Can we save lives with thermodynamics? Nanoengineering and Thermofluids for the Water-Food-Energy Nexus

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Global Preventable Causes of Death



WHO, -factsheets 2014

In 2015 World Economic Forum named "Water Crisis" as the most likely and most impactful global economic risk

World Economic Forum, Geneva, Switzerland, "Global risks 2015 10th edition," 2015.





Growing Water Focus

Water Researchers



Government(funding)Image: Image: I

\$72 million/year NSF: Innovations at the Nexus of Food, Energy and Water Systems (INFEWS) (2016)

Publishers: Two new journals in 2016:



[1] "Global desalination market set to grow 320.3% by 2020 - driven by RO," Membrane Technology, vol. 2011, no. 10, pp. 7 –, 2011.

[2] U. E. I. Administration, International Energy Outlook 2016. U.S. Department of Energy, 2015.

[3] The Water and Food Nexus: Trends and Development of the Research Landscape, Stockholm International Water Institute and Elsevier, 2012

Thermo-nano scientific techniques for water



My Research





Desalination Systems Level



Definitions



$$\begin{array}{ll} \mathbf{2}^{\mathrm{nd}}\text{-law} & \\ \text{efficiency} & \eta_{II} = \frac{\dot{W}_{\mathrm{least}}^{\mathrm{min}}}{\dot{W}_{used}} \end{array}$$





Multistage Vacuum MD



Multiple Effect Distillation (MED)



Multistage Flash (MSF) (once through)



Mechanical Vapor Compression



Humidification-Dehumidification (HDH)



Multistage Vacuum MD



Multiple Effect Distillation (MED)



Multistage Flash (MSF) (once through)



Humidification-Dehumidification (HDH)









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with **desalination**

Membrane Distillation Advantages









MEMSTILL

aquaver





XZERO AB



3/24/2017





AGMD Computational Cell



Primary trade off:

Flux $J = B * \Delta P_{vapor \, pressure}$ thermal $\eta_{MD} = \frac{\dot{Q}_{evap}}{\dot{Q}_{evap} + \dot{Q}_{cond}}$ subscript{gevap} $\sum_{evap} Q_{evap}$

J	flux	[kg/m²s]
В	MD membrane permeability	m²s/kg
Ż	Heat transfer rate	[W]
Sub	script Key	
evap	evaporation	
cond	conduction	

[21] Warsinger et al., IHTC-15, Paper No. IHTC15-9351, (Kyoto, Japan August 2014).

Jumping droplet condensation



Video recorded by N. Miljikovic

Air Gap Membrane Distillation: Flow Regimes



- David Warsinger, Jaichander Swaminathan, Laith Maswadeh, and John Lienhard V. Superhydrophobic condenser surfaces for air gap membrane distillation. In planned submission to Desalination, October 2014.
- 2. 2. David Warsinger, Jaichander Swaminathan, and John. Lienhard V. Superhydrophobic condensing surfaces for air gap membrane distillation, October 2014. reference number 16942.



Air-Gap Membrane Distillation Experimental Setup



CNC Plates for Membrane Module





Sapphire condensing surface (visualization)

CuO Superhydrophobic Surface Fabrication



CuO Superhydrophobic surface desired properties

- High roughness (hydrophobicity)
- Low surface energy coating (hydrophobicity)
- Thin self-limiting layer (thermal conductivity)
- Materials with high thermal conductivity (CuO)
- Robustness for long duration operation
- Scalable to large sizes cheaply (via bath process)



Hydrophobic condensing in MD



Summary of the influence of gap and configuration changes on permeate flux

parameter	Spacer Orientation	Surface Hydrophobicity	Spacer Hydrophobicity	Mesh Thermal Conductivity	Tilt Angle	
range/details	horizontal & diagonal	Contact angle of <20° to 164°	Contact angle of ~80° to ~150°	~0.3 to 400 W/m ² K	Module tilt of - 60° to 85°	
Flux Increase	<5%	0-110%	-22-2%	21-119%	0-54%	

Jumping Droplet Condensation in Membrane Distillation CuO Coated and silanized surfaces

Improved Condensate Flux



Warsinger et al., Journal of Membrane Science, vol. 492, pp. 578–587, 2015.

