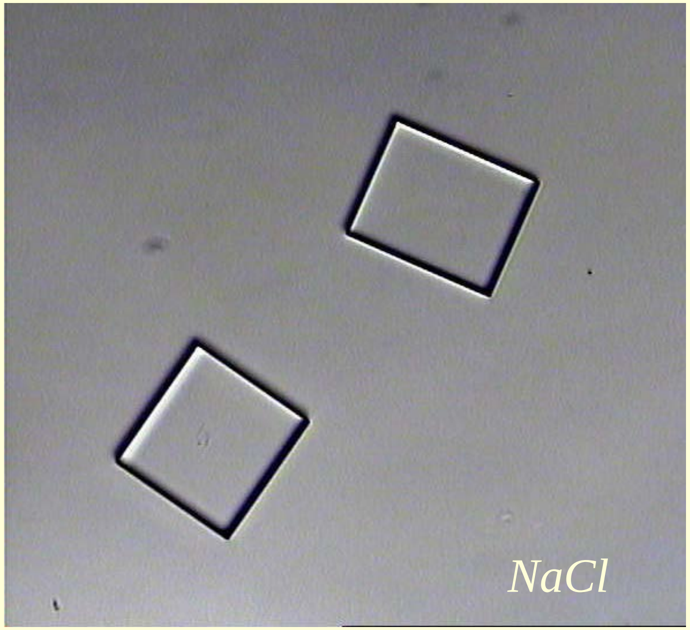
- *Calcium sulphate:* To limit calcium sulphate precipitation, Ca^{2+} ions are recovered as $CaCO_3$ through reactive precipitation with Na_2CO_3

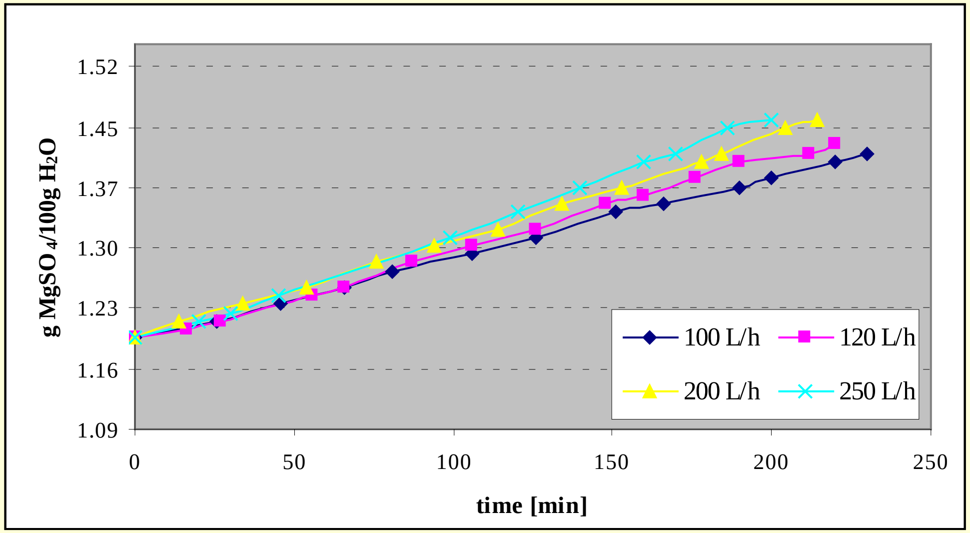




- *NaCl* (ΔH_{sol} = 0.93)

RO brine crystallization: type of produced salts





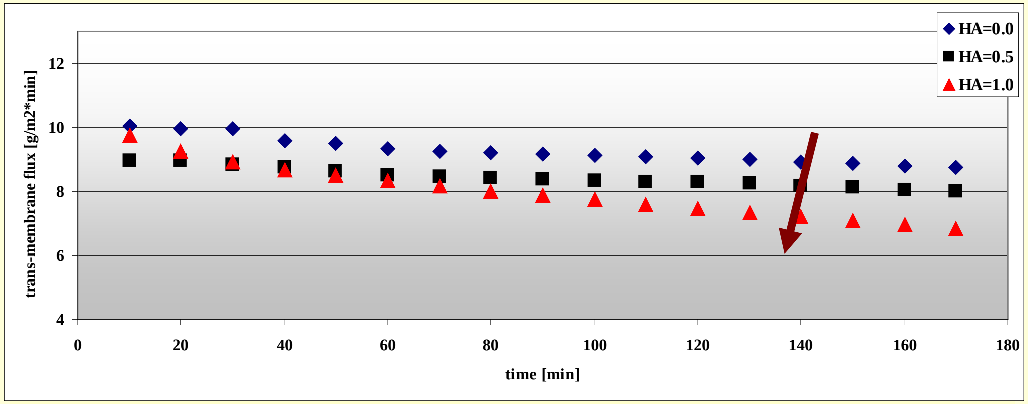
Magnesium sulphate concentration vs time at different feed flow rates for the lab tests of aqueous solution of NaCl.

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

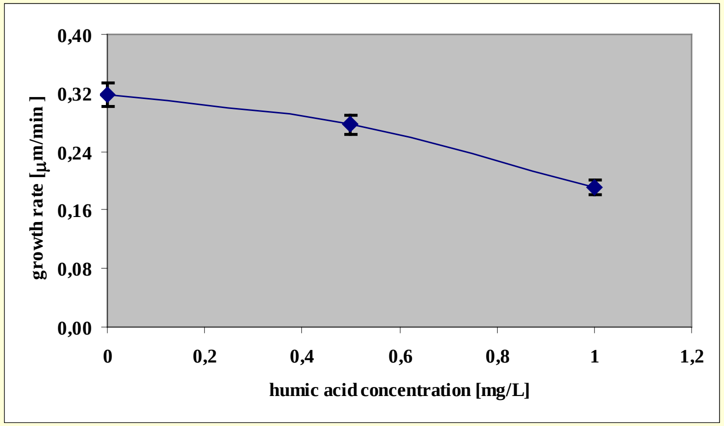
✓ The crystallization tank work at 25°C and atmospheric pressure. At this temperature, the solubility of magnesium sulphate in water is 25.6g/100g H_2O, much higher of $MgSO_4$ concentration in the carried out tests.

Indispensable optimization of pre-treatment steps for the control of the crystallization process.

MCr tests on NF/RO brine with humic acid: effect of organic components



Flux vs time for *RO* brine. (Q_{feed}= 200 L/h, $T_{in, feed}$= 38±1 °C.)



Humic acid concentration [mg/L]	0.0	0.5	1.0
G [μm/min]	0.3174	0.2764	0.1910
CV [%]	30.25	43.00	57.35
d_m [μm/min]	49.97	42.72	34.23
MCr recovery factor[%]	78.66	78.11	77.55

- Lower water recovery factor
- smaller crystals
- higher CVs
- lower crystals growth rate

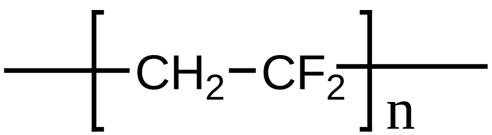
with respect to the ones obtained from inorganic RO brine solutions

Indispensable optimizing of the pre-treatment steps in order to control the crystallization processes that are linked with the nature and the amount of the foreign species existing in the highly concentrated brines emerging from the NF and RO stages.

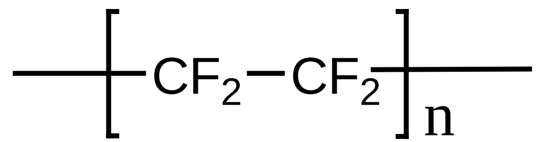
E. Drioli et al., Desalination and Water Treatment, 18 (2010) 224-234.

Fluoropolymers for membranes

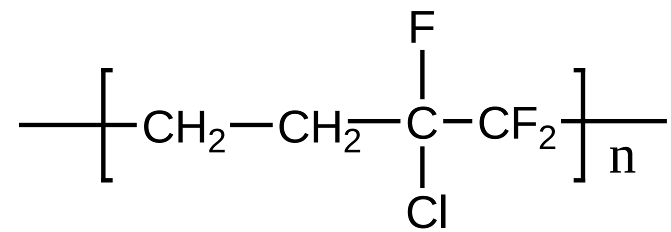
- Most of the fluoropolymers for membranes are homopolymers and copolymers based on PVDF and PTFE.
- ECTFE, which is starting to catch researchers' attention, is a novel fluoropolymers for membranes.



PVDF homopolymer



PTFE homopolymer



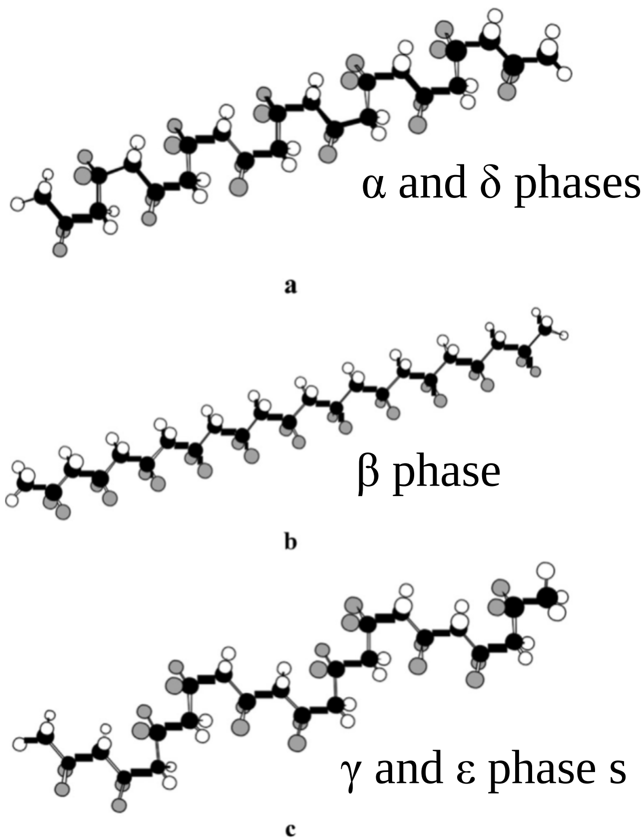
ECTFE copolymer

- PVDF membranes are used in MF, UF, MD, MCr, ME, PV.
- PTFE membranes are used in MD, MC, PV, MGA.
- ECTFE membranes are used in PV, has potential in MD, MC and MF/UF.

Cui Z, et al. Recent progress in fluoropolymers for membranes. Prog Polym Sci (2013), http://dx.doi.org/10.1016/j.progpolymsci.2013.07.008

PVDF homopolymers

- Homopolymers of PVDF are semicrystalline and long chain macromolecules which contain 59.4 wt.% fluorine and 3 wt.% hydrogen.
- PVDF typically has a crystallinity of 35-70%, depending on the preparation and thermal mechanical history.



- Three molecular conformations are TGTG’ (α and δ phases), TTT (β phase) and TTTGTTTG’ (γ and ε phases).
- The α-form is kinetically favorable, while the β-form is the most thermodynamically stable form.
- α phase is non-polar, β and γ phases are polar.
- The polar property and the relatively higher mechanical strength makes β phase is the most interesting phase.
- γ phase presents higher melting point and solvent resistance.

Ameduri B. Chem. Rev 2009; 109: 6632-86; Dillon DR, et al. Polymer 2006; 47: 1678-88; Hasegawa R, et al. Polym J 1972; 3: 600-10; Boccaccio T, et al. J Membr Sci 2002; 210: 315-29.

Structure data of different PVDF crystals

	α-phase	β-phase	γ-phase
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Polarity	Nonpolar	Polar	Polar
Space group	$P2_1/c(C\frac{5}{2h})$	$Cm2m(C\frac{14}{2v})$	$C121(C\frac{3}{2})$
Lattice constants	a=4.96Å	a=8.58Å	a=8.66Å
	b=9.64Å	b=4.91Å	b=4.93Å
	c(f.a.)=4.62Å	c(f.a.)[a]=2.56Å	c(f.a.)=2.58Å
	β=90 °C		β=97 °C
Number of chains per lattice	2	2	2
Molecular conformation	TGTG'	TTT	TTTGTTTG'
Density, Obsd at 30 °C	1.76_9 g/ml	1.80_6 g/ml	1.80_4 g/ml
Calcd (X-ray)	1.93 g/ml	1.97 g/ml	1.94 g/ml
FTIR peak (cm^{-1})	408, 532, 612, 766, 795, 855, 976, 1182, 1400	445, 470, 511, 600, 840, 1270	431, 512, 776, 795, 812, 833, 840, 1233
Peak of 2θ of X-ray diffraction	17.66, 18.30, 19.90, 26.56	20.26	18.5, 19.2, 20.4

Cui Z, et al. Recent progress in fluoropolymers for membranes. Prog Polym Sci (2013), http://dx.doi.org/10.1016/j.progpolymsci.2013.07.008

Solvents/diluents for PVDF membrane preparation

Author	Polymer type	Type of diluent	The geometry	Year
Lloyd [12]	Polypropylene (PP), high density polyethylene (HDPE), poly(4-methyl-1-pentene) (TPX), PVDF	Mineral oil, Kel-F oligomer oil, DBP	Flat sheet	1990
Lloyd et al. [13]	iPP	N,n-bis (2-hydroxyethyl) Tallowamine	Flat sheet	1991
Kim et al. [14]	iPP	Eicosane, eicosanoic acid, N,n-bis (2-hydroxyethyl) Tallowamine	Flat sheet	1991
Gordon et al. [15]	iPP	Mineral oil, eicosane, tetradecane, dotriacontane	Flat sheet	1991
Kim et al. [16]	iPP	Tetradecane, dotriacontane, pentadecanoic acid, eicosane, eicosanoic acid	Flat sheet	1991
Alwattari et al. [17]	iPP	Hexamethylbenzene (HMB)	Flat sheet	1991
McGuire et al. [18]	iPP	Dotriacontane	Flat sheet	1993
Laxminarayan et al. [19]	iPP	Diphenyl ether (DPE)	Flat sheet	1994
McGuire et al. [20]	iPP	DPE	Flat sheet	1994
Song et al. [21]	Atactic polystyrene	Cyclohexane	Flat sheet	1994
Cha et al. [22]	Nylon 12	Polyethylene glycol (PEG)	Flat sheet	1995
Song et al [23]	Polystyrene	Cyclohexanol	Flat sheet	1995
Berghmans et al. [24]	Poly(2,6-dimethyl-1,4-phenylene ether) (PPE)	Cyclohexanol	Hollow fiber	1996
McGuire et al. [25]	iPP	DPE	Flat sheet	1996
Caplan et al. [26]	Poly(tetrafluoroethylene-co-perfluoro-(propyl vinyl ether)) (Teflon® PFA)	Chlorotrifluoroethylene	Flat sheet	1997
Matsuyama et al. [27]	iPP	DPE	Flat sheet	2000
Sun et al. [28]	HDPE	Liquid paraffin (LP)	Hollow fiber	2000
Matsuyama et al. [29]	iPP	DPE	Flat sheet	2002
Shang et al. [30]	Poly(ethylene-co-vinyl alcohol) (EVOH)	Glycerol	Hollow fiber	2003
Matsuyama et al. [31]	HDPE	Diisodecyl phthalate (DIDP), LP	Hollow fiber	2003
Yave et al. [32]	Syndiotactic polypropylene (sPP)	DPE	Flat sheet	2005
Yave et al. [33]	iPP, sPP	DPE	Flat sheet	2005
Fu et al. [34]	Poly(vinyl butyral) (PVB)	PEG 200, 400, 600	Hollow fiber	2005
Yang et al. [35]	iPP	DBP, DOP	Hollow fiber	2006
Yang et al. [36]	iPP	DBP, DOP	Hollow fiber	2006
Fu et al. [37]	PVB, EVOH	PEG 200	Hollow fiber	2006
Gu et al. [6]	PVDF	Dioctylsebacate (DOS), DOP and dimethyl-phthalate (DMP)	Flat sheet	2006
Gu et al. [38]	PVDF	DMP	Flat sheet	2006
Su [39]	PVDF	Butyrolactone, cyclohexane (CO), DBP	Flat sheet	2007
Su [40]	PVDF	Butyrolactone, propylene carbonate (PC), DBP, dibutyl sebacate (KD)	Flat sheet	2007
Luo et al. [41]	iPP	Soybean, DBP	Flat sheet	2008
Ji et al. [42]	PVDF	DBP, di(2-ethylhexyl) phthalate (DEHP)	Flat sheet	2008
Ji et al. [43]	PVDF	DBP, DEHP, LP	Hollow fiber	2008
Rajabzadeh et al. [44]	PVDF	Glycerol triacetate (triacetin)	Hollow fiber	2008
Yang et al. [45]	PVDF	DPK	Flat sheet	2008
Han et al. [46]	Poly phenylene sulfide (PPS)	DPK	Flat sheet	2008
Li et al. [47]	PVDF	DBP	Flat sheet	2008
Qiu et al. [48]	PVB/Pluronic F127	PEG 200	Hollow fiber	2008
Lu et al. [49]	PVDF	DBP, DOP	Flat sheet	2009
Rajabzadeh et al. [50]	PVDF	Glycerol triacetate (triacetin)	Hollow fiber	2009
Lin et al. [51]	PVDF	DPC	Flat sheet	2009
Lin et al. [52]	iPP	Diamyl phthalate (DAP)	Flat sheet	2009
Qiu et al. [53]	PVB/Pluronic F127	PEG 200, 300, 400, 600	Hollow fiber	2009
Tang et al. [54]	PVDF	DPK, 1,2-propylene glycol (PG)	Flat sheet	2010
Qiu et al. [55]	PVB	PEG 200	Hollow fiber	2010
Ma et al. [56]	PVDF/poly methyl methacrylate (PMMA)	Methyl salicylate (MS), benzophenone (BP)	Flat sheet	2011
Li et al. [57]	UHMWPE	Mineral oil	Hollow fiber	2011
Ghasem et al. [58]	PVDF	Glycerol triacetate (triacetin)	Hollow fiber	2011
Ghasem et al. [59]	PVDF	Glycerol triacetate (triacetin)	Hollow fiber	2012
Rajabzadeh et al. [60]	PVDF	Diethyl phthalate (DEP)	Hollow fiber	2012

Cui, Z., et al., J Membr Sci, 444 (2013): 223-236.

Membrane preparation:

Solvents for NIPS process: DMAc, DMF, DMSO, HMPA, ,NMP, TMU, TEP, TMP, THF…

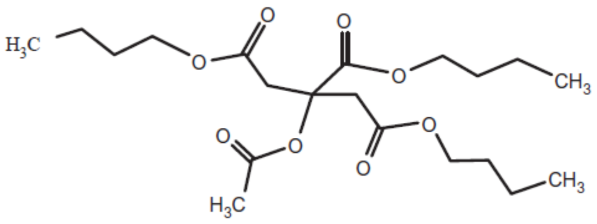
Diluents for TIPS process: DMP, DEP, DBP, DHP, GTA, EAA, PGC, DPK, DPC…

- Most of These solvents/diluents are toxic.
- The toxic solvents/diluents reduce the contributions of membranes to environmental protection.
- With the environmental protect act becoming more and more severe, finding more environmental solvents/diluents is becoming an important topic in membrane preparation fields.

ATBC (Tributyl O-Acetylcitrate) for PVDF membr

Formula	$C_{20}H_{34}O_8$
Molecular weight, g/mol	402.5
Purity, %	>97 (GC)
Specific gravity	1.05
Boiling point, ºC	343
Flash point, ºC	204
Melting point/freezing point, ºC	-80
Soluble in	Ethanol, alcohol ether
Insoluble in	Water

Chemical structure



- **ATBC is one of the environmental friendly solvents.**

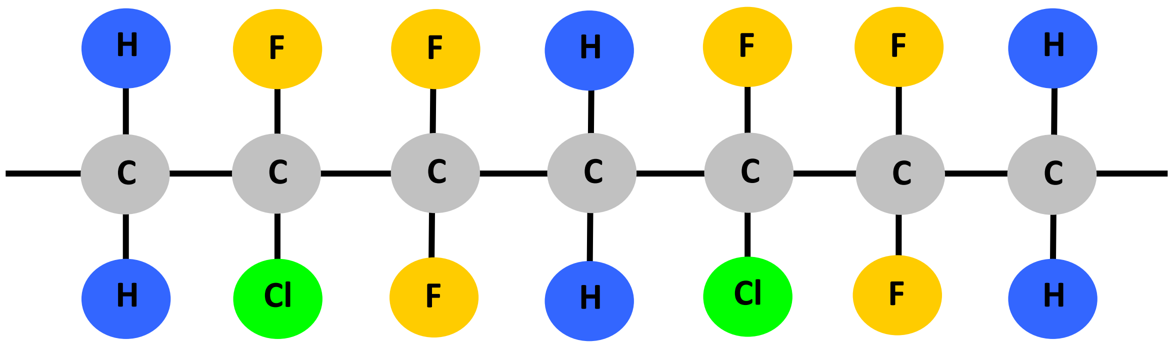
- **ATBC has a solubility parameter of 18.34 $MPa^{1/2}$ according to the group contribution method.**

- **It is expected that PVDF is insoluble in ATBC at room temperature but possibly soluble in ATBC at suitable temperatures. It is possible to be used for PVDF membrane preparation *via* TIPS process.**

Cui, Z., et al., J Membr Sci, 444 (2013): 223-236.

ECTFE membranes

ECTFE (Ethylene–Chlorotrifluoroethylene copolymer) is a copolymer of formula –(–CH2–CH2–CFCl–CF2–)n–, composed of alternating ethylene and chlorotrifluoroethylene units.



Since it is very hydrophobic, an ECTFE porous membrane is more suitably used in membrane processes in which vapor or gas passes through the membrane pores, like MD, and a dense ECTFE membrane can be used in PV. This material has been studied primarily in preparing flat sheet and hollow fiber membranes, microporous membranes for UF/MF processes, and dense membranes for the PV process.

INTEGRATED MEMBRANE OPERATIONS

Enrico Drioli[1,2,3,4]

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KACST, February 2014

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

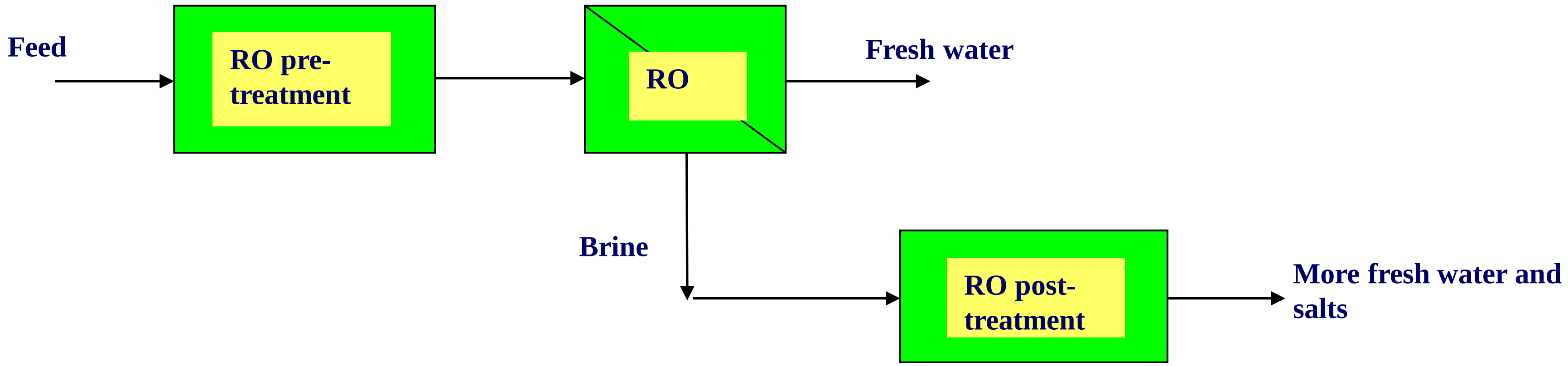
1) Integrated Membrane Systems

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.**

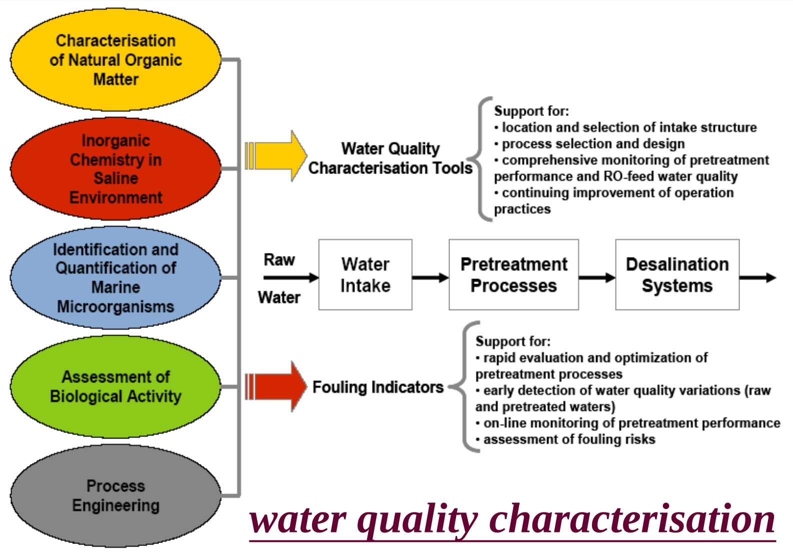
CASE 1: Integrated Membrane System for Desalination



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".

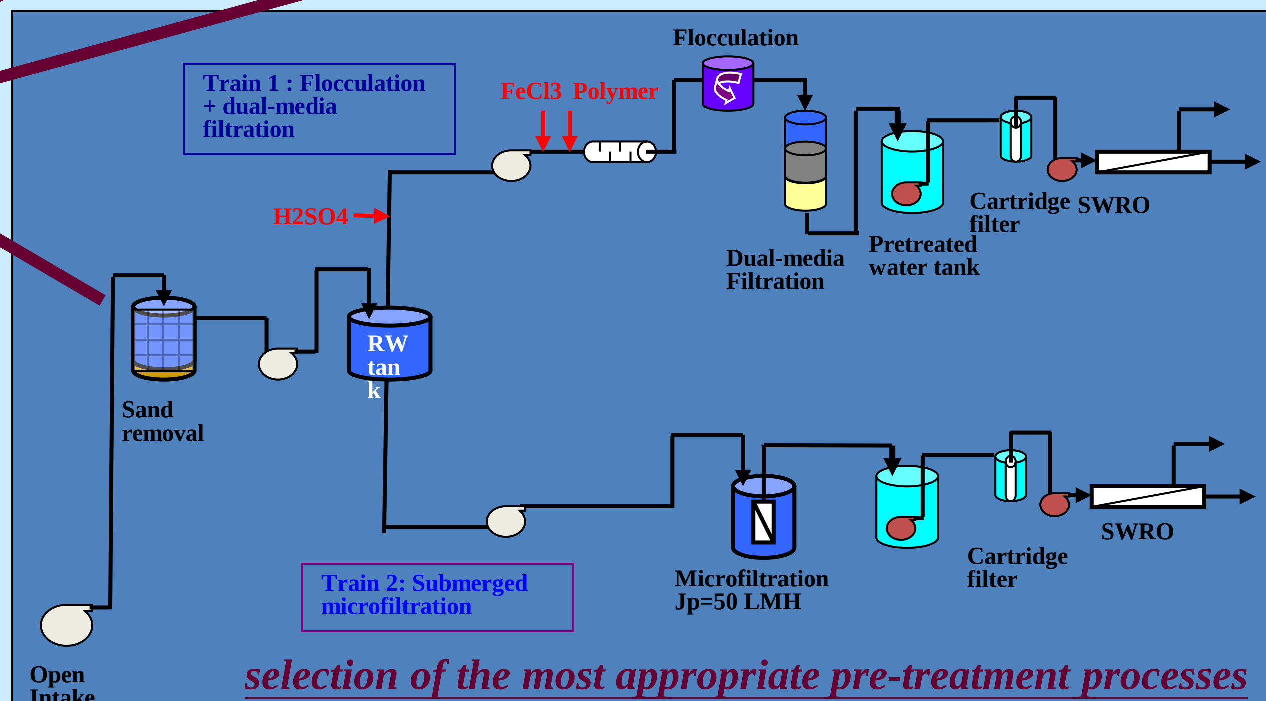
The proposed approach is based on the integration of different membrane operations in RO pre-treatment (MF/UF/Membrane Bioreactor/NF/Membrane Contactor) and post-treatment stages (MC/MD/Membrane Crystallizer/working on the concentrates) according to the philosophy of Process Intensification.

In the RO pre-treatment steps, the integration of



membrane cleaning strategies

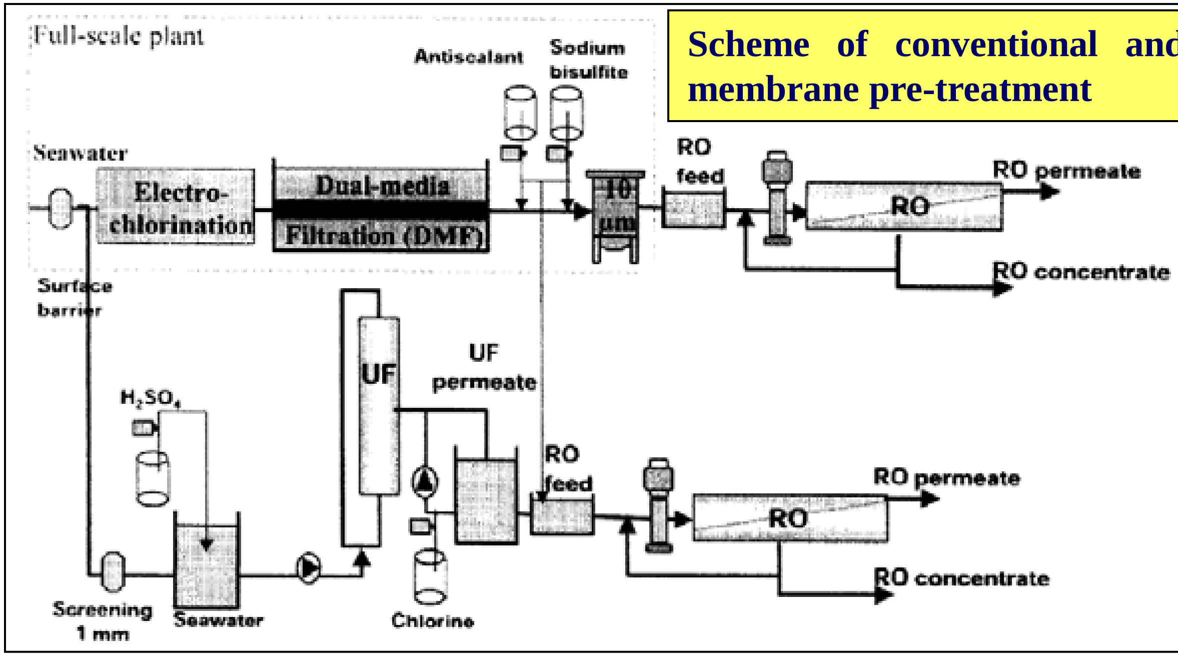
tools for RO fouling characterization and understanding



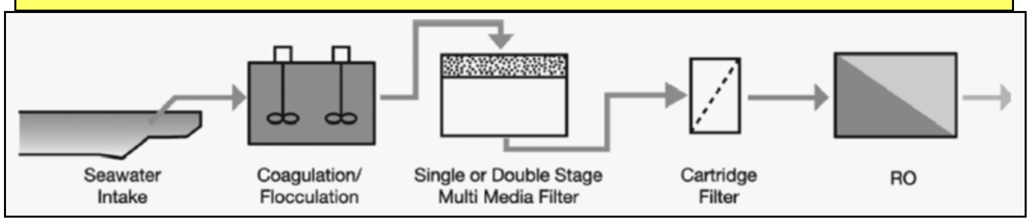
leads to the minimisation of membrane replacement needs thereby reducing the operating costs

RO pre-treatment

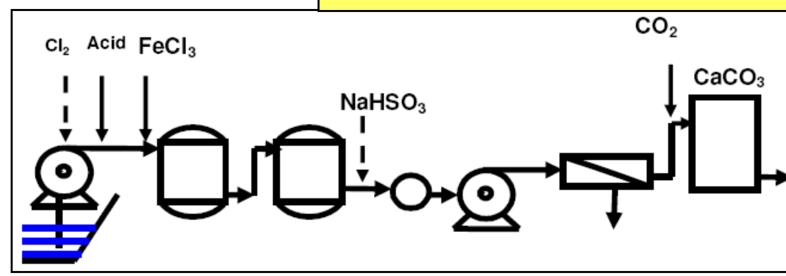
Scheme of conventional and membrane pre-treatment



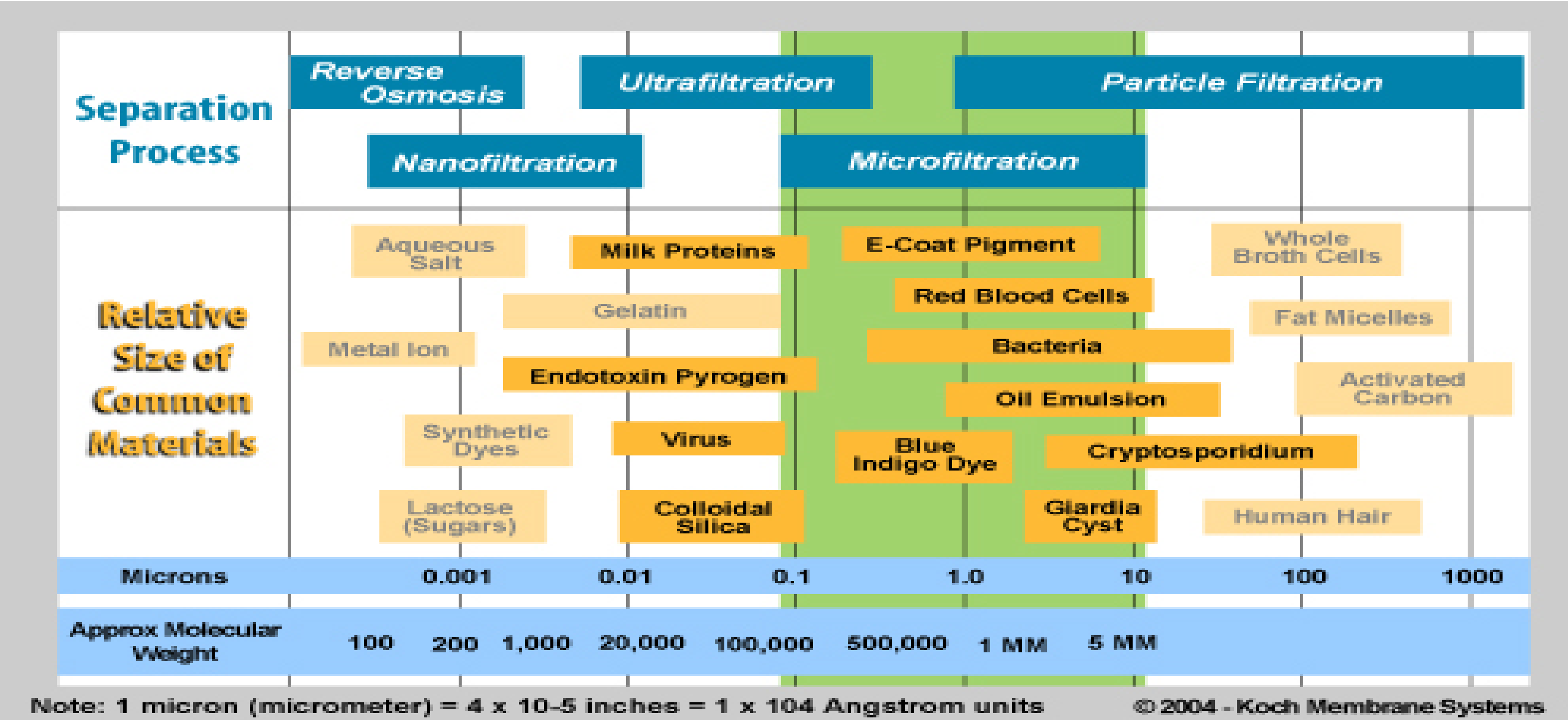
Conventional pre-treatment scheme (chemical and physical)



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.

