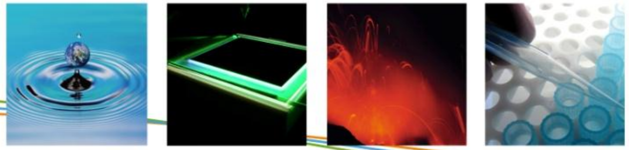


28/09/2012

Membranes in salinity gradient power generation

Chris Dotremont (VITO)
Willem van Baak (FUJI)

Outline

- Salinity gradient power (SGP)
  - Concept and some figures
- Overview of technologies
  - Pressure Retarded Osmosis (PRO)
    - ✓ Current status and developments
    - ✓ Market Players
    - ✓ Challenges
  - Reverse Electrodialysis (RED)
    - ✓ Current status and developments
    - ✓ Market Players
    - ✓ Challenges

Salinity gradient power (SGP) – concept

Gibbs free energy of mixing low concentration (LC) and high concentration (HC) streams, ΔG_{mix}:

$$-\frac{\Delta G_{\text{mix},V_{\text{LC}}^0}}{\nu RT} \approx \frac{c_{\text{M}}}{\phi}\ln c_{\text{M}} - c_{\text{LC}}\ln c_{\text{LC}} - \frac{1-\phi}{\phi} c_{\text{HC}}\ln c_{\text{HC}}$$

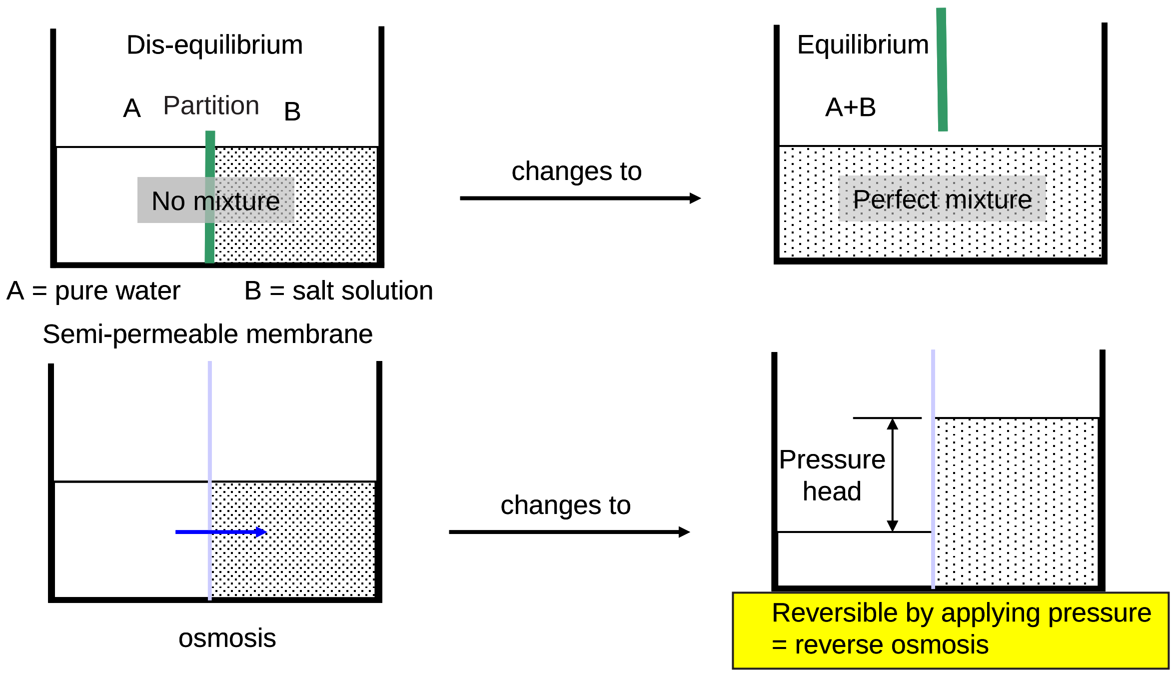
C	molar concentration
ϕ	volume fraction of low concentration (LC) stream
ν	number of electrolyte ions (e.g., 2 for NaCl)
R	gas constant
T	absolute temperature

Subscripts:

M – mixture; LC – low conc stream; HC – high conc stream

vito
vision on technology

Salinity gradient power (SGP) - concept



- seawater (35 kg of salt per m³): osmotic pressure = 2,700,000 Pa => 27 bar => 270 m of water column
- to squeeze potable water out of seawater, a pressure of over 27 bar must be applied

Salinity gradient power (SGP) – some figures

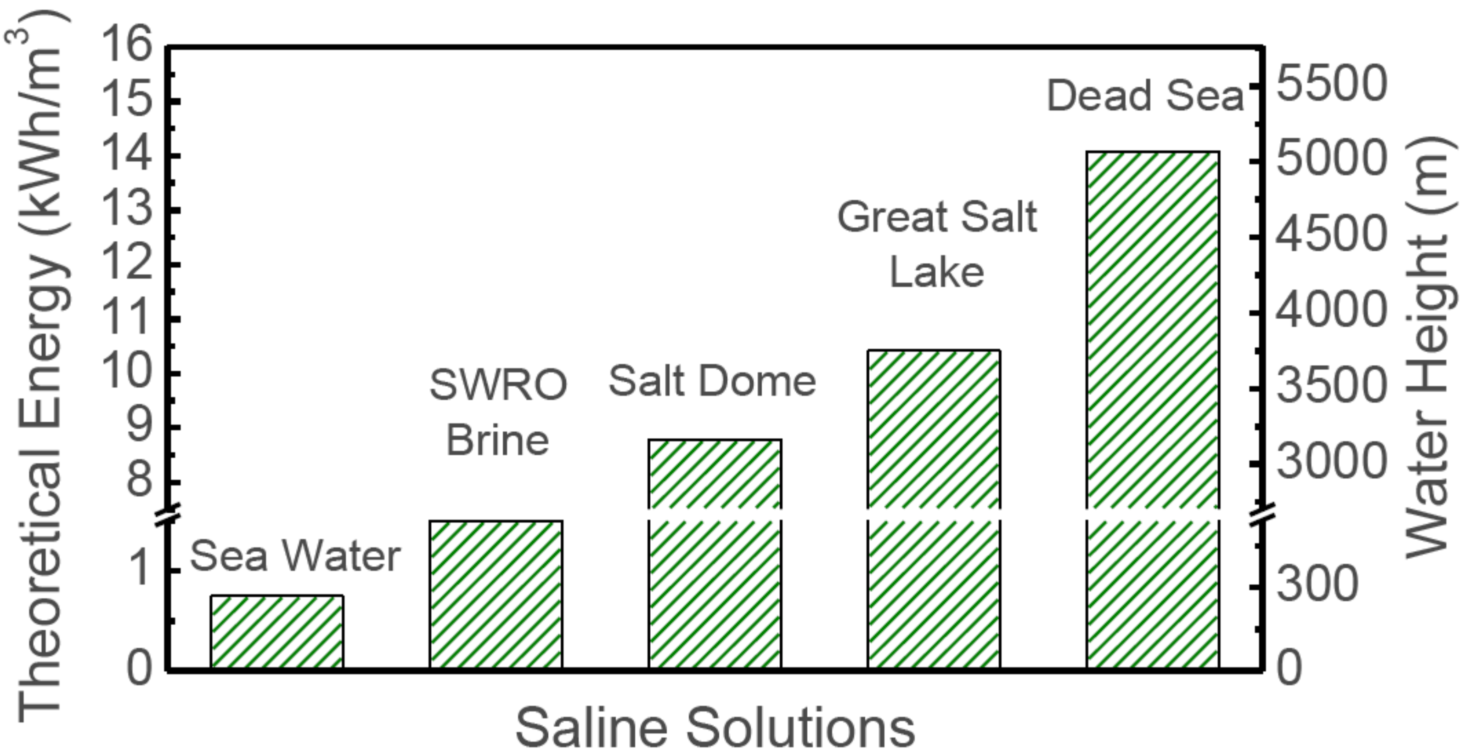
» Indirect calculation: seawater osmotic energy content:

$$E = P \times V = P \times S \times d$$

- ✓ producing one m³ fresh water from an infinite amount of seawater : $E = 2{,}700{,}000\ N/m^2 \times 1\ m^2 \times 1\ m = 2{,}700{,}000\ Nm =$ 2,7 MJ
- ✓ seawater : 2.7 $MJ/m^3 = 0.75\ kWh/m^3$
- ✓ equals the potential energy "m x g x h" of 1 m^3 of water (1000 kg) at a height of about 270 m
- ✓ in theory: the osmotic energy within 1 m^3 of seawater allows to lift 1 m^3 of water to a height of 270 m