Warsinger et al., October 2014. Full Patent Application, US Application No. 14/517,342

Improved Flux vs

Implications of hydrophobic condensing

- It improves flux substantially, and overall efficiency (GOR). Are similar gains possible in other thermal desalination technologies?
- Can other condensing and micro-fluidic nanotechnologies improve this and others, including directional wicking?
- How will technologies be designed differently at the nano and system-level with these techniques?

Fouling Types in MD

Inorganic scale



 $CaSO_4$

Particulate fouling



Iron Oxide

Biofouling



Streptococcus faecalis

Membrane degradation



cracking from intermittent operation

David M. Warsinger, **Jaichander Swaminathan**, **Elena Guillen-Burrieza**, **Hassan A. Arafat**, **and John H. Lienhard V.** Scaling and fouling in membrane distillation for desalination applications: A review. *Desalination*, in press, 2014.

Polymer thin films deposited using initiated chemical vapor deposition (iCVD)

iCVD chamber





Roll-to-roll iCVD system



A. Servi

iCVD for hydrophobic membranes

iCVD parameters to optimize



1. Chemistry

- -Safe?
- -Hydrophobicity?
- -Stability & performance



- 2. Thickness and conformality
 - -Avoids pore blocking
 - -Avoids gaps in surface coverage





Top: submerged superhydrophobic MD membrane, visibly shiny due to the thin air layer on its surface.

Bottom: SEM images of MD membrane surface. PVDF membrane coated with PFDA via iCVD for superhydrophobicity

[6] Warsinger et al. Journal of Membrane Science in June 2015 505, 241–252 (2016).

[19] Warsinger et al. In Proceedings of ACE15, Anaheim, CA, USA, (2015).

[29] Warsinger et al. " Provisional Patent Application Submitted, mit-17920pro, 2015

Wetting Occurrence





Membrane type	Manufactu rer	Trade name	Polymer	Thickness (μm)	Nominal pore size (μm)	IPA bubble point (kPa)	Air flowrate (l/min/cm ² @ 0.7 bar)	Contact angle
Flat sheet	Enka	Accurel 2E-PP	PP	177	0.2	114.5	1.3	113°
Flat sheet	Donaldson	Tetratex 6532	PTFE/ PES	130	0.1	200	3	153°

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Properties of polymeric membranes





air vs none = with air layer recharging or not

	Membrane	Feed side		Permeate side		Maximum SDS
Experiment		Air recharg- ing	Spacer	Air recharg- ing	Spacer	Conc. before wetting
E1 (Default 1)	PP	-	-	-	-	0.2
E2	PP	-	+	+	+	0.3
E3	PP	+	-	-	+	0.3
E4 (Default 2)	PTFE	-	-	-	-	0.4
E5	PP	+	+	-	+	0.4
E6	PTFE	+	+	-	+	0.8< (no wetting)

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Concept: providing air at high pressure from the backside (from pure permeate) to reverse wetting



Membrane Distillation



Salty water penetrates through membrane



Percent Change in Liquid Entry Pressure (LEP) after breakthrough





Warsinger et al. *Provisional Patent Application Submitted, mit-18467Kpro (2016).* Warsinger et al. , *MTC16, February 1-5, 2015, San Antonio, Texas*, February (2016).



Reverse Osmosis (RO)




D. M. Warsinger et al., Water Research, vol. 106, pp. 272-282, 2016.

What is Batch?

- A set volume of liquid is concentrated
- Pressure varies over time





Batch RO: High Pressure Tank Concept



How to make a high pressure tank Batch Process?

Need: simultaneously set ideal pressure while volume changes over time, done reversibly!

Idea?

- Motor? Small inefficiencies dominate
- Springs? No $\frac{dP}{dt}$ control



Batch RO: High Pressure Tank Concept



Analysis details



Volume discretization of membrane module for batch models.

