UNIVERSITY OF TWENTE.

MESA+ INSTITUTE FOR NANOTECHNOLOGY

The power of Blue Energy

Kitty Nijmeijer

Membrane Science & Technology

wetsus

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MST Membrane Science & Technology

Acknowledgements

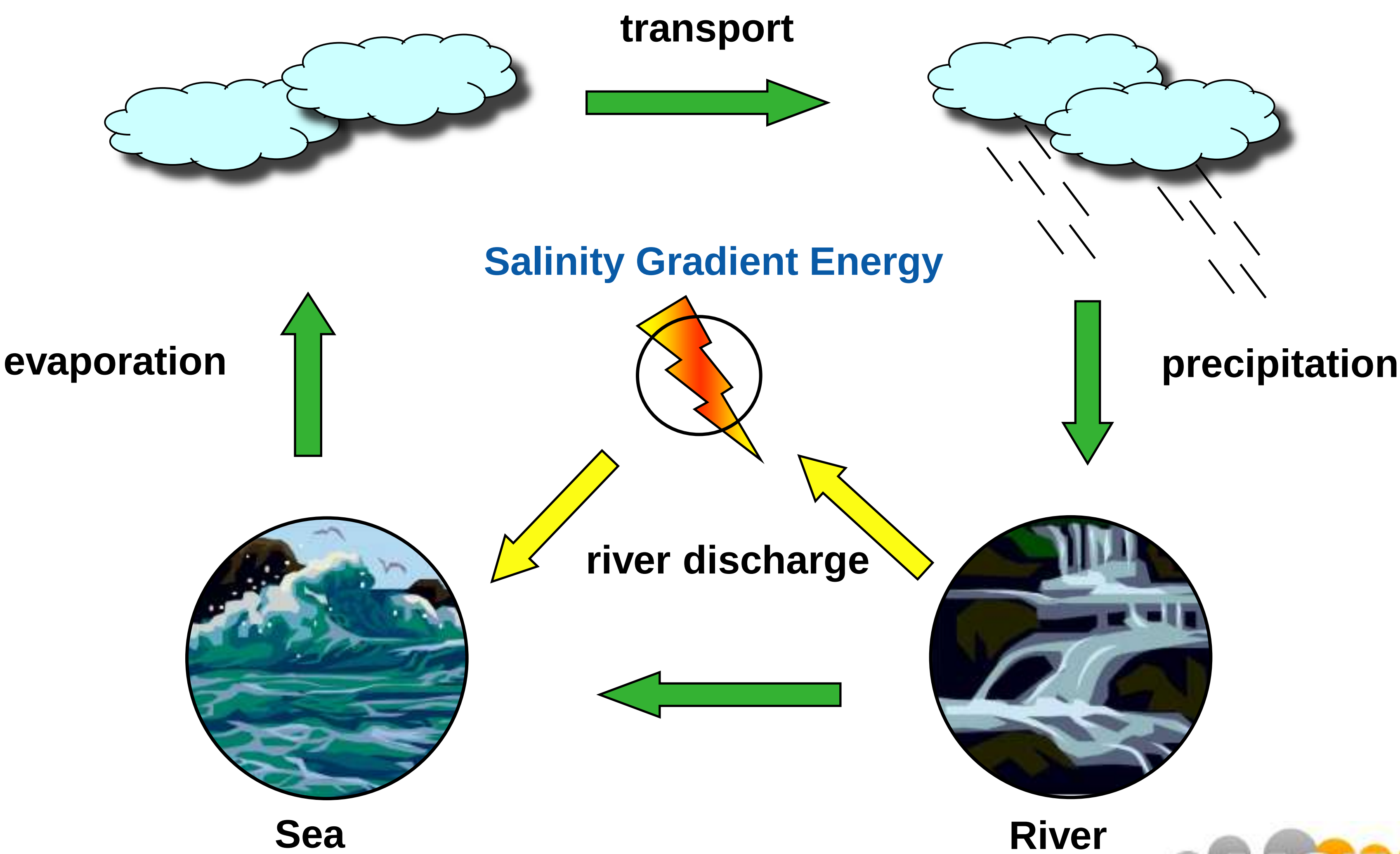
- Jordi Moreno, Timon Rijnaarts, Enver Guler, David Vermaas, Piotr Długołęcki, Michel Saakes, Matthias Wessling, Yali Zhang, Rianne Elizen

- Blue Energy Team Wetsus:

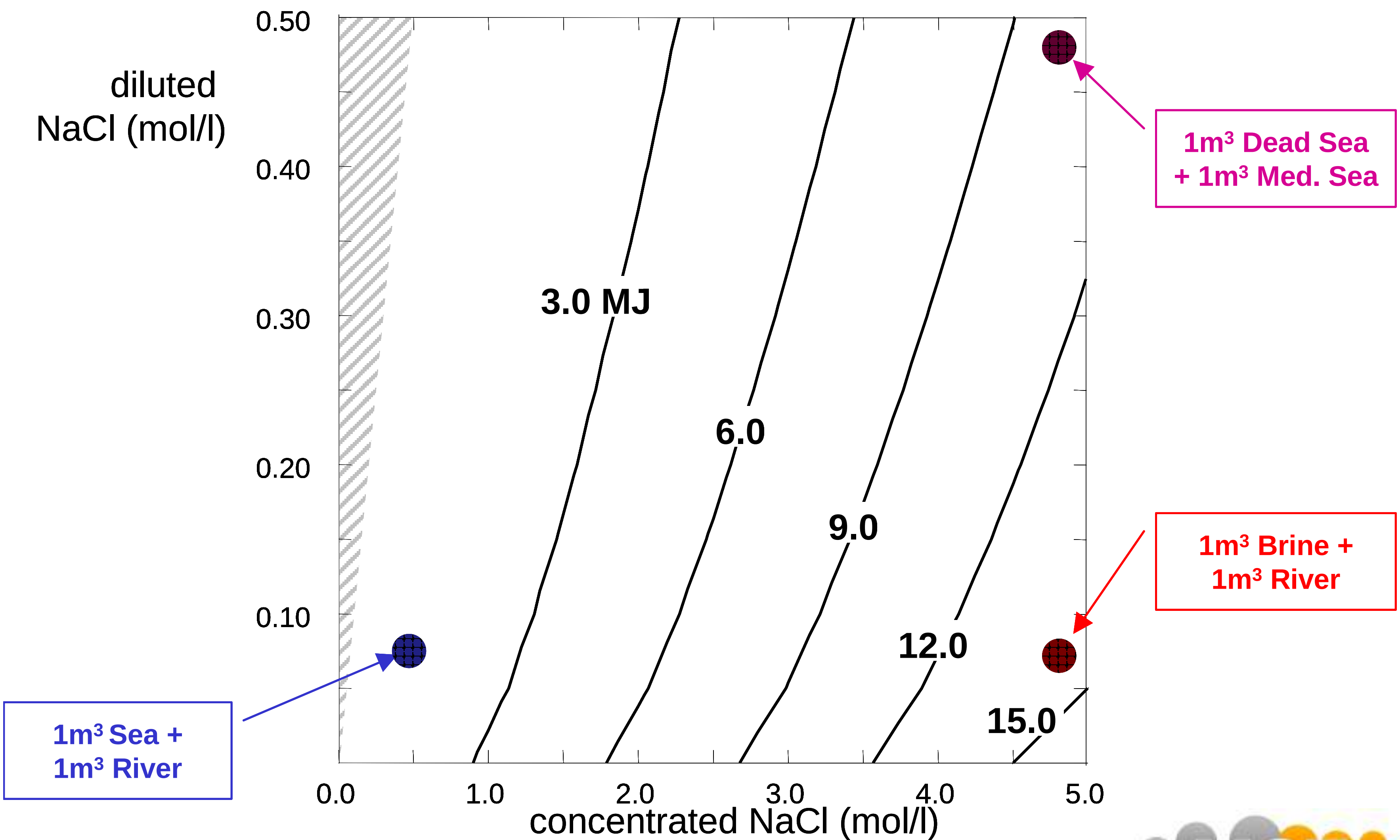
wetsus
european centre of **excellence**
for sustainable **water technology**

Alliander | Landustrie
Eneco Energy | Magneto Special Anodes
Frisia Zout | A.Hak
Fuji Film | MAST Carbon

Salinity Gradient Energy



Theoretical potential: Gibbs energy of mixing



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

Energy Potential

- Global potential: 2.4 TW (2.4×10^{12} W)
- Sustainable energy
- Fuel readily available
- No emission of CO_2, SO_2, No_x
- 3300 m^3/s fresh water into sea

  Rine: 2200 m^3/s

  IJssel: 600 m^3/s

  Maas: 200 m^3/s
- Rhine: energy supply 80% Dutch households

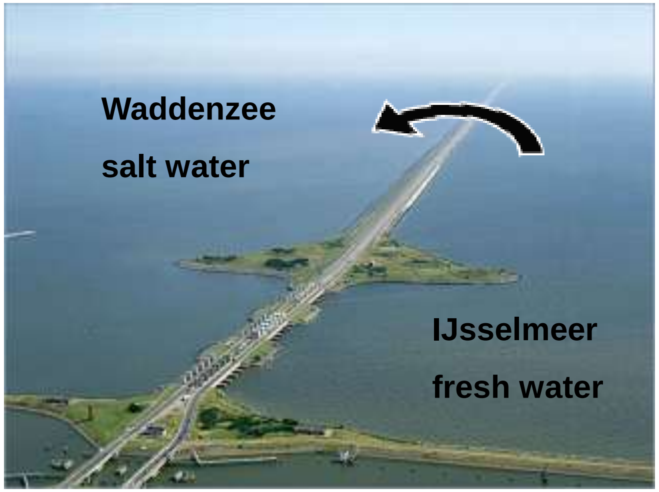
Energy Potential

The Netherlands:

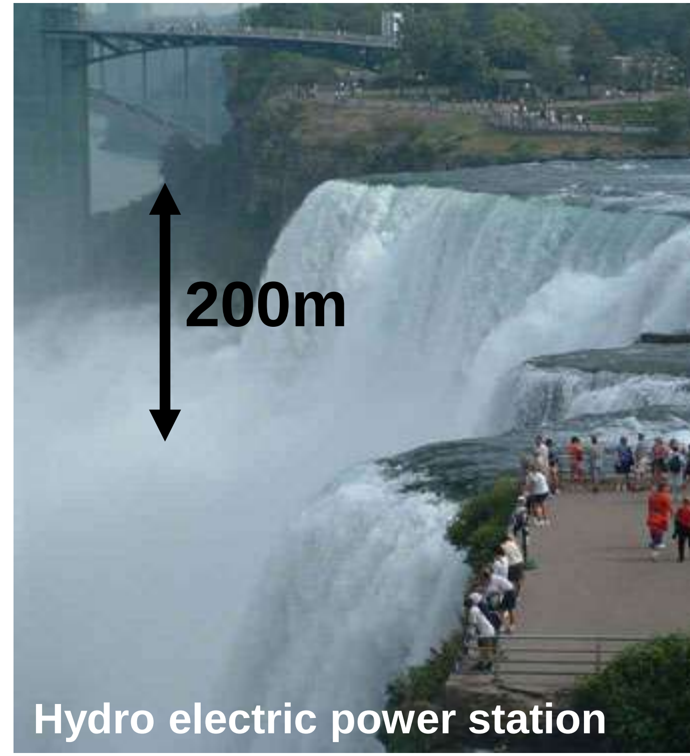
- Electricity demand 2002: 12500 MW
- Theoretical potential: 7000 MW (50%!)
- Practice: 3000 MW?
- Objective:
  - ~3 kW/m^3 reactor volume
  - ~3 W/m^2 membrane area

- **Challenge: increase in power output**

Energy Potential



Energy Potential

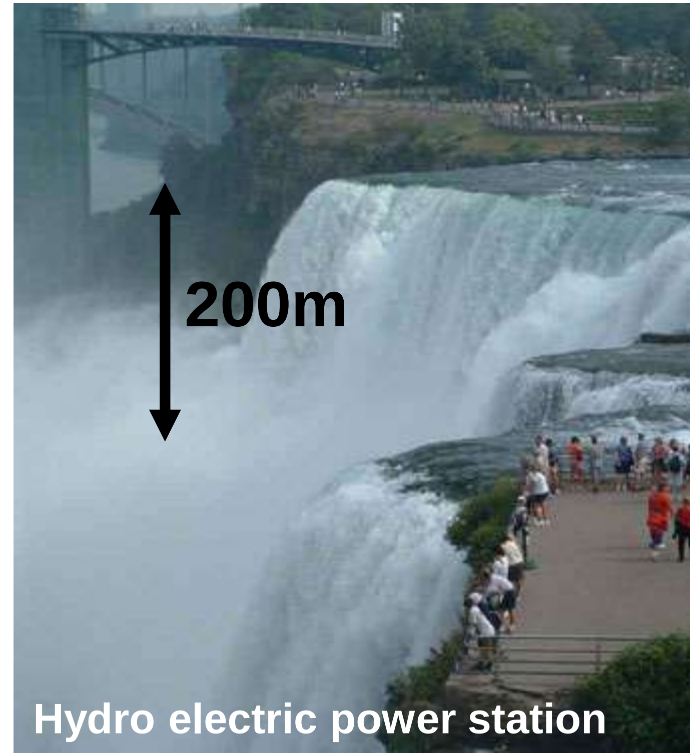


Potential worldwide: 1.4-2.6 TW

Practical potential NL: 1.5 GW

(10-15% of Dutch consumption)

Energy Potential

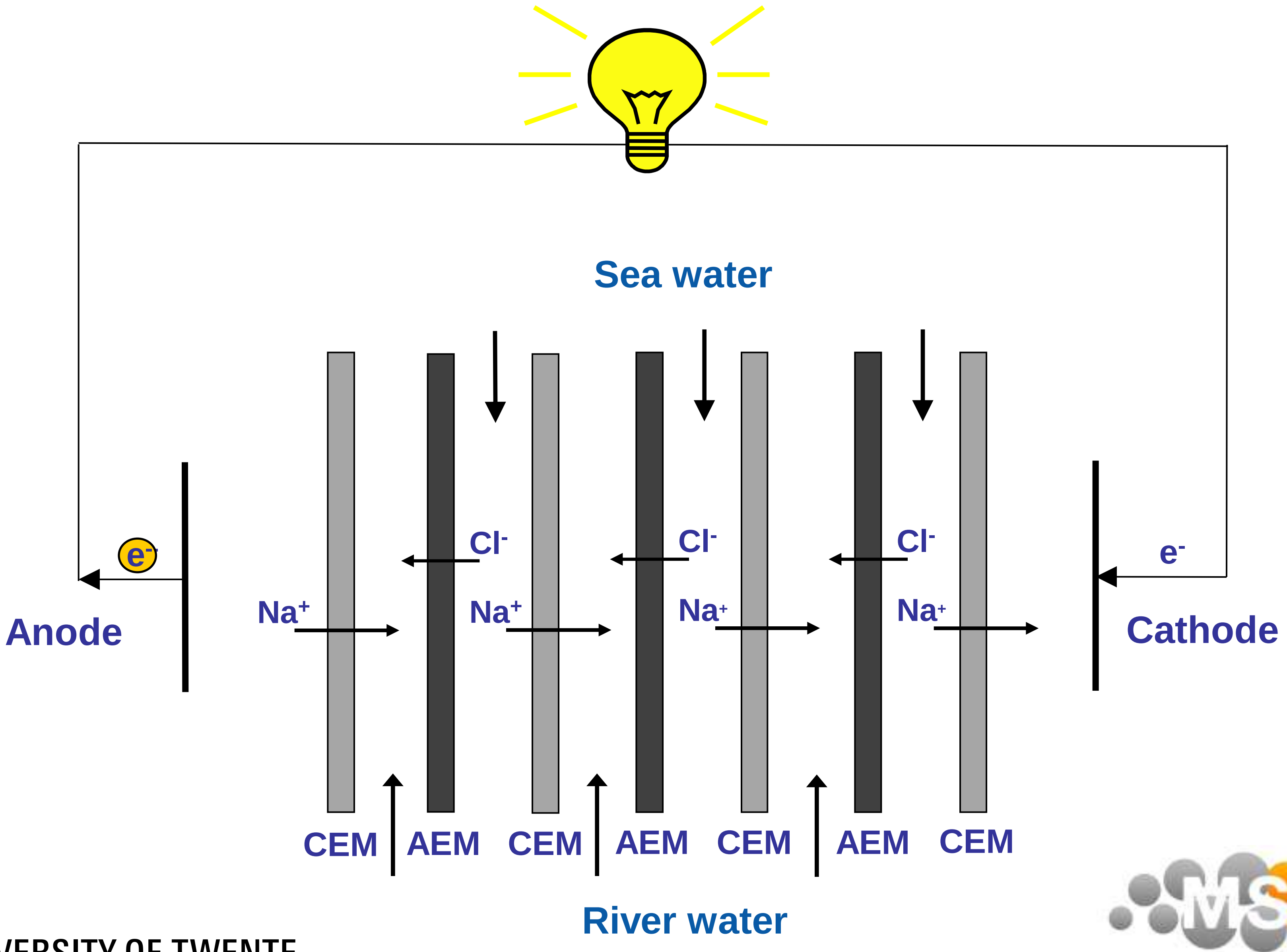


Potential worldwide: 1.4-2.6 TW

Practical potential NL: 1.5 GW

(15% of Dutch consumption)

