

2.500 Desalination & Water Purification

Spring 2009 Summary



Haiti

Photos by Amy Smith. Used with permission.



Department of Mechanical Engineering Massachusetts Institute of Technology Ghana



Context



Safe water supply ... is not universal



Image from Wikimedia Commons Tanzania

More than 1 billion people lack access to clean drinking water

Half the hospital beds in the world are occupied by patients with easily prevented water-borne disease Half the people in the world do not have sanitation systems as good as those in Ancient Rome.

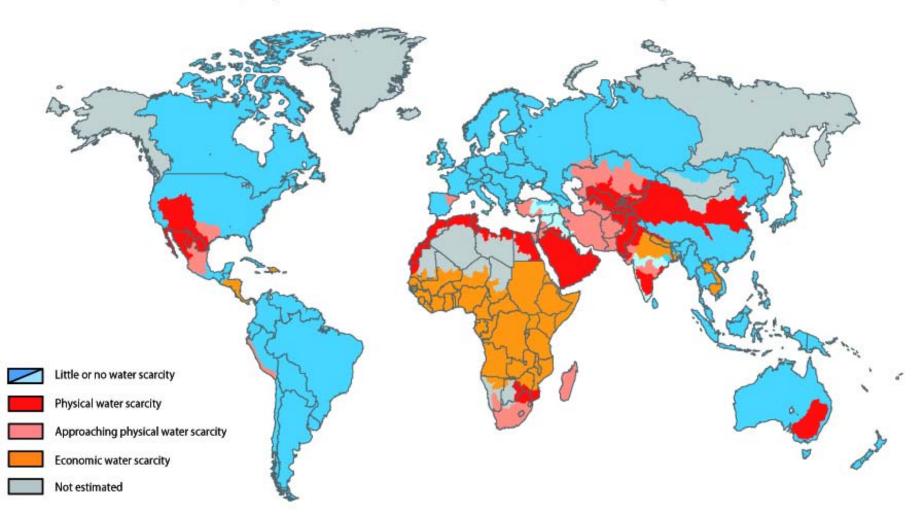
In 2000, unsafe water mortality amounted to 80 million years of lost life (*Science*, 25 Jan 2008)

This situation is expected to get WORSE.



Images removed due to copyright restrictions. Please see http://www.flickr.com/photos/andrewheavens/100063338/ http://jimbicentral.typepad.com/photos/uncategorized/2007/09/18/water_scarcity.jpg

Areas of physical and economic water scarcity



UNEP/GRID-Arendal. "Areas of Physical and Economic Water Scarcity." UNEP/GRID-Arendal Map and Graphics Library. UNEP/GRID-Arendal, 2008. Accessed September 25, 2009.



Yangon, Myanmar

May 2008 ...after cyclone

Images removed due to copyright restrictions.

Please see http://www.nytimes.com/slideshow/2008/05/05/world/0505-MYANMAR_index.html http://graphics8.nytimes.com/images/2008/05/05/nytfrontpage/23097528.JPG

Source: Wikipedia



Historical Population Density - 1994

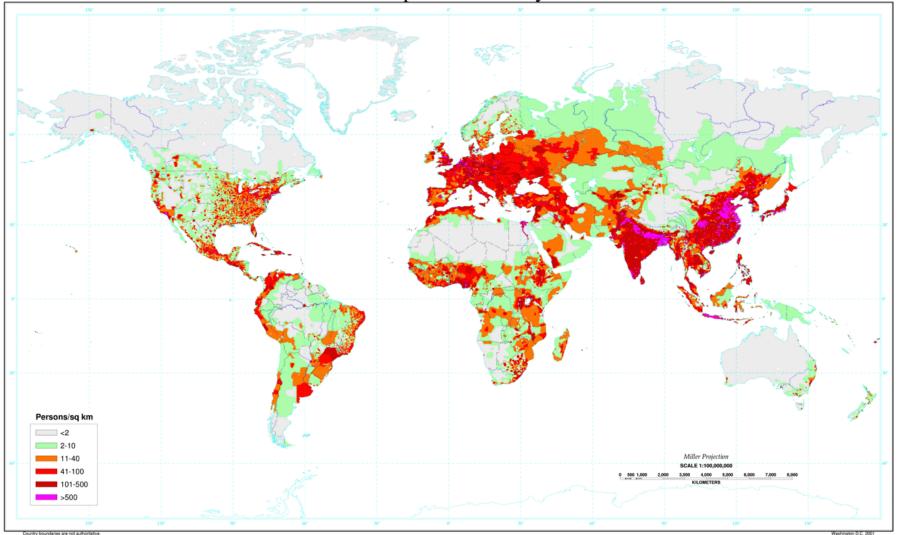


Image from Tobler, W., et al. "The Global Demography Project." TR-95-6. Santa Barbara, CA: National Center for Geographic Information Analysis, 1995. Image is in the public domain.

Department of Mechanical Engineering Massachusetts Institute of Technology



Per capita water consumption (m³/y)

2

	Worldwide average	800
с.	Nigeria	50
с.	China	300
с.	Mexico	800
с.	Italy	1000
	USA	2000

World desalting capacity



Source: Science, v. 319, 25 Jan 2008

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Please see http://www.flickr.com/photos/peggyarcher/975676140/in/set-72157601398334771/

Cleaning a sidewalk in Long Beach, CA

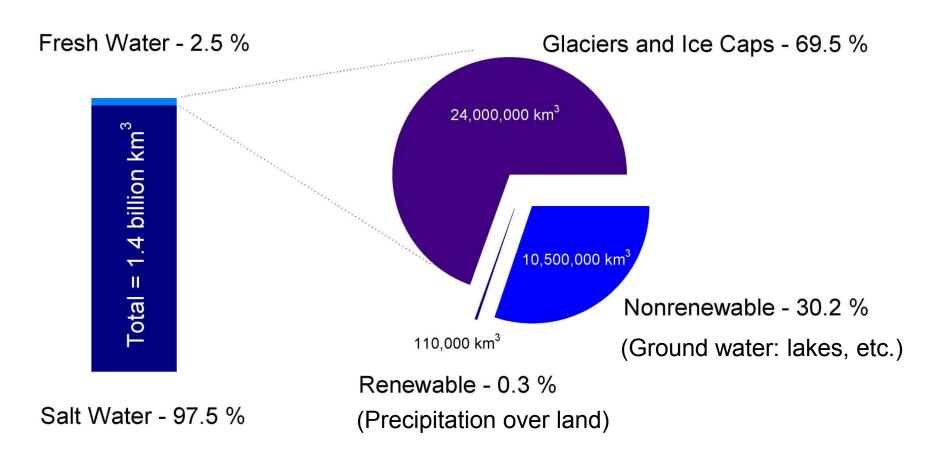


July - September, 1989

August 12, 2003

Images from NASA Earth Observatory. Aral Sea – water diverted for agriculture

Source: infranetlab.org

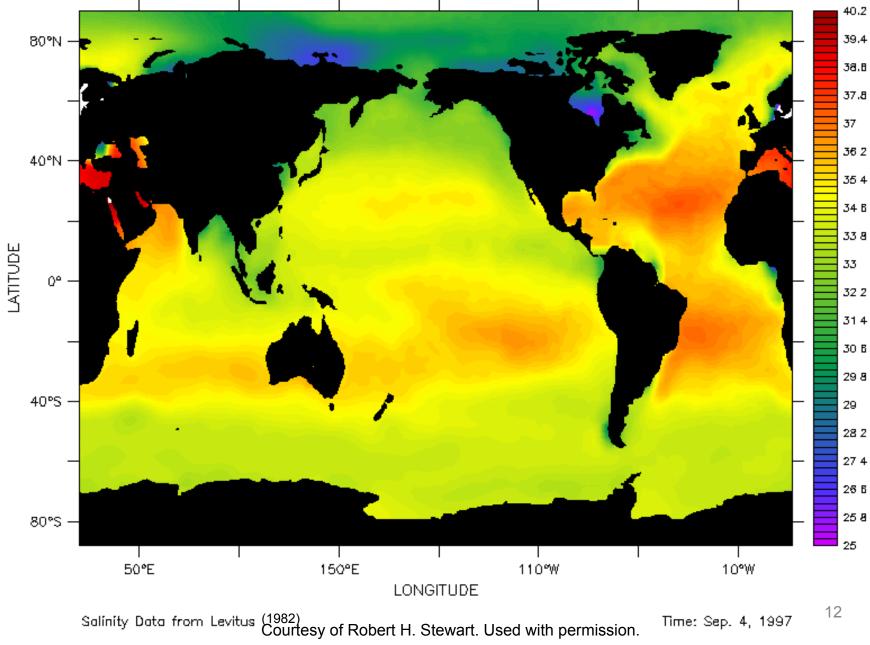


Courtesy of Sandia National Labs. Used with permission.

