Fouling Resistant Membranes for Treating Concentrated Brines for Water Reuse in Advanced Energy Systems

Zachary Hendren[1], Rachael Guenter[1], Elliot Reid[1], Young Chul Choi[1], Wenyan Duan[2], Alexander Dudchenko[2], David Jassby[2]

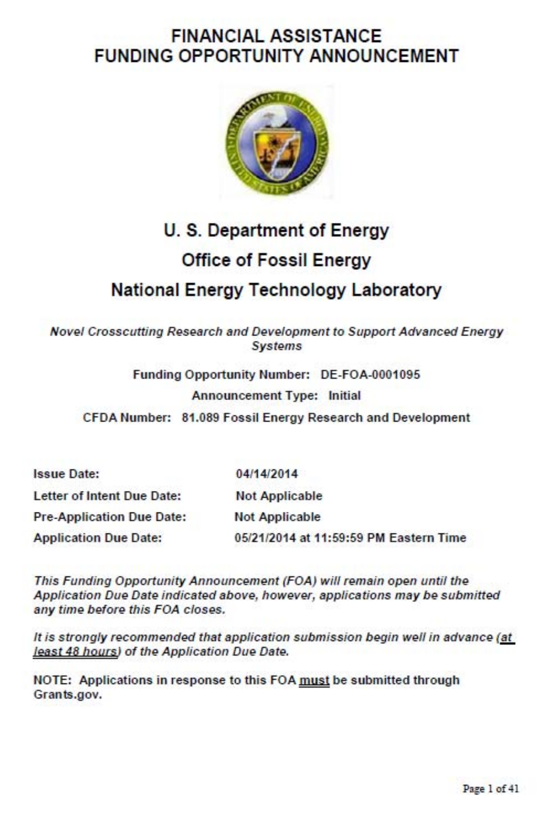
Crosscutting Research Portfolio Review
March 23rd 2017, Pittsburgh PA

DOE Award No. DE-FE0024074

Period of Performance: 10/1/2014 to 9/30/2017

[1] RTI International, Energy Technology Division (zhendren@rti.org)
[2] UC Riverside, Bourns College of Engineering

Project Goals and Objectives



FINANCIAL ASSISTANCE
FUNDING OPPORTUNITY ANNOUNCEMENT

U. S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Novel Crosscutting Research and Development to Support Advanced Energy Systems

Funding Opportunity Number: DE-FOA-0001095
Announcement Type: Initial
CFDA Number: 81.089 Fossil Energy Research and Development

Issue Date:	04/14/2014
Letter of Intent Due Date:	Not Applicable
Pre-Application Due Date:	Not Applicable
Application Due Date:	05/21/2014 at 11:59:59 PM Eastern Time

This Funding Opportunity Announcement (FOA) will remain open until the Application Due Date indicated above, however, applications may be submitted any time before this FOA closes.

It is strongly recommended that application submission begin well in advance (at least 48 hours) of the Application Due Date.

NOTE: Applications in response to this FOA must be submitted through Grants.gov.

Page 1 of 41

- **Project Objectives**:
  - Demonstrate the efficacy of membrane distillation (MD) as a cost-savings technology to treat concentrated brines that have high levels of total dissolved solids (TDS) for beneficial water reuse.
  - Develop a novel, fouling-resistant nanocomposite electrically conductive membrane that will reduce the need for chemicals to address membrane scaling due to the precipitation of divalent ions in high-TDS wastewaters.

#	Milestone Title	Milestone Completion Date	Verification Method
1	Successful demonstration of ECMD membrane	4/15/15	Experimental demonstration of simultaneous MD and EC applied.
2	Feasibility of MD technology for treating produced waters with total-dissolved-solids concentration of at least 180,000 mg/L	9/4/15	Experimental data showing that at least 50% clean water recovery can be achieved
3	Enhanced fouling resistance of conductive MD membranes	5/31/17	Experimental data showing that relative water flux of at least 0.8 can be maintained with highly scaling waters
4	Conductive membrane model validation	6/30/17	Model validated ($r^2 > .8$) with experimental data

Presentation Outline

- Background
- Experimental results
- Modeling results
- Preliminary cost assessment comparison
- Future work and summary

RTI International

delivering **the promise of science**
for global good

RTI International is an independent, nonprofit research institute dedicated to improving the human condition. We combine scientific rigor and technical expertise in social and laboratory sciences, engineering, and international development to deliver solutions to the critical needs of clients worldwide.

Energy Technology Research at RTI International

ENERGY TECHNOLOGIES

Developing advanced process technologies for energy applications by partnering with industry leaders