vito
vision on technology

Energy of mixing from natural salinity gradient



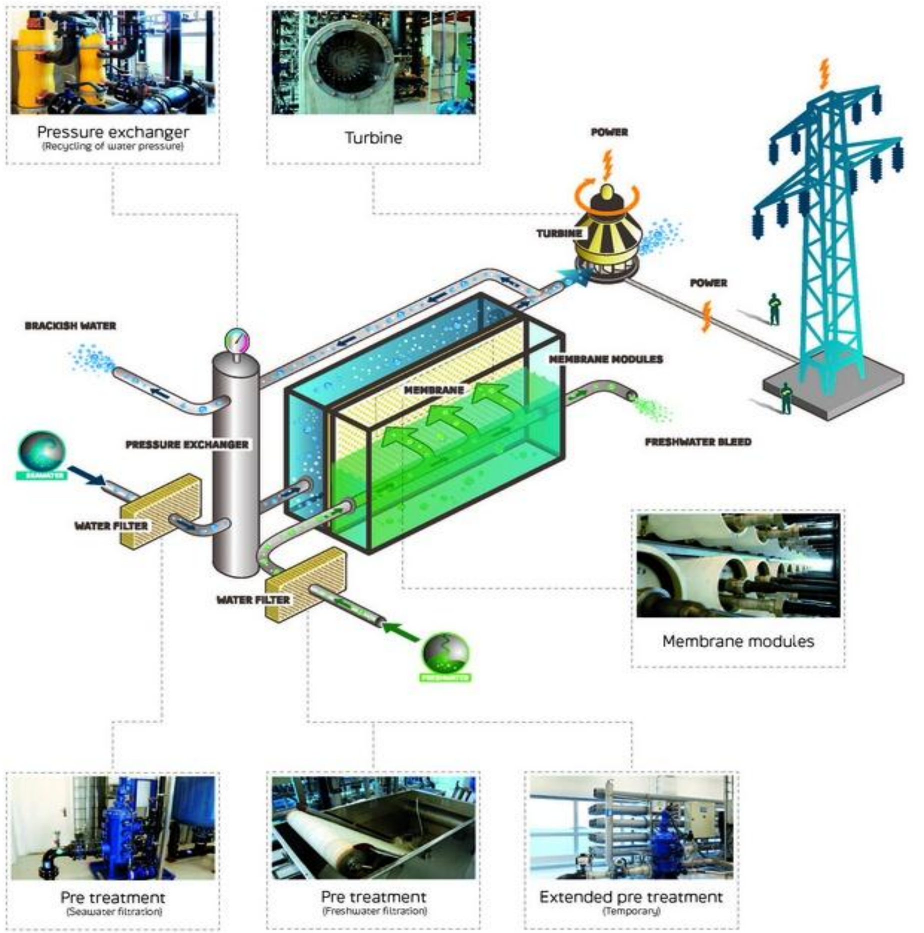
For river water–seawater mixing: $\Delta G_{mix} \sim 0.8$ kWh/m^3

Outline

- Salinity gradient power (SGP)
  - Concept and some figures
- Overview of technologies
  - Pressure Retarded Osmosis (PRO)
    - ✓ Current status and developments
    - ✓ Market Players
    - ✓ Challenges
  - Reverse Electrodialysis (RED)
    - ✓ Current status and developments
    - ✓ Market Players
    - ✓ Challenges

SGP-PRO (Pressure retarded osmosis)

- Most intensely studied and advanced SGP principle: research initiated by Sydney Loeb (1976)
- Principle of operation:
  - Transport of water through membrane from low concentration to high concentration
  - Skin layer in contact with high salinity side
  - Back pressure on high salinity side and increase of volume



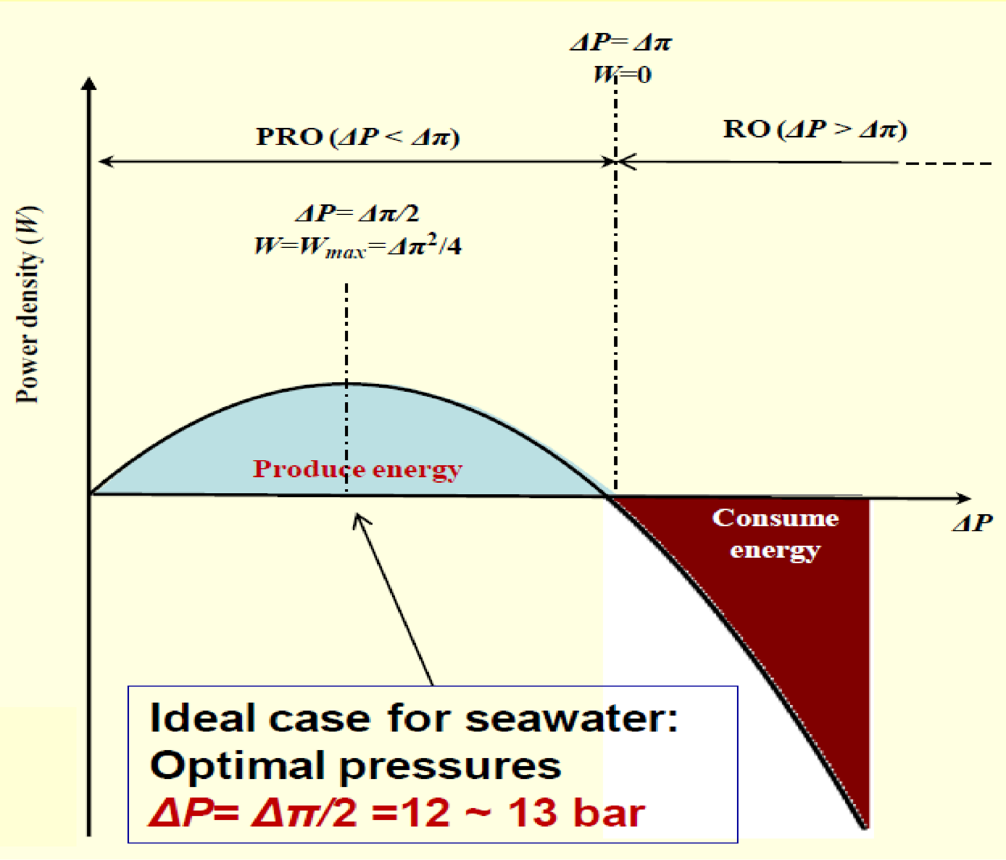
SGP-PRO (Pressure retarded osmosis)

- RO versus PRO
  - $\Delta p = 0$ →FO
  - $0 < \Delta p < \Delta\pi$ →PRO
  - $\Delta p > \Delta\pi$ →RO

- Work delivered by transport of water through membrane

$$W = A.(\Delta\pi - \Delta p).\Delta p$$

$$W_{MAX} = \frac{\Delta\pi^2}{4}$$



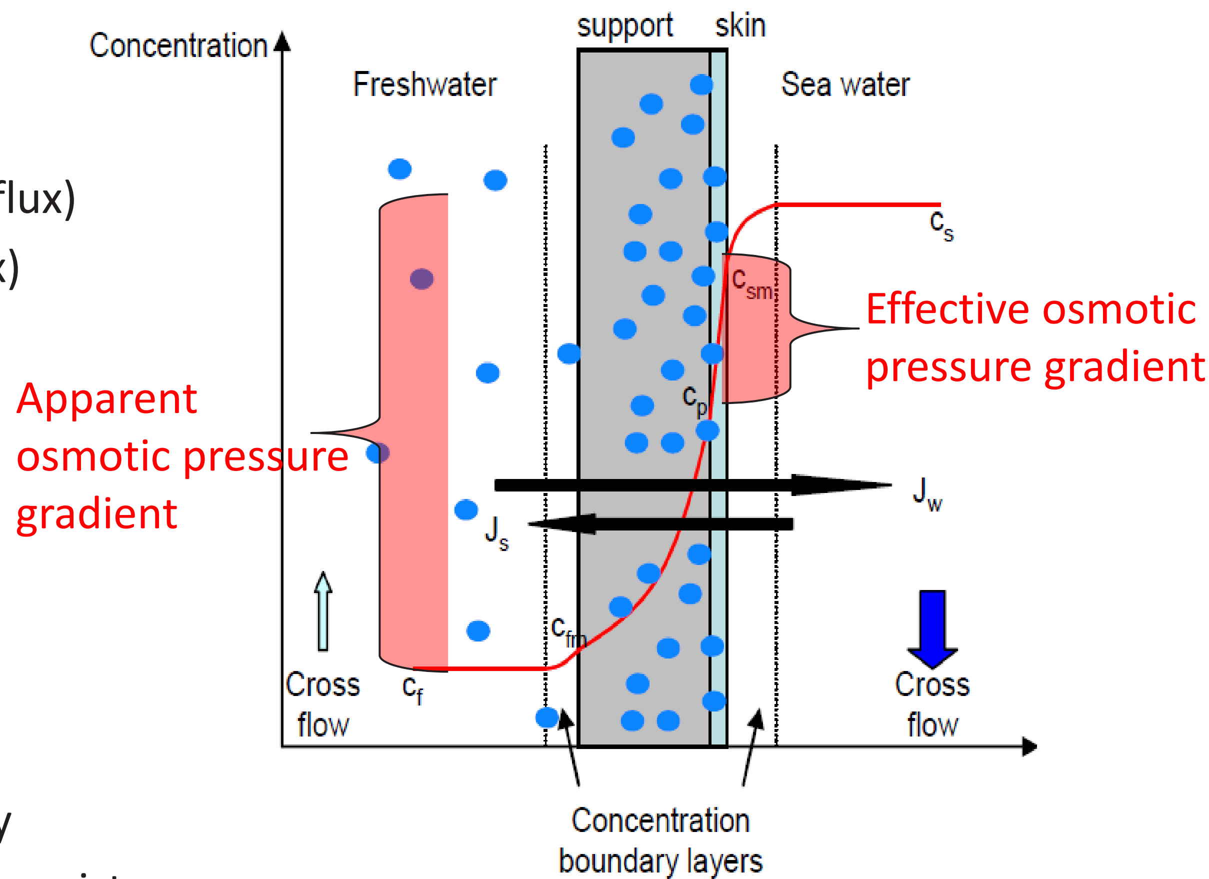
SGP-PRO (Pressure retarded osmosis)