Approximately 23% of renewable water is appropriated for human uses, including agriculture. Accessible annual run-off is about 12,500 km³/y, of which about 54% is acquired for human use.

Source: Miller, 2003.

Annual Mean Sea Surface Salinity



Water flows (km³/y)

Precipitation on land 120,000

- Evaporation on land 70,000
- River runoff and groundwater recharge 50,000

Available river flow and recharge 12,000

- Withdrawal for human use
 - Agriculture 3,500
 - Industry 1,000
 - Domestic 500

World desalting capacity = 13 km³/y

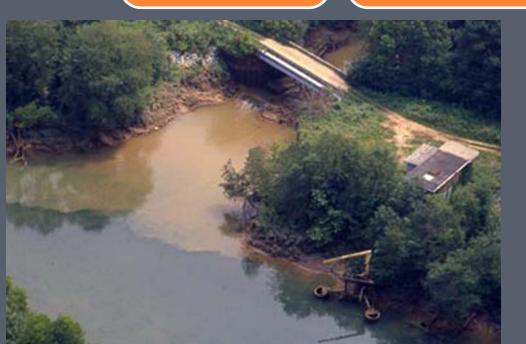
Source: *Science*, v. 319, 25 Jan 2008

Water Quality

Water Quality Characteristics

Ref: Reynolds & Richards

Biological Characteristics *microorganisms* Physical Characteristics *taste, odor, color,...* Chemical Characteristics natural or manmade





Images from Wikimedia Commons, http://commons.wikimedia.org

Biological

- Bacteria
- Viruses
- Protozoa
- Coliform bacteria (indicate human waste)
- Helminths
- Fungi, algae

Physical

- Total solids (dissolved and suspended)
- Turbidity
- Color (apparent and true)
- Taste & odor (organic compounds in surface water; dissolved gases in ground water)
- Temperature

Chemical

- pH
- Anions & cations (dissolved solids)
- Alkalinity (HCO₃⁻, CO₃²⁺,OH⁻ system)
- Hardness (*Ca*^{2+,} *Mg*²⁺)
- Dissolved gases (O₂, CO₂, H₂S, NH₃, N₂, CH_{4...})
- Priority pollutants (organic and inorganic)

Microbial contamination is the #1 concern for water

- Protozoans
 - Amoeba, cryptosporidium, giardia, algae,...
- Bacteria
 - Salmonella, typhus, cholera, shigella, ...
- Viruses
 - Polio, hepatitis A, meningitis, encephalitis,...
- Helminths
 - Guinea worm, hookworm, roundworm,...
- Principal transmission is by human waste
- Principal purification technique is chlorination, especially for bacteria.

Ref: Faust and Aly, 1998.

Disinfection of water

• Chlorination

- Highly effective for bacteria, and effective for viruses
- Not effective for protozoa
- Inexpensive, very common
- Ozonation
 - Highly effective
- Ultraviolet radiation
 - Effective for low turbidity
- Boiling
 - Complete sterilization possible

Physical characteristics

- Suspended solids include silt, clay, algae, colloids, bacteria...remove by settling, filtration, or flocculation
- Turbidity interferes with passage of light, usually as the result of colloidal material
- Color is due to dissolved (true color) or colloidal (apparent color) material...iron, manganese, clay,...
- Taste/odor ...typically treated by aeration (to release dissolved gas from ground water) or activated carbon (to remove organics from surface water)

EPA Primary Standards for ~130 chemicals

- Toxic metals Arsenic, lead, mercury, cadmium, chromium,...
- Organic compounds insecticides, herbicides, PCBs, petrochemicals, PAH, benzene, halogenated hydrocarbons,...very long list
- Nitrate or nitrite fertilizer byproduct
- Fluorine damages teeth and bones at high concentrations
- Radionuclides mainly natural alpha emitters...

Secondary standards for taste, odor, appearance: Cl⁻, SO₄²⁻, pH, color, odor, iron, manganese, copper, zinc, foaming agents...

Substance (amounts in mg/kg)	Standard Seawater	Cambridge City Water	Massachusetts Water Resources Authority	Poland Springs Bottled Water	Maximum Allowable
Sodium, Na⁺	10781	79	30	2.6-5.6	aesthetics: 200
Magnesium, Mg ²⁺	1284	5	0.8	0.7-1.9	-
Calcium, Ca ²⁺	412	25	4.5	3.5-9.5	-
Potassium, K⁺	399	nr ^[1]	0.9	0.74-0.88	-
Strontium, Sr⁺	13	nr	nr	nr	-
Chloride, Cl ⁻	19353	140	21	1.5-6.6	250
Sulfate, SO ₄ ²⁻	2712	27	8	0.87-5.9	250
Bicarbonate, HCO ₃ -	126	nr	nr	13-28	-
Bromide, Br-	67	nr	0.016	not detected	-
Boric Acid, B(OH) ₃	26	nr	nr	nr	-
Fluoride, Fl-	1.3	1	1	0.0-0.27	2-4
Water	965000	-	-	-	-
Total dissolved solids	35200	320	110	33-57	500
Nitrate, NO ₃		0.46	0.11	0.12-0.42	10
Retail Cost, US\$/m ³	free?	1.05	1.18	~300 to 3000	-

^[1] nr = not reported.

Concepts from Physical Chemistry

- Gibbs energy
- Chemical activity
- Colligative properties (especially osmosis)
- Electrolyte behavior
- Osmotic coefficient
- Ion transport
- Colloidal Stability

G = H - TS

Measures of concentration

- Mass fraction (% by mass, ppm,...), w_i
- Mole fraction (% of total moles), x_i
- Total dissolved solids is a mass fraction
- Molality (mol solute/kg solvent), m_i

Dissolution of salts

$$A_{\nu+}B_{\nu-} \longrightarrow \nu_{+}A^{z+} + \nu_{-}B^{z-}$$
Electroneutrality:
$$\begin{cases}
\nu_{+}z_{+} + \nu_{-}z_{-} = 0 \\
z_{+}c_{+} + z_{-}c_{-} = 0
\end{cases}$$

 $MgCl_2 \longrightarrow Mg^{2+} + 2Cl^{-}$

Salts that dissociate completely are called *strong electrolytes.*

NaCl, MgCl₂, MgSO₄, CaSO₄, K₂SO₄, KBr, ...CaCO₃ are related to seawater

Partial molar Gibbs energy

 $\underline{G} = x_a G_a + x_b G_b$

 $\overline{G_i} = \underline{G}_i + RT \cdot \ln(a_i)$

mixture, J/mol

partial molar, J/mol

For pure substance in reference state

For equilibrium between two phases or solutions, the partial molar Gibbs energy of each species is the same.

Chemical Activity

$$a_{solvent} = \gamma_{solvent} x_{solvent}$$

$$a_{electrolyte} = (\gamma_{\pm} m_{\pm})^{\nu}$$

$$\ln(a_{solvent}) = -\phi \cdot M_{solvent} \left(10^{-3} \text{ kg/g} \right) \cdot \sum m_i$$

Note that the osmotic coefficient provides a less error sensitive means of calculating the partial molar Gibbs energy of the solvent.