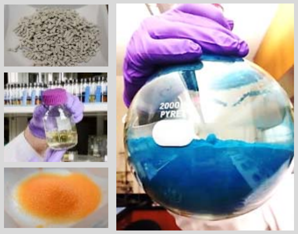

Carbon Capture & Utilization

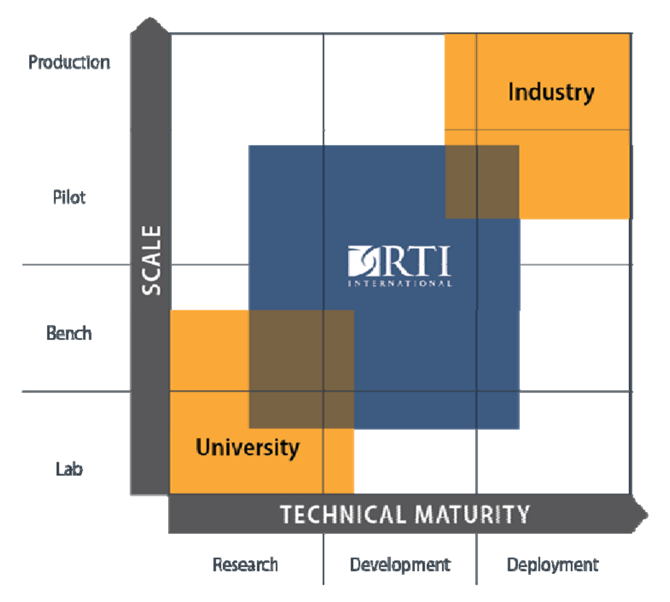

Industrial Water Treatment


Biomass Conversion


Natural Gas


Syngas Processing

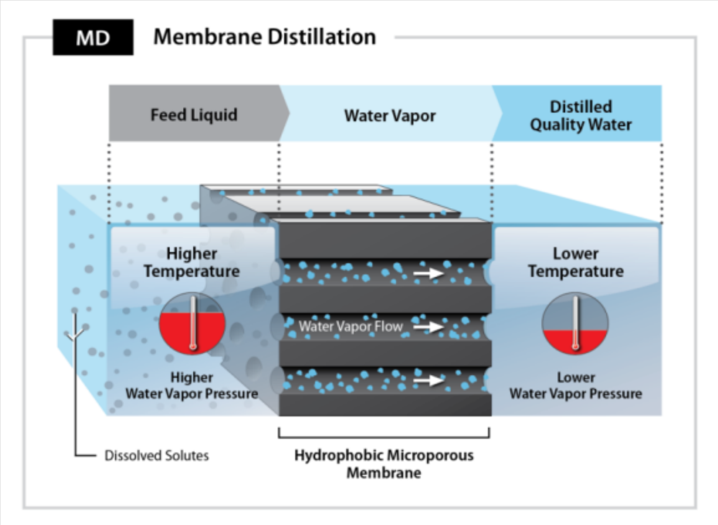

Advanced Materials

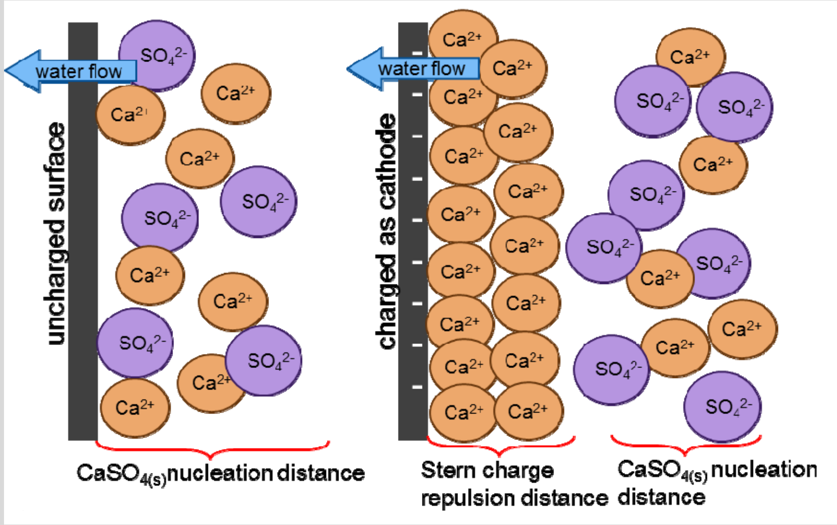


Focused on Applied Research
(concept to demonstration) in Partnership with
Government Agencies, Academia, and Industry

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy | BIOENERGY TECHNOLOGIES OFFICE
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy | ADVANCED MANUFACTURING OFFICE
arpa-e
EMISSIONS REDUCTION ALBERTA
GASSNOVA
CASALE
CLARIANT
BASF We create chemistry
SINTEF
HALDOR TOPSOE
VEOLIA
Masdar
THE LINDE GROUP
BERKELEY LAB
MIT
CLEMSON UNIVERSITY
NC STATE UNIVERSITY
STANFORD UNIVERSITY
Duke UNIVERSITY
UNIVERSITY OF CALIFORNIA UC RIVERSIDE

Project Concept: Electrically Conductive Membranes + Membrane Distillation = ECMD





Increasing TDS concentration & scaling potential

No desalination

Brackish RO

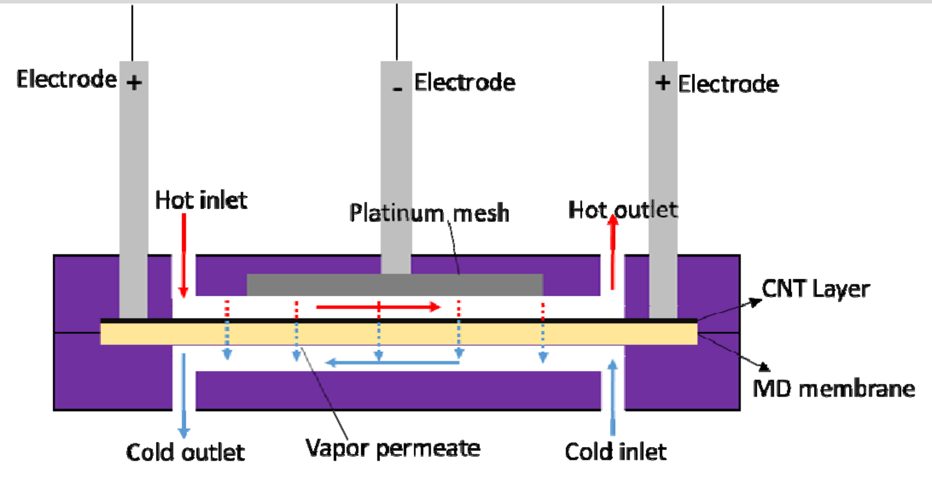
Seawater RO

Evaporation

Crystallization

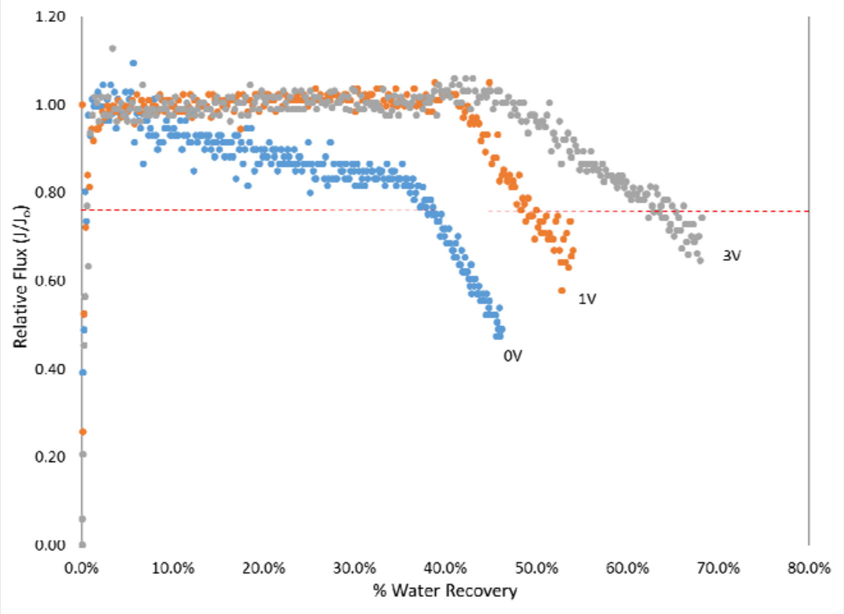
Membrane Distillation (MD)

ECMD Test Cell



- Plate-and-frame flat sheet single membrane test cell
- Continuous data logging of operating parameters
- Test run in countercurrent configuration
- External electrical supply for AC/DC voltages
- Membrane as anode or cathode

Scaling Resistance for Calcium Sulfide



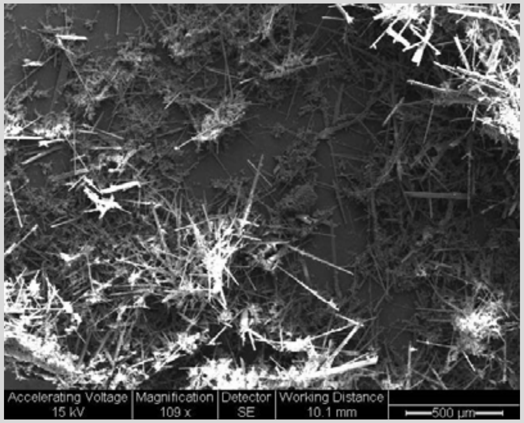
Feed = $CaSO_4$ scaling solution:

- 0.0134M Na_2SO_4
- 0.0200M $MgSO_4$
- 0.0164M $CaCl_2$

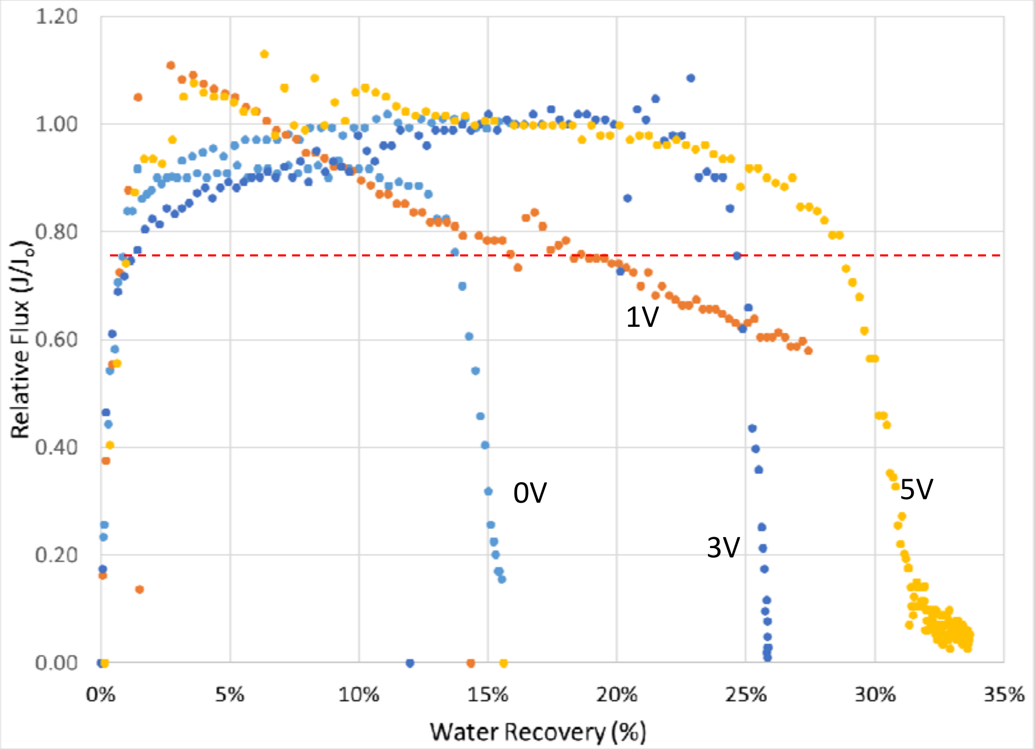
T_f = 60°C
T_p = 20°C
Average salt rejection >99.99%

Membrane	Feed T (°C)	EC voltage	Time (min)	Volume recovered (%)
CNT-PVDF	60	0V	1079	39%
CNT-PVDF	60	1V	993	49%
CNT-PVDF	60	3V	1382	64%

To reach 75% relative flux



Scaling Resistance for Calcium Chloride



Feed = $CaCO_3$ scaling solution:

- 0.0072 $CaCl_2$
- 0.0107M KCl
- 0.0047 $MgCl_2$
- 0.0094M Na_2CO_3

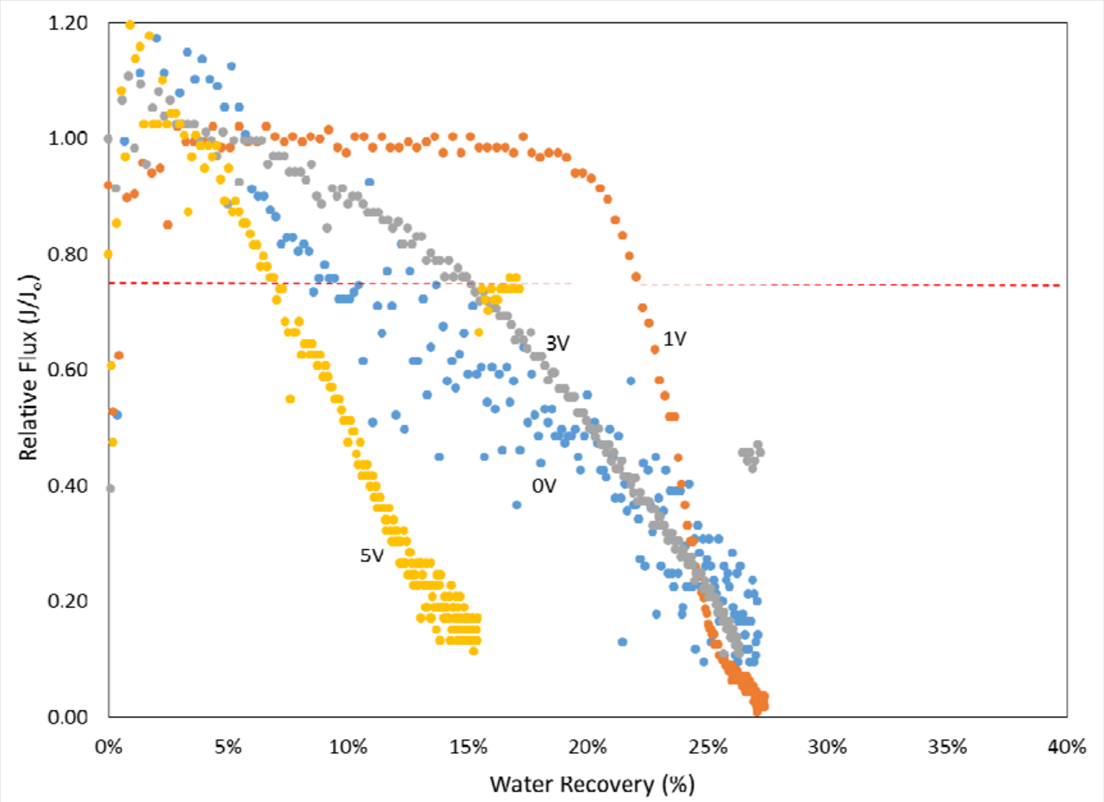
T_f = 60°C

T_p = 20°C

Average salt rejection >99.99%

Membrane	Feed T (°C)	EC voltage	Volume recovered (%)
CNT-PTFE	60	0V	14%
CNT-PTFE	60	1V	17%
CNT-PTFE	60	3V	25%
CNT-PTFE	60	5V	29%

Scaling Resistance for Strontium Sulfide



Feed = $SrSO_4$ scaling solution:

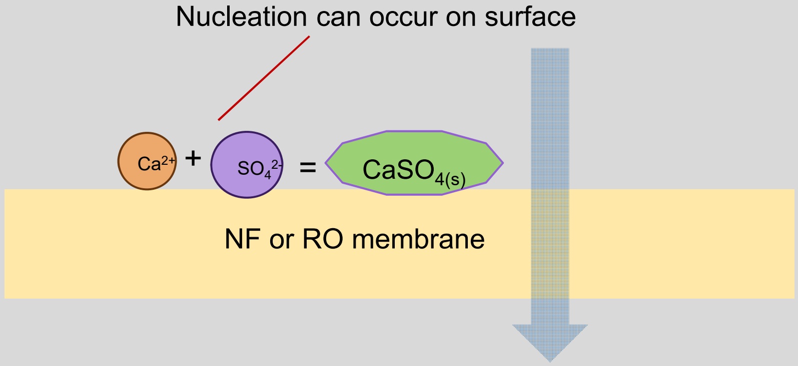
- 110 g/L NaCl
- 61 g/L $MgCl_2$*6H_2O
- 40 g/L KCl
- 1.25 g/L $SrCl_2$*6H_2O
- 2.5 g/L Na_2SO_4