- Membrane challenges
  - Rejection layer:
    - High A-value (water flux)
    - Low B-value (salt flux)
  - Support layer:
    - Small S-value

$$S = \frac{\tau \times t_{sm}}{\varepsilon}$$

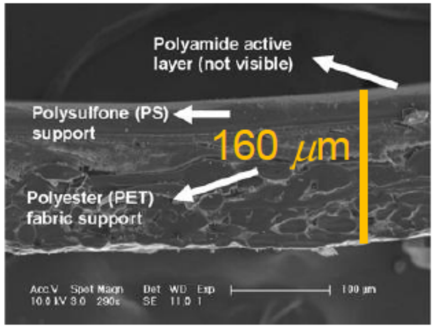
- Thinner
- More porous
- Lower tortuosity

    - Higher back-pressure resistance



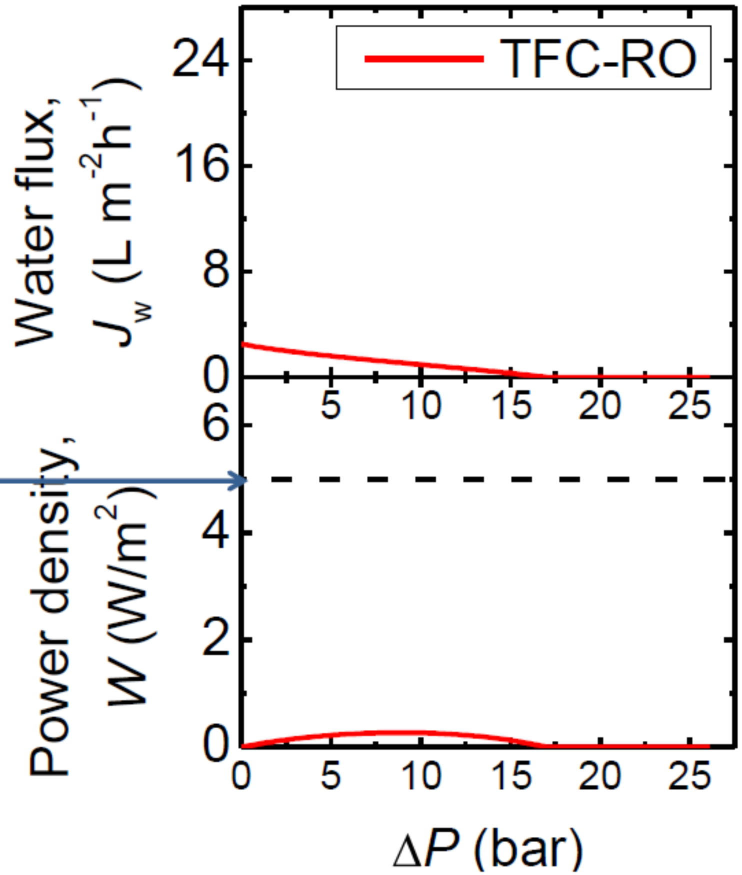
RO Membranes Perform Poorly in PRO

Commercial RO polyamide thin-film composite membrane



Target:
5 W/m²

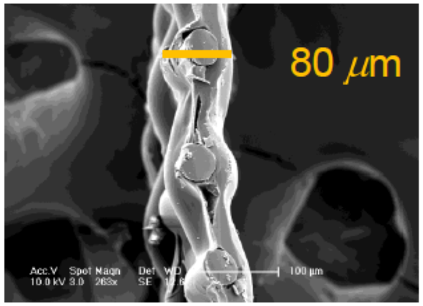
Skilhagen *Desal. & Water Treatment* **2010**, 15 (1-3), 271-278



Draw: Seawater
Feed: River water

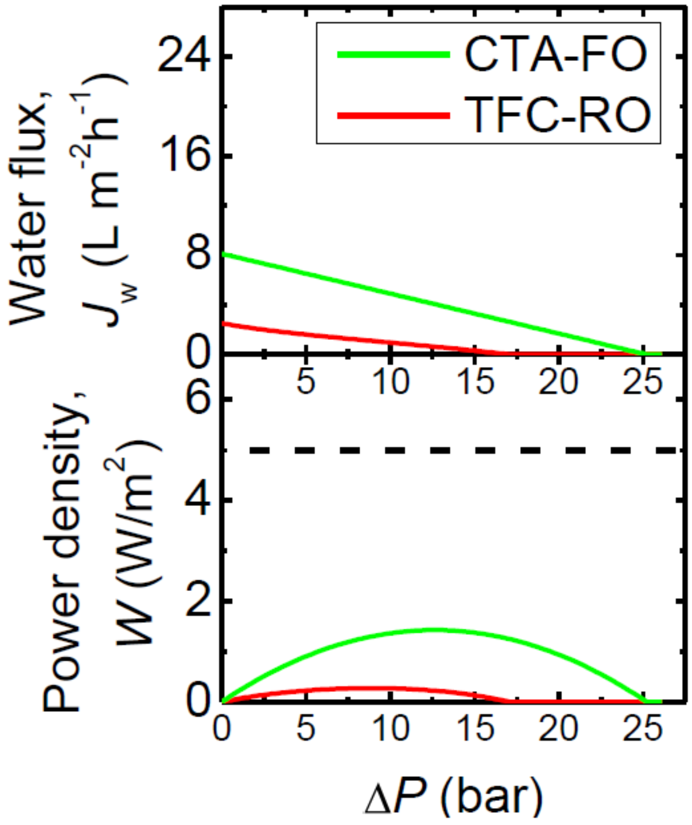
Commercial Cellulose Acetate FO Membrane has Limitations

Commercial FO cellulose triacetate asymmetric membrane



Limitations

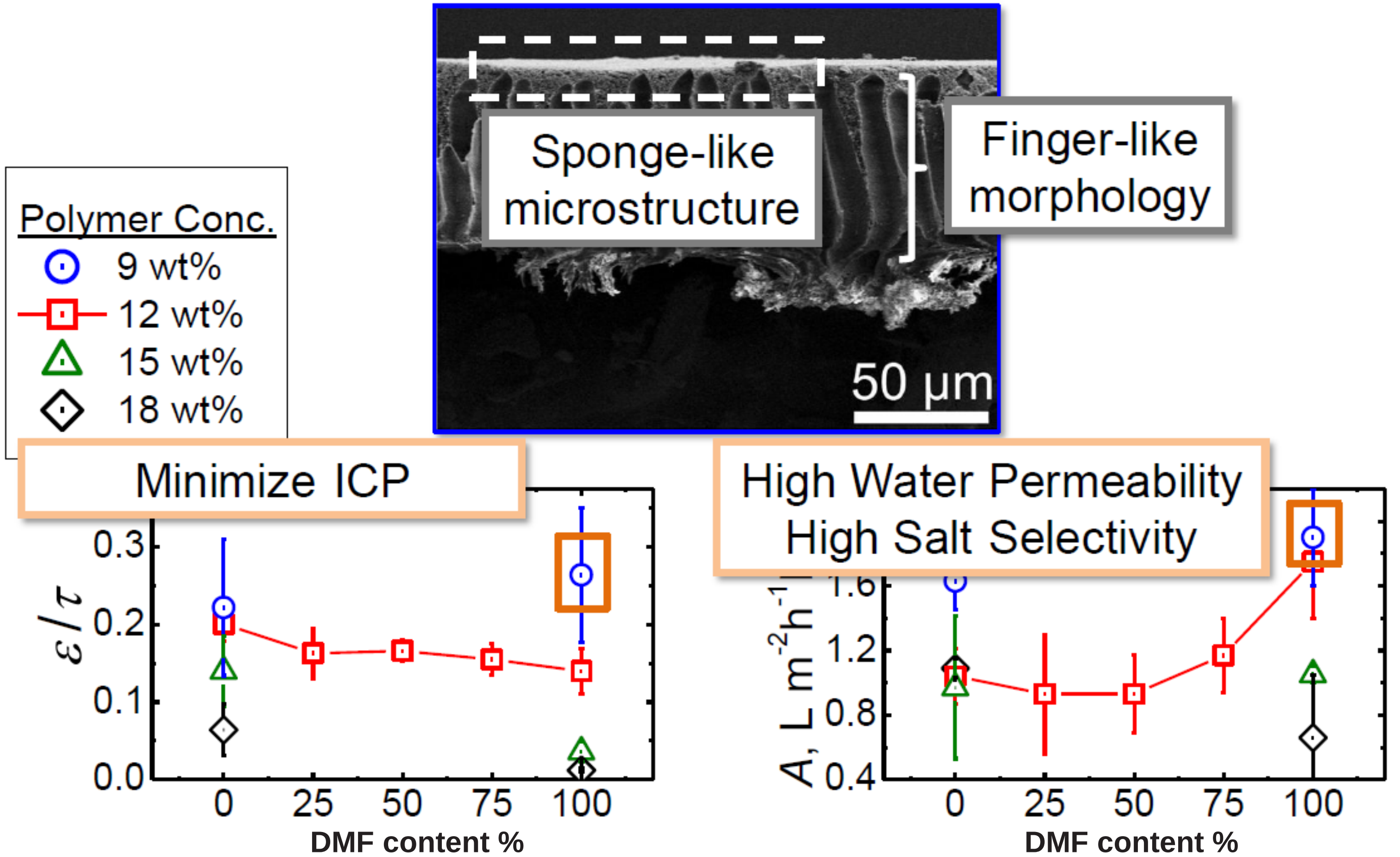
- Low intrinsic water permeability
- Low salt rejection
- Narrow operable pH range



Draw: Seawater
Feed: River water

vito
vision on technology

Performance Determined by Active and Support Layer Properties



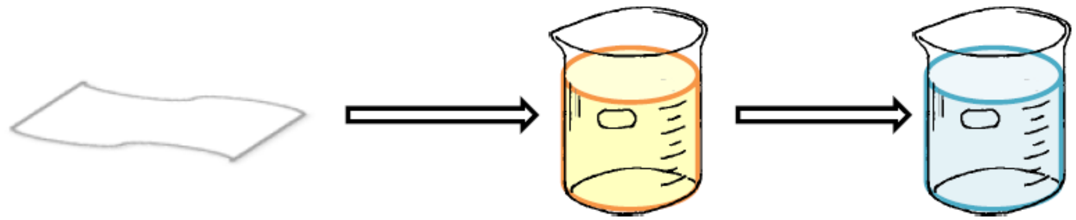
Tiraferri et al. *J. Membr. Sci.* **2011**, 367, 340-352

PSf /NMP-DMF phase-inversion process

vito
vision on technology

Increase Membrane Permeability on the Expense of Membrane Selectivity

- Post-treatment of polyamide selective layer

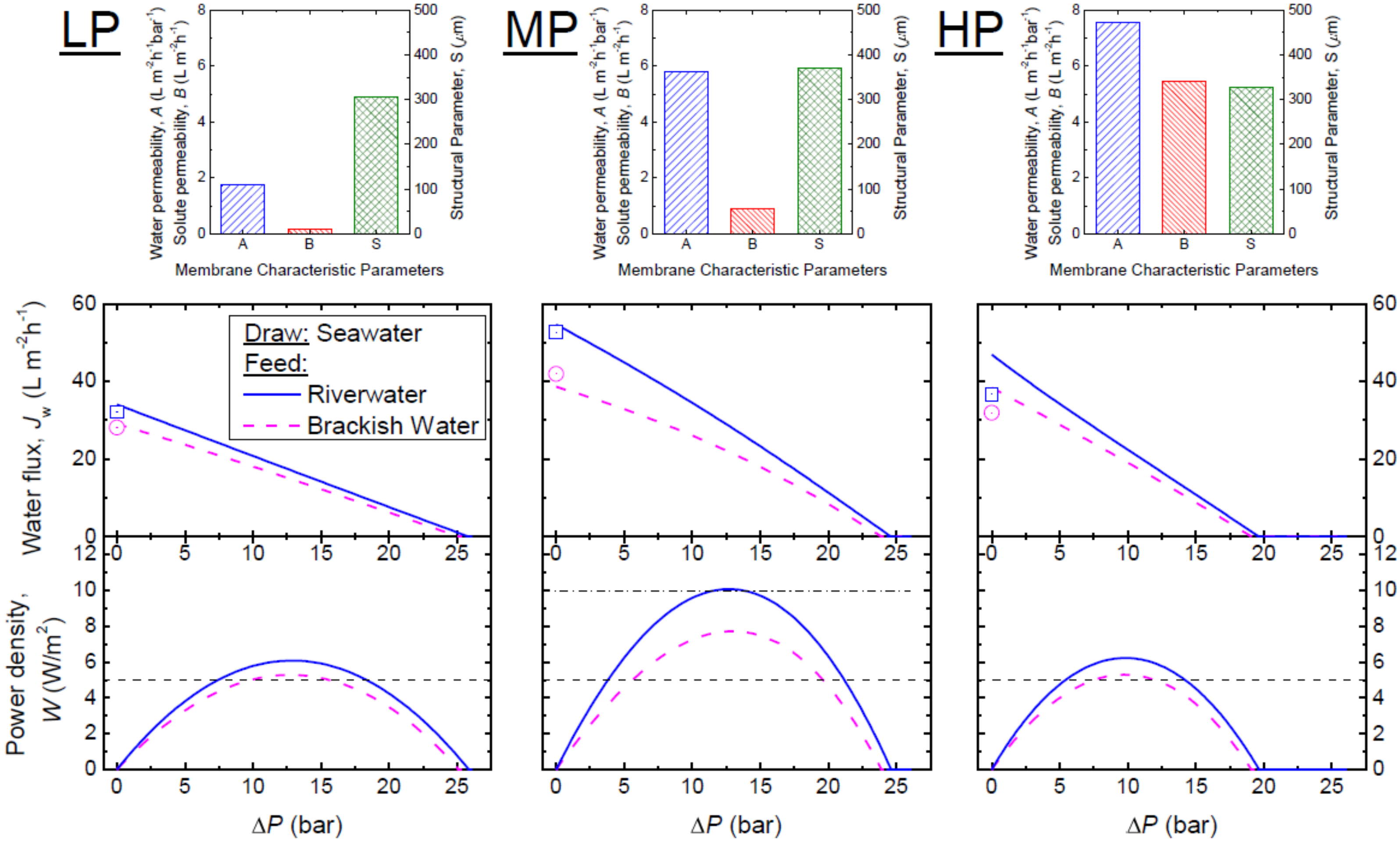


Membrane	Chlorine	Alkaline	Δpermeability
"LP" Low permeability	No post-treatment		–
"MP" Medium permeability	1,000 ppm NaOCl @ pH 7.0, 60 mins	0.1 M NaOH, 16 h	
"HP" High permeability	2,000 ppm NaOCl @ pH 7.0, 120 mins	0.1 M NaOH, 62 h	

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

vito
vision on technology

TFC-PRO Membrane Performance



SGP-PRO Market Players

❑ **HTI: supplier CTA FO membrane (first generation)**

OsMEM™ FO Cellulose Triacitate Flat Sheet Membrane

- **Commercial 40 inch production**
- **Woven and non-woven backed versions**
- **Spiral FO modules** (2.5", 4" and 8" diameter by 40" lengths, single element and multi-element configuration)
- **Plate and frame cassette modules**
- **Available for large production orders**

HTI's historical and founding membrane product. Extremely hydrophilic and oleophobic (contact angle 60°). Excellent non-fouling properties. Long lived and Chlorine tolerant.

- Average flux in FO mode - 9.0 LMH (1M NaCl vs DI water)
- NaCl rejection - 99% (<500 mg/ liter)
- Operating pH range - 3 to 8

HTI Hydration Technology Innovations

4

vito vision on technology

SGP-PRO Market Players

- ❑ **HTI: supplier TFC FO membrane (novel product)**

Announcing Commercial Availability of OsMEM™ FO TFC Flat Sheet Membrane Modules

- **High performance thin film composite (TFC) polymer membrane**
- **40 inch production on durable woven backing – very robust**
- **Spiral FO modules** (2.5", 4" and 8" diameter by 40" length, single and multi-module configuration)
- **Available for large production orders**

HTI's high performance FO membrane product is hydrophilic (contact angle 45°). Excellent non-fouling properties.

- Average flux in FO mode - min 20 LMH (1M NaCl vs DI water)
- NaCl rejection - 99.4 % (<300mg/L salt leakage)
- PRO rating (flat cell - 160psi, 10 C) - 3.5 Watts/M^2
- Operating pH range - 2 to 11

Hydration Technology Innovations

5

SGP-PRO Market Players

- **Perifera Inc.: new membrane supplier FO**
  - New FO membranes ready for commercial production (June 2012)
  - TFC membranes → stable in wide range of pH & solvent, low propensity to foul
  - High power density ~ 10-12 W/m^2
- **Pilot- / Demo-projects**
  - Norway: Statkraft project (Statkraft + Hydranautics / Nitto Denko)
  - Japan: Mega-ton Water System project (Toray)

vito
vision on technology

Statkraft project

MAIN EXPERIENCES

--> No environmental showstoppers detected

--> Increased belief in commercial possibility

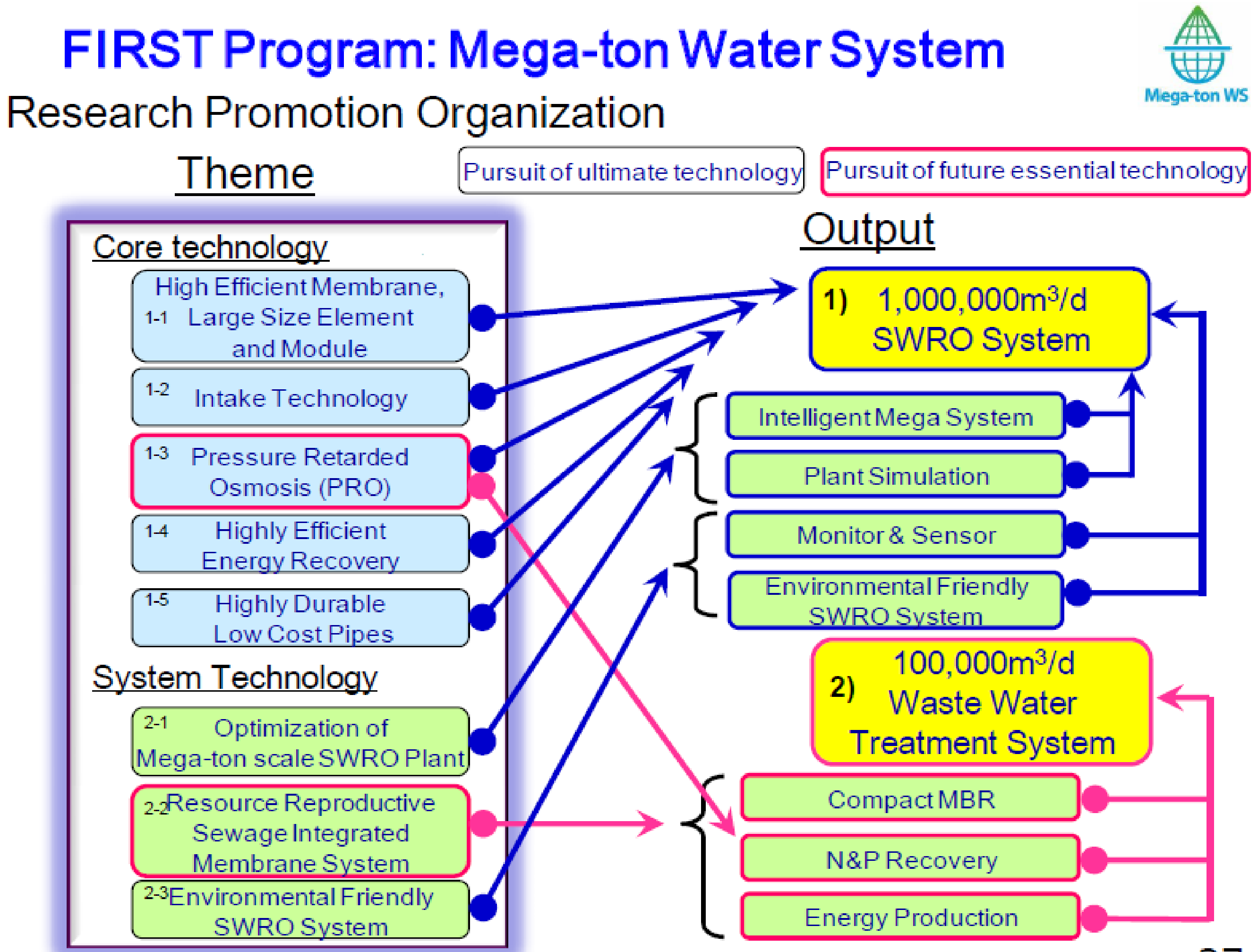
--> Possible to operate throughout seasonal variations

--> PRO membranes behave different in real conditions than in the lab

--> NOM fouling on FW side, main fouling issue

vision on technology

Mega-ton Water System



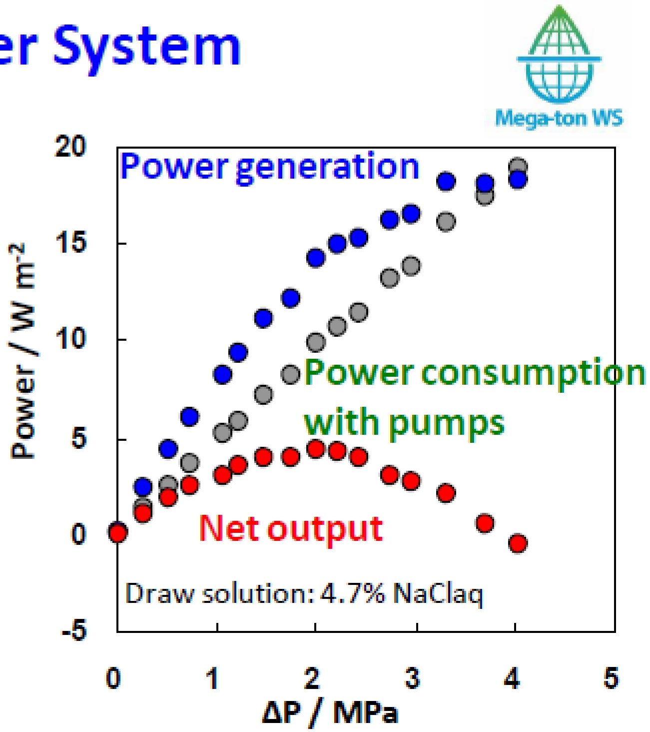
Mega-ton Water System

FIRST Program: Mega-ton Water System

Topics

Pressure Retarded Osmosis

- Hollow fibre membrane for power generation by PRO using seawater brine was newly developed.
- Net output was estimated at 4.4 W/m² when 4.7% of NaClaq was used, 9 W/m² is promising at 7% of seawater brine.
- Energy recovery for seawater desalination process was optimized by detailed PRO simulations.



PRO output corresponding to operation pressure

SGP-PRO

» **Main challenges for the coming years**

- High performance membranes
- Develop low-cost pretreatment
- Fouling issues
- Module design (spiral wound/HF)
- Upscaling (membrane production and PRO-systems)

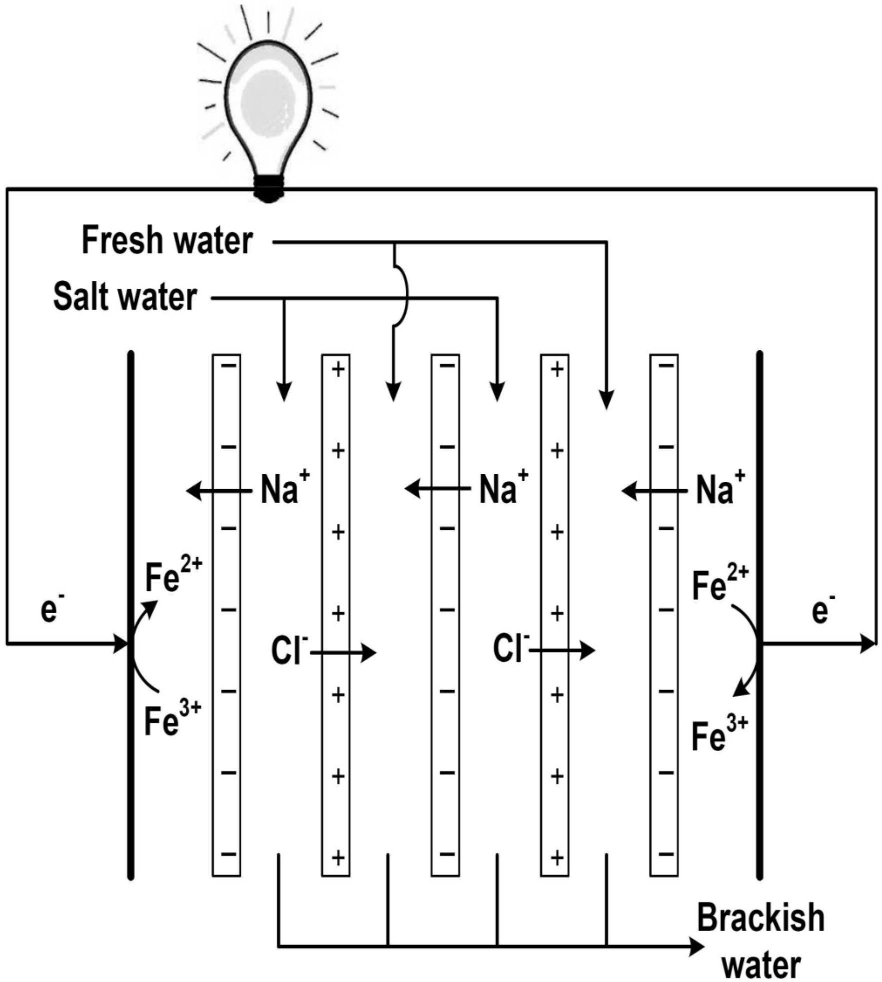
vito
vision on technology

Outline

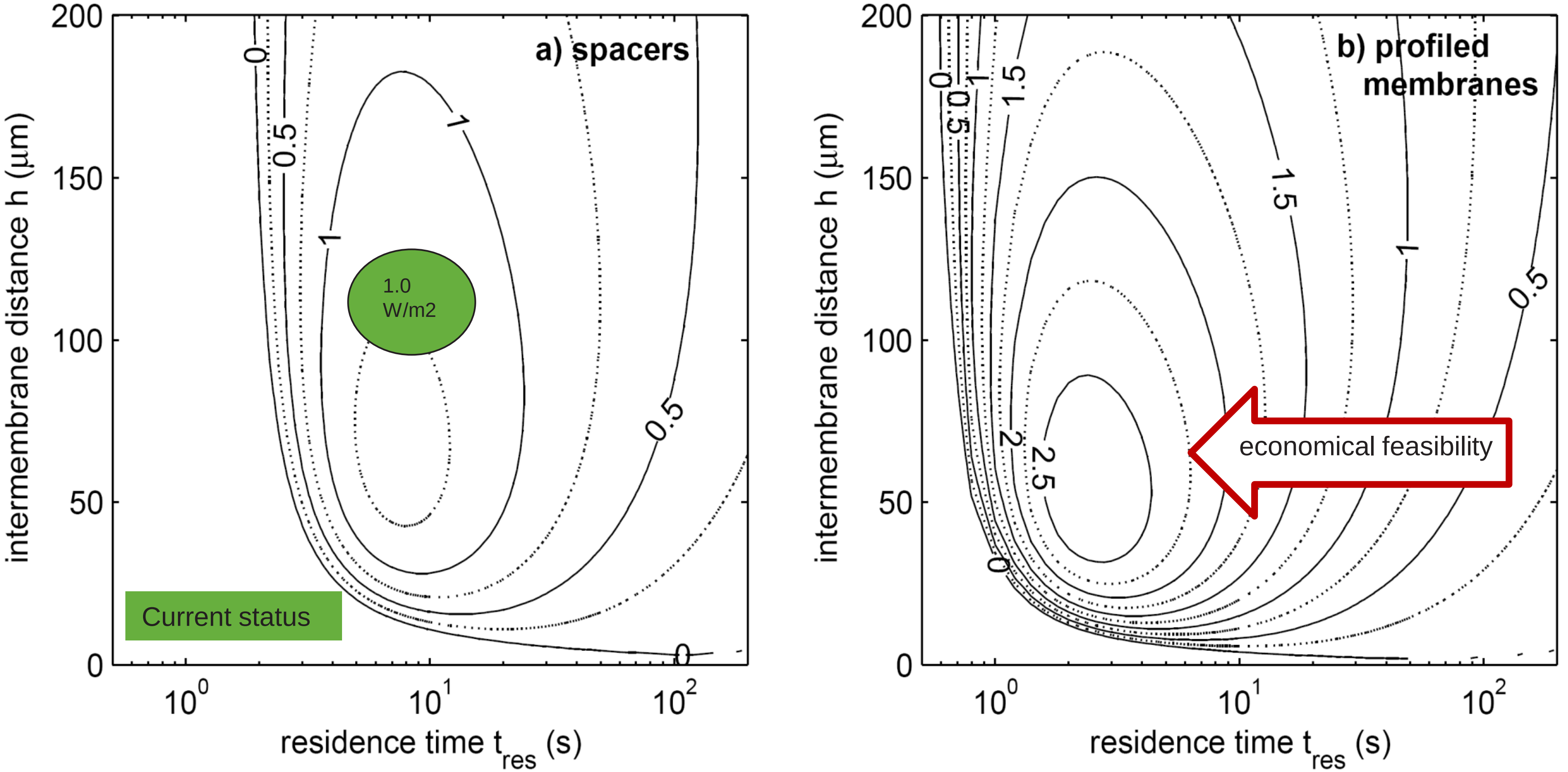
- » Salinity gradient power (SGP)
  - Concept and some figures
- » Overview of technologies
  - Pressure Retarded Osmosis (PRO)
    - ✓ Current status and developments
    - ✓ Market Players
    - ✓ Challenges
  - Reverse Electrodialysis (RED)
    - ✓ Current status and developments
    - ✓ Market Players
    - ✓ Challenges

SGP-RE (Reverse Electrodialysis)

- Principle of operation:
  - Ions are transported through membrane due to concentration gradient
  - Cell potential is generated by selective diffusion of ions
  - Electrode reactions induce electric current
  - Applicable at different salinity gradients
    1. river – sea water
    2. brine – sea water

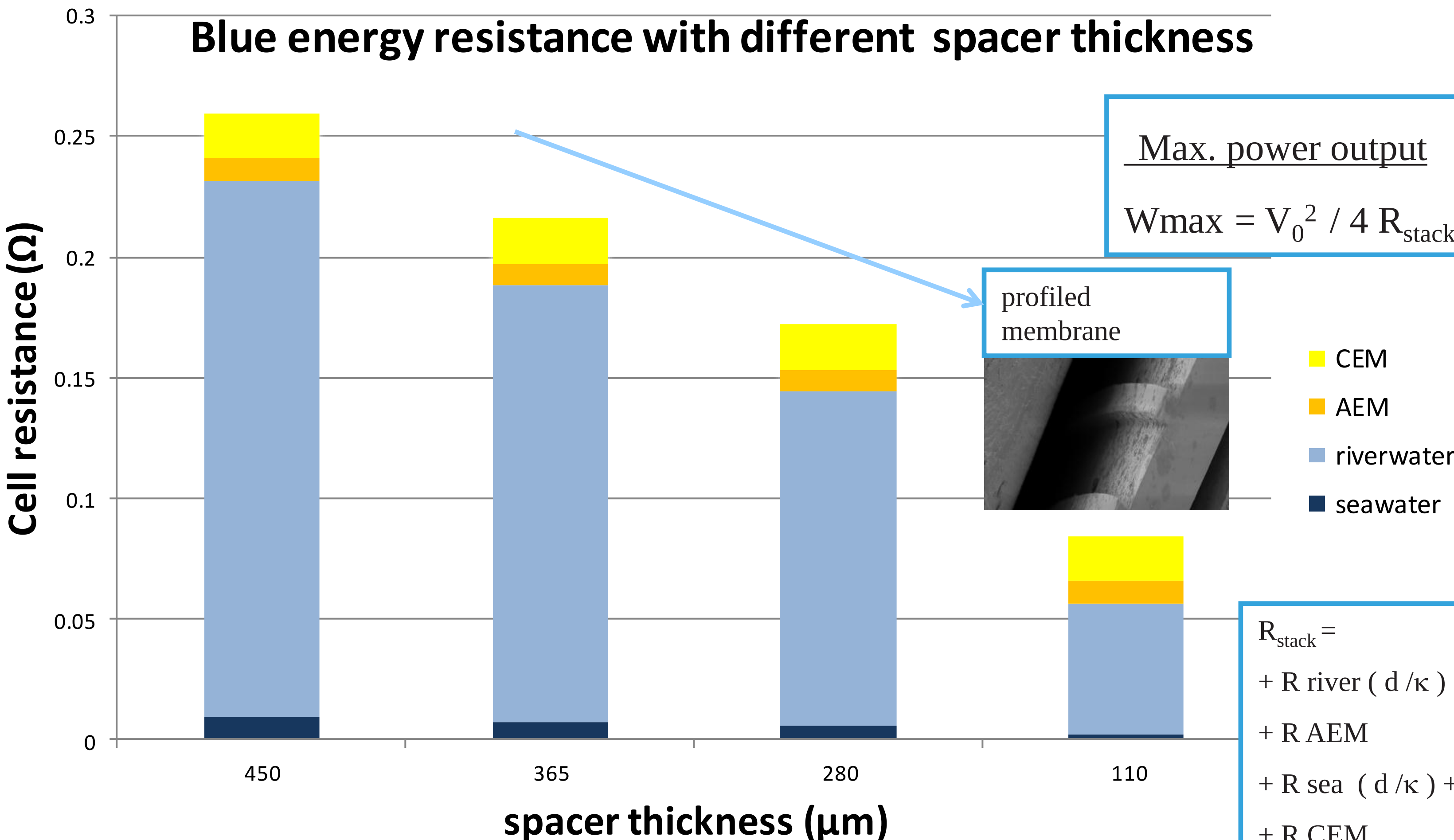


SGP-RE: Blue Energy (river-sea) status



Vermaas et al./ Energy Procedia (2011)

SGP-RE: Blue Energy (river-sea) development



Max. power output

$W_{max} = V_0^2 / 4 R_{stack}$

R_{stack} =

+ R river (d /κ) + spacer

+ R AEM

+ R sea (d /κ) + spacer

+ R CEM

SGP-RE: REAPower (brine – sea) status

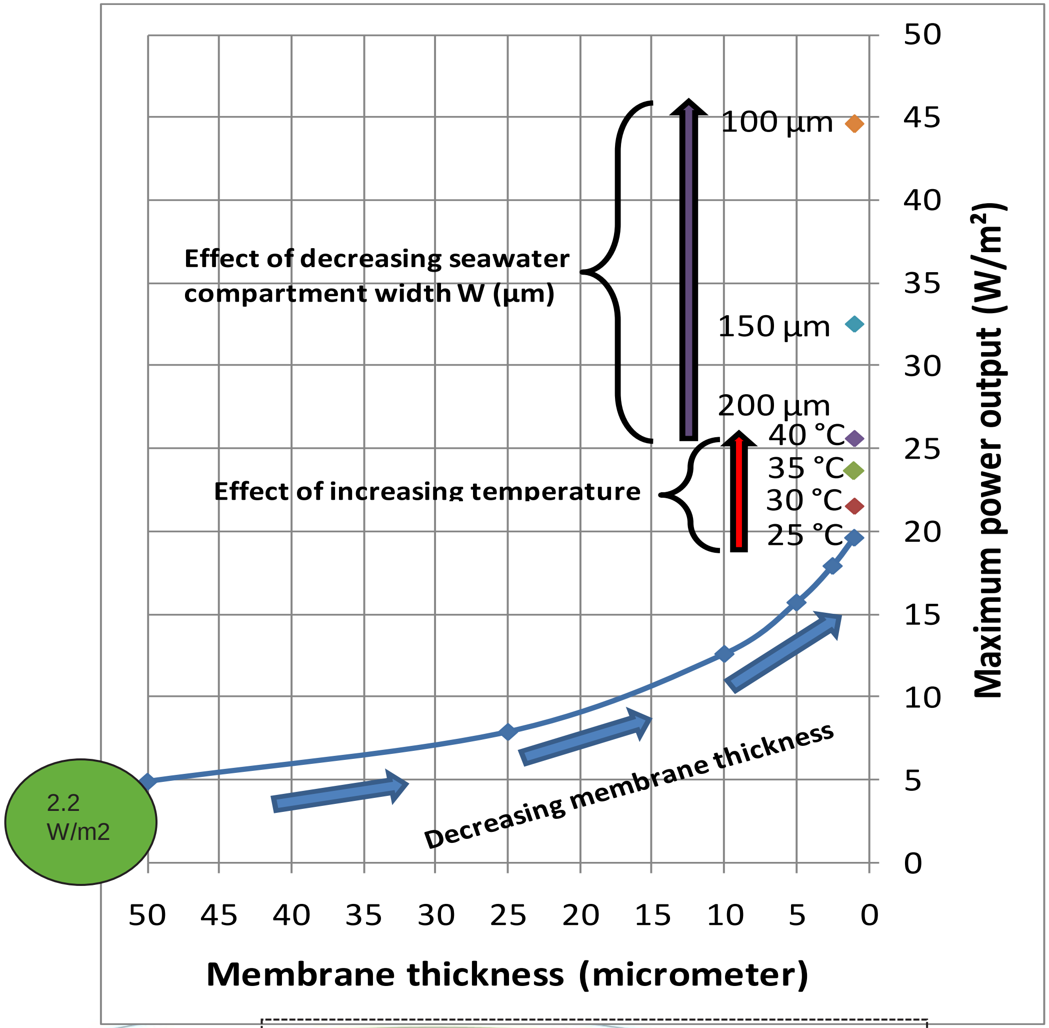
- REAPpower status
  - 0.5 - 4.0 m NaCl
  - FUJI R1 membranes

    - 120 micron thick

    - homogeneous
  - 300 micron spacer

- Highest value:

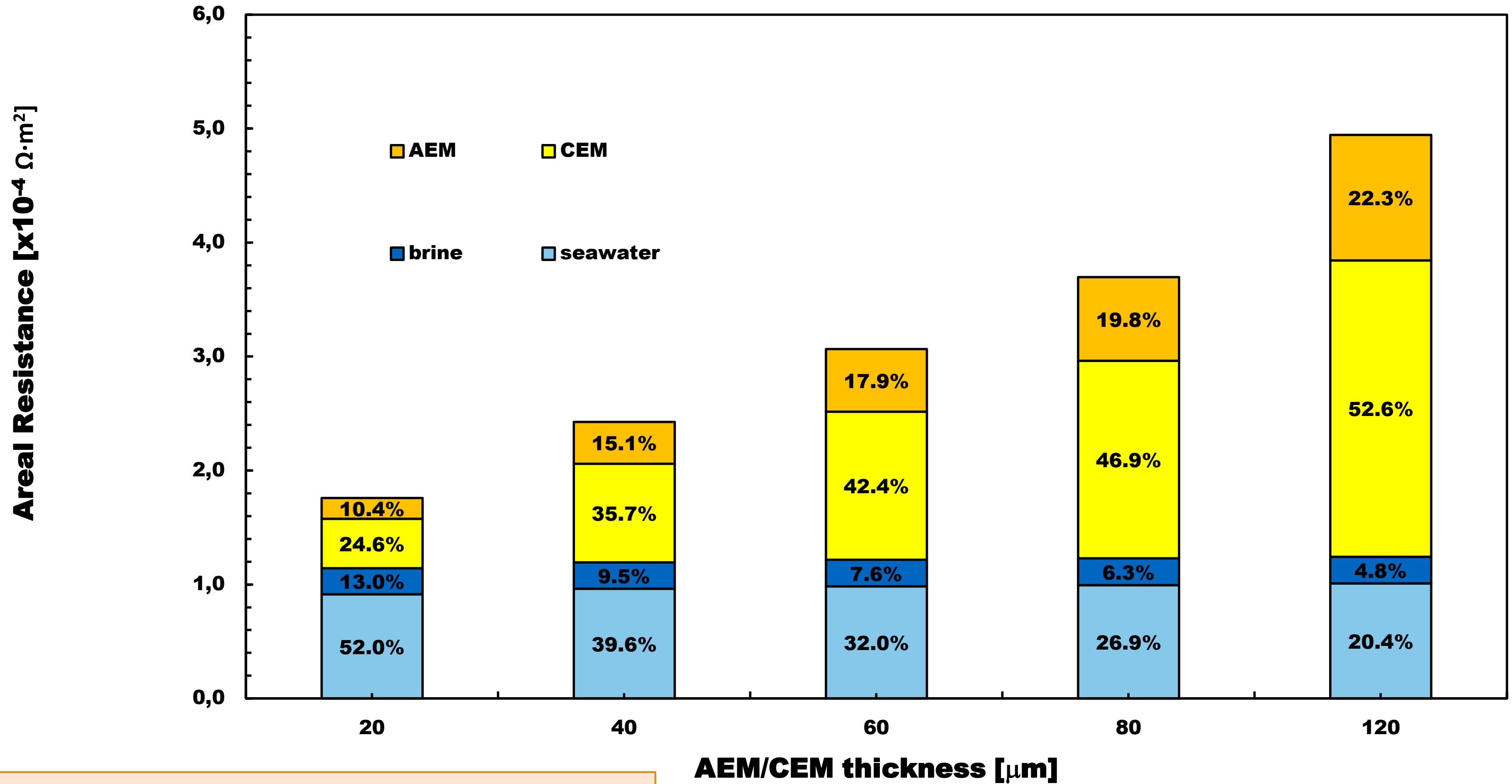
  2.2 W/m2 cell pair



E. Brauns, Desalination 237 (2009) 378–391

SGP-RE: REAPower (brine – sea) development

development towards thinner membranes

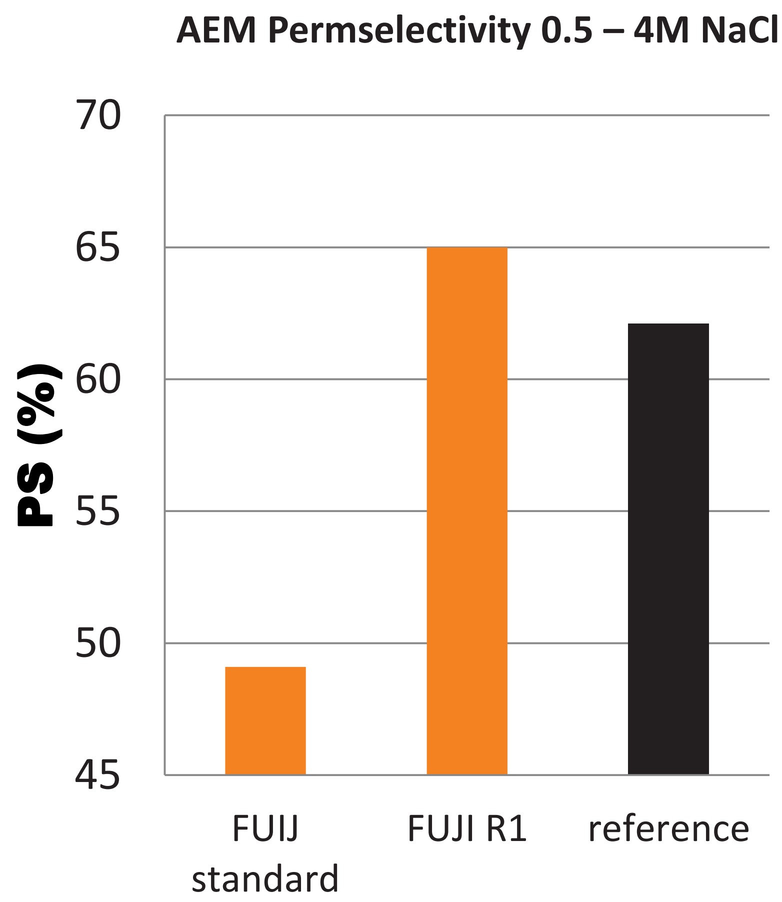


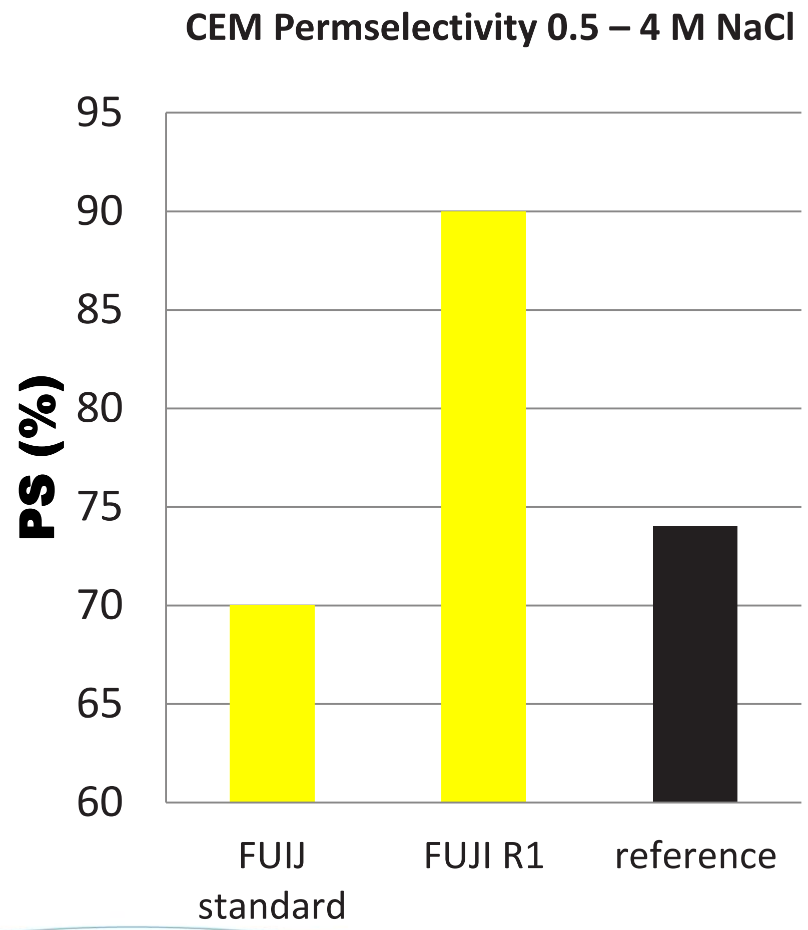
<u>Influence of IEMs thickness on resistance of the system.</u>
- Simulation of a 1000 cells stack assuming a linear decreasing of IEMs resistance with IEMs thickness.
- α_{AEM} = 0.65, α_{CEM} = 0.90.
- spacer thickness of seawater/brine compartments d = 200 micron.

Source: A multi-scale model for the Reverse ElectroDialysis process with seawater and concentrated brines by M. Tedesco University Palermo

SGP-RE: REAPower (brine – sea) development

development high PS membranes at high salt concentration





SGP-RE: Membrane market players

- **Main players**
  - **FUJI FILM**
    - cost competitive membranes
    - commercially available (max. width 50 cm)
  - **Kraton (only CEM), Fumatech**

- **Increasing interest other IEM manufacturers**

SGP-RE: main challenges coming years

» Blue Energy

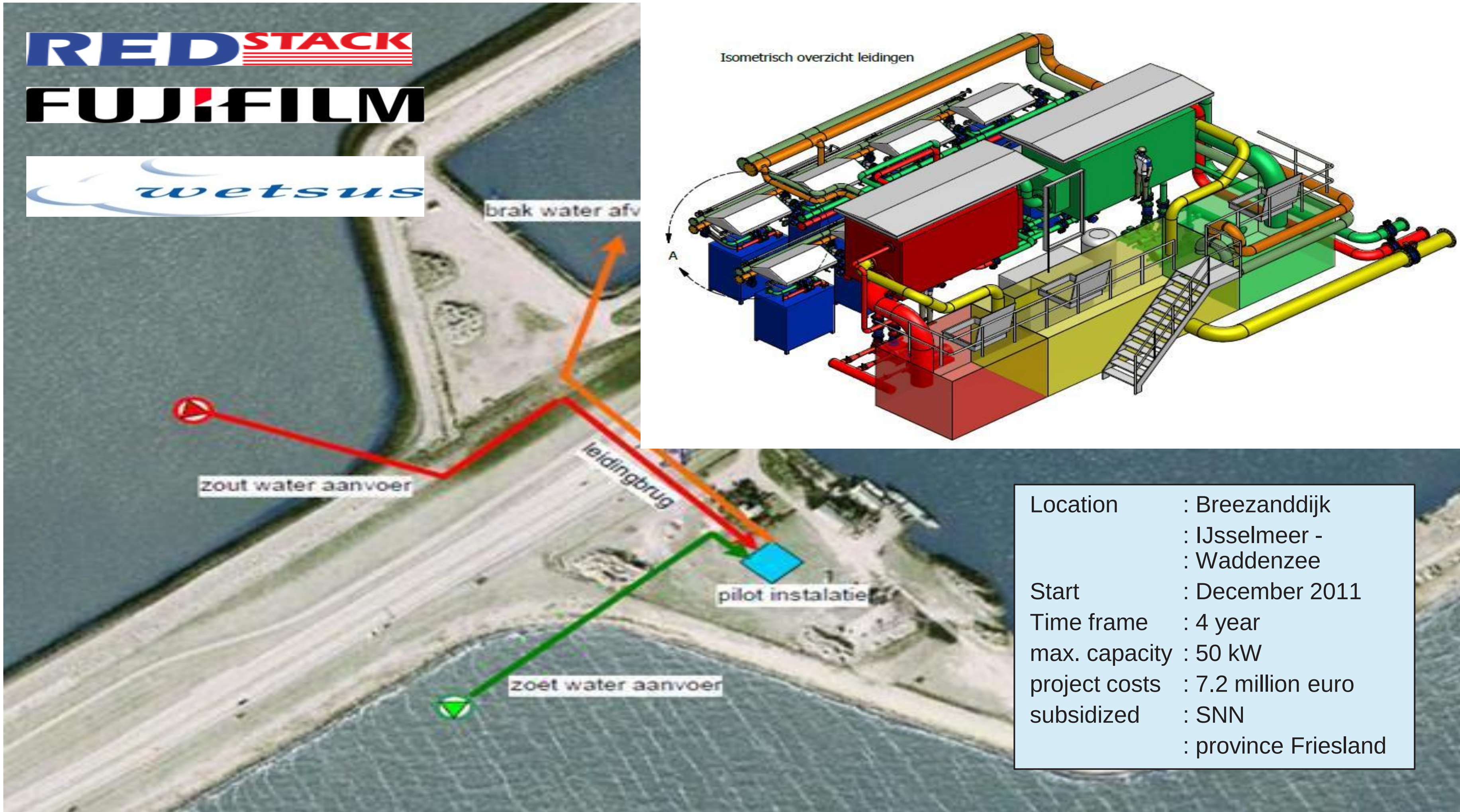
- » river – sea water
- ○ powerdensity increase > 2 W/m2
- ○ reduce river channel resistance

» REAPower

- » brine – sea water
- ○ powerdensity increase to 4-5 W/m2
- ○ reduce membrane resistance

- ○ feed pre-filtration at low cost
- ○ fouling
- ○ scaling
- ○ prove technology
- ○ scale up to fieldtest pilots

SGP-RE: Blue Energy pilot Afsluitdijk



Location	: Breezanddijk
	: IJsselmeer -
	: Waddenzee
Start	: December 2011
Time frame	: 4 year
max. capacity	: 50 kW
project costs	: 7.2 million euro
subsidized	: SNN
	: province Friesland

vito
vision on technology

FUJIFILM

SGP-RE: REAPower in Trapani salt pond - Sicily

Field test: 2013 -2014

COOPERATION

REAPower

REDSTACK · UNIVERSITÀ DELLA CALABRIA · FUJIFILM · NEXT TECHNOLOGY · KEMA · MANCHESTER · UNIVERSITÀ DEGLI STUDI DI PALERMO · Kraton · SolarSpring · vito · WIP

Thanks for your attention !