AACHENER VERFAHRENSTECHNIK

The future of membranes in water and waste water technology

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Chemical Process Engineering

RWTH

Outline

- Water scarcity --> alternative water ressources --> membranes
- Energy consumption as critical barrier to membrane application
- Way to procede:
  - Reduce resistance
    - new membrane materials,
    - optimised module geometry, hydrodynamics and mode of operation
  - Reduce driving force
    - revolutionary reverse osmosis concept

Water scarcity, water management and reuse

AquaStress

Water scarcity *is a* *shortage of water of adequate quality.*

Criteria: per capita water availability, ratio of water resources to abstraction (wsi)

But: Average values mislead, regional and seasonal view needed

Water scarcity impairs health, quality of life, economy, food production

Water management *tries to* *control* *water availability and demand.*

Demand control: water pricing, rationing, public campaigns, crop selection, watering techniques, water saving appliances, internal recycling, piping maintenance, permits for industry, parks and settlements

Availability expansion: **Dams**, pipelines, wells, **desalination**, surface and ground water treatment, **water reuse**

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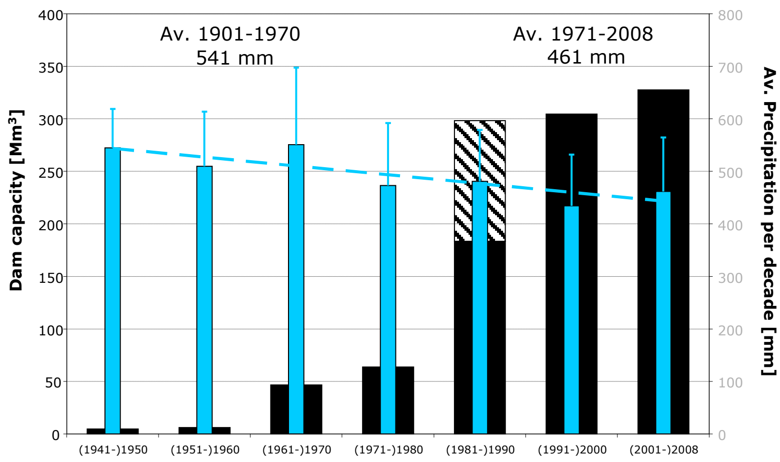
Water availability – new dams? Example Cyprus



Source: Hochstrat et al.(2009) EDS Conference on Desalination for the Environment, Clean Water and Energy, Baden-Baden

* Data Source: Meteorological Service / WDD - Ministry of Agriculture, Natural Resources and Environment

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Time window for water resources planning

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Alternative water ressources, membranes and energy

Water supply challenges: Need to tap alternative resources

- desalination
- water reuse

- Membrane technology dominates today's desalination market
- Membrane technology is an undisputed part of high quality reuse:
  - MF / UF for particle retention / hygienic quality improvement and as pretreatment
  - NF / RO (additionally) for removal of salts, nutrients and chemical contaminants

But: membrane technology is energy intensive and not affordable for all

Our Goal: reduce energy consumption and cost of membrane technology

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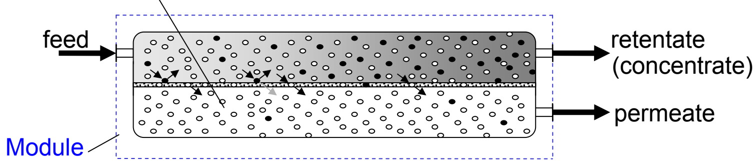
Basics of membrane processes

Membranes are planar, semi-permeable structures



flux = driving force / resistance

Membrane processes are non-equilibrium-processes.
→ energy use generally well above thermodynamic minimum.
→ we don' t have any excuses.