T_f = 60°C
T_p = 20°C
Average salt rejection >99.99%

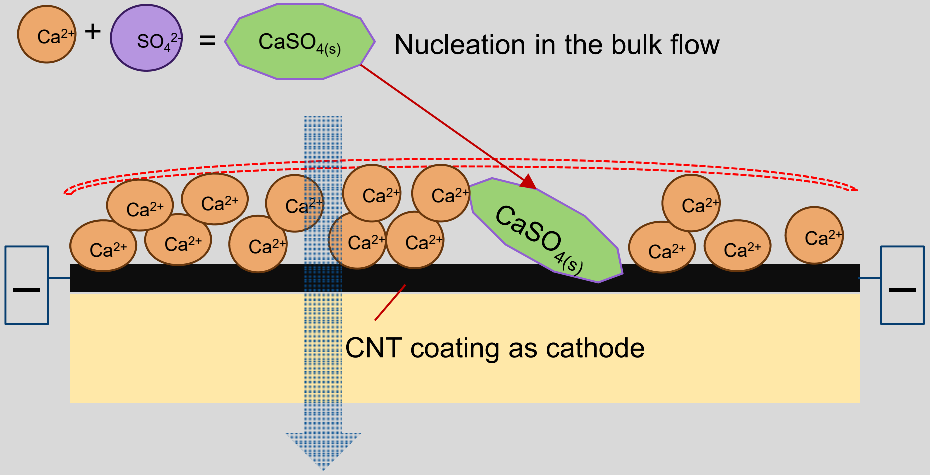
Scaling inhibition not observed with increased voltage for SrSO4 (solution unstable)

Mechanisms for Scaling of Membrane Surface

Scaling on normal membrane surface



Charge repulsion using electrically conductive membrane

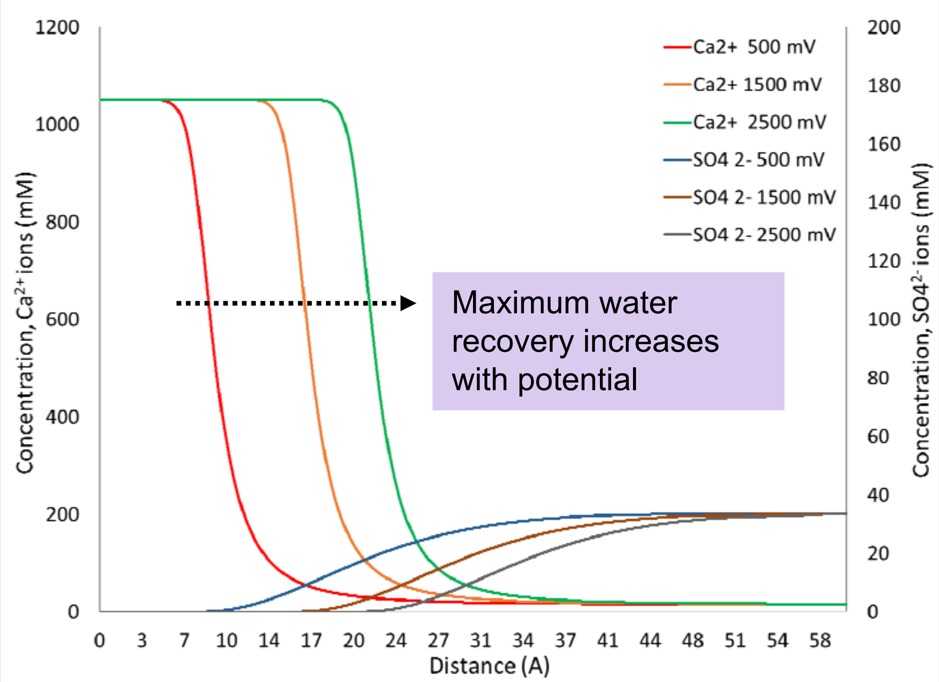


- Charge barrier is ~20Å at 3V
- The diameter of $CaSO_4$ nuclei ~15Å*
- Deposition of non-ionically charged particles accounts for scaling buildup

*Lochhead, M.J., Letellier, S.R., & Vogel, V. (1997). Assessing the role of interfacial electrostatics in oriented mineral nucleation at charged organic monolayers. The Journal of Physical Chemistry B, 101(50), 10821-10827.

Modeling Ion Concentrations and Charge on ECMD Surface

Feed Temperature = 60°C



Maximum water recovery increases with potential

Increasing surface charge increases the thickness of the ion layer along the surface, with a corresponding decrease in the rate of scaling for a given concentration.

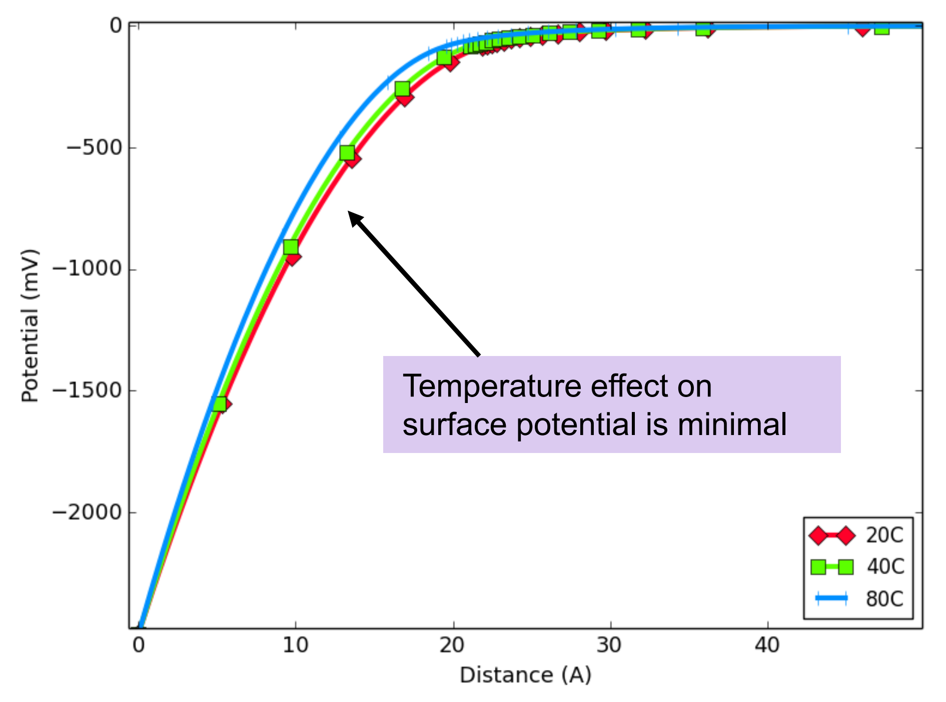
For charged surfaces >200mV use modified Poisson-Boltzmann (MPB) to predict ion concentrations near a charged surface.