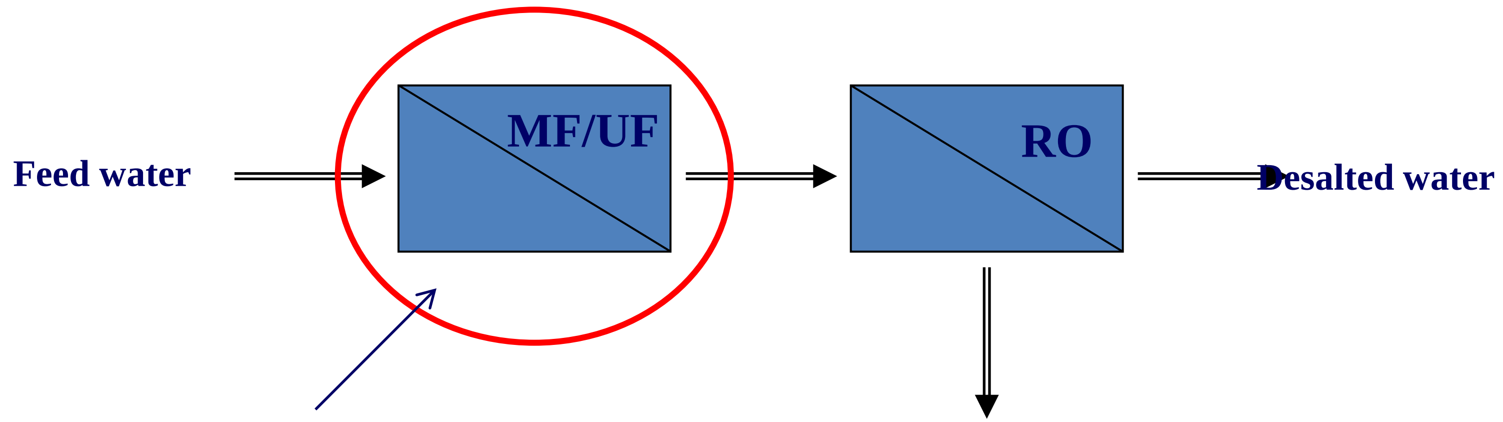


- **MF use include: bacteria and pigment removal and elimination of other particulates with particle sizes in the submicron range.**

- **UF use include: bacteria and viruses removal, and can separate macromolecules as well as colloidal particles.**

- **NF is useful, e.g., for color and dye removal or for removing hardness or sulfate from water supplies.**

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.

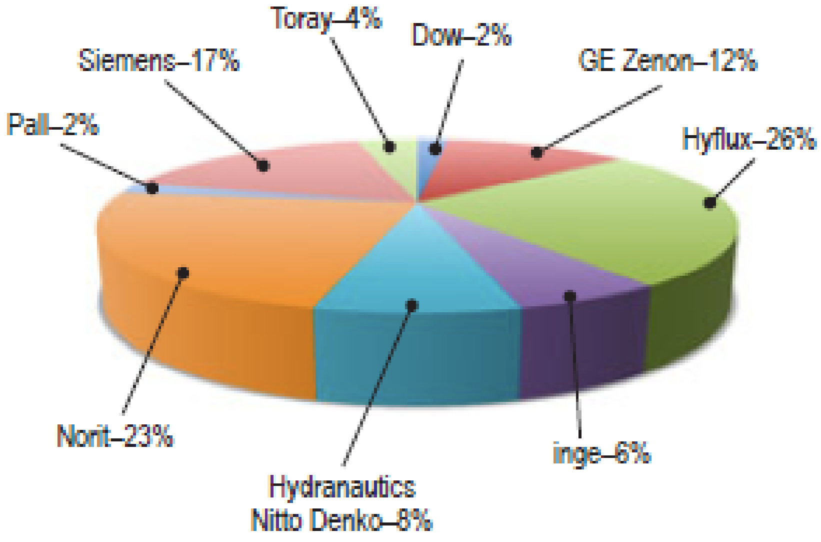
Chemical cost comparison for different pre-treatment options

	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

A growing trend in the use of low-pressure MF/ UF membranes for SWRO pretreatment is observed.



MF/UF Membrane Suppliers for SWRO Pretreatment
% of Installed/contracted Capacity

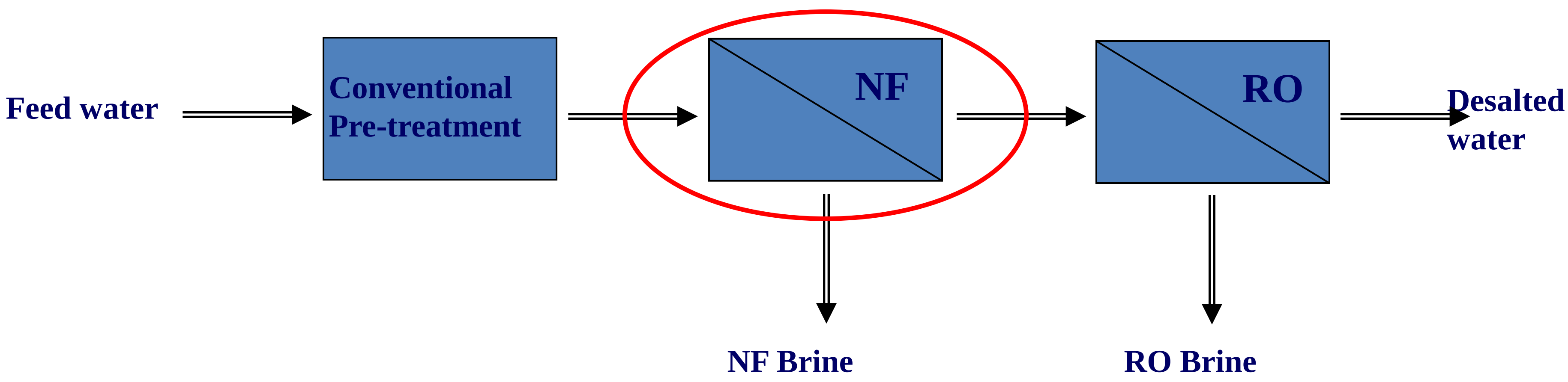
Hyflux has the largest share of the market. Its capacity includes the 500,000 m^3/d (131 MGD) Mactaa SWRO plant in Algeria, which is contracted but not yet constructed.

Water Desalination Report, Volume 46, Number 26, 12 July 2010

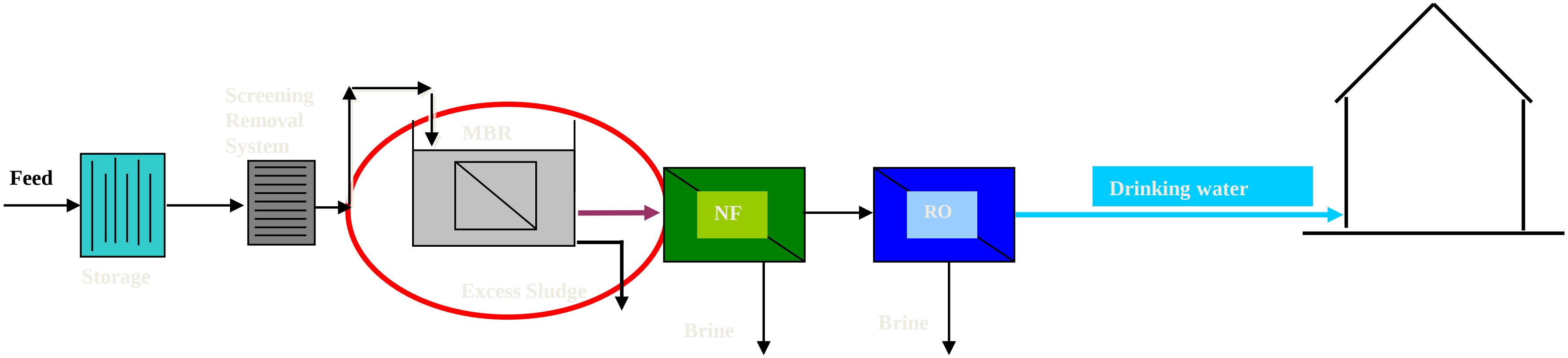
Nanofiltration (NF) as "Softening" Step for RO

- 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)



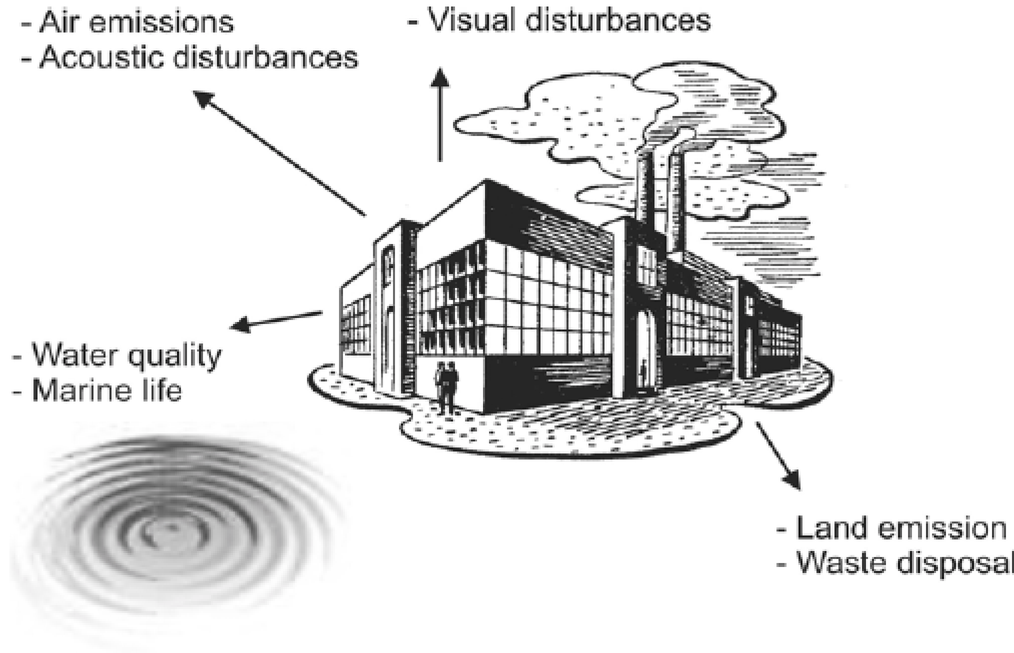
Membrane Bioreactor as SWRO pre-treatment and not only for municipal and industrial wastewater treatment



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.

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

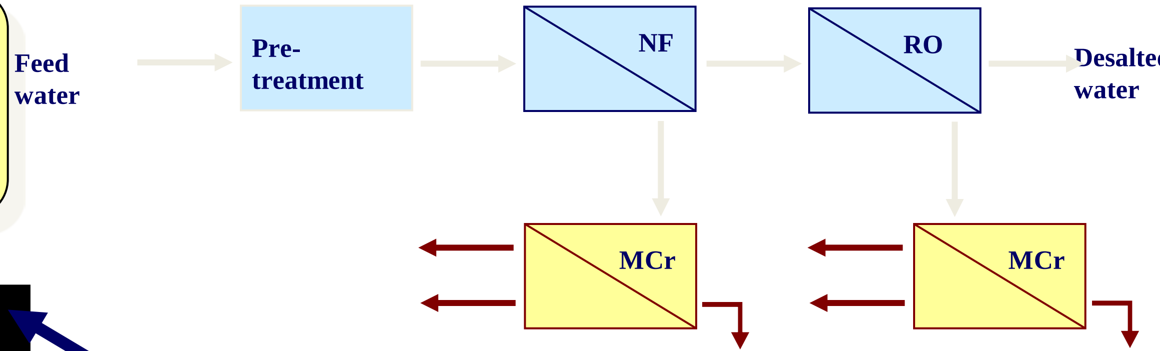
- backwash water from physical pre-treatment (high loads of solids, containing biological, mineral and organic matter),
- saline concentrate from the reverse osmosis separation unit, often containing anti scalants
- membrane cleaning solutions

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.

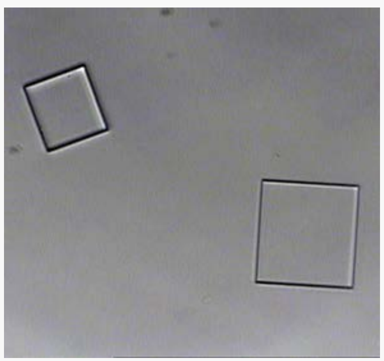
For desalination plants not located close to the shore several al options are available:
- discharge into solar evaporation ponds,
- disposal to wastewater systems,
- land application (spray irrigation, percolation ponds),
- injection into deep saline aquifer (non drinking water aquifer),
- disposal onto land surface,
- disposal into the sea through long pipeline systems.

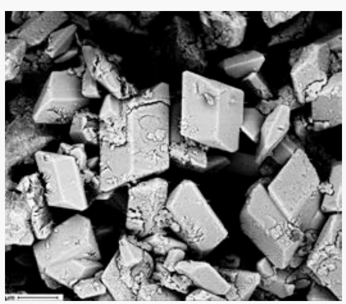
Membrane Contactors for NF/RO post-treatment



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

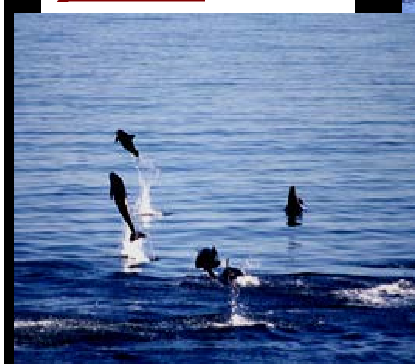
increasing recovery factor





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

reducing brine disposal problem



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

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

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.**

Conventional Integrated Membrane Systems for Seawater Desalination

FS1: *RO unit alone*

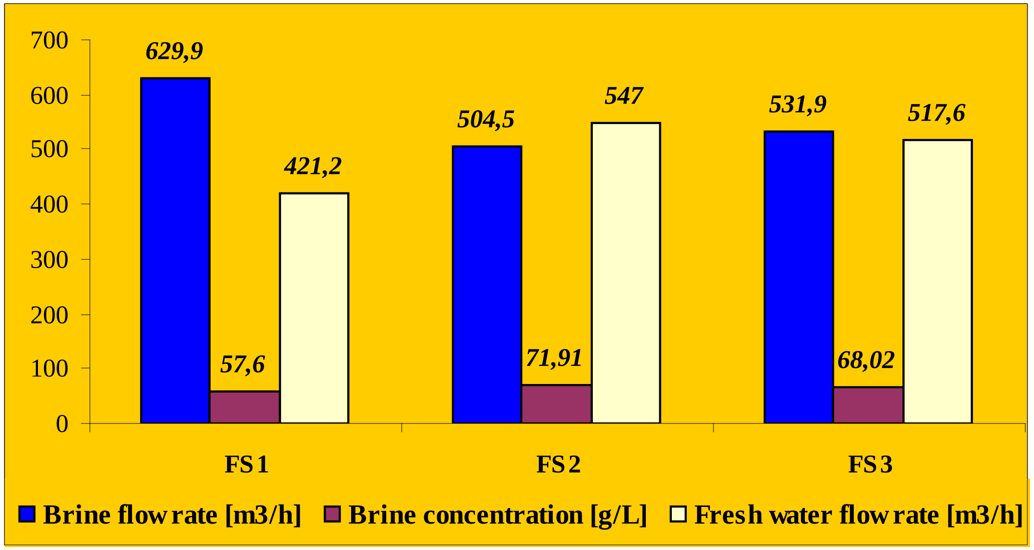
FS2: *RO operating on NF permeate*

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%

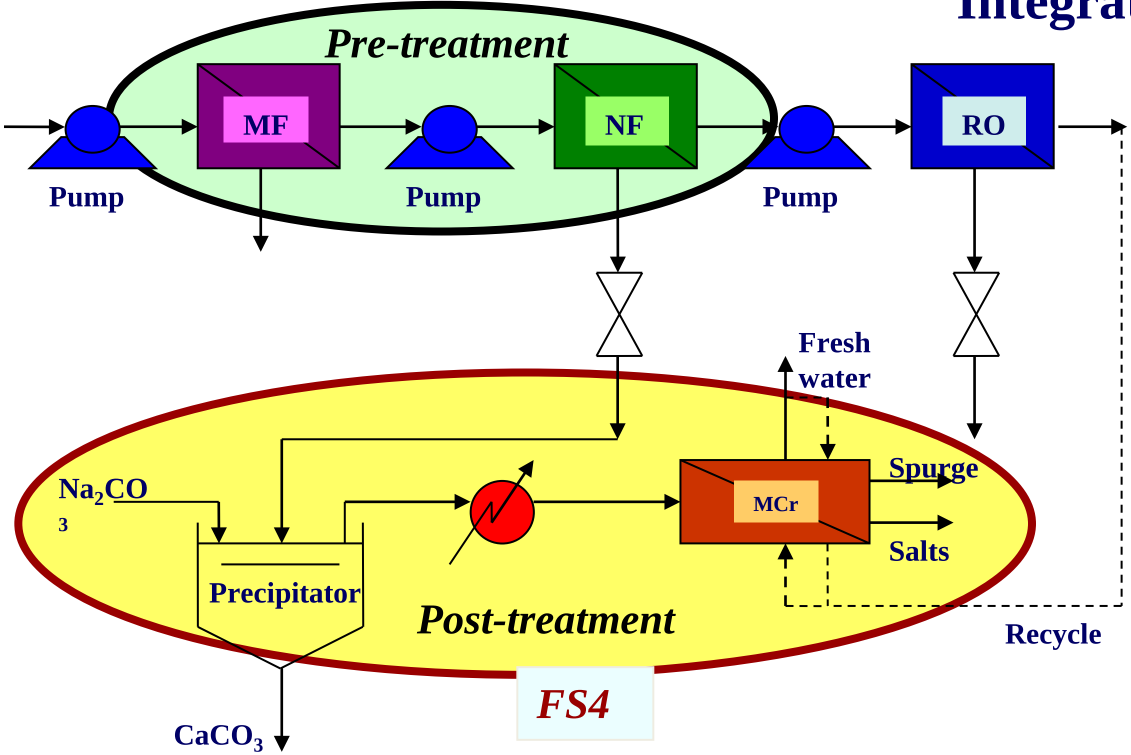


Rejection values

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*



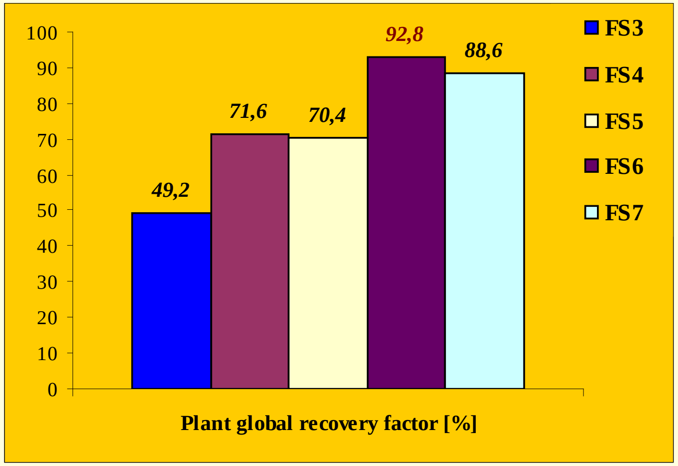
FS4: MF-NF-RO, MCr on NF brine

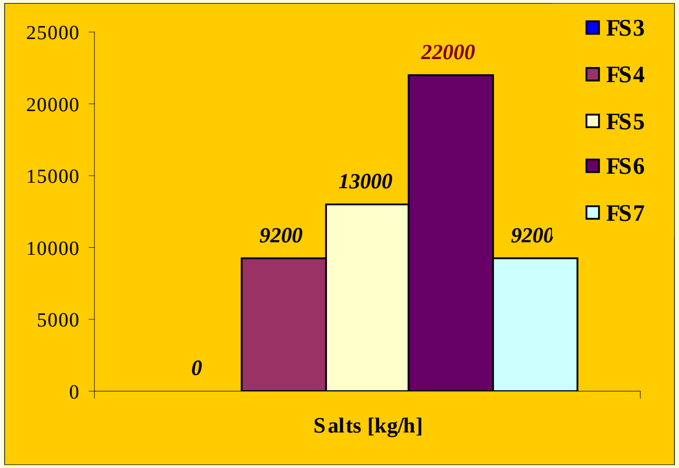
FS5: MF-NF-RO, *MCr on RO brine*

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* [$/m³]	0.61/0.40[a]	0.47/0.40[a]	0.46/0.39[a]	0.68/0.63[a]	0.59/0.54[a]	0.73/0.69[a]	0.74/0.71[a]
Unit cost*, b [$/m³]	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*

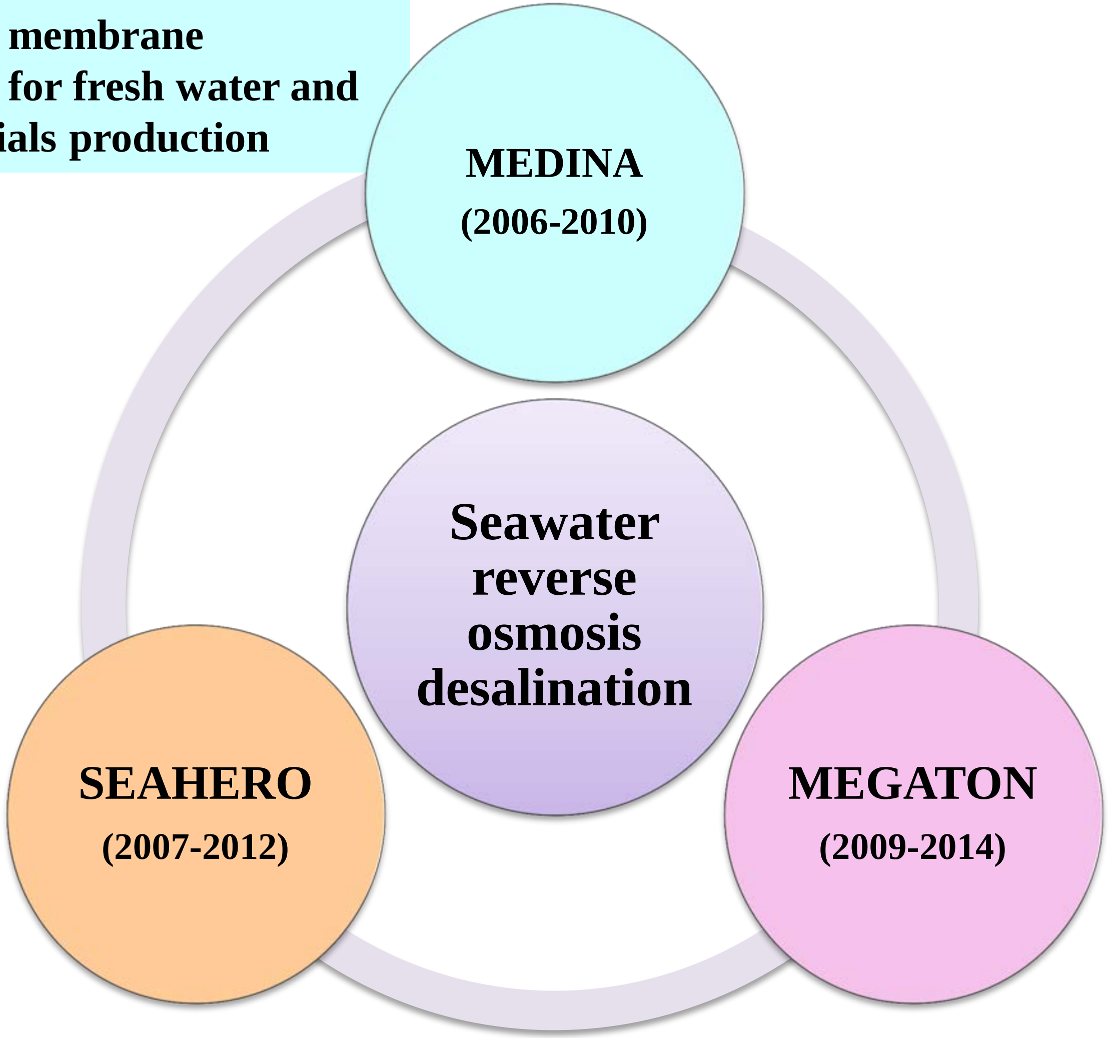
* Desalted water unit cost without consider the gain for the salts sale. (a) If Pelton turbine is used as energy recovery device. (b) If thermal energy is available in the plant or the stream is already at the operating temperature of the MCr unit.

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.

Membrane based desalination projects

Integrated membrane operations for fresh water and raw materials production



Large scale: **largest SWRO unit** (27,000 m^3/d)
Low energy: reduction by 4 kWh/m^3.
Low fouling: reduction of 50 %

Efficient design to obtain capacity of **1,000,000 m^3/d.** Large size element and module, intake technology, **pressure retarted osmosis, energy recovery,** pipe design

http://medina.unical.it
M. Kurihara, M. Hanakawa / Desalination 308 (2013) 131–137.
S. Kim et al. / Desalination 238 (2009) 1–9

Membrane-Based Desalination: An Integrated Approach (acronym MEDINA)

SIXTH FRAMEWORK PROGRAMME - PRIORITY 1.1.6.3 - Global Change and Ecosystems

Aim: **to improve the overall performance of membrane-based water desalination processes through the integration of different membrane operations in RO pre-treatment and RO post-treatment stages.**

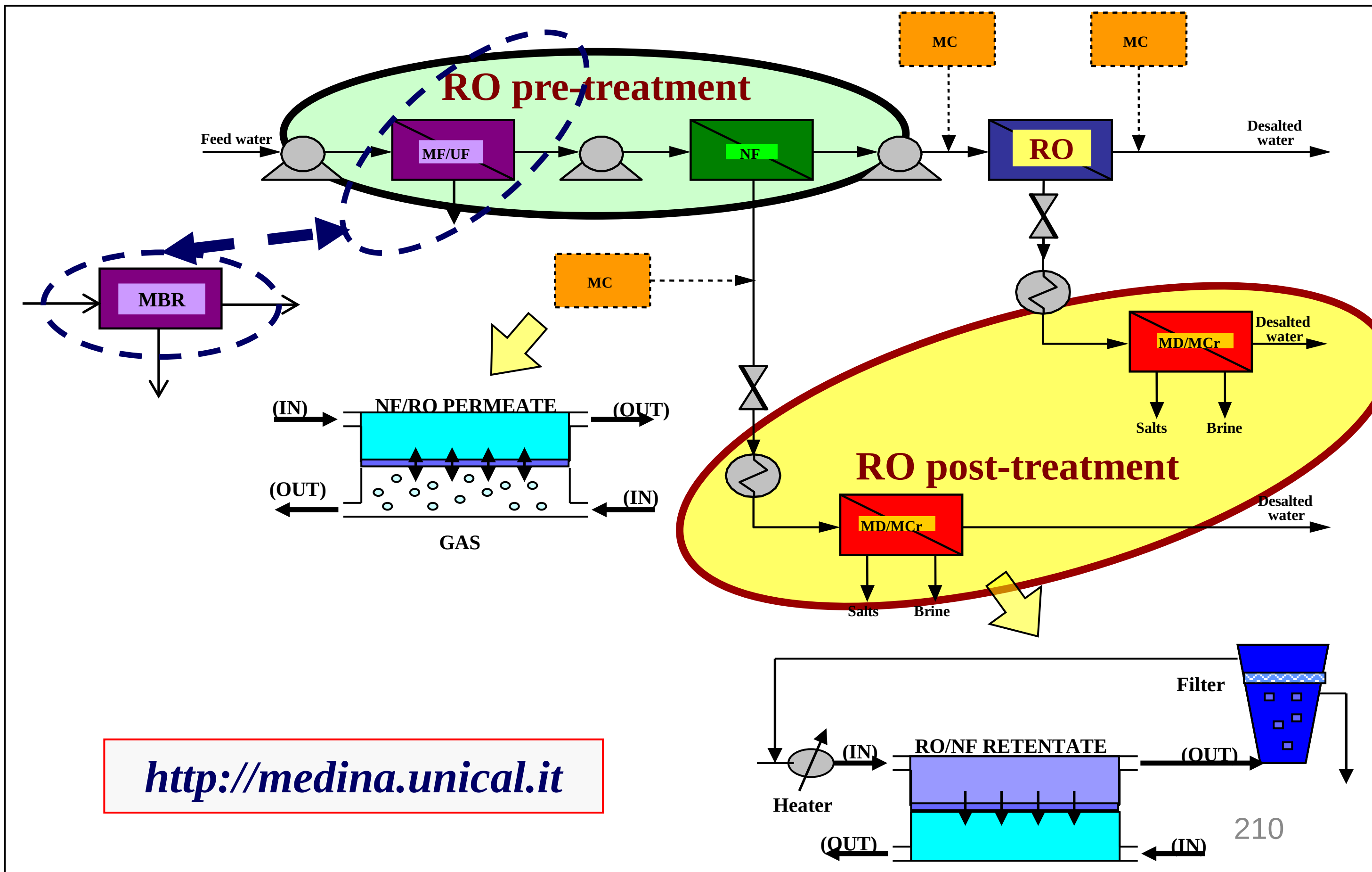
Objectives:

1. to minimise environmental impacts

2. to optimise energy sources and consumption

3. to increase fresh water production

4. to optimize sea-brackish water desalination by understanding, controlling and minimizing fouling phenomena.



Mega-Ton Water System project

Research Organization

Research Supervise

Pursuiting Extremely-High Technology

Pursuiting Basic Technology for the future

Chief Scientific Director

JSPS※1

Fund

Research Support Organization (NEDO)※2

Contract

Elemental Technology

- High-Efficiency/Large Scale Membrane Element Modules
- Seawater Intake Technology
- Osmotic Power Generation
- Highly Efficient Energy Recovery
- Low-Cost/Highly Durable Piping

System Technology

- Optimization of 1 million m3 class plants
- Resource Producing Innovative Sewage integration Membrane System
- No Chemical Seawater Desalination System

University The University of Tokyo, Tokyo Institute of Technology, Hokkaido University, Kobe University etc… 10 Universities in total

Company TORAY, HITACHI, TOSHIBA, MITSUBISHI HEAVY INDUSTRIES, etc… 17 companies in total

Others Tokyo Bureau of Sewage, Japan Sewage Works Agency

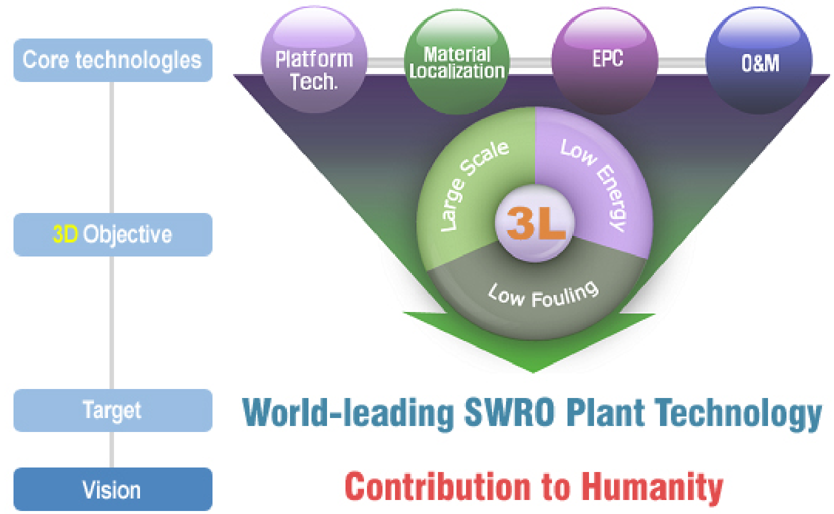
Registered Researcher 140 people total. (20 from University, 120 from company)

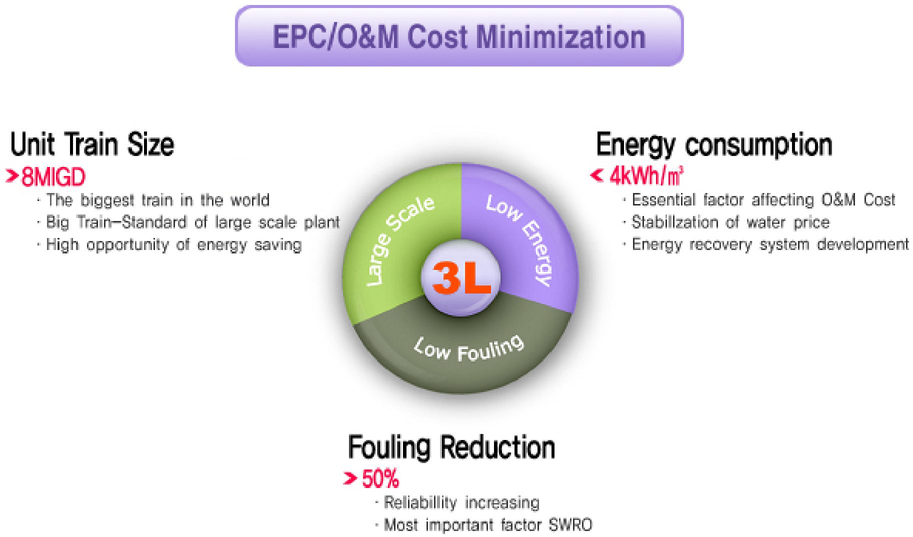
※1 JSPS・・・Japan Society for the Promotion of Science

※2 NEDO・・・New Energy and Industrial Technology Development Organization

Seawater Engineering & Architecture of High Efficiency Reverse Osmosis (SeaHERO) project is targeting to get the top SWRO technologies in the world

Center for Seawater Desalination Plant pursues the RO membrane technique which meets 3L skills. *3L* means the three main technical objectives including *large scale, low energy, and low fouling* for SWRO plants. At first, large scale is to design and construct the largest unit SWRO train [8MIGD = 36,368 m^3/d] in the world.