The module is divided into unequal volumes, and in each step, equal amounts of permeate are removed from each section and the remaining liquid moves to the next section.

$W_{\text{batch},\text{HP}} =$



Which is discretized across the membrane module for spatial effects, and also calculated over time



Salinity profiles in the membrane module as recovery increases during each cycle for the batch process with 3 ppt at 75% recovery.

Dimensionless distance (The abscissa) is defined as the fraction of the module recovery achieved as the fluid traverses the module (equivalently, i/n). Lines are equally spaced by permeate production; arrows indicate the direction of cycle progression.

Batch Improvement



Percent reduction in energy requirements of batch RO systems compared to continuous, single-stage RO with pressure recovery. D. M. Warsinger et al., *Water Research*, vol. 106, pp. 272-282, 2016.

Applications

• Large-scale desalination

- Agricultural water use: more efficient, cheaper, water savings
- Household disinfection for India etc. 70% water savings
- Mining Water treatment







Batch Cost Savings



Batch RO in the News

WATER DESALINATION REPORT

The international weekly for desalination and advanced water treatment since 196

Volume 52, Number 41



Fort Irwin Water Plant nears completio

hardness to less than 1 mg/L as CaCO3, before it undergoes crystallization in a 40 gpm (2.52 L/s) Encon forced circulation evaporator with mechanical vapor compression (MVC).

Initially, the RO permeate and evaporator distillate are returned to the head of the plant; however, upon California Department of Public Health approval, both flows will be blended with the EDR product water.

The non-recoverable portion of the RO concentrate, spent regenerant, crystallizer blowdown, lime sludge and CIP wastes are discharged to the eight active, and one standby, solar evaporation ponds. The ponds have an average water depth of 16 inches (41cm) and a combined surface area of 6.74 acres (2.7ha). It is anticipated that a pond will be removed from service once every eight years for cleaning, with the solids hauled to a landfill for disposal.

process, this was not an absolute energy minimum for RO desalination, adding, "It may be that better designs can move us even closer to the true thermodynamic limit.

31 October 2016

WDR has reviewed two recently accepted Journal papers in which researchers have evaluated several RO configurations as they consider various strategies of approaching greater energy efficiency.

The first paper is entitled "Energy efficiency of batch and semi-batch reverse osmosis desalination" by MIT's David Warsinger, Emily Tow, Kishor Navar, Laith Maswadeh and John Lienhard V. The paper was published in Elsevier's Water Research journal online on 25 September. The second paper is entitled "Can batch or semi-batch processes save energy in reverse-osmosis desalination?" by Yale University's Jay Werber, Akshay Deshmukh and Menachem Elimelech. It is scheduled for January 2017 publication in Desalination.

The semi-batch process referred to in both papers is Desalitech's Closed Circuit Desalination (CCD) process, which recirculates pressurized concentrate until a desired recovery level is achieved. The concentrate is then displaced from the system with new feedwater without interrupting the feed or permeate flows.

Both papers also analyzed pressure exchanger batch ROs, agreeing that batch processes may be "the least energy possible RO processes," while acknowledging that scalable, energy-efficient batch systems have not yet been developed Although the Yale authors consider a variable volume tank arrangement to be "relatively impractical", they believe it to be "ideal from an energetics perspective".

Administration in the Administration and a second s



Batch desalination configuration bests standard reverse osmosis approach

Researchers develop a new way to create more clean water with less energy, thanks to clever timina.

School of Engineering November 18, 2016

With water scarcity affecting nearly 2 billion people - many of whom live near the oceans -"water, water everywhere and not a drop to drink" has become a common cry for more than iust wayward sailors. Desalination through reverse osmosis (RO) has long offered one solution to help meet global water needs in the face of population growth, development, and climate change. However, removing salt from water is energy-intensive.



