RECENT PROGRESSES AND PERSPECTIVES IN DESALINATION WITH INTEGRATED MEMBRANE SYSTEMS

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SAUDI INTERNATIONAL WATER TECHNOLOGY CONFERENCE

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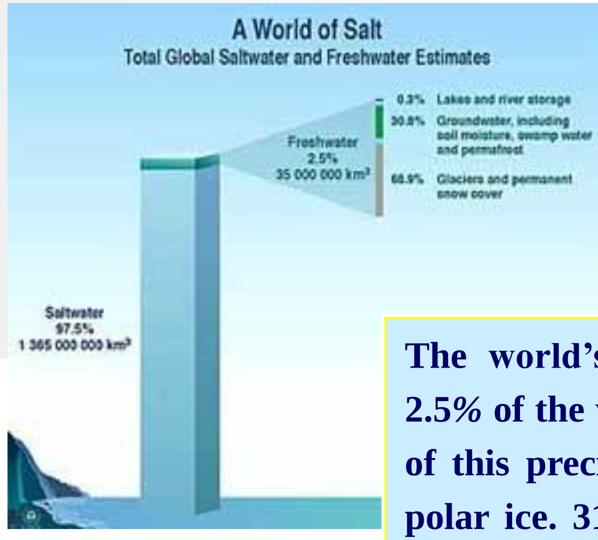
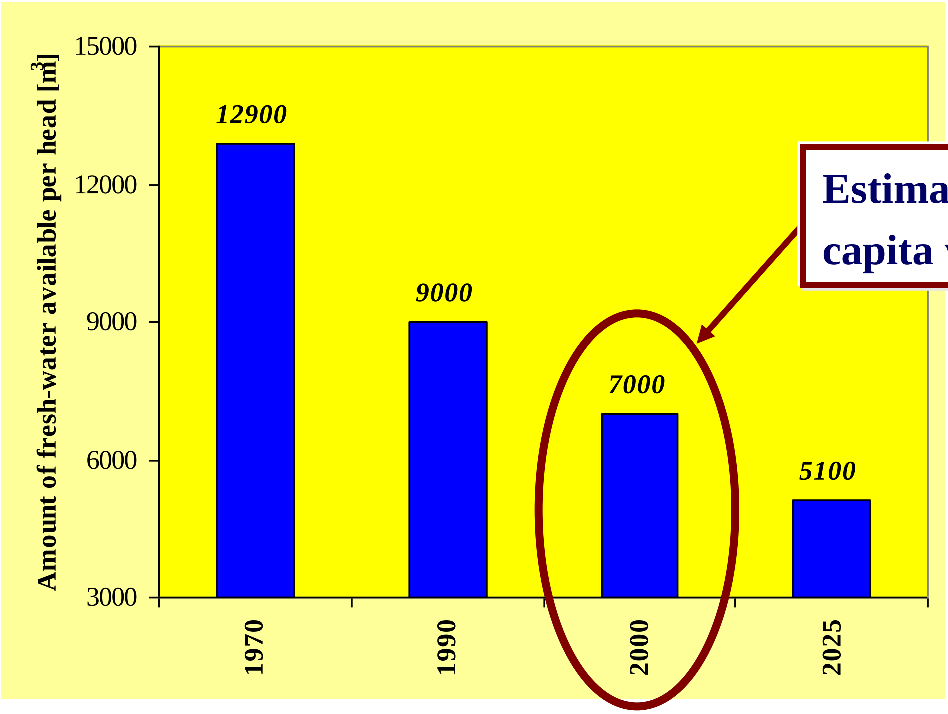
Water usage is globally increased by *six* times in the past 100 years and will *double* again by 2050.



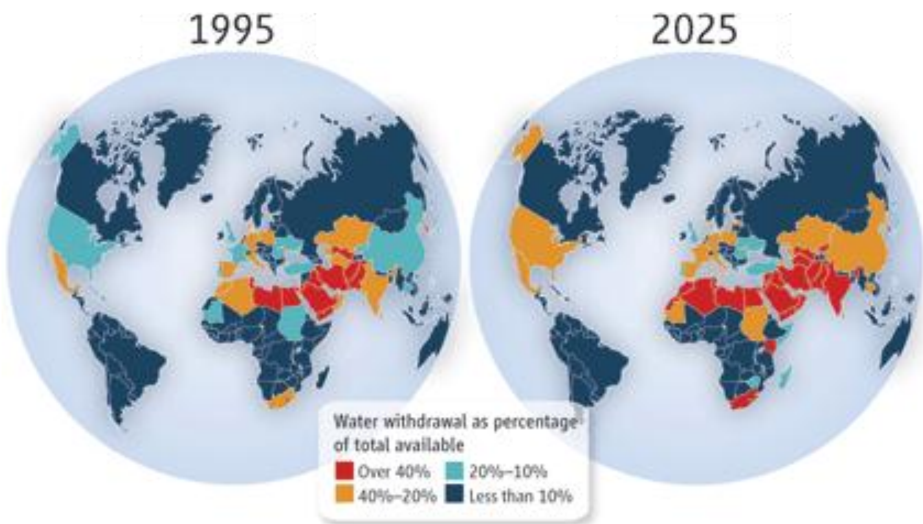
The world's potable water reserve represents 2.5% of the world's total water resources. 68.9% of this precious limited supply is locked in the polar ice. 31.1% can be found as groundwater, lakes, natural reservoirs and rivers.

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.***

Solution to the water shortage problem requires today significant update level of innovations, which can be reached through different ways:

- **by sea/brackish and marginal water sources desalination;**
- **by recovering and reusing treated industrial/municipal waste waters;**
- **by supplying water of diverse quality to the final users depending from their requirements (drinking, washing, agriculture, irrigation and industrial use).**

Actually water reuse and sea/brackish water desalination are well established water production processes also for communities using conventional water treatment and fresh water resources.

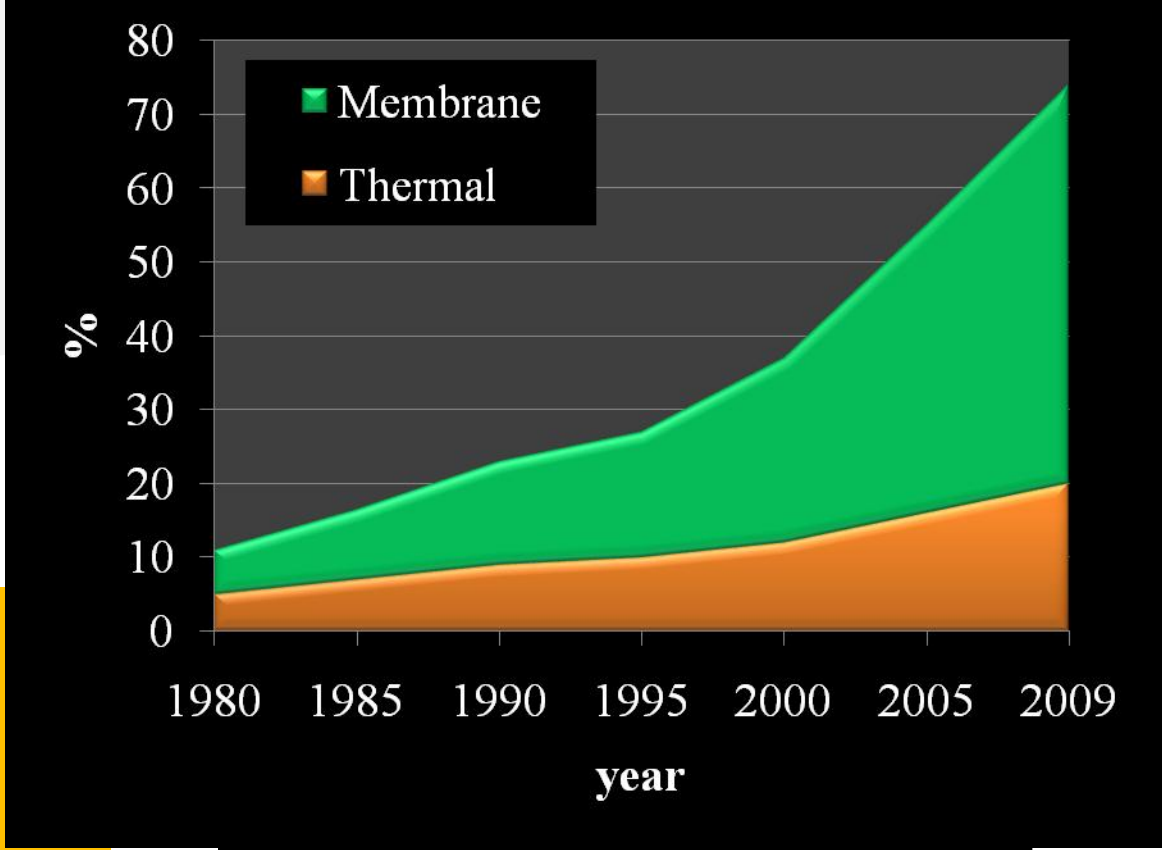
In particular desalination has become the most important source of drinking water production.

WATER DESALINATION

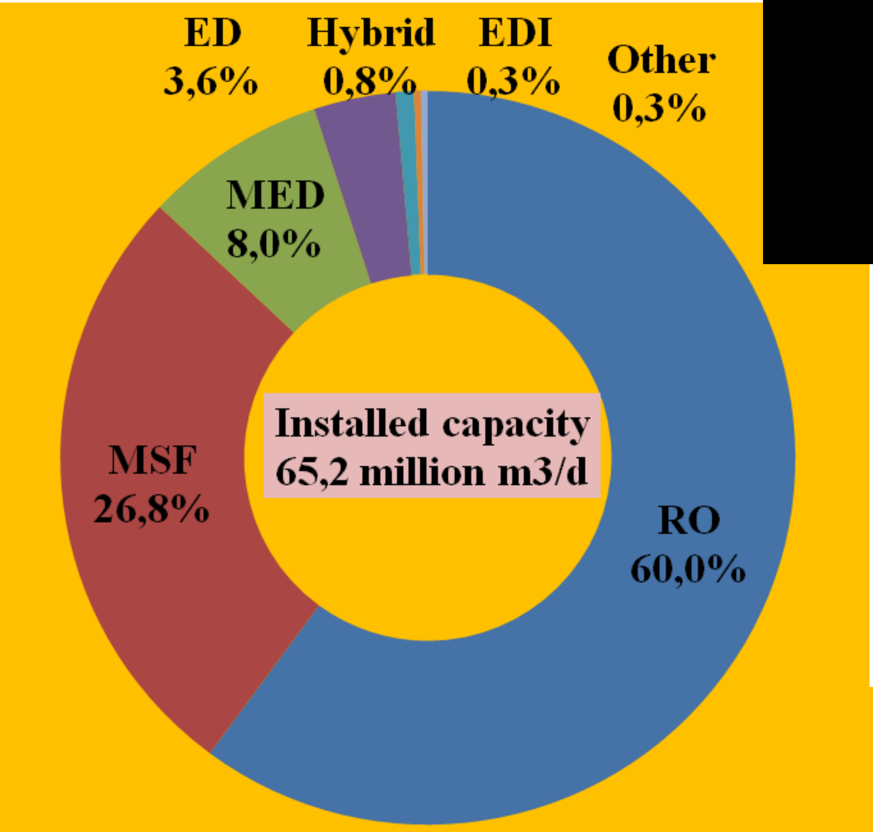
Seawater desalination through membrane operations (RO) epitomises the success of membrane technology and is probably the clearest example today of what can be achieved through the integration of different membrane operations.

- ✓ ***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)**
- ✓ ***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.**



Installed membrane and thermal capacity, 1980-2009 (cumulative)



Total worldwide installed capacity by technology

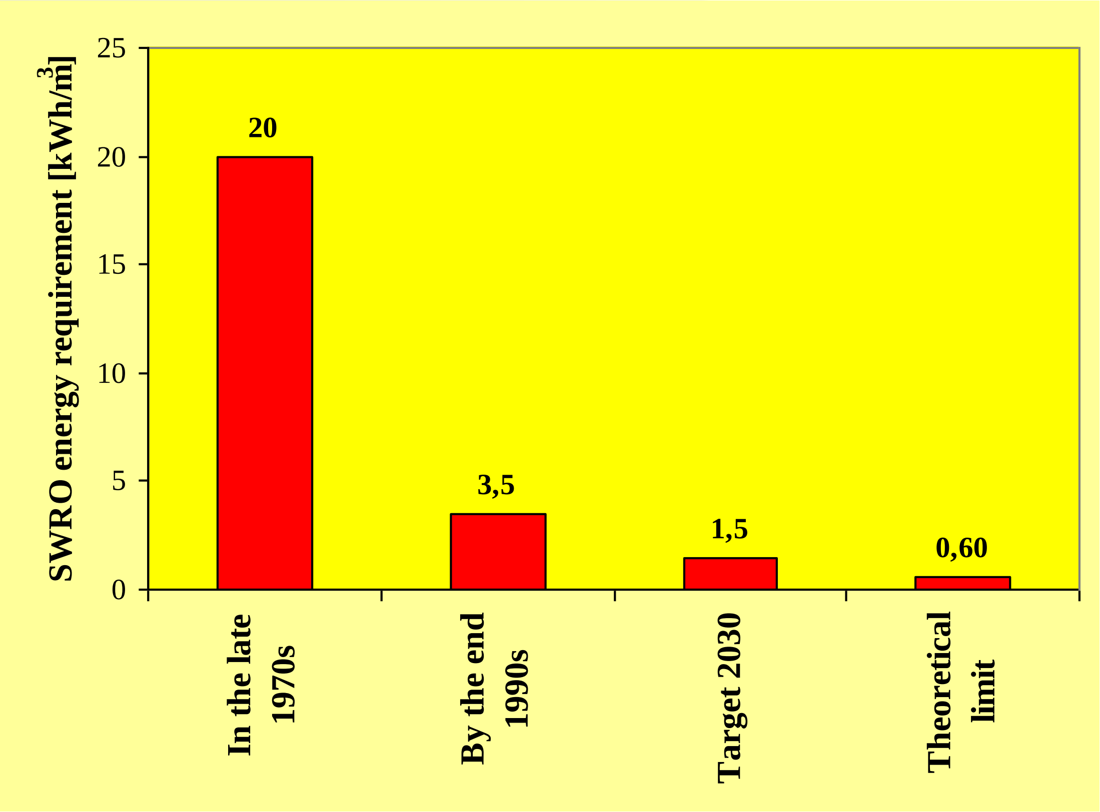
Why RO is the leader in current desalination installations?

Because …

Thermal desalination processes (MSF, MED, VC)	Membrane desalination processes (RO)
Energy consumption (MSF) = 17 ÷ 18 kWh/m^3	Energy consumption =2.2 ÷ 6.7 kWh/m^3
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 \$/m^3 (MSF) ÷ 0.7-1.0 (MED, TVC)	Desalted water cost ≈ 0.50 ÷ 0.70\$/m^3 (in the most part of SWRO plants) and 0.36\$/m^3 (from brackish water sources)

Because …

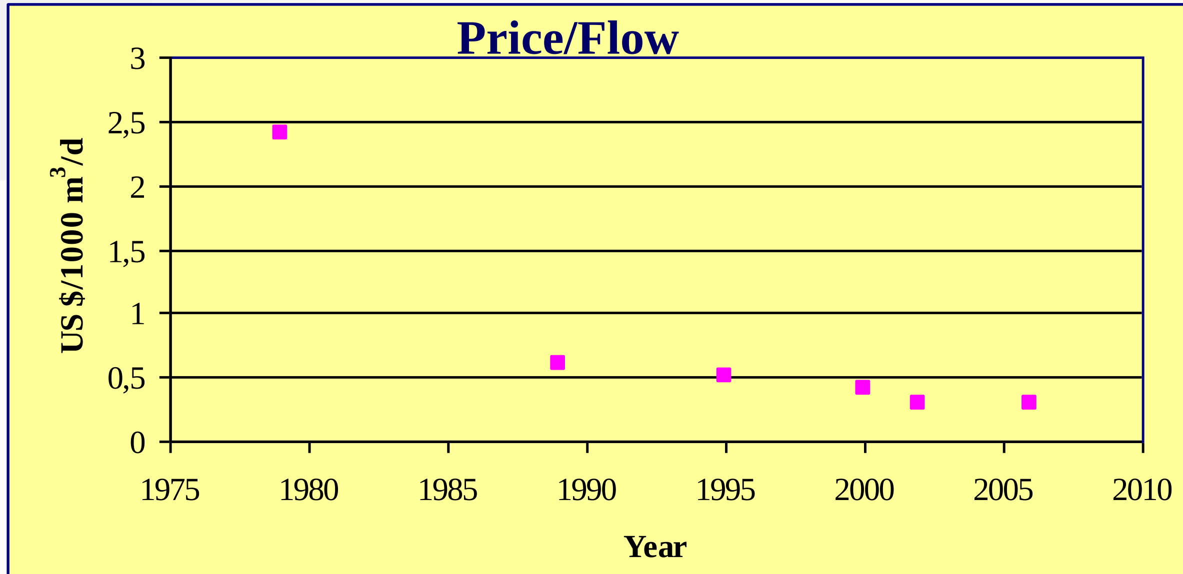
… currently, the lowest energy consumption is achieved by RO desalination processes.