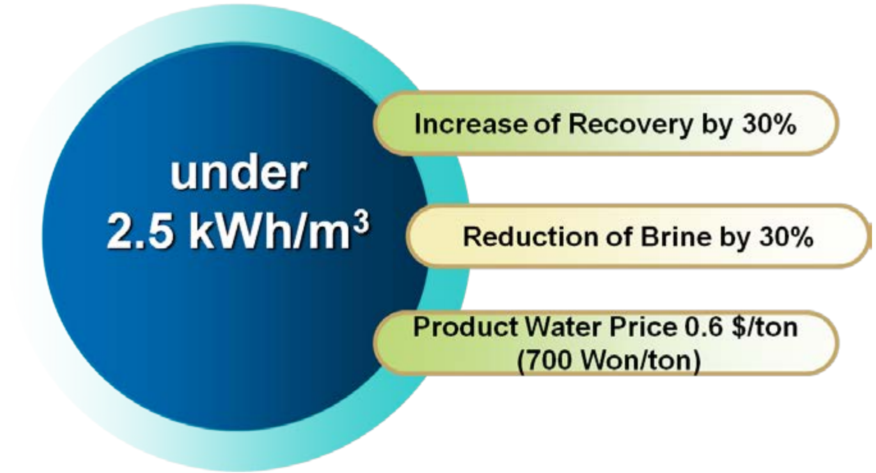


Second, low energy means to lower energy consumption of whole SWRO plant including intake, pretreatment, SWRO systems, and so on by 4kWh/m^3. At last, low fouling is to reduce fouling effect by 50% in terms of silt density index [SDI] and a new fouling parameter developed.

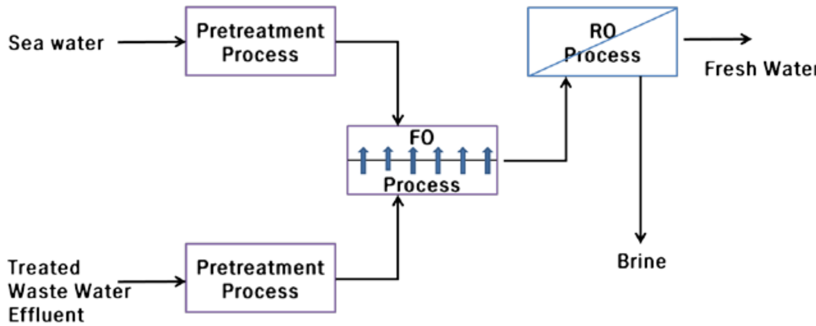
http://www.seahero.org/eng/

FO-RO Hybrid Desalination Process

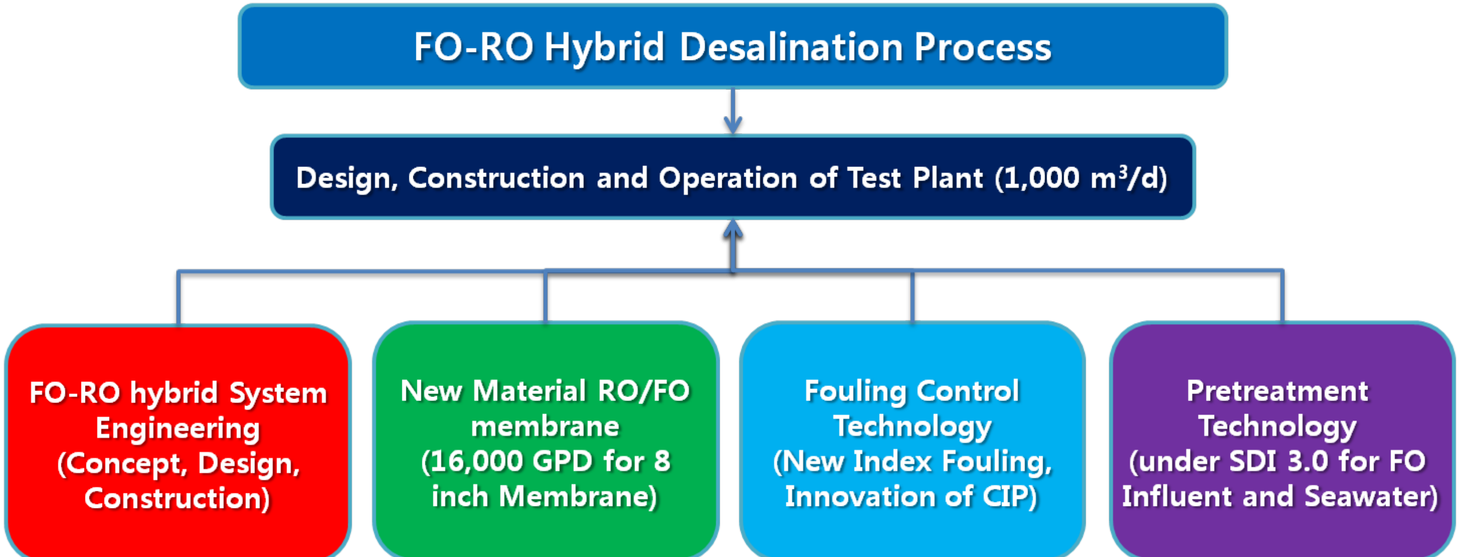
Technical Target : under 2.5 kWh/m³



FO-RO Process Concept

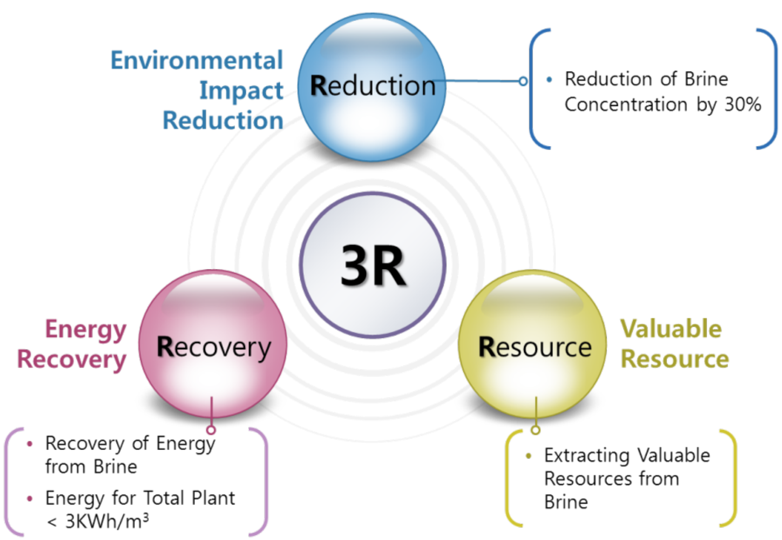


Research Center Structure

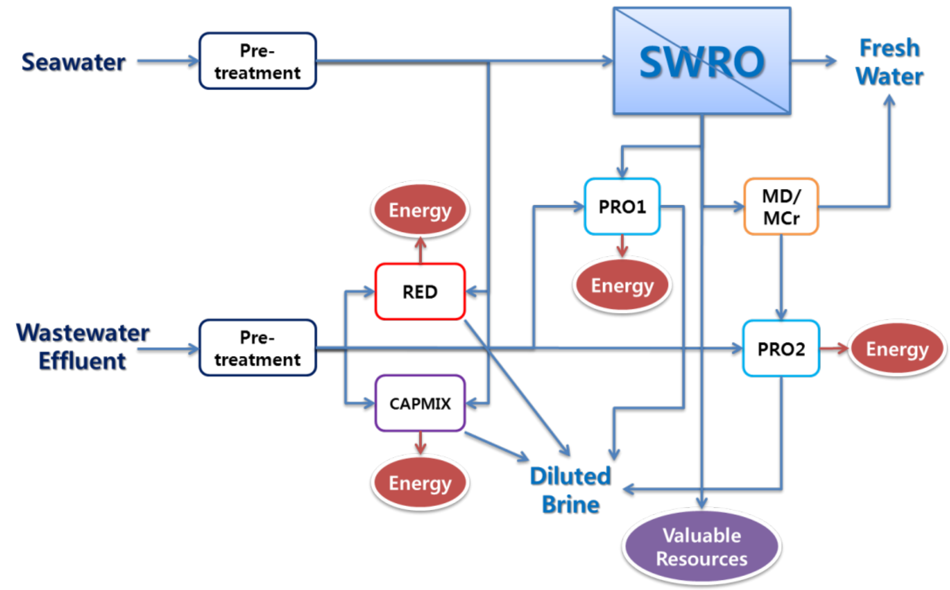


Hybrid Desalination Process for Energy/Resources Recovery

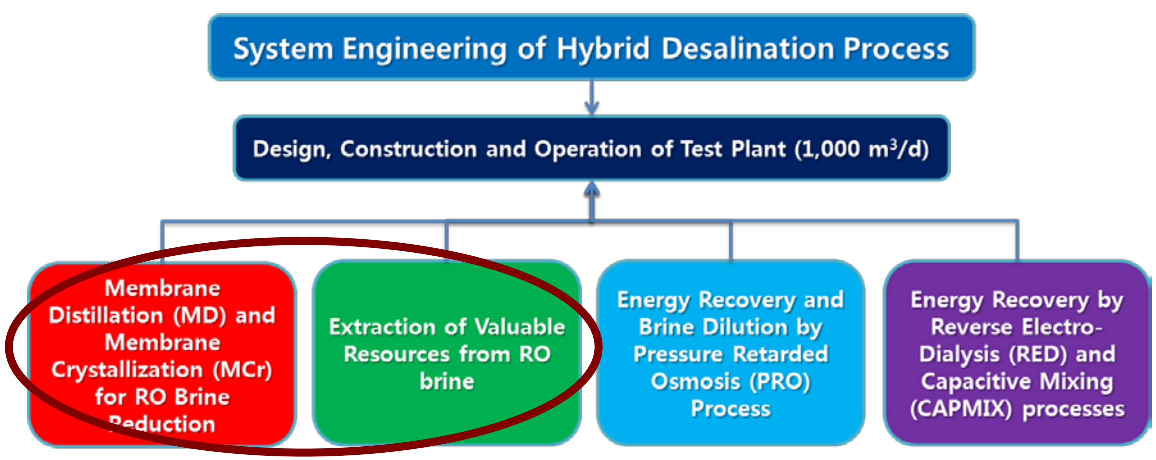
Vision: 3R



Concept

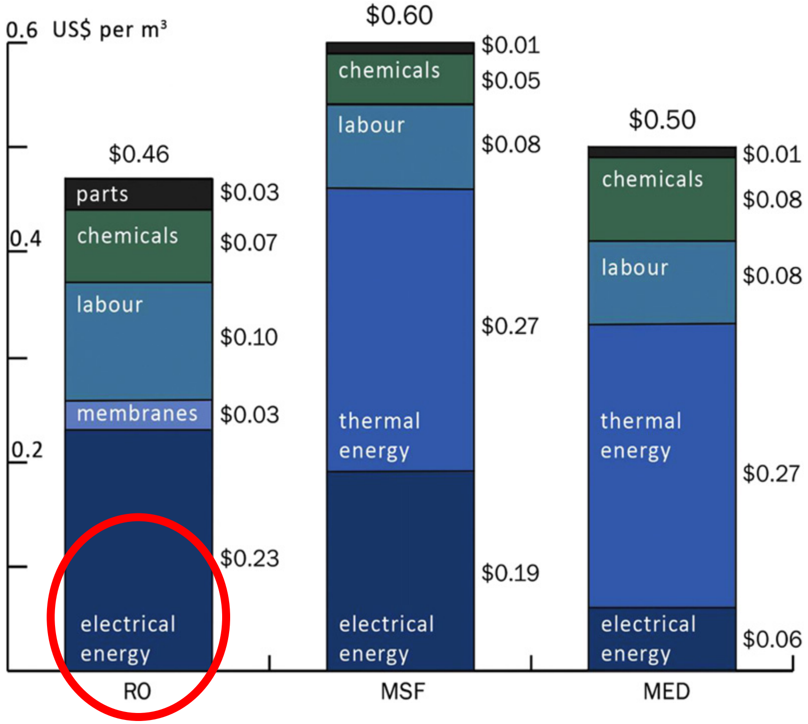


Research Center Structure

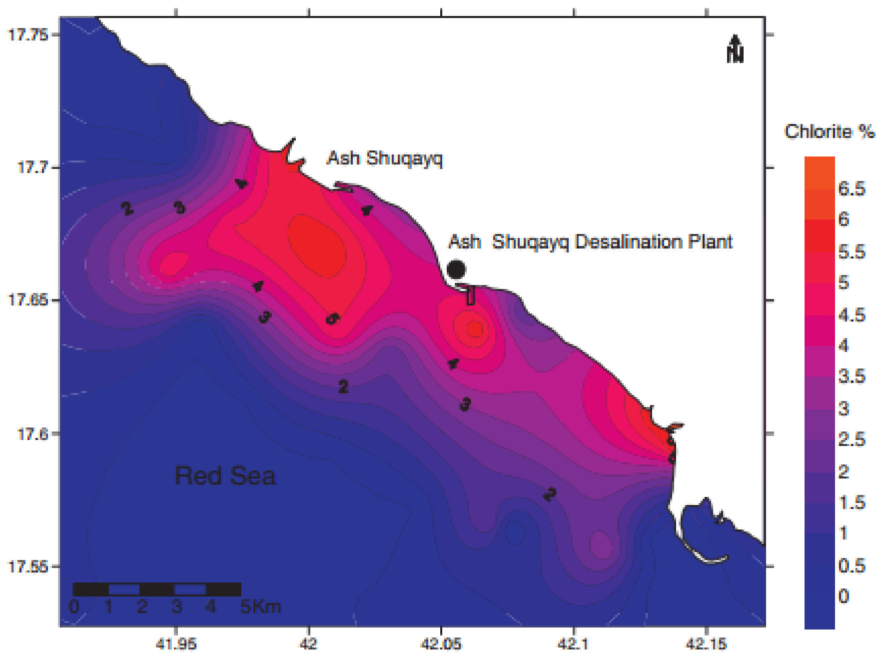


After SeaHERO projects.

Energy-intensive process



Brine treatments

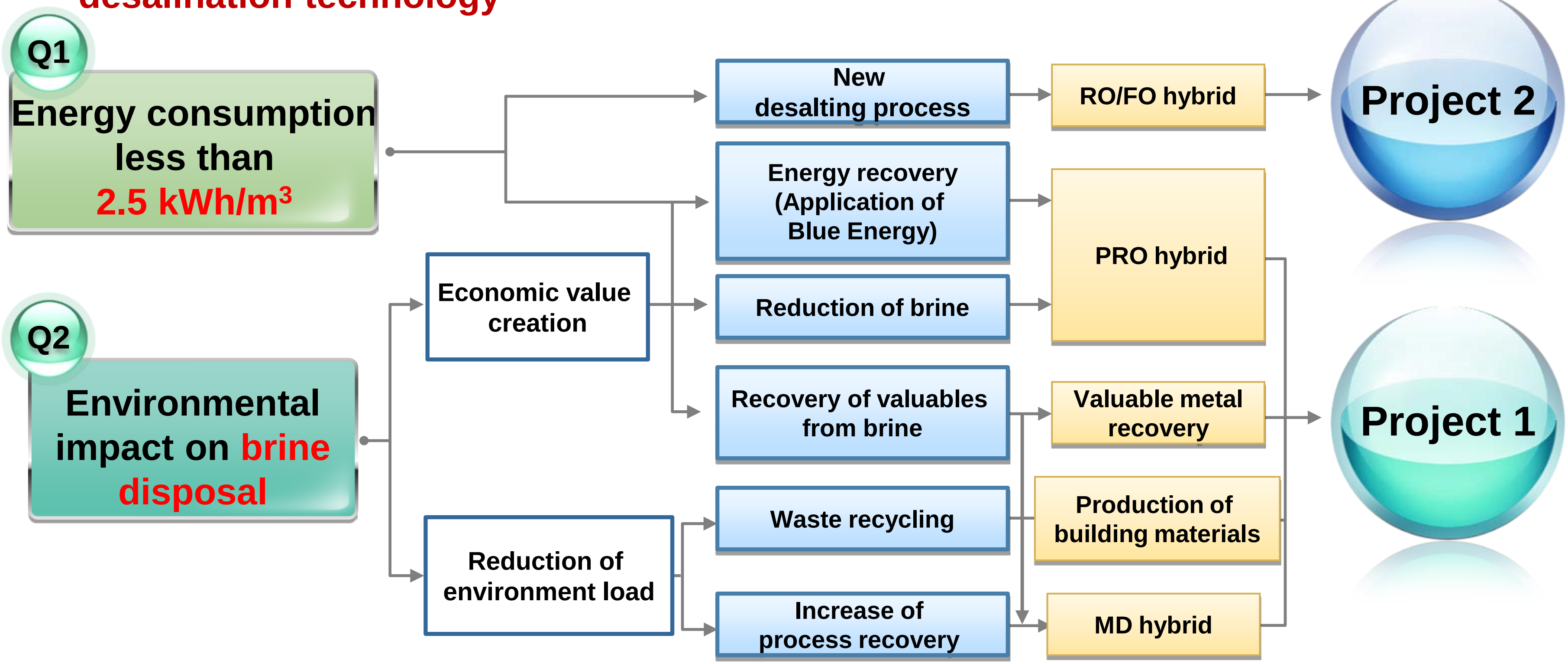


We still have problems related to energy and environmental issues of desalination.

2nd SeaHERO R&D Project

Problems of current desalination technology

Solutions for problems

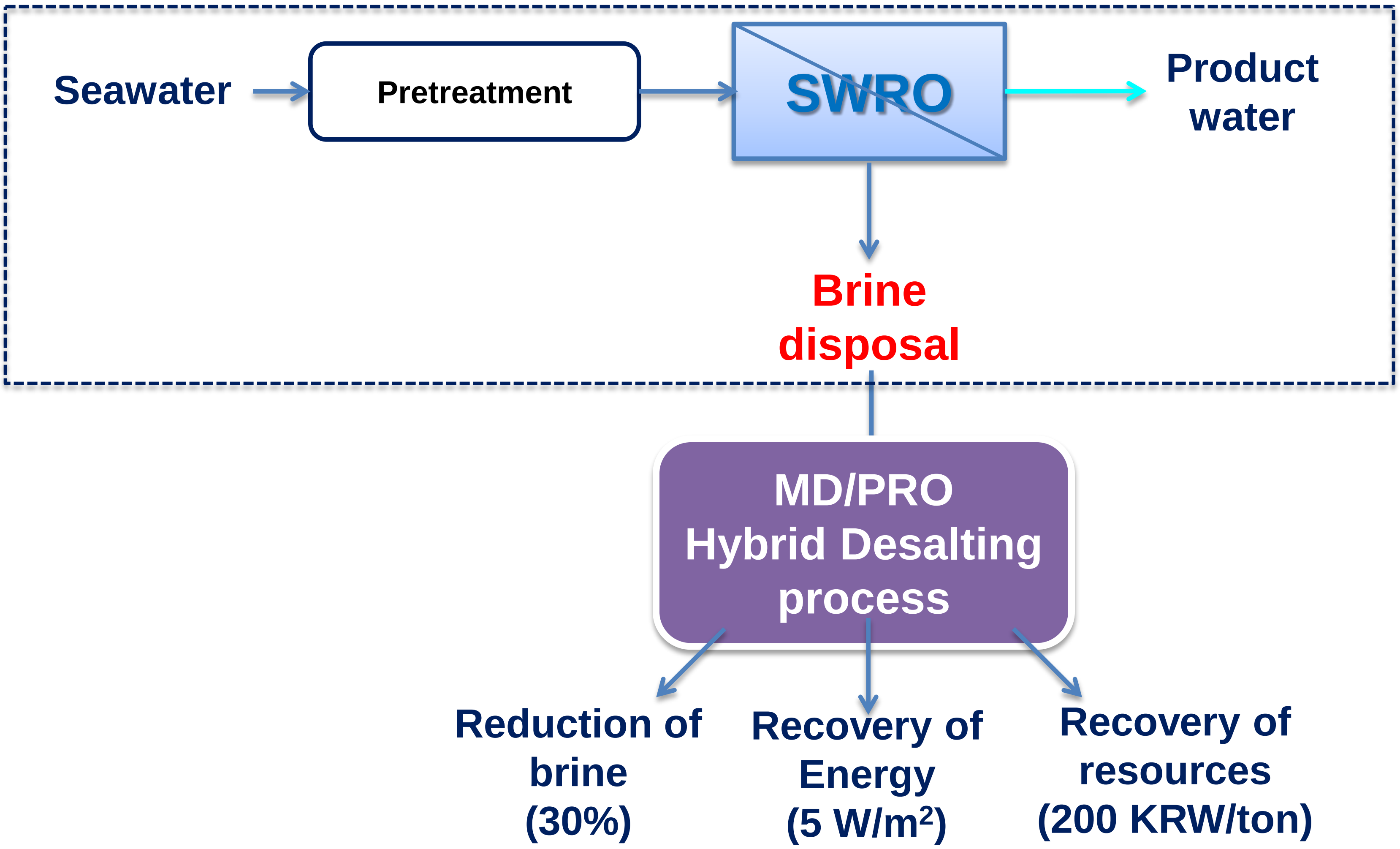


Hybrid project 1	Hybrid project 2
MD/PRO hybrid desalting technology	FO/RO hybrid desalination process

Acronyms: Forward Osmosis (FO), Membrane Distillation (MD), Pressure Retarded Osmosis (PRO)

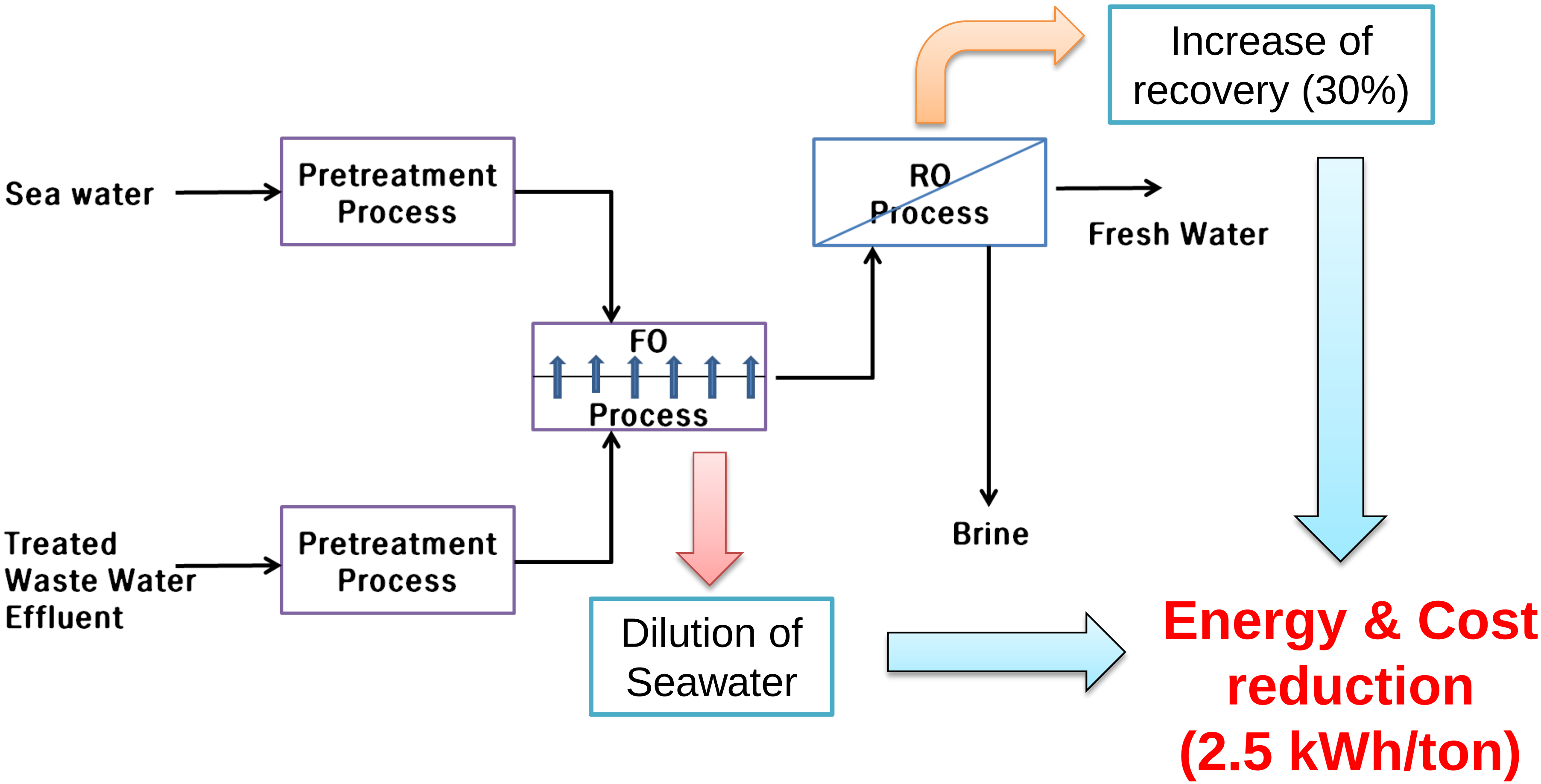
MD/PRO Hybrid process

Conventional desalination plant (Recovery < 40-50%)



FO/RO Hybrid process

Osmotic dilution of seawater using FO process



Plans for 2nd SeaHERO projects

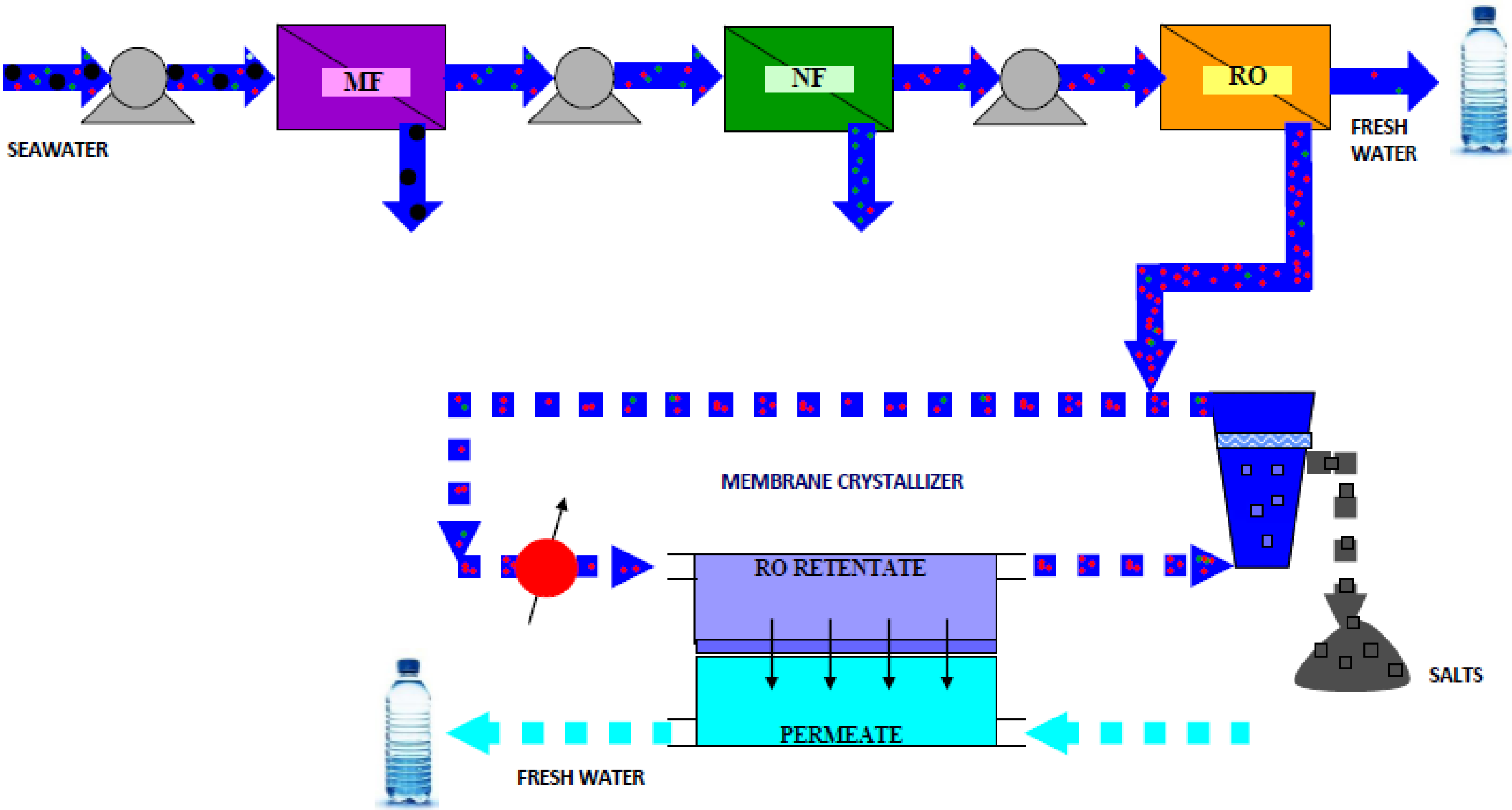
1. MD/PRO Hybrid (Launched)

- Duration : **2013. 05 ~ 2018. 04 (5 yr)**
- Budget : 26 Billion KRW + α

2. FO/RO Hybrid (To be)

- Duration : **2014. 05 ~ 2019. 04 (5 yr)**
- Budget : 32 Billion KRW + α

Integrated Mebrane Desalination System for Water and Raw Material



- Suspended solids, bacteria
- Divalent ions
- Monovalent ions

Modern, Late Modern, Post Modern Ages
To be sustainable on the10-Billion Earth

:

WATER DISTRICT

- Establishment of much more closed urban aquatic metabolic systems for high population density and high activity areas.
- Water district is more ergonomic system than ecological.
- Membrane technologies (reuse /desalination) are key to establish the systems.
- Fast breeder reactor energy are requested if ample renewable natural energy can not obtainable in the future.
- Integrated river basin management and resource conservation are improved remarkably by introducing the water district concept.

IN THE POST MODERN PERIOD

ESSENTIAL USE OF POTENTIAL WATER QUALITY

being supported by

- Separated or cascaded use of Water Quality selecting appropriate multiple water systems or its alternatives with least amount of energy and resource consumption.

・Conservation of natural water body clean as more important subject than ever. (Keep diversity of ecosystem)

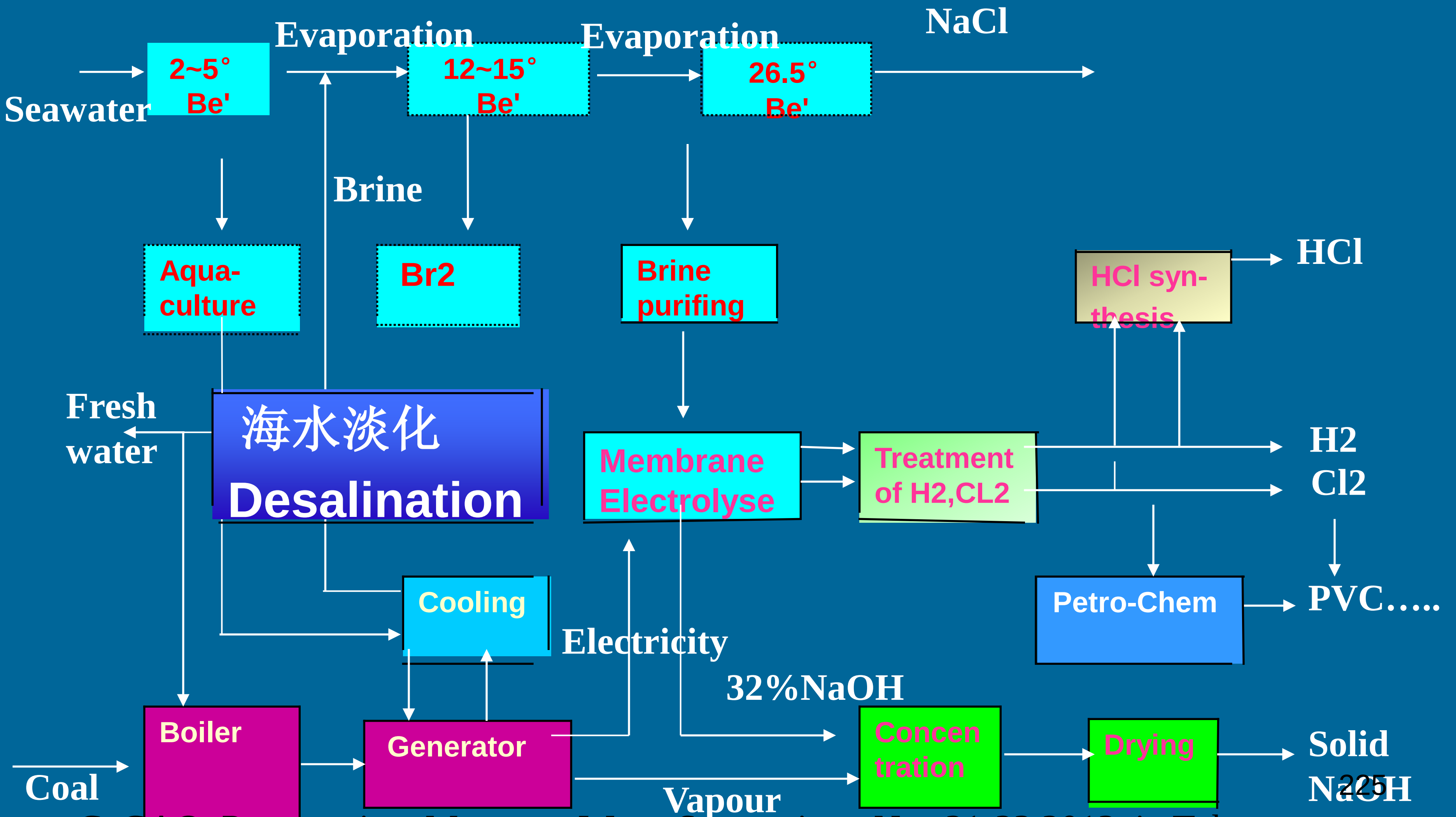
・Select dispersed but closed social metabolic systems without too much long distance bulk transportation and too much energy consuming treatments.

- Various membrane technology is a key to make up post modern urban water metabolic system.