Improvements from all of the following are welcome:
- *materials science (membranes), nano-materials?*
- *hydraulics (module design, operation)*
- *process technology (process design)*

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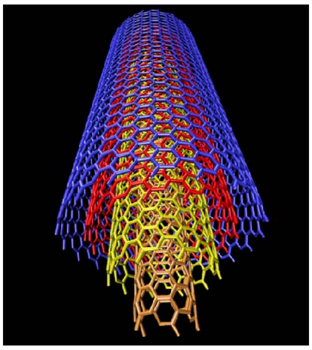
Membrane materials: Carbon Nano Tubes

- What are they ?
  - Tube-like nanostructured (d around 1 nm) set of carbon-molecules (L/d up to & beyond 10^6)
  - Belong to fullerene structural family
  - Two types: Singe walled (SWNT) and multi walled (MWNT)



- What makes them special?
  - Measured tensile strength up to 65 GPa
  - Counter-intuitive mass transport properties

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Desalination Potential of CNT-based Membranes

- Molecular Dynamics Study

			maximal pore density		2.5 x 10^{11} pores per cm²	
CNT type	internal diameter [Å]	salt rejection	flow rate	improve-ment	flow rate	improve-ment
(5,5)	3.2	100%	45.2	682	0.16	2.42
(6,6)	4.7	100%	78.8	1189	0.27	4.21
(7,7)	5.9	95%	119.5	1801	0.42	6.39
(8,8)	7.5	58%	182.9	2759	0.65	9.76

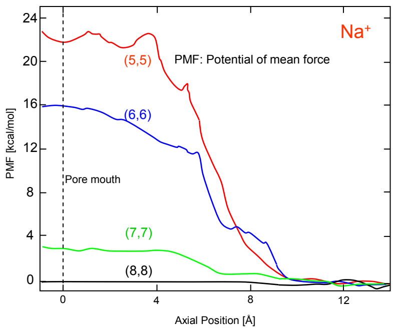
➢ Salt rejection heavily depends on pore size

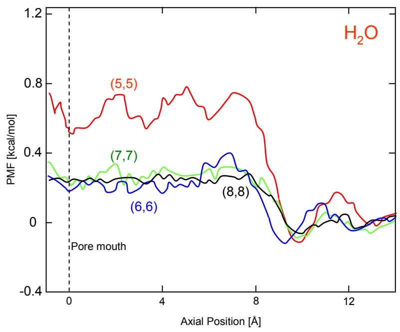
➢ Low pore densities

➢ Little improvement over today's membranes

Numbers assume an operating pressure of 5.5 MPa and allow for an osmotic pressure of 2.4 MPa. Flow rates are measured in L cm^{-2} day^{-1}. Improvements in efficiency are quoted relative to published values for a FILMTEC SW30HR-380 commercial reverse osmosis membrane

Desalination Potential for CNT-based membranes



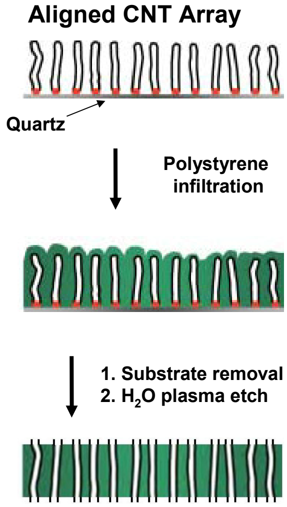


- Salt (left): The smaller the pore, the more water molecules need to be stripped off from the solvation shell (very large energetic entry barrier)
- Water (right): Breakage of hydrogen bounds at the pore entrance (energy barrier small)
- PMF stays flat inside the CNT (no additional energy barriers inside; frictionless transport)

Preparation of CNT Membranes

- Fabrication process:
  - •Step 1: CVD process ferrocene-xylene-argon-H_2 on quartz 5-10 µm at 700 °C
  - •Step 2: Polystyrene / toluene spincoating
  - •Step 3: Quartz removal with HF
  - •Step 4: H_2O plasma oxidation to remove polymer and end-caps / to open pores; Polymer oxidation rate faster than that of CNTs.