Principle of RED



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Application of reverse electrodialysis

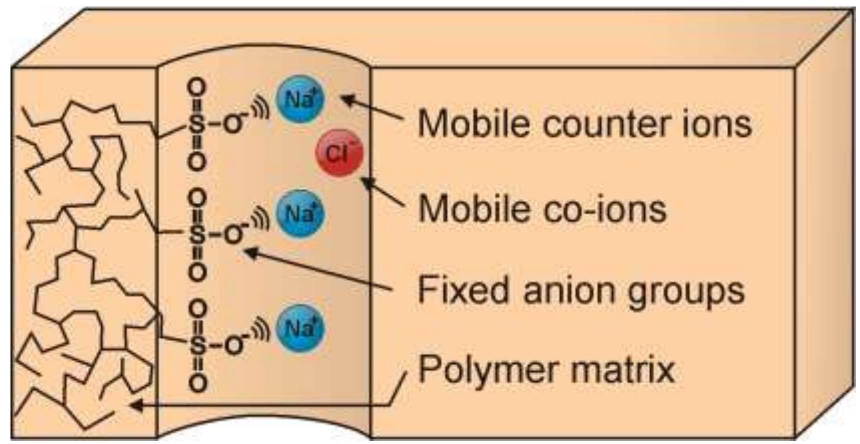
- Type of salt solutions
  - Mostly NaCl
  - Industrial salt streams[1]
  - Thermolytic solutions (e.g. ammonium bicarbonate, higher Δc)[2]

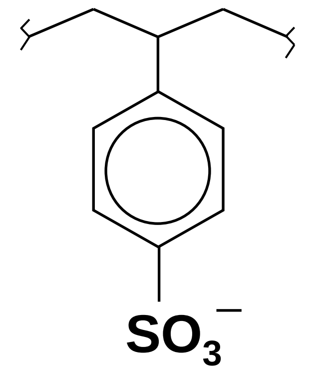
- Combination with other technologies
  - RED with seawater desalination and solar ponds[3]
  - RED with reverse osmosis (RO)[4]
  - Closed-loop ammonium carbonate RED cells for H_2 recovery[5]
  - RED combined with microbial fuel cell technology[6]

1. R. Audinos, J. Power Sources, 1983, 10, 203
2. G. M. Geise et al., ACS Macro Lett., 2013, 2, 814; M. C. Hatzell, B. E. Logan, J. Membr. Sci., 2013, 446, 449; X. Luo et al., Electrochem. Commun., 2012, 19, 25
3. E. Brauns, Desalin. Water Treat., 2010, 13, 53
4. W. Li et al, Appl. Energ., 2013, 104, 592
5. M. C. Hatzell, et al., Phys. Chem. Chem. Phys., 2014, 16, 1632
6. Y. Kim, B.E. Logan, Environ. Sci. Technol. 2011, 45, 5834

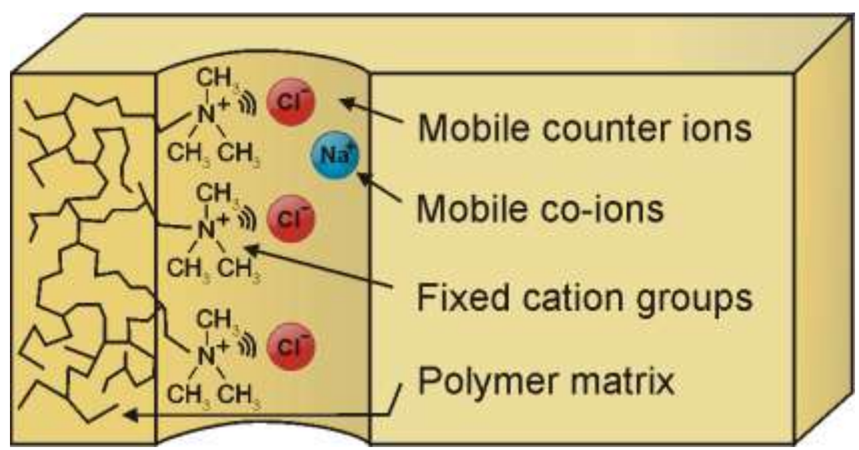
Ion exchange membranes for RED

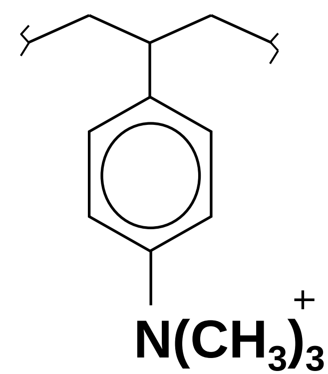
Cation exchange membrane (CEM)





Anion exchange membrane (AEM)





Membrane properties

Cation Exchange Membranes					
Membrane	Thickness (µm)	IEC (meq/g dry)	Permselectivity (%)	Resistance ($\Omega \times cm^2$)	
Fumasep®					
FKE	34	1.36	98.6	2.5	Electrodialysis, high selectivity
FKD	113	1.14	89.5	2.1	Diffusion dialysis for NaOH
Neosepta®					
CM-1	133	2.30	97.2	1.7	Low electrical resistance
CMX	164	1.62	99.0	2.9	High mechanical strength
Ralex®					
CMH-PES	764	2.34	94.7	11.3	Heterogeneous, Electrodialysis, Electrodeionization
Selemion®					
CMV	101	2.01	98.8	2.3	Electrodialysis

Dlugolecki et al., Journal of Membrane Science 319 (2008) 214.

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Membranes in RED

Comparaison de l'énergie obtenue en fonction de la nature et de la concentration de l'électrolyte pour les membranes Asahi (1, 3, 5) et Rhône-Poulenc (2, 4, 6): cas du recyclage total

Numéro de l'essai	1	2	3	4	5	6
Nature de l'électrolyte	NaCl		$ZnSO_4$			
ΔU(mesuré) (mV)	387	374	179	77	118	114
$\eta/I - r$ (Ω)	52	24	51	114	11	7
i (A/m^2)	3,82	4,61	0,37	0,15	0,25	0,24
$\dot{W}$ (mW)	5,92	6,24	0,26	0,05	0,12	0,11
$\dot{\omega}$ (mW/m^2)	148,0	156,0	6,50	1,25	3,00	2,75

1, 3, 5: Homogeneous; 2, 4, 6: Heterogeneous; Maximum power output: 0.4 W/m^2

R. Audinos, J. Power Sources, 1983, 10, 203.

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Membranes in RED

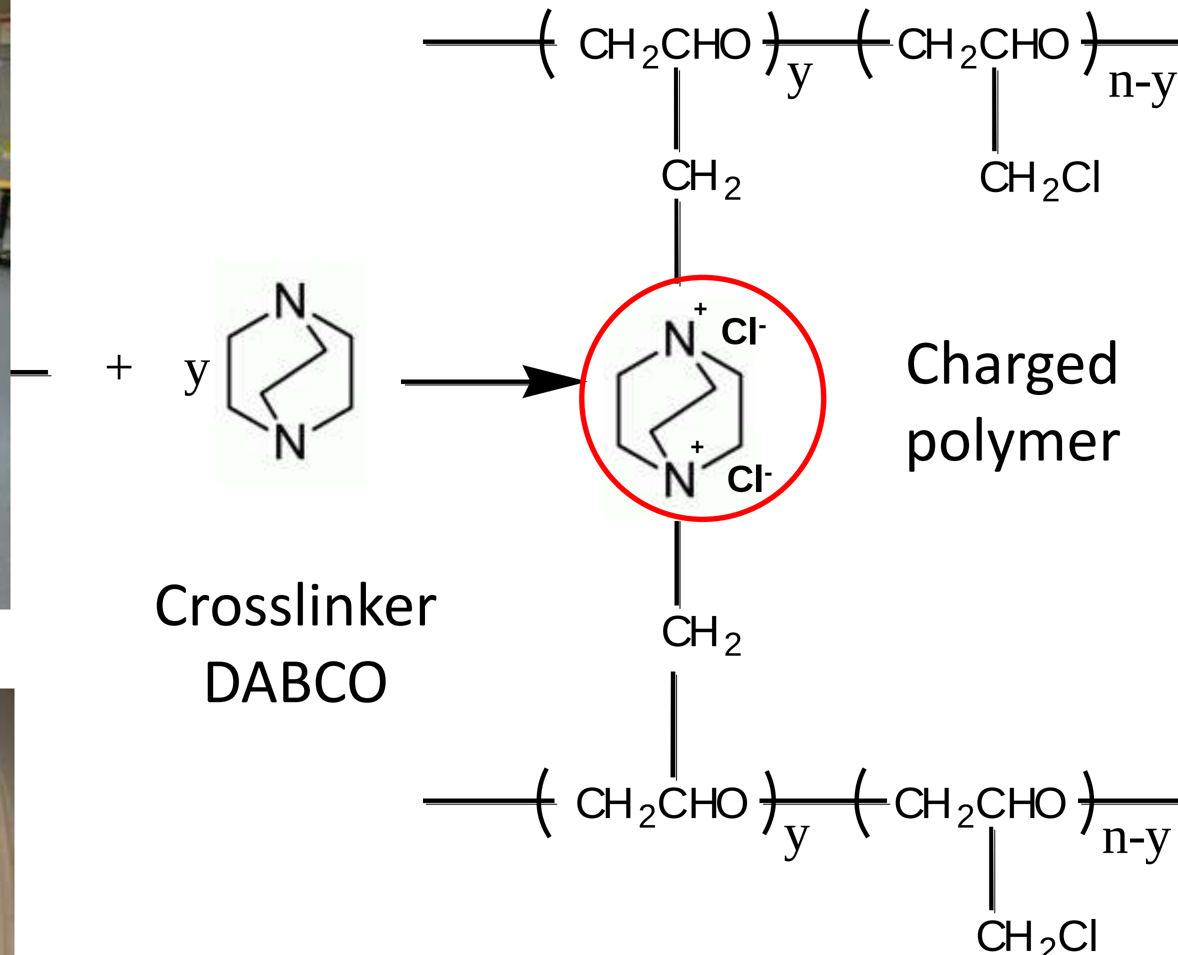
	a	b	c	d	e	f
	Qianqiu heterog.	Qianqiu homog.	Fumasep FAD/FKD	Selemion AMV-CMV	Neosepta ACS-CMS	Neosepta AMX-CMX
Values at optimal current density ($J = J_{opt}$)						
Exergy decrease feed (X_{cons}) (W/m²)	1.88	5.09	5.08	4.07	1.70	4.80
Thermodynamic exergy eff. (η_T) (%)	26	21	23	29	35	14
Power density (P_u) (W/m²)	0.49	1.05	1.17	1.18	0.60	0.65
Response product ($R_P = P_u * \eta_T$) (W/m² %)	13	22	27	34	21	9

- Response product = Power density x Thermodynamic efficiency
- Highest for Selemion AMV-CMV
- No clear relationship between response product and individual membrane properties (selectivity)
- Membrane resistance, osmosis and co-ion transport affect performance

J. Veerman et al., J. Membr. Sci., 2009, 327, 136.

Membrane design

Polymer
PECH

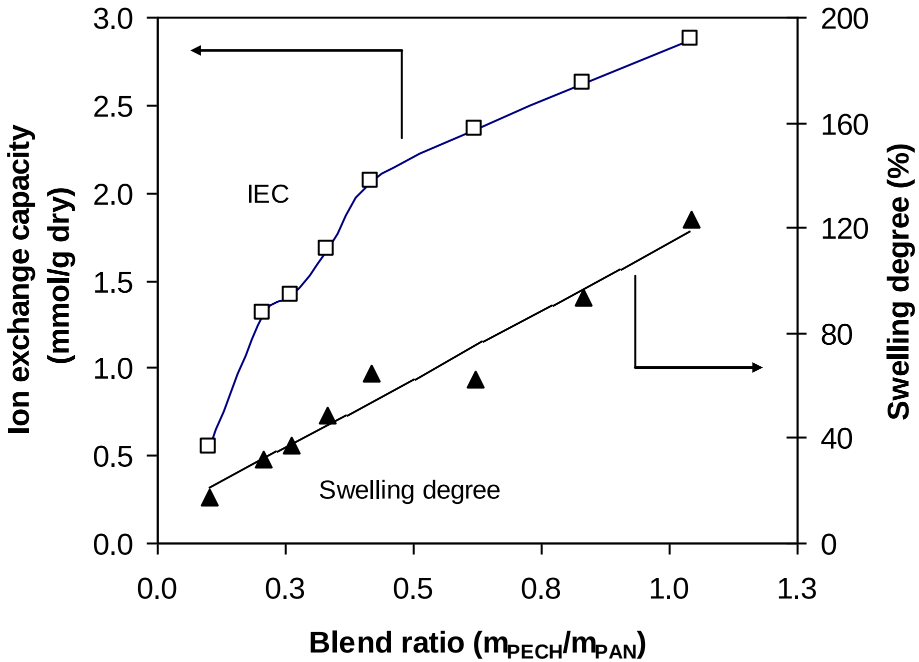


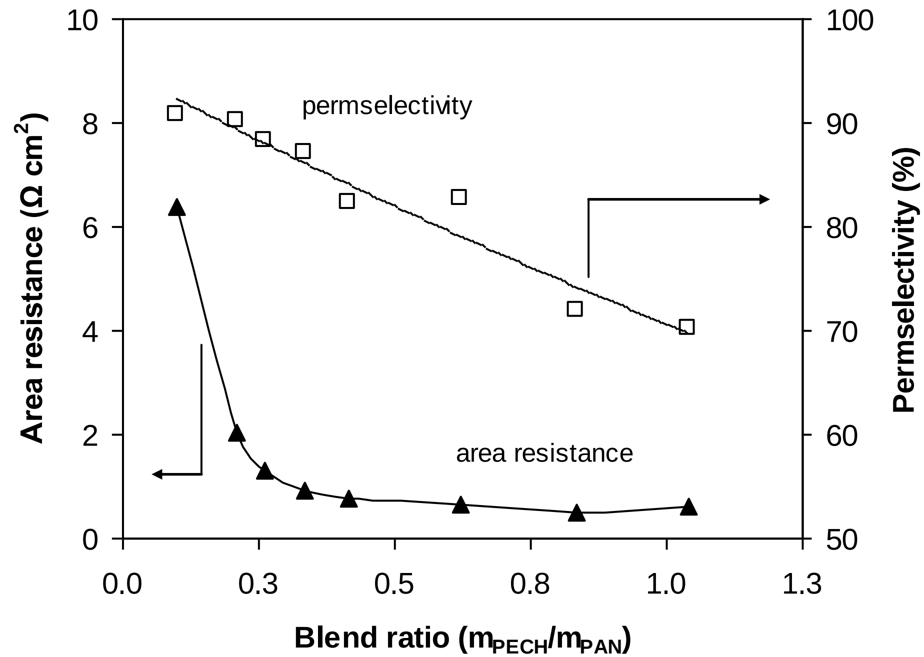
Crosslinker
DABCO

Charged
polymer

P. Altmeier, Patent 5,746,917 (1998); Bolto and Jackson, Reactive polymers 2 (1984) 209-222.

Membrane design





Membrane resistance
is essential

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Enver Guler et al., ChemSusChem
5 (11) (2012) 2262-2270.