- **In prediction, the annual output value of desalination will be 10 billion RBM in the coming 5~10 years.**

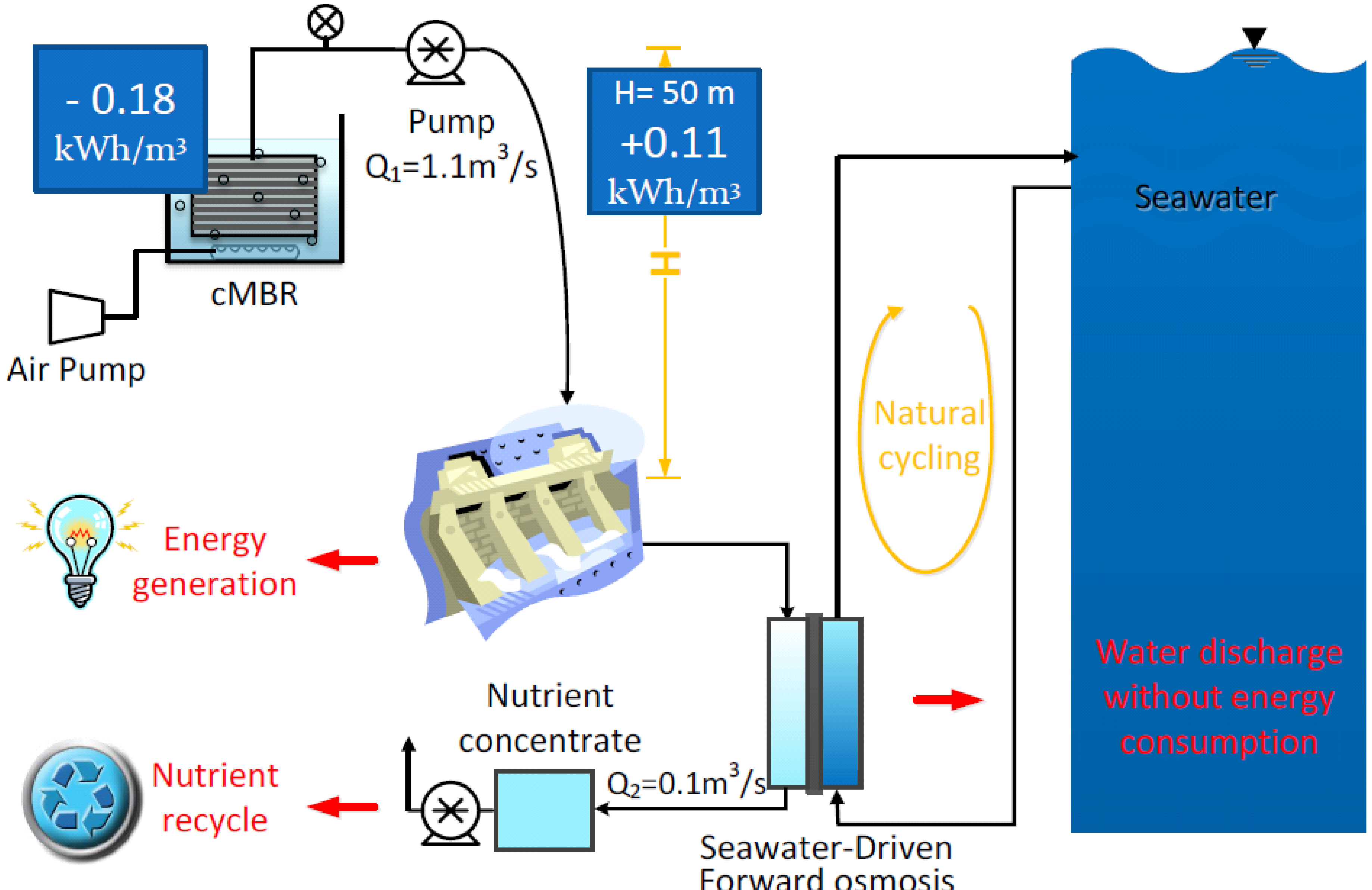
- **The integration of desalination with power production, heat supply and multipurpose use of seawater should be encouraged for better economical benefit and environmental protection.**
- **Pay much attention to impact on environment of seawater desalination, and offer related countermeasures**

Fig.5-4 The integration of desalination with power production, heat supply and multipurpose use of seawater



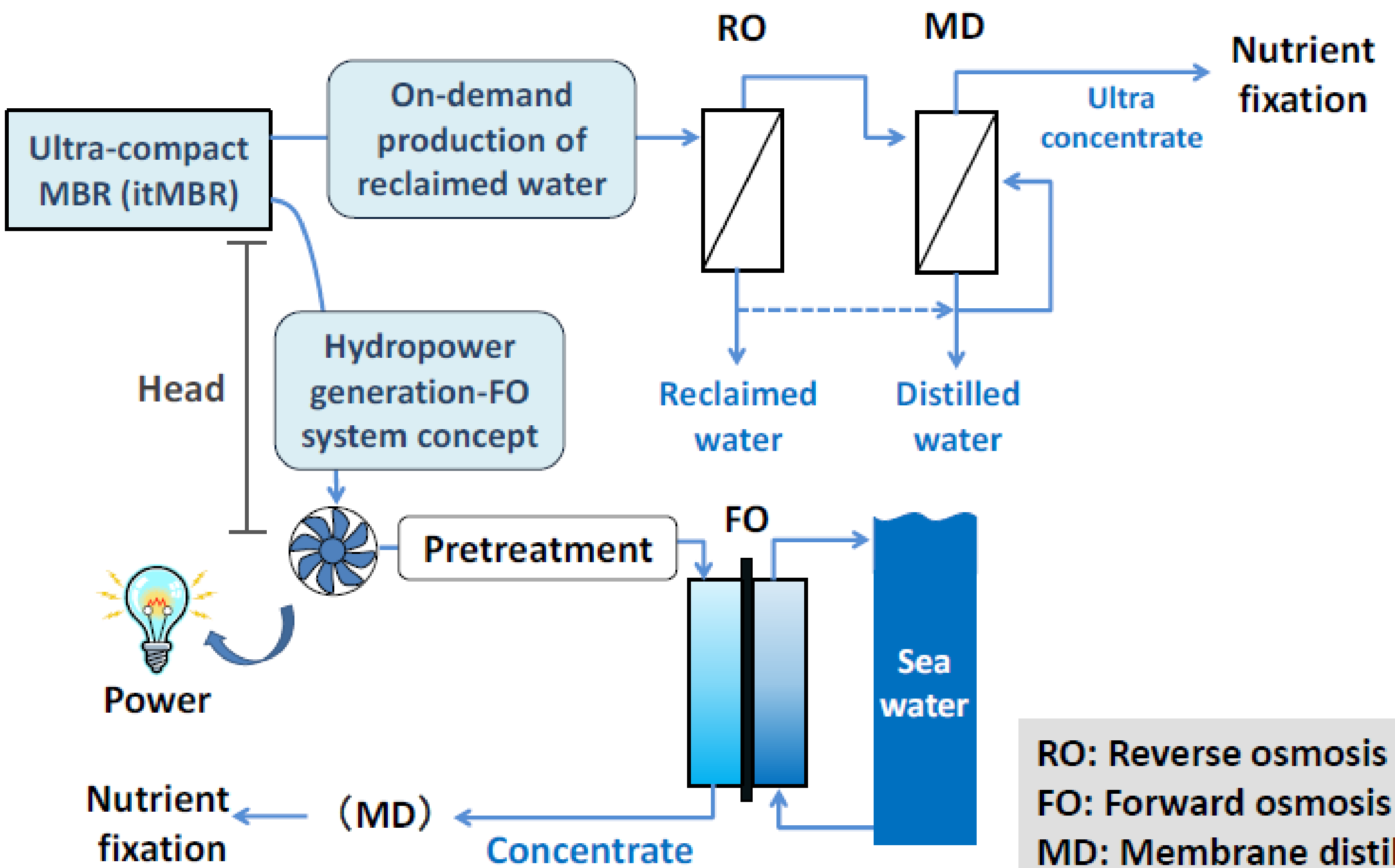
C. GAO: Presentation, Mega-ton Water Symposium, Nov.21-23,2013 in Tokyo

A novel thought of Electricity generation Forward osmosis



K. YAMAMOTO: Presentation, Mega-ton Water Symposium, Nov.21-23,2013 in Tokyo

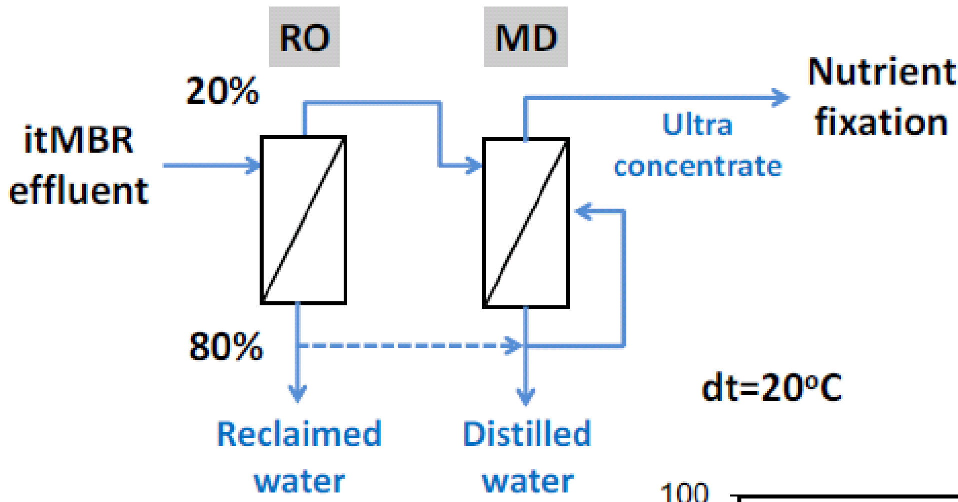
Hybrid Membrane System (HMS)



RO: Reverse osmosis filtration
FO: Forward osmosis filtration
MD: Membrane distillation

K. YAMAMOTO: Presentation, Mega-ton Water Symposium, Nov.21-23,2013 in Tokyo

HMS: Ultra-high water recovery by RO + MD



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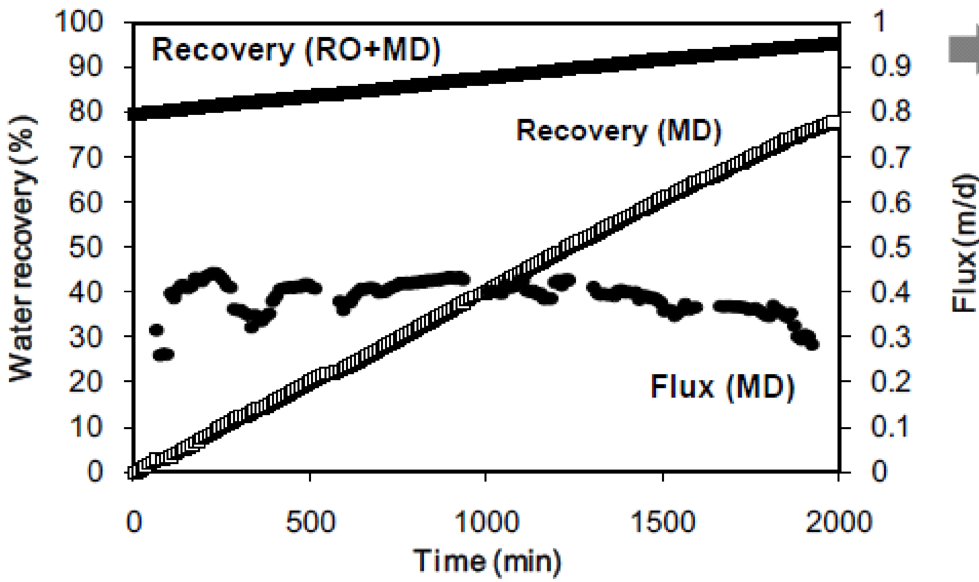
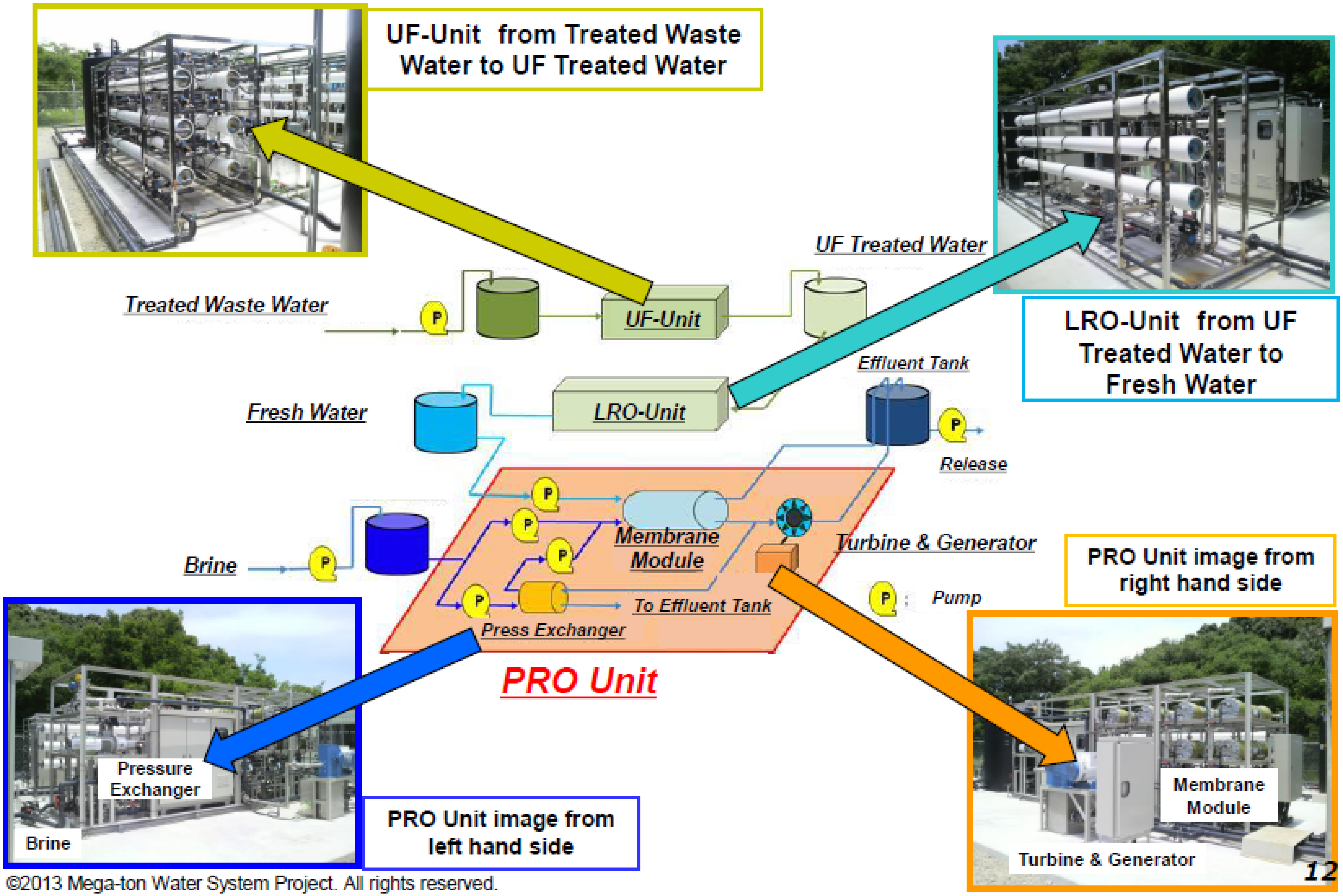


95% water recovery

K. YAMAMOTO: Presentation, Mega-ton Water Symposium, Nov.21-23,2013 in Tokyo

Prototype plant operation of PRO



A. TANIOKA: Presentation, Mega-ton Water Symposium, Nov.21-23,2013 in Tokyo

Comparison of water flux, specific salt flux and power density of various PRO membranes

Salty water	Fresh water	Operation pressure ΔP (bar)	Water flux J_v (LMH)	Power density W (W/m^2)	Specific salt flux J_s/J_w (mole/L)	Membrane	Reference
1.0M NaCl[b]	1 mM NaCl	15.1	49.9	**20.9**	**0.03**	TFC-PEI hollow fiber membrane	Current work
	10 mM NaCl	15.1	44.7	18.7	0.03		
0.5M NaCl[c]	10 mM NaCl	5.0	32.0	4.4	-	TFC-PES hollow fiber membrane	[14]
	40 mM NaCl	8.9	22.7	5.6	-		
	80 mM NaCl	8.9	16.7	4.1	-		
1.0M NaCl[b]	10 mM NaCl	8.4	47.2	11.0	-		
	40 mM NaCl	9.0	42.5	10.6	-		
	80 mM NaCl	9.1	33.3	8.4	-		
1.0 M NaCl[b]	10mM NaCl	15.0[a]	8.9[a]	3.7[a]	0.1[a]	HTI CTA-W	[12]
1.06 M NaCl[b]	0.9 mM NaCl 80 mM NaCl	15.2 15.2	36 27	15.2 11.4	>0.1[a]	TFC nanofiber flat sheet	[29]
1.0M NaCl[b]	DI water	15	-	12	-	TFC flat sheet	[30]

a. The data were estimated from the figure; b. synthetic seawater brine; c. synthetic seawater

R. WANG: Presentation, Mega-ton Water Symposium, Nov.21-23,2013 in Tokyo

BLUE ENERGY AND METALS RECOVERY FROM SEAWATERS AND BRACKISH WATERS

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[2]Department of Chemical Engineering and Materials, University of Calabria, via P. Bucci, Rende (CS)

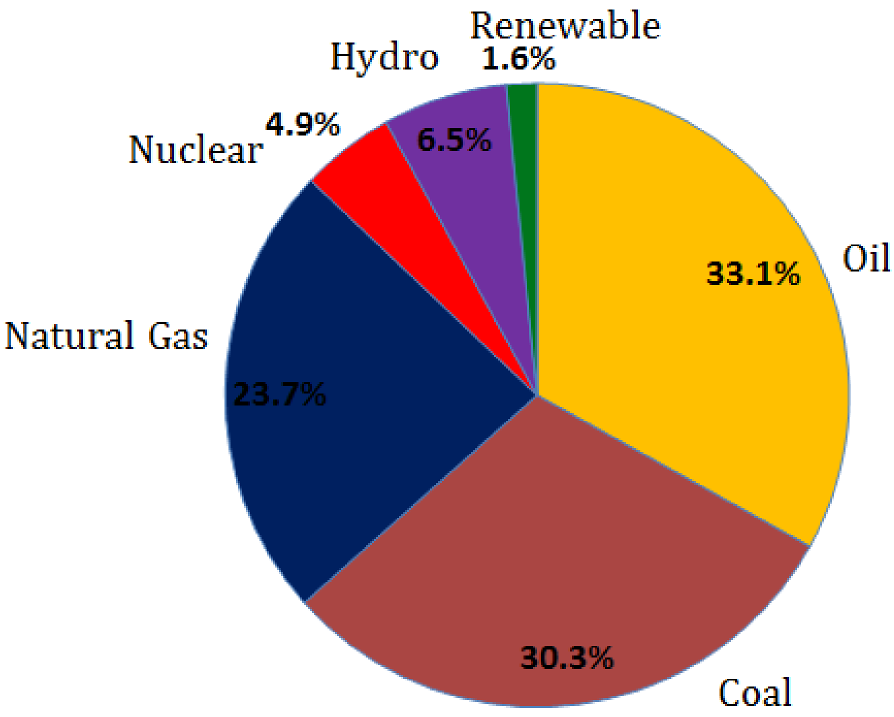
[3]WCU Energy Department, Hanyang University, Seoul 133-791 S. Korea

[4] Distinguished Adjunct Professor, Center of Excellence in Desalination Technology, King Abdulaziz University, Jeddah Saudi Arabia

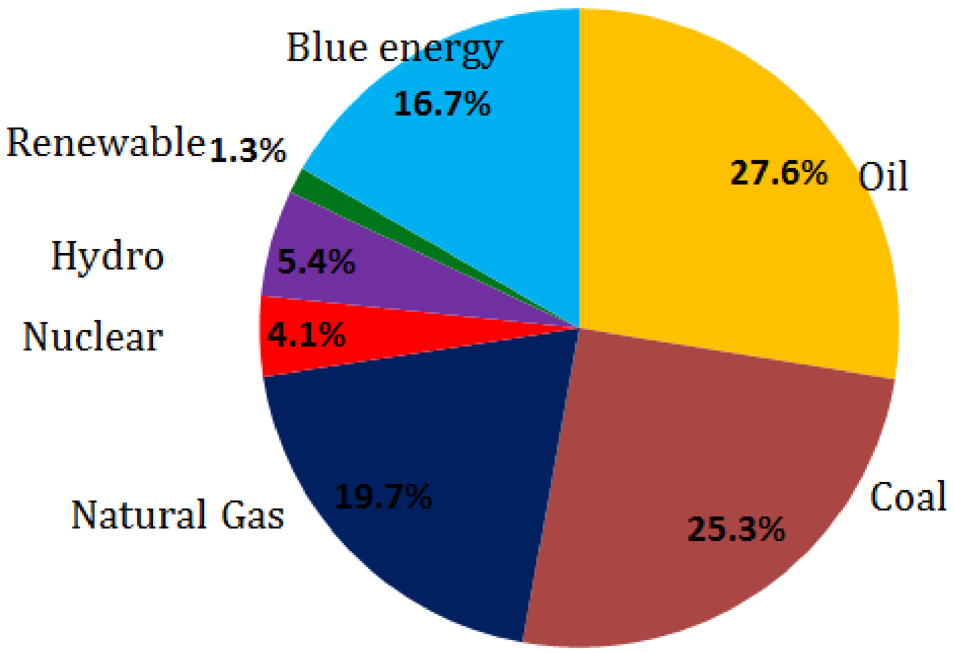
KACST, February 2014

Energy Resources

- **According to some optimistic estimations, 80 % of the worlds power consumption can be generated from the salinity gradient (osmotic power) which can reduce 40 % emission of green house gases.**



BP: Statistical review 2011



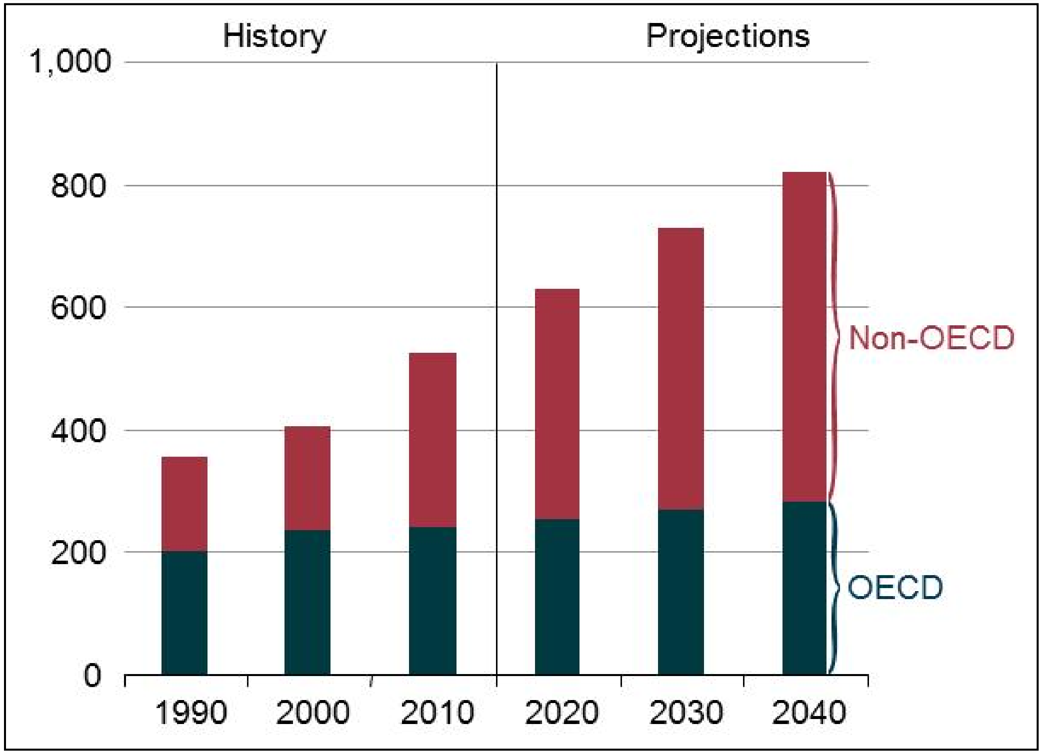
Recalculated

J.W. Post, PhD thesis, Wageningen University, Wageningen The Netherlands (2009)

World Energy Demand

- **Global energy demand will increase in more than 85 % from 2010-2040 in the developing nations outside the Organization for Economic Cooperation and Development (non-OECD)**
  - Economic expansion
  - Population growth
  - Improvement in Living standard
- **OECD member countries are already more mature energy consumers with slower economic and pulsation growth.**

World total energy consumption, 1990-2040 (quadrillion Btu)



EIA, International Energy Outlook 2013

Salinity Gradient Power

- **The salinity-gradient energy (blue energy) is the energy that can be obtained from mixing water streams with different salt concentrations.**
- **Blue energy could is available where;**
  - **Fresh water streams flow into the sea**
  - **Natural or industrial salt brines are achievable**
- **Up to 0.8 KW/m^3 extracted from a salinity gradient - corresponding to water falling over a dam more than 280 metres high**
- **Advantages:**
  - **No fuel cost**
  - **No CO_2 emissions or other significant effluents**
  - **Inefficient extraction is acceptable as long as an adequate return on investment is possible**

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

Blue energy: Learning from nature

- **The concept of using electrochemical potential between the solutions of different ion gradient to produce the energy that has been explored in producing the energy from salinity gradient.**
- **Since the difference in ionic gradient between the seawater and fresh water is higher than that for the biological solutions, the energy density for such systems is much higher than the natural ones.**

***''The tremendous energy flux available in the natural salination of fresh water is graphically illustrated if one imagines that every stream and river in the world is terminated at its mouth by a waterfall 225 m high… ''* Norman, R.S., Science 186 (1974), p. 350-352**

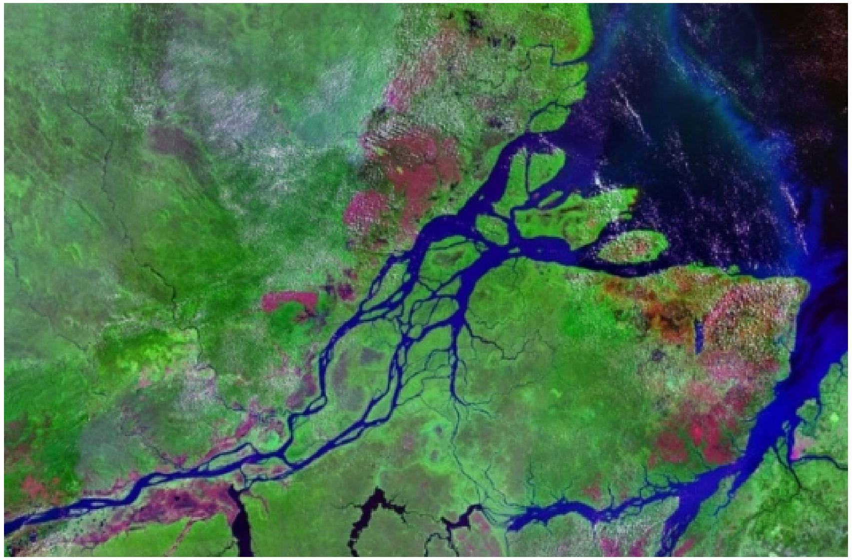
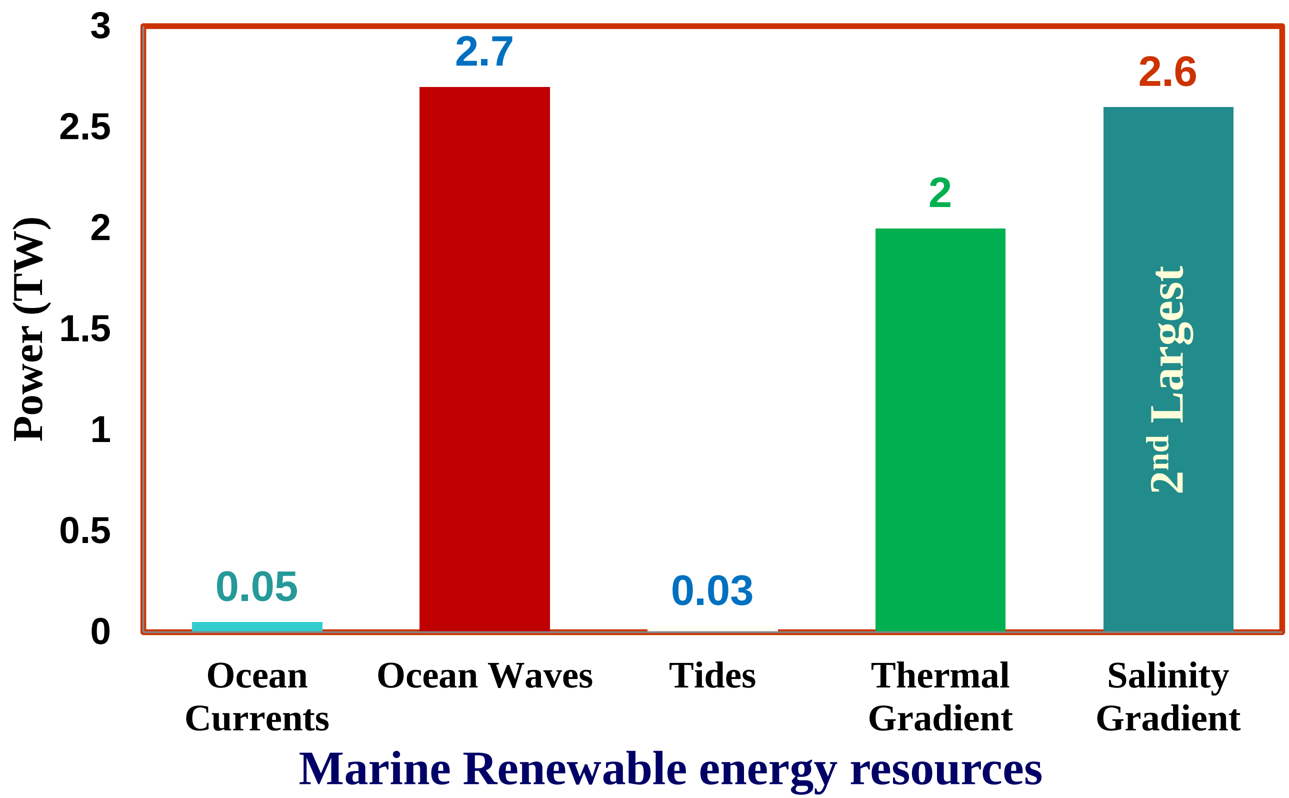


Image of AMAZON Estuary taken by NASA

Blue Energy and Other Marine Energy Resources

- **Global energy output from estuaries is estimated to be 2.6 TW**
  - **Approximately 20 % of the present worldwide energy demand**
  - **Around 980 GW is extractable**
  - **Additional 18 GW could be generated from wastewater**



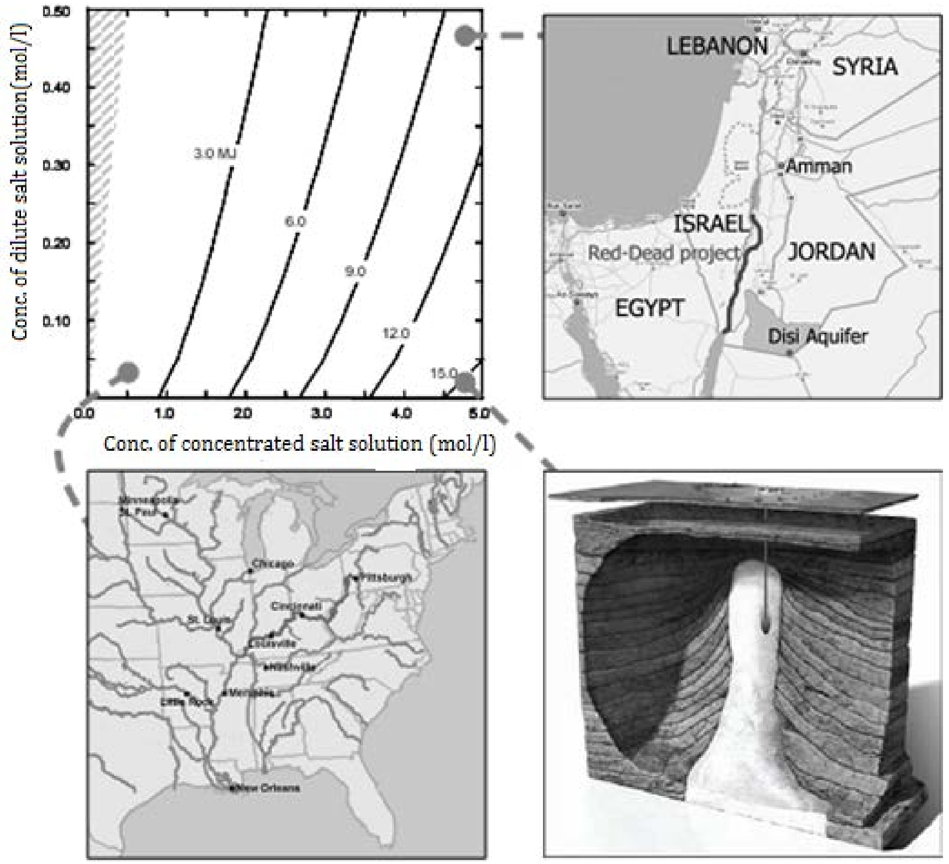
Recent Developments in Salinity Gradient Power, OCEANS 2003. Proceedings (Vol:4), 2284 – 2287.