CNT density in the order of 10^{11} cm^{-2}



[4]

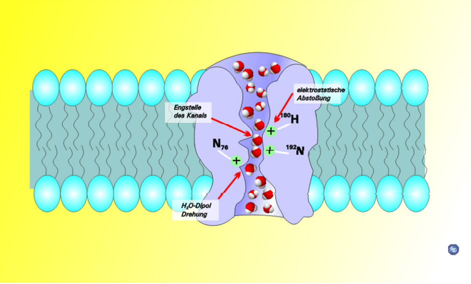
Conclusions on CNT-Membrane Production

- Porosity
  - Low CNT density
    ➔ No real improvement in transmembrane flux compared to commerically available polymer-membranes
- Production Process
  - Not straight forward
  - Not (economically) applicable in large scale
  - High temperatures in CNT production impede one-step processes
  - Alternative production methods suffer from failing alignment of CNTs

Membrane materials, the next step: Aquaporins?

Aquaporins are water transporting proteins embedded in cell walls, behaving very much like CNTs, except:

- Shorter (= cell wall)
- More selective (--> ultra pure water)
- Easier to make and embed (?)



Open questions:

- fraction of open area
- stability in case of significant differential presures

For answers follow the EU-project "MEMBAQ" coordinated by Hans Enggrob, DHI, Denmark

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Back to reality: Membrane materials of today

Attempts to increase flux (--> reduce membrane thickness) conflict with demand for increased mechanical stability.

Classical solution: anisotropic membrane,
-- > very thin active top layer on highly porous, stable support structure.

Disadvantages:

- tortuosity and porosity of top layer unsatisfactory
  --> new pore forming / membrane structuring techniques

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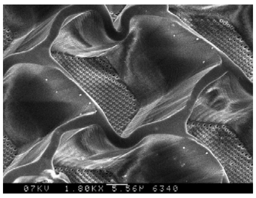
Microsieve: first tries

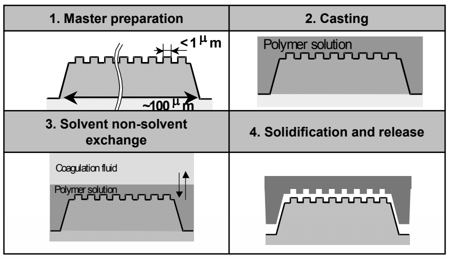
Source: M. Wessling, AMK 2005

a) Hot embossing of polymer film on microstructured mould
Microarchitecture: Fields of holes,
Macrostruture: support beams

Problems:
- Film sticking to mould
- holes not cleanly cut
- bent macrostructure



b) Phase separation micromoulding



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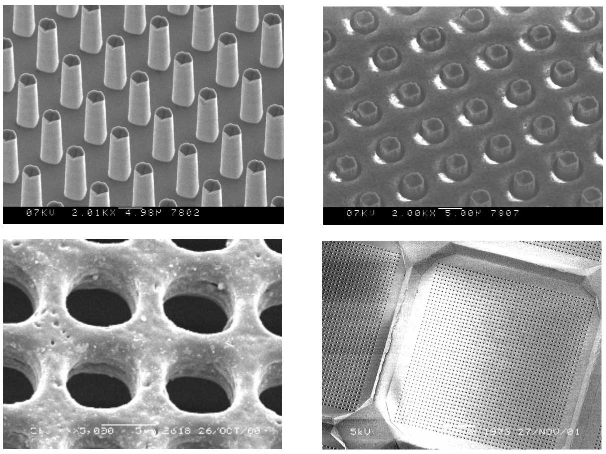
Microsieve: first tries

Source: M. Wessling, AMK 2005

Phase separation micromoulding (continued)



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Phase separation micromoulding Source: M. Wessling, AMK 2005

Status and evaluation

- Low cost material used in a moderate cost process
- Shrinking during manufacturing is key to success
- Up to now pore sizes of 3 micron possible
- Minimum target: 1 micron,complete retention of bacteria requires 0.2-0.3µm
- No information on performance
- No details on module design and operational concept
- No motivated manufacturer

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Membrane materials: Call it “microsieve“

The ideal membrane

- Equally sized, equally spaced pores
- Straight bore pores, pore length → 0
- High hole density, large total open area

Expected benefits

- Very high flux
- Perfect retention of all particles > d_{pore}
- Perfect passage of all particles < d_{pore}
- Minimal adsorption (no inner area to adsorb on)
- Minimal cake compression (little differential pressure needed)

Doubts

- Can it be made and how?
- What good does a perfect pore do, if it gets plugged at once?