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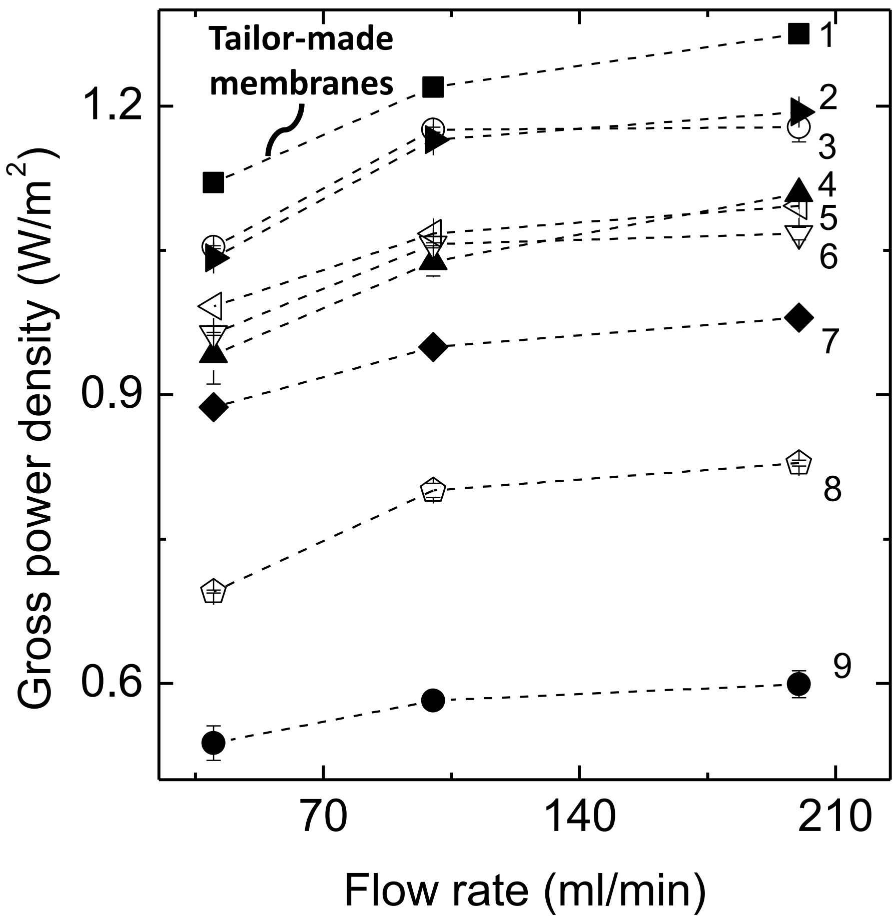
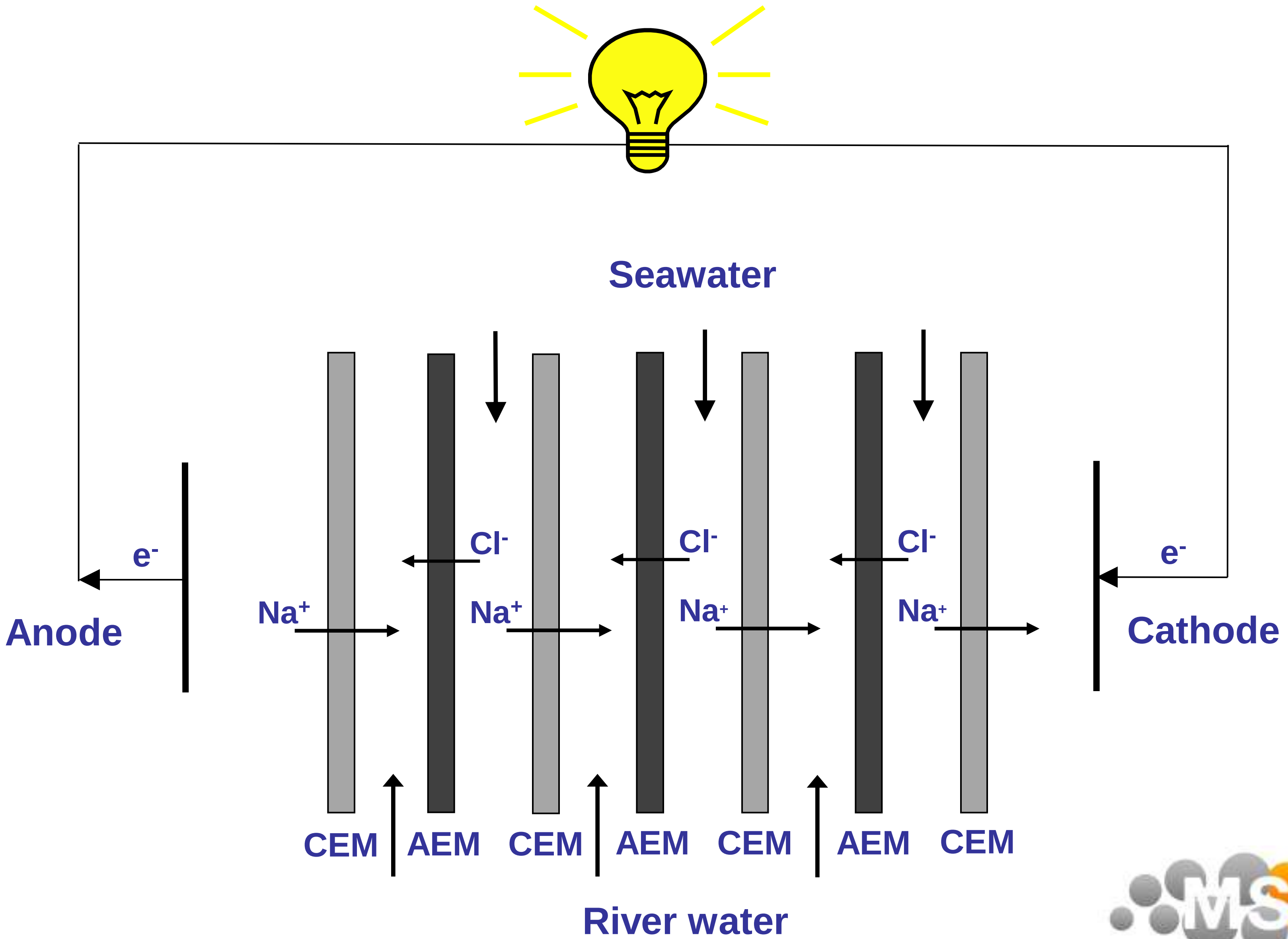
Membrane design



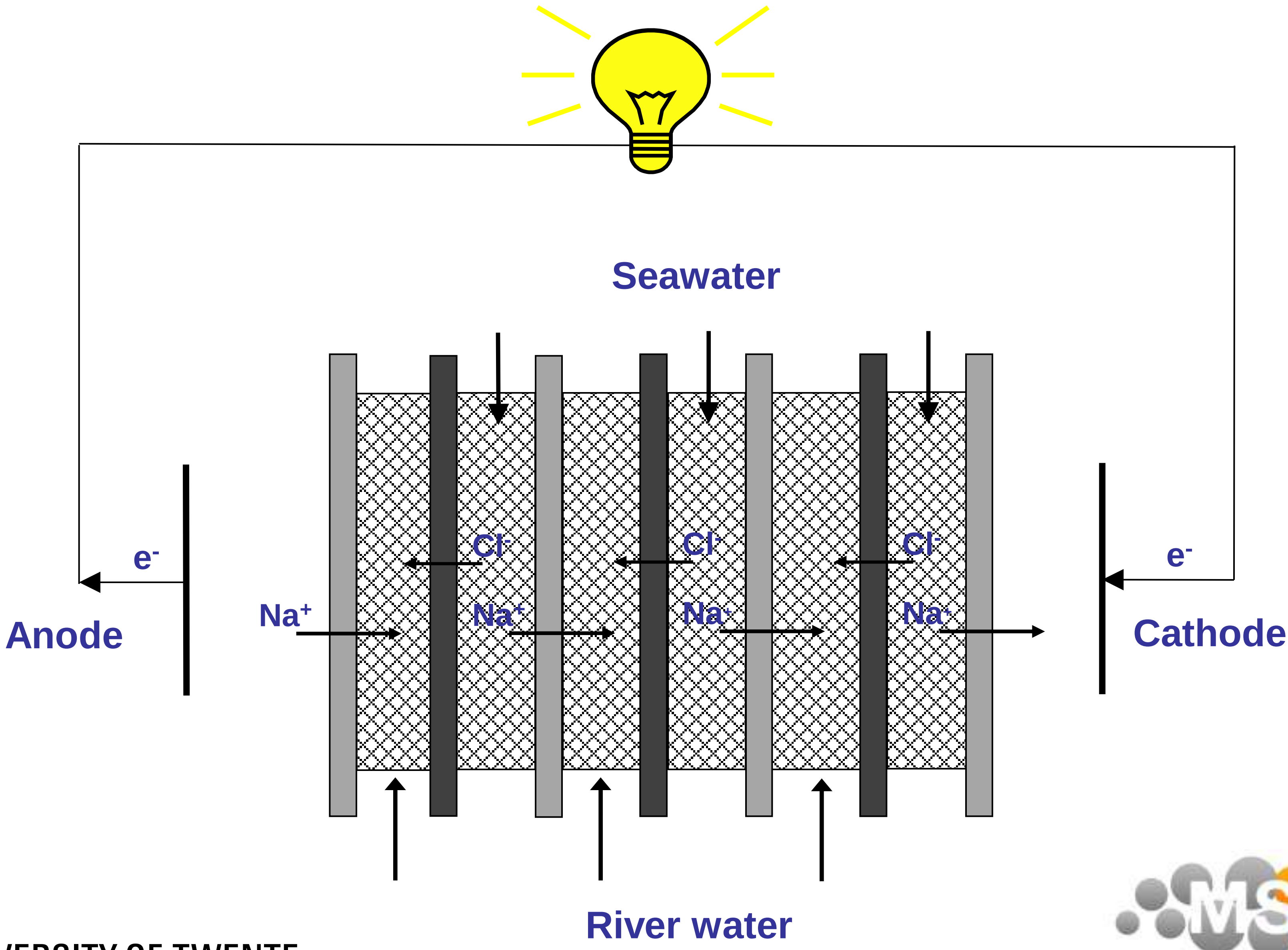
1 SPEEK 65/PECH B2
2 CMX/PECH B2
3 SPEEK40/PECH B2
4 FKS/FAS
5 SPEEK 65/AMX
6 CMX/AMX
7 SPEEK 40/AMX
8 Qianqui
9 CMH-PES/AMH-PES

Enver Guler et al., ChemSusChem 5 (11) (2012) 2262-2270;
Journal of Membrane Science 446 (2013) 266–276.

Principle of RED

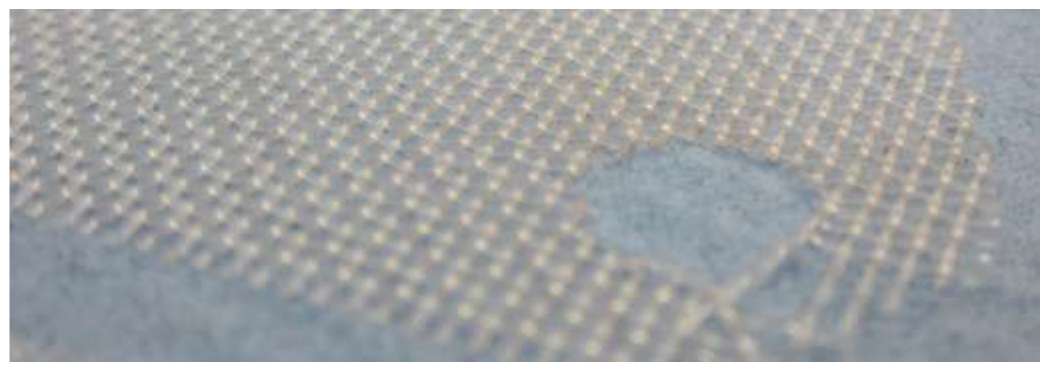


Principle of RED



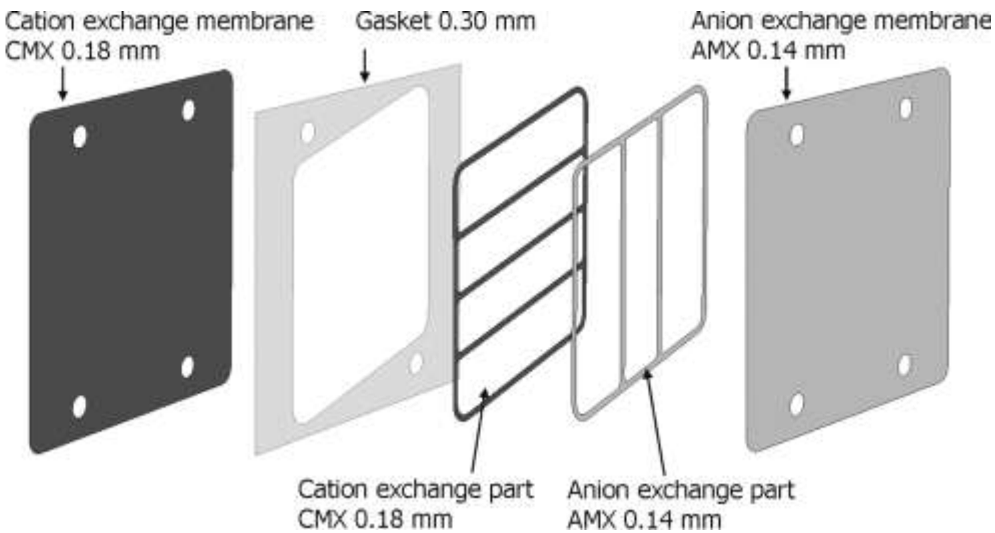
Spacers in RED

- Thinner spacers: higher gross power densities but higher pressure drop
- Membranes traditionally separated by non conductive spacers