$$\varepsilon_e \frac{d^2\psi}{dx^2} = \frac{-eN_A \sum_{i=1}^{m} z_i c_i^{\infty} \exp\left(-\frac{z_i e\psi}{kT}\right)}{1 + \sum_{i=1}^{m} \frac{c_i^{\infty}}{c_i^{\max}} \left[\exp\left(-\frac{z_i e\psi}{kT}\right) - 1\right]}$$

$$c_i = \frac{c_i^{\infty} \exp\left(-\frac{z_i e\psi}{kT}\right)}{1 + \sum_{i=1}^{m} \frac{c_i^{\infty}}{c_i^{\max}} \left[\exp\left(-\frac{z_i e\psi}{kT}\right) - 1\right]}$$

Where:
ψ = electrical potential,
z = valence of ions
e = elementary charge,
N_A = Avogadro's number
T = Temperature
c = ion concentration
k = Boltzmann constant

Modeling Ion Concentrations and Charge on ECMD Surface



Temperature effect on surface potential is minimal

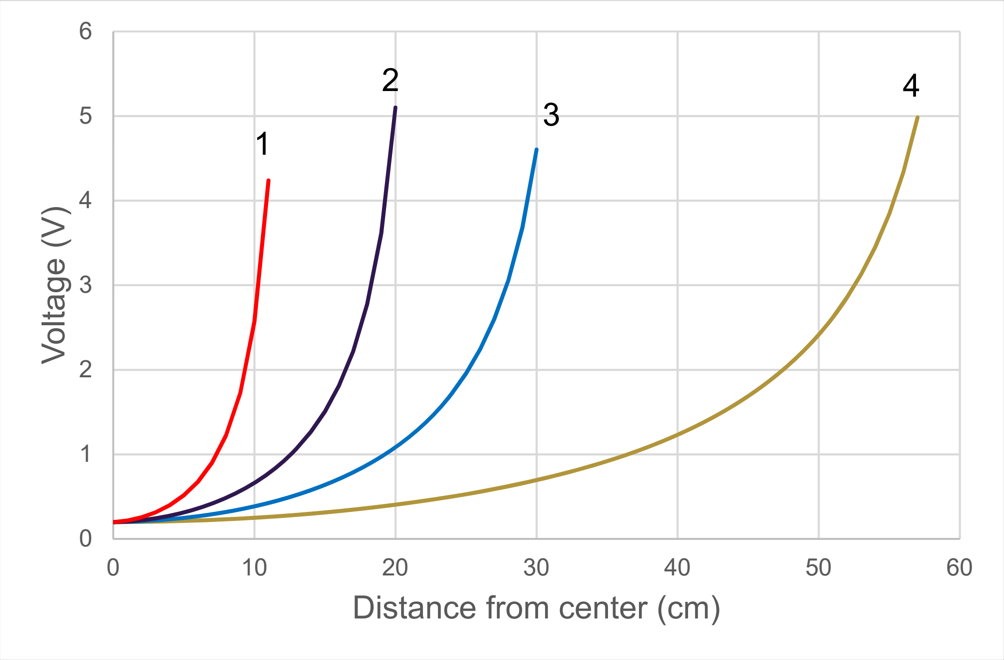
For charged surfaces >200mV use modified Poisson-Boltzmann (MPB) to predict ion concentrations near a charged surface.

$$\varepsilon_\mathrm{e} \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{-eN_\mathrm{A} \sum_{i=1}^{m} z_i c_i^{\infty} \exp\left(-\frac{z_i e\psi}{kT}\right)}{1 + \sum_{i=1}^{m} \frac{c_i^{\infty}}{c_i^{\max}} \left[\exp\left(-\frac{z_i e\psi}{kT}\right) - 1\right]}$$

$$c_i = \frac{c_i^{\infty} \exp\left(-\frac{z_i e\psi}{kT}\right)}{1 + \sum_{i=1}^{m} \frac{c_i^{\infty}}{c_i^{\max}} \left[\exp\left(-\frac{z_i e\psi}{kT}\right) - 1\right]}$$

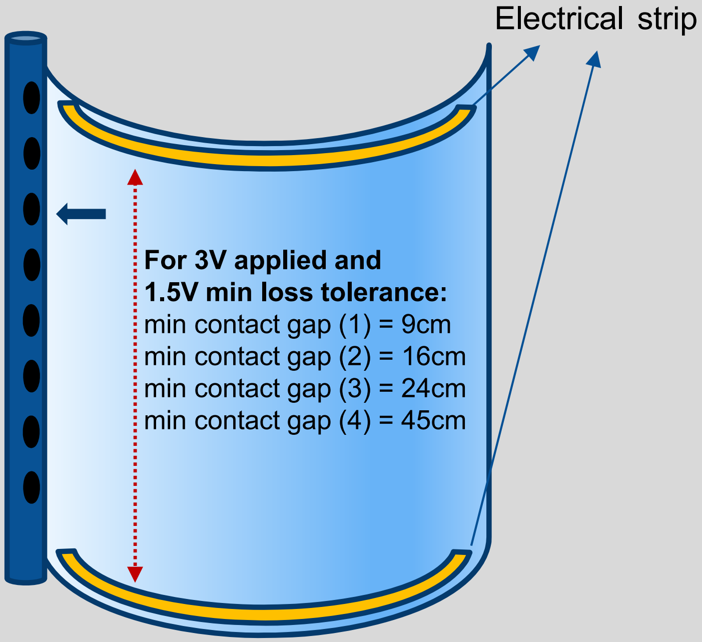
Where:
ψ = electrical potential,
z = valence of ions
e = elementary charge,
N_A = Avogadro's number
T = Temperature
c = ion concentration
k = Boltzmann constant