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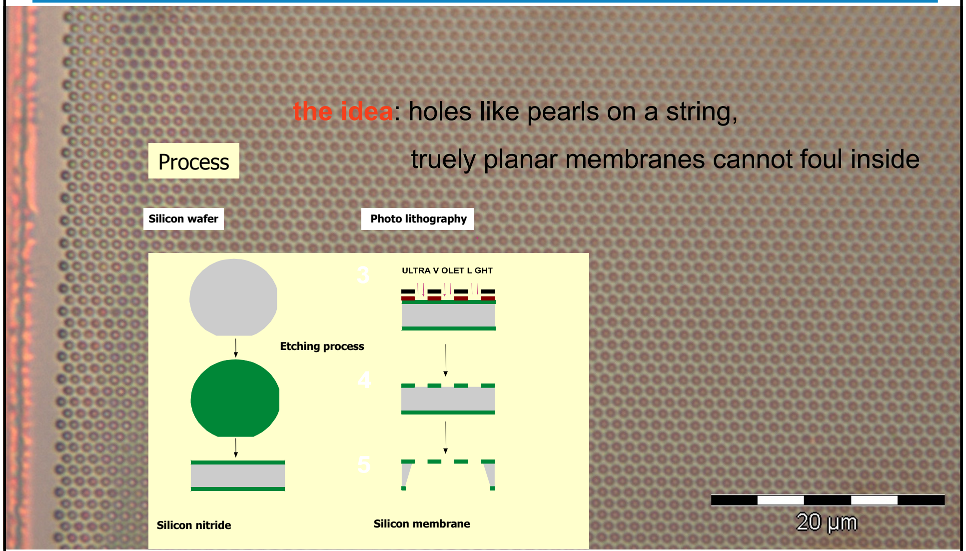
Silicon nitride microsieve

source: own work (8)

the idea: holes like pearls on a string,
truely planar membranes cannot foul inside



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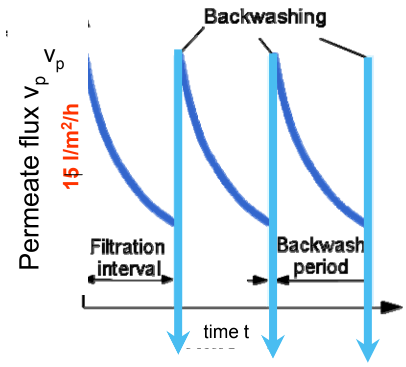
New operating mode needed: backpulsing



Backwashing: typical filtration interval (min) and backwashing period (sec) - Standard technique in “dead-end" membrane filtration and MBR with flux around 15 LMH

Microsieve:
clear water flow > **10m³/m²/h**

- Plugging within 1 sec at moderate solid load
- Backwash frequency must go up!
- Ideal: **4 to 10 Hz**

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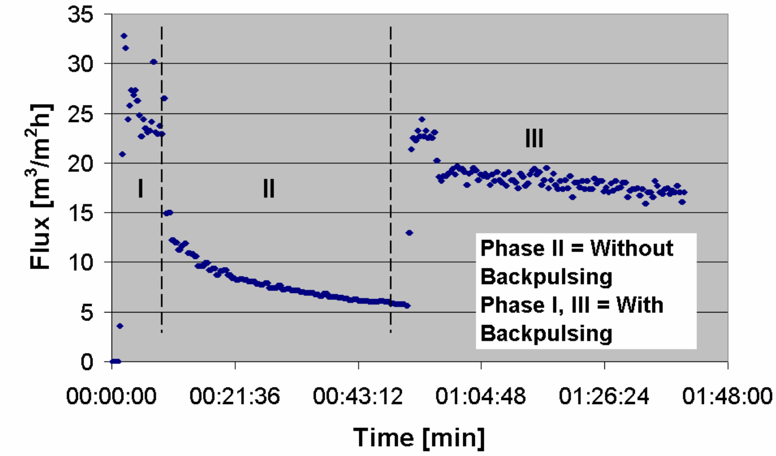
Microsieve

