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

RTI International, Energy Technology Division, Research Triangle Park, NC

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**Crosscutting Research & Rare Earth Elements