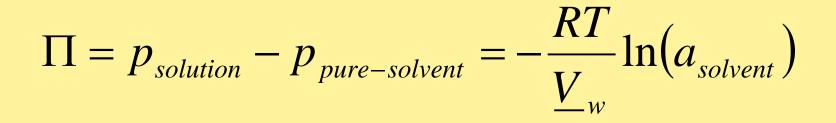
Colligative Properties

- Properties that depend upon the amount of dissolved solute but not the identity of the solute
 - Vapor pressure lowering (Raoult's Law)
 - Boiling point elevation,
 - Freezing point depression
 - Osmosis
- Amount: molality (mol solutes/kg solvent)
- These properties refer to equilibrium between phases or solutions of differing composition, and all are related to partial molar Gibbs energy

Property	Ideal Solute	Real Solute
Osmotic pressure	$\Pi = RTc_{solutes}$ $(\phi = 1)$	$\Pi = \phi RT \rho_{solvent} \sum m_i$
Freezing point depression	$\delta = k_f \times \sum m_i$	$\delta = \phi \times k_f \times \sum m_i$
Boiling point elevation	$\delta = k_b \times \sum m_i$	$\delta = \phi \times k_b \times \sum m_i$
Vapor pressure lowering	$p_{vap} = p_{sat, pure} x_{solvent}$	$p_{vap} = p_{sat, pure} a_{solvent}$

Osmotic coefficient, Φ , is a function of solute, solvent, temperature, and molality

Osmotic pressure



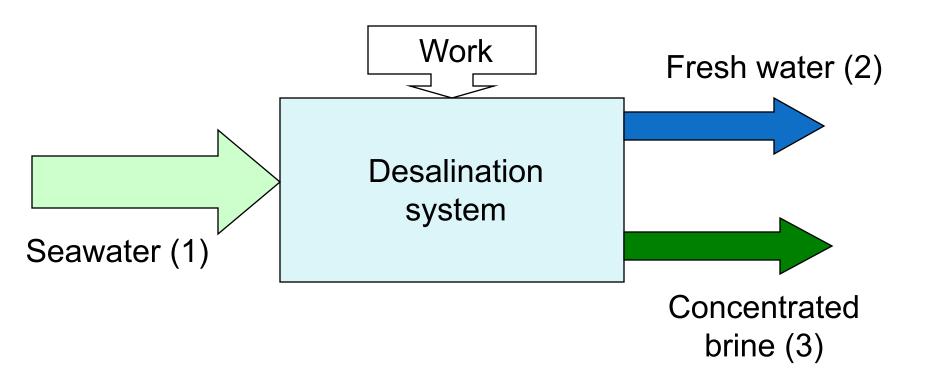
$$\Pi = \phi RT \rho_{solvent} \sum m_i$$

$$\Pi_{seawater} \approx (7.6 \times 10^{-4}) (\text{TDS in ppm})$$

Comparing seawater to aqueous sodium chloride

- Seawater with 35,000 ppm TDS
 - 0.62 molal NaCl solution has the same TDS or mass fraction of dissolved salts
 - 0.55 molal NaCl solution has the same chemical activity

Seawater purification



Ideally, this requires 2.5 to 7 kJ per kg fresh water produced.

Practically, it takes an order of magnitude more energy.

Work of separation $\dot{W} = [(\dot{N}\underline{G})_2 + (\dot{N}\underline{G})_3] - (\dot{N}\underline{G})_1 + T\dot{S}_{gen}$

Least work of separation (consider 0.62 molal aqueous NaCl)

- 1 kg removed from "ocean": 3.05 kJ/kg-fresh
- 38% recovery of water: 3.82 kJ/kg-fresh
- Remove salt from salt water: 8.32+3.05 = 11.37 kJ/kg-fresh

Least work varies with salinity and recovery (about 15% lower for 0.55 molal NaCl; much lower for brackish water)

Scale Formation

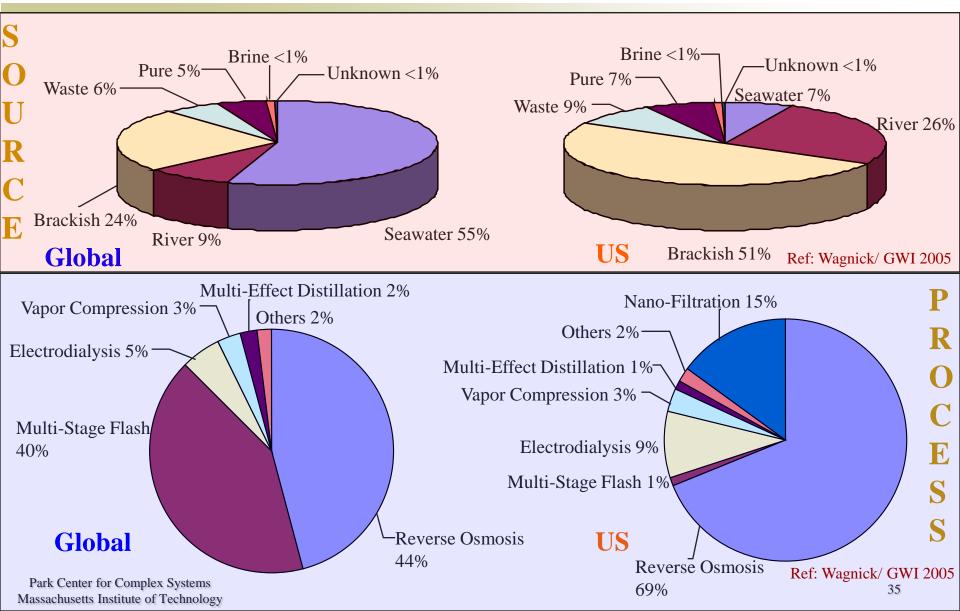
- Certain relatively insoluble salts precipitate easily when seawater is concentrated and heated
 - CaCO₃
 - Mg(OH)₂
 - CaSO₄
- These salts substantially impact the design of thermal desalination systems
 - Acid scale control (T < 120°C)
 - Polyphosphate control (T < 85°C)
- CaSO₄ has no economical control, so regimes where it precipitates are avoided (concentration factors of 2 or less for temperature below 120°C)

Principal desalination techniques

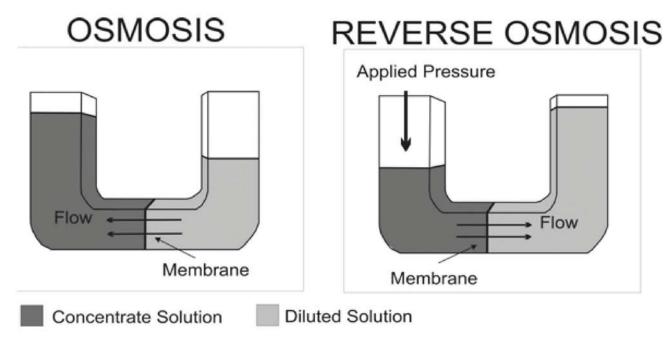
• Membrane techniques

- Reverse osmosis (SWRO or BWRO)
- Electrodialysis (ED)
- Capacitative deionization (CDI)
- Nanofiltration (NF)
- Distillation techniques
 - Multistage flash evaporation (MSF)
 - Multieffect distillation (MED or MEE)
 - Vapor compression distillation
 - Solar thermal distillation (concentrating or not)
- Related methods
 - Deionization
 - Water softening

Installed desalination capacity



Reverse Osmosis



Courtesy of Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

If pressure is applied to the solution, the direction of osmotic flow can be reversed. In this way solvent can be driven through the membrane, purifying it.