Voltage Distribution at Large Scale



0 is center of film between
metal electrodes

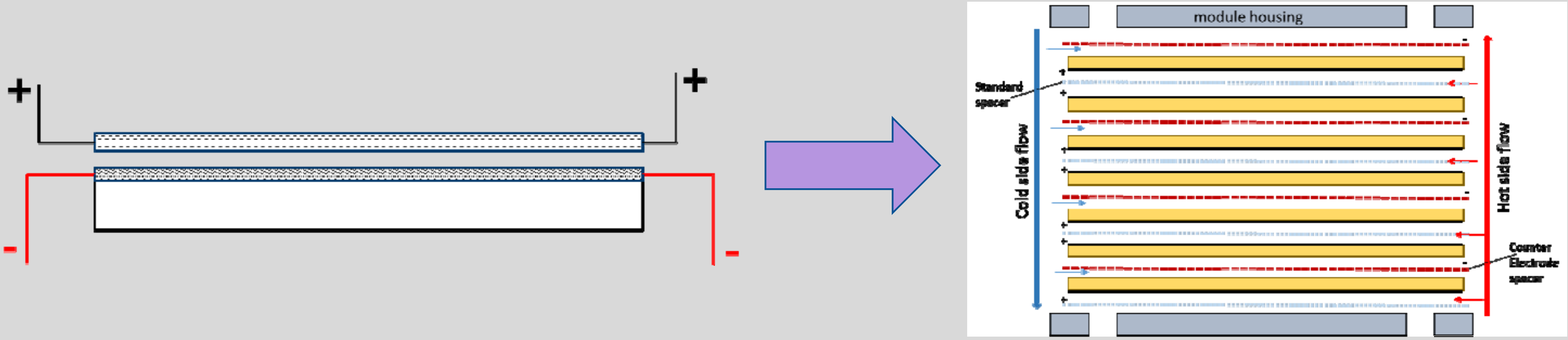
- 1 - 6300 Ω/square CNT, 600 Ω/square counter electrode
- 2 - 3000 Ω/square CNT, 600 Ω/square counter electrode
- 3 - 1000 Ω/square CNT, 600 Ω/square counter electrode
- 4 - 100 Ω/square CNT, 600 Ω/square counter electrode



For 3V applied and
1.5V min loss tolerance:
min contact gap (1) = 9cm
min contact gap (2) = 16cm
min contact gap (3) = 24cm
min contact gap (4) = 45cm

Full Scale ECMD Module Design Considerations

- **Electricity delivery**
  - Ensure leak free module design
  - Maintain charge along larger surface
- **Counter electrode**
  - Carbon cloth as substitute for titanium?
  - Vary location and size of counter electrode
- **Power consumption**
  - Current leakage across high TDS fluid
  - Effect of module configuration/spacer distance on potential power consumption

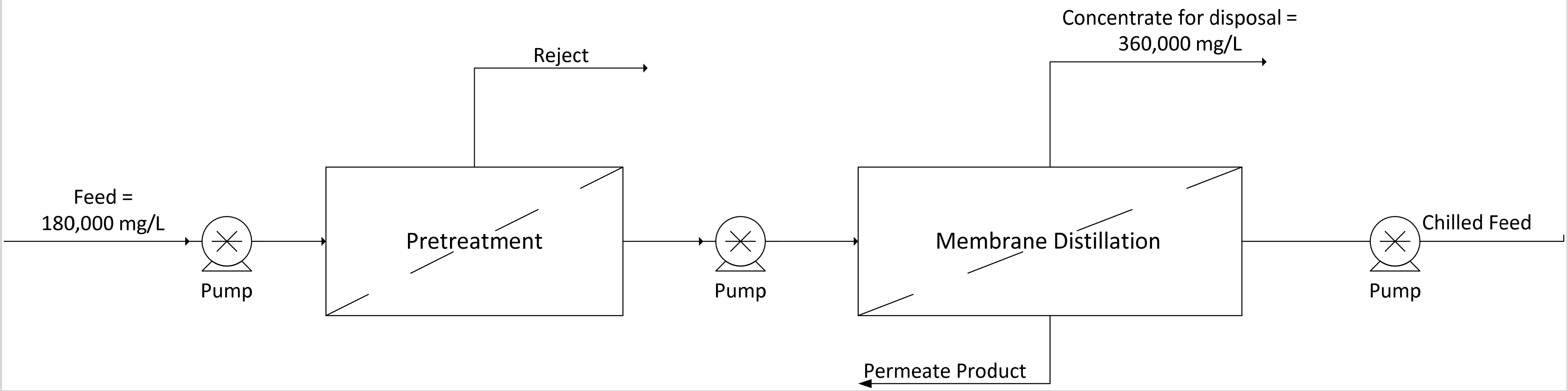


ECMD vs MD Cost Comparison Projection

- Use 1 million gallons/day capacity to compare costs of MD to ECMD.
- Assume 180,000 mg/L feed and 50% recovery.
- Pre-treatment and energy heat energy consumption not yet accounted for.

MD/ECMD operating conditions:

- 8 LMH nominal flux (without scaling)
- Module membrane surface area 26 m^2
- $T_f = 70^oC$
- $T_p = 20^oC$
- Average salt rejection >99.99%

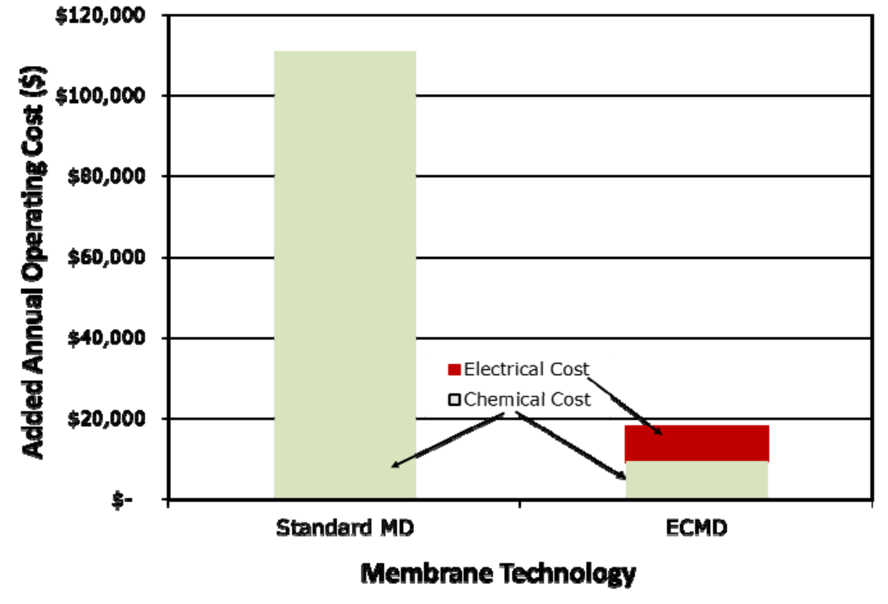


ECMD vs MD Cost Comparison Projection

- Two areas where cost trade-offs occur when comparing standard MD and ECMD:
  - Operating costs – chemical usage and electricity usage
  - Differences in the capital costs will be expressed: (1) membrane module costs (CNT addition, added hardware components) and (2) the effective processing capacity (EPC) that will dictate overall system size
- Baseline MD/operating assumptions include:
  - 26 m^2 membrane area per module
  - Chemical cleaning at relative flux = 0.75
  - Each cleaning event takes 8hrs, uses both acid/base membrane CIP
  - Target recovery for plant = 50%