A team of MIT researchers has responded by creating new designs for reverse osmosis



TECH IDOL

BIOGRAPHY



Dr. David Warsinger completed his B.S. and M.Eng at Cornell, and his PhD in Mechanical Engineering at MIT: he completed his oraduate studies in a combined 3 years. David's research focuses on the water-energy nexus, with approaches from thermofluids and nanoengineering. Currently, David is a PostDoc at MIT and beginning a joint PostDoc at Harvard. Prior to starting his PhD, David worked at the engineering consulting firm Arup, where he performed energy and sustainability analysis and designed heating and cooling systems. David is a coauthor of 22 published and 6 submitted journal or conference papers, and a co-inventor on 13 filed or awarded patents. He is also involved with entrepreneurial endeavors, including demonstrating batch reverse osmosis with MIT startup Sandymount, and cofounding Coolify, a startup providing cold storage for farmers in developing economies. Notable awards David has earned include the national dissertation award from UCOWR, the highest GPA award for his masters, and the MIT Institute Award for Best Research Mentor for Undergraduate Students.



DAVID WARSINGER







Commercialization Strategy



Commercialization and additional funding implementation plan of batch desalination research

Can we get big benefits too from improving not just the process, but its nanomaterials?



Ultrapermeable RO Membranes: Graphene Oxide (GO)

- Reduces membrane area $(\$_{\downarrow})$
- Energy savings: less overpressure
- Potentially fouling resistant
- **Emerging contaminants (PFOA)**



Decrease in "l"



D. M. Warsinger et al. (in progress)

C. Amandei D. M. Warsinger et al. (in progress)



Visualizing Water Stress









Phase-change thermal storage

- Freezing packed-bed heat transfer
- Thermodynamic system design
- Phase change materials



Packed bed of solid materials







Cooling Load (kW)

Vision & Collaboration



Energy-Water Nexus Funding Ecosystem



Water-Energy-Food Nexus



Acknowledgements







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Can we save lives with thermodynamics?



Questions?



Feed Modeling

 $Nu = \frac{(f/8) \cdot (Re - 1000) \cdot Pr}{1 + 12.7 \cdot (f/8)^{1/2} \cdot (Pr^{2/3} - 1)}$

$$Sc_f = \frac{\mu_f}{(\rho_{feed} \cdot D_{s,w})}$$

$$K_{cond} = \frac{k_m \cdot (1 - \xi) + k_{air} \cdot \xi}{\delta_m}$$

Main Flux eqn
$$J_i = B \cdot (P_{f,m,i} - P_p \cdot x_{a,m,i})$$

Concentration along flow direction $x_{f,b,i} = S_{in} \cdot \left(\frac{m_{f,i}}{\dot{m}_{f,in}/n_{sheets}}\right)$

Effect of concentration polorization

$$x_{f,m,i} = x_{f,b,i} \cdot \exp\left(\frac{J_i}{k_{mass} \cdot \rho_{feed}}\right)$$

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$$P_{f,m,i} = \mathcal{P}_{\text{sat}}\left(Water, \ \mathbf{T} = T_{f,m,i}\right) \cdot \left(1 - \left(\frac{\frac{x_{f,m,i}}{MW_{solute}}}{\left(\frac{x_{f,m,i}}{MW_{solute}}\right) + \left(\frac{1000 \ [\text{g/kg}] - x_{f,m,i}}{MW_{water}}\right)}\right)\right)$$

 $q_{out,i} = J_i \cdot (h_{fg,f,i}) + q_{m,i} - J_i \cdot (h_{f,b,i} - h_{f,m,i})$

Air Gap & Condensate

Diffusion Equation

$$\left(\frac{J_i}{M_{H2O}}\right) = \frac{c_{a,i} \cdot D_{wa}}{d_{gap} - \delta_i} \cdot \ln\left(1 + \left(\frac{x_{i,i} - x_{a,m,i}}{x_{a,m,i} - 1}\right)\right)$$

$$T_{a,m,i} - T_{i,i} = \left(\frac{q_{conv,i}}{k_{mix,i}}\right) \cdot \left(\alpha_{mix,i} \cdot \frac{\rho_{mix,i}}{J_i}\right) \cdot \left(\exp\left(\frac{J_i}{\rho_{mix,i} \cdot \alpha_{mix,i}} \cdot (d_{gap} - \delta_i)\right) - 1\right)$$

$$\nu_{f,i} = \frac{\mu\left(Water, \mathbf{P} = P_p, \mathbf{T} = T_{av,film,i}\right)}{\rho_f}$$