Ion conductive spacers

- Integration of spacer and membrane functionality
- Microstructured membranes



P. Dlugolecki et al., J. Membrane Sci. 347 (2010) 101;
Environ. Sci. & Tecnol. 43 (2009) 6888

Ion conductive spacers

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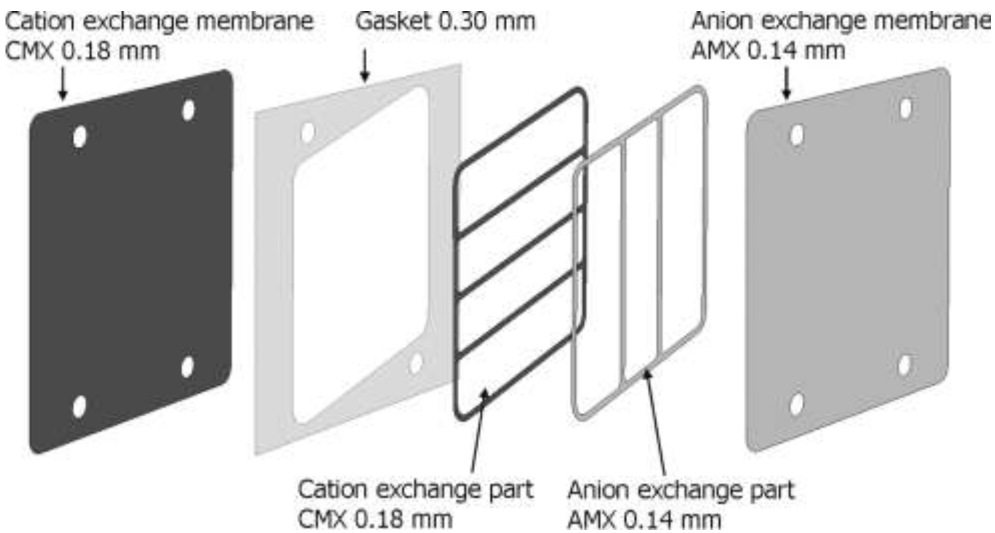

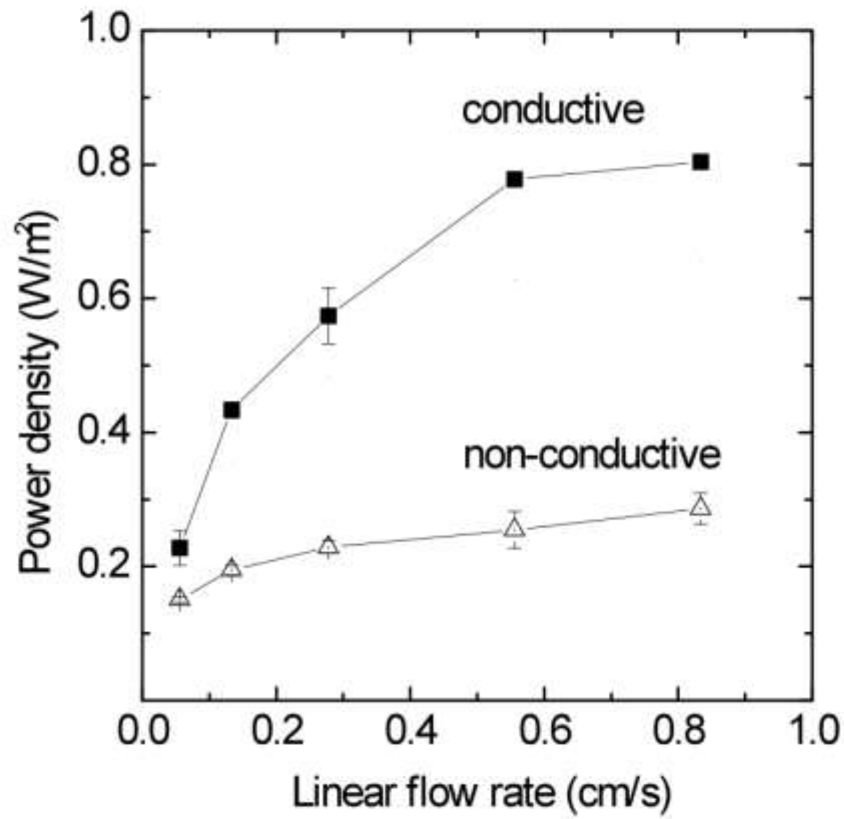

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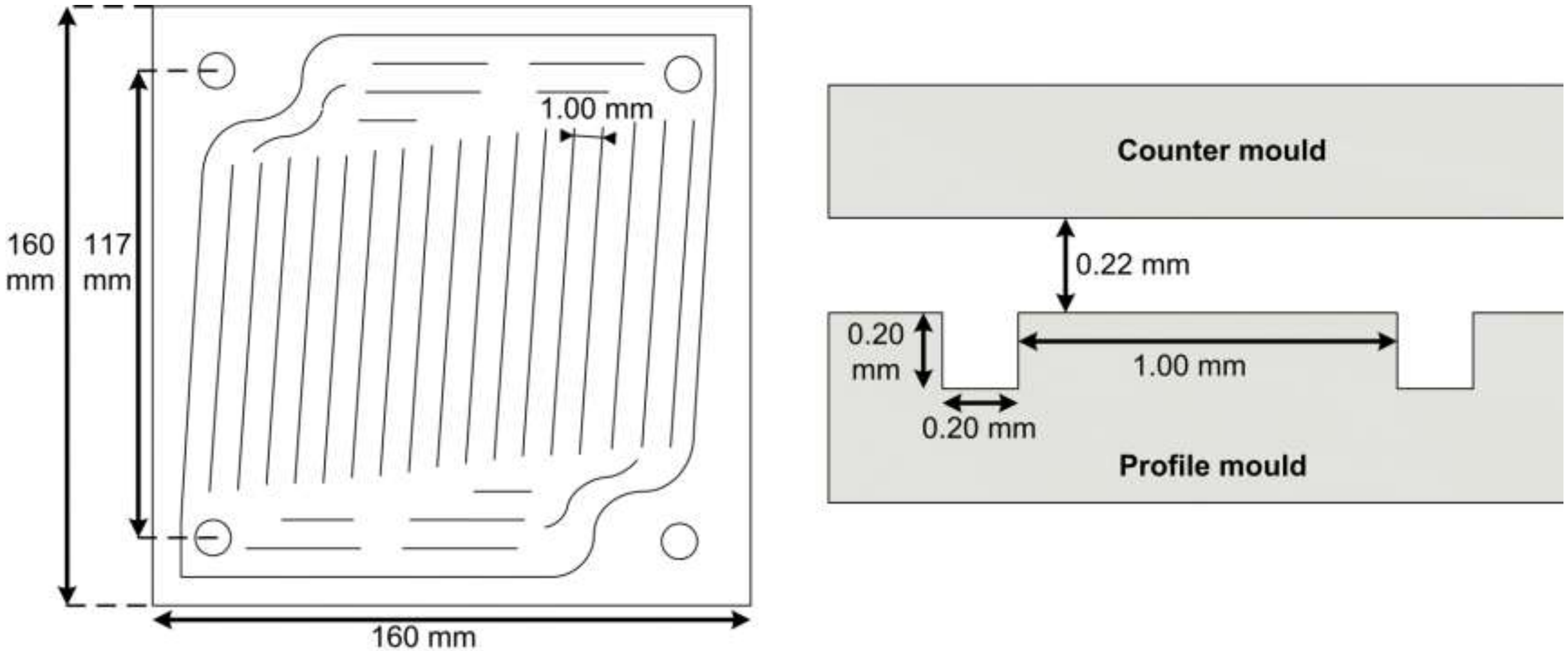
Microstructured membranes – hot pressing

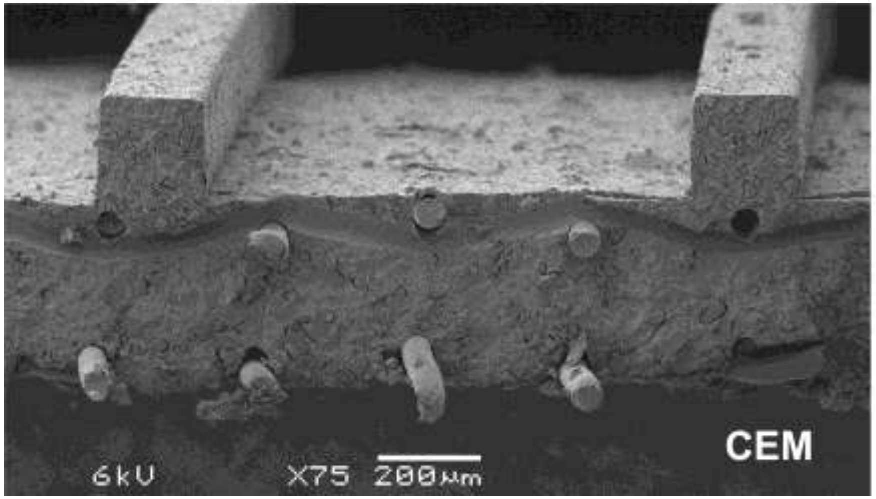


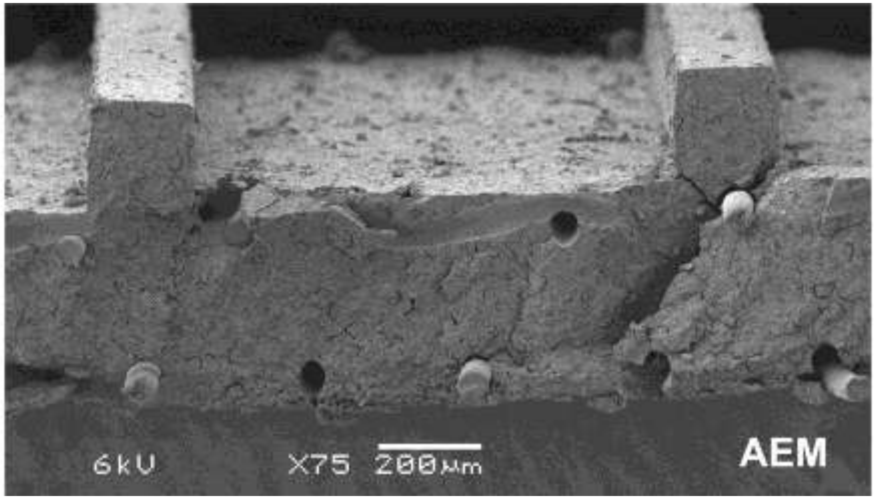
Hot-pressing of commercial membranes

David Vermaas et al., Journal of Membrane Science 385-386 (2011) 234-242.

Microstructured membranes – hot pressing

Profiled CEM (Ralex - CMH) and AEM (Ralex - AMH)





David Vermaas et al., Journal of Membrane Science 385-386 (2011) 234-242.

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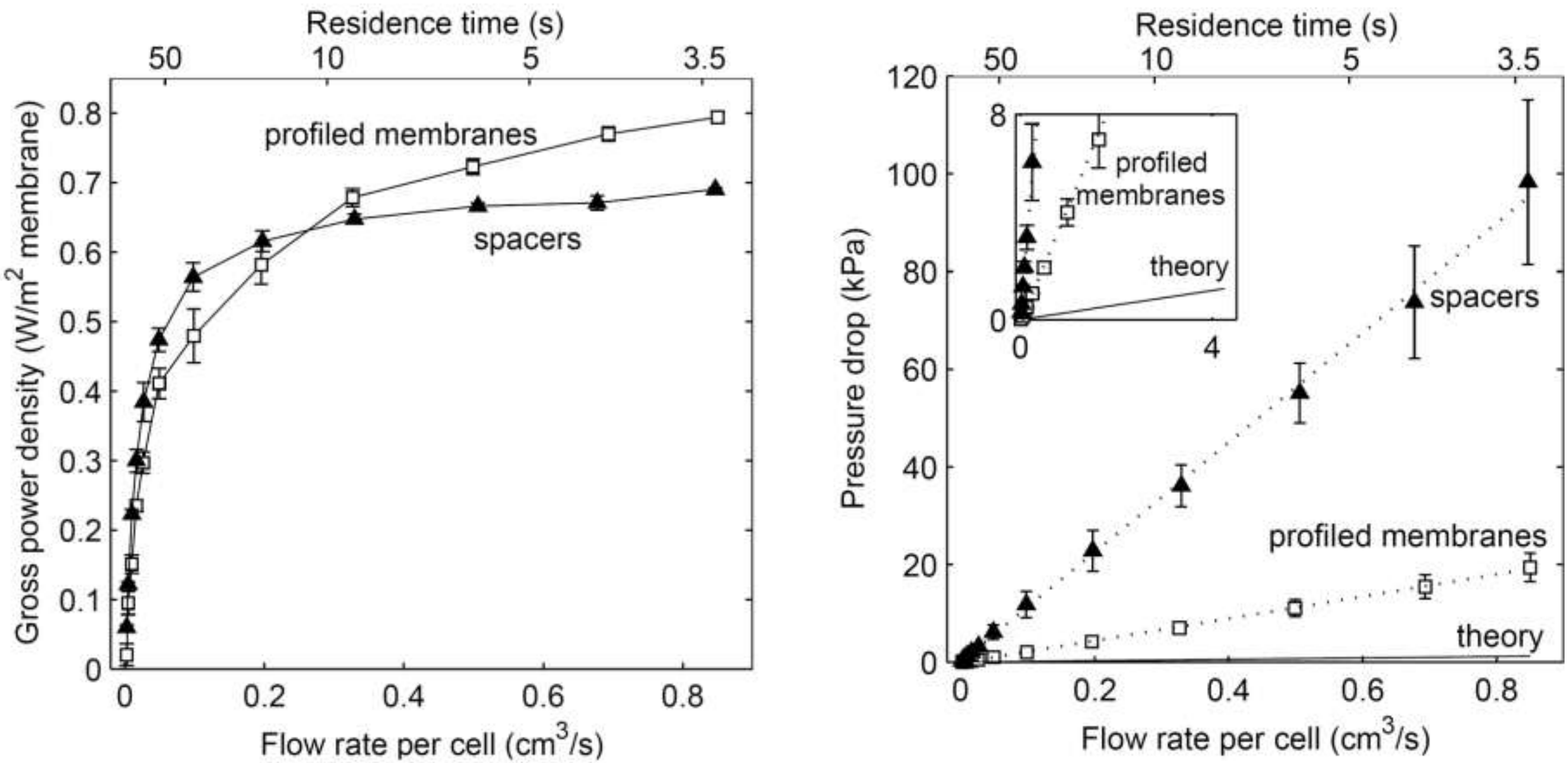
Microstructured membranes – hot pressing



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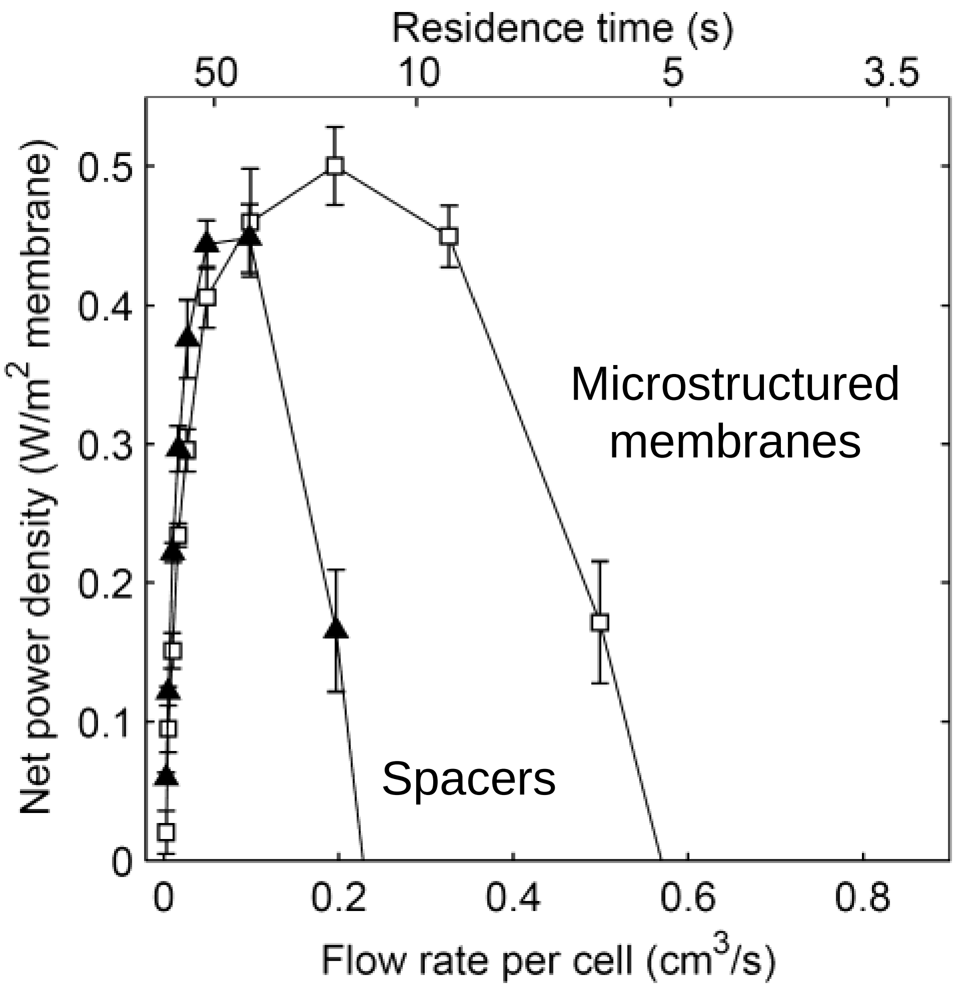

David Vermaas et al., Journal of Membrane Science 385-386 (2011) 234-242.