The power consumption rate decreased due to *(i) new low energy RO membranes with improved salt rejection and lower price, (ii) high efficiency pumps and motors, (iii) more efficient energy recovery devices.* A recent request is to aim for a consumption of 1.5 kWh/m^3 by 2030, not far from the theoretical inferior limit that remains around 0.6 kWh/m^3 due to the osmotic pressure of the fed seawater.

Due …

…to the decreasing trend of the membranes price 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%).

Reverse Osmosis for water desalination: from domestic use to large scale

Reverse osmosis under-skin desalination system

RO-NF spiral-wound modules for large scale plant

Ashkelon Seawater Reverse Osmosis (SWRO) Plant, Israel
Production capacity: 330,000m^3/day (100 million m^3/y)

Problems still to be solved

- ✓ bio-fouling and fouling
- ✓ brine disposal
- ✓ energy consumption
- ✓ recovery factor
- ✓ water quality
- ✓ costs

Membrane Technology represented for process engineering a significant improvement towards innovation and rationalization of production cycles, and towards sustainable development.

Low energy consumption, modularity, operational simplicity and flexibility, compactness, high selectivity and permeability for the transport of specific components, and good stability under a wide spectrum of operating conditions represent the *strong points* of a technology addressed to "*Process intensification*" technology.

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.

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.

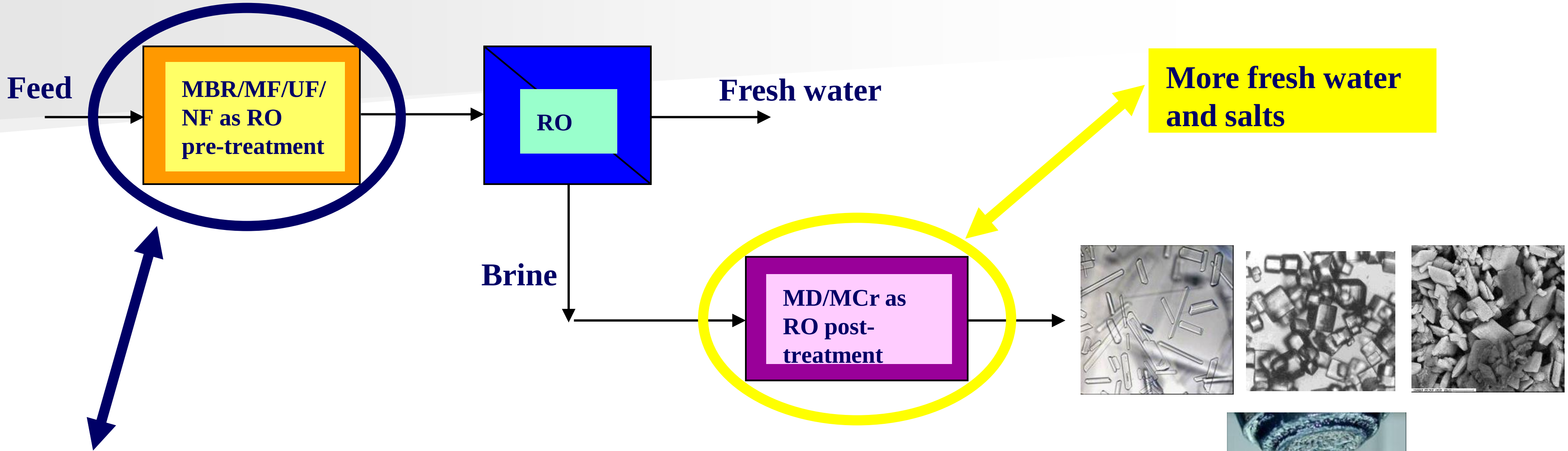
Membrane Operations

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!

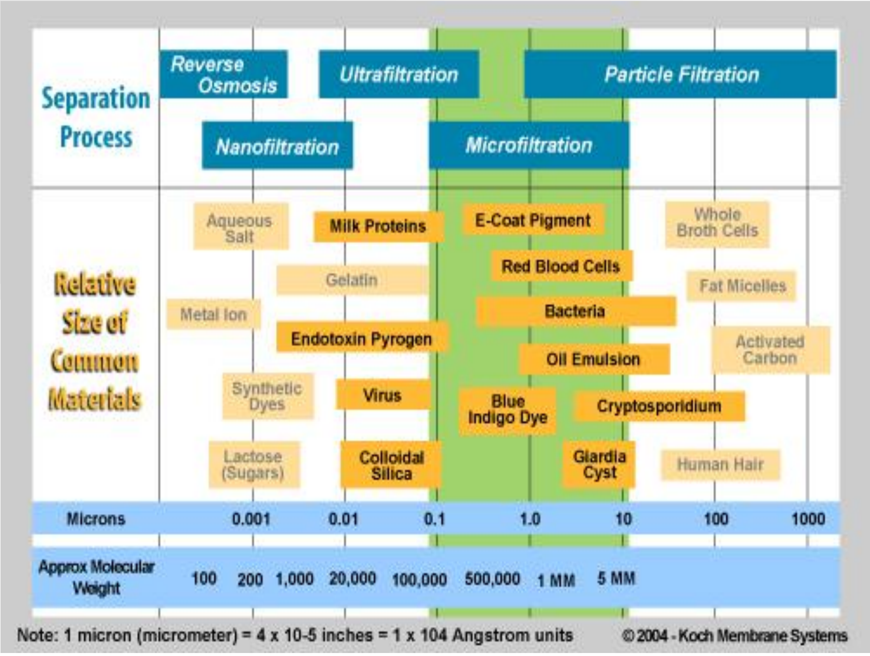
MR conversion much *higher (5 times)* than TR

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.

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



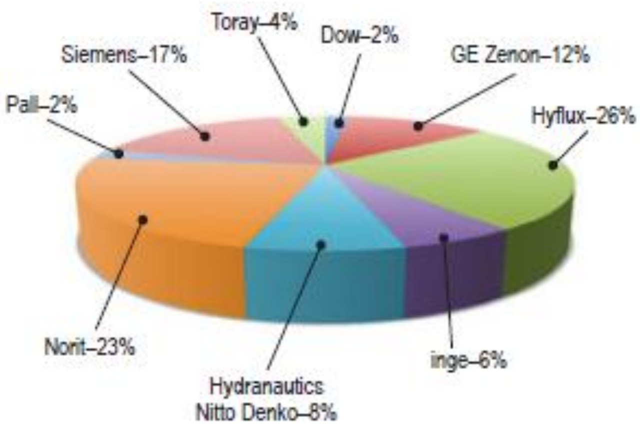
- *RO feedwater of good quality* with lower COD/BOD and SDI
- *Reduction in capital and operating cost*:
  - ✓ Elimination of fine filters in the RO systems
  - ✓ Less membrane replacement cost (due to the lengthened membrane useful life)
  - ✓ Less chemical consumption cost (less chemicals are needed 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)



- 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.

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

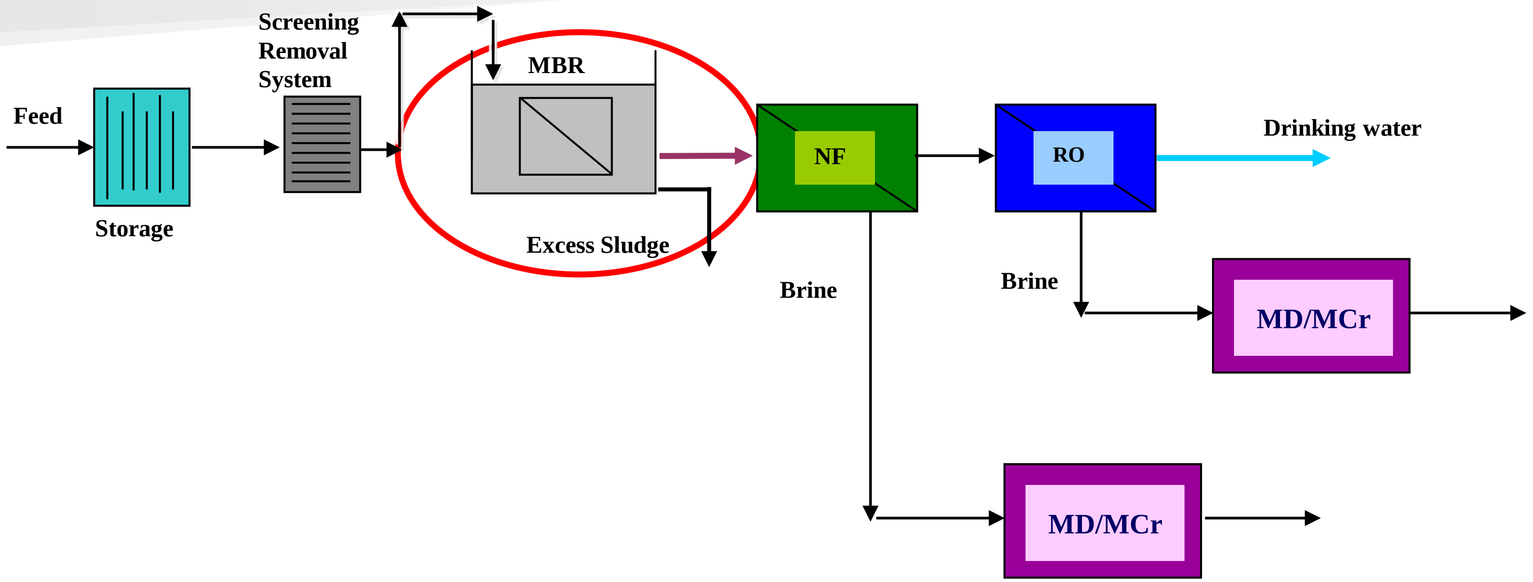
Only in 2010, CH2M Hill's Rob Huehmer has identified 94 such SWRO installations in operation or contracted .



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

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

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



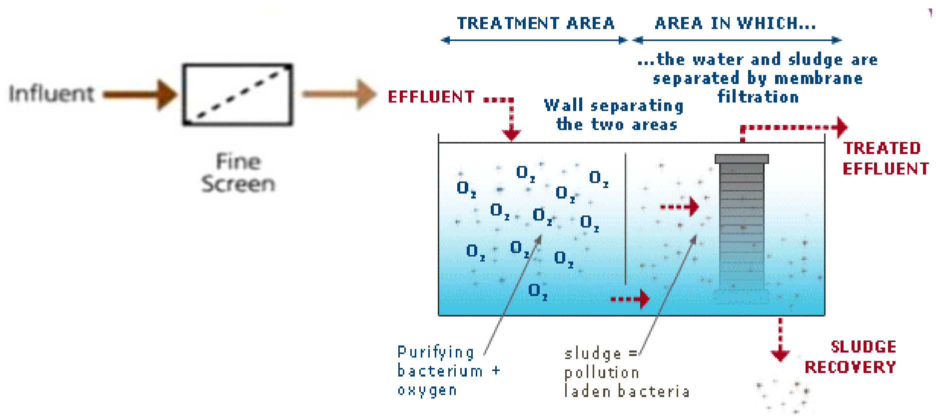
The possibility to use Membrane Bioreactor as SWRO pre-treatment could be of interest for the removal of a variety of anthropogenic organic pollutants and fouling agents that are increasingly present in sea/brackish-water.

MBR as RO pre-treatment

Membrane bioreactor (MBR) is a membrane operation in which low-pressure membrane filtration, either MF or UF, is used to separate effluent from activated sludge.

In a MBR the membranes are directly immersed in the tanks containing the biological sludge and the treated permeate is extracted.

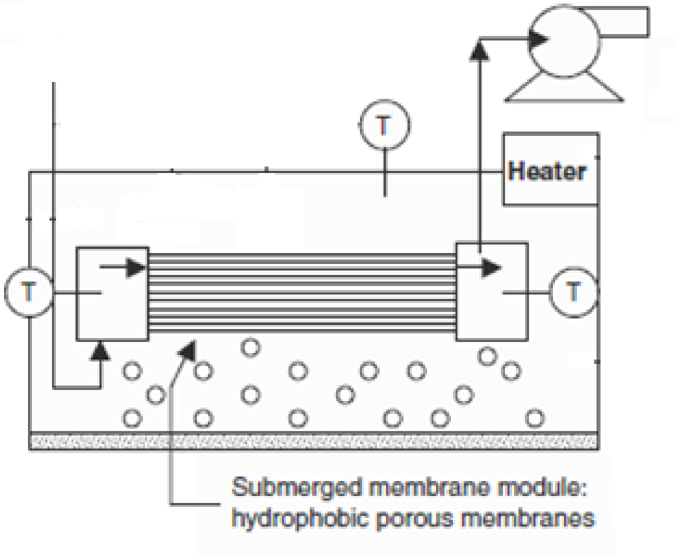
Membrane Bioreactor



MBR combines biological treatment with membrane separation. The treated water is separated from the purifying bacteria (active sludge) by a process of membrane filtration rather than in a settling tank as in conventional systems. Only the treated effluent passes through the membrane. It is then pumped out. The sludge is recovered and dewatered.

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

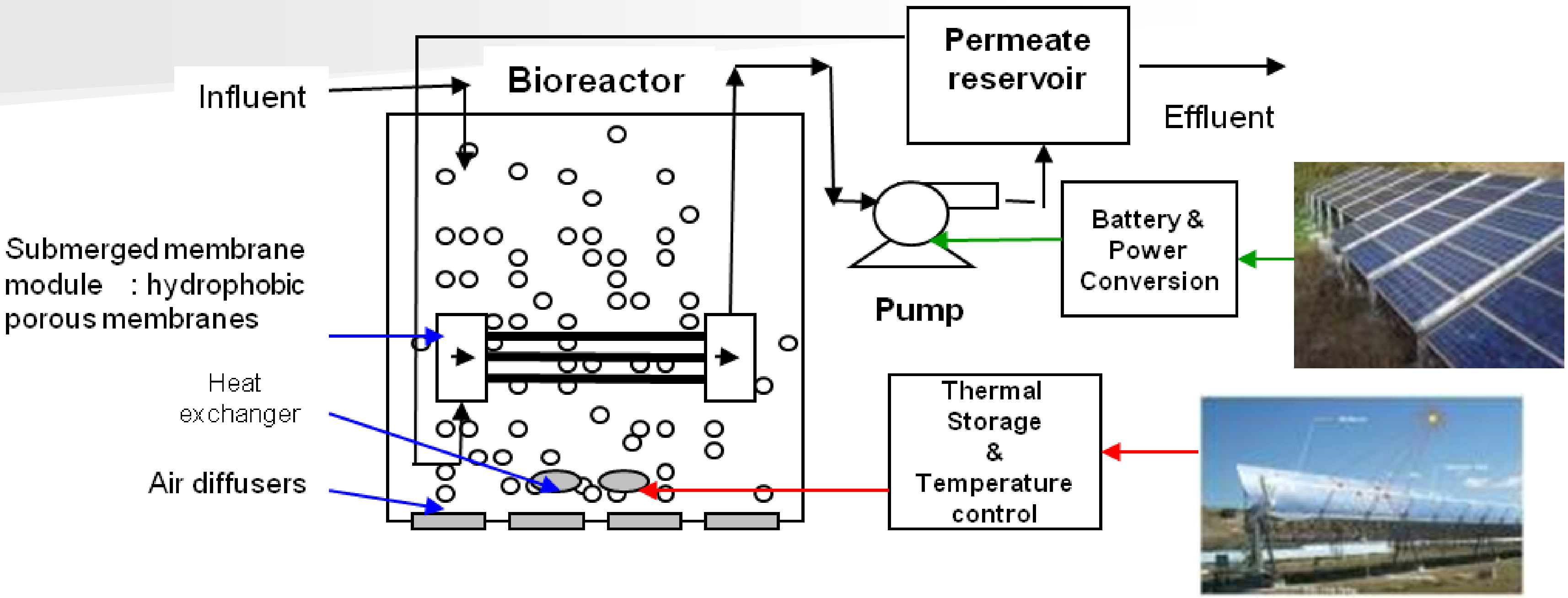
MEMBRANE BIOREACTOR CONFIGURATION (MDBR)



More recently membrane distillation has been also used in membrane bioreactor configuration (MDBR) for the treatment of industrial and municipal used waters.
The development of MDBR system was due to the fact that, in a conventional MBR, the molecular weight cut-off of the utilized MF/UF membranes delivers a portion of the organic species of the feed. The effect of this is that recalcitrant organics may not be well degraded, and the direct reuse potential of the permeate may be limited.

MDBR advantages
Effectively retention of small size and persistent contaminants, which facilitates their biodegradation in the bioreactor, thereby producing higher quality product water.
Potentially possess comparative economical advantage in removing pollutants from the used water more effectively.