Effect of backpulsing on filtration of latex suspension ($D_{Latex} > D_{Pore}$)



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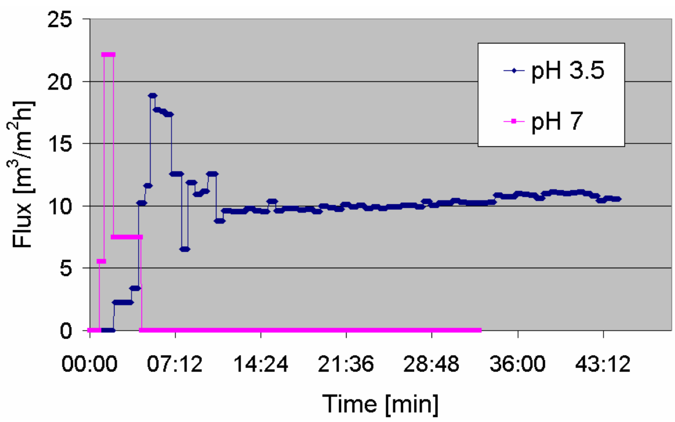
Microsieve

Effect of solution properties on filtration of yeast suspension with backpulsing



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More basics: Concentration polarization (module design)

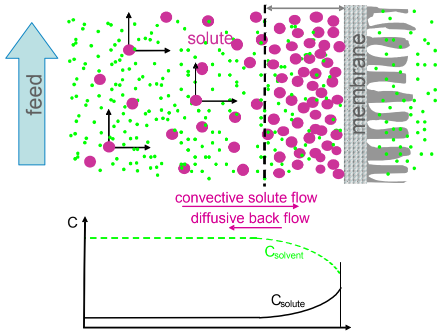
- Retained substances are concentrated at membranes
- Influencing factors:
  Flux j, Diffusivity D, Mass transfer coefficient k

For completely retained component j:

$$(c_{ji} - c_{jb}) / c_{jb} = \exp(j / Dk)$$

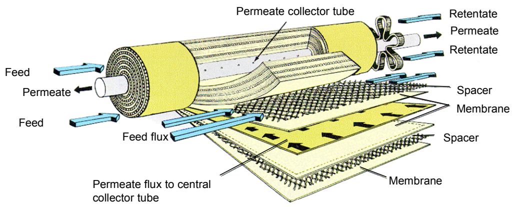
Concentration polarization
= major cause of fouling,
reduced flux and retention

Concentration polarization reduced by:
• higher cross-flow
(--> higher energy consumption),
• Intelligent spacer design



Spacers: Introduction

- Spacers are used in various flat sheet membrane process
  - Spiral wound UF / NF / RO modules
  - Electrodialysis stack
  - Membrane distillation modules

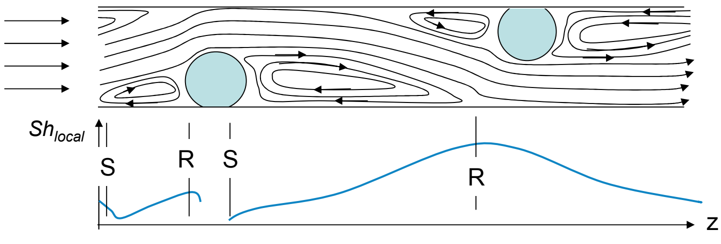


[1]

- Provide defined distance between individual membrane sheets / layers
- Increase mass transport to the membrane due to introduction of eddies
- Reduced concentration polarization
- Influence fouling behaviour

[1] T. Melin 2008, Membranverfahren, 3rd edition, Springer, Heidelberg

Spacer Induced Mass Transfer Enhancement



[Fimbres et al., Ind. Eng. Chem. Res 45 (2006) 6594-6603]

- Recirculating regions prior and behind spacer filaments
- Highest mass transport rates at the re-attachement zones
  - Low concentration bulk fluid transported to the membrane wall surface
- High pressure loss