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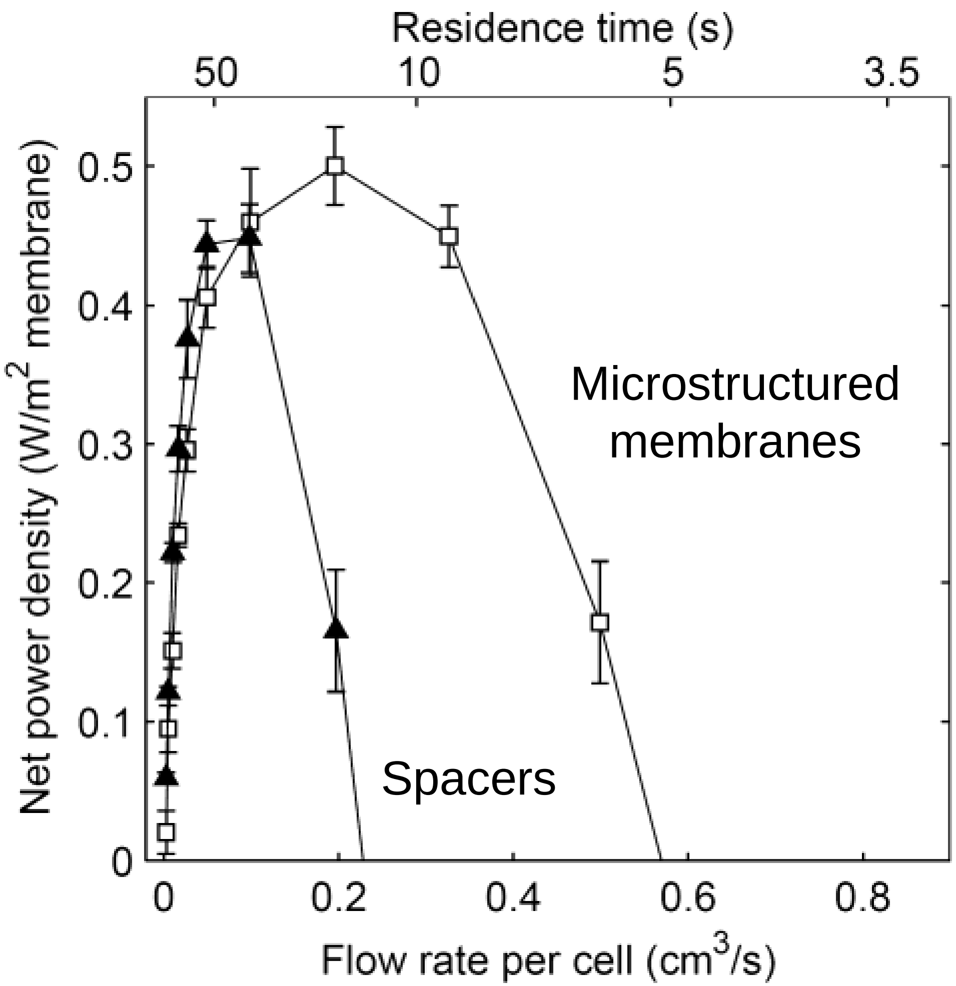
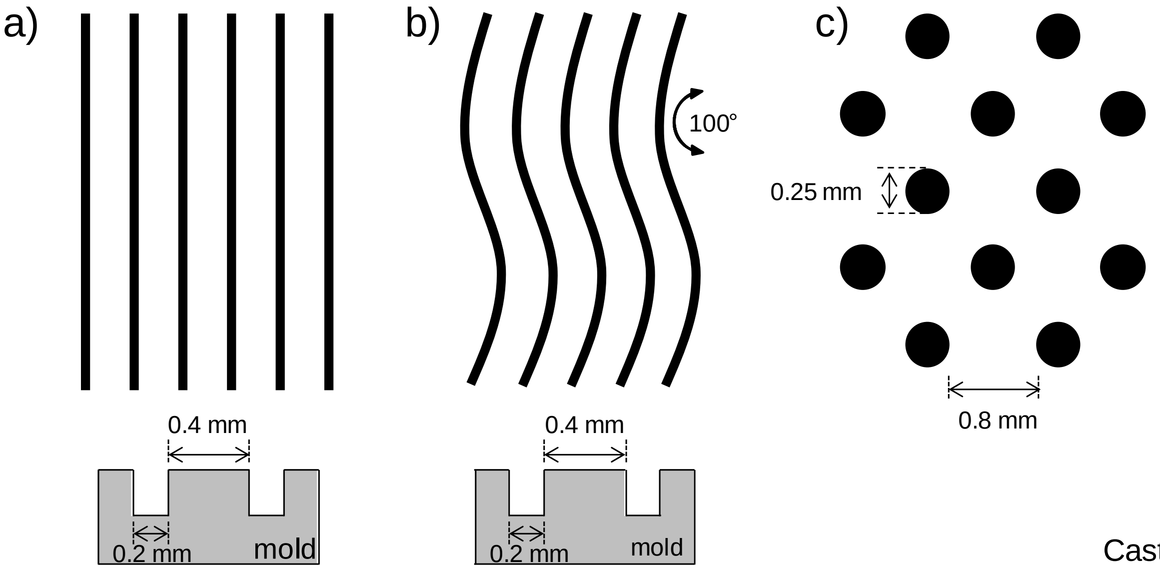
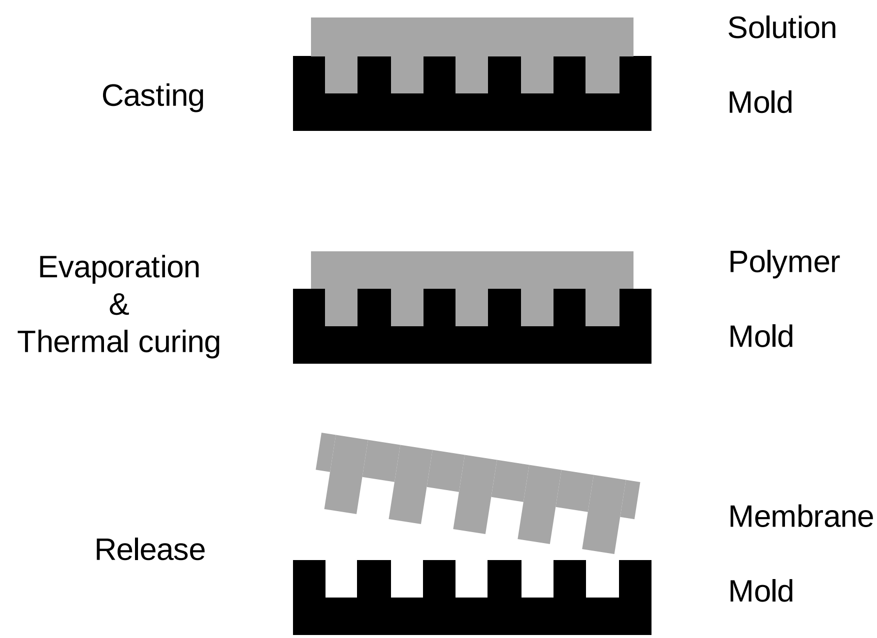


- Microstructured spacers: small improvement in net power
- But: due to geometry of the structures, mixing is poor and effect of boundary layers is dominant

David Vermaas et al., Journal of Membrane Science 385-386 (2011) 234-242.

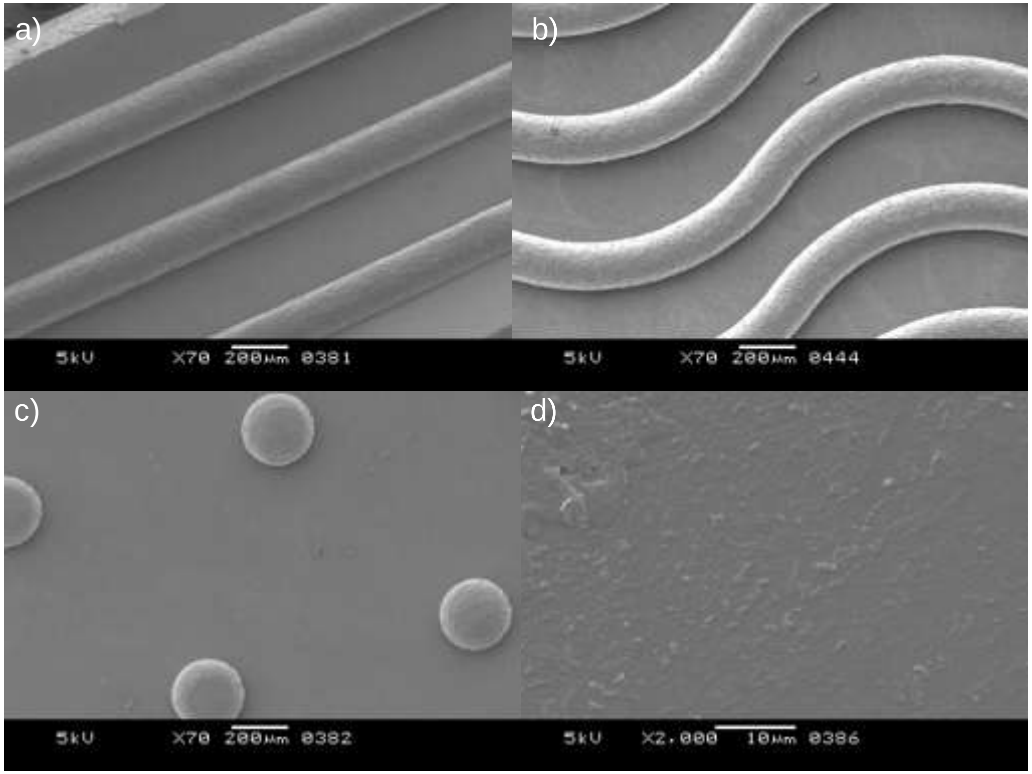
Microstructured membranes – Membrane casting





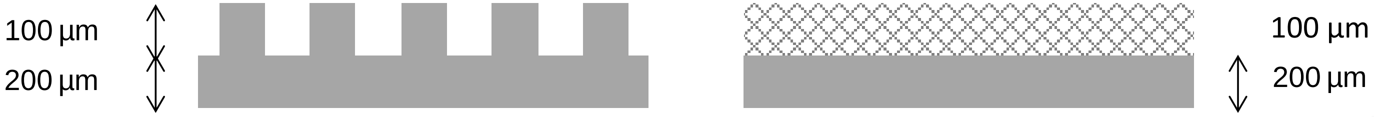
Guler et al., Journal of Membrane Science 458 (2014) 136

Microstructured membranes – Membrane casting



Structured membrane

Flat membrane



Guler et al., Journal of Membrane Science 458 (2014) 136

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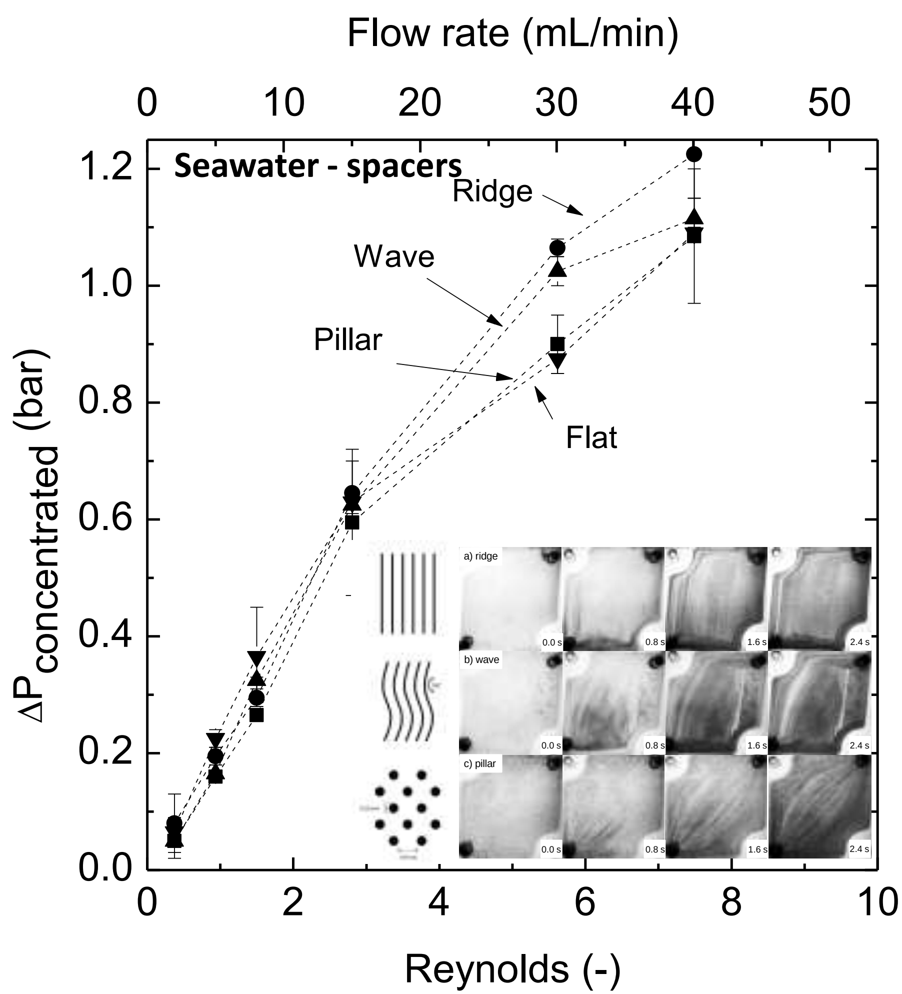
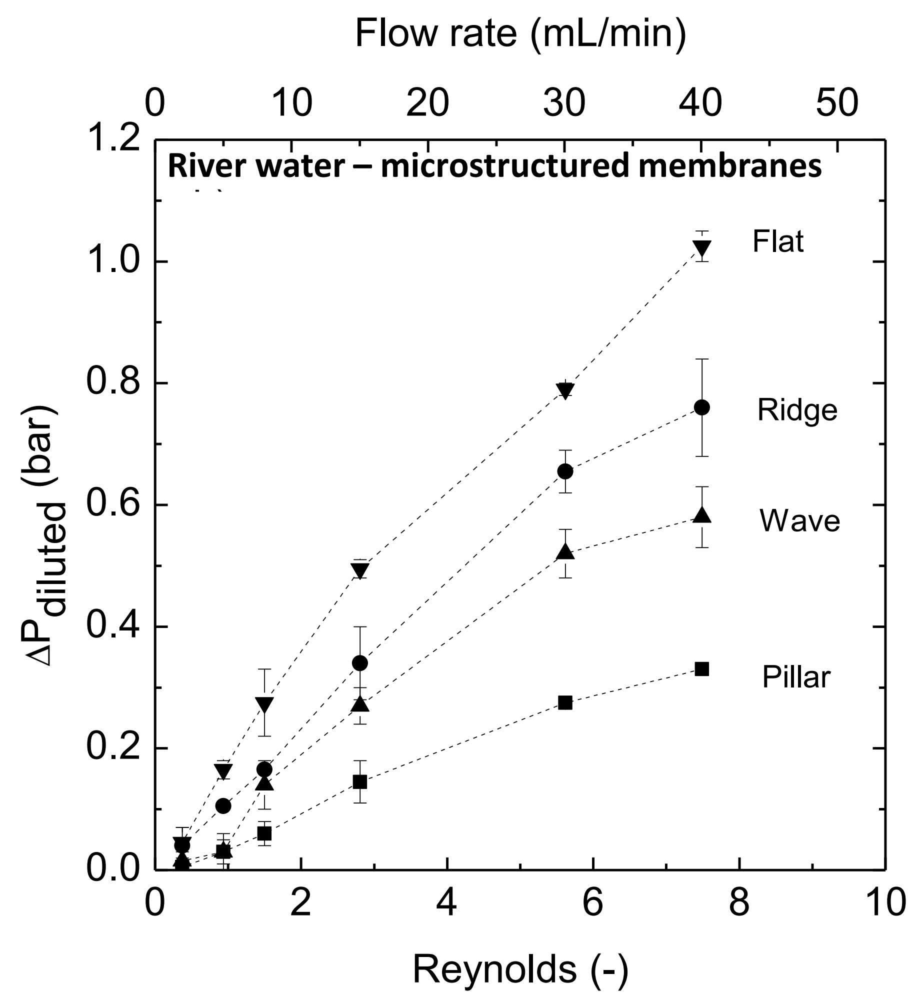
Microstructured membranes – Membrane casting