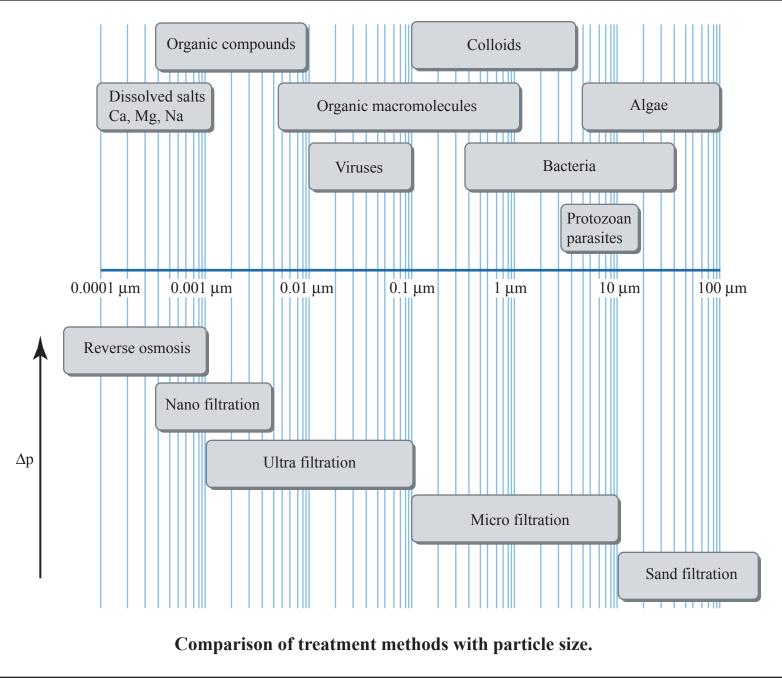


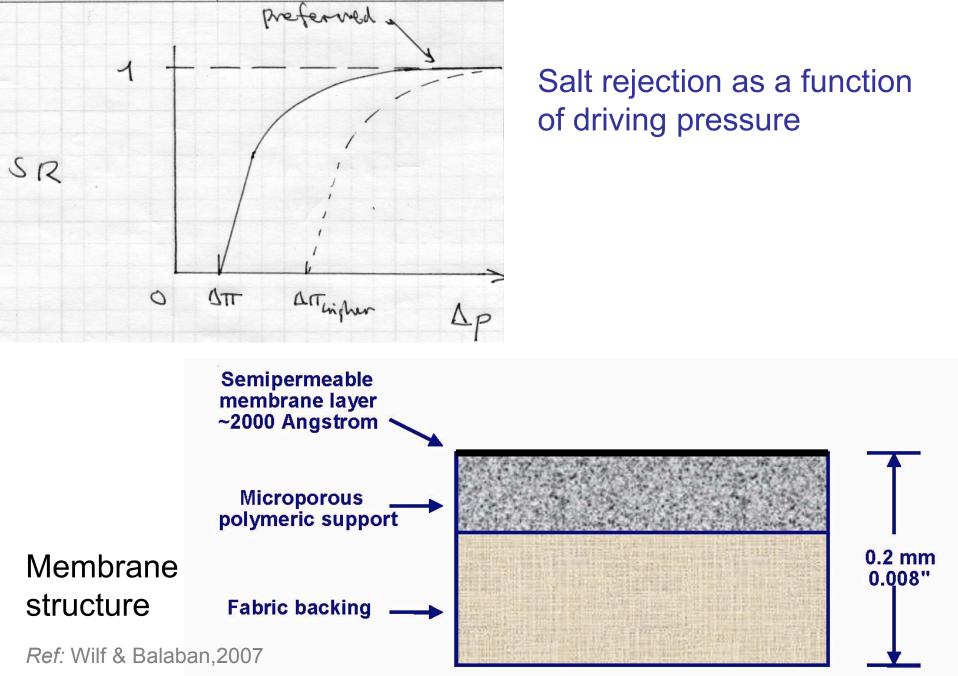
Figure by MIT OpenCourseWare.

Source: Twort et al.

Solution-diffusion model

 Transport through membranes is controlled by the solubility of ions and water in membrane and their diffusion through the membrane.

$$\begin{split} J_{v} &= A \Big(\Delta p - \Delta \Pi \Big) \quad \text{Volume flux, L/m^2-s} \\ J_{s} &= B \Big(c_{s,f} - c_{s,p} \Big) \quad \text{Salt flux, mol/m^2-s} \\ SR &\equiv 1 - c_{s,p} / c_{s,f} = \frac{(A/B)(\Delta p - \Delta \Pi)}{1 + (A/B)(\Delta p - \Delta \Pi)} \quad \text{Salt rejection} \end{split}$$



Figures from Wilf, M., and M. Balaban. *Membrane Desalination and Membrane Filtration*. L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

Concentrations for crossflow RO separator

$$\frac{c_{s,r}}{c_{s,f}} = \left(1 - R_p\right)^{-SR}$$

Salt concentration of retentate

$$\overline{c_{s,p}} = \left(\frac{c_{s,f}}{R_p}\right) \left[1 - \left(1 - R_p\right)^{1 - SR}\right]$$

Average salt concentration of permeate

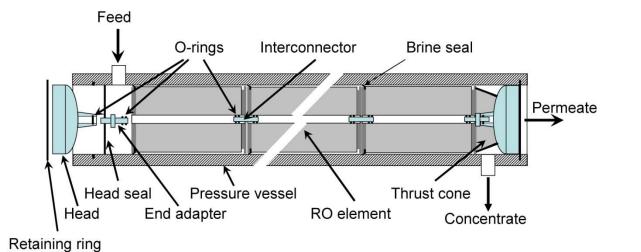


Spiral-wound element 20 cm diam by 1 m length

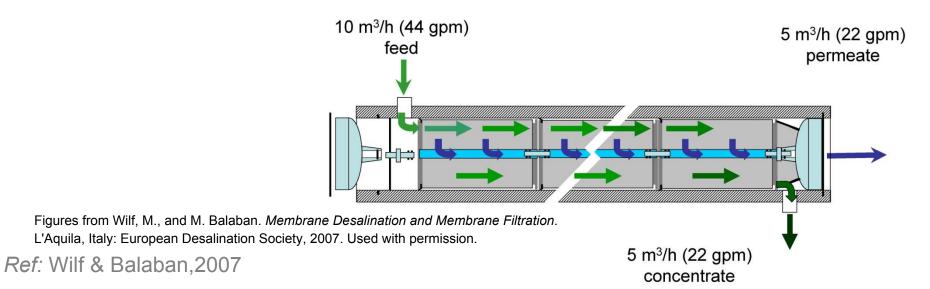
Figures from Wilf, M., and M. Balaban. *Membrane Desalination and Membrane Filtration*. L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

Ref: Wilf & Balaban, 2007

Configuration of a pressure vessel assembly



Water flow in a pressure vessel assembly





Figures from Wilf, M., and M. Balaban. *Membrane Desalination and Membrane Filtration*. L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

Pressure Vessels and Vertical Centrifugal Pumps

Ref: Wilf & Balaban, 2007

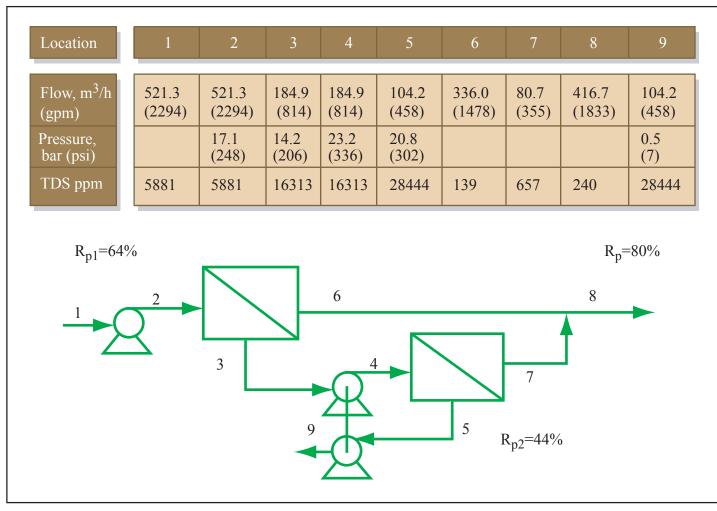


Figure by MIT OpenCourseWare.