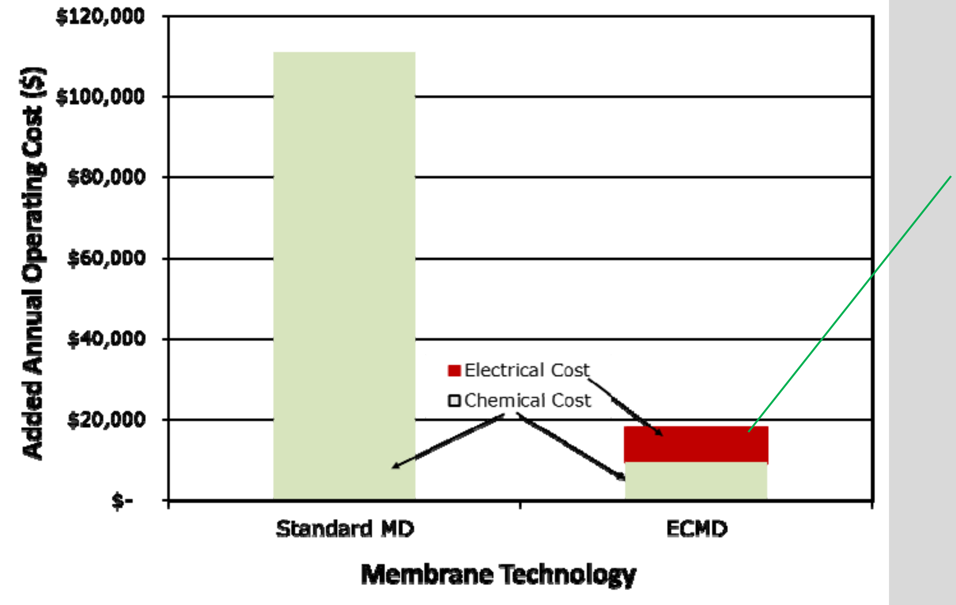
ECMD/MD Cost Comparison – operating costs Δ

	MD	ECMD
Feed Flow (MGD)	1	1
Recovery (%)	50%	50%
Required membrane area (m^2)	~17,000	~10,000
No. of modules	400	650
Citric acid use (kg/yr)	85400	7500
Sodium Hydroxide use (kg/yr)	56900	4990
Additional electricity (kWh/yr)	N/A	69241
Chemical cost ($/yr)	$111,003	$9,734
Additional elec. use ($/yr)	N/A	$8,309
Module Cost ($/req. membranes)*	$325,000	$400,000



*de Lannoy, C. F., Jassby, D., Davis, D., & Weisner, M. (2012). A highly electrically conductive polymer -- multiwalled carbon nanotube nanocomposite membrane. Journal of Membrane Science.

ECMD/MD Cost Comparison – operating costs Δ

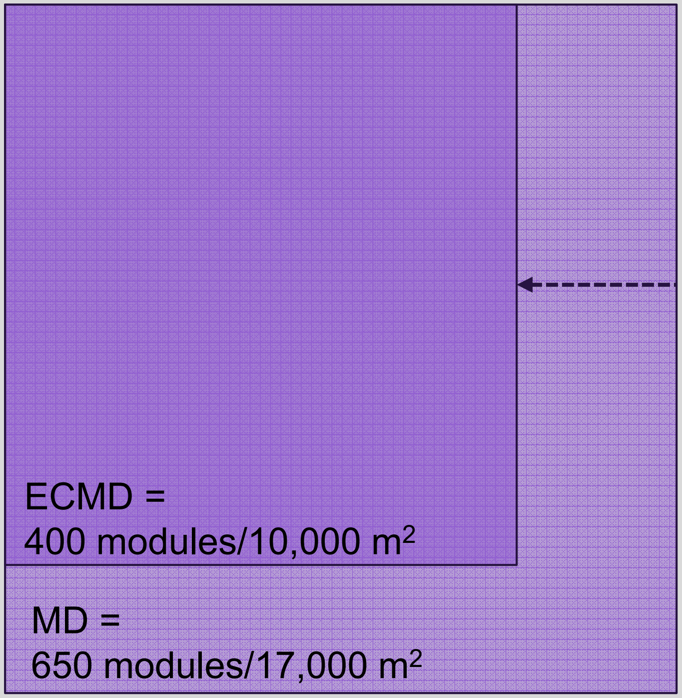


Lab results showed 2.7 mA/m^2 at 3V, we assumed 10-fold increase in power requirements for scale up so used 270 mA/m^2 current density ~ 20 kWh/day for 1 MGD system.

The reduction in scaling needed (and corresponding decrease of acetic acid/sodium hydroxide) to break even from a daily operational cost standpoint is **9%.**

ECMD/MD Cost Comparison – capital cost Δ

	MD	ECMD
Feed Flow (MGD)	1	1
Recovery (%)	50%	50%
Required membrane area (m^2)	~17,000	~10,000
No. of modules	400	650
Citric acid use (kg/yr)	85400	7500
Sodium Hydroxide use (kg/yr)	56900	4990
Additional electricity (kWh/yr)	N/A	69241
Chemical cost ($/yr)	$111,003	$9,734
Additional elec. use ($/yr)	N/A	$8,309
Module Cost ($/req. membranes)*	$325,000	$400,000



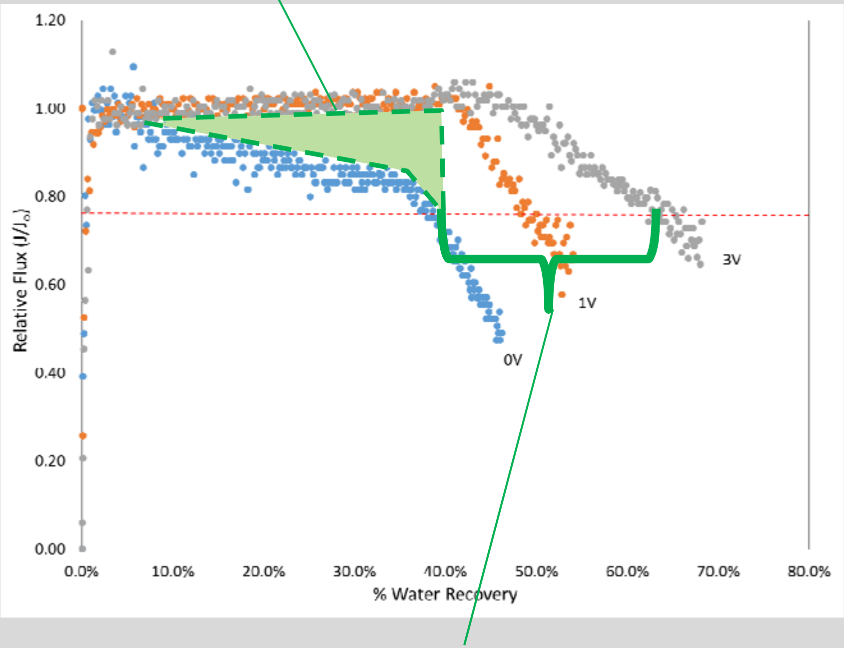
ECMD =
400 modules/10,000 m^2

MD =
650 modules/17,000 m^2

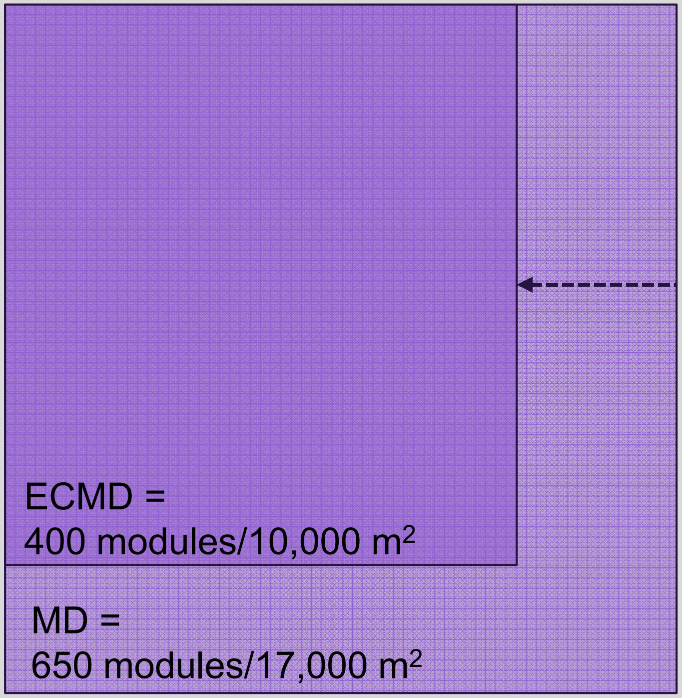
38% smaller footprint since fewer modules needed for same flow due to increased EPC