Guler et al., Journal of Membrane Science 458 (2014) 136

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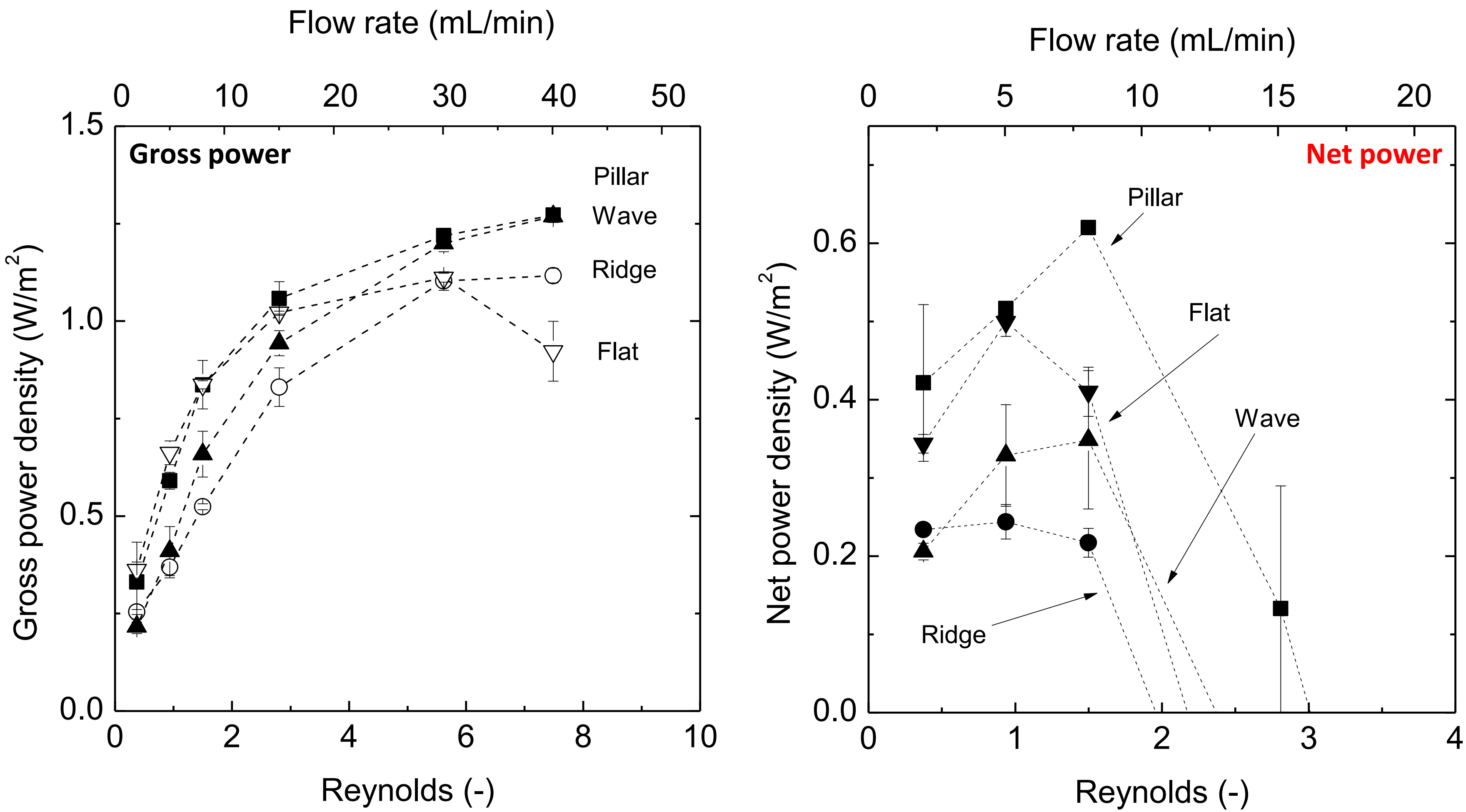
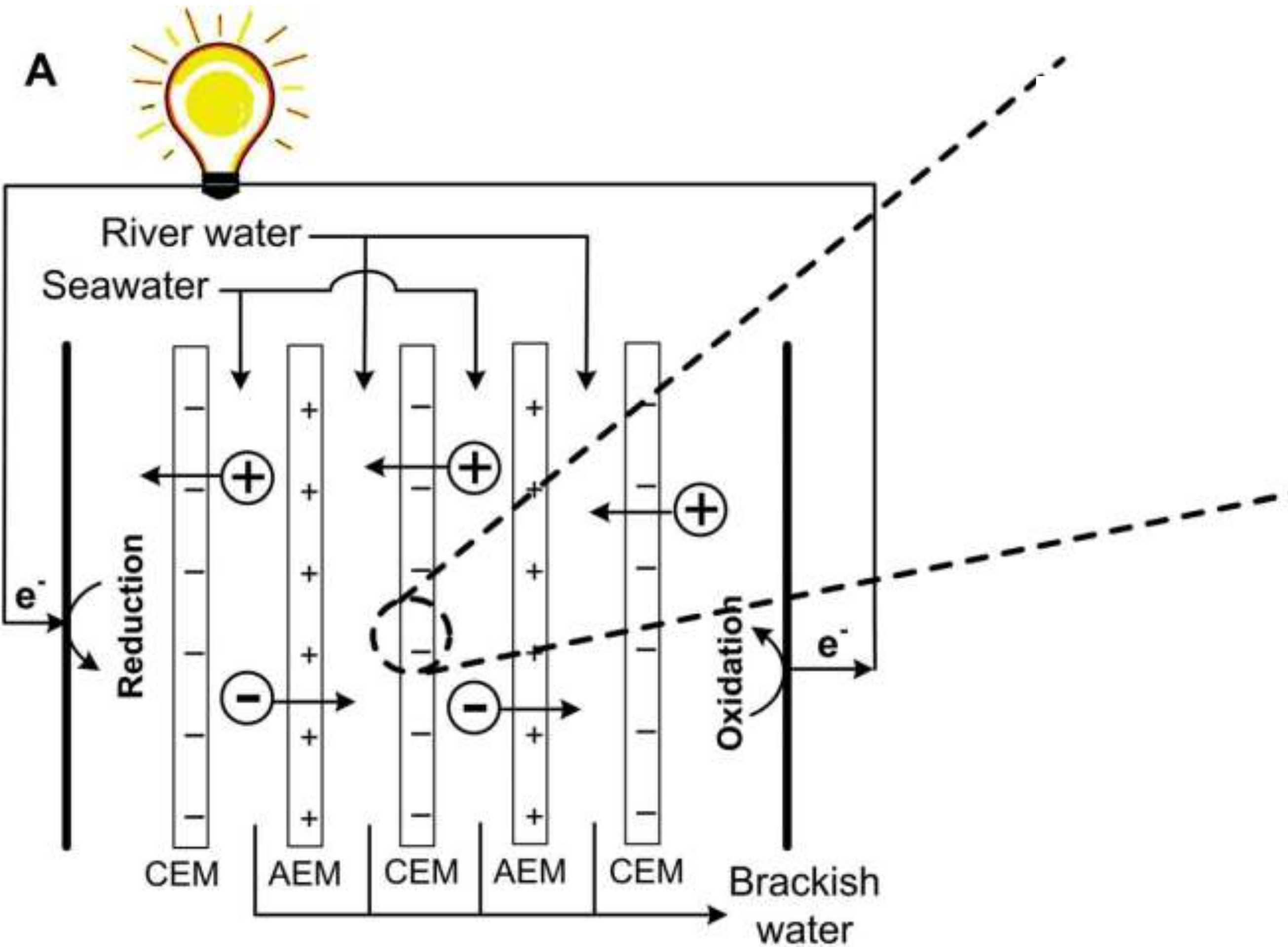


Guler et al., Journal of Membrane Science 458 (2014) 136

Towards the application: Real feed waters



J.W. Post et al., Journal of Membrane Science 330 (2009) 65; D Vermaas et al., Water Research 47 (2013) 1289

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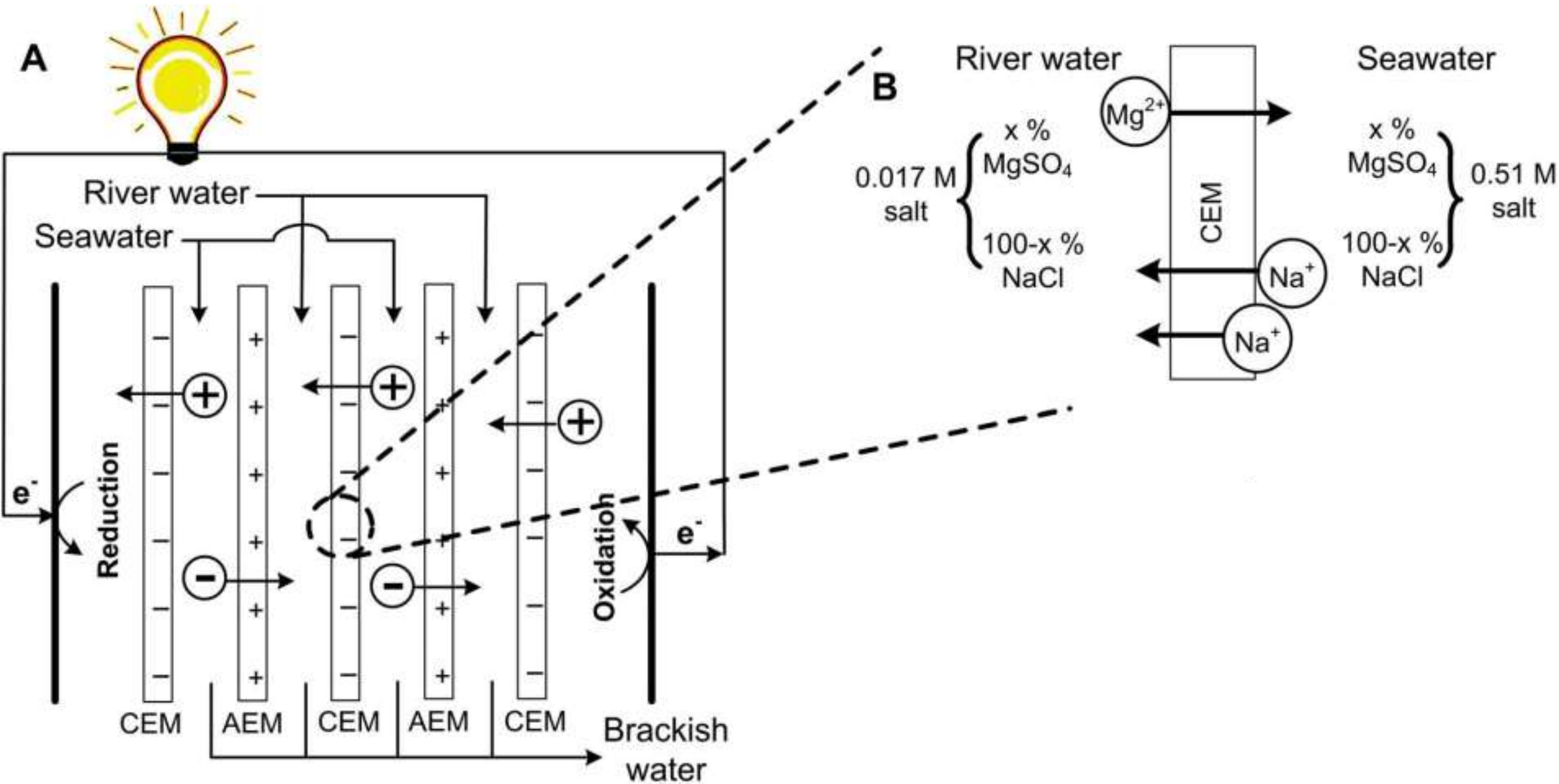
Real seawater and river water: $MgSO_4$



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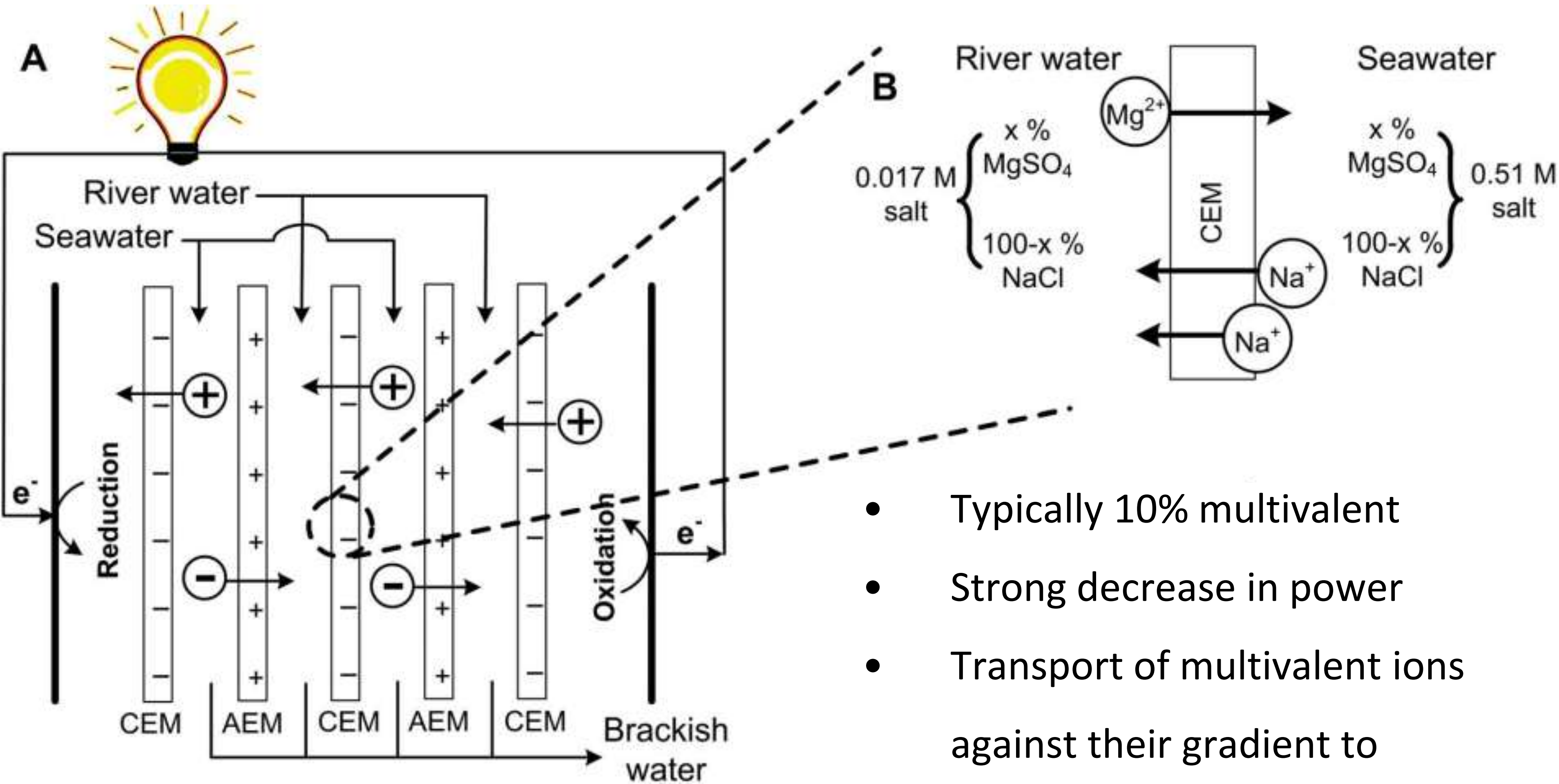