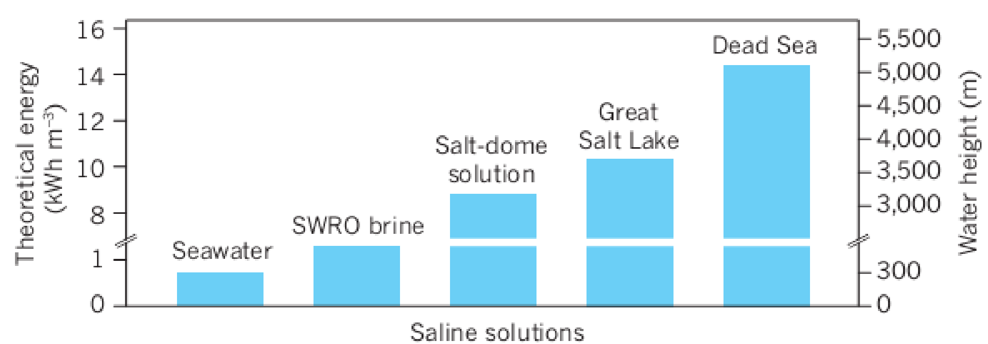
Potential of Blue Energy

- **Theoretical amount of energy(MJ) available by mixing NaCl solutions with various concentrations.**

Examples:

- **Mixing fresh river water from;**
  - **The Mississippi with sea water from the Gulf of Mexico would gain 1.4 MJ**
  - **The Dead Sea would gain 10 MJ**
  - **A vacuum salt mining industry with 15 hypersaline brine from a salt cavern would gain 15 MJ**

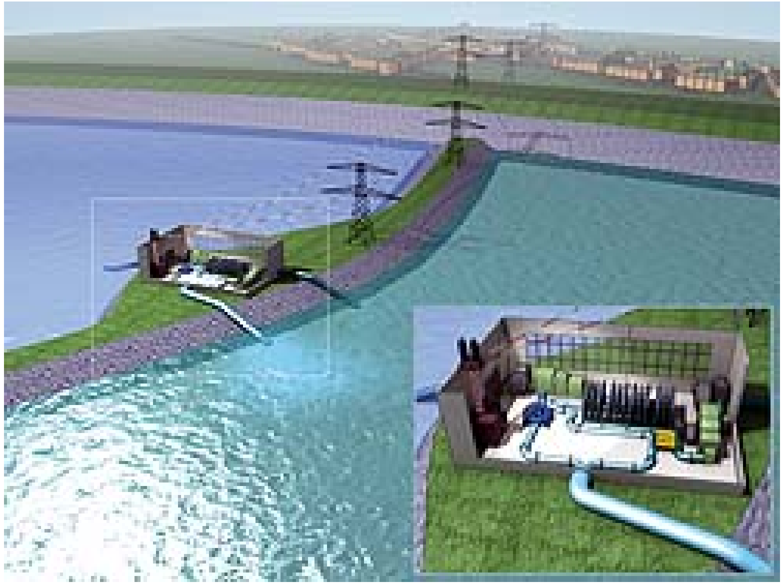




J.W. Post, PhD thesis, Wageningen University, Wageningen The Netherlands (2009)

Blue energy and PIS

- ✓ Each m^3 of river water can yield 1.4 MJ when mixed with the same amount of sea water.
- ✓ The production of energy from the salinity gradient is an emerging field and an attractive way to achieve the objective of sustainability.



- ✓ The technique can be extremely useful in reducing the reliance on fuel for energy production and an important step to cut down the CO_2 emission.
- ✓ Brine can be a useful candidate to increase the salinity gradient. These considerations make this technique in good agreement with the recommendations of PIS.

Approaches for Blue Energy Generation

- **Membrane-based processes to generate power from salinity gradient**

Pressure Retarded Osmosis

Reverse Electrodialysis

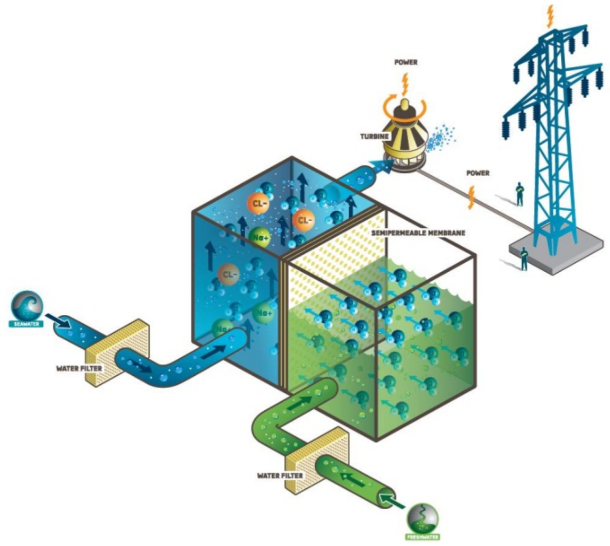
Most Promising

- **Others**
  - **Capacitive mixing (CAPMIX)**
  - **Vapor pressure difference utilization**
  - **Nano Battery Electrodes (NBE)**

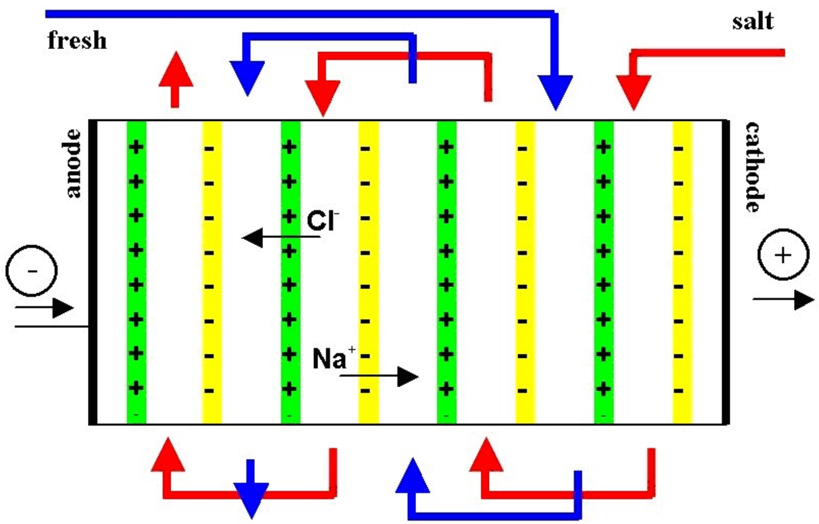
J.W. Post et al., Journal of Membrane Science 288 (2007) 218–230

Approaches for Blue Energy Generation

- **Pressure retarded osmosis (PRO) involves the flow of water from low salinity water to high salinity water through a semipermeable membrane to produce pressurized water that generates electricity through mechanical turbines.**
- **Reverse electrodialysis (RED) is based on the transport of ions and electrical current is generated directly from the flow of ions.**



PRO



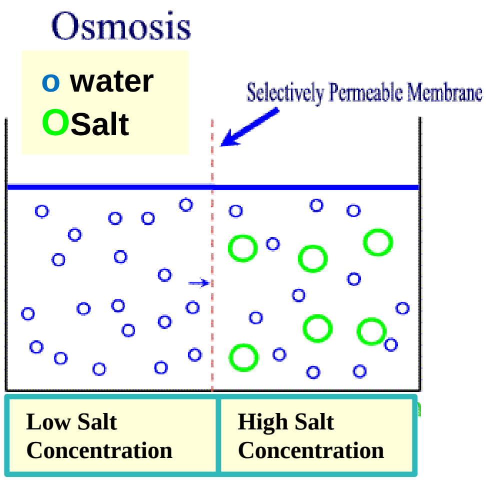
RED

- **Both techniques are close to commercialization but still suffering some challenges**
  - **High cost of the membranes**
  - **Fouling of the membranes which adversely affects the useful lifetime of the membrane modules**

Pressure Retarded Osmosis

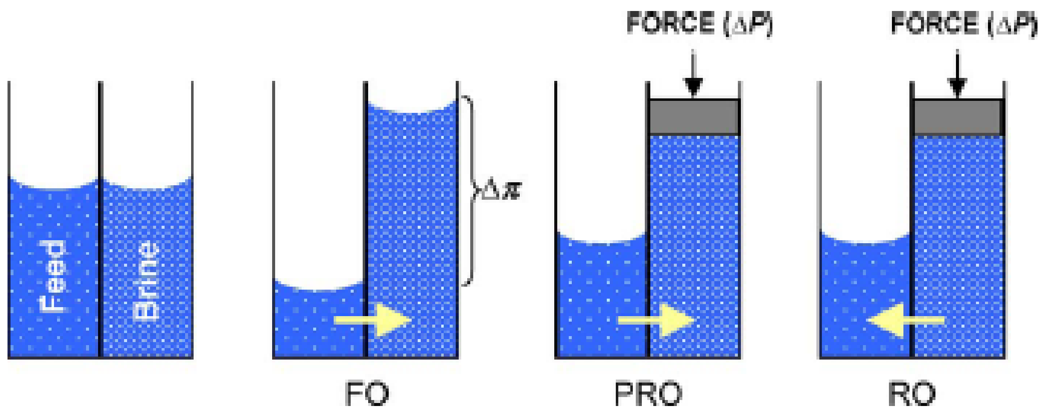
Osmotic processes

- 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.

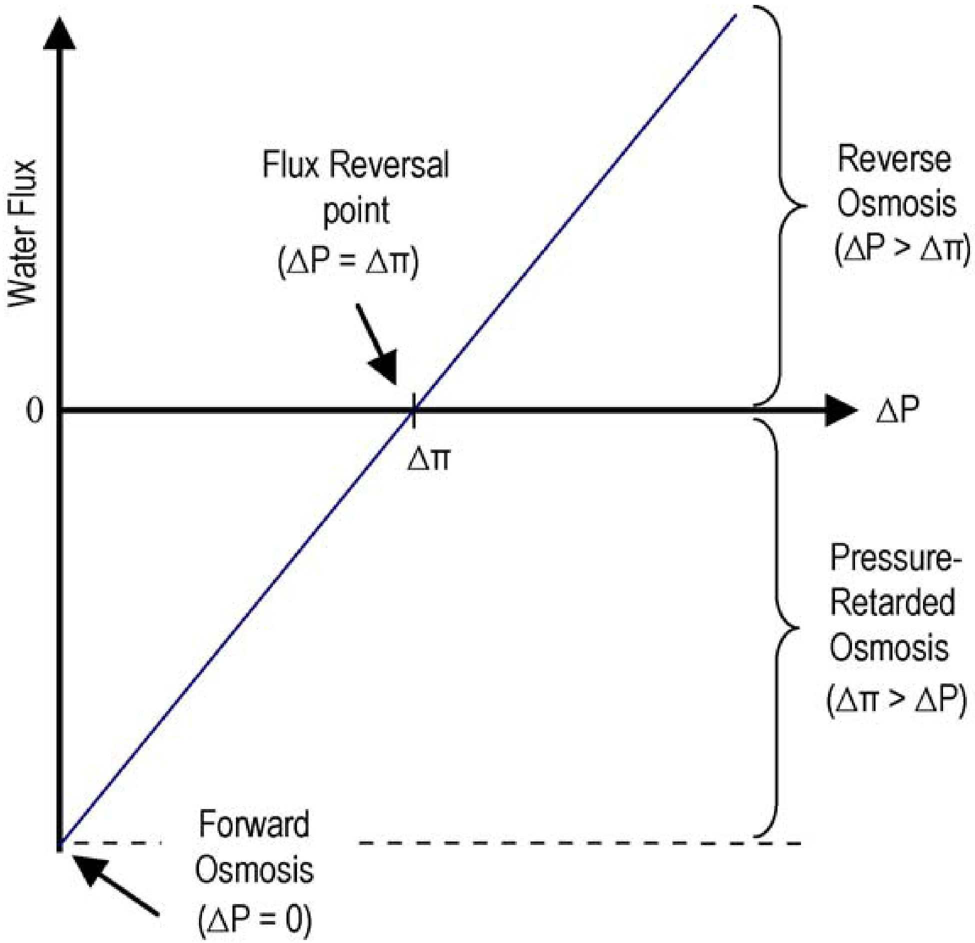
Classification of osmotic processes



- **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

Transport in Osmotic Processes



- **The general equation describing water transport in FO, RO and PRO is**

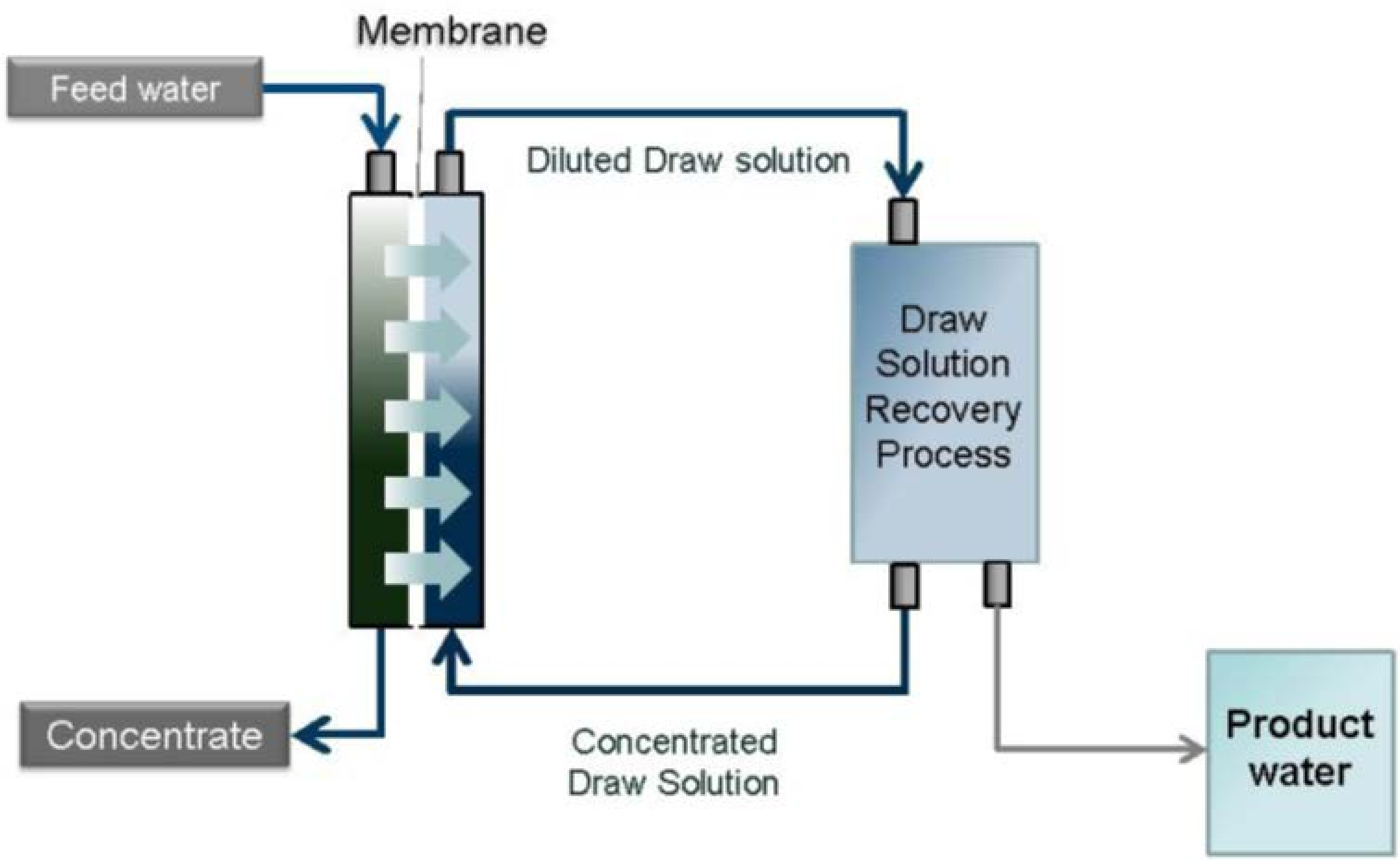
$$J_w = A(\sigma\, \Delta\pi - \Delta P)$$

where J_w is the water flux, A the water permeability constant of the membrane, σ the reflection coefficient, and ΔP is the applied pressure.

- **For FO, ΔP is zero;**
  - ✓ **for RO, $\Delta P > \Delta\pi$;**
  - ✓ **for PRO, $\Delta\pi > \Delta P$.**

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

Forward Osmotic Processes



FO advantages and Applications

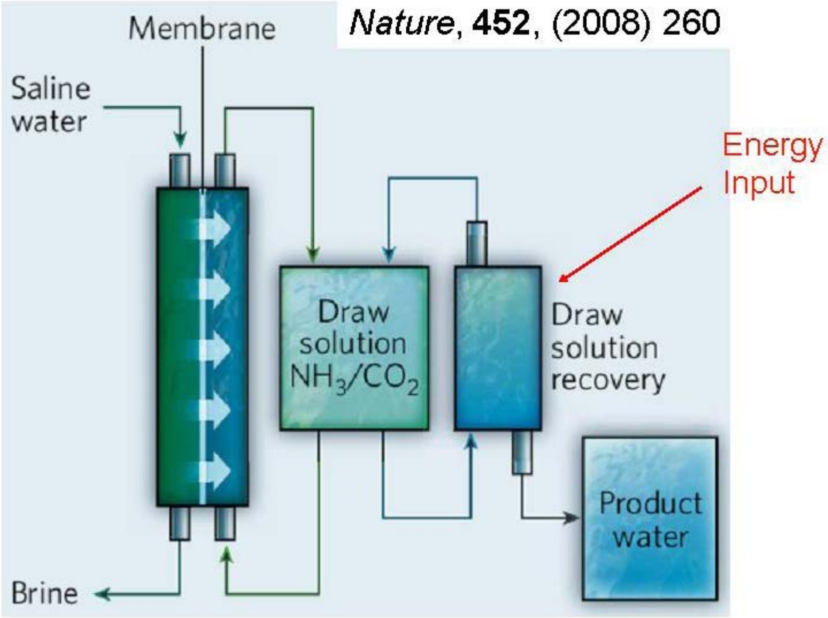
- FO advantages:
  - Low or no hydraulic pressures
  - High rejection of a wide range of contaminants
  - Lower membrane fouling propensity than pressure-driven membrane processes
  - Equipment used very simple and membrane support less of a problem due to the low pressure involved
- FO has been used in the following fields:
  - Desalination of seawater;
  - Treatment of industrial wastewaters (at bench-scale);
  - Concentration of landfill leachate (at pilot- and full-scale);
  - Treatment of liquid foods in the food industry (at bench-scale).

A Forward Osmosis Desalination Pilot Plant

- **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 which makes it ideal for drawing water from saline feeds.**

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

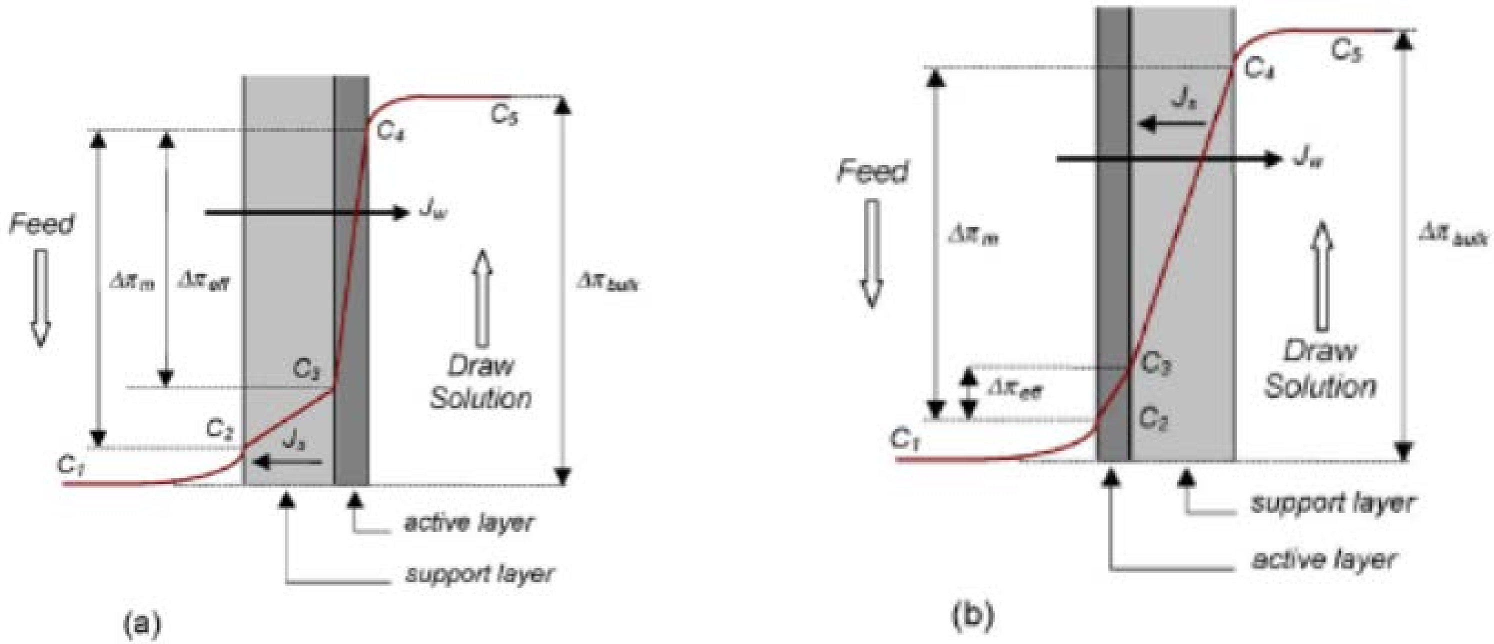
Nature, **452**, (2008) 260



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

✓ **These salts have the ability to decompose into ammonia and carbon dioxide gases when heated allowing for their efficient complete removal and reuse**

Major Challenge: Internal Concentration Polarization (CP)



(a) Concentrative internal CP

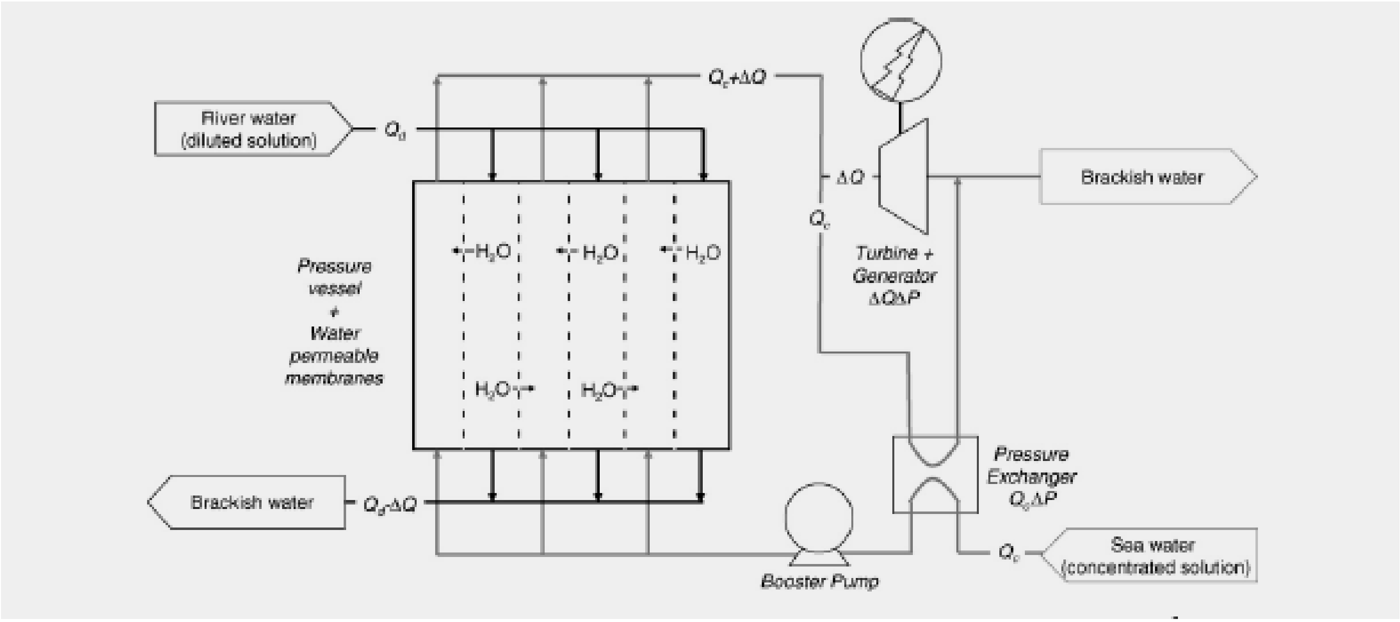
(b) dilutive internal CP across a composite or asymmetric membrane in FO

- **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.**

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,**
  - **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.**

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 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 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.**

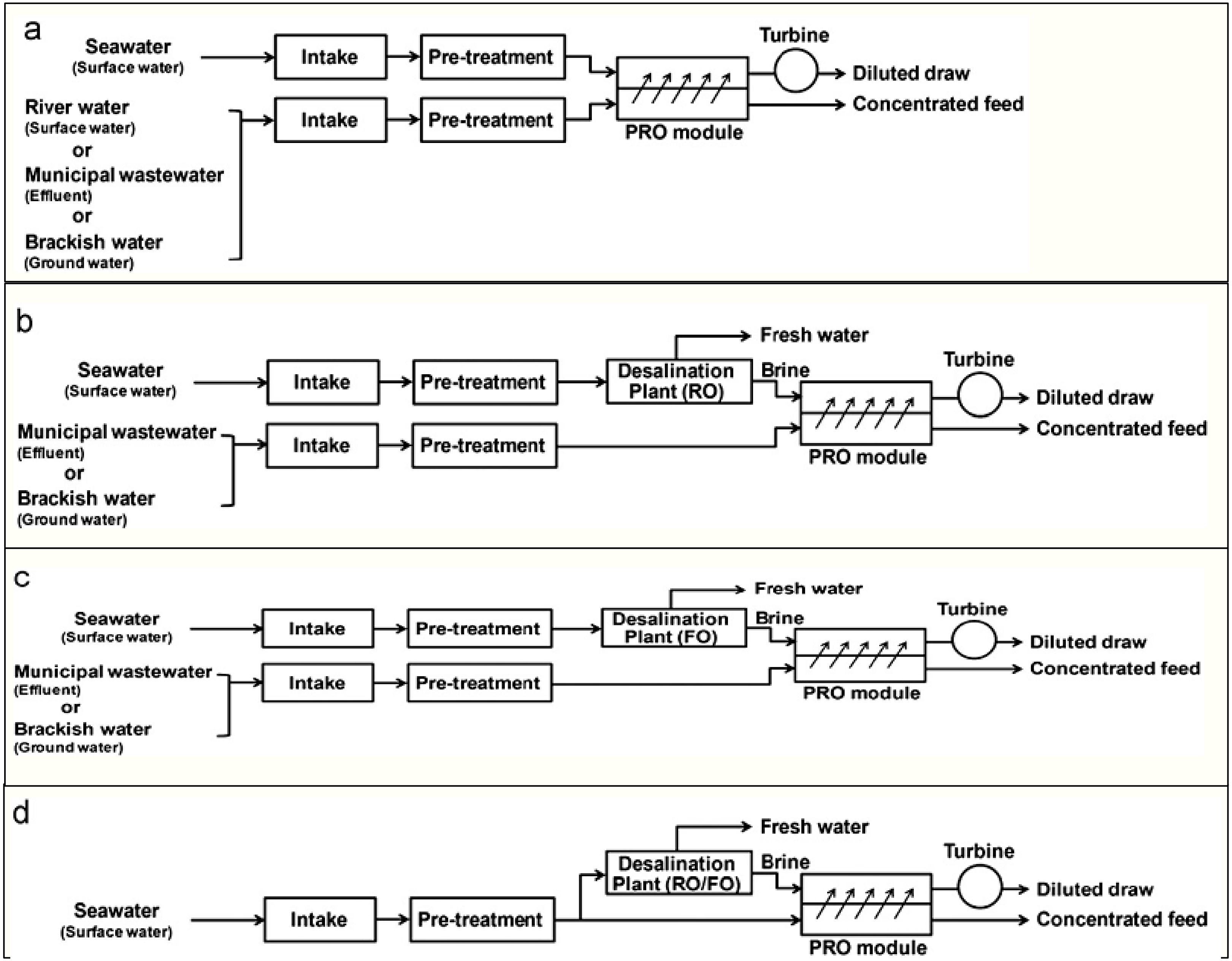
Seawater/Brine pair for PRO

- **The most commonly used seawater/river water for the generation of energy through PRO does not have the appropriate membranes for viable operation.**
- **The other possible solution can be tried to use the different salinity gradient resources more efficiently.**
- **Alternative draw/feed solutions for PRO;**
  - **Brine from RO (or future FO) / municipal wastewater**
  - **Seawater/RO (or future FO) brine**
- **A current study reveals that the use of 2M draw solution in combination with 0.5 M feed solution has the potential to generate a power density of 4.7 W/m^2 by using the existing commercial membranes.**

The pretreatment of draw solution can be avoided in this way

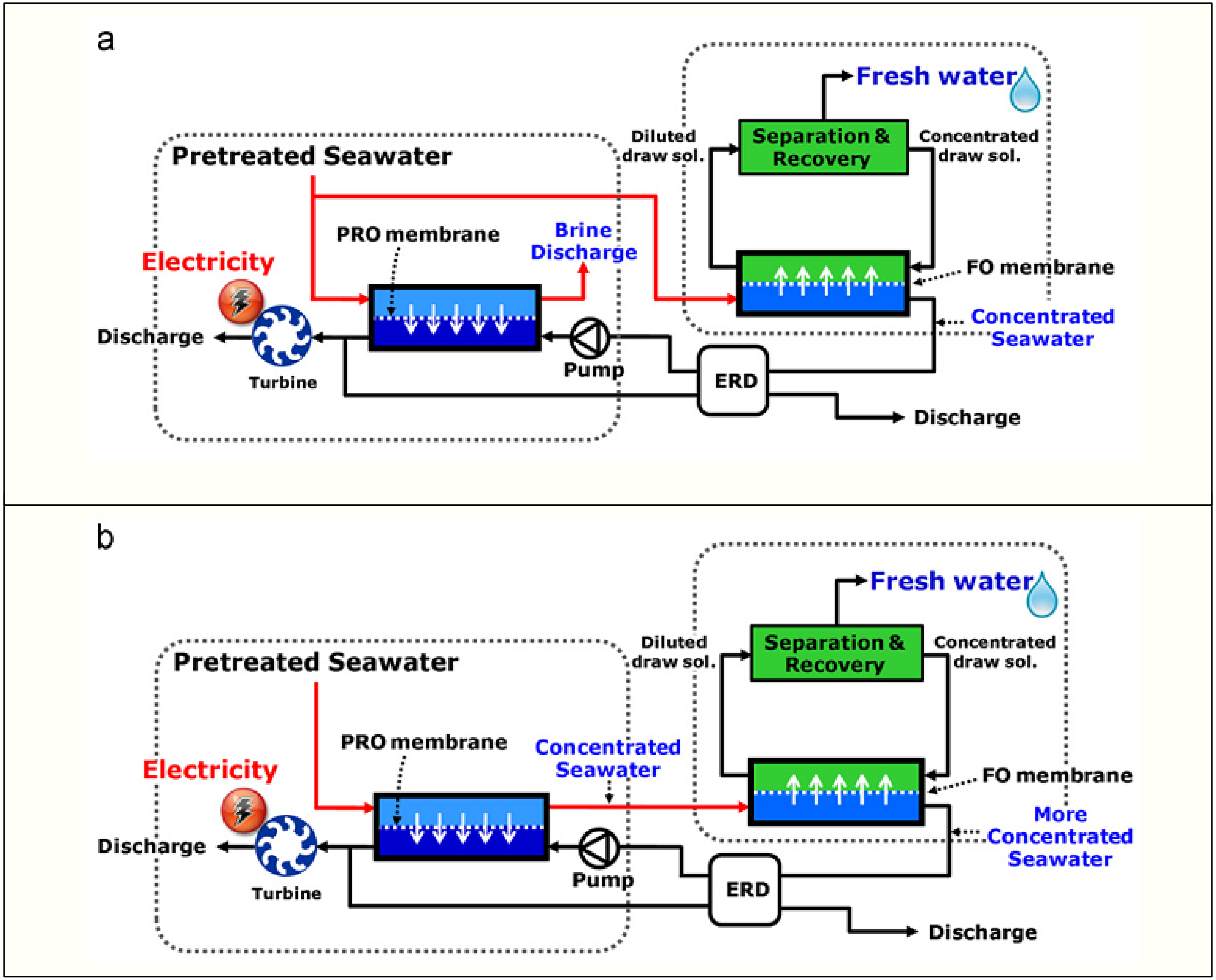
Y. C. Kim and M. Elimelech, J. of Mem. Sci. 429 (2013) 330–337

Resources of Salinity Gradient for PRO

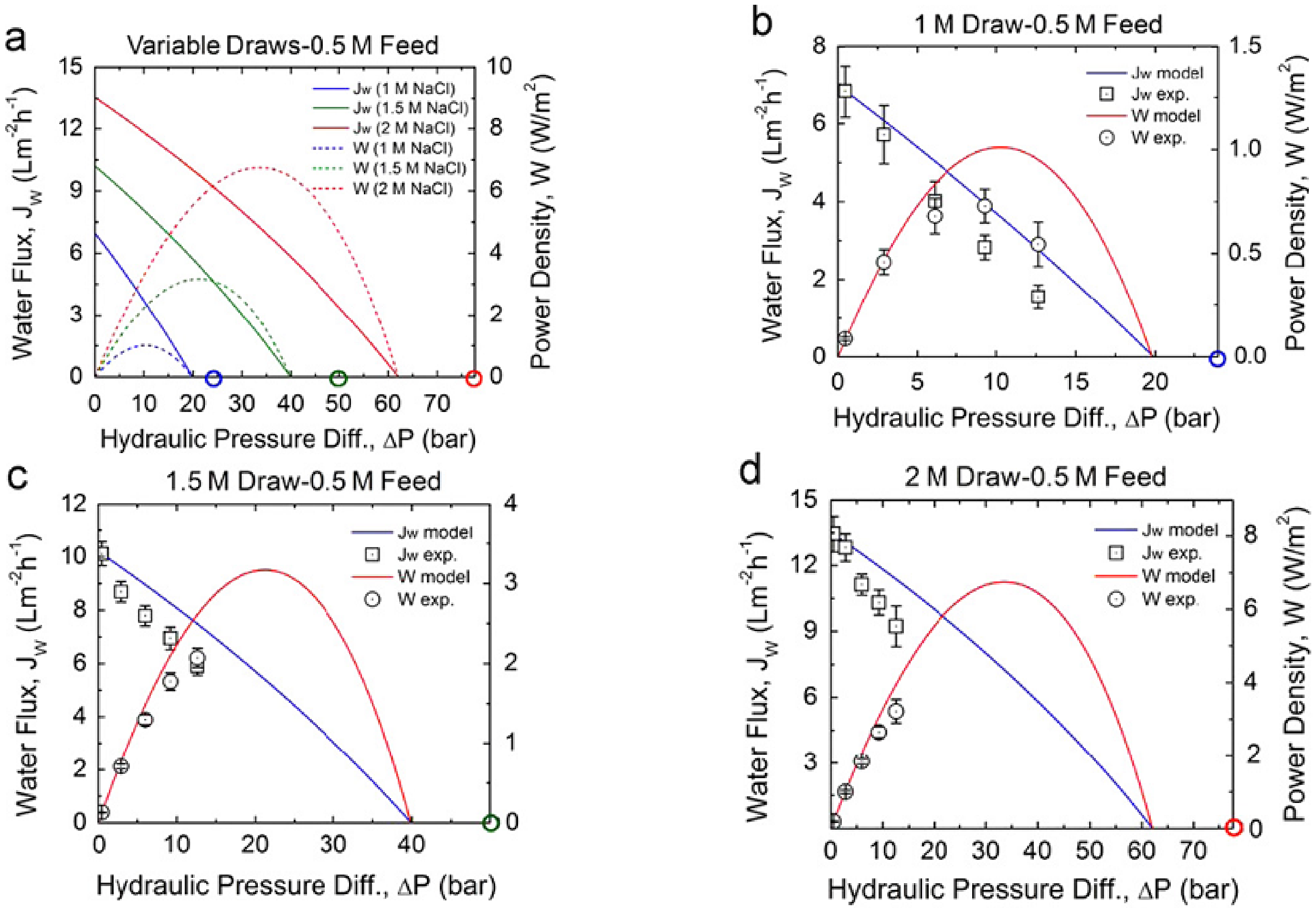


Y. C. Kim and M. Elimelech, J. of Mem. Sci. 429 (2013) 330–337

PRO Configurations



Effect Of Draw and Feed Solution Concentration on Power Density



- **The water flux decreases linearly and power density shows a quadratic function curve with a peak point as a function of the hydraulic pressure difference**
- **For the higher salinity gradient conditions using 1.5 and 2 M NaCl draw solutions, the projected power density have an increasing trend**