Concentrate staging in a high-salinity brackish RO system with 80% recovery. Note turbine assisted booster pump.

from M. Wilf, 2007



Figures from Wilf, M., and M. Balaban. Membrane Desalination and Membrane Filtration. L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

Turbocharger applied as interstage booster pump

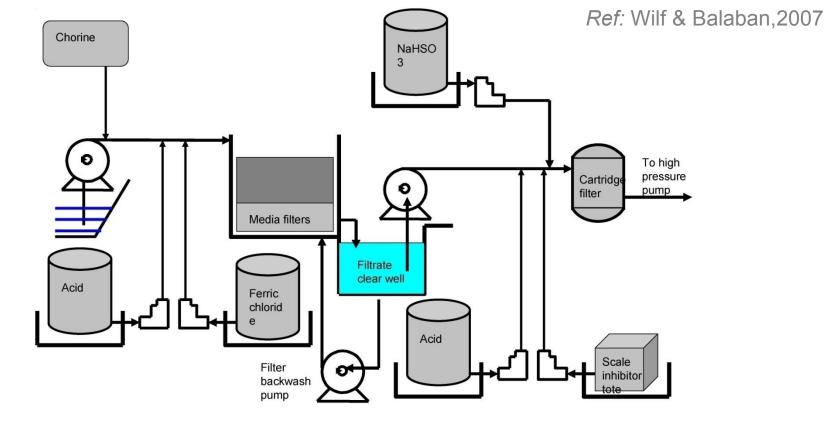
Ref: Wilf & Balaban, 2007



Pumping system at Larnaca plant. (Cyprus)

Figures from Wilf, M., and M. Balaban. Membrane Desalination and Membrane Filtration. L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

Ref: Wilf & Balaban, 2007



Configuration of a conventional RO pretreatment system treating surface water source.

Figures from Wilf, M., and M. Balaban. Membrane Desalination and Membrane Filtration.

Seawater pretreatment.

L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

Disinfect with chlorine

Add ferric chloride to coagulate small particulates

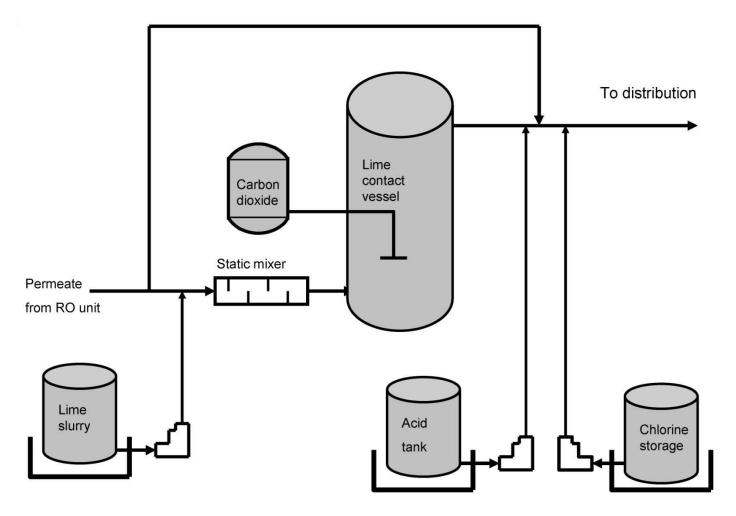
Filter, adjust pH to protect membranes, add scale inhibitor

dechlorination (by sodium bisulfate), cartridge filtration (5-15 µm porosity)



Figures from Wilf, M., and M. Balaban. Membrane Desalination and Membrane Filtration. L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

Ref: Wilf & Balaban, 2007



Seawater RO Post-treatment.

Figures from Wilf, M., and M. Balaban. Membrane Desalination and Membrane Filtration. L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

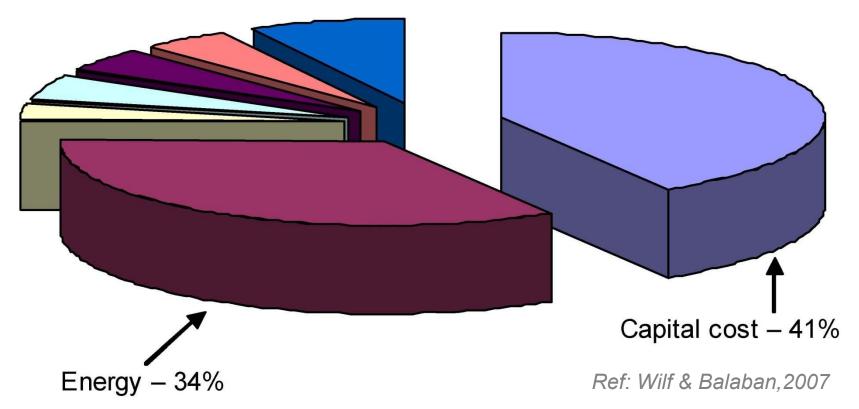
Add alkalinity and hardness via: $CO_2+Ca(OH) \rightarrow Ca(HCO_3)_2$

Disinfect with additional chlorine, control pH

Ref: Wilf & Balaban, 2007

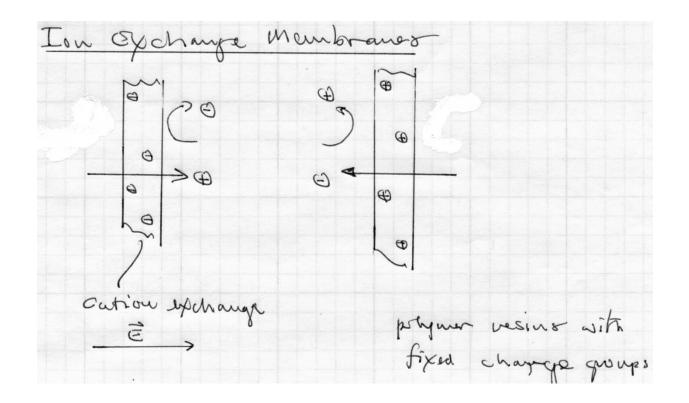
Total water cost distribution in SWRO

Membrane replacement – 3% Labor – 5% Maintenance and parts – 5% Consumables – 5% Others & contingency – 7%



Figures from Wilf, M., and M. Balaban. Membrane Desalination and Membrane Filtration. L'Aquila, Italy: European Desalination Society, 2007. Used with permission.

Electrodialysis

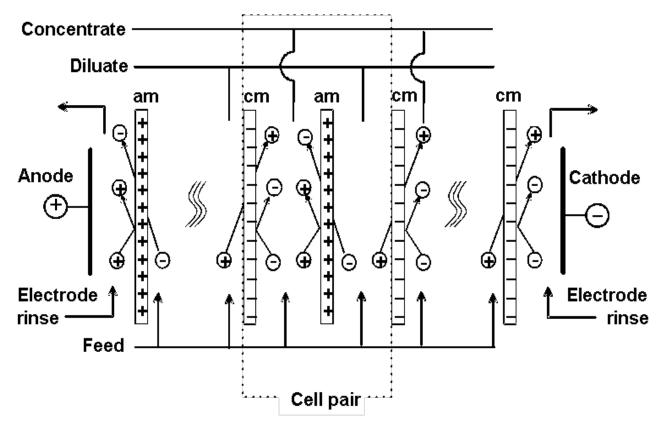


Cation exchange membranes contain fixed negative charges. *Donnan exclusion* prevents anions from passing through membrane.

Anion exchange membranes contain fixed positive charges.

CONVENTIONAL ELECTRODIALYSIS

The process principle



Courtesy of Heiner Strathmann. Used with permission.

ions are removed from a feed solution and concentrated in alternating cells

a cation and an anion-exchange membrane, and a diluate and concentrate cell form a cell pair Strathmann, 2007

Currents in electrodialysis systems are tied to concentrations of ions

$$I = \frac{\Delta c_d \dot{V_d} F |z| \nu}{\xi}$$

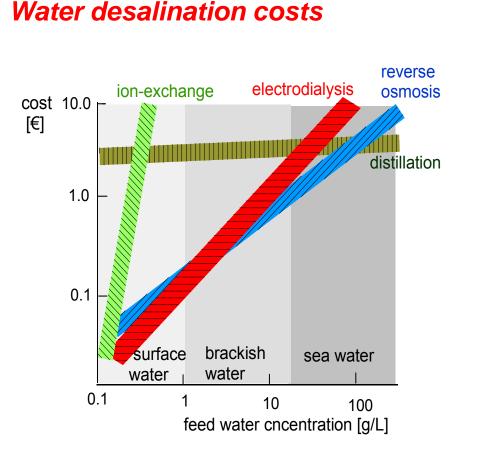
Operating current

$$i_{\rm lim} \cong \frac{2|z|Fc_{d,bulk}D}{\delta}$$

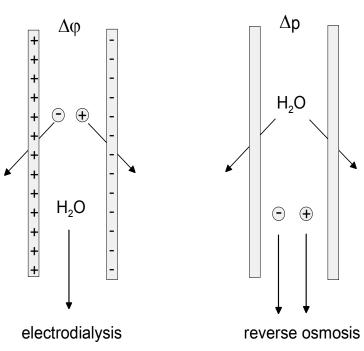
Limiting current density, due to concentration polarization

CONVENTIONAL ELECTRODIALYSIS





Process principles of electrodialysis and reverse osmosis



costs estimated for a required product concentration of < 0.2 g/L

irreversible energy loss proportional to ion transport $(E_{irr} = z_i \vdash \Delta C_i \cup V)$ irreversible energy loss proportional to water transport ($E_{irr} = \Delta p V_{water}$)

Strathmann, 2007

Courtesy of Heiner Strathmann. Used with permission.