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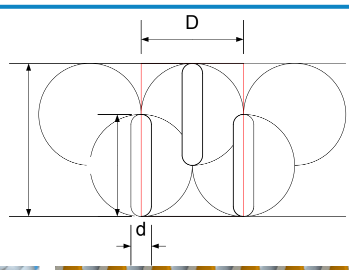
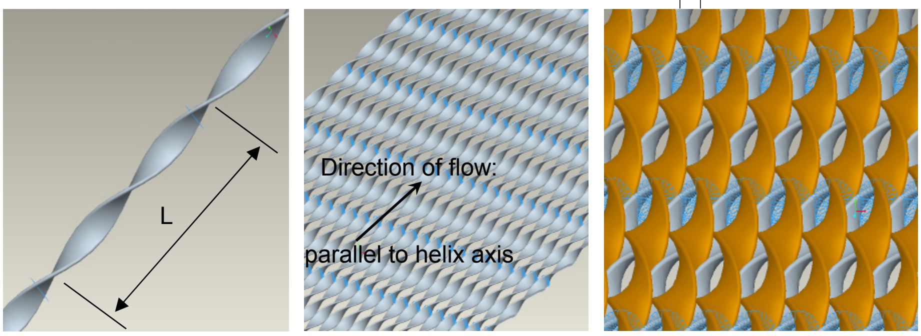
Micro-stuctured membrane spacer

- Doube-helix form filaments
- 2 layers of filaments
- Geometrical parameters:
  - D, d, L, (h_{sp})





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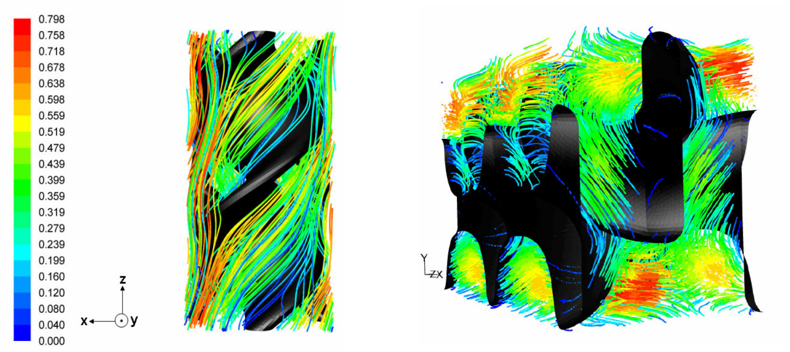
CFD Simulation of Flow

- Flow conditions
  - Transport of high concentration fluid away from the membrane
  - Bulk fluid is directly forced to the membrane
  - No eddies have been found in simulations



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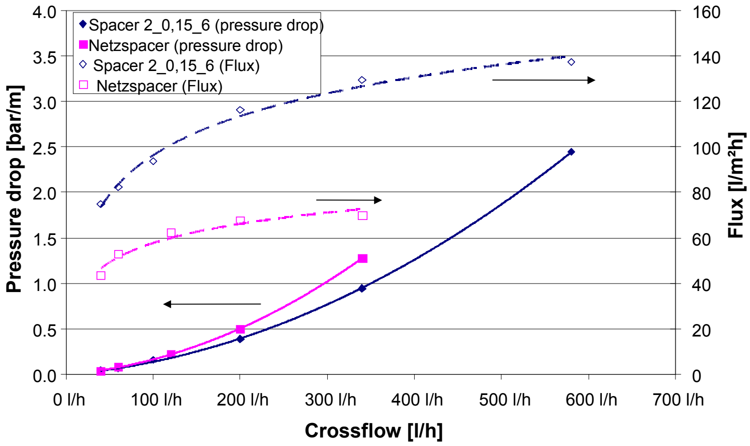
UF of a dextran solution 15 – 100 k Dalton

- Experimental comparison with commercial net-spacer (80 mil)
  - Filtration 5g/L at 1,5 bar trans-membrane pressure (TMP)



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New engineering concepts: Deep see desalination

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New engineering concepts: Deep see desalination

Starting points:

- Classical RO operates too far away from the thermodynamic optimum (70 bar instead of 30 bar, pressurized volume = 250 % of permeate) - -> high energy cost.
- Pre-treatment drives up the investment cost.
- Modul and piping cost equal cost of membranes.
- Chemicals (anti-scalants) and salt content in outfall make concentrate disposal ecologically questionable.