Y. C. Kim and M. Elimelech, J. of Mem. Sci. 429 (2013) 330–337

Membranes for PRO

❖ **Desirable membranes for practical applications in PRO, must possess the following features**

- **Minimization of internal concentration polarization**
- **Good mechanical strength of the membrane**
- **Very less tendency towards fouling**

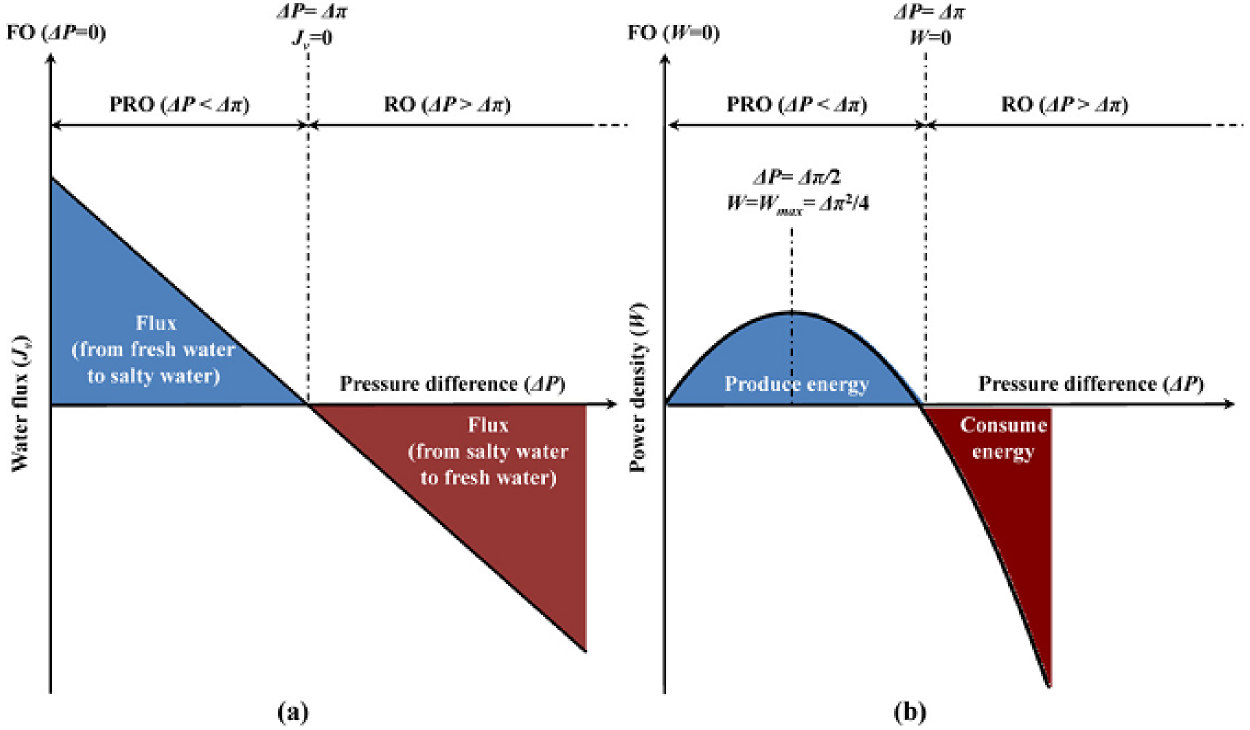


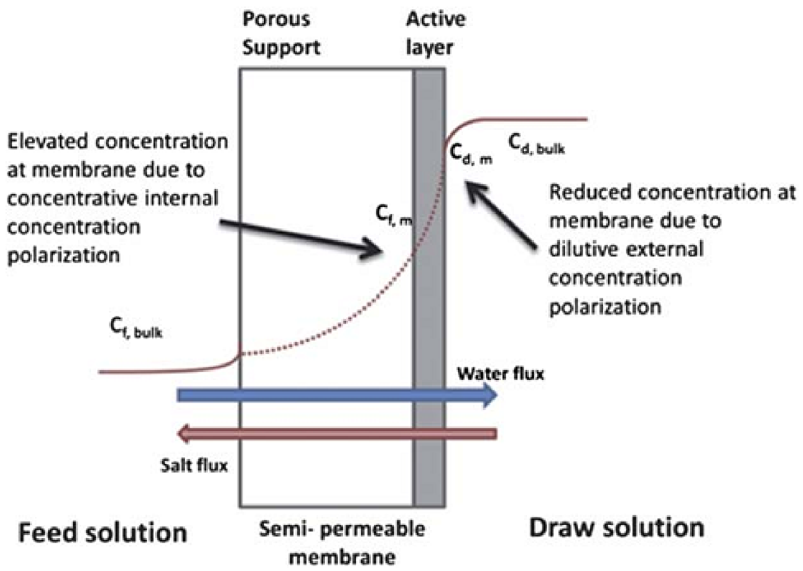
Fig. 1. Water flux direction and energy consumption/production in FO, PRO and RO using a semi-permeable thin film.

S.Chou et al., Journal of Membrane Science 389 (2012) 25 – 33

Membranes for PRO

Membranes	Water Permeability $\times 10^{-12}$ m/Pa•s	Salt Permeability $\times 10^{-7}$ m/s	Structure factor µm	Power density (W/m²) Seawater	RO Brine[b]
Lab Cellulose-Acetate-FO[25]	0.41	0.22	52	0.7	2.7
Lab TFC-FO[26]	5.27	0.91	312	6.1	15.3
Lab TFC-FO[24]	3.22	1.3	492	3.8	10.1
Lab TFC-FO (hollow fiber)[23]	6.2	0.56	595	5.5	8.7
Commercial FO Cellulose Tri-Acetate[11,24]	2.2	1.2	625	2.8	7.8
Lab TFC-FO[22]	7.1	1.1	670	4.7	6.5
Commercial RO Cellulose-Acetate[a24]	2	0.6	1000	2.4	5.9
Commercial TFC-RO*[a24]	1.6	0.8	2200	1.2	2.1

[a] without fabric support. [b] Dilute stream concentration 0.02M, representative of wastewater.



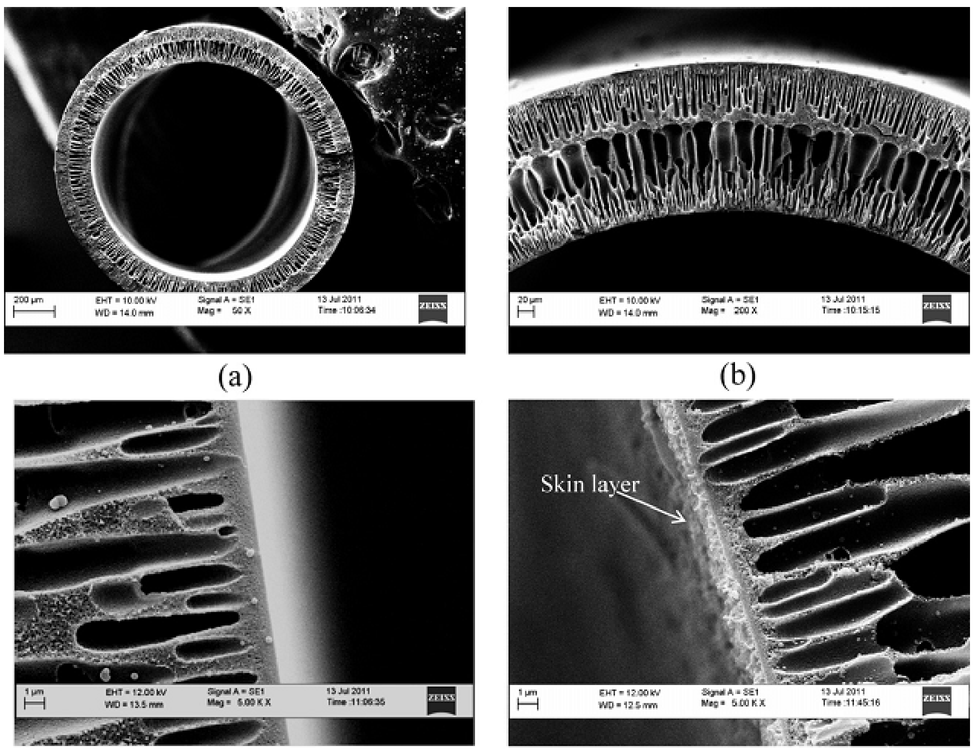
Internal CP is caused by two mechanisms

- **The first is the rejection and subsequent accumulation of salt present in the dilute stream**
- **Diffusive salt diffusion through the membrane driven by the concentration gradient from the concentrated to the dilute side.**

G. Z. Ramon et al, Energy Environ. S ci. , 2011, 4, 4423

Thin Film Composite Hollow Fiber Membranes For PRO

- A major milestone achieved in the preparation of PRO membranes is the formation of thin film composite hollow fiber membranes which enable to achieve the power density as high as 10.6 W/m^2 by using the seawater brine and wastewater brine as the draw and feed solution respectively.



Morphology of hollow fibers:

a)Cross-section of substrate at 50×

b)Substrate enlarged at 200 ×

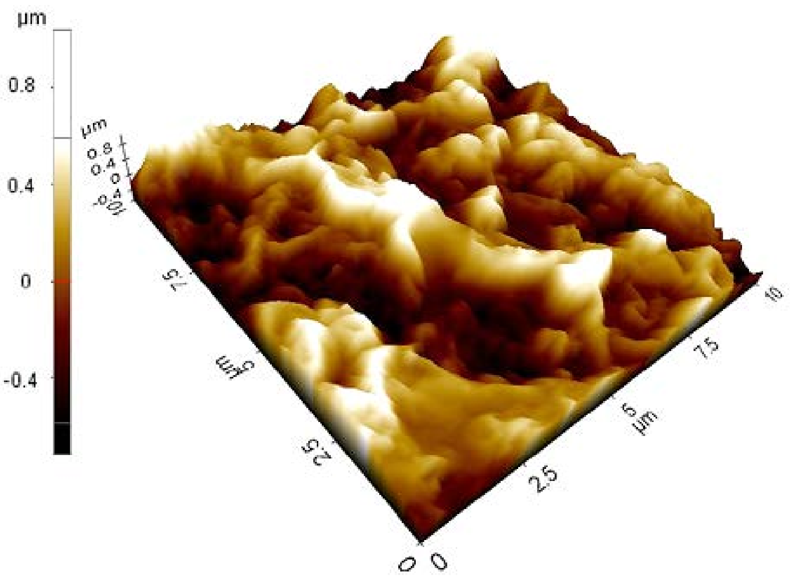
c)Enlarged lumen side of substrate at 5000×

d)Enlargedlumen side of TFC hollow fibers at 5000×

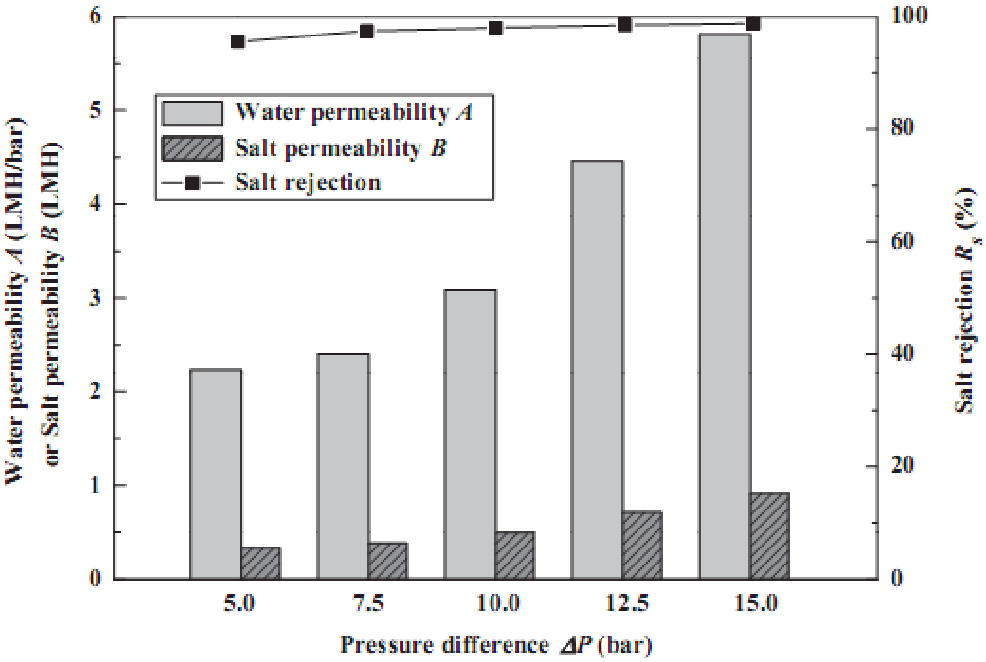
S.Chou et al., Journal of Membrane Science 389 (2012) 25– 33

Thin Film Composite Hollow Fiber Membranes For PRO

- **Newly developed TFC hollow fiber membrane can achieve a power density of 20.9 W/m^2 at a pressure of 15 bar, using synthetic seawater brine (1.0 M NaCl) as the draw solution and synthetic river water (1 mM NaCl) as the feed water, respectively.**



AFM 3D micrographs of the hollow fiber membranes inner surface of the TFC membrane



Water and salt permeability of the TFC-PEI hollow fiber membrane at various trans-membrane pressures

Shuren Chou et al., Journal of Membrane Science, 448 (2013) 44-54.

Thin Film Composite Hollow Fiber Membranes For PRO

- **TFC membranes consisting of a selective polyamide layer formed by interfacial polymerization on top of a polysulfone support by phase separation have been fabricated for high performance in PRO process**

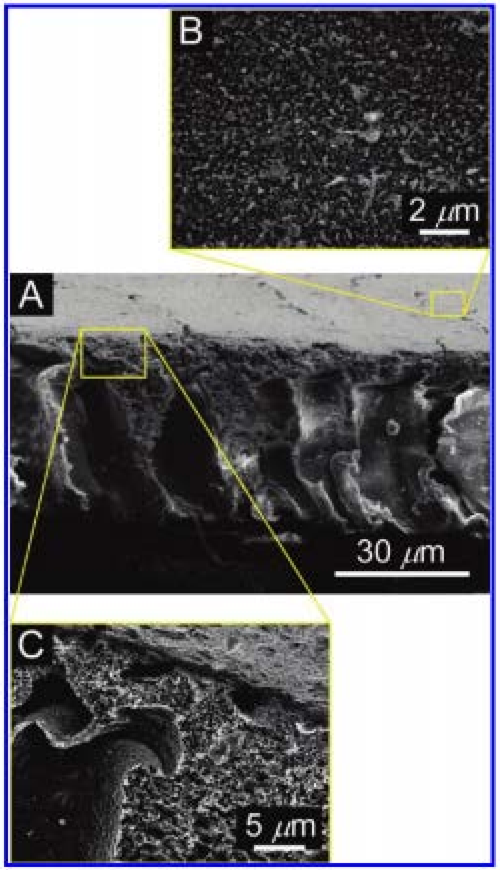


Table 1. Summary of Membrane Characteristic Parameters and Modeled Peak Power Densities for All TFC-PRO Membranes Fabricated

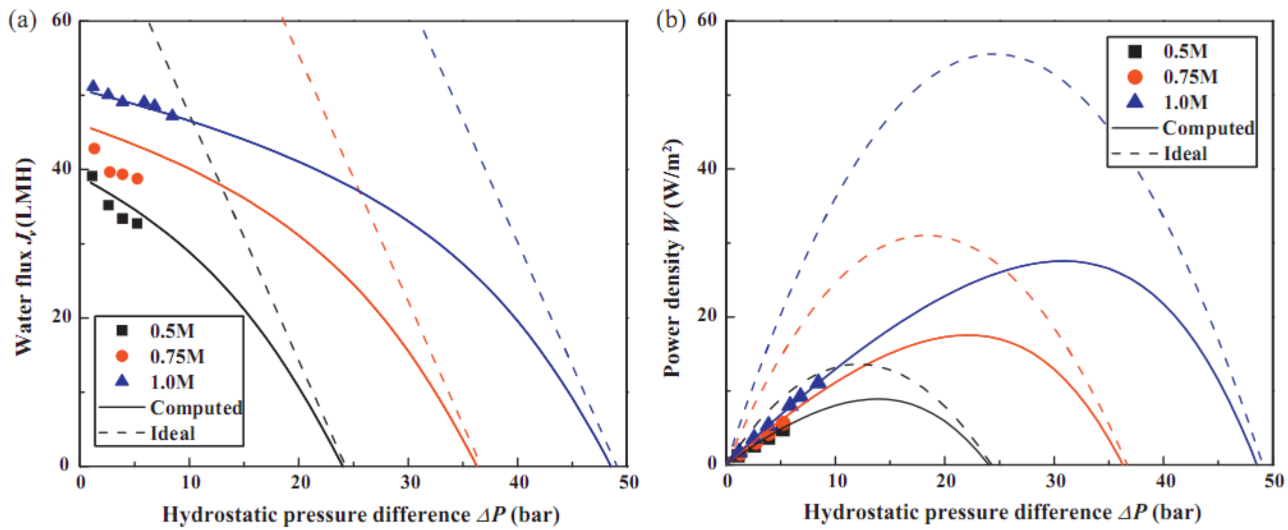
membrane	intrinsic water permeability,[a] A (L m^{-2} h^{-1} bar^{-1})	solute permeability coefficient,[b] B (L m^{-2} h^{-1})	structural parameter,[b] S (μm)	peak power density,[c] W_{peak}: river water (W/m^2)	peak power density,[c] W_{peak}: brackish water (W/m^2)
LP#1	1.74	0.16	307	6.09	5.29
LP#2	1.42	0.08	355	5.24	4.56
LP#3	1.71	0.09	384	6.03	5.09
avg	**1.63**	**0.11**	**349**	**5.79**	**4.98**
SD	**0.18**	**0.04**	**39**	**0.47**	**0.38**
MP#1	5.81	0.88	370	10.0	7.69
MP#2	4.08	0.77	332	9.21	7.38
MP#3	3.16	0.61	316	8.37	6.90
avg	**4.35**	**0.76**	**340**	**9.21**	**7.33**
SD	**1.34**	**0.14**	**28**	**0.84**	**0.40**
HP#1	7.55	5.45	327	6.08	5.16
HP#2	7.35	4.12	336	6.82	5.71
HP#3	7.76	3.86	416	5.78	4.80
avg	**7.55**	**4.48**	**360**	**6.23**	**5.22**
SD	**0.20**	**0.85**	**49**	**0.54**	**0.46**

N.Y Yip et al, Environ. Sci. Technol. 2011, 45, 4360–4369

Membrane Performance in PRO process

Comparison of water flux and power density of various PRO membranes.

Salty water	Fresh water	Operation pressure ΔP (bar)	Water flux J_v (LMH)	Power density W (W/m^2)	Membrane used	Reference
	River water (10 mM NaCl)	5.0	32.0	5.7	TFC hollow fiber membrane	Current work
	Waste water	4.9	24.3	3.3		
Seawater (0.5 M NaCl)	brine(40 mM NaCl)	8.9	22.7	5.6		
	Concentrated waste water brine	4.7	21.2	2.8		
	(80 mM NaCl)	8.9	16.7	4.1		
	River water (10 mM NaCl)	8.4	47.2	11.0		
Seawater brine (1.0 M NaCl)	Waste water brine	5.1	44.1	6.2		
	(40 mM NaCl)	9.0	42.5	10.6		
	Concentrated waste water brine	5.0	33.8	4.7		
	(80 mM NaCl)	9.1	33.3	8.4		
35 g/L NaCl (0.6 M NaCl)	DI water	9.72	10.12	2.73	HTI membrane	[6]
60 g/L NaCl (1.03 M NaCl)			18.76	5.06		
π = 25.3 bar	Water	12.16	1.04	0.35	Permasep B-10 membranes	[3]
π = 78.0 bar	Water	40.53	2.77	3.12		[4]
π = 81.1 bar	Water with 0.2% formaldehyde	40.53	2.92	3.27		[22]
π = 101.3 bar	Water	19.25	2.92	1.56	FRL composite membrane	[21]



- **A significant benefit of using seawater brine presents in the PRO operation compared with seawater.**
- **This is due to the lower chemical potential of water in seawater which results in higher chemical potential difference and thus larger free energy capacity.**

S.Chou et al., Journal of Membrane Science 389 (2012) 25-33

Performance limiting effects for PRO

- ✓ **The following have been identified as the performance limiting phenomena in PRO process.**
  - ❖ **Internal concentration polarization**
  - ❖ **External concentration polarization**
  - ❖ **Reversal draw salt flux**
- ✓ **The power density is trade-off between the membrane permeability and selectivity.**
- ✓ **The membrane performance can be maximized by tailoring the salt and water permeabilities to the membrane structure parameter.**
- ✓ **External concentration polarization is the main parameter limiting the performance of the process at high power densities and can be reduced by improving the hydrodynamic conditions in the membrane feed channel.**

➢ **The loss factor (LF) describes the effect of ICP, ECP or reverse draw salt flux on power density and can be defined as;**

$$LF = \frac{W_{peak/hyp} - W_{peak}}{W_{peak/hyp}}$$

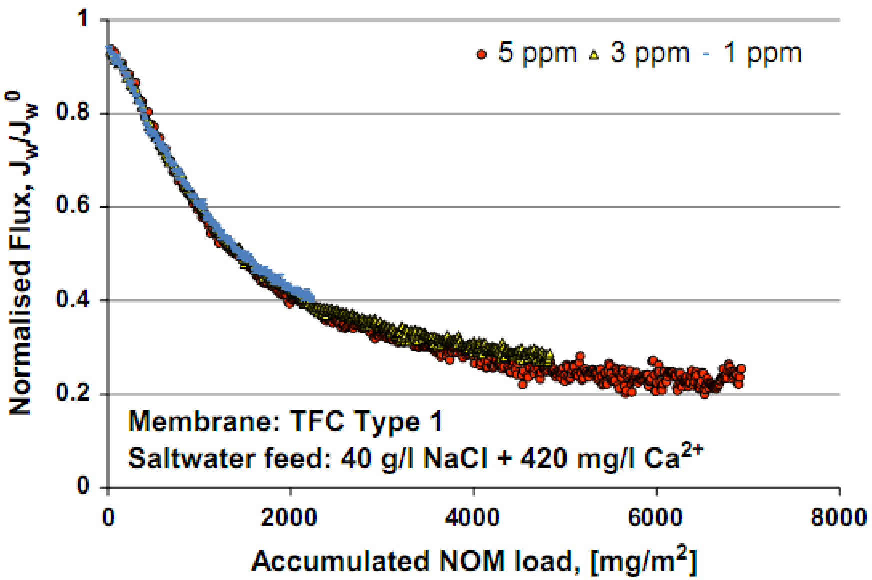
Where W_{peak} and $W_{peak/hyp}$ are actual and hypothetical peak densities respectively.

N.Y. Yip and M. Elimelech, Environ. Sci. Technol. 2011, 45, 10273 -10282

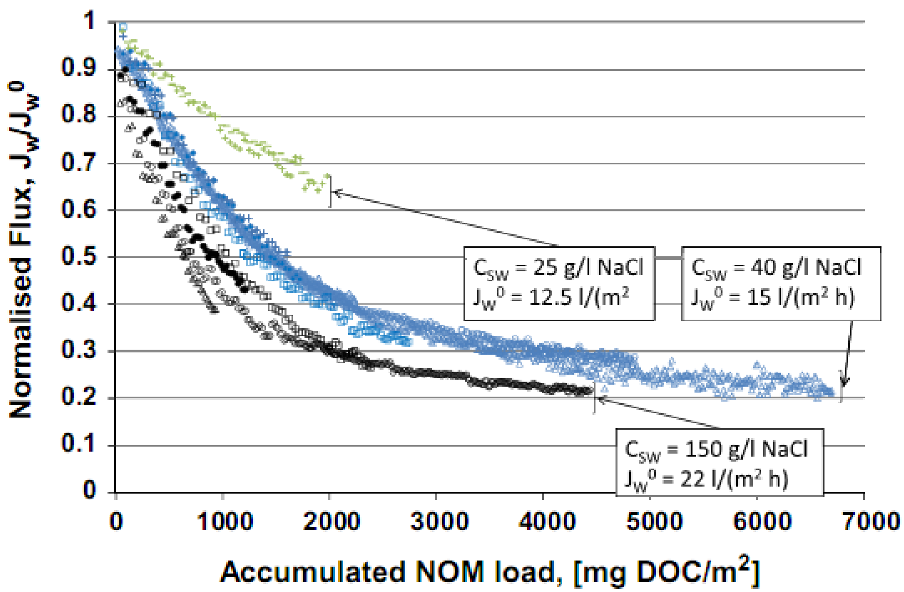
Natural Organic Fouling in PRO

- **Among the challenges for PRO is the development of economically feasible procedures and measures for fouling control and mitigation that ensures a stable long term performance of the PRO membrane.**
    - ***Thus, effective fouling control is imperative for successful operation.***
- **For maximum specific power output in PRO, the membrane skin must be oriented towards the seawater. This orientation is different from pressure driven filtration processes (the membrane skin faces the feed solution)**
    - ***This will worsen the fouling situation in PRO.***
- **In PRO, foulants are brought into the support layer of the membrane by water permeation in PRO.**
    - **Thus, fouling will occur uncharacteristically within the membrane porous support, rather than the membrane surface.**

Natural Organic Fouling in PRO



Normalised water flux plotted as a function of accumulated NOM load for TFC

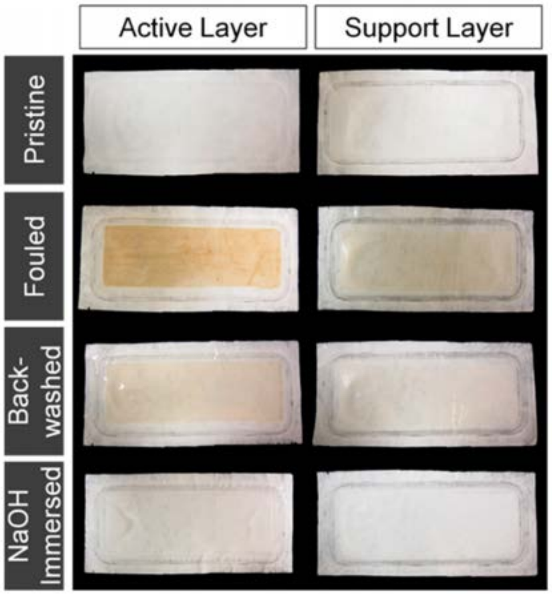


Normalised water flux as a function of accumulated NOM load obtained with three different concentrations of NaCl in the saltwater feed.

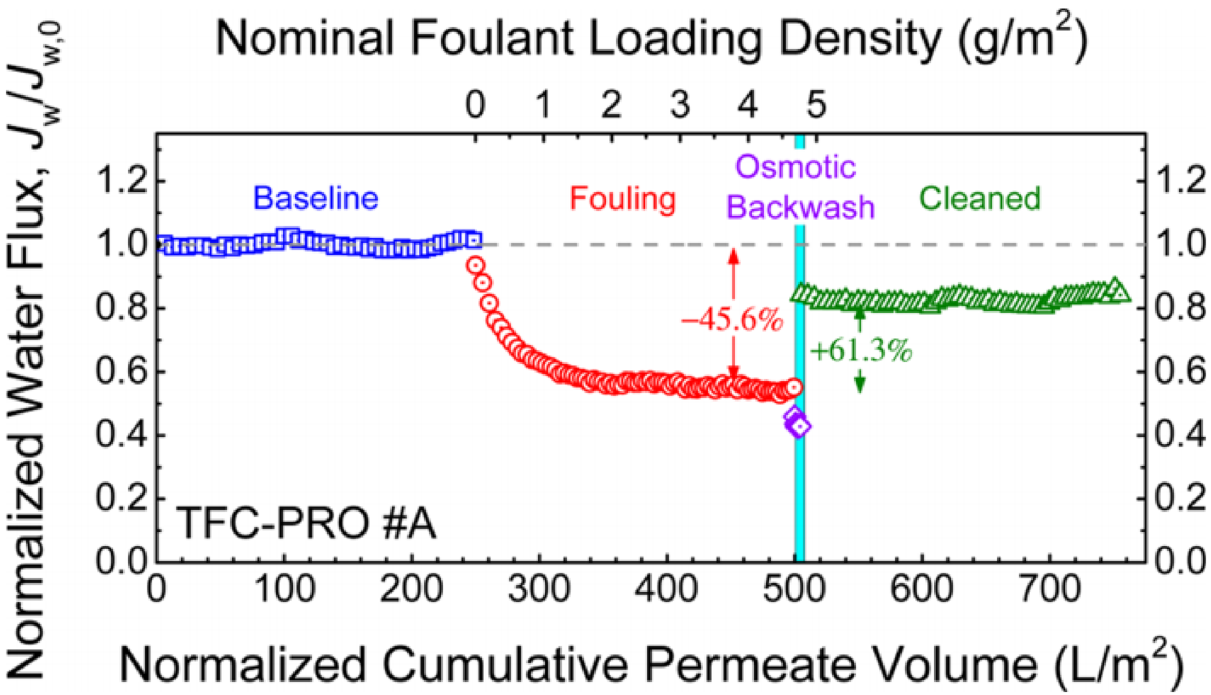
- **Flux decline at a given accumulated NOM load will be independent of the concentration of NOM in the feed water. However, at higher concentration of NOM in the freshwater feed, accumulated NOM load will be higher and as a consequence the flux will decline faster.**
- **Increased ionic strength promote NOM fouling due to double layer compression and charge screening at high ionic strength in the support structure.**

W.R. Thelin et al., Journal of Membrane Science 438 (2013) 46-56.

Natural Organic Fouling in PRO



Active and support layer of a hand-cast TFC membrane



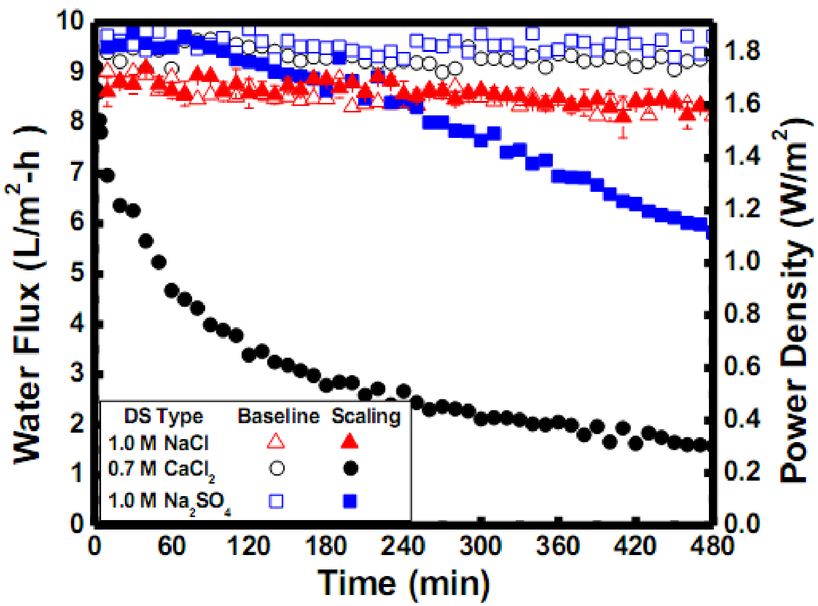
- **The normalized water flux for hand-cast TFC-PRO membrane;**

  The water flux for the baseline, fouling, osmotic backwash, and cleaned experiments (blue square, red circle, violet diamond, and green triangle symbols, respectively) is normalized with the baseline water flux.

Yin yip *et al., Influence of Natural Organic Matter Fouling and Osmotic Backwash on Pressure Retarded Osmosis Energy Production from Natural Salinity Gradients, Environ. Sci. Technol. (accepted on sept. 19, 2013)*

Scaling in PRO

- **Due to the different transport phenomena like internal concentration polarization (ICP) and reverse solute diffusion additional scaling mechanisms are likely applicable in PRO compared to FO**
- **PRO requires a high concentration DS to drive its water permeation through the membrane, and the chemistry of the DS can potentially play a critical role in PRO scaling.**



Compared to the Na_2SO_4 draw solutions, the $CaCl_2$ draw solution induced more severe scaling, which could be attributed to the greater reverse diffusion of $CaCl_2$

Effects of draw solution type on PRO gypsum scaling

Minmin Zhang et al., Gypsum scaling in pressure retarded osmosis: Experiments, mechanisms and implications, water research xxx (2013) 1-9.

Commercialization of PRO

- The successful commercial implementation of PRO technique faces the challenges due to the following facts.
  - Unavailability of low cost and robust membranes with minimum ICP.
  - Potential environmental impact caused due to the disruption of natural flow of water.
  - Extensive pretreatment required for the streams involved.
- A commercial plant based on PRO produced 1Wm^{-2} of electricity using cellulose acetate membranes which is quite low than the feasible value of 5 Wm^{-2}
- Considerable amount of energy is consumed in pretreating the streams. It has been estimated that in a PRO plant with a 50 % overall efficiency, the actual extractable energy from the mixing of river water and sea water is 0.3 - 0.4 kWh m^{-3} leaving about 0.1 kWh of drivable useful energy from per cubic meter of fresh water.
- Increasing the water permeability of the membrane skin layer and optimizing the thickness of the support layer can further enhance the efficiency of the process.