Distillation methods

Least work of separation

$$\dot{W}_{least} = \left[\left(\dot{N}\underline{G} \right)_2 + \left(\dot{N}\underline{G} \right)_3 \right] - \left(\dot{N}\underline{G} \right)_1$$

Least heat of separation

$$\dot{Q}_{least} = \frac{\dot{W}_{least}}{(1 - T_c / T_h)}$$

Energy consumption in distillation

- For single stage distillation or single stage flashing: q (kJ/kg) ≈ h_{fg}
- This is far larger than the theoretical least heat of distillation (about 12 kJ/kg-fresh). The reason is both irreversibility and wasted available work (due to hot discharge).
- Performance ratio:

$$R = \frac{h_{fg}}{q}$$

Key steps to improving distillation energy efficiency

- Regeneration:
 - use hot brine or distillate to preheat feed
- Multiple effects:
 - latent heat released by condensing vapor from stage n
 drives vaporization in stage n+1 as lower pressure (MED)
 - hot brine is flashed in successively lower pressure stages (MSF)
- Can achieve performance ratios *R~10* with these methods

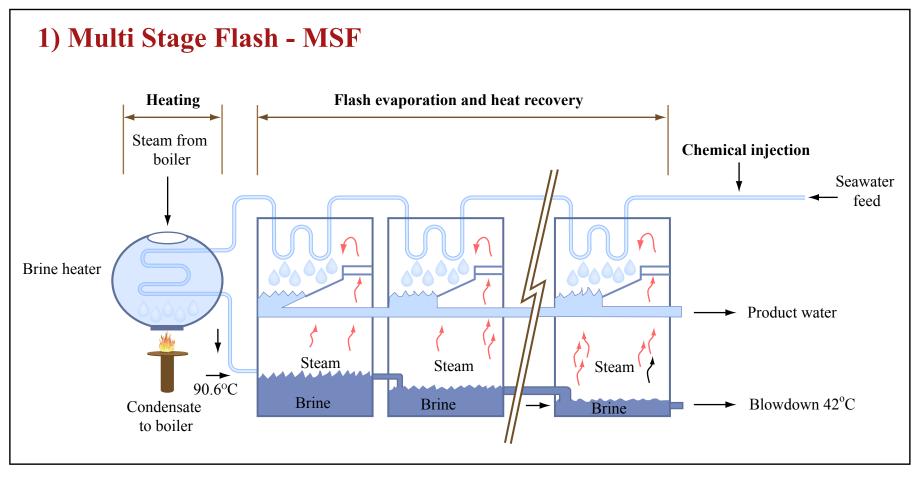
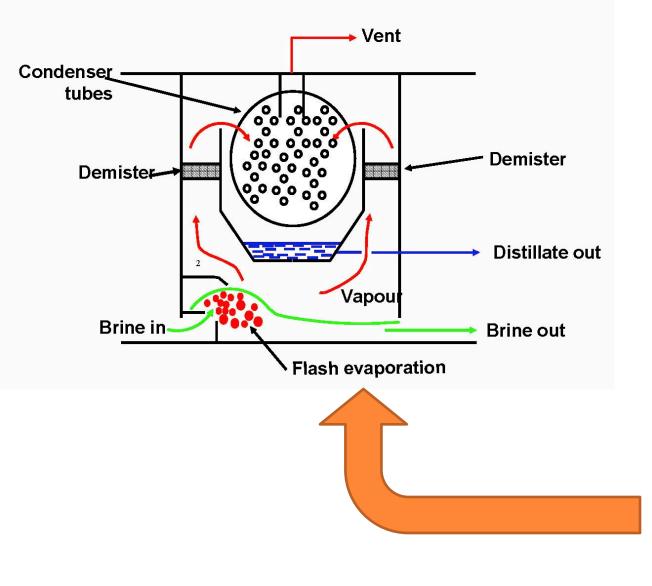


Figure by MIT OpenCourseWare.

Typical stage arrangement of a large MSF plant

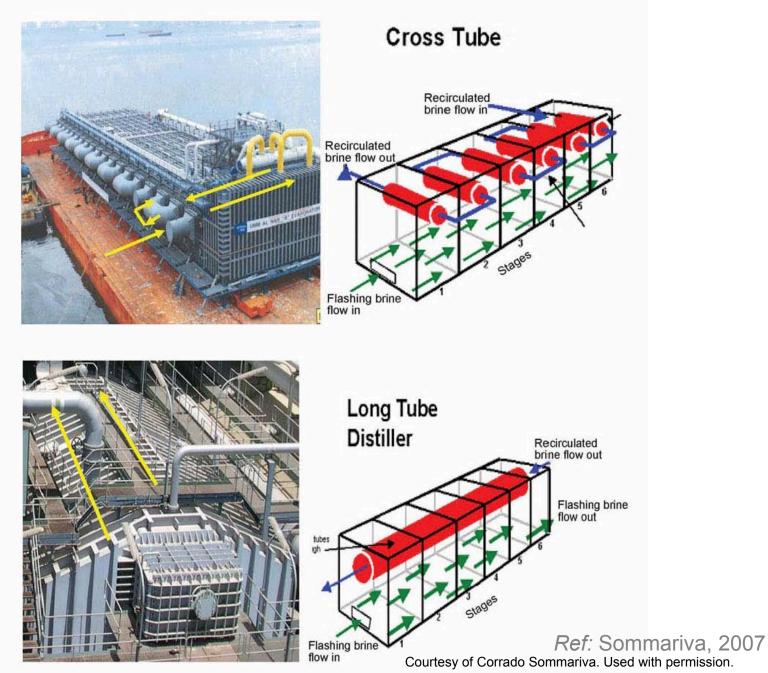


Ref: Sommariva, 2007

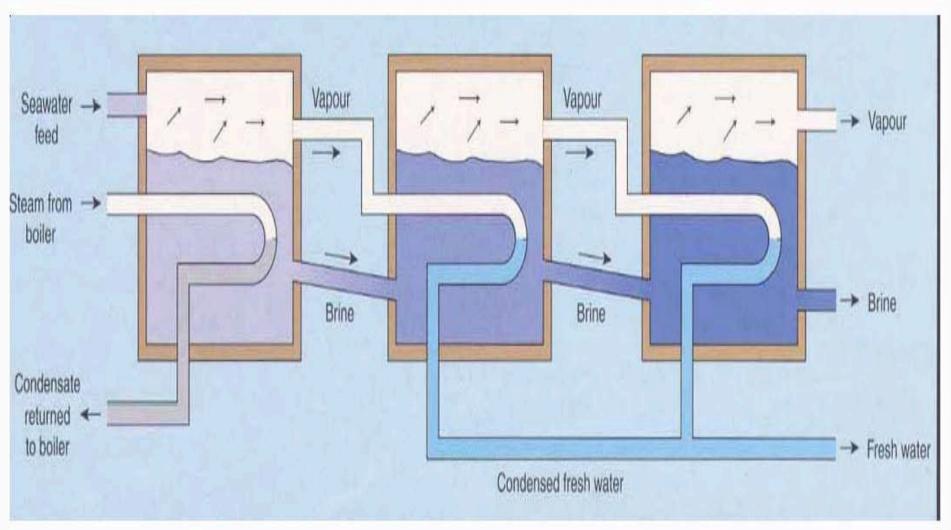
Courtesy of Corrado Sommariva. Used with permission.