Condesnation film thickness

$$J_i \cdot dA = g \cdot \frac{\rho_f - \rho_g}{3 \cdot \nu_{f,i}} \cdot w \cdot \left(\delta_{i+1}^3 - \delta_i^3\right)$$

heat absorbed by condensate

$$q_{c,i} = J_i \cdot h_{fg,c,i} + q_{m,i}$$

film conduction resistance

$$q_{c,i} = \frac{k_{film,i}}{\delta_i} \cdot (T_{i,i} - T_{wall,i})$$

Cooling Channel Modeling

$$d_{h,c} = 4 \cdot \frac{w \cdot d_{cond}}{2 \cdot (w + d_{cond})}$$

BL resistance

$$T_{wall,i} = T_{c,b,i} + \left(\frac{q_{c,i} + J_i \cdot (h_{c,i,i} - h_{c,wall,i})}{h_{t,c}}\right)$$

conserve energy in bulk stream

 $h_{c,b,i+1} = h_{c,b,i} - (q_{c,i} + J_i \cdot (h_{c,i,i} - h_{c,wall,i})) \cdot \frac{dA}{\dot{m}_{f,1} + (\dot{m}_{c,ex}/1)}$



Efficiency Definitions Typical Value Definitions

Parameter

ε

Flux
$$J = \frac{\dot{m}_{\rm p}}{A}$$

GOR Energy Efficiency 1.5-15 $GOR = \frac{\dot{m}_{p}h_{fg}}{\dot{Q}_{f}}$ **M** MD Thermal Efficiency .5-.93 $\eta = \frac{\dot{Q}_{vap}}{\dot{Q}_{vap} + \dot{Q}_{cond}}$

NTU Dimensionless size 4-35 $NTU = \frac{UA}{\dot{m}c_p}$

Heat transfer effectiveness 0.3-0.95

$$\varepsilon = \frac{h_{\rm c,out} - h_{\rm c,in}}{h_{\rm f,in} - h_{\rm c,in}} = \frac{T_{\rm c,out} - T_{\rm c,in}}{T_{\rm f,in} - T_{\rm c,in}}$$

2-10 L/m²hr

pure water flux (J, measured in L/m²-hr). Where $\dot{m}_{\rm p}$ is the mass flow rate of feed, A is the area.

 $h_{\rm fg}$ is the enthalpy of vaporization (2257 kJ/kg $\dot{Q}_{\rm f}$ is the total heat energy input.

Heat transfer by conduction across the membrane (\dot{Q}_{cond})

NTU, or number of transfer units

U is the overall heat transfer coefficient $c_{\rm p}$ is the specific heat.

Model Validation



η and \mathcal{E}



GOR vs Flux Seawater salinity





Figure 7: A comparison of GOR and Flux for AGMD and CGMD, $s_f = 250 \text{ g/kg}^{-58}$

GOR vs Flux High salinity



Impact of salinity AGMD



Figure 8: AGMD. The GOR-flux curves at high salinity exhibit decreasing GOR and flux at large system size $(L > L^*)$ or correspondingly $J < J^*$. The J^* value increases as s_f increases, but is not as easy to see.

Dimensionless framework



Figure 12: GOR as a function of NTU from the discretized and simplified HX model of MD. Dotted lines are results from the HX model, and show that the HX model is also capable of capturing the NTU* beyond which flux begins to decline. Just like J* increases at high salinity, the critical system size (or NTU*) decreases with feed salinity. Shorter module lengths have to be used when treating high salinity water with MD. The * indicates optimal system size to maximize GOR

Maximum Performance



Figure 16: Max GOR possible by using the ideal membrane thickness at each salinity and flux for CGMD