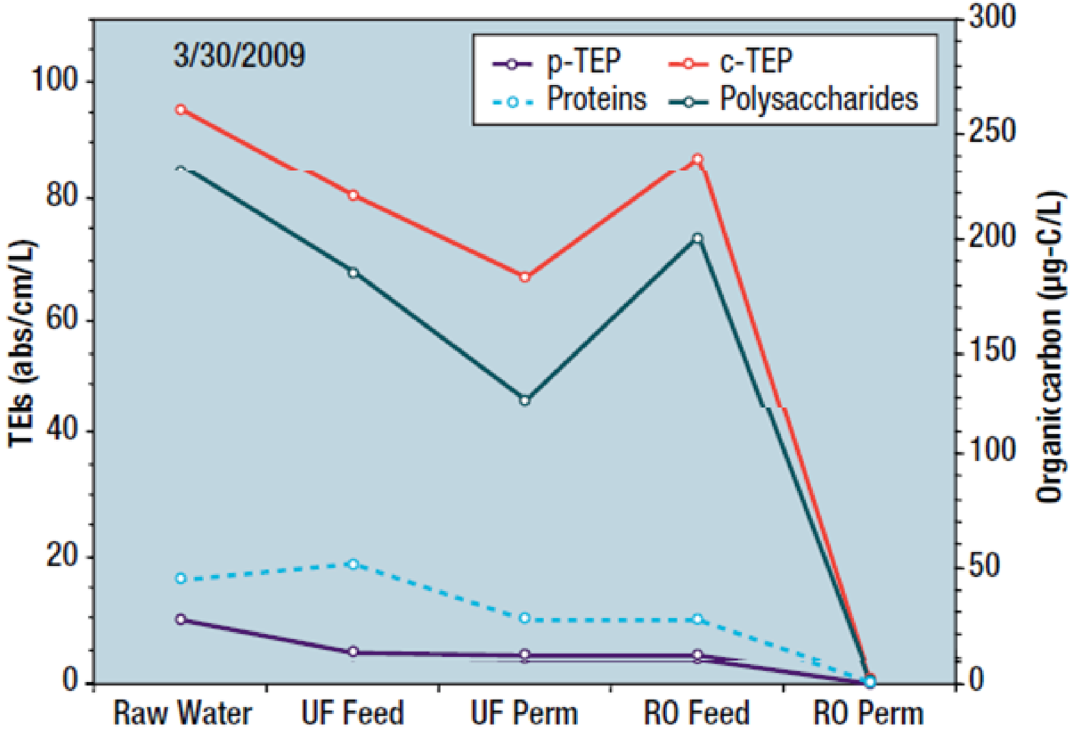
Energy Efficient Water Purification



Combined-cycle Solar Energy Self-sustaining Membrane Distillation (MD) - Membrane Distillation Bioreactor (MDBR) Water Production and Recycling System for Sea-water desalination and waste water recycling using membrane distillation and bioreactor.

Source: Nanyang Technological University (http://www.exquisitus.eee.ntu.edu.sg/Research/Pages/EnergyEfficientWaterPurification.aspx)

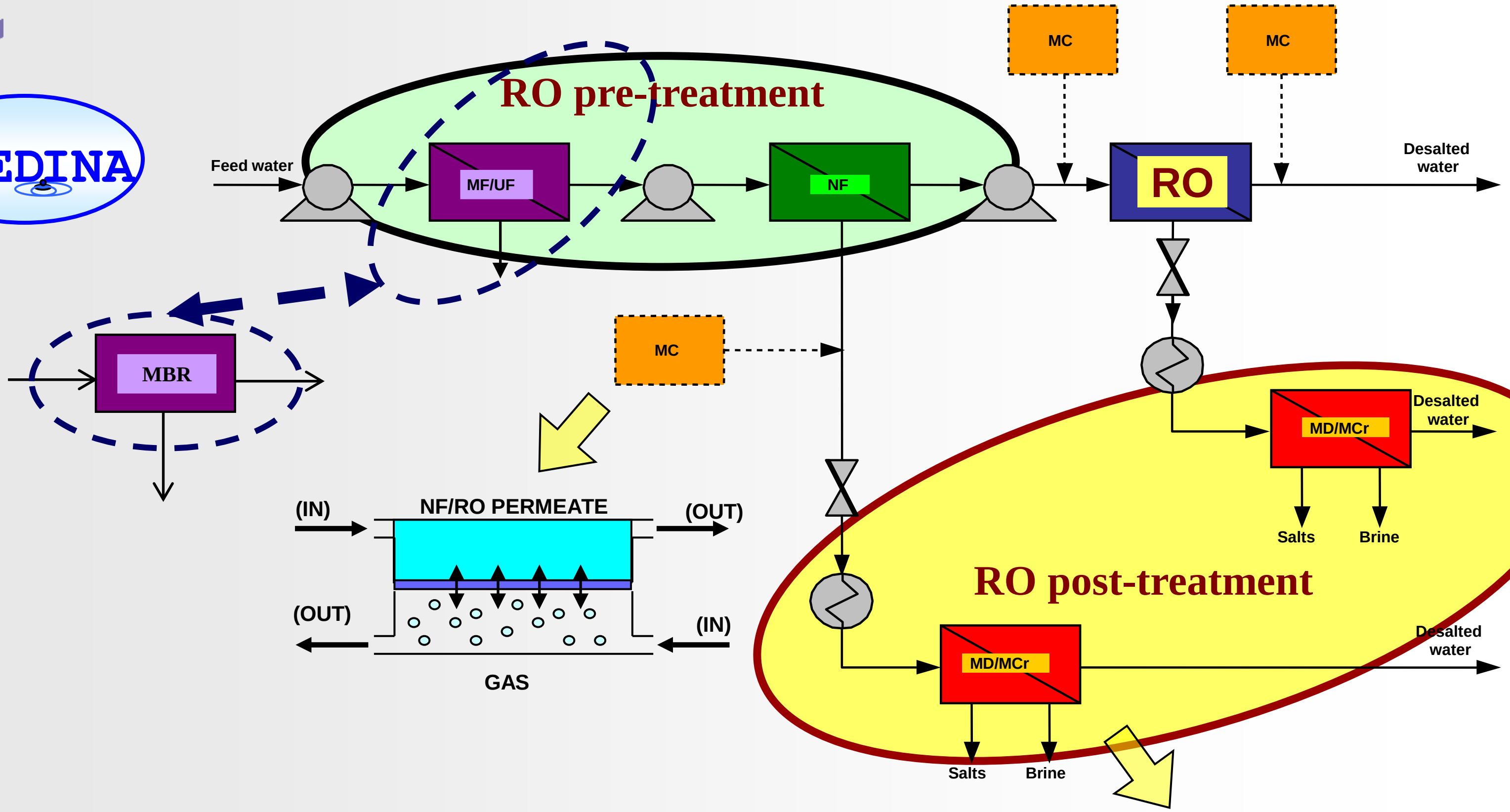
Solution to biofouling might require dramatic transformations of the traditional pre-treatment and disinfection methodologies (such as the use of chlorine).

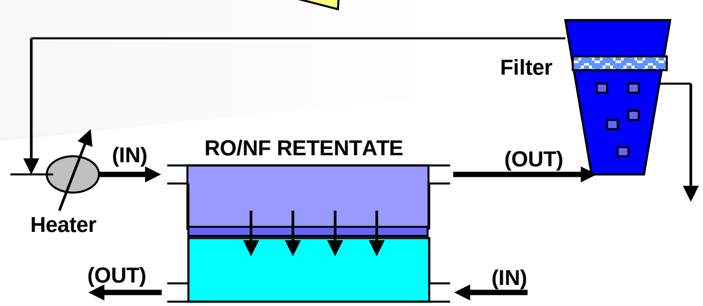


Usually, in the conventional pre-treatment, the seawater is acidified and chlorinated to control bacterial and organic fouling. Biological fouling, after dechlorination can be observed on the piping and fouling on the RO membrane occurrs. The bacterial counts are greater in the RO feed than in the seawater itself.

H. Winters, Desalination, 110 (1997) 93-96.; Y.P.Zhang, et al., Desalination 220 (2008)371-379.

Integrated Membrane Strategy for Desalination



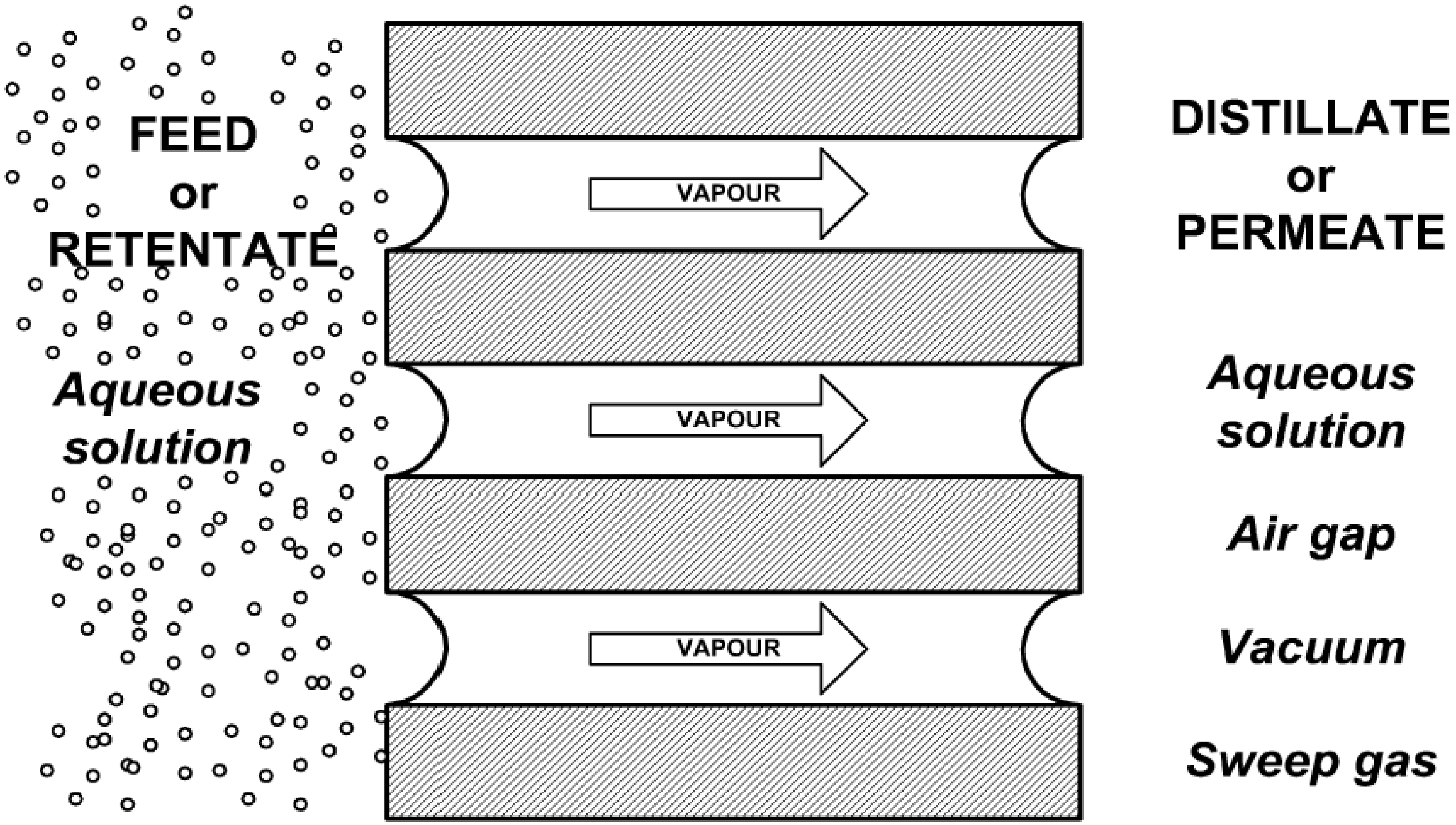


Possible integrated membrane desalination system at the basis of MEDINA project (one of the European funded projects in the Sixth Framework Programme)

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

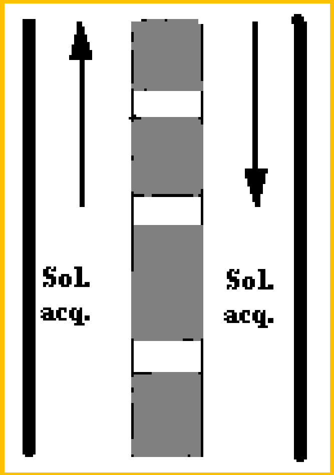
MEMBRANE DISTILLATION IN SEAWATER AND/OR BRACKISH WATER DESALINATION

MD PRINCIPLE

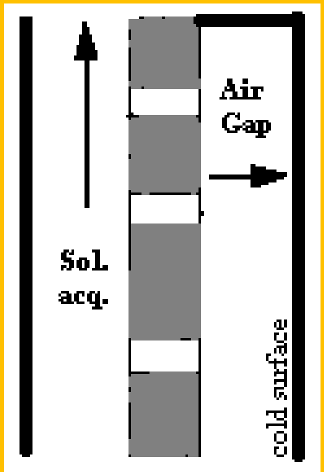


Volatile compounds **evaporate at the interface of a** *microporous hydrophobic membrane*, **diffuse and/or convect across the membrane, and are condensed and/or removed on the opposite side (permeate or distillate) of the system.**

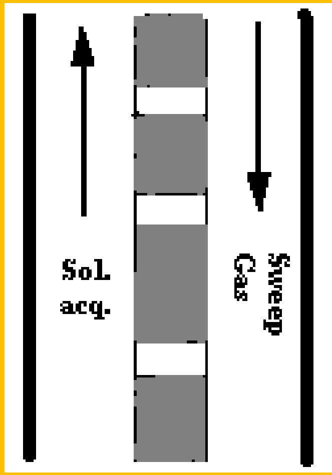
MD CONFIGURATIONS



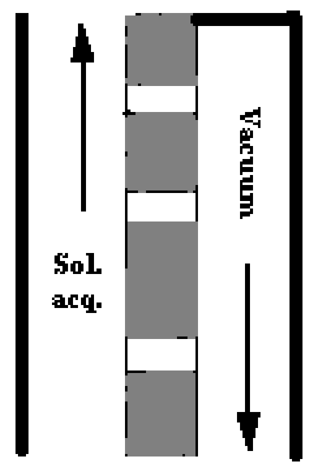
Direct Contact Membrane Distillation (DCMD). The permeate side of the membrane consists of a condensing fluid (often pure water) that is directly in contact with the membrane.



Air Gap Membrane Distillation (AGMD). The permeate side of the membrane consists of a condensing surface separated from the membrane by an air gap.

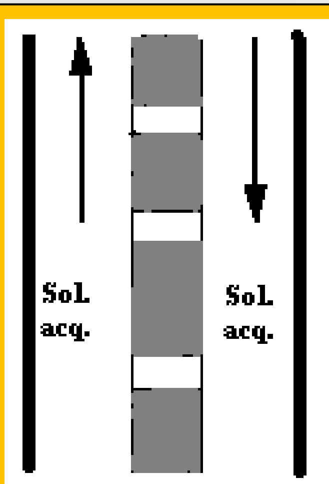


Sweeping Gas Membrane Distillation (SGMD). The vaporized solvent is removed by a sweep gas.



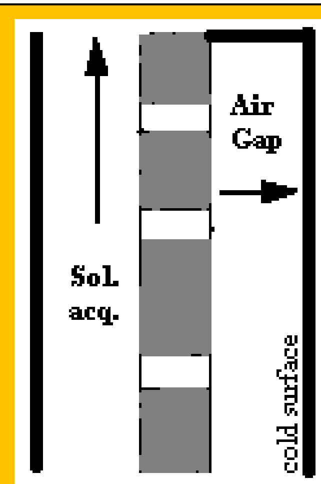
Vacuum Membrane Distillation (VMD). The vaporized solvent is recovered by vacuum.

MD CONFIGURATIONS: ADVANTAGES AND DRAWBACKS



DCMD:

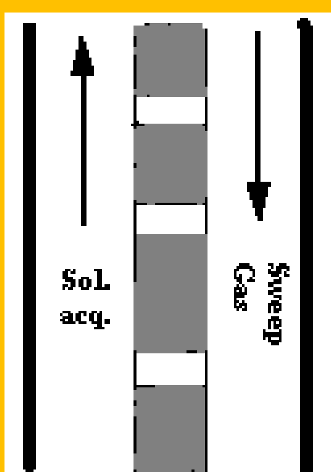
- Low efficiency of heat utilization due to the high heat lost by conduction through the membrane.