Bruce E. Logan & Menachem Elimelech, doi:10.1038/nature11477

Commercialization of PRO

Tofte Prototype Plant

- ✓ First demonstration of salinity-gradient power plant becoming operational in Statkraft's Osmotic power prototype at Tofte (Norway)
- ✓ Projected capacity of 10 kW, while a 25 MW installation
- ✓ Is expected to become operational in 2015

❑ Kyowakiden Industry Co., Ltd., in Fukuoka, Japan

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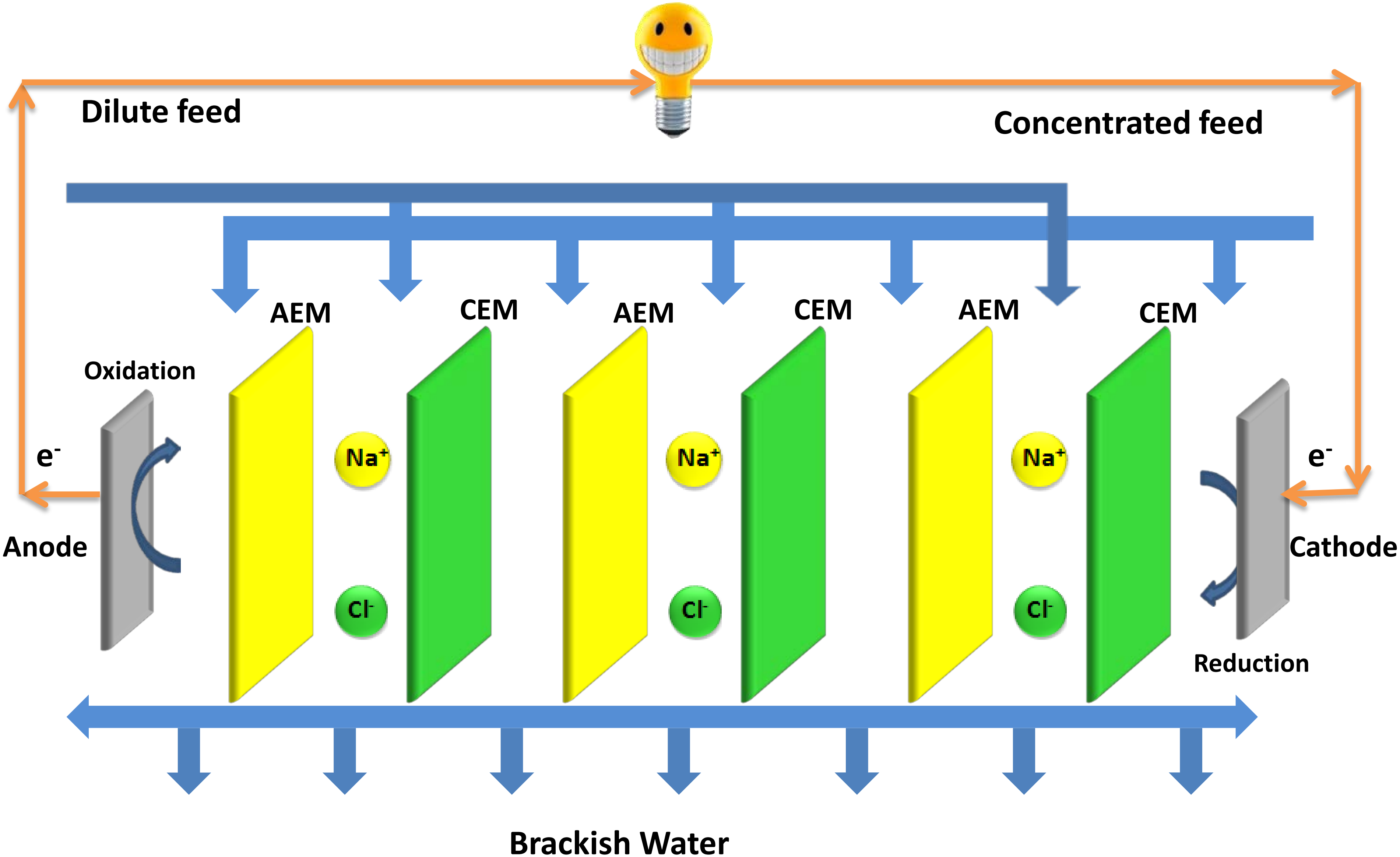
http://news.cnet.com/8301-11128_3-10404158-54.html, accessed on June 2013.

Reverse Electrodialysis

Principle of Reverse Electrodialysis

- **In a reverse electrodialysis (RED) 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.*** **(Theoretically, about 1.7 MJ/m^3 is obtained from a river water mixed with the same volume of sea water).**

Principle of Reverse Eectrodialysis



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Energy and Power in RED

- The energy released due to the potential difference can be expressed as **Gibbs free energy (ΔG)**,

$$\Delta G = 2RT\left[V_d C_d \ln\frac{C_d}{C_M} + V_c C_c \ln\frac{C_c}{C_M}\right]$$

$$C_M = \frac{V_d C_d + V_c C_c}{V_d + V_c}$$

- **Power density from the stack open circuit voltage**

$$P_d = \frac{V_s}{4AR_{stack}}$$

- **Power density from known maximum power output**

$$P_d = \frac{P_{\max}}{AN}$$

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J. Veerman et al., Journal of Membrane Science 327 (2009) 136–144

RED Performane and Progress

❑ Power Production:

- ❖ 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.

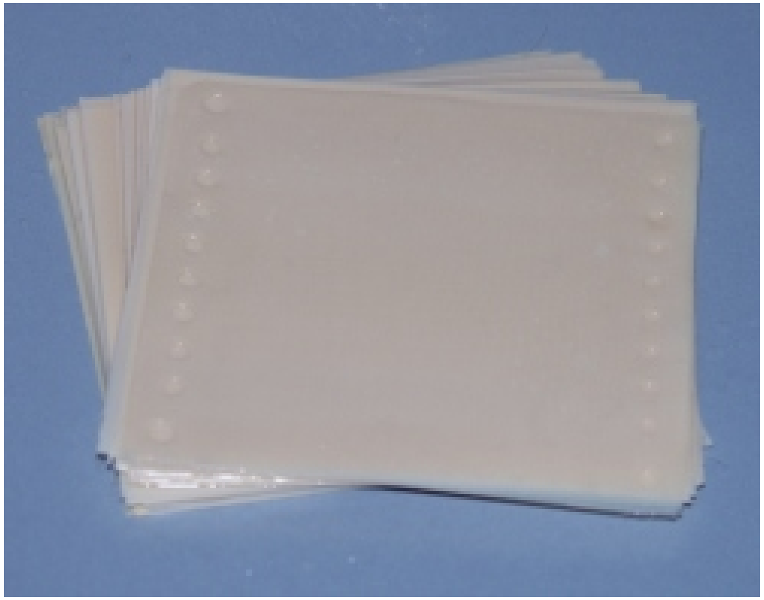
❑ Project:

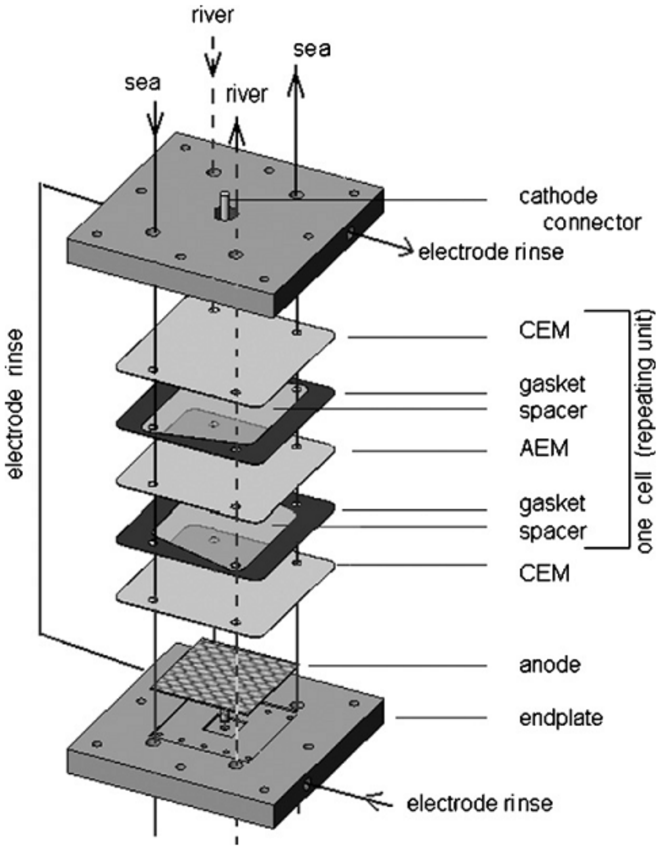
- ❖ **REAPower-** an FP7 European project - develop a pilot plant with power density above 5 W/m^3

http://www.reapower.eu/

Main Components of RED

- **Ion exchange membranes**
  - **Anion exchange membranes (AEM)**
  - **Cation exchange membranes (CEM)**





- **Spacers**
- **Electrodes**
- **Electrolytes**

A reverse electrodialysis stack with one cell

J. Veerman et al., Journal of Membrane Science, 327 (2009) 136-144.

Ion Exchange Membranes for RED

- **Ion exchange membranes are the key component in RED process. Their resistance must be as low as possible while the selectivity is marginally important.**

Membrane	IEC (mequiv./g dry)		Permselectivity[a] (%)		Resistance[b] ($\Omega\,cm^2$)		SD (%)		Thickness (μm)		Properties
Cation exchange membranes											
Fumasep®											
FKE	**1.36**	> 1.0	**98.6**	>98	**2.46**	<3.0	**12**	15	**34**	50–70	Electrolysis, high selectivity
FKD	**1.14**	> 1.0	**89.5**	>95	**2.14**	<3.0	**29**	25–30	**113**	90–100	Diffusion dialysis for NaOH
Neosepta®											
CM-1	**2.30**	2.0–2.5	**97.2**	>96[c]	**1.67**	1.2–2.0	**20**	35–40	**133**	120–170	Low electric resistance
CMX	**1.62**	1.5–1.8	**99.0**	>96[c]	**2.91**	1.8–3.8	**18**	25–30	**164**	140–200	High mechanical strength
Ralex® (heterogeneous)											
CMH-PES	**2.34**	2.2	**94.7**	>92	**11.33**	<10	**31**	<55	**764**	<700	Electrodialysis, electrodeionization
Selemion®											
CMV	**2.01**	N/A	**98.8**	>92	**2.29**	3.0[d]	**20**	N/A	**101**	130.0	Electrodialysis
Anion exchange membranes											
Fumasep®											
FAD	**0.13**	> 1.5	**86.0**	>91	**0.89**	<0.8	**34**	25	**74**	80–100	Diffusion dialysis for acid
Neosepta®											
AM-1	**1.77**	1.8–2.2	**91.8**	>96[c]	**1.84**	1.3–2.0	**19**	25–35	**126**	130–160	Low electric resistance
AFN	**3.02**	2.0–3.5	**88.9**	>96[c]	**0.70**	0.4–1.5	**43**	40–55	**163**	150–200	Resistant against organic fouling
AMX	**1.25**	1.4–1.7	**90.7**	>96[c]	**2.35**	2.5–3.5	**16**	25–30	**134**	160–180	High mechanical strength
Ralex® (heterogeneous)											
AMH-PES	**1.97**	1.8	**89.3**	>90	**7.66**	<8	**56**	<65	**714**	<850	Electrodialysis, electro deionization
Selemion®											
DSV	**1.89**	N/A	**89.9**	N/A	**1.03**	1.0[d]	**28**	N/A	**121**	100.0	Diffusion dialysis, low resistance
APS	**0.29**	N/A	**88.4**	N/A	**0.68**	0.5[d]	**147**	N/A	**138**	150.0	Diffusion dialysis, oxidant proof

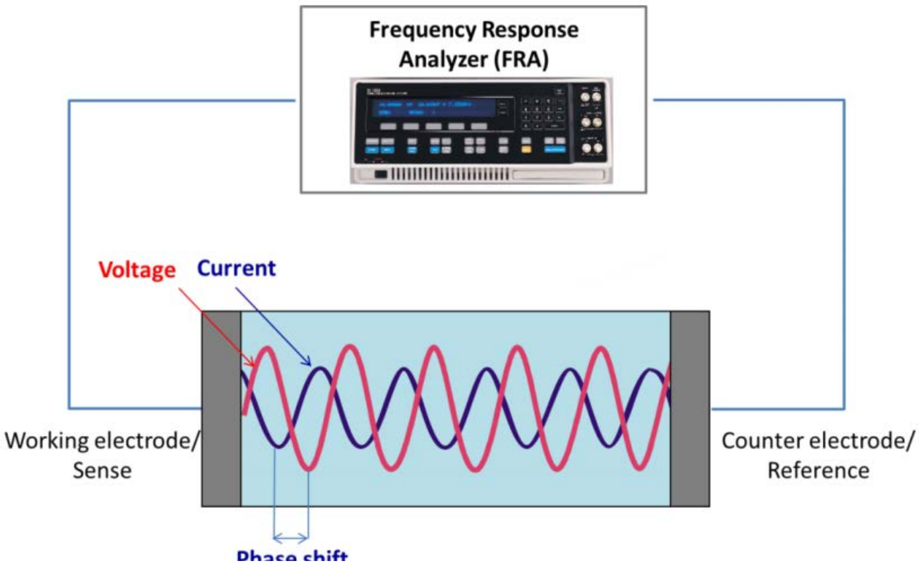
Bold represents the experimental data while the normal foot is commercial data

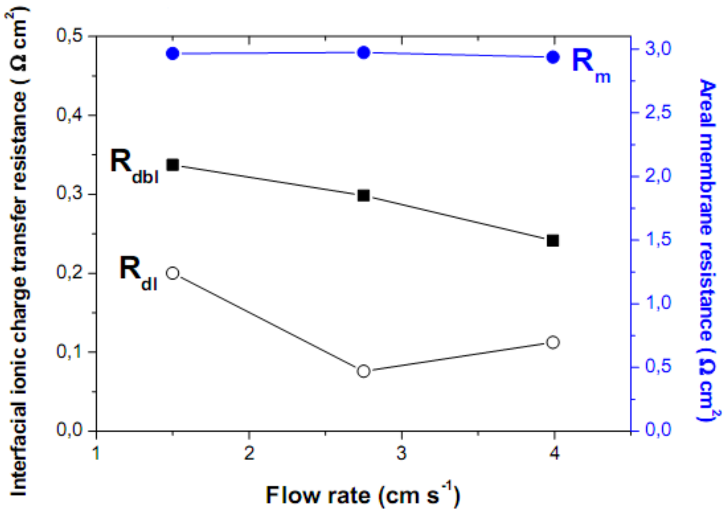
- **The most desired properties of ion-exchange membranes are:**
  - **high permselectivity**
  - **low electrical resistance**
  - **good mechanical and form stability**
  - **high chemical and thermal stability**

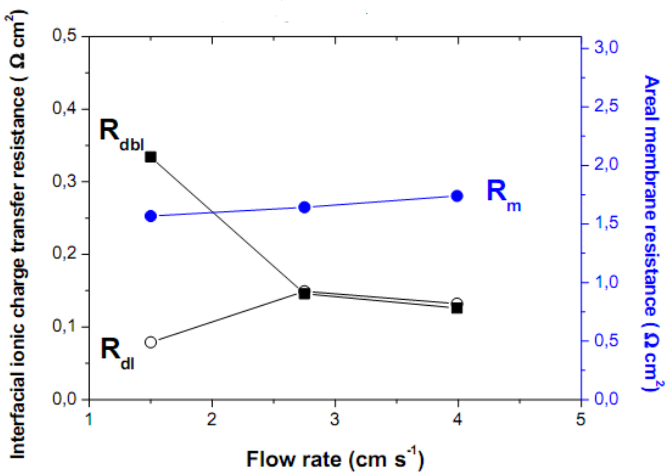
Piotr Długołecki et al, J. of Mem. Sci. 319 (2008) 214–222

Study of Membrane Resistance

❖ **Electrochemical Impedance Spectroscopy power fool tool for study of membrane resistance**



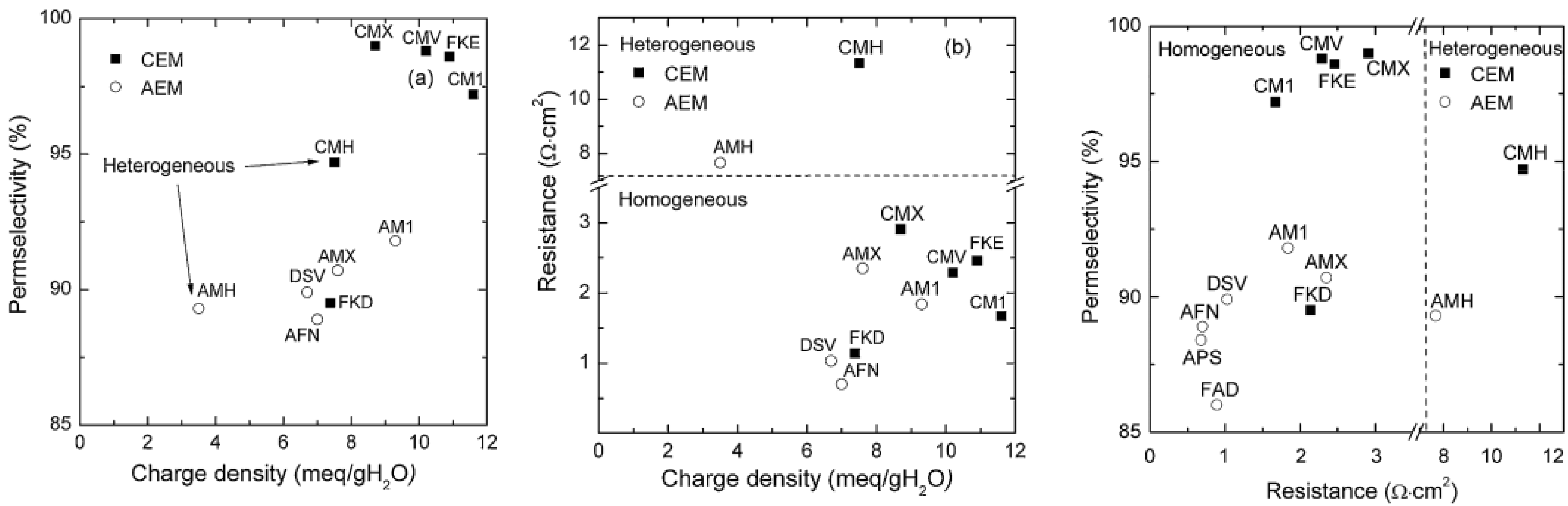




R_m is areal membrane resistance

R_{dbl} and R_{dl} are Interfacial membrane resistances

Membrane Properties and RED performance

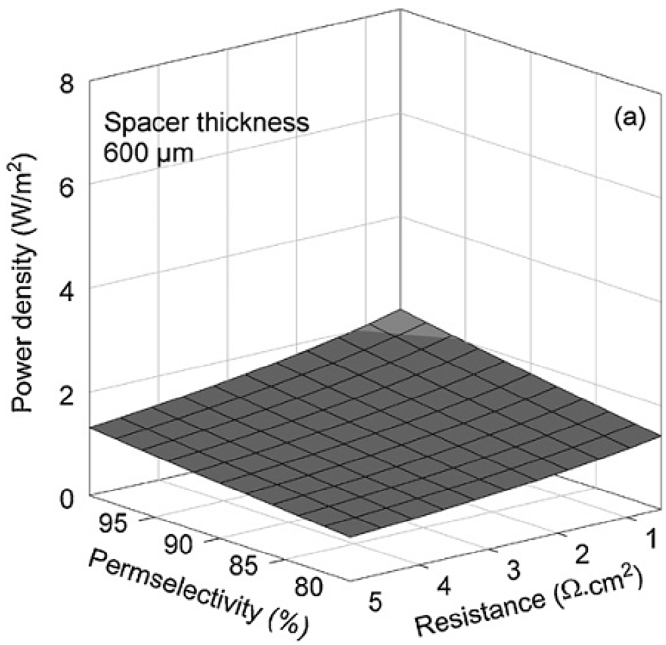


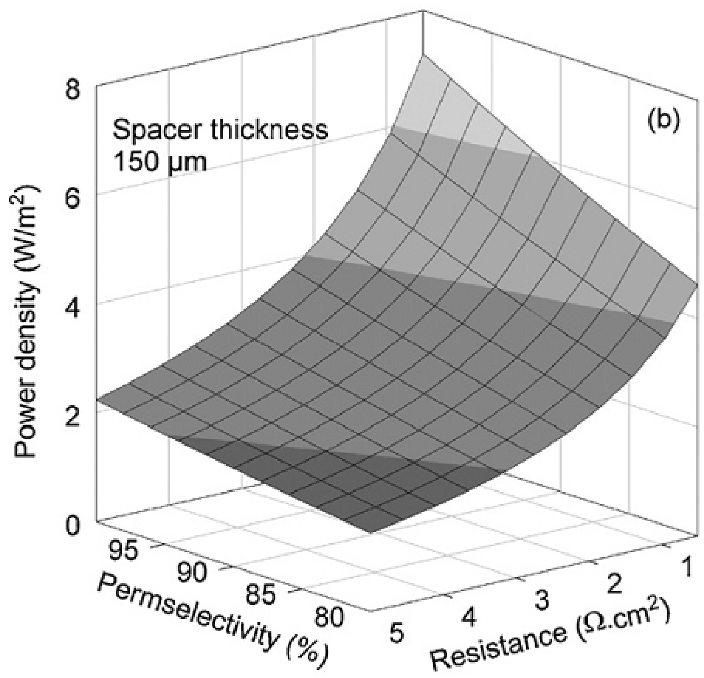
- **Membranes with a lower fixed charge density have a lower selectivity resulting in less effective co-ion exclusion.**
- **Generally, cation exchange membranes have a higher charge density and a corresponding higher permselectivity than anion exchange membranes (but also higher membrane resistance).**
- **A high concentration of fixed ionic charges in the membrane matrix leads to a low electric resistance, but causes a high degree of swelling combined with poor mechanical stability.**

Piotr Długołecki et al, J. of Mem. Sci. 319 (2008) 214–222

Membrane Properties and RED performance

➤ **Power density vs Permselectivity and Resistance for different spacer thickness**





Membrane pair with 600 µm thick spacers

Membrane pair with 150 µm thick spacers

➤ **The membrane resistance and permselectivity are of minor importance when thicker spacers are used. However, with thinner spacers, the membrane properties do play a role and a large increase in power density (up to values of 6-7 W/m^2) can be obtained at low membrane resistance and high perm selectivities.**

Piotr Długołecki et al, J. of Mem. Sci. 319 (2008) 214–222.

Membrane Properties and RED performance

- **Membrane properties as variables and experimental and theoretical power density**

No.	Membranes	R ($10^{-4}\,\Omega\,m^2$)	α (dimensionless)	$P_{exp.}$ (W/m^2)	$P_{pred.}$ (W/m^2)	Residual (W/m^2)
1	SPEEK65/PECH B2	9.05	0.88	1.28	1.15	0.12
2	FKS/FAS	12.65	0.92	1.11	1.18	−0.07
3	SPEEK40/PECH B2	13.20	0.91	1.18	1.16	0.01
4	CMX/PECH B1	18.65	0.93	1.27	1.15	0.13
5	CMX/PECH B2	19.25	0.93	1.19	1.14	0.05
6	CMX/PECH C	20.25	0.89	1.15	1.08	0.06
7	SPEEK65/AMX	17.85	0.90	1.10	1.11	−0.02
8	CMX/PECH B3	21.15	0.93	1.07	1.13	−0.06
9	CMX/PECH A	24.80	0.95	1.08	1.12	−0.05
10	CMX/AMX	26.30	0.95	1.07	1.12	−0.05
11	SPEEK40/AMX	22.00	0.93	0.98	1.12	−0.14
12	Qianqui (CEM/AEM)	24.11	0.84	0.83	0.99	−0.16
13	Ralex CMH/AMH	94.95	0.92	0.60	0.56	0.04
14	FKD/FAD	15.15	0.88	1.19	1.10	0.09
15	CMV/AMV	27.20	0.93	1.13	1.09	0.04

R is total membrane resistance in the 5-cell RED stack and α is average permselectivity

Enver Güler et al., Journal of Membrane Science 446 (2013) 266-276

Electrode Material/Redox Couple Systems for RED

- **Electrode systems can be grouped in two categories: with or without opposite electrode reactions where the direct and the reversed reaction take place at anode and cathode, respectively.**
- **The nature of redox processes affects the external output and different proper external membranes have to be selected for each redox process to avoid the contamination of concentrated and dilute solution.**

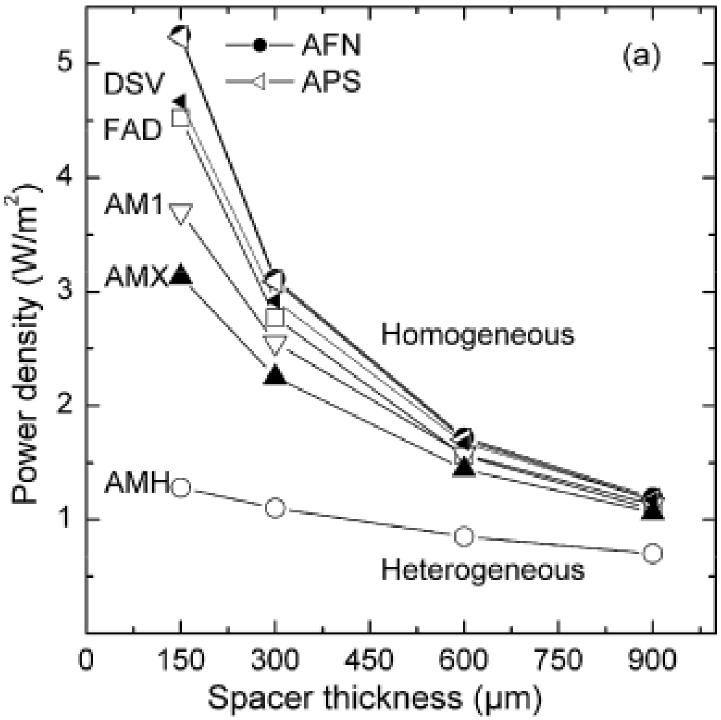
Maximum power output for stack of 40 cells pairs with different redox systems

Redox processes and electrodes	Maximum power (W)	Maximum power density computed with respect to geometric area of cathode (P) and with respect to total area of cationic membranes (P_{mem}) (W/m^2)	Corresponding ΔV (V) and current density (A/m^2)
$H_2O \rightarrow 2H^+ + 0.5\ O_2 + 2e^-$ / $H_2O + e^- \rightarrow OH^- + 0.5\ H_2$ Pt based cathode and Ti/IrO_2–Ta_2O_5 anode	0.07	$P = 7.1$ $P_{mem} = 0.18$	1.8 V 4.1 A/m^2
$Cl^- \rightarrow 0.5\ Cl_2 + e^-$ /$H_2O + e^- \rightarrow 0.5\ H_2 + OH^-$ Pt based cathode and Ti/RuO_2–IrO_2 anode	0.11	$P = 11.03$ $P_{mem} = 0.27$	2.4 V 5.3 A/m^2
$Fe^{3+} + e^- = Fe^{2+}$ carbon felt electrodes	0.26	$P = 26.2$ $P_{mem} = 0.66$	3.24 V 8.1 A/m^2
$[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-}$ carbon felt cathode and Ti/RuO_2–IrO_2 anode	0.31	$P = 31.25$ $P_{mem} = 0.78$	2.5 V 12.5 A/m^2

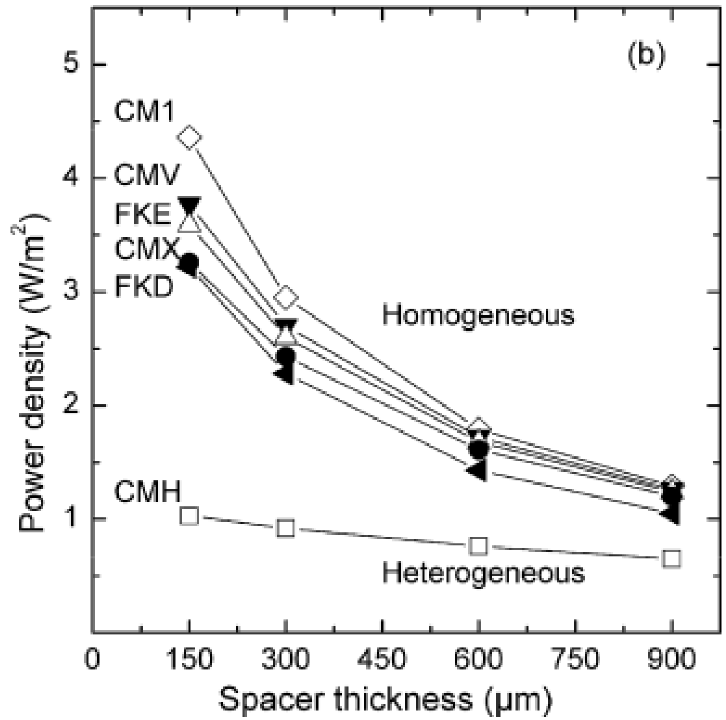
- **Power density depend on nature of redox material, concentration of redox species and on the number of cell pairs**

O. Scialdone et al. / Journal of Electroanalytical Chemistry 704 (2013) 1-9

Effect of Spacer Thickness



Effect of spacer thickness on power density for anion exchange membranes

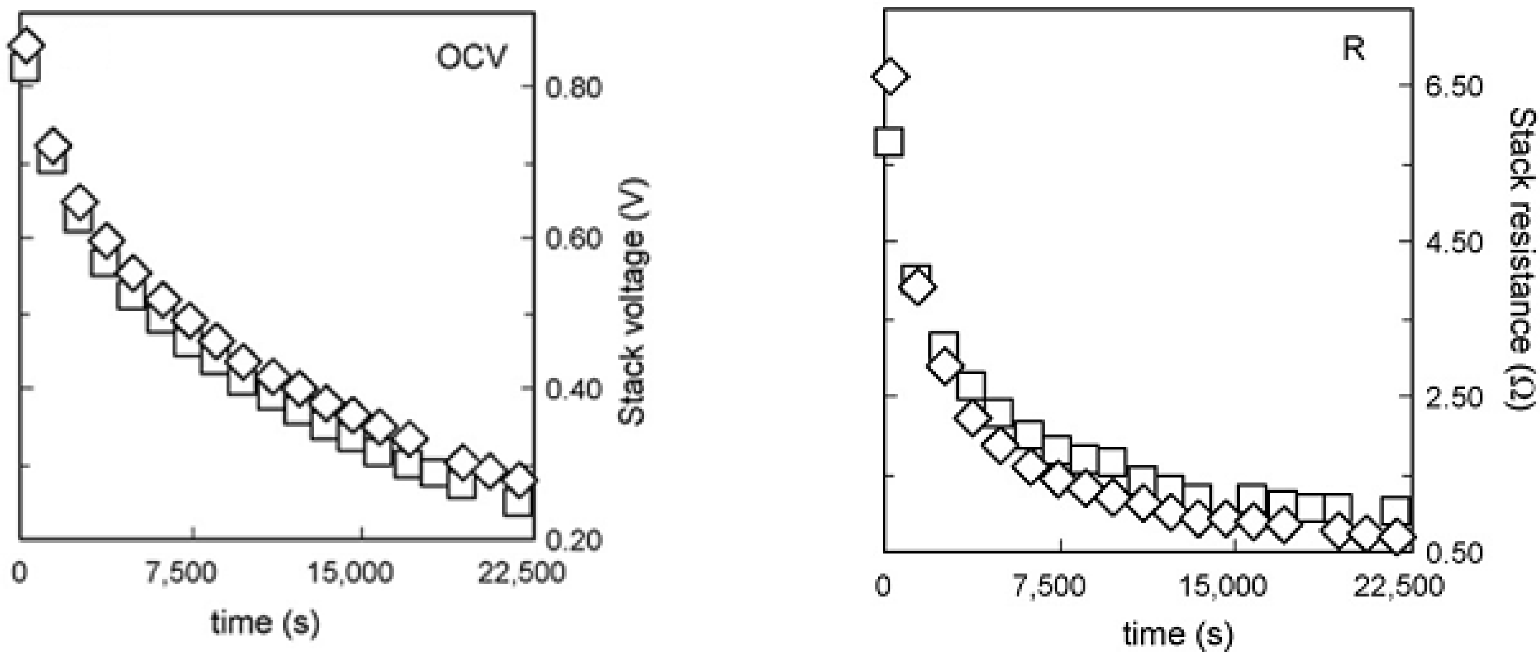


Effect of spacer thickness on power density for cation exchange membranes

- **When relatively thicker spacers are used, the difference in power density for various types of membranes is only marginal. The effect of membrane properties becomes prominent only for thinner spacers.**

Piotr Długołecki et al, J. of Mem. Sci. 319 (2008) 214–222

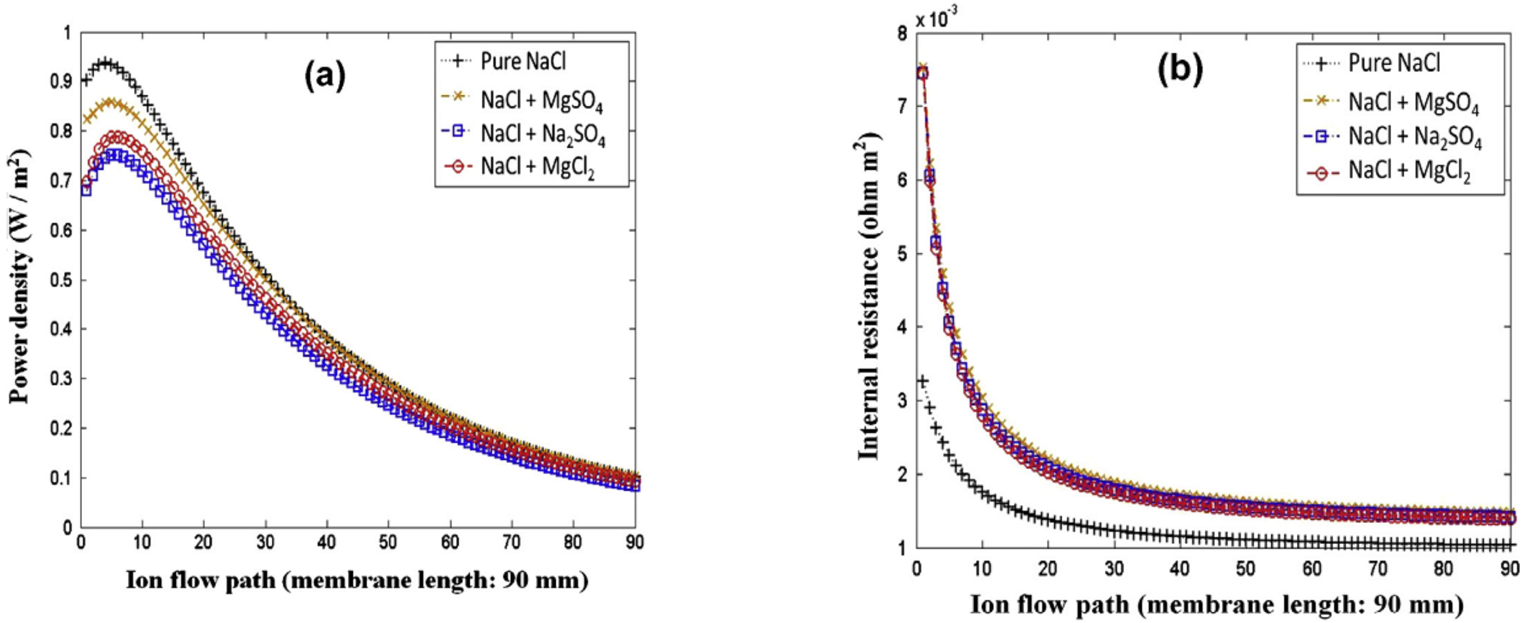
Effect of Multivalent Ions



Open-circuit voltage and resistance R of a stack with monovalent-selective membranes during recycling of feed solutions (pure sodium chloride solutions (NaCl, ◊), or with added magnesium sulphate (MgSO4,)