ECMD/MD Cost Comparison – capital cost Δ

provides greater production
prior to cleaning (12.5%)



Less downtime due to required
cleaning events (87.5%)



ECMD =
400 modules/10,000 m^2

MD =
650 modules/17,000 m^2

38% smaller footprint since fewer modules needed for same flow due to increased EPC

ECMD/MD Cost Comparison – capital cost Δ

	MD	**ECMD**
Feed Flow (MGD)	1	1
Recovery (%)	50%	50%
Required membrane area (m^2)	~17,000	~10,000
No. of modules	400	650
Citric acid use (kg/yr)	85400	7500
Sodium Hydroxide use (kg/yr)	56900	4990
Additional electricity (kWh/yr)	N/A	69241
Chemical cost ($/yr)	$111,003	$9,734
Additional elec. use ($/yr)	N/A	$8,309
Module Cost ($/req. membranes)*	$325,000	$400,000

- Increased capital cost of membrane modules will likely be offset by reduced capital needed for additional piping, valves, etc. as well as reduced overall footprint.
- Membrane module cost estimation will vary depending on materials of construction, hardware, and power supply.

Remaining Items to be Included in TE Analysis

- Determine maximum recovery and scaling resistance of high TDS real wastewater
- Identify pre-treatment requirements
- Heat source costs and recovery method for MD
- Comparison to include thermal evaporator technology (energy efficiency vs. lower capital investment) and deep well injection
- Residuals management and disposal

Summary of Results

- ECMD shown to be effective for calcium sulfate and calcium chloride scaling, not for strontium sulfide scaling (real wastewater TBD).
- The charge repulsion is minimally impacted by temperature and concentration.
- The expected tradeoffs between the increased electricity requirement and the reduction in required chemicals is likely to be favorable.

Acknowledgements/Disclaimer

- Department of Energy - National Energy Technology Laboratory project manager: Jessica Mullen
- RTI: Rachael Guenter, Elliot Reid, Young Chul Choi
- UC Riverside: Wenyan Duan, Alexander Dudchenko, David Jassby
- Veolia: Adrien Moreau, Herve Buisson

Thank You!

delivering **the promise of science** for global good

Zachary Hendren, PhD.
Energy Technology Division
zhendren@rti.org
(919) 541-6605

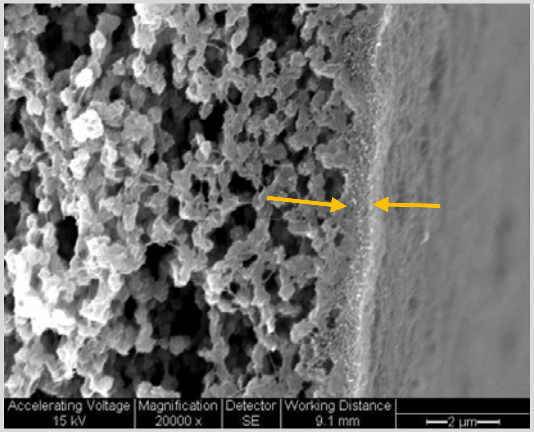
Baseline MD & ECMD Membrane Performance (1M NaCl)

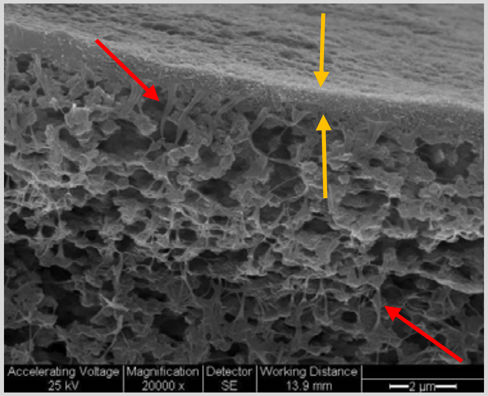
Feed Temp (°C)	PVDF 0.22μm		CNT-PVDF 0.22μm		PVDF 0.45μm		CNT-PVDF 0.45μm	
	Flux (LMH)	Rejection (%)	Flux (LMH)	Rejection (%)	Flux (LMH)	Rejection (%)	Flux (LMH)	Rejection (%)
50	12.0	99.98	11.4	99.99	19.0	99.97	n/a	n/a
60	22.0	99.99	19.1	99.99	31.3	99.99	n/a	n/a
70	39.4	99.99	33.1	99.99	53.3	99.99	n/a	n/a

(Permeate T=20°C)

CNT coating decreases flux;
salt rejection is maintained.

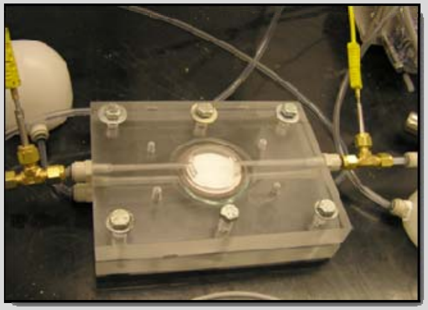
!!!CNT coating entered pores and allowed liquid to pass through





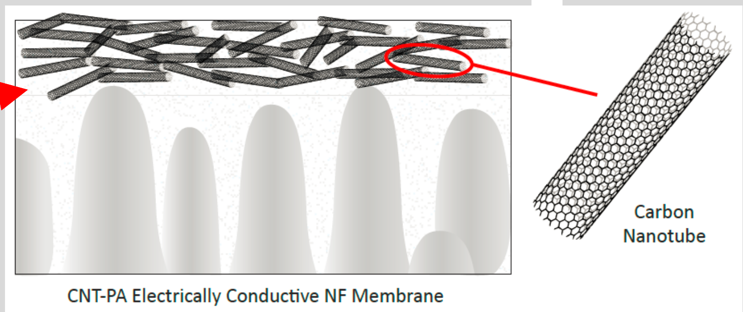
Technology Development Concept – From Bench to Pilot to Full Scale

Test Cell: 1 mL/min



Full size plant: 50 million gallons/day

Address Scaling/Fouling with Carbon Nanotube



Smallest Commercial membrane: 2.2 L/min