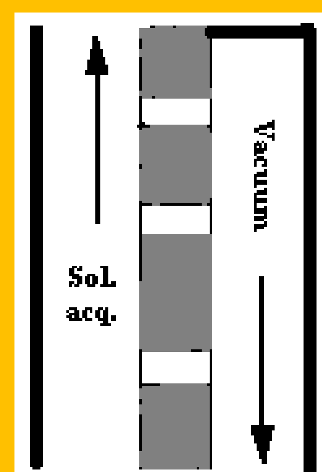
AGMD:

-Low conductive heat loss with respect to DCMD

-- Higher mass transfer resistance than DCMD



SGMD combines the low conductive heat loss of AGMD with the reduced mass transfer resistance of DCMD. The problem is that the permeate is condensed in an external surface.

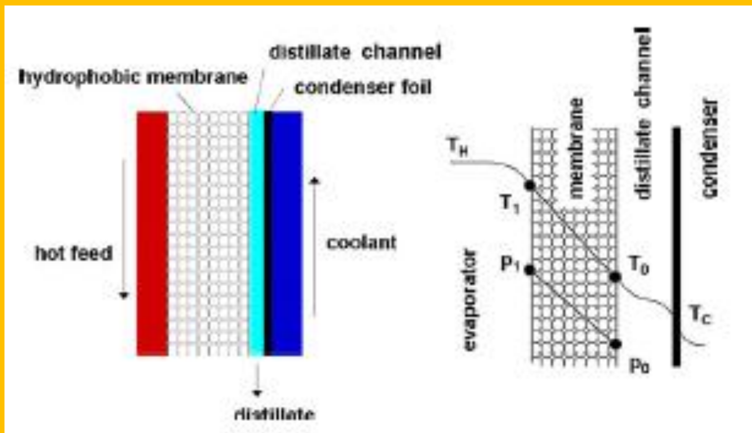


VMD:

-Negligible conductive heat loss through the membrane

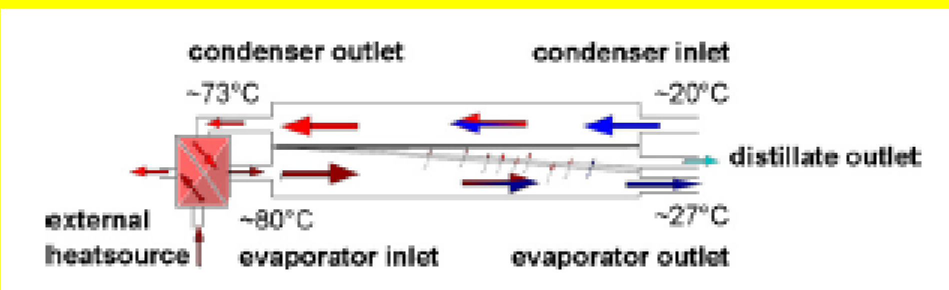
-High sensibility to membrane wetting

Permeate gap membrane distillation (PGMD)



PGMD is an enhancement of DCMD in which a third channel is introduced by an additional non-permeable foil.

One significant advantage of PGMD is the separation of the distillate from the coolant. Therefore the coolant can be any other liquid, such as cold feed water. This offer the opportunity to integrate an efficient heat recovery system.

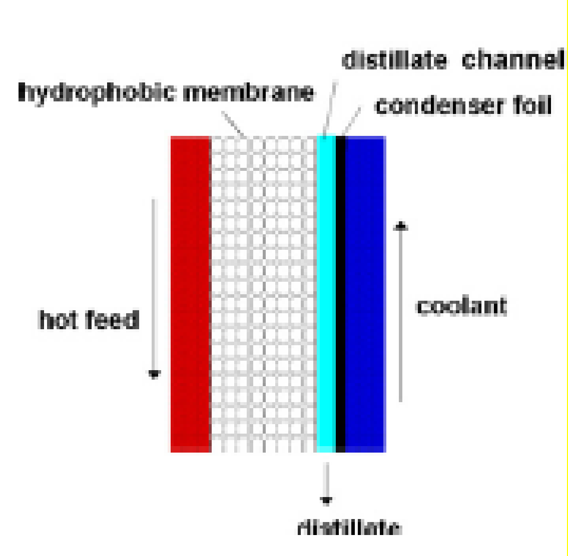


Cold feed water enters the condenser channel and gains heat to about 73°C by internal heat recovery. An external heat source (e.g. solar collector) heats the feed water up to 80°C.

Water vapour passes through the membrane and condenses in the distillate channel. The latent and sensible heat is transferred through the condenser foil to preheat the feed water in the condenser channel. Pure distillate exits the module at the distillate outlet.

Winter et al., Journal of Membrane Science 375 (2011) 104-112.

Permeate gap membrane distillation (PGMD)



Basic channel arrangment for PGMD

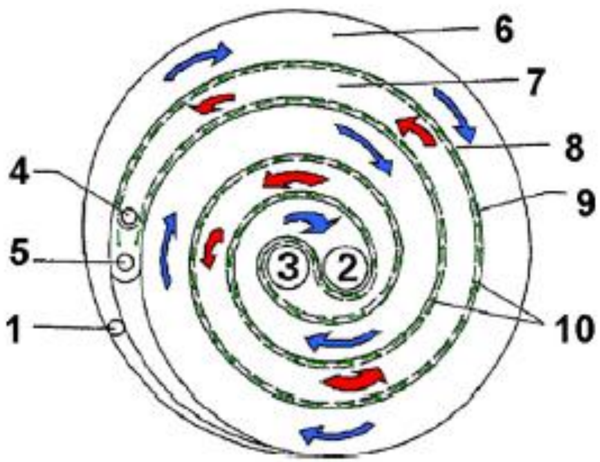


Fig. 5. Schematic of the spiral wound module concept: (1) condenser inlet, (2) condenser outlet, (3) evaporator inlet, (4) evaporator outlet, (5) distillate outlet, (6) condenser channel, (7) evaporator channel, (8) condenser foil, (9) distillate channel and (10) hydrophobic membrane.

PGMD channel arrangment transferred into a compact spiral package.

The hot zones of the channels are in the module center and the cold zones are at the module's shell side. Therefore even without module insulations, only minimal heat losses to ambient occur.

Winter et al., Journal of Membrane Science 375 (2011) 104-112.

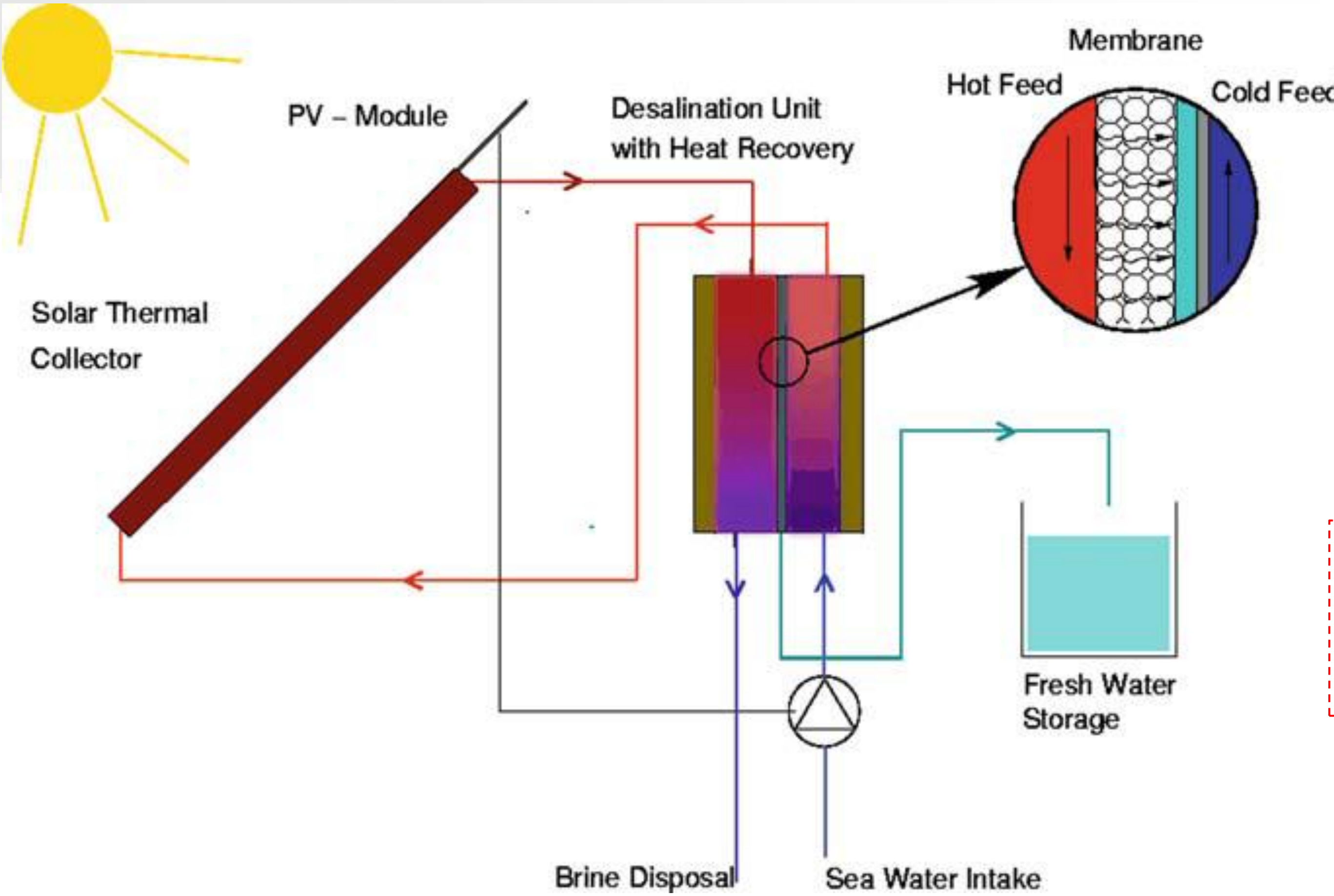
Some of MD advantages with respect to conventional distillation and reverse osmosis

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

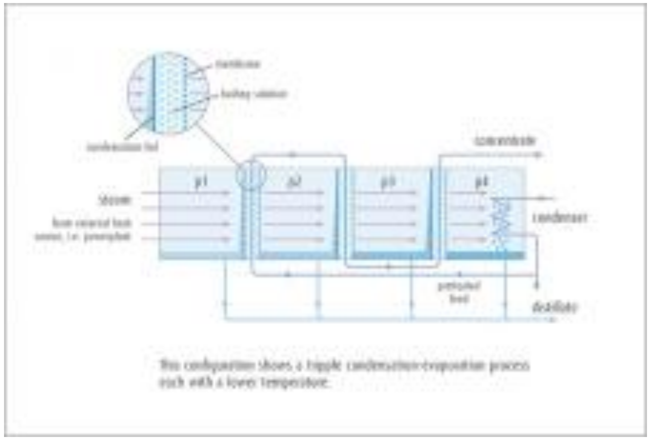


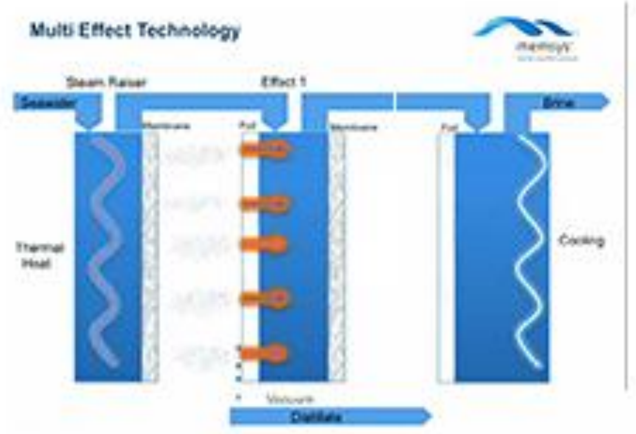
J. Koschikowski, M. Wieghaus, and M. Rommel, Membrane Distillation for Solar Desalination

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

<u>Memsys clearwater distribution Pte Ltd</u> 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:

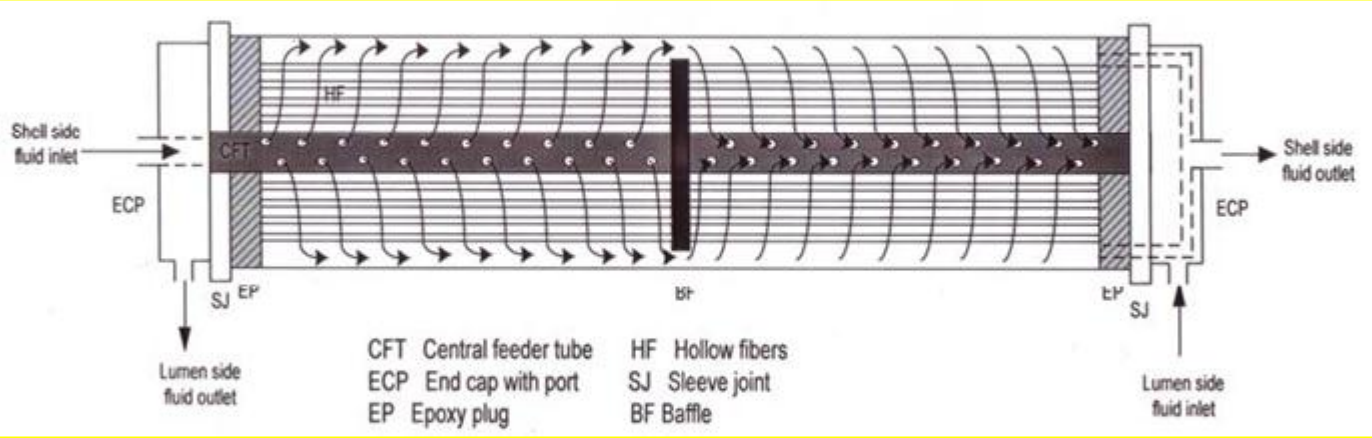
- ✓**Energy advantages through the use of low level waste energy**
- ✓**Investment cost advantages though use of non steel materials**
- ✓**Operational cost advantages because of low maintenance**
- ✓**Ecological advantages because of less need of water treatment**
- ✓**Full modularity increases flexibility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

Polymeric Hollow Fiber Heat Exchanger for Heat Recovery

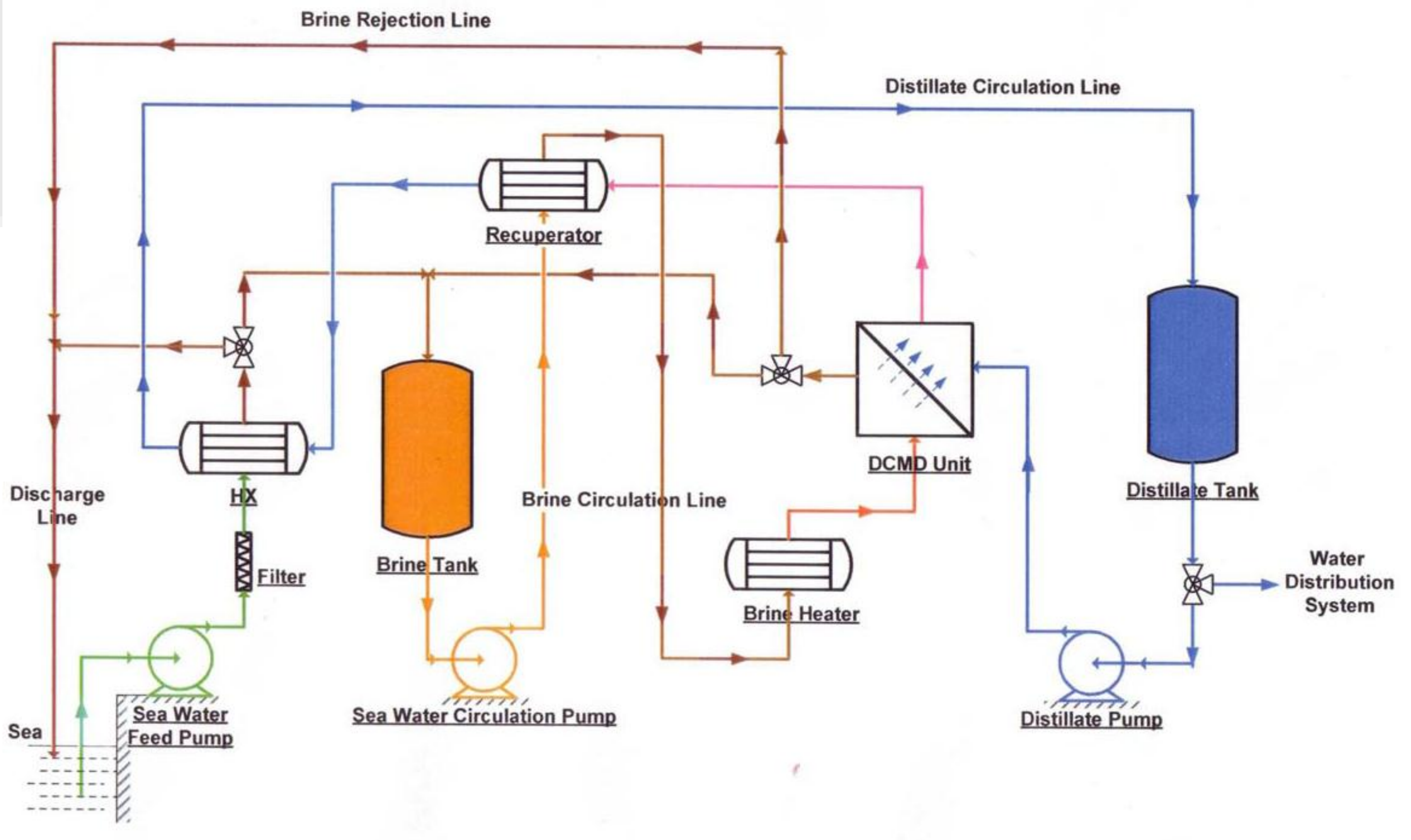
Solid polypropylene hollow fiber heat exchanger HEPP4 (effective area 3.9 m^2 based on fiber I.D.).

A large crossflow polymeric solid hollow fiber-based heat exchanger (HX) was obtained from Membrana Inc.. This HX has a surface area per unit volume of 22.5 cm^{-1} , a total heat exchange surface area of around 4 m^2 , polypropylene hollow fibers of the internal diameter 430 µm and the outside diameter 580 µm. The overall dimensions of this heat exchanger are: 38 cm long, shell side housing I.D. 9.7 cm.

Schematic view of the baffled crossflow HX module



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/m³, which is much cheaper than RO ($1.02/m³);

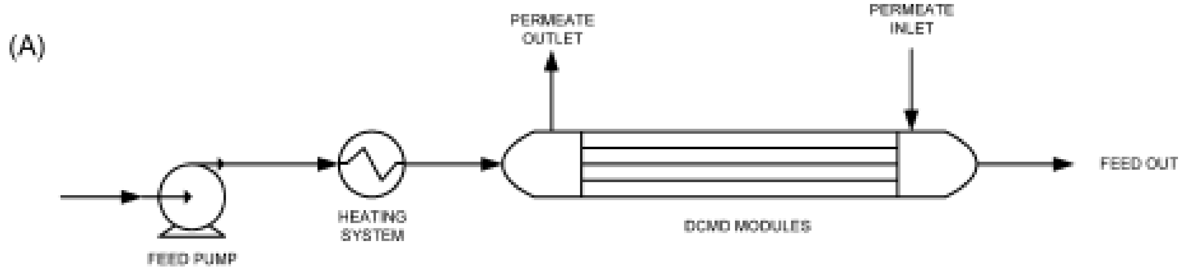
-when the cost of steam is taken into account, DCMD water cost is = 0.76 – 1.04 $/m³ (depending on the steam cost).

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.

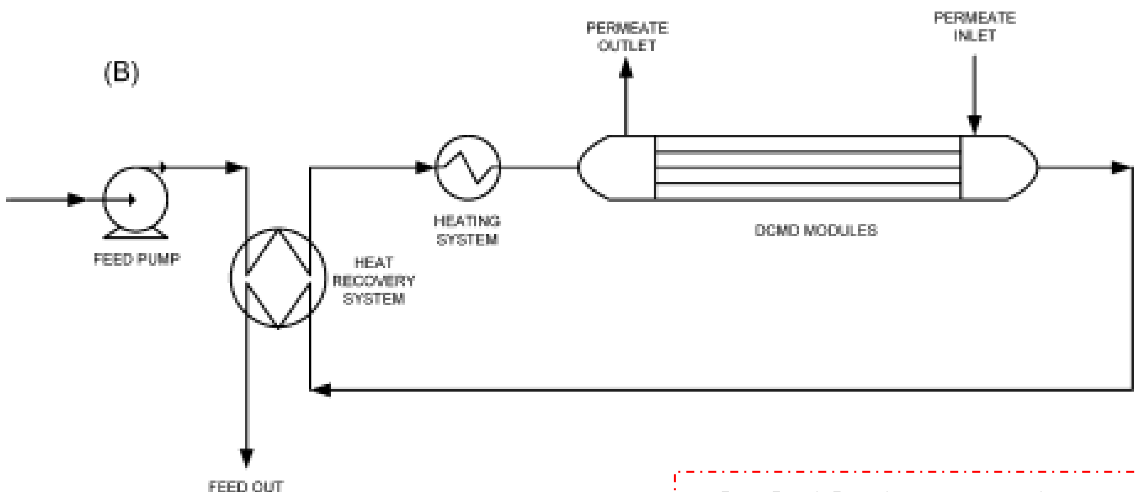
**** RO operative conditions: operating pressure 1,000 psi; 30% recovery; energy recovery, 30%; lifetime 3 years)**

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%)

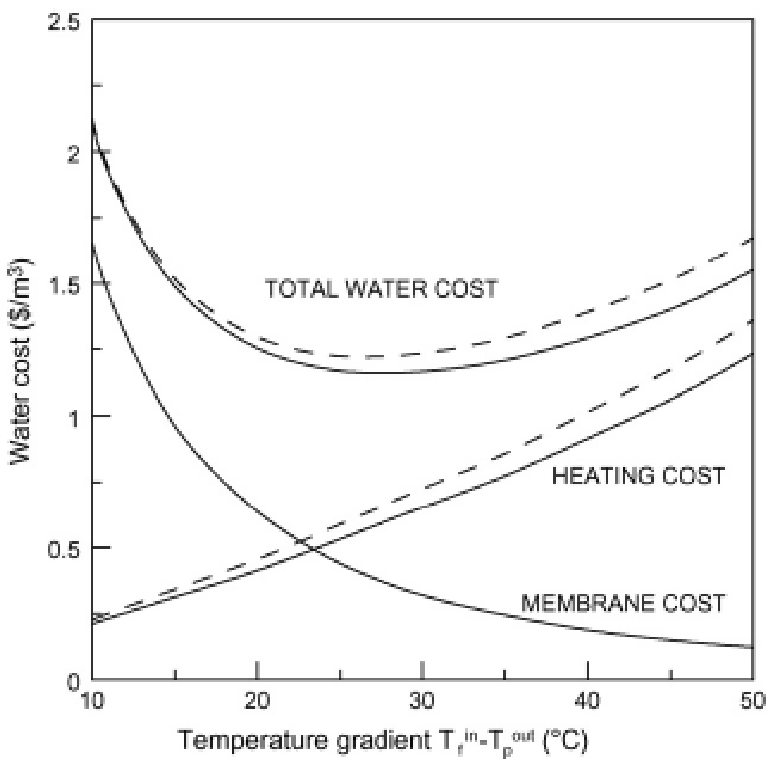


Scheme of Direct Contact Membrane Distillation (DCMD) operating: (A) without heat recovery (HR) system and (B) with HR system



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)

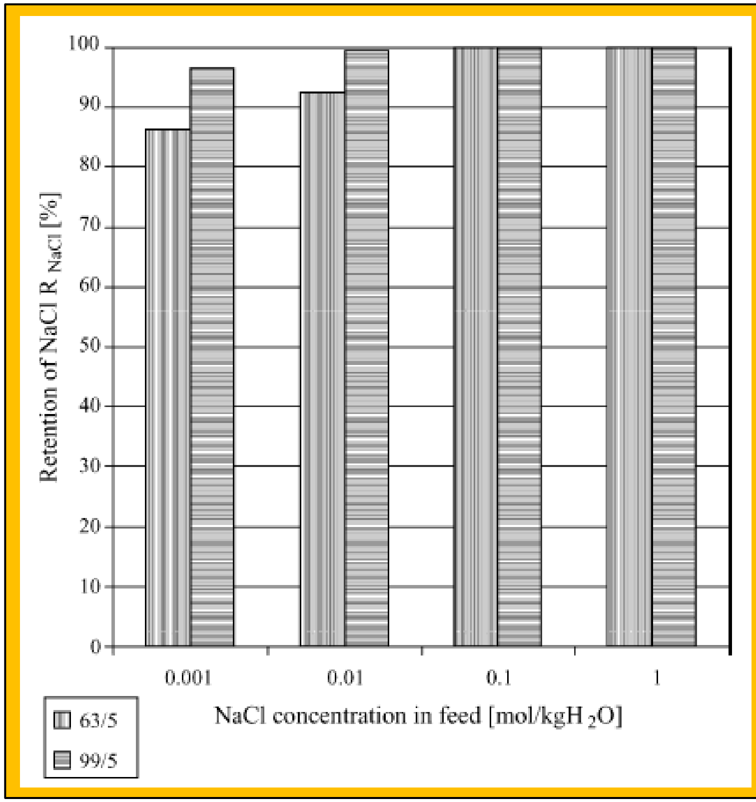
The minimum water cost is $1.23m^3 for DCMD without HR (feed temperature= 55 ◦C, DT = 25 ◦C).
The minimum water cost is $1.17m^3 for DCMD with HR (feed temperature close to 60 ◦C and DT=30).

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.		

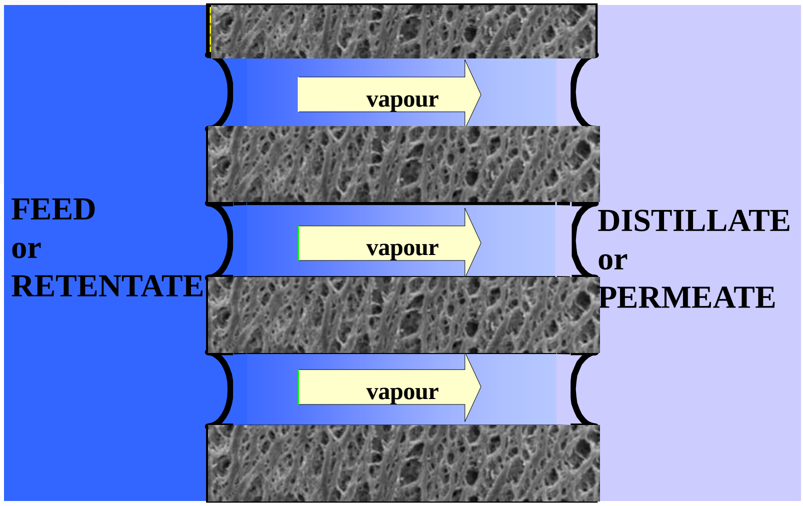


Retention coefficient for NaCl solutions at different concentration in MD process using fluoroalkylsilanes grafted zirconia membrane. Feed/permeate temperatures: 63°C/5°C and 99°C/5°C.

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

MCr technology

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

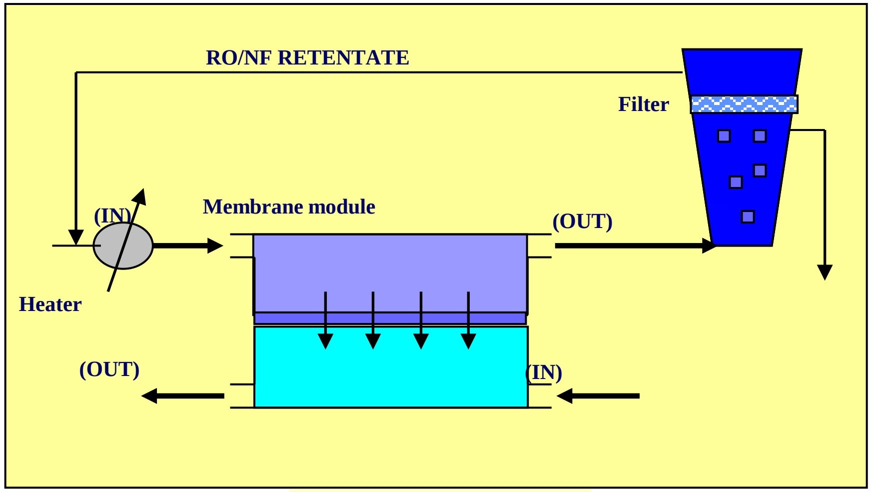


Mcr principle

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

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

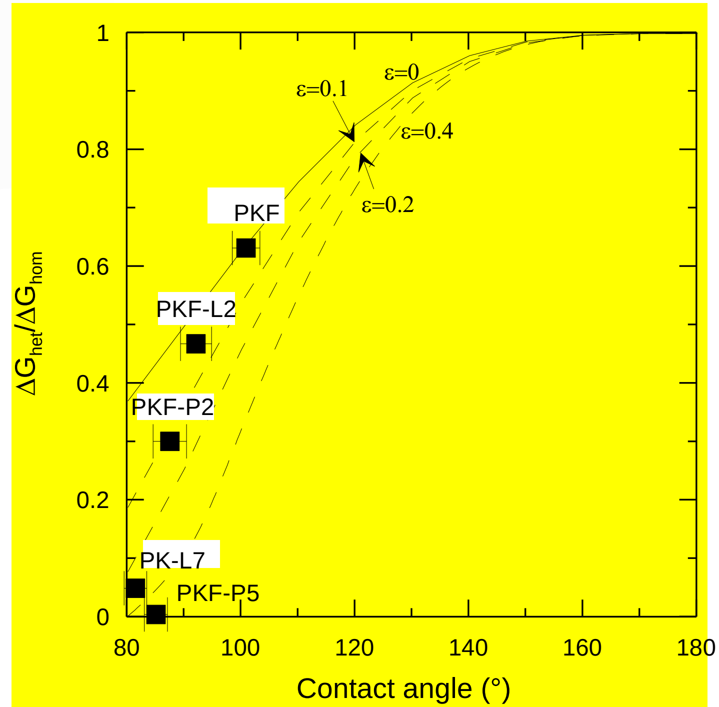
- ✓ **The process is not limited by concentration polarization phenomena as it is the case in pressure driven operations → pure water can also be obtained from highly concentrated feeds with which RO cannot operate.**
- ✓ **In MCr the membrane induces heterogeneous nucleation.**

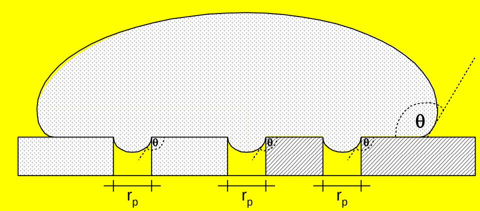


MCr process

Advantages of Membrane Crystallization compared to traditional techniques

- ✓ **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**
- ✓ **Surface effect (heterogeneous nucleation)**
- ✓ **Control of the kinetic/thermodynamic balance in the polymorphic crystallization of organic molecules.**
- ➢ **Possibility to work in continuous mode**
- ➢ **Application in anti-solvent crystallization process**
- ➢ **Reduction in the free energy of nucleation as a function of the contact angle with the polymeric surface**





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	$5.4\cdot10^{-1}$

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

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

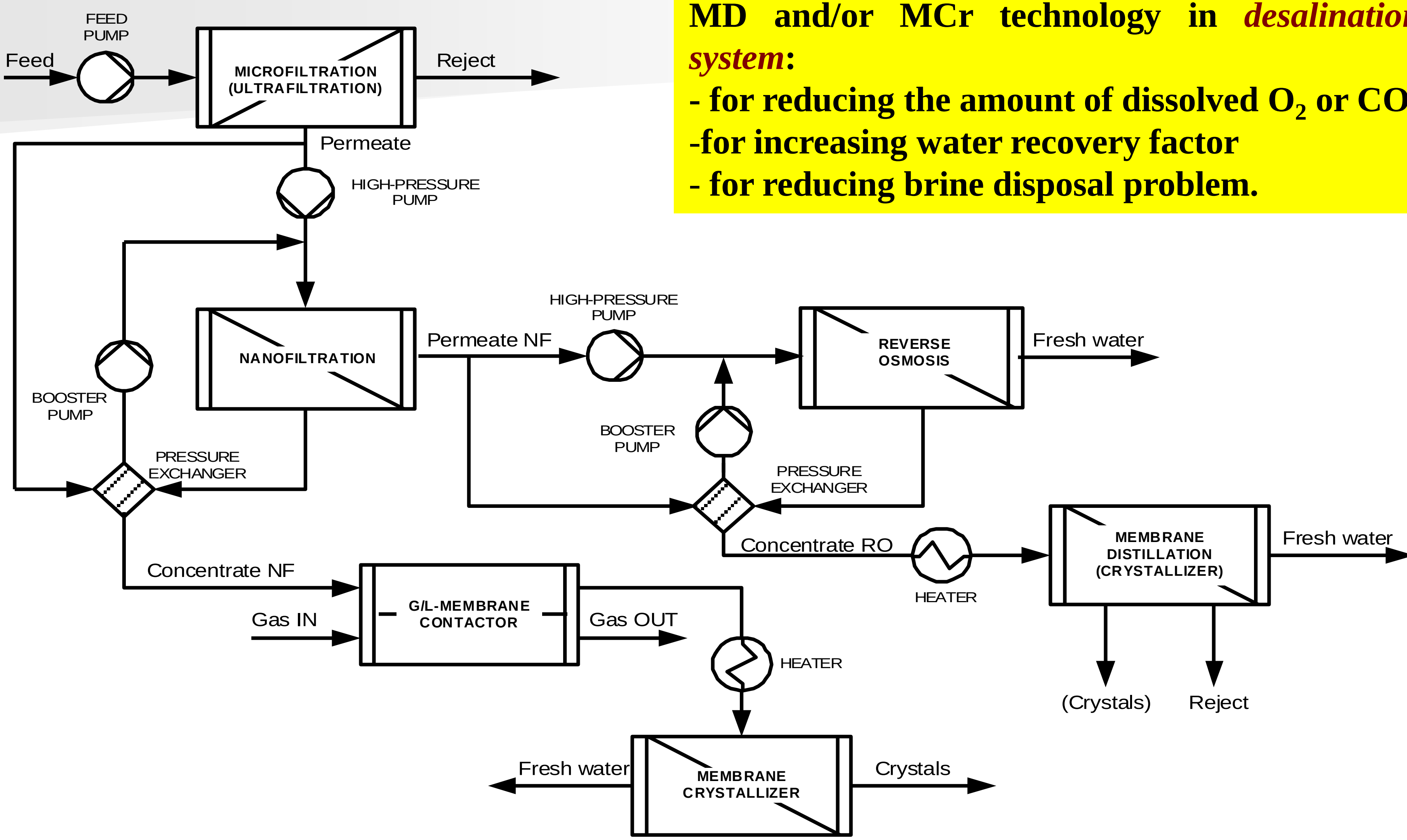
INTEGRATED MEMBRANE DESALINATION SYSTEM

MD and/or MCr technology in *desalination system*:

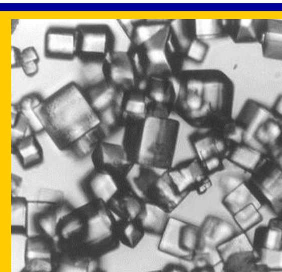
- for reducing the amount of dissolved O_2 or CO_2

-for increasing water recovery factor

- for reducing brine disposal problem.



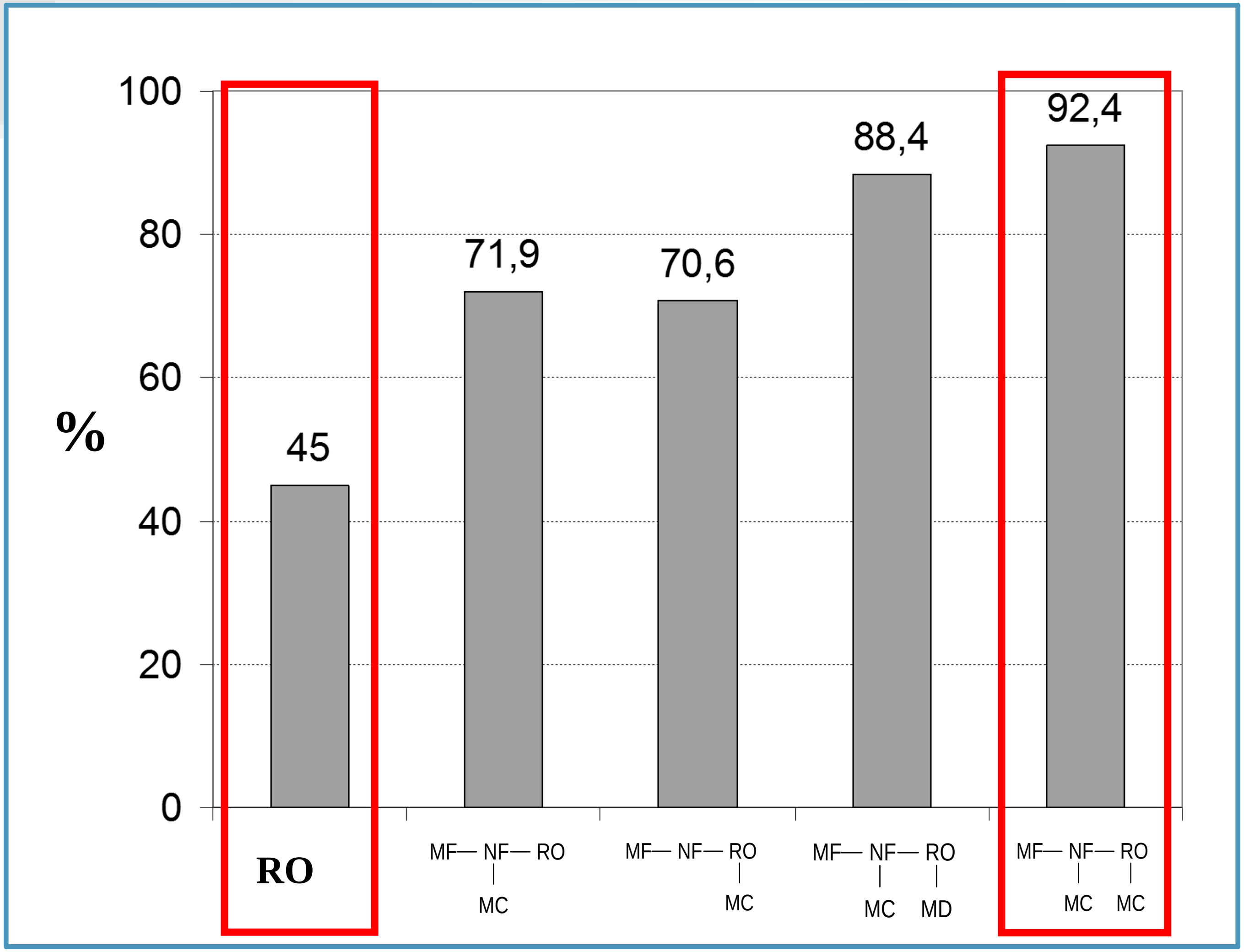
Amount of salts produced per cubic meter of NF brine*

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

*Seawater =3.5%; NF recovery factor=5.3%

Pressure-Driven Membrane Operations and Membrane Contactor Technology Integration. Strategy not only for recovery factor increase but also for the recovery of *the ions contained in nanofiltration and reverse osmosis brine.*

Pressure-Driven Membrane Operations and Membrane Contactor Technology Integration for Seawater Desalination. *Recovery factor increase.*



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

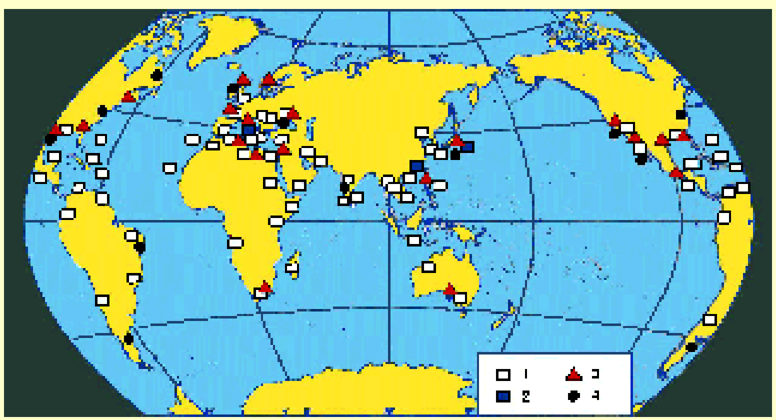
E. Drioli et al., Chemical Engineering Research and Design, 84 (A3) (2006) 209–220. - E. Drioli et al., Desalination and Water Treatment, 18 (2010) 224-234.

Chemical resources of the ocean waters – open sky mines

Element	ppm	Element	ppm
Sodium	*10,800*	Lithium Li	0.170
Chlorine	*19,400*	Rubidium Rb	0.120
Magnesium	*1,290*	Molybdenum Mo	0.01
Sulfur	*904*	Phosphorus P	0.088
Potassium	*392*	Iodine I	0.064
Calcium	*411*	Zinc Zn	0.005
Bromine	*67.3*	Uranium U	0.0033
Carbon C	28.0	Arsenic As	0.0026
Nitrogen ion	15.5	Vanadium	0.0019
Fluorine F	13	Selenium Se	0.0009
Strontium Sr	8.1	Copper Cu	0.0009
Boron B	4.450	Argentum (Ag)	0.00028
Silicon Si	2.9	Mercury Hg	0.00015
Argon Ar	0.450	Aurum (gold) Au	0.000011

Detailed composition of seawater (at 3.5% salinity)

Geographical distribution of some of the chemicals currently extracted from marine water by means of conventional processes

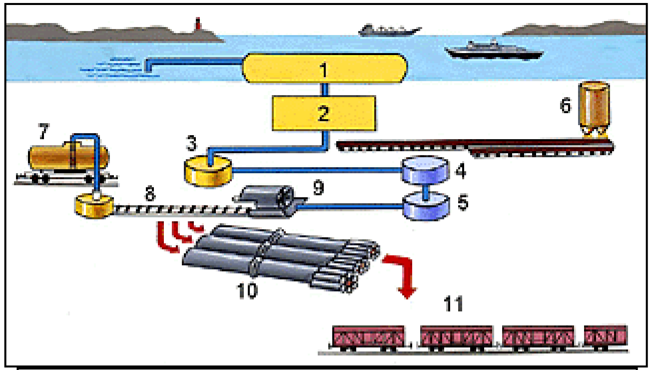


Places of extraction:
1.Cooking salts 2. Potassium
3. Magnesium 4. Bromine

Waters of the World Ocean contain so many organic and inorganic elements that they are figuratively called "*liquid polymetallic ore*". Marine water is *a reserve of raw material for the production of fertilisers, salts, acids, alkalis, various metals and a number of chemical products*.

Components recovered from Seas and Oceans

- The Ocean provides more than *40%* of all *magnesium* produced World-wide. Presently, only England and the USA have more than *20 plants* producing a majority of magnesium from sea water, the most part of which is consumed within these countries. *Simple magnesium* and *its compounds* are widely used in the construction of rockets, aircraft and spacecraft. Textiles, building materials, paper, rubber, pharmaceuticals and agriculture are also customers.



Method used to extract dolomite lime from sea water

- *One-third* of the World's supply of *salts* comes already from the seas and Oceans: *cooking salt, potassium salts* (the bases for various agricultural fertilisers), *bromine (*practically unobtainable from land minerals. Current World-wide extraction of bromine is about 10,000 tons/year), *iodine.*

Components recovered from Seas and Oceans: some examples

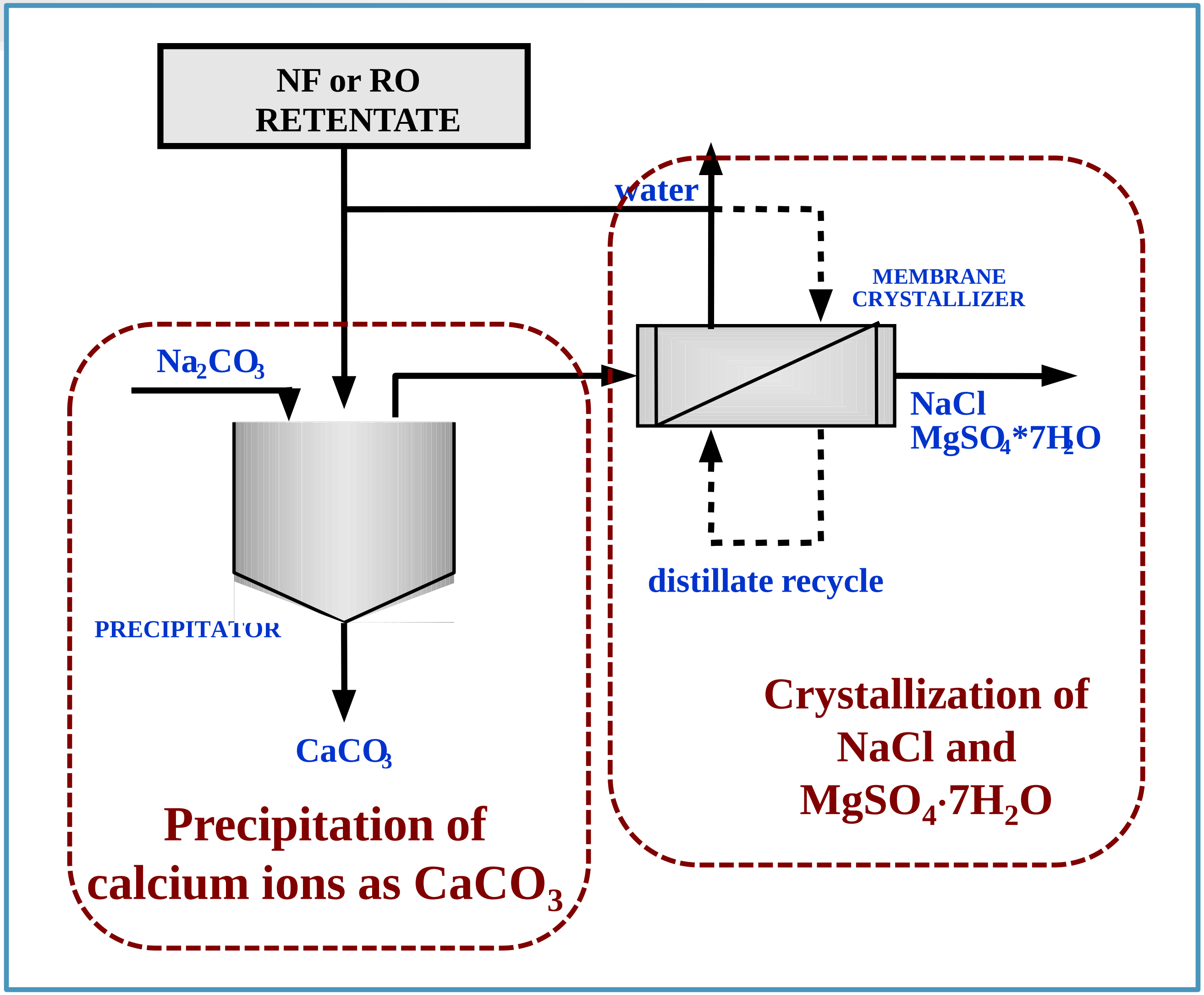
The supply of bromine, chloride, potassium and magnesium salts in Dead Sea is practically unlimited. These resources are widely used by private companies for the extraction of salts such as potash salts, industrial salts and food grade salts.

The salts production of the Dead Sea Works (DSW) industry for the year 1994 [Source: HARZA & JRV, 1997].

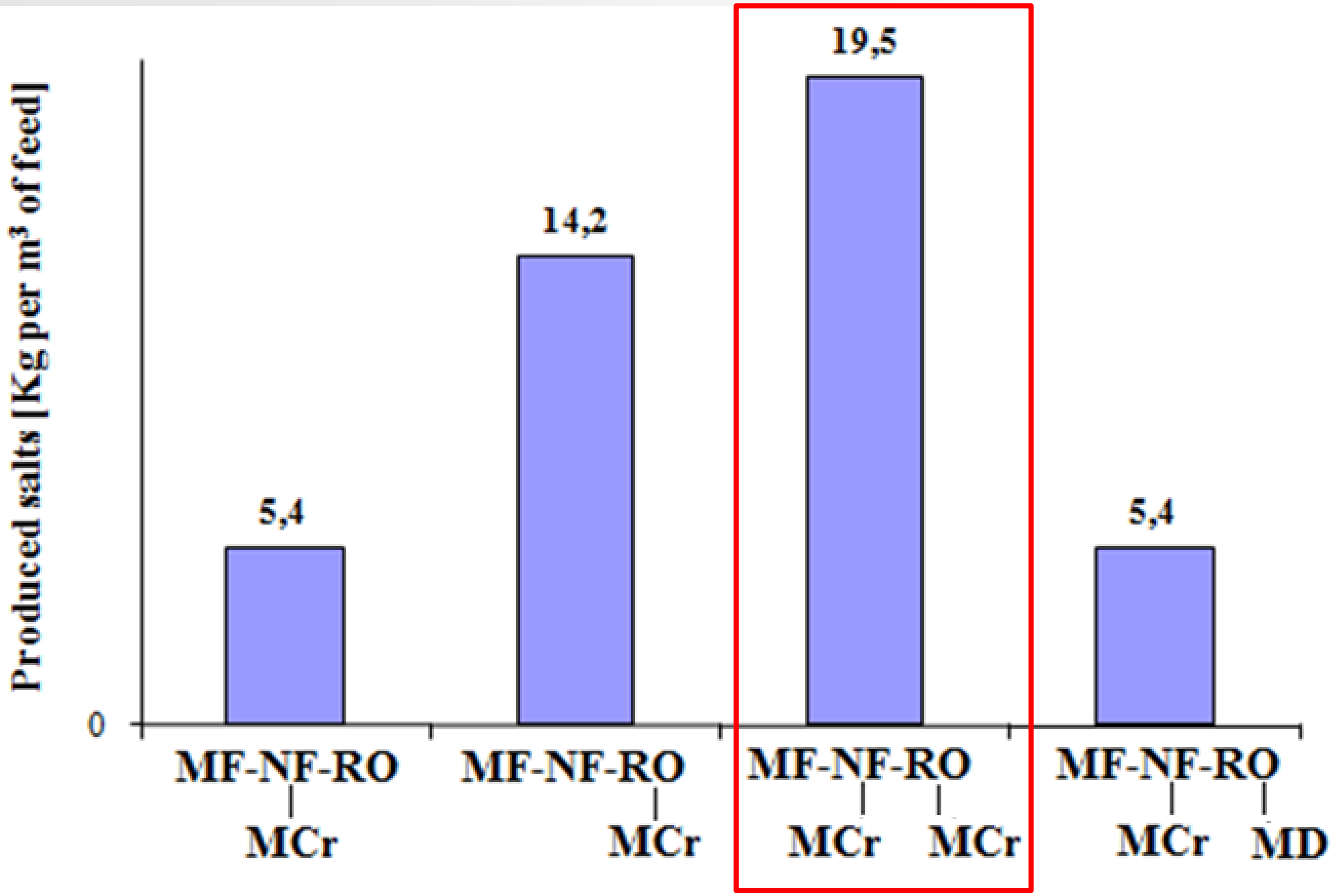
ITEM	PRODUCTION RATE
Potash	2.3 Million tonnes
Industrial Salts	235,000 tonnes
Bromine	180,000 tonnes
Magnesium Chloride Flakes	74,000 tonnes
Table Salts	63,000 tonnes
Magnesium metal	2,500 tonnes
Bath salts	2,200 tonnes

The Murray-Darling Basin Commission (MDBC), in order to reduce the environmental problem of the salinity in the Murray Basin, converts the salts present in the water in commercial products addressed to the market: first the retentate is evaporated and then it is sent to a conventional crystallizer for the extraction of (NaCl) and epsomite ($MgSO4 \cdot 7H_2O$). The fine quality salts are produced at a cost of 18.49 and of 329 $/t, respectively.