- Typically 10% multivalent
- Strong decrease in power
- Transport of multivalent ions against their gradient to compensate for charge transport of monovalent ions

J.W. Post et al., Journal of Membrane Science 330 (2009) 65; D Vermaas et al., Water Research 47 (2013) 1289

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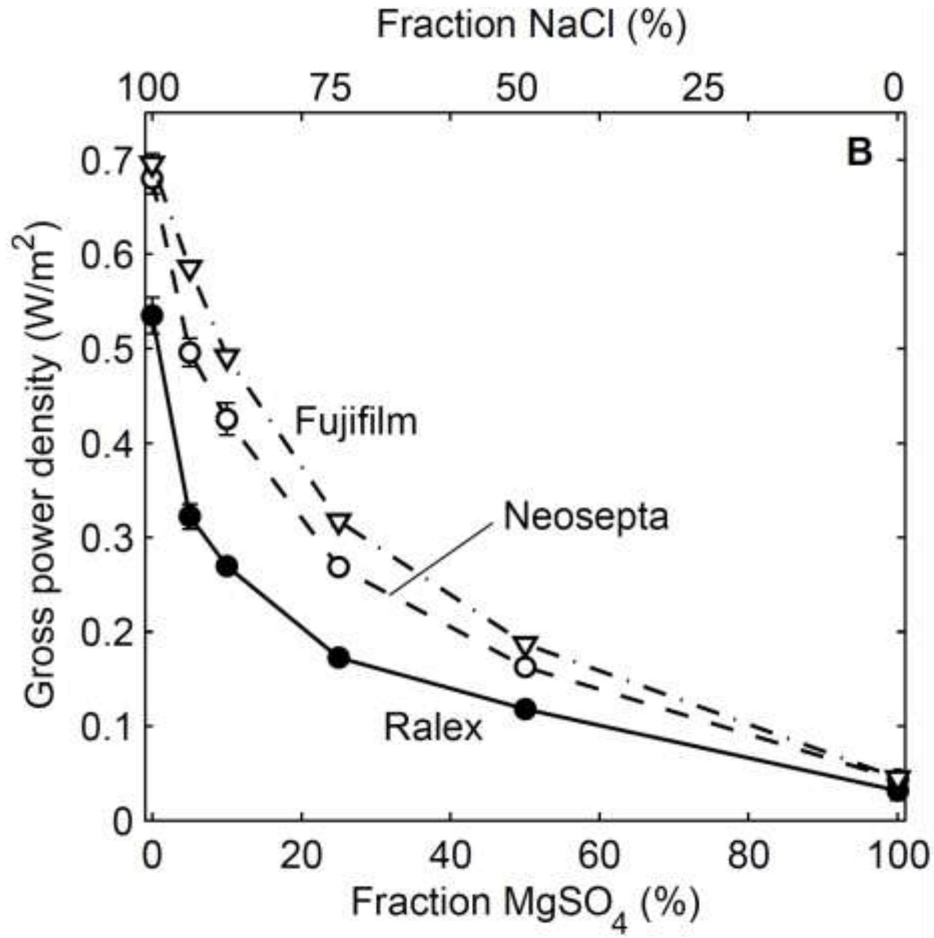

D. Vermaas et al., Water Research 47 (2013) 1289

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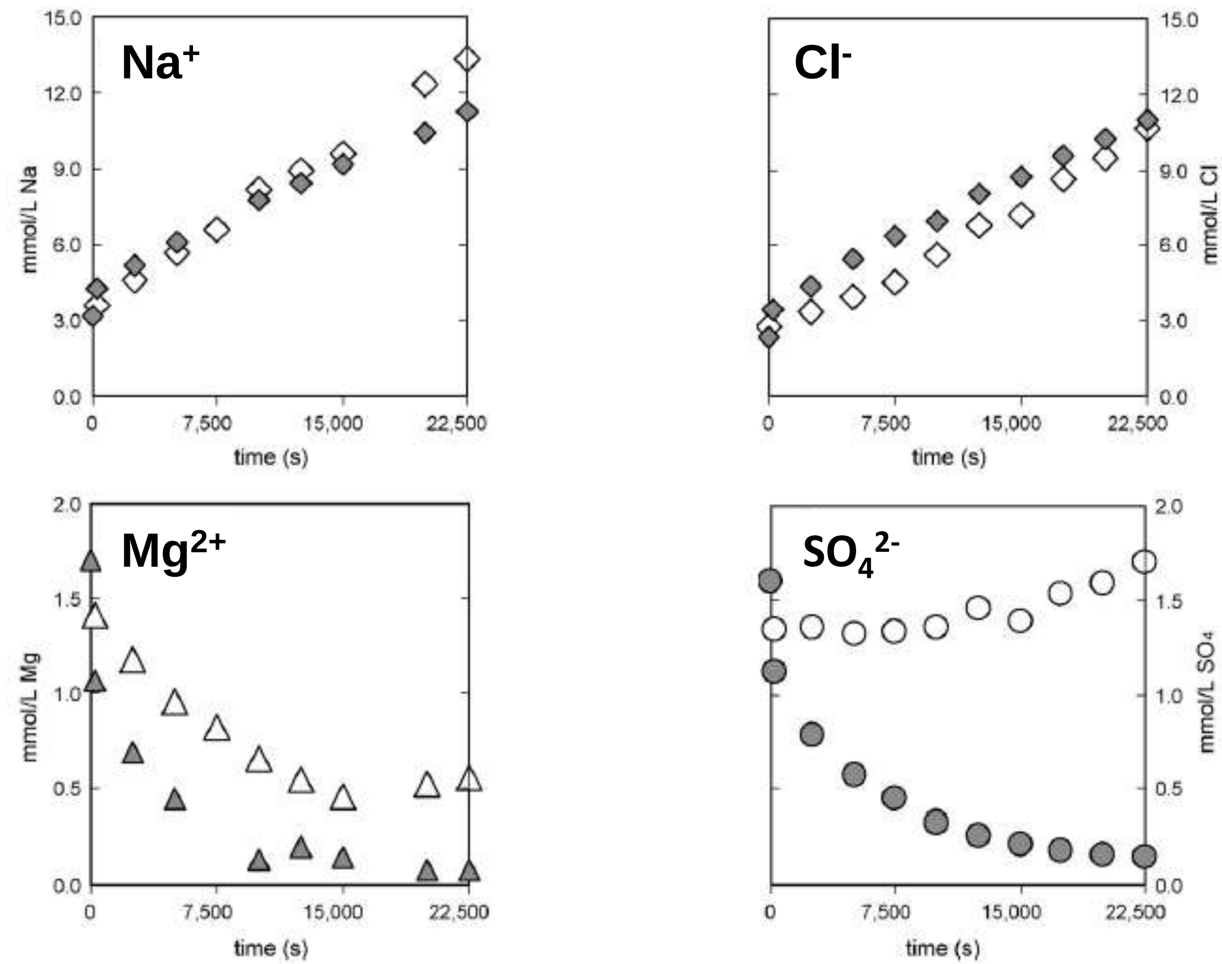
Monovalent ion selective membranes?

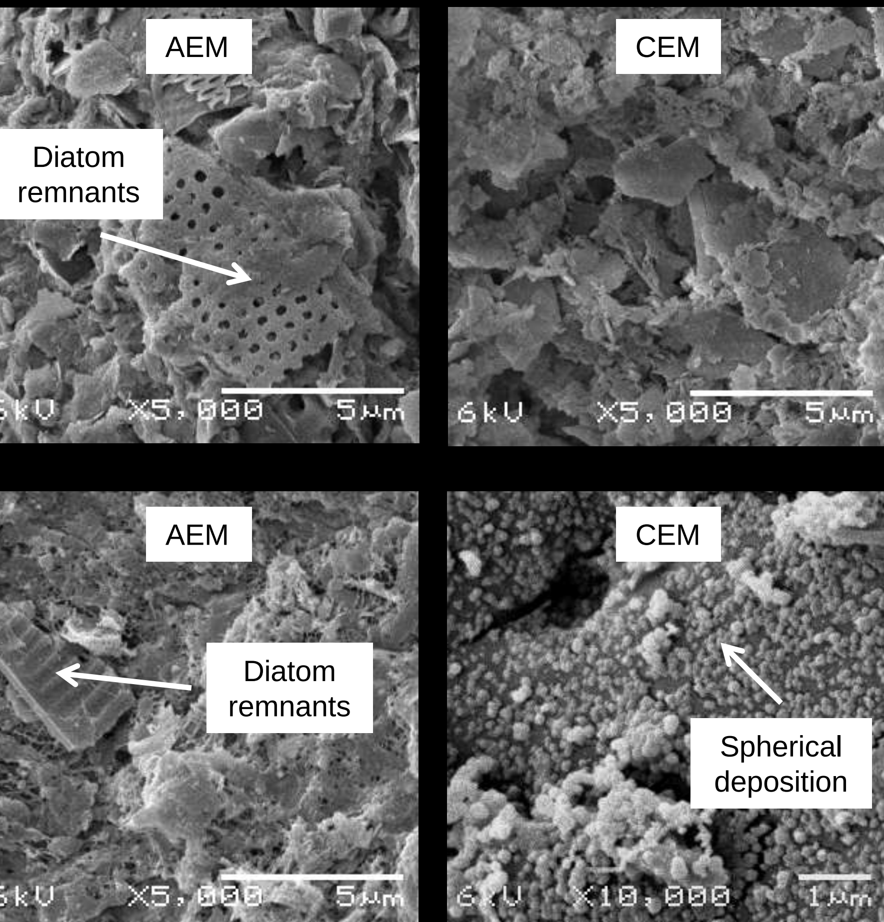


Ion concentrations in river water compartment

Filled symbols: standard-grade; open symbols: monovalent-ion selective membranes

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

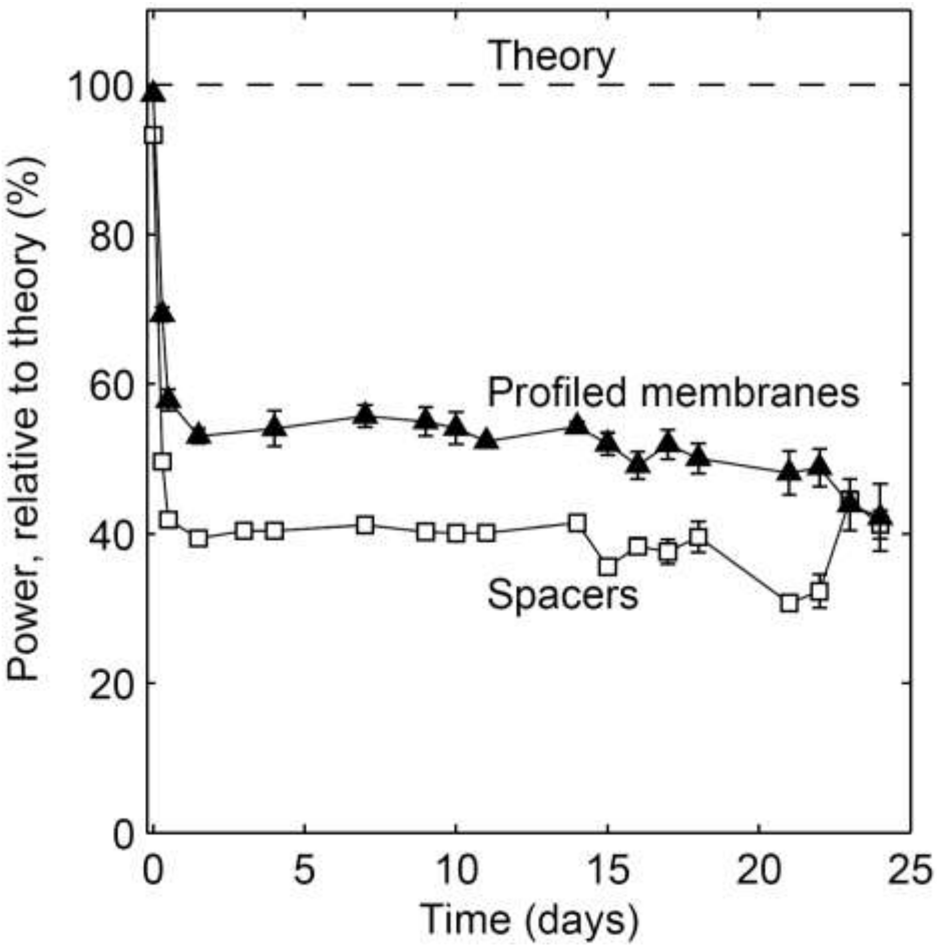
Real river water



Real seawater

- Grey-brown material in spacer open area
- Fouling especially on AEM (HA)
- Less fouling on CEM
- Membrane charge is important
- Spacers strongly enhance fouling