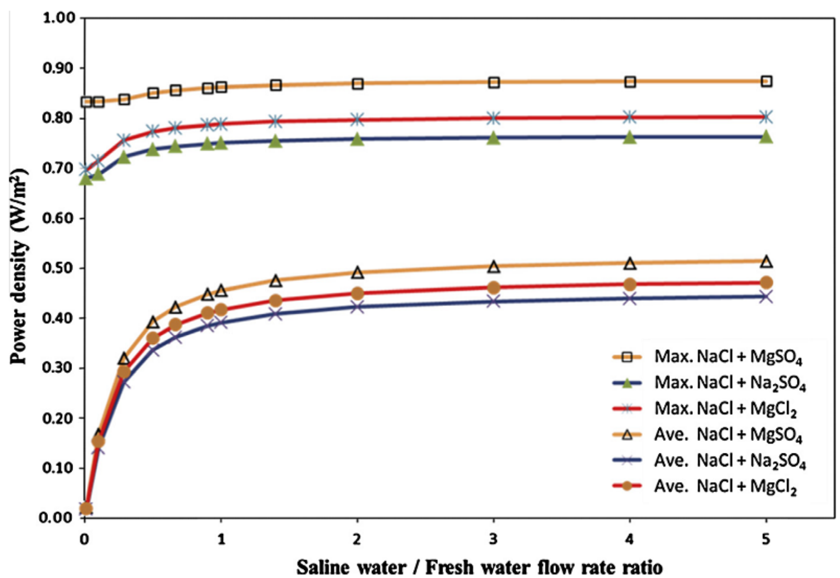
- **The presence of multivalent ions like magnesium and sulphate in the feed solutions (more often in dilute compartment) gives a lowering effect on stack voltage as well as enhancement of the stack resistance.**

J.W. Post et al., Journal of Membrane Science 330 (2009) 65-72



Effect of multivalent ions on power density generation

Effect of multivalent ions on Internal stack resistance

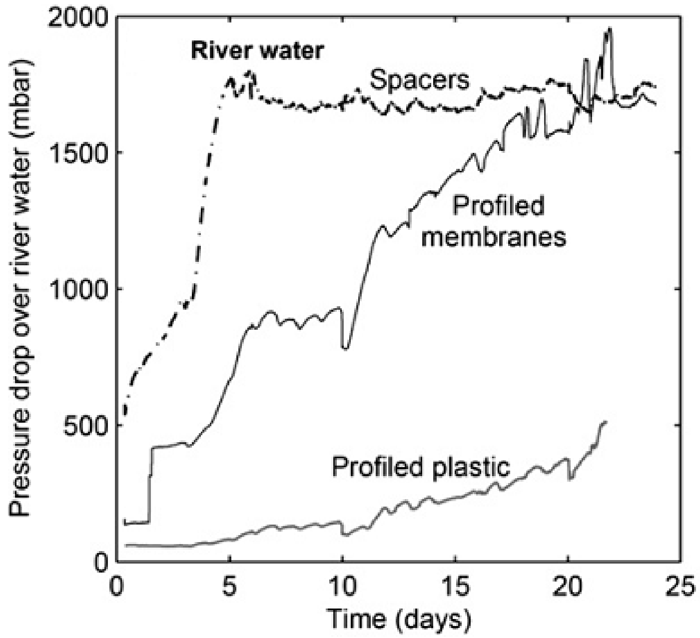


Effect of saline water and freshwater flow rate ratios

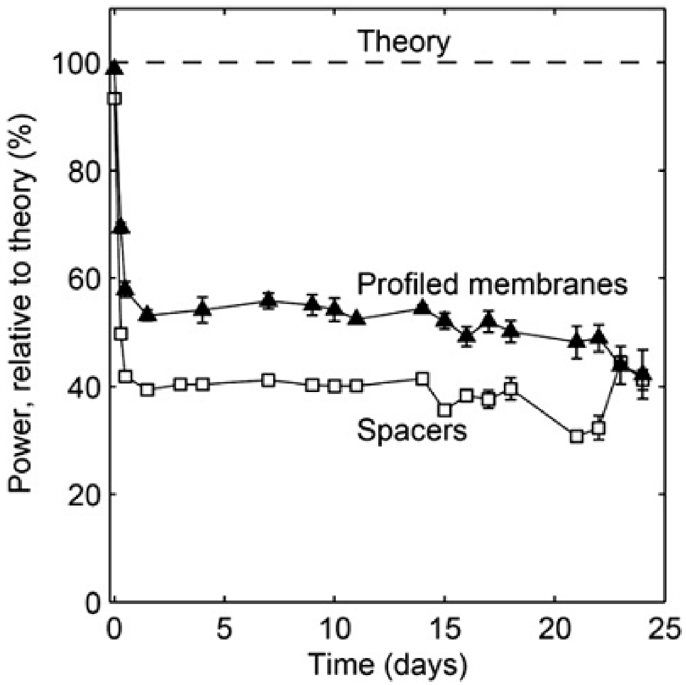
J.G. Hong et al. / Applied Energy 110 (2013) 244-251

Fouling in Reverse Electrodialysis

- Fouling in RED is expected to be less pronounced than in PRO
- Anion exchange membranes, as they are most sensitive for organic and colloidal fouling



Pressure drop over the river water



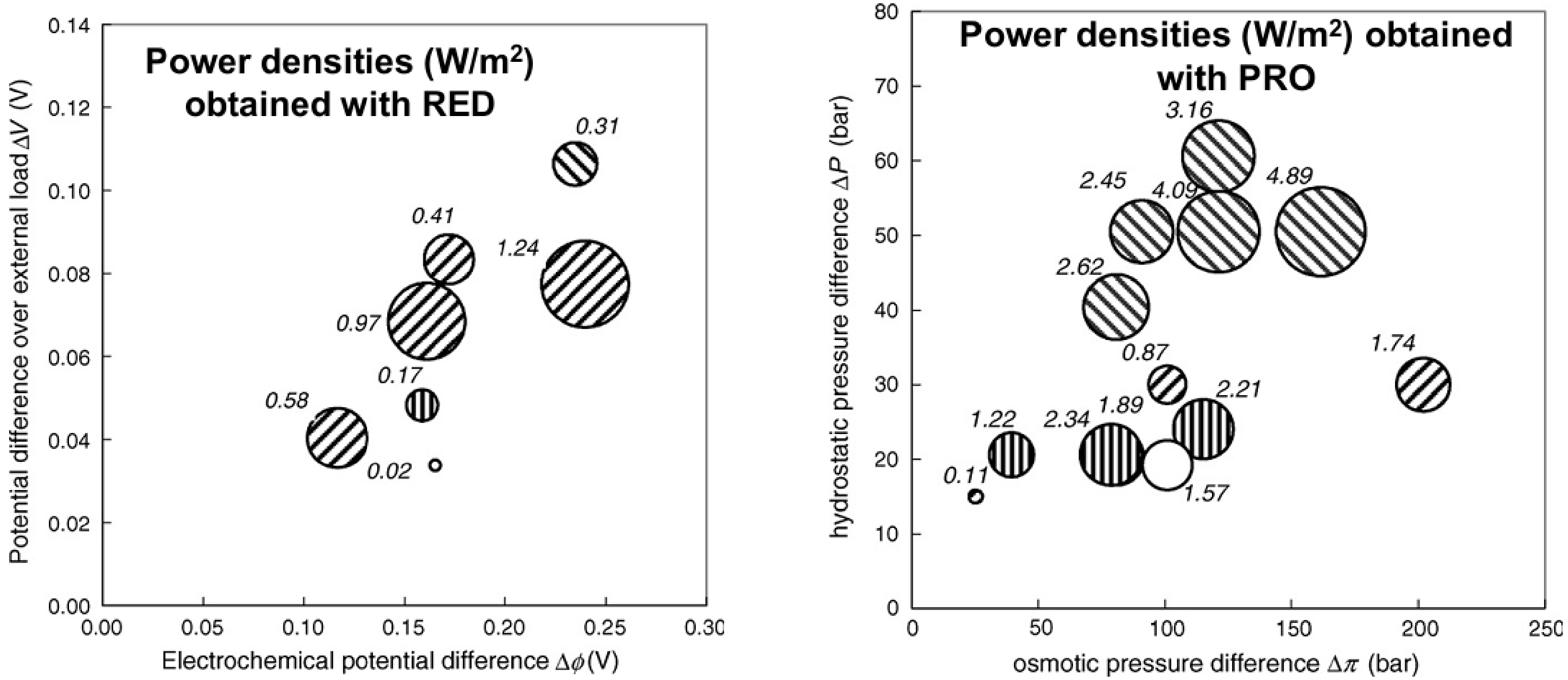
Power density vs time

- The decrease in power density occurs faster than the increase in pressure drop indicating strategies against non-colloidal fouling are required to maintain a high power density.

David A. Vermaas et al. , water research 47 (2013) 1289-1298

Evaluation of the Performance of RED and PRO

- **Power density and energy recovery can be used as measure of the performance to compare the two techniques.**

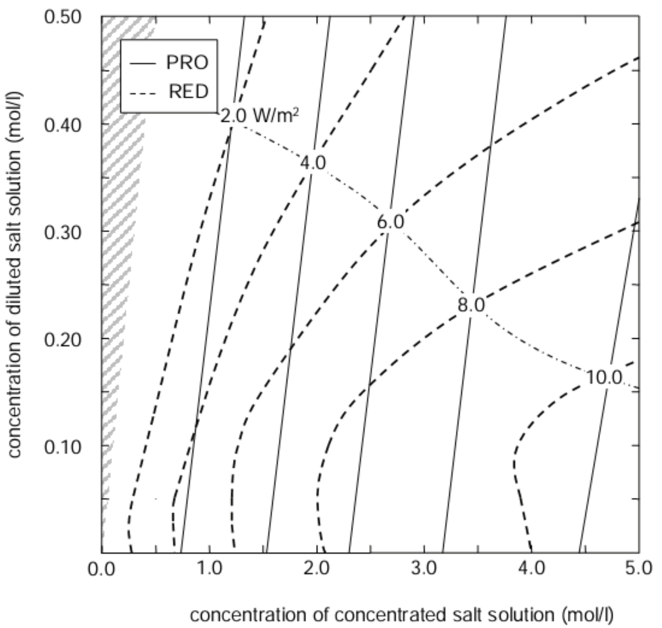


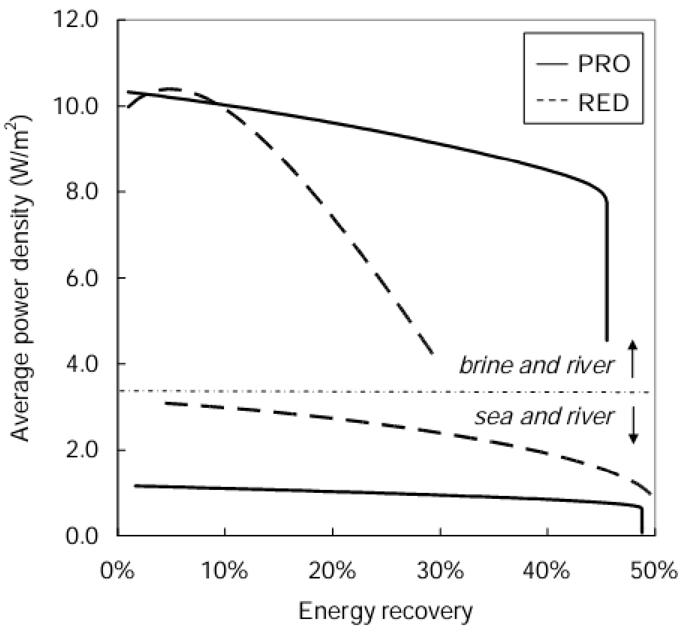
Diameter of the bullets represents the power densities reported in the literature

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

Evaluation of the Performance of RED and PRO

- **The power density is dependent on solution concentrations and in practical situations on energy recovery or residence time.** ***With increasing recovery or residence time, power density decreases.***
- **The maximum energy recovery for river and seawater through PRO and RED are limited, resepctively, due to** ***internal concentration polarization and due to permeselectivity value of less than unity.***





Calculated maximum power density and average power density for PRO and RED

- **PRO is more feasible for brine and river water while RED is suitable for river water and seawater**

J.W. Post PhD thesis, Wageningen University, Wageningen The Netherlands (2009)

Hybrid Technologies

RO and PRO Hybrid Process

- **RO and PRO are promising processes to alleviate water and energy demands and thus the enhancement of these two processes can potentially reduce water and energy stresses.**
- **It would be beneficial to hybridize the two processes (the concentrated brine of**
- **RO is utilized as a draw solution of PRO) due to the reliance of the two membrane processes on the concentration of solutions.**
    - ***Enhance power generation***
    - ***Reduce cost of post treatment for brine disposal***
- **Water and energy return (WERR) rate is a good criterion to simultaneously assess the efficiency of hybrid system configurations;**
    - **However, under-estimation of each unit process could be possible since it only concerns energy production/consumption and water production.**
    - **Simulation results confirm RO plays an important role in determining the WERR value.**

J. Kim et al., Desalination 322 (2013) 121–130

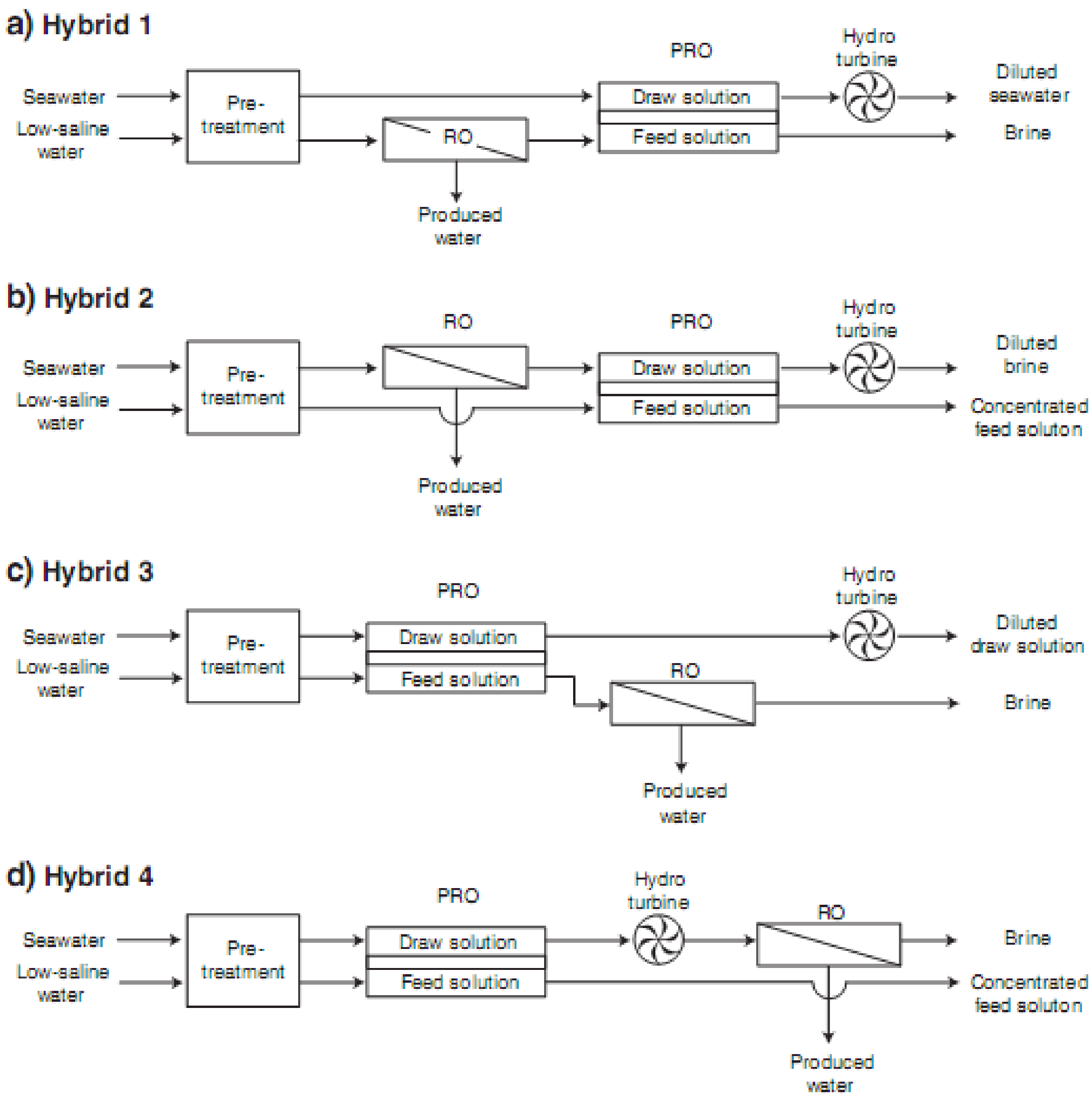
RO and PRO Hybrid Process

(RO → PRO mode)
Low-saline water as a RO feed

(RO → PRO mode)
Seawater as a RO feed

(PRO → RO mode)
Concentrated low-saline water as a RO feed

(PRO → RO mode)
Diluted seawater is supplied as a RO feed



Four possible RO-PRO hybrid configurations

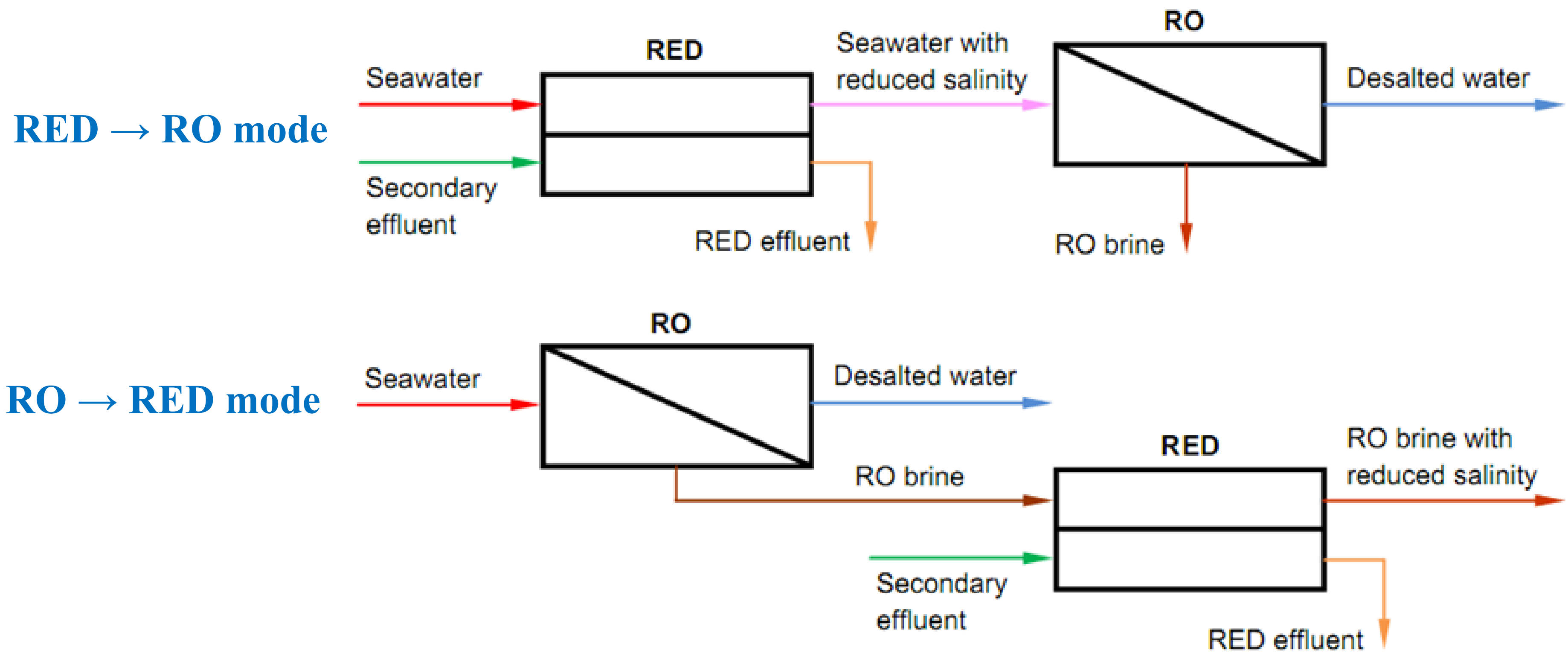
J. Kim et al., Desalination 322 (2013) 121-130

RED in Hybrid Process involving RED

- **The requirement of a concentrated solution as an input system makes RED a potentially suitable technology that can be integrated with sea water desalination technologies (SWDT) and a solar power desalination technologies (SPDT).**
- **The integrated approach of RED process involves direct feeding of brine concentrates from SWDT to RED system.**
- **RO and MD can be integrated to RED system either separately or in a combined way depending on level of efficiency required and affordability of the system setup.**
- **In integrated SWDT-RED process, the RO process can supply the concentrated brine as the high salinity feed solution for a higher power density.**
  - **Advantages :**
    - ✓ **Minimization of SWDU brine toxicity**
    - ✓ **Energy consumption of SWDU reduced by pretreatment with RED**
- **The process as a whole could then help in prevention of the environmental problems related to brine disposal allowing the production of electricity simultaneously.**

E. Brauns, Desalination 219 (2008) 312-323

Integrated Technologies Involving RED



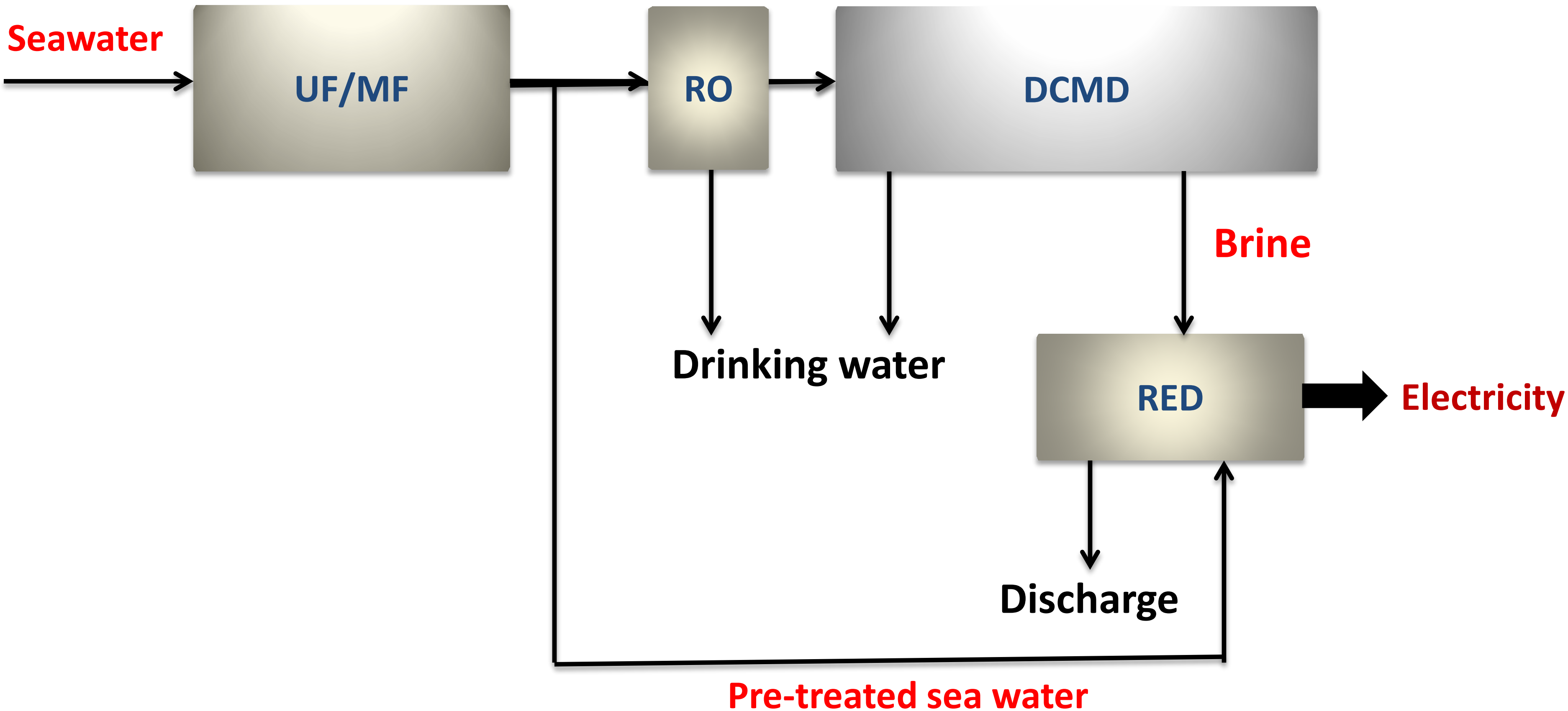
Basic RED-RO hybrid processes

- **Advantages of the RED–RO hybrid process configurations over conventional SWRO processes**
  - ✓ **Reduction of total energy consumption**
  - ✓ **Brine management permits a zero-discharge system with a higher recovery**
  - ✓ **Easy modification of the RED-RO configuration**
  - ✓ **Possibility of using biologically treated effluents as the low salinity feed to RED for a higher efficiency**

W. Li et al., Applied Energy 104 (2013) 592–602

Integrated Technologies Involving RED

Integration with RO and MD



- *Brine of up to 6 M can be generated with Direct Contact Membrane Distillation (DCMD) to be used as a feed of RED*

Challenges and Future prospective

- For pressure retarded osmosis, **the development of specific membranes must gain some special attention.**
- For RED, **the system characteristics majorly internal resistance mainly determined by width of the spacers are more important**.
    - Inadequate know how on the requirements for stack design in relation to initial pre-treatment and process losses
    - Insufficient availability of data on economical evaluation for the RED process in large scale
- The required water quality parameters are still unknown
- On operational end, fouling is the common problem for both techniques.
- The feasibility of the techniques, especially for RED, is mainly determined by the membrane cost.
    - Unavailability of specially developed low cost membranes
- Hybrid processes is designed to fully obtain the synergy of all the processes

DCMD can produce the brine to be used for energy generation. Moreover DCMD can be used as a membrane crystallization unit which is just an extension of MD.

Thus seawater can be used for energy generation and metals recovery.

How much brine is discharged from the current desalination plants ? How much salts can be potentially recovered?

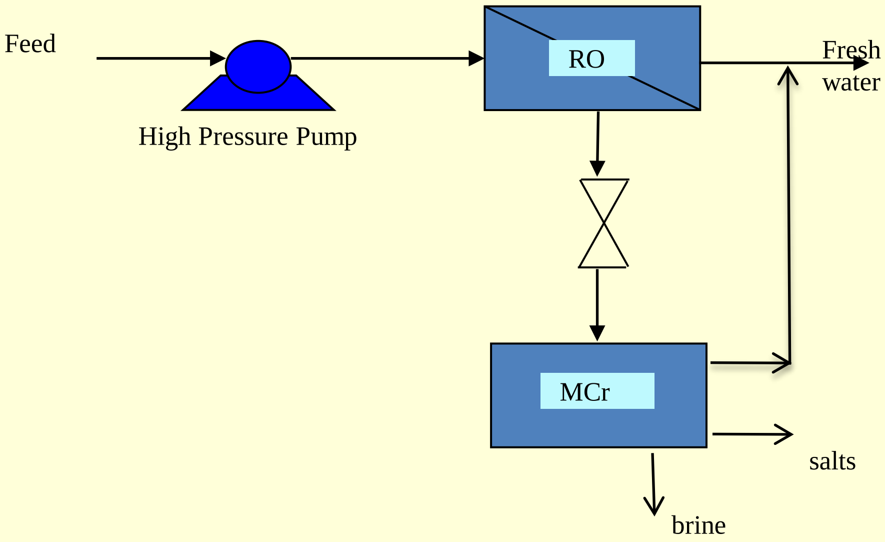
Desalination plant

Salt deposit

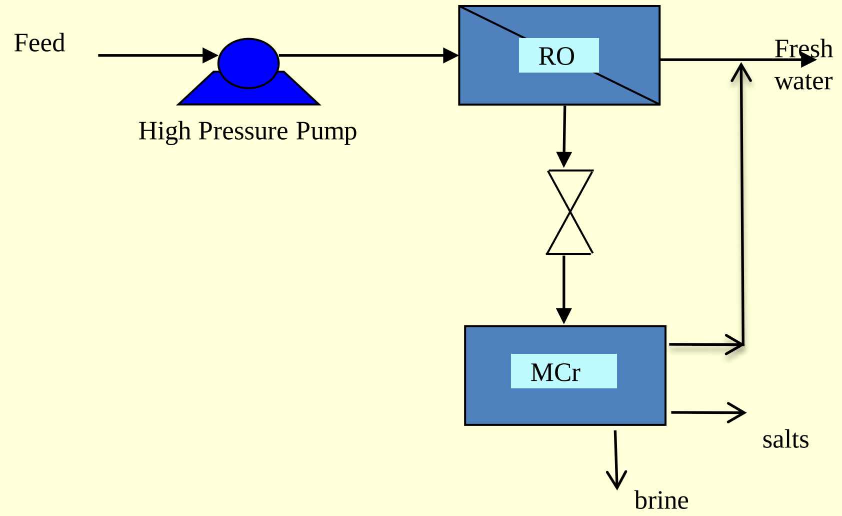
How much salts can be recovered from the current desalinated seawater?

INPUT DATA:

- Technology = RO+MCr
- *Capacity = 65.2 *10^6 m^3/d*
- RO recovery factor = 50%
- RO rejection = 99.6%
- RO inlet pressure = 55.8 MPa
- Seawater flow rate = 7.01*10^7 m^3/d



How much salts can be recovered from the current desalinated seawater?



RESULTS:

- Brine flow rate = $4.82*10^6$ m^3/d
- Brine concentration = 460.3 g/l
- Fresh water flow rate=$65.2*10^6$ m^3/d
- Fresh water concentration= 0.074 g/l
- Plant recovery factor = 93%
- Salts:
  - NaCl= 150 ton/day
  - $CaCO_3$ = 68.3 ton/day

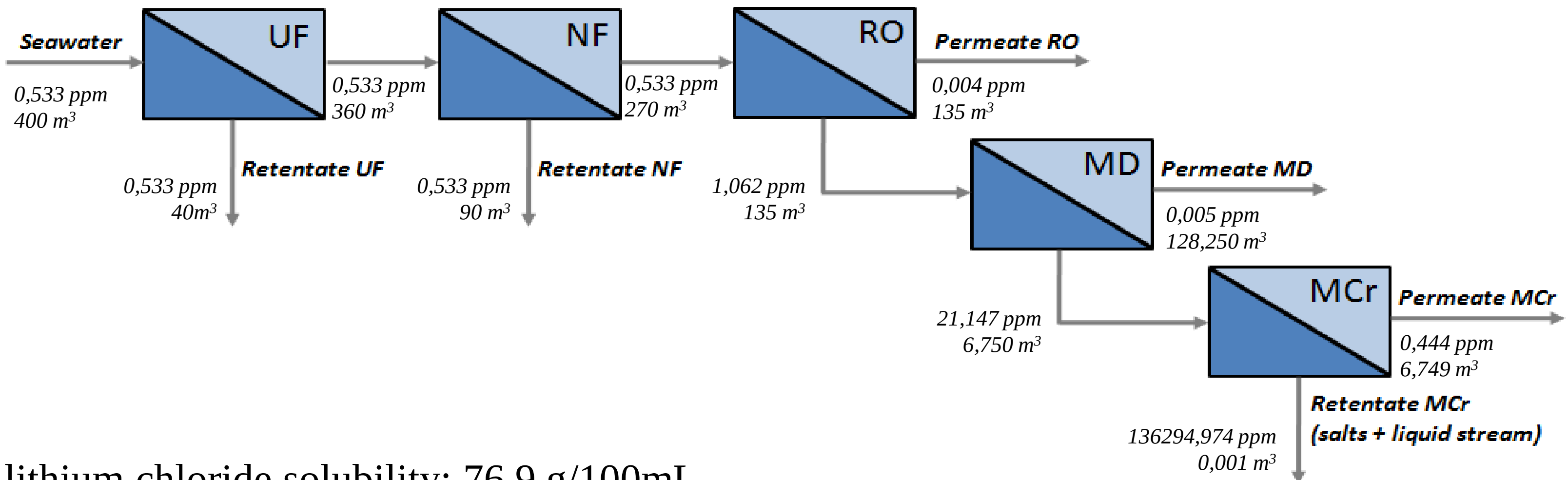
Ion	Seawater [ton/day]	Brine [ton/day]
Cl	1.332.043	1.234.555
Na	736.129	685.862
SO4	189.290	188.350
Mg	94.645	94.175
Ca	28.043	558
HCO3	9955	9906
K	26.640	244
CO3	245	1639
Br	4557	4534
Li	11,9	*11,9*
U	0,231	0,230

higher than the annual worldwide magnesium demand

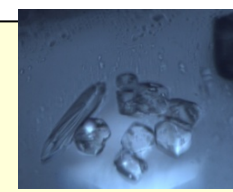
27% of the annual worldwide lithium demand

Lithium crystallization

It is necessary to start from 400 m^3 of seawater and to concentrate up to 1L of satured solution to obtain the crystallization of lithium chloride.



lithium chloride solubility: 76.9 g/100mL



	Feed	PT (perm.)	NF (perm.)	RO (ret.)	MD (ret.)	MCr (ret.)
Recovery (%)	-	90	75	50	95	99.98
Rejection (%)	-	0	0	99.25	99.54	97.90
Volume (m^3)	400	360	270	135	6.75	0.001
Concentration (ppm)	0.533	0.533	0.533	1.062	21.147	136295
Concentration factor (-)	-	0	0	2	20	6445