Multi stage flash

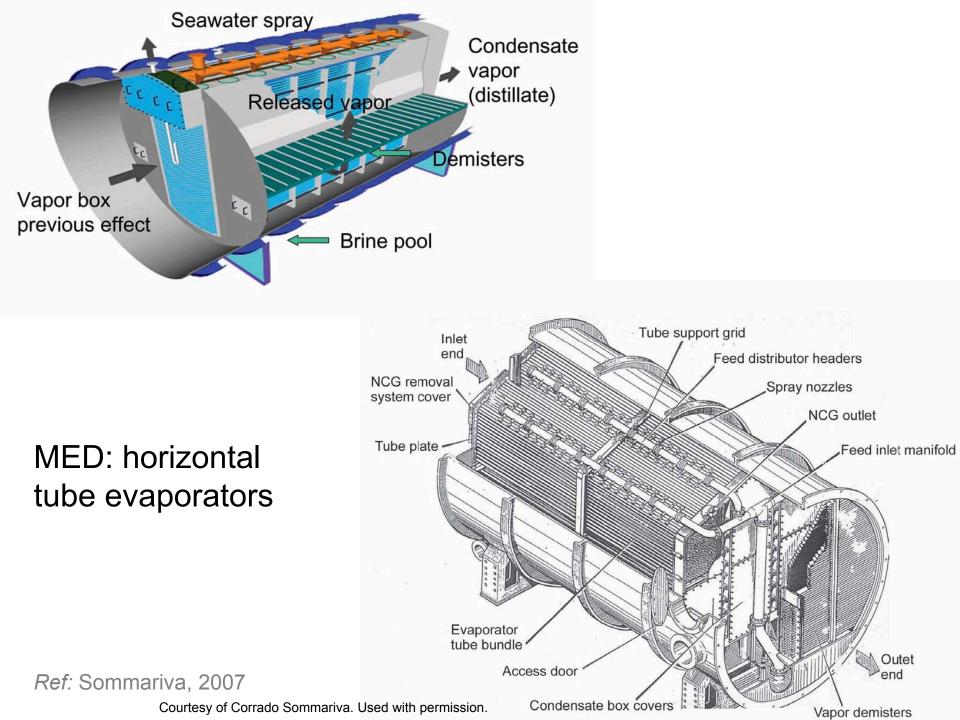


Multieffect distillation concept



Courtesy of Corrado Sommariva. Used with permission.

Ref: Sommariva, 2007



Combined power production and MSF distillation – substantially lowers cost of energy for distillation



Courtesy of Corrado Sommariva. Used with permission.



Solar Desalination

World Insolation (kWh/m²-day)

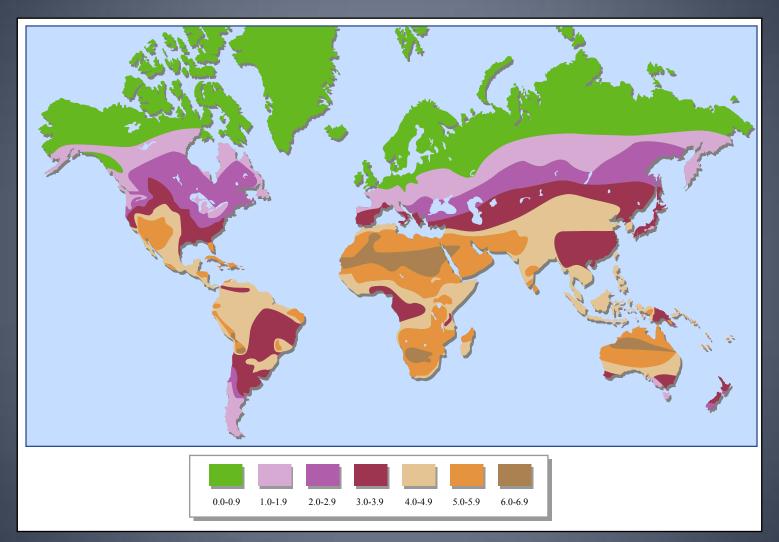
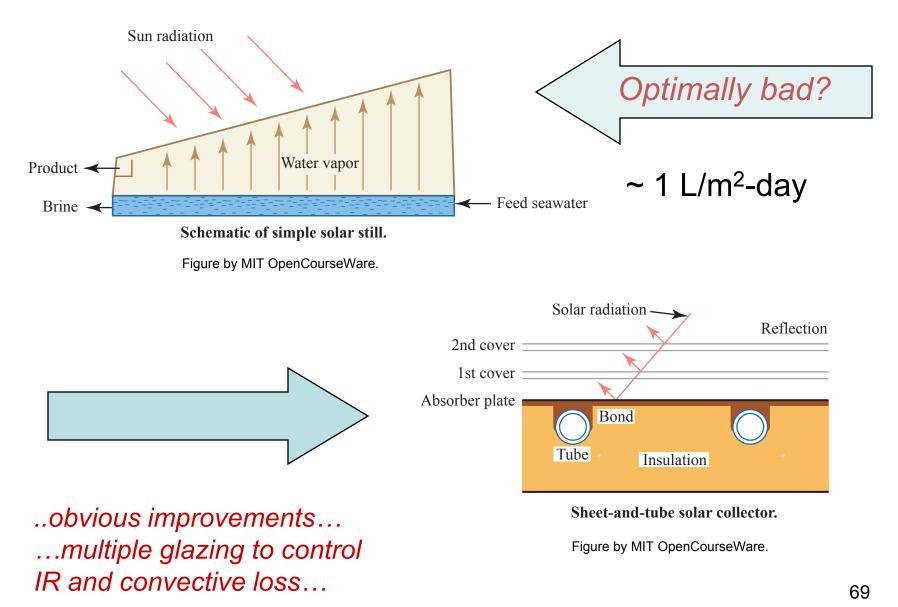
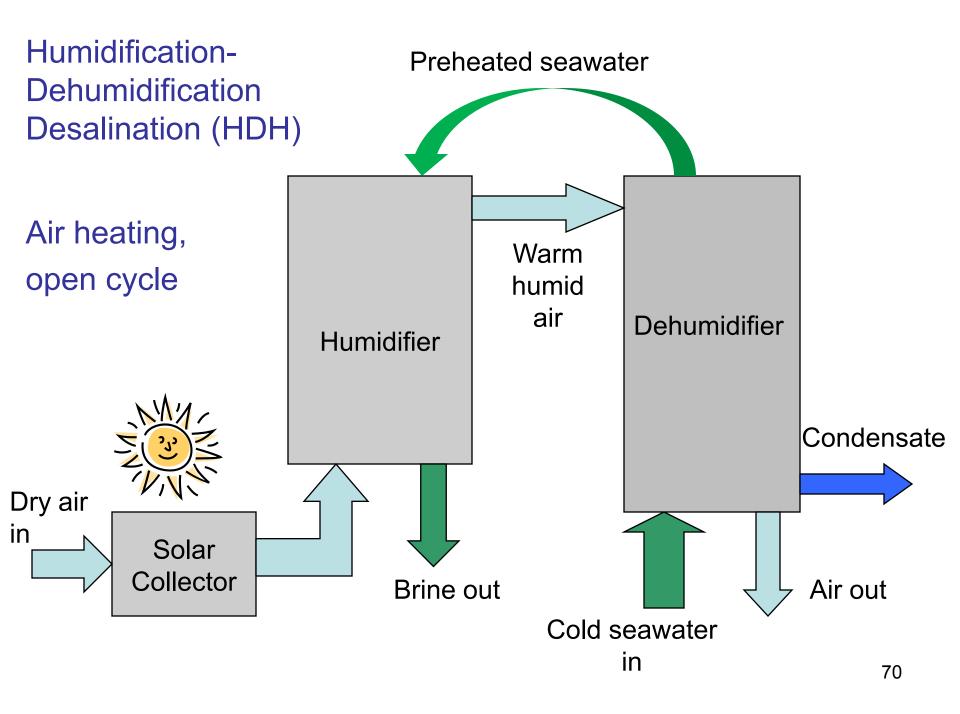


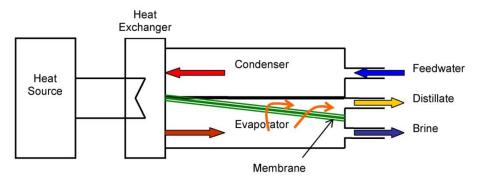
Figure by MIT OpenCourseWare.