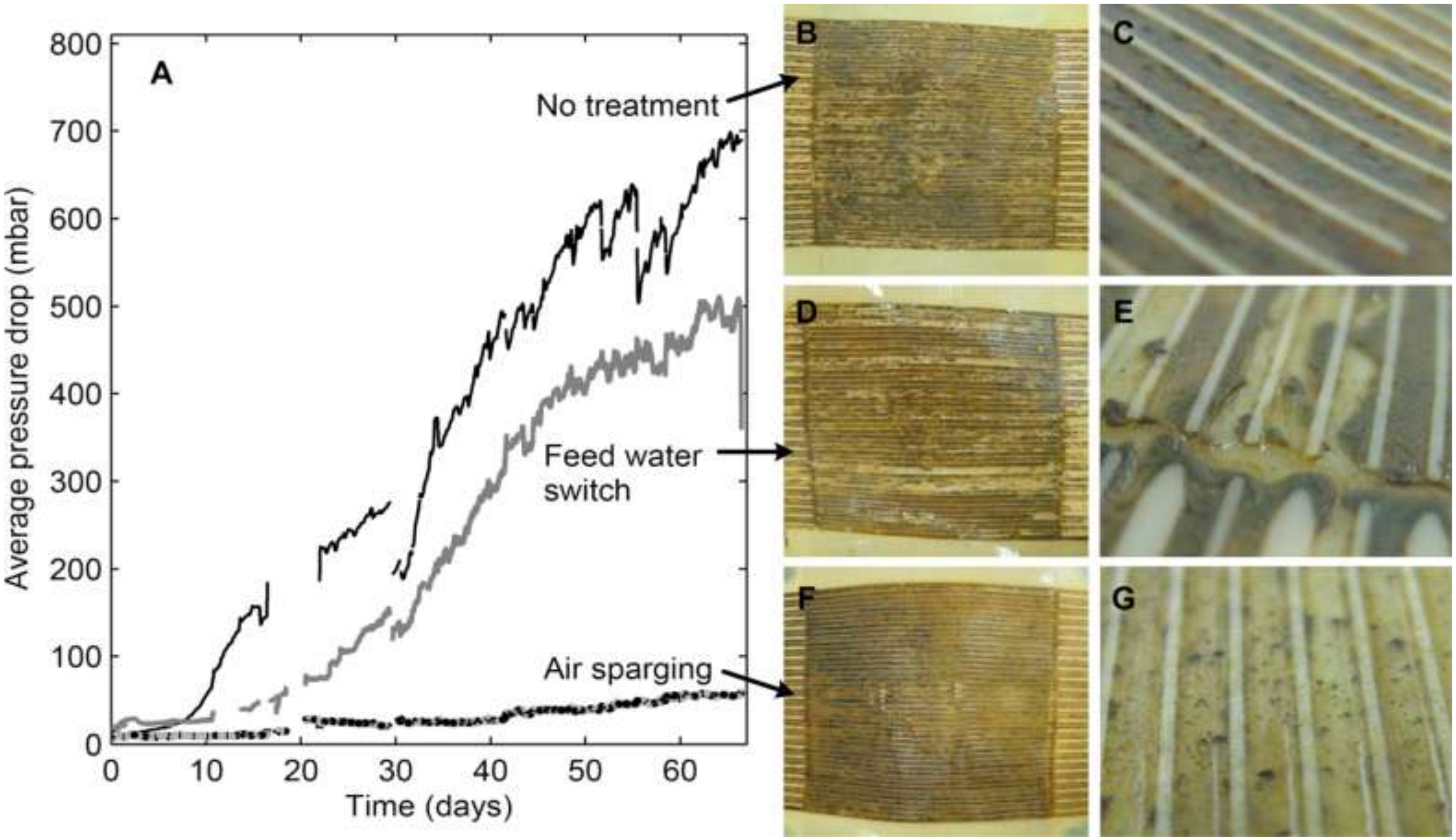
Real seawater and river water: Fouling



- Values 'normalized' (net power)
- Organic fouling covers the charge of the membrane
  → Selectivity and resistance
- Profiled membranes show reduced fouling
- Fouling control?

David Vermaas et al., Water Research 47 (2013) 1289

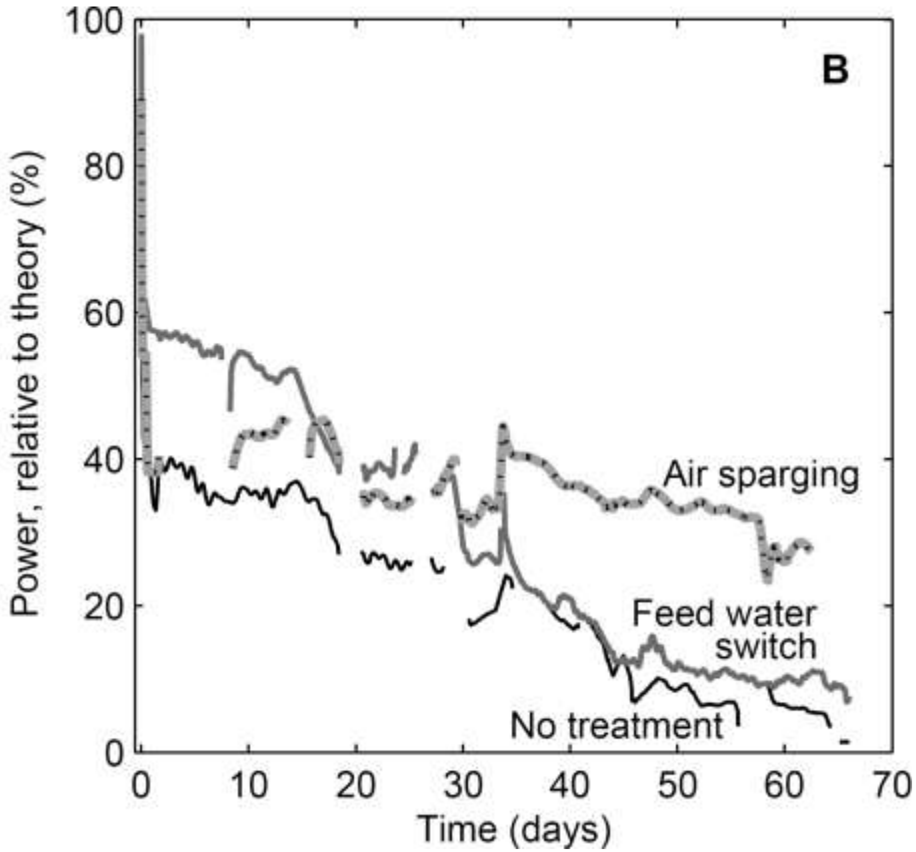
Real seawater and river water: Fouling reduction



- Feed water switching: every 30 minutes
- Air sparging: every 30 minutes, 30 sec.

David Vermaas et al., Environ. Sci. Technol. 2014, 48, 3065

Real seawater and river water: Fouling reduction



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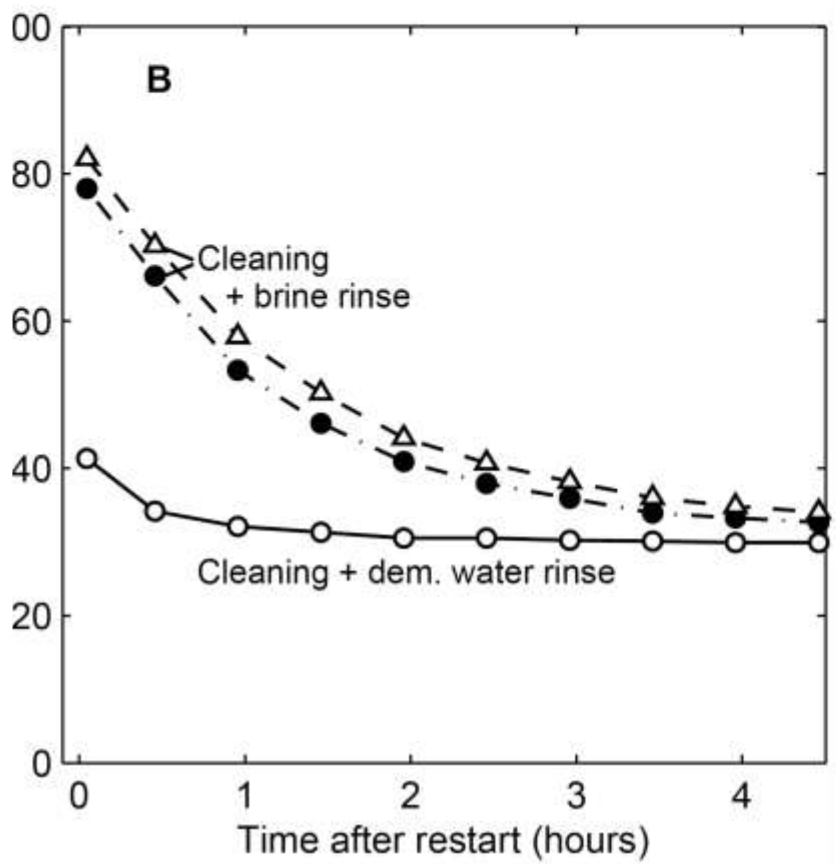


- Stop, cleaning manually with a brush and stored in demineralized water or 5 M NaCl (brine) for 3 days, followed by power generation.

David Vermaas et al., Water Research 47 (2013) 1289

Future perspective

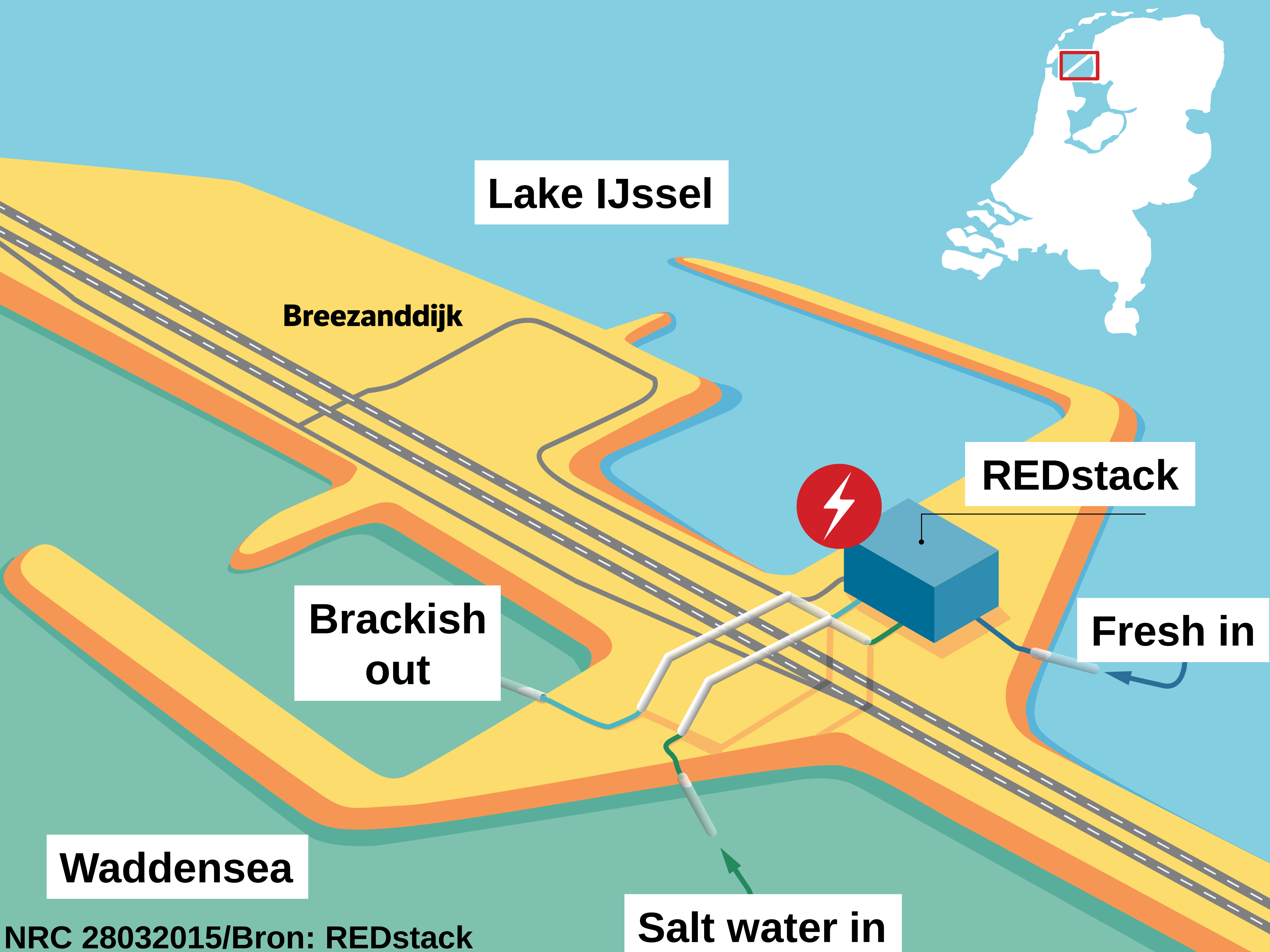
- Fouling significantly reduces power output
- Operational strategies for fouling reduction
- Chemistry allows tailoring the membrane properties:
  - Improved power output
  - Monovalent ion selective membranes to mitigate against the negative effect of multivalent species
  - Anti-fouling membranes

Towards the real application

Demonstration at the Afsluitdijk (NL)

Demonstration installation at the Afsluitdijk

- 2005: Foundation REDstack BV
- 2006 - present: Fundamental Research Wetsus
- 2007 - 2010 First tests on real feed water
- About the Afsluitdijk project:
  - December 2011: Public Funding
  - May 2012: Private Funding
  - May 2012: Start Design process Afsluitdijk-plant
  - June 2013: Permits obtained + start building + testing
  - November 2014: Official opening by the King of The Netherlands


Lake IJssel
Breezanddijk
REDstack
Brackish out
Fresh in
Waddensea
Salt water in
NRC 28032015/Bron: REDstack

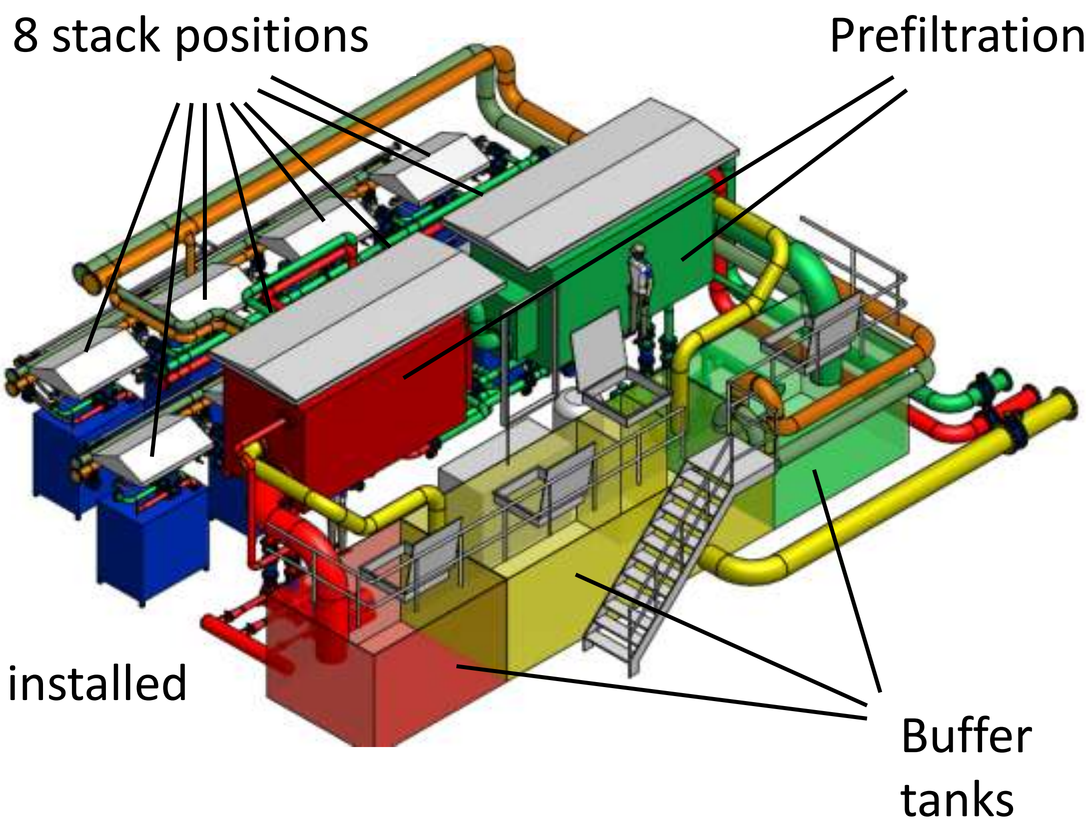
Demonstration installation at the Afsluitdijk

REDSTACK FUJIFILM wetsus SNN VOOR DE NOORDELIJKE ECONOMIE provinsje fryslân provincie fryslân

Demonstration installation at the Afsluitdijk

After 10 years of research……. Pilot plant on the Afsluitdijk (NL).

- 7.33 M€
- 8 stacks, 50 m^2/stack
- 25 W/stack
- 5 W for pumping/stack
- Fuji membranes
- 220 m^3/h seawater
- 220 m^3/h fresh water
- Goal: after 4 years: 50 kW installed



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