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Goals:

- Pump the permeate, not the feed
- Leave pressure near minimum
- No chemicals, no pretreatment, no concentrate disposal

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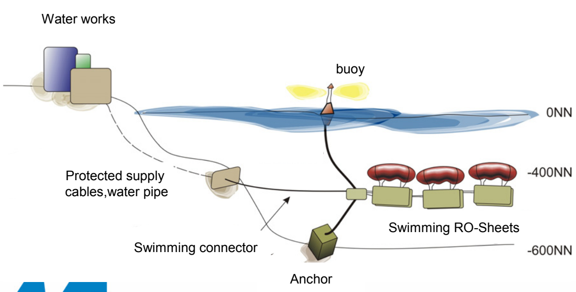
Towards minium energy consumption: Deep sea RO

Strategy:

- Avoid any concentration increase on the feed side
- Do not pump the feed, pump the permeate
- Read old literature: B.C. Drude (Siemens AG), Desalination, 2 (1967) 325.
- --> Deep sea RO



Abstract The hydrostatic pressure in several hundred fathoms' depth may be employed for desalination by reverse osmosis, if the pressure at the permeate side is maintained near atmospheric. The work to be performed consists merely of the energy required for lifting the product water to the surface. Maintenance-free sub mersible pumps are available. The membranes outside of the pressure vessel may be of any desired shape and arrangement. Due to natural currents there will as a rule be no salt concentration in front of the membranes. For smaller depths a cascade type may be envisaged.(abbreviated)

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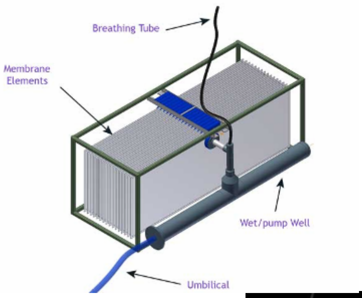
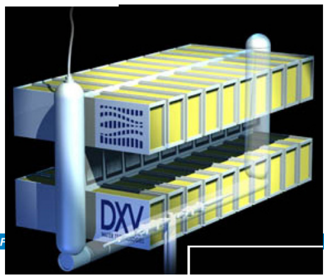
Deep sea RO – new approach

DEMWAX
Depth **E**xposed **M**embrane for **Wa**ter E**x**traction



- No forced feed circulation
  - natural flow of water between membrane sheets (6 mm spacing)
  - Gravity driven provision of feed and removal of concentrate
- Low recovery (2%)
  - → Low pressure demand
  - → Low concentrated "brine" close to background salinity
- Low flux (2.6 – 3.4 LHM)
- Operable at depths of around 260 m



Source: DEMWAX^{TM} Technical White Paper, DXV Technologies

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Towards minium energy consumption: Deep sea RO

Towards Realization: DEMWAX project by DXV (Ca, USA)

- Hanging flat sheet membranes (unwound spiral wound module, like bed sheets on clothes lines) in a gitter box.
- Small distance between membranes (6 mm), very low flux (2,5-3,5 L/m²/h)
- 190m³/d pilot plant planned, pump is only moving part
- **Claimed: 1,25 kwh/m³ (conventional: >3kwh/m³)**

Other advantages

- No intake buildings
- No pretreatment
- No pressure vessels

--> Reduced investment

Open points

- membrane life?
- piping cost
- maintenance strategy?

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Summary

Membranes have come a long way.

For their continued success story, energy consumption is critical.

We need a concerted effort of:

Materials science (better membranes)
+
Engineering (modules, mass transfer, operational concepts)

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Thank you for your attention

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First Announcement

13th Aachener Membran Kolloquium

27th-28th October 2010

Topics

- Industrial waste water treatment,
- Process and drinking water treatment,
- Food and beverage industry,
- Process industry,
- Gas and vapour separation applications
- Life Sciences.

Find futher information on ***www.amk.rwth-aachen.de***

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