Solar Distillation



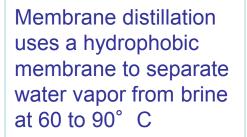
Refs: Ettouney & Rizzuti, 2006; Duffie & Beckman, 2006





Ref: Fath et al., *Desalination*, 2008

Fig. 1. Membrane distillation principles.



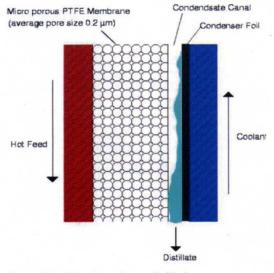
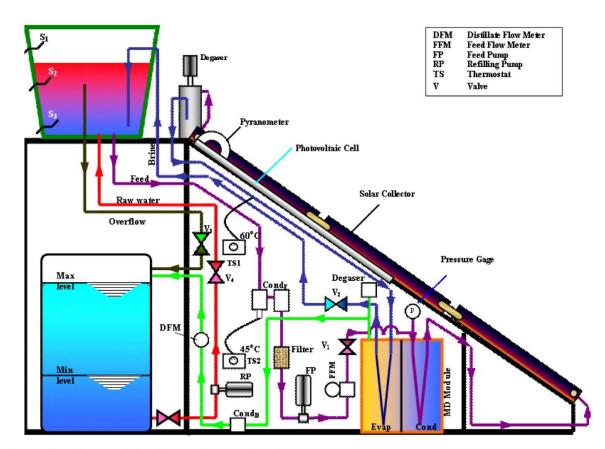


Fig. 1. Principle of membrane distillation.





Concentrating solar power...





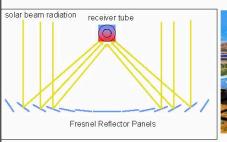
Images by NREL and Schlaich Bergermann und Partner, from Wikimedia Commons, http://commons.wikimedia.org

...achieves higher *T* and higher thermodynamic efficiency



Linear Fresnel Concentrating Solar Thermal Collector

Animation by FhG-ISE



receiver

reflect

Parabolic Trough Concentrating Solar Thermal Collector



Concepts from concentrating solar power can be applied to solar distillation generate

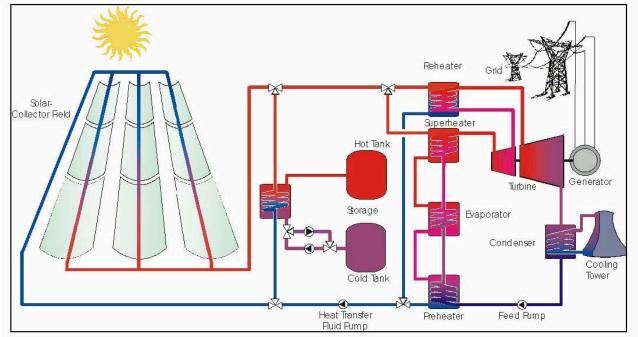
distillation...generate electricity, then make water from waste heat or electricity

Courtesy of Franz Trieb and DLR. See www.dlr.de/tt/aqua-csp. Used with permission.

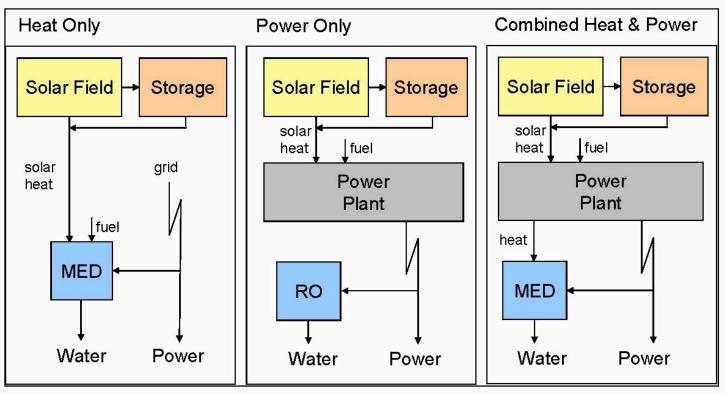
...theoretical performance can be ~100X better than solar still

Ref: Trieb et al., Nov. 2007

Courtesy of Franz Trieb and DLR. See www.dlr.de/tt/aqua-csp. Used with permission.



Combined concentrating solar power and desalination



Courtesy of Franz Trieb and DLR. See www.dlr.de/tt/aqua-csp. Used with permission.

Performance of 35 to 185 L/m²-day

Cost at present is still high by ~2x or more

Ref: Trieb et al., Nov. 2007

Relative performance of desalination techniques

Major concerns in desalination systems

- Cost: hardware, site development
- Cost: energy consumption
- Cost: maintenance
 - Scaling, from precipitation of salts (has a *controlling* influence on design of thermal systems)
 - Fouling, from bacteria and other deposits
 - Degradation of membranes
 - Corrosion of hardware
- Disposal of brine efflux, environmental impact
- Reliability, distribution,...

Energy used	thermal		mechanical	
Process	MSF	MED/TVC	MVC	RO
State of the Art	commercial	commercial	commercial	commercial
World Wide Capacity 2004 (Mm ³ /d)	13	2	0.6	6
Heat Consumption (kJ/kg)	250 – 330	145 - 390		
Electricity Consumption (kWh/m ³)*	3 - 5	1.5 - 2.5	8 - 15	2.5 - 7
Plant Cost (\$/m³/d)**	1500 - 2000	900 - 1700	1500 - 2000	900 -1500
Time to Commissioning (months)	24	18 - 24	12	18
Production Unit Capacity (m ³ /d)	< 76000	< 36000	< 3000	< 20000
Conversion Freshwater / Seawater	10 - 25%	23 - 33%	23 - 41%	20 - 50%
Max. Top Brine Temperature (°C)	90 - 120	55 - 70	70	45 (max)
Reliability	very high	very high	high	moderate (for seawater)
Maintenance (cleaning per year)	0.5 - 1	1 - 2	1 - 2	several times
Pre-treatment of water	simple	simple	very simple	demanding
Operation requirements	simple	simple	simple	demanding
Product water quality (ppm)	< 10	< 10	< 10	200 - 500

Courtesy of Franz Trieb and DLR. See www.dlr.de/tt/aqua-csp. Used with permission.

Ref: Trieb et al., Nov. 2007

Reference	MSF	MEE	VC	Seawater	Brackish RO	Brackish
			2	RO		ED
А	1.10-1.50	0.46-85	0.87-0.92	0.45-0.92	0.20-0.35	6
В	0.80	0.45		0.72-0.93		
С	0.89	0.27-0.56		0.68		e
D	0.70-0.75			0.45-0.85	0.25-0.60	
E				1.54	0.35	7
F				1.50	0.37-0.70	0.58
G	1.31-5.36			1.54-6.56		
Η	1.86	1.49				
I		1.35		1.06		
J				1.25		
K	1.22					2 2
L					0.18-0.56	
М			0.46			
Ν				1.18		
Ο		1.17				
Р			0.99-1.21			
Q				0.55-0.80	0.25-0.28	
R				0.59-1.62		
S				1.38-1.51		
Т				0.55-0.63		
U				0.70-0.80		91;
V					0.27*	
W				0.52		

Table 4. Desalination Costs (\$/m³ fresh water – multiply by 3.8 for \$/1000 gal)

Courtesy of Sandia National Labs. Used with permission.

Ref: Miller (2003)

Prices for consumers in office spaces occupying 4180 m² of city space and using 10,000 m³/y

Country	\$/M ³
Germany	\$1.91
Denmark	\$1.64
Belgium	\$1.54
Netherlands	\$1.25
France	\$1.23
United Kingdom	\$1.18
Italy	\$0.76
Finland	\$0.69
Ireland	\$0.63
Sweden	\$0.58
Spain	\$0.57
U.S.A.	\$0.51
Australia	\$0.50
South Africa	\$0.47
Canada	\$0.40

Figure by MIT OpenCourseWare.

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