Pressure-Driven Membrane Operations and Membrane Contactor Technology Integration for Seawater Desalination. ***Proposed strategy for the recovery of NaCl, $CaCO_3$, $MgSO_4$*$7H_2O$ from NF and/or RO brines.***



Pressure-Driven Membrane Operations and Membrane Contactor Technology Integration for Seawater Desalination. *Amount of produced salts.*



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.

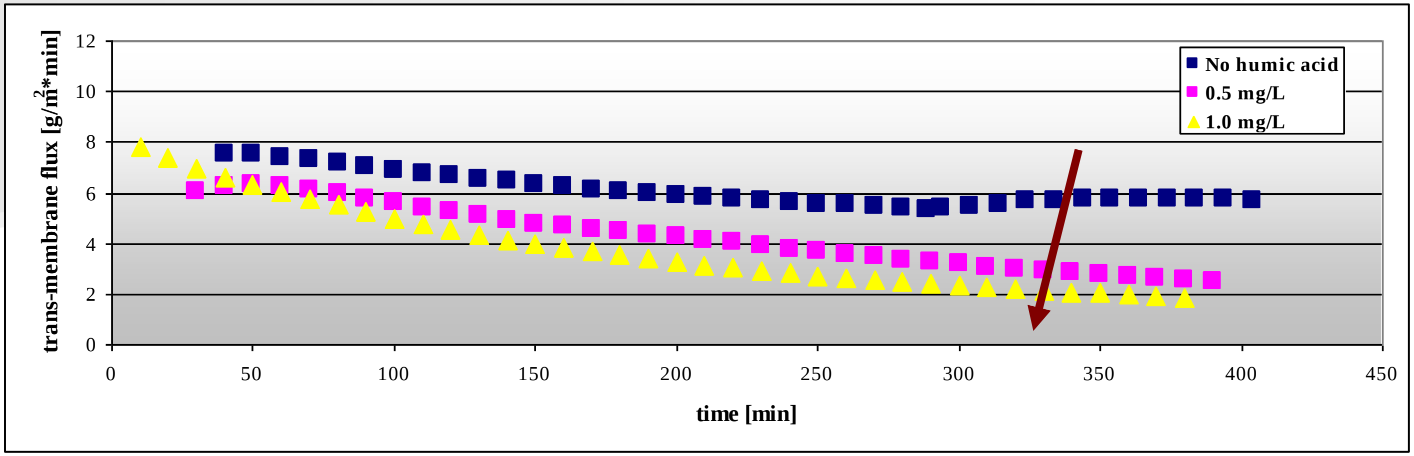
Indispensable optimization of pre-treatment steps for the control of the crystallization process.

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

Natural waters contain natural organic matter (NOM), largely composed of humic substances, which are macromolecular mixtures of humic acid (HA), fulvic acids and humin.

The removal of NOM from feed water is necessary in potable water production because it is responsible for colour in the water, formation of carcinogenic disinfection by-products (DPB's) during water disinfection, complexation with heavy metals and calcium, etc. Moreover, dissolved organics (e.g. humic acids, proteins, carbohydrates and tannins) are the most serious foulants and they are difficult to remove via conventional pre-treatment.

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

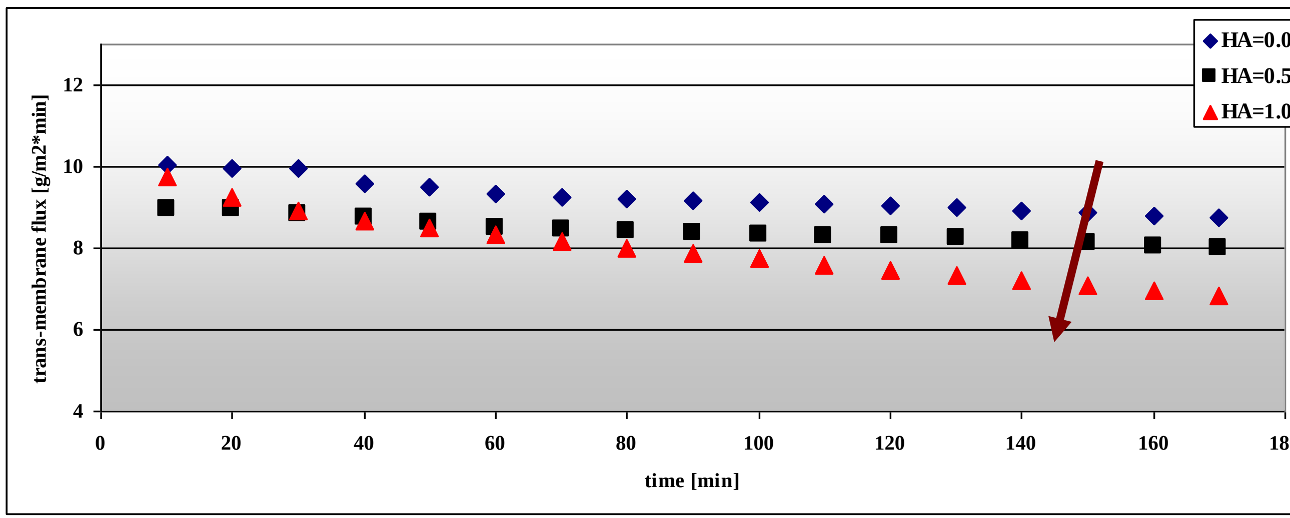


Flux vs time for *NF* brine.

Q_{feed}= 207 L/h, $T_{in,\ feed}$= 39±1 °C.

Flux vs time for *RO* brine.

Q_{feed}= 200 L/h, $T_{in,\ feed}$= 38±1 °C.



The deterioration of flux due to the fouling layer may be attributed to the reduction of surface area available for vaporization as the fouling layer blocked the pore entrances.

MCr tests on *NF* brine with humic acid: effect of organic components on crystallization kinetics

Humic acid concentration [mg/L]	0.5	1.0
Crystal growth [μm/min]	0.0407	0.0612

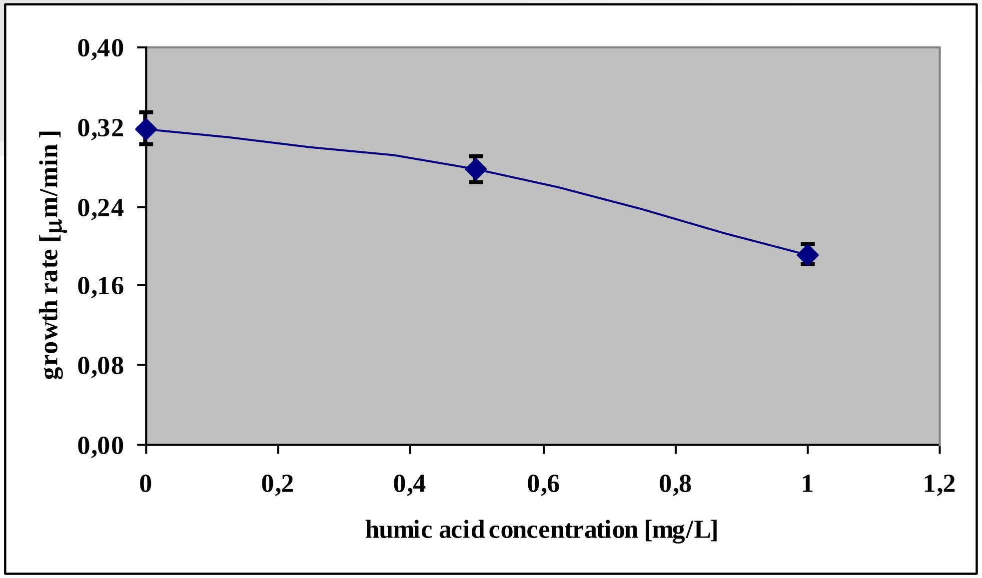
Feed/Permeate flow rate = 207/100 L/h; Feed Temp.= 39±1 °C

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

with respect to the ones obtained from inorganic NF brine solutions

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

MCr tests on RO brine with humic acid: effect of organic components on crystallization kinetics



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.

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

Desalination plant

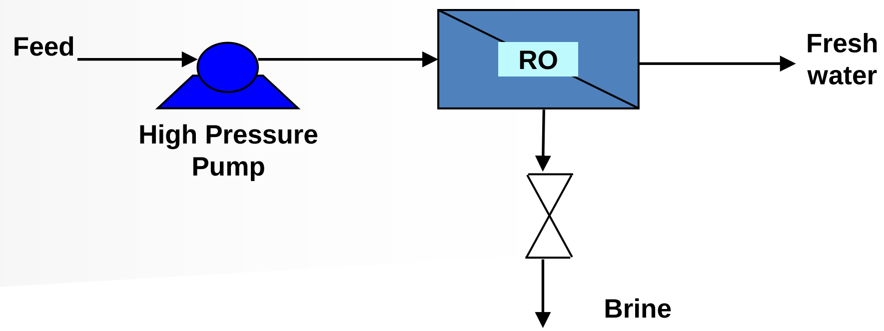
Salt deposit

Example # 1: Perth SWRO Desalination Plant - Australia

Capacity	**140,000 m^3/d**
Population supplied	**1.5 million**
Anticipated water cost	**AU$ 1.17/kL**
Power supply	**Renewable (Emu Downs wind farm)**
Seawater temperature	**16°C to 24°C**
Salinity	**35,000mg/L to 37,000mg/L**
Recovery factor	**45%**

	Seawater (3,5%) [ppm]	Brine [ppm]
Chloride Cl	19345	35067
Sodium Na	10752	19490
Sulfate SO4	2701	4896
Magnesium Mg	1295	2347
Calcium Ca	416	754
Potassium K	390	707
Bicarbonate HCO3	145	263
Bromide Br	66	120
Borate BO3	27	46
Strontium Sr	13	24
Floride F	1	1,8
Total	35151,00	63716,00

Conventional SWRO process: discharged brine



INPUT DATA:

- Technology = Reverse osmosis
- *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 = 1.30*10^8 m^3/d
- Seawater composition:

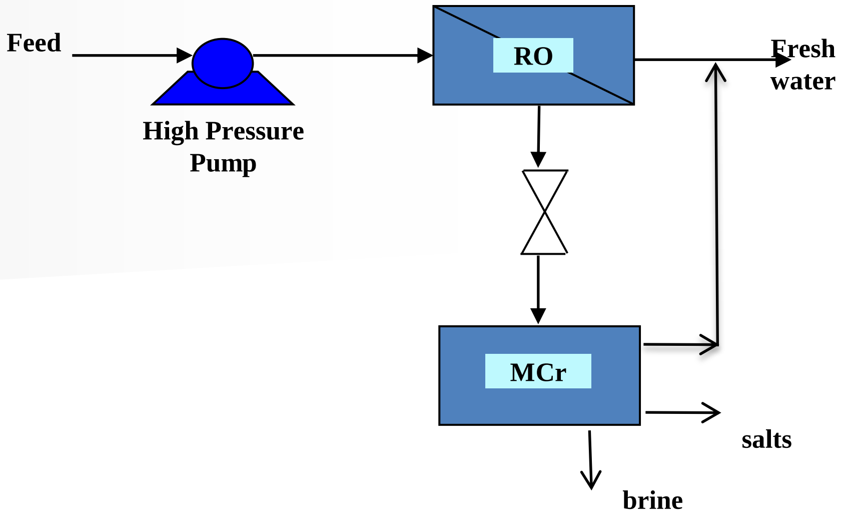
Seawater composition	[g/L]	[ton/day]
Cl	19,00	2.477.600
Na	10,50	1.369.200
SO4	2,70	352.080
Mg	1,35	176.040
Ca	0,40	52.160
HCO3	0,14	18.516
K	0,38	49.552
CO3	0,004	456
Br	0,07	8476
Li	0,00017	22,2
U	0,0000033	0,430

RESULTS:

- Brine flow rate = 65*10^6 m^3/d
- Brine concentration = 68943 g/l
- Fresh water flow rate = 65,2 *10^6 m^3/d
- Fresh water concentration = 0,138 g/l

Ion	RO brine composition [ton/day]
Cl	2.472.644
Na	1.366.461
SO4	351.375
Mg	175.687
Ca	52.055
HCO3	18.479
K	49.452
CO3	455
Br	8459
Li	22,1
U	0,429

How much salts can be recovered from the current SWRO plants?

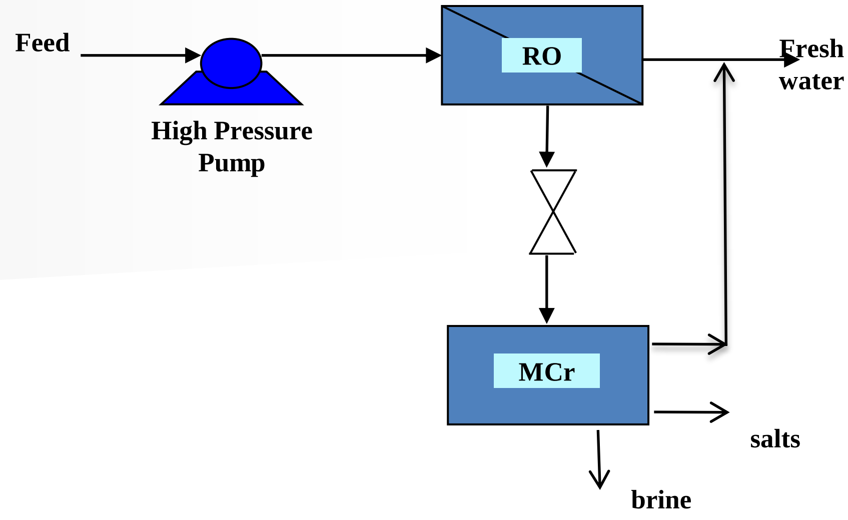


INPUT DATA:

- 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
- Plant recovery factor = 93%

Seawater composition	[g/L]
Cl	19,00
Na	10,50
SO4	2,70
Mg	1,35
Ca	0,40
HCO3	0,14
K	0,38
CO3	0,004
Br	0,07
Li	0,00017
U	0,0000033

How much salts can be recovered from the current SWRO plants?



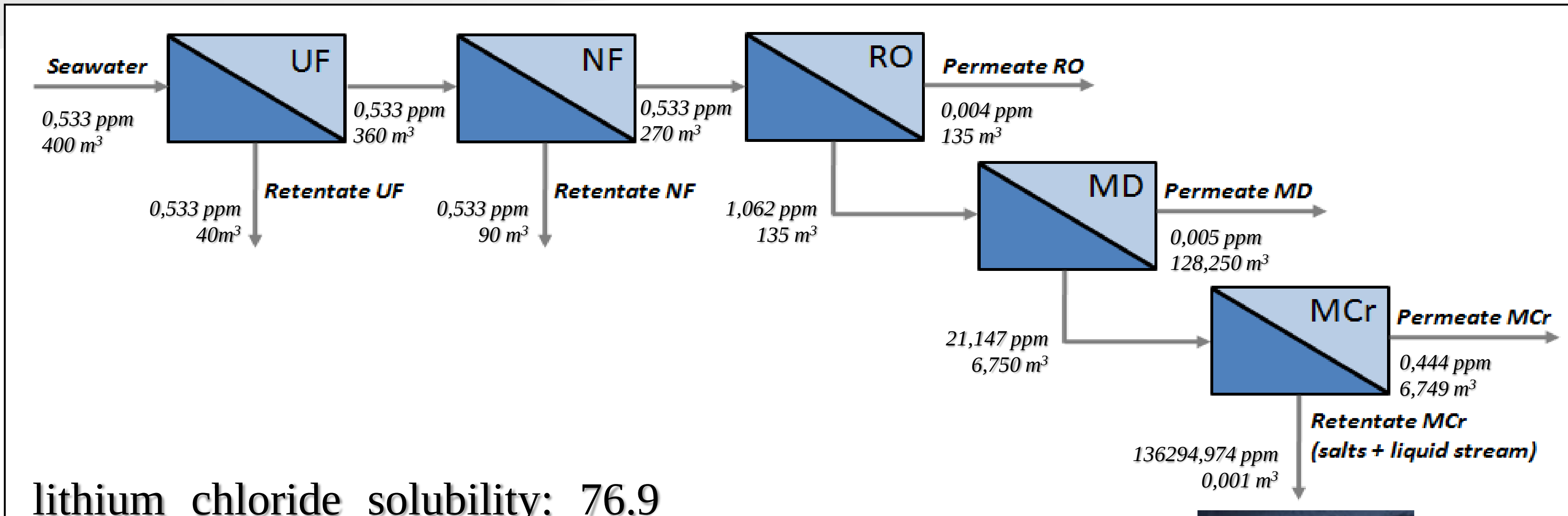
RESULTS:

- **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
  - 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

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

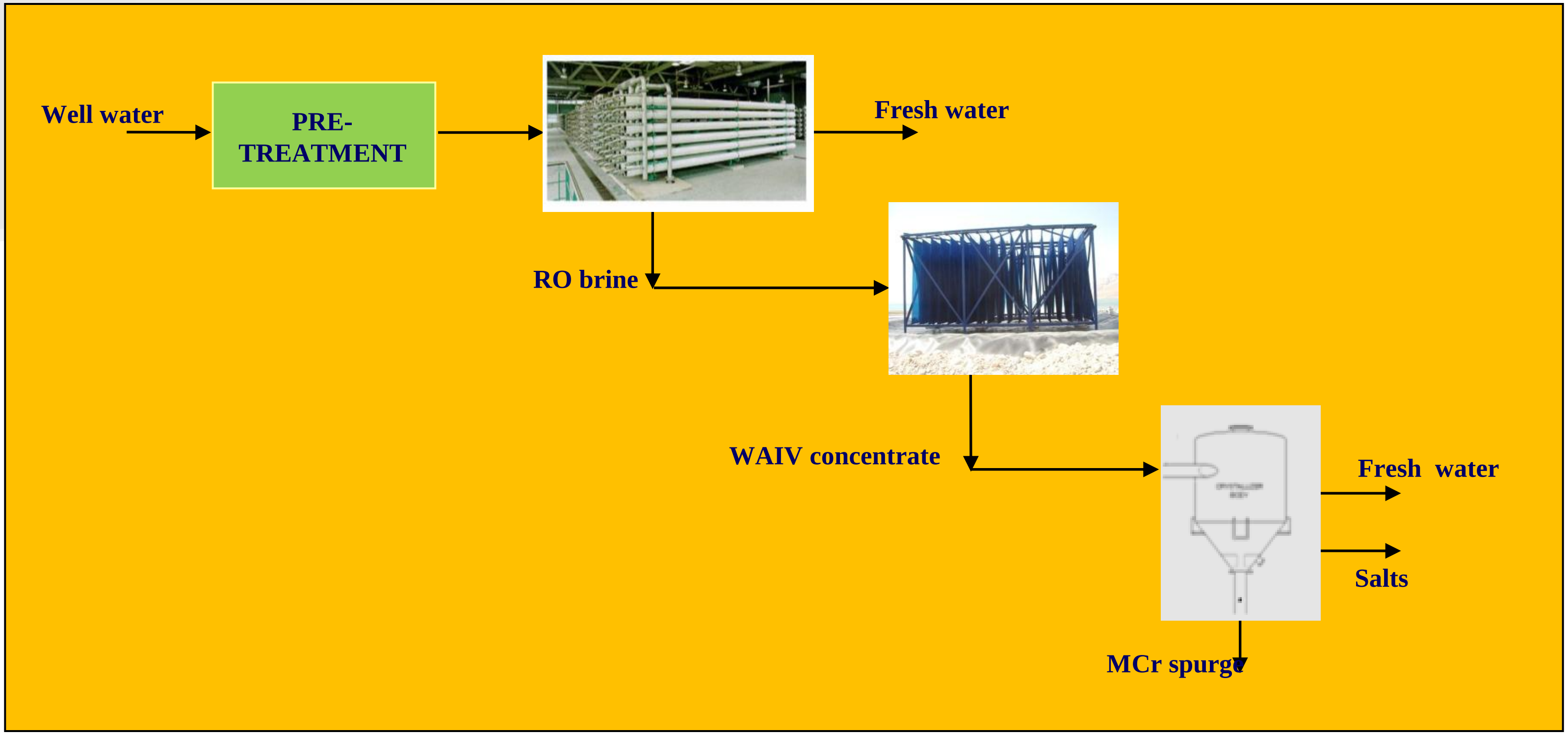
	Feed	PT (perm.)	NF (perm.)	RO (ret.)	MD (ret.)	MCr (ret.)
Recovery (%)	-	90	75	50	95	99.98
Rejection (%)	-	0	0	99.25	99.54	97.90
Volume (m^3)	400	360	270	135	6.75	0.001
Concentration (ppm)	0.533	0.533	0.533	1.062	21.147	136295
Concentration factor (-)	-	0	0	2	20	6445

Brackish water desalination

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

The application of novel concentrate treatment options (such as MCr and Wind Aided Intensified eVaporation - WAIV) can help in developing inland brackish water RO, minimizing the impact of concentrates on the environment towards zero discharge.

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



Three different types of WAIV super-concentrates were concentrated through the MCr process:

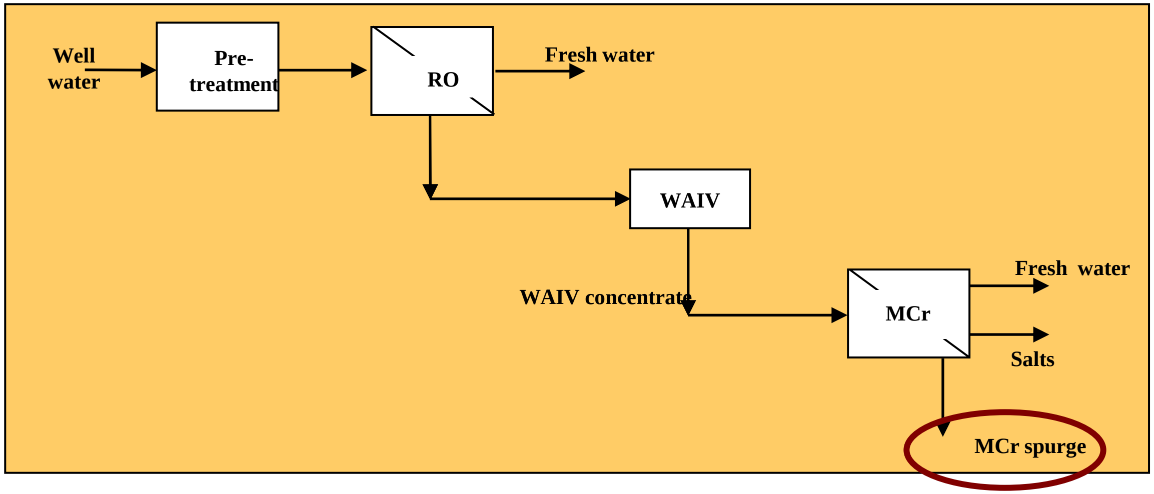
a) a first sample named *BGU 1 without antiscalant or organics and RO recovery factor* equal to *75%*,

b) a second sample named *BGU 2 with organics*, sodium hexametaphosphate as *antiscalant and* RO recovery factor equal to *75%*,

c) a third sample named *BGU 3 with organics*, PC-191 as *antiscalant* and RO recovery factor equal to *88%*.

F. Macedonio, J. Gilron et al., Desalination, 273 (2011) 127–135

	BGU 1 (no antiscalant/organics - 75%)	**BGU 2** (organics/antiscalant - 75%)	**BGU 3** (organics/antiscalant - 88%)
MCr **recovery factor [%]**	**75.0**	**69.9**	**77.2**
Volume Concentrator Factor (VCF) of WAIV	**12**	**10**	**10**
Pre-treatment+RO **recovery factor [%]**	**75.0**	**75.0**	**88.0**
Pre-treatment+RO+WAIV+MCr **recovery factor [%]**	**76.6**	**76.8**	**88.9**
MCr_spurge [%]	**0.52**	**0.75**	**0.27**
Amount of produced salts [g/10 L of MCr feed]	**26.53**	**18.73**	**71.8**



If the amount of brine discharged from the system is considered, it represents only 0.27 ÷ 0.75% of the RO feed!

F. Macedonio, J. Gilron et al., Desalination, 273 (2011) 127–135

CONCLUSIONS

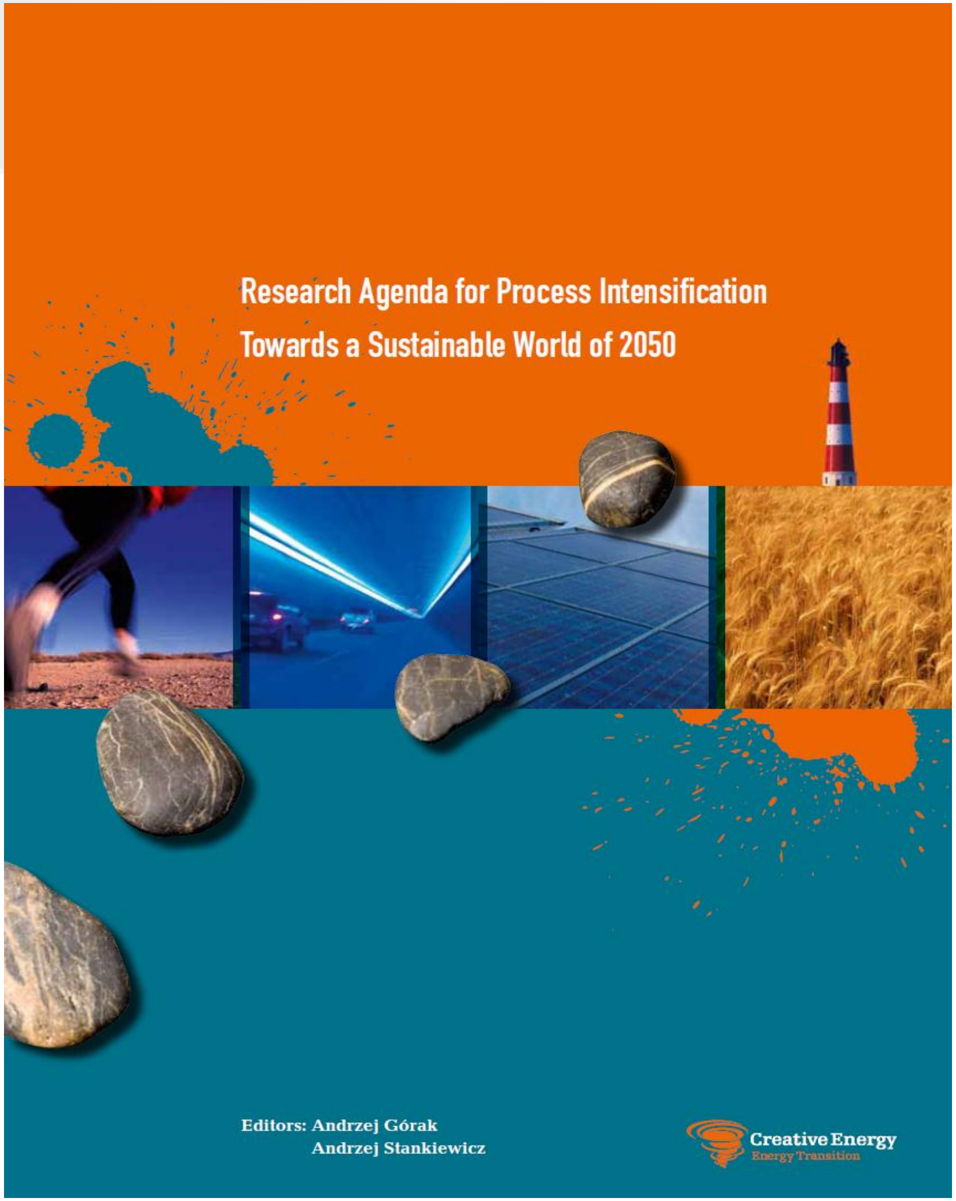
- **New Membrane operations (Membrane Distillation, Membrane Crystallisers, ...) are today of interest for mass and energy transfer between different phases.**

- **The possibility of integrating these membrane units for solving existing problems or limits in various industrial production is interesting.**

- **Increasing recover factor and minimising brine disposal problems in seawater and brackish water desalination is a typical case.**

- **Important progress in the process intensification strategy can be reached by the further development of these units.**

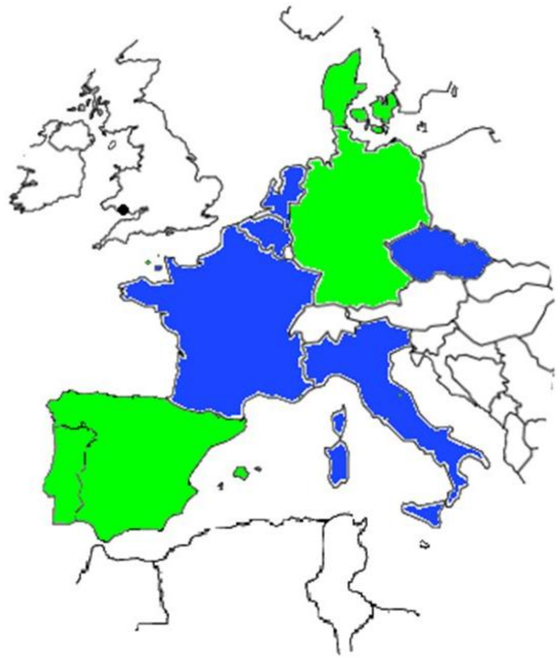
Sustainable growth - how to answer?



http://eudime.unical.it

EUDIME: Erasmus Mundus Doctorate in Membrane Engineering

The *Erasmus Mundus Doctorate in Membrane Engineering (EUDIME*) is designed to implement excellence, innovation, mobility and multi-disciplinarity in investigation approaches related to membrane engineering.



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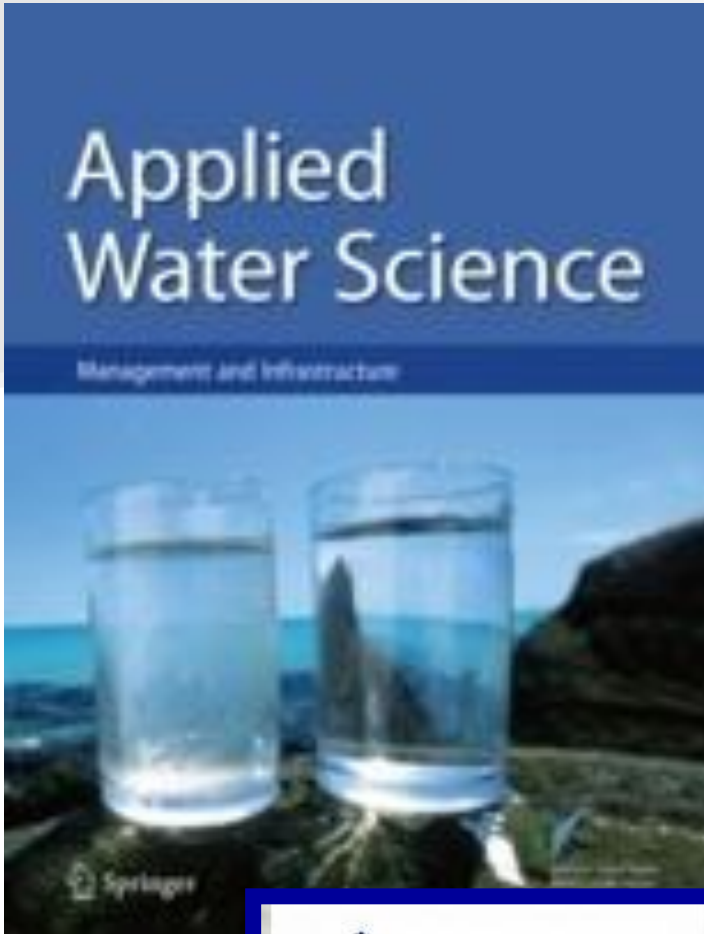

Applied Water Science explores water scarcity solutions from a holistic system oriented viewpoint. From the sustainable management of natural water resources to the development of the technologies and infrastructure for the production of clean fresh water from natural and waste water.

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