# INTEGRATED MEMBRANE OPERATIONS FOR WATER, ENERGY AND MINERALS PRODUCTION FROM THE SEA

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**1st UNION FOR THE MEDITERRANEAN STAKEHOLDER CONFERENCE ON THE BLUE ECONOMY**

**Workshop 4: Energy from the Mediterranean Sea – innovative financial schemes and technological advancements**

**November 29, 2017 - Hotel Excelsior , Naples ( Italy )**

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- **IUPAC's mission** is to advance the worldwide aspects of the chemical sciences and to contribute to the application of chemistry in the service of Mankind.

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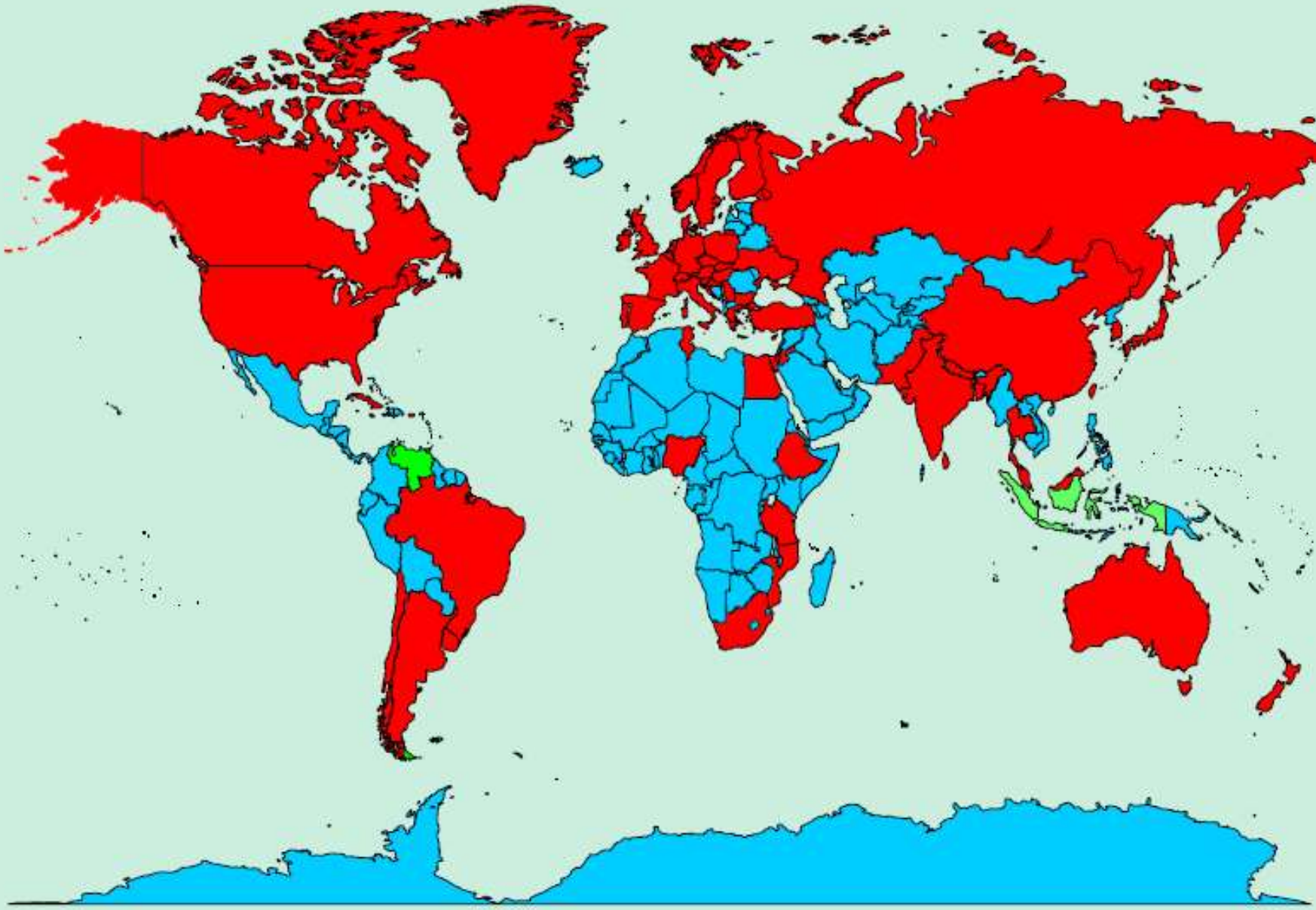
  - Advocates free exchange of scientific information and access of scientists
  - Addresses global issues as a scientific, international, non-governmental, objective body

# IUPAC NAOs and ANAOs



# µMED

## INTERNATIONAL CONFERENCE ON MICROPLASTIC POLLUTION IN THE MEDITERRANEAN SEA

CAPRI SEPTEMBER 26th - 29th 2017 HOTEL LA RESIDENZA - CAPRI (NA) - ITALY

**Nowadays, water scarcity is a worrying reality and the related environmental and societal aspects have become a major priority. All this leads scientists and industries towards the development of technologies for reducing the production of waste streams and, when present, for their reuse.**

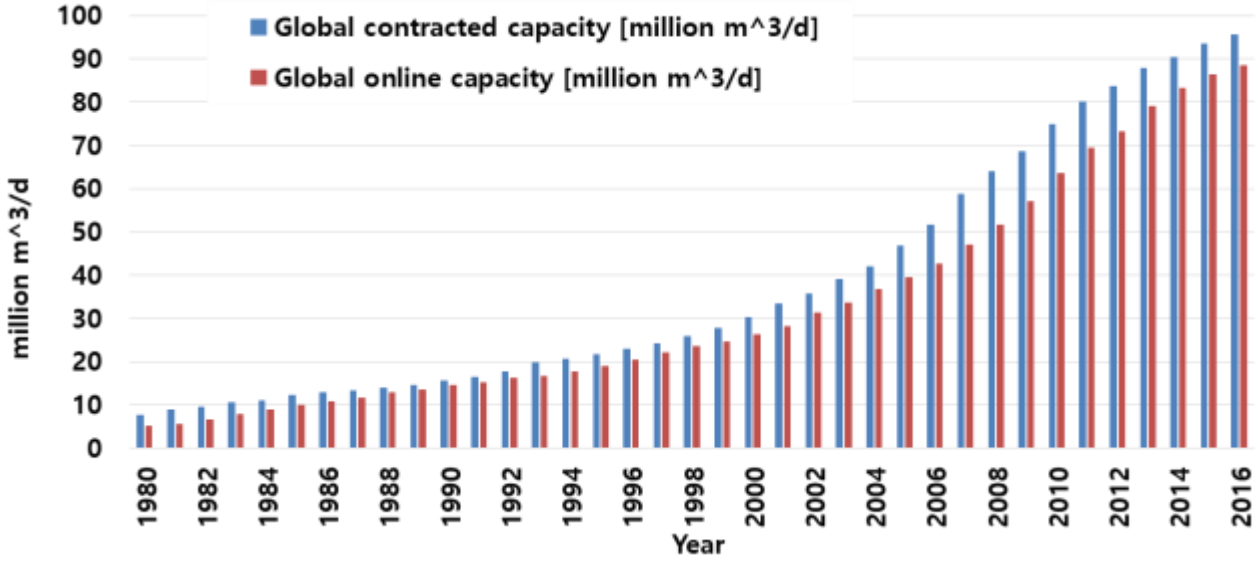
**Picture from:** ***The United Nations world water development report 2017. Published in 2017 by the United Nations Educational, Scientific and Cultural Organization, 7, place de Fontenoy, 75352 Paris 07 SP, France***

# SEAWATER DESALINATION: ALREADY A WELL ESTABLISHED SOLUTION TO WATER SHORTAGE

**Some numbers**

- ✓ **18426: The total number of desalination plants worldwide***
- ✓ **88.56 million $m^3$/d: the global online capacity****
- ✓ **95.59 million $m^3$/d: the global capacity of commissioned desalination plants****
- ✓ **150: The number of countries where desalination is practiced**
- ✓ **More than 300 million: The number of people using desalinated water**

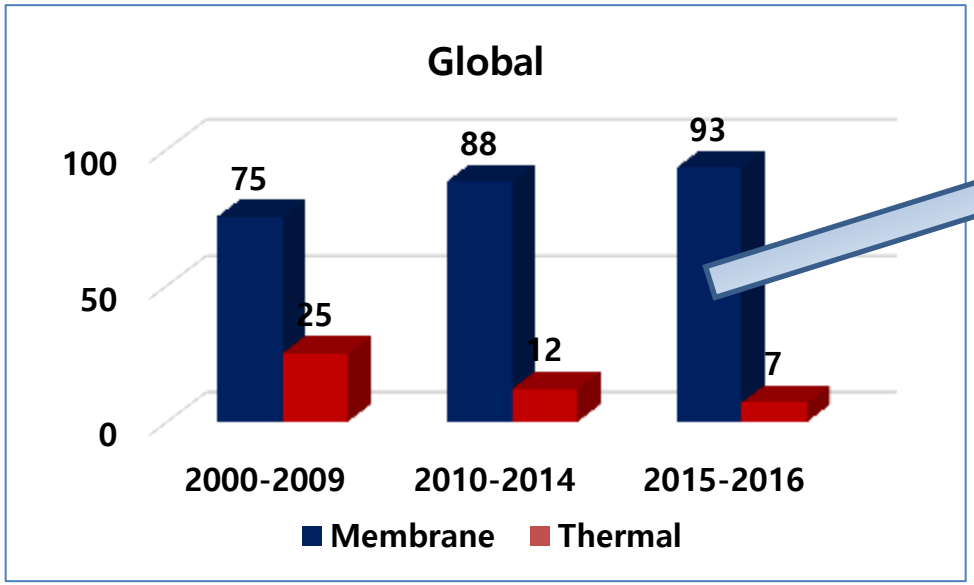
*** As of June 30, 2015 - **As of June 30, 2016**




**IDA Desalination Yearbook 2016-2017. ISBN: 978-I-907467-49-3**

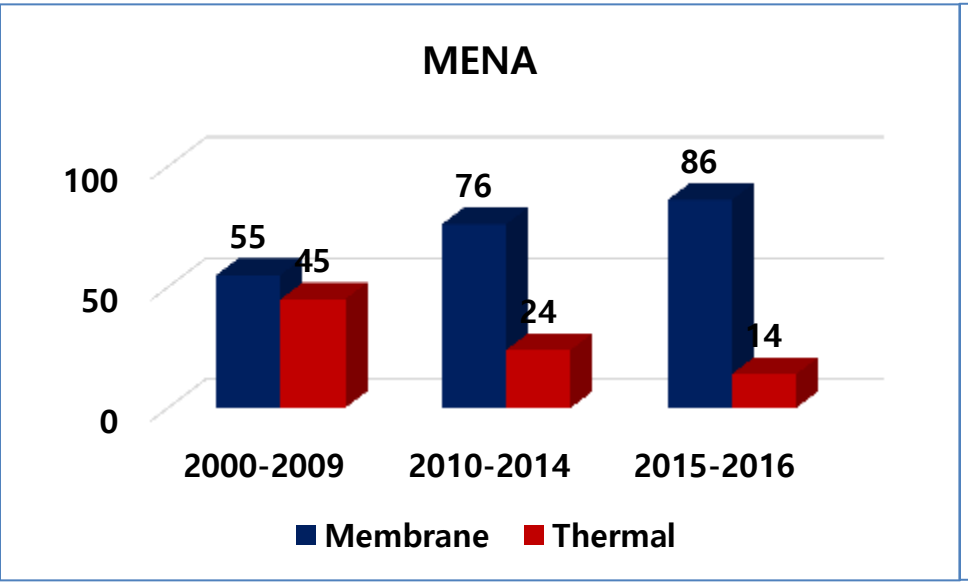
**http://idadesal.org/desalination-101/desalination-by-the-numbers/**

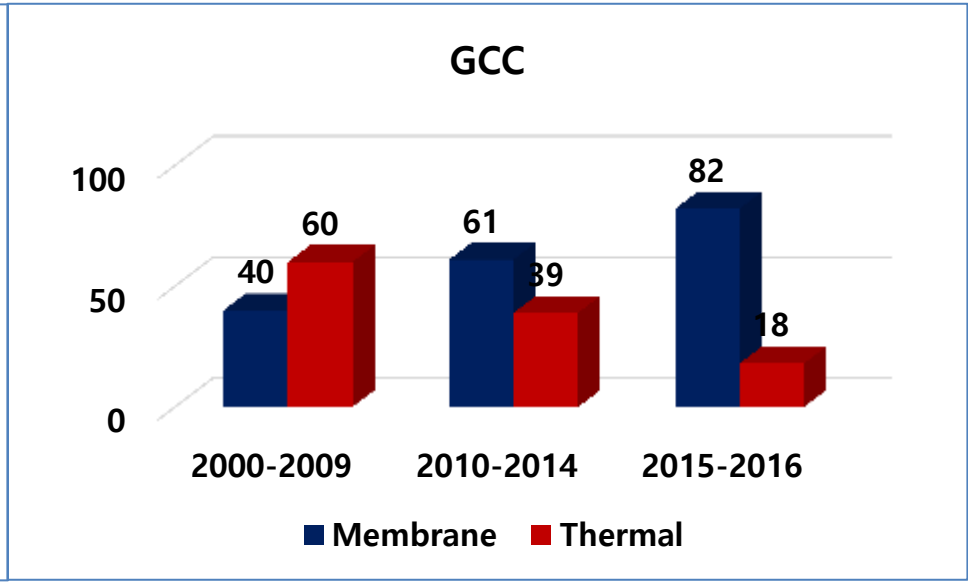
# TIME EVOLUTION OF MEMBRANE VS THERMAL TECHNOLOGIES




**82.4 million $m^3/d$: the global online capacity obtained via membrane processes (mostly through *reverse osmosis*)**

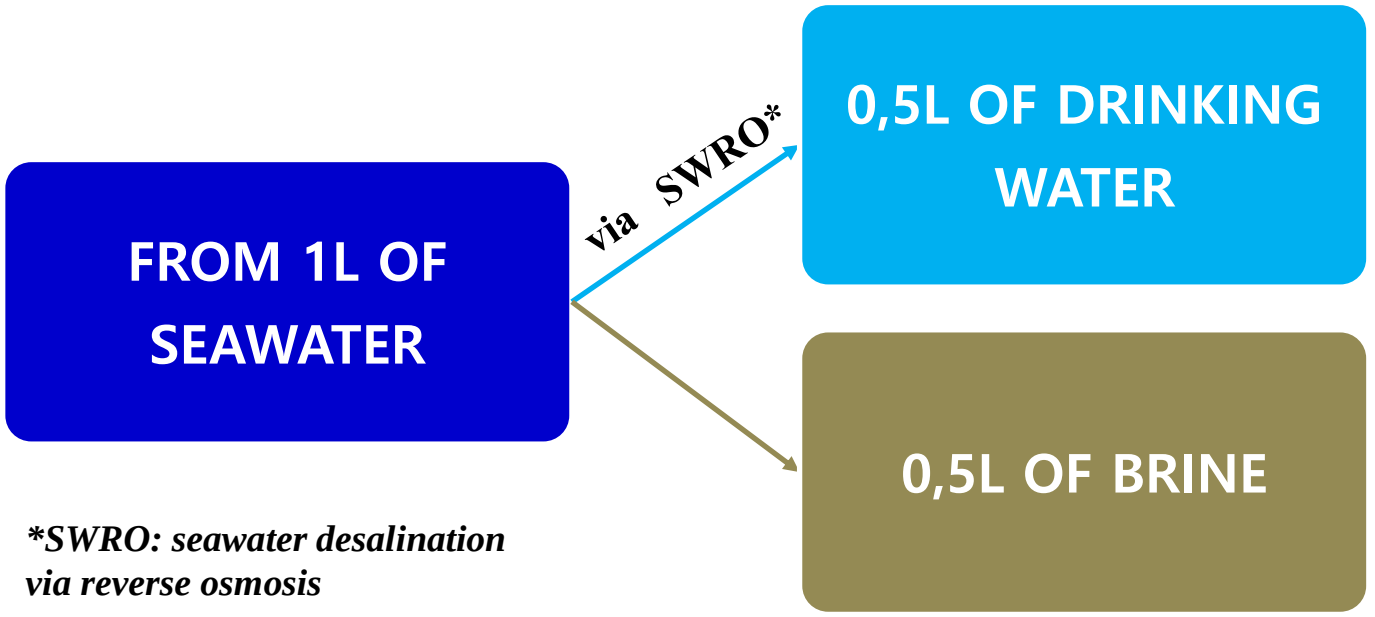
**Global: global situation; MENA: Middle East and North Africa Countries situation; GCC: Gulf Cooperation Council Countries situations**




**IDA Desalination Yearbook 2016-2017. ISBN: 978-I-907467-49-3**

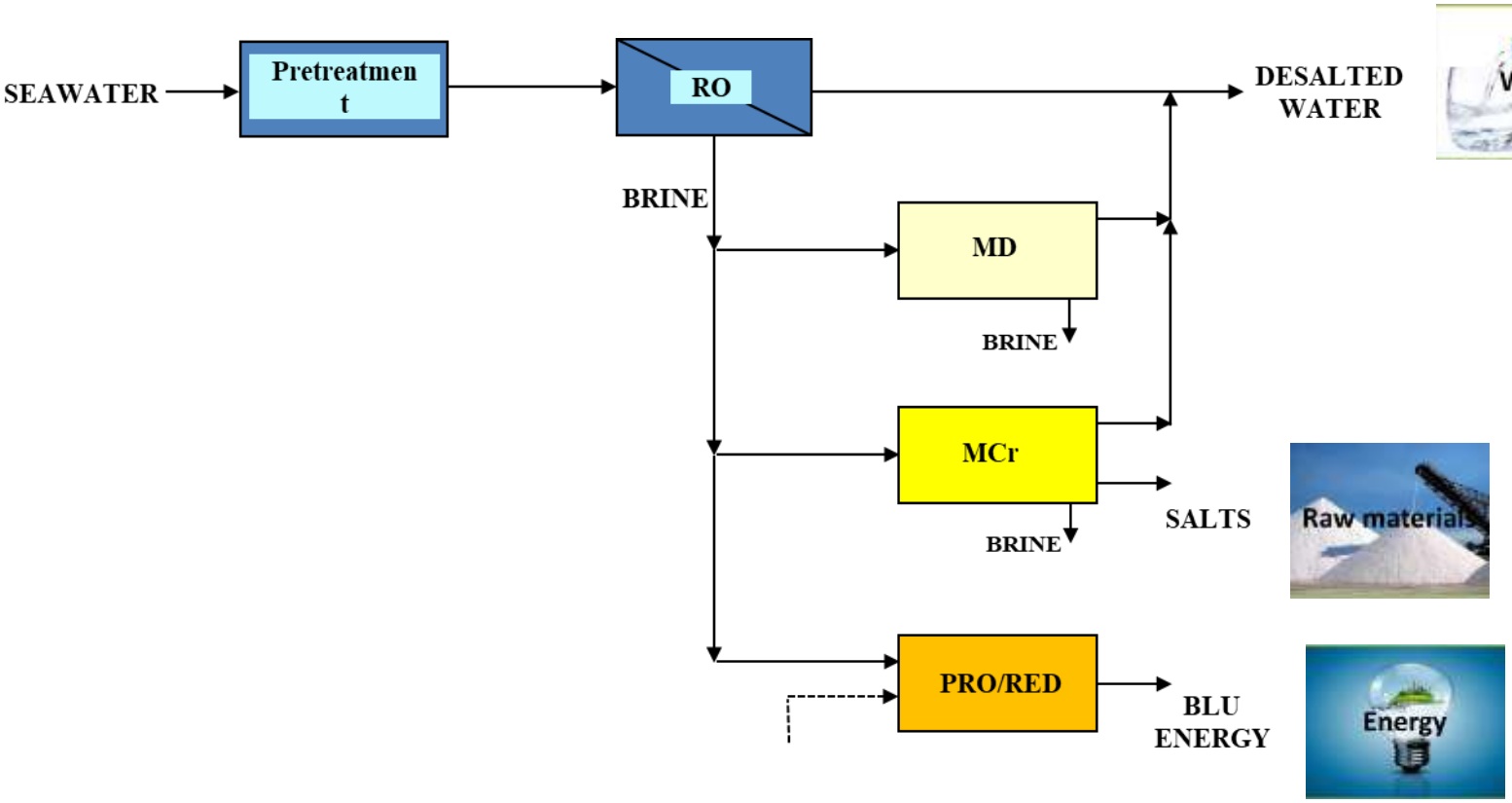
# MANAGEMENT OF BRINE: THE DRAWBACK OF SEAWATER DESALINATION




**POSSIBLE MEASURES (1) TO MITIGATE ENVIRONMENTAL IMPACT OF THE DISCHARGED BRINE, (2) TO INCREASE WATER RECOVERY AND (3) TO ACHIEVE ZERO LIQUID DISCHARGE**

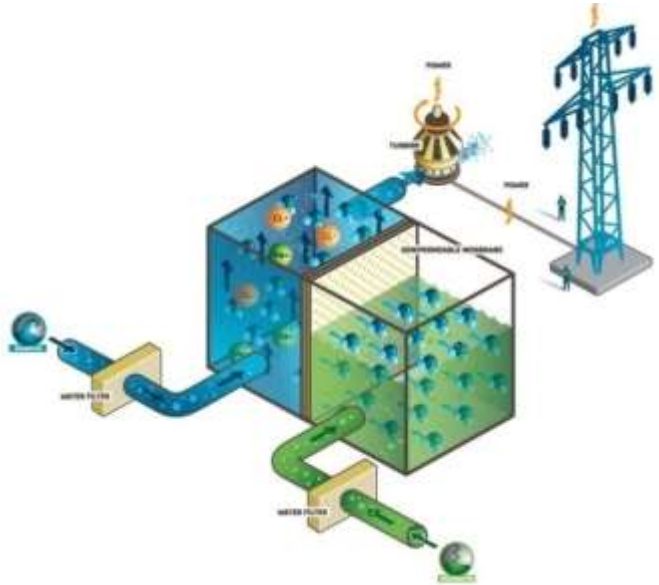
- **RETHINK THE MANAGEMENT OF BRINE**
- **EMBRACE NEW TECHNOLOGIES**

# MEMBRANE TECHNOLOGIES FOR BRINE EXPLOITATION

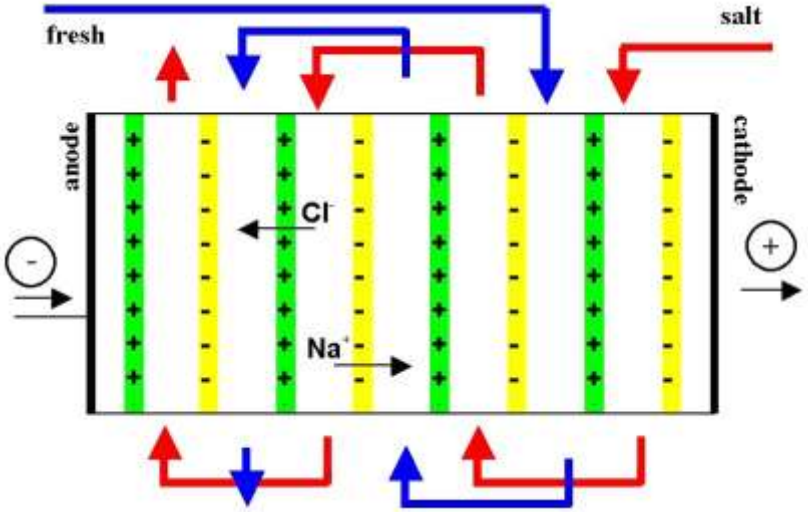



| MEMBRANE TECHNOLOGY | GOAL |
|---|---|
| MEMBRANE DISTILLATION (MD)<br>MEMBRANE CRYSTALLIZATION (MCr) | FRESH WATER RECOVERY<br>RAW MATERIALS EXTRACTION |
| PRESSURE-RETARDED OSMOSIS (PRO)<br>REVERSE ELECTRODIALYSIS (RED) | POWER GENERATION *(BLUE ENERGY)* |

# BLUE ENERGY: THE POSSIBILITY TO GENERATE POWER FROM SALINITY GRADIENT



**Pressure retarded osmosis (PRO)**




**Reverse electrodialysis (RED)**

In PRO, two solutions of different salinity are brought into contact by a semi-permeable membrane. The chemical p otential difference between the solutions causes the transport of the solvent (i.e. water) from the low-pressure diluted salt solution to the high-pressure concentrated salt solution (because hydrostatic pressure is applied to the concentrat ed solution). This results in a pressurization of the volume of transported water that ca be used to generate electrical power in a turbine.

RED is based upon the transport of the ions through a stack of cationic and anionic membranes (alternately filled wit h a concentrated and a diluted salt solution). The salinity gradient results in a potential difference over each membra ne. This chemical potential difference causes the transport of ions through the membranes from the concentrated sol ution to the diluted solution. The potential difference over the electrodes can be used to generate electrical power, w hen an external load or energy consumer is connected to the circuit.

- **Zhang and Chung** [*S. Zhang, T.S. Chung, Minimizing the instant and accumulative effects of salt permeability to sustain ultrahigh osmotic power density, Environ. Sci. Technol. 47 (2013) 10085–10092*] **report that hollow fiber PRO membranes can produce 24 W/m$^2$ at 20 bar.**

- **Sarp et al.** [S. Sarp, Z. Li, J. Saththasivam, Pressure retarded osmosis (PRO): past experiences, current developments, and future prospects, Desalination 389 (2016) 2–14] **has projected that an integrated PRO process can provide about 20% reduction in SWRO specific energy consumption for a typical SWRO brine.**

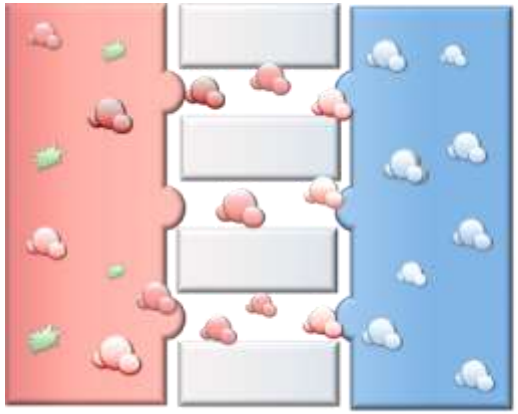
- **In Japan, the recent MEGATON project achieved a power density higher than 10 W/m$^2$ using a 7% SWRO brine in a demonstration-scale study using PRO membrane modules** [M. Kurihara, Role of pressure retarded osmosis (PRO) in the MEGATON project, http://www.desaltech2015.com/assets/presenters/Kurihara_Masaru.pdf2015 ].

- **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$^2$.**

- **Membranes in a RED application on more concentrated brines and fresh water could yield a power density of 1.2 W/m$^2$.**

# MEMBRANE DISTILLATION / MEMBRANE CRYSTALLIZATION FOR DESALTED WATER *AND/OR* MINERALS PRODUCTION FROM BRINE STREAMS

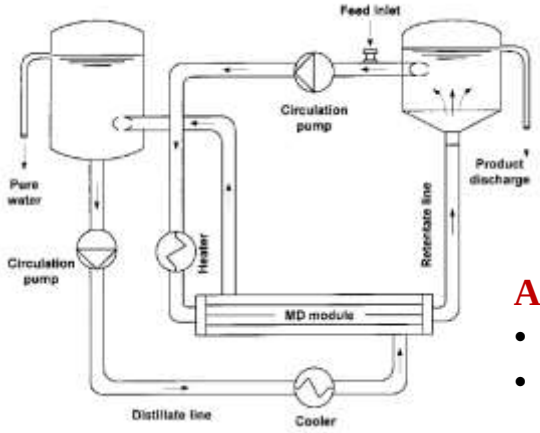
## Membrane Distillation



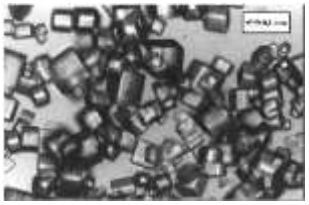

**ADVANTAGES**

- **Not limited by osmotic pressure**
- **100% theoretical rejection of all nonvolatile compounds**
- **Low-grade heat could be employed (no high pressure pump required)**

## Membrane Crystallization

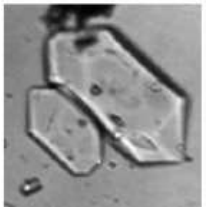



**$CaCO_3$**



**NaCl**

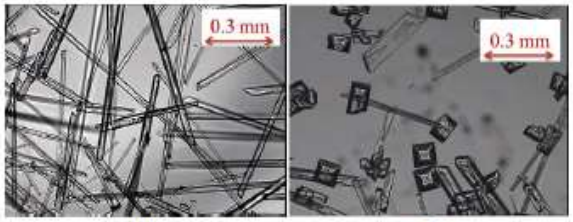
**Some salts recovered from brine.**



**$MgSO_4 \cdot 7H_2O$**

**ADVANTAGES**

- **Heterogeneous Nucleation**
- **Possibility to control the nucleation kinetics, energy level, and crystal polymorphism**

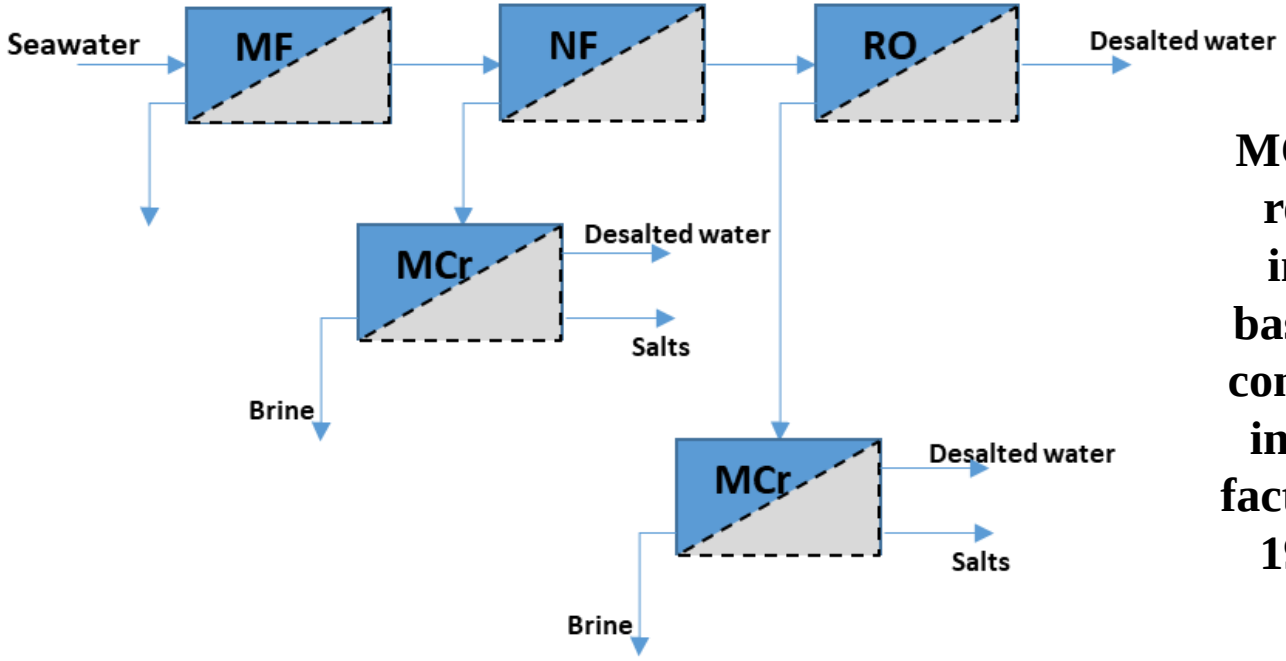



**LiCl crystals from single salt solution**

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

SIXTH FRAMEWORK PROGRAMME - PRIORITY 1.1.6.3 - Global Change and Ecosystems

***Aim:*** **improving 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.**

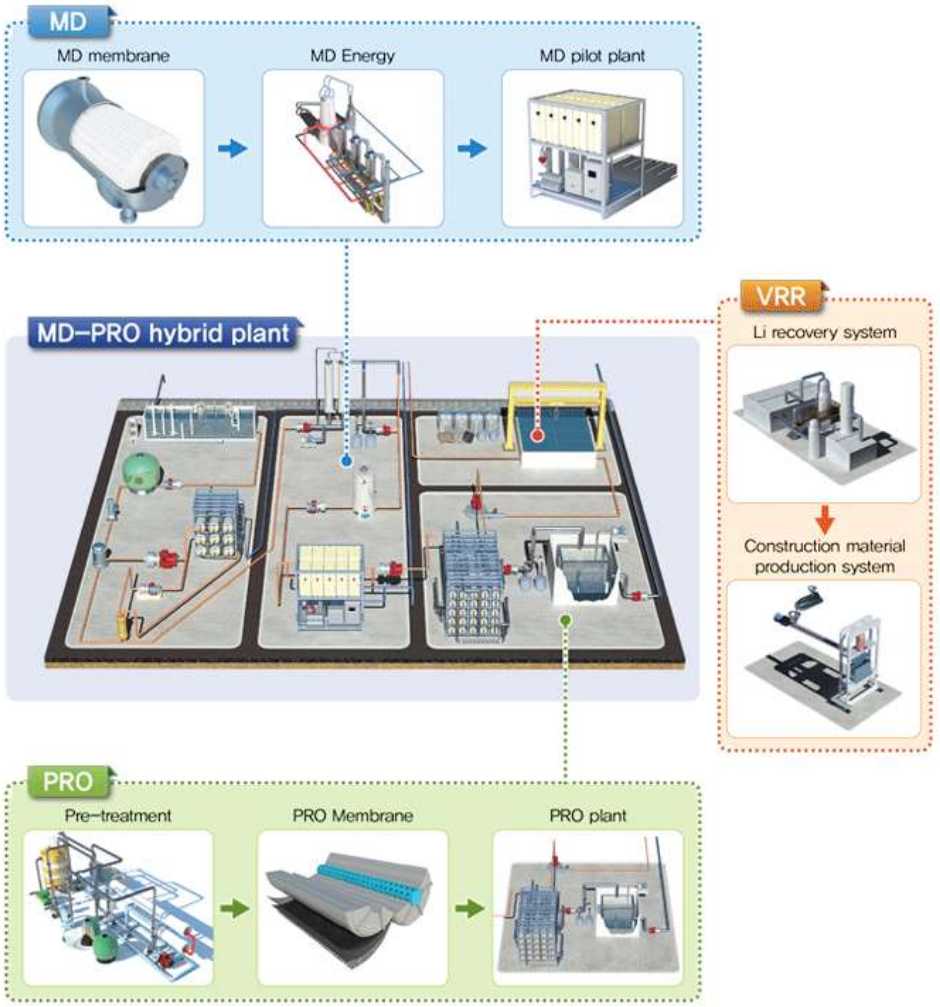



**MCr units on NF and RO retentate streams of an integrated membrane-based desalination system constituted by MF/NF/RO increases plant recovery factor until 92.8%. Around 19.5kg of salts ($CaCO_3$, NaCl and/or $MgSO_4*7H_2O$) are produced per $m^3$ of seawater**

Membrane-based Desalination: An Integrated Approach. Edited by E. Drioli, A. Criscuoli, F. Macedonio. IWA Publishig. 2011. ISBN: 9781843393214

# Five years Global MVP research program (2013-2018) in progress in Korea

- **Recourse to MD and/or MCr for water recovery factor increase, brine disposal reduction, raw materials production**
- **Use of PRO for blue energy production from the sea**
- **New design of desalination process via Integrated membrane based desalination systems**




http://www.globalmvp.org/

# *Conclusions*

- **In the last decades, membrane operations have been already assigned a key role in water reclamation schemes that are aimed at higher water quality reuse applications**
- **Despite the enormous success of membrane desalination technology, improvements are still required in terms of desalted water cost, higher productivity (that means higher water recovery factors), better water quality and enhanced eco-sustainability of the desalination process (solving brine disposal problem).**
- **Membrane engineering can help to enhance seawater desalination by a proper re-design of desalination processes, by combining various membrane operations.**
- **MD/MCr technology is a powerful tool for inter-phase mass transfer driven by partial pressure gradients, not limited by concentration polarization, and offers the opportunity to recover salts dissolved in seawater (sodium chloride, epsomite etc.) as crystalline product. Moreover, also blue energy production from salinity gradients through PRO or RED might be integrated in the system.**

***Thank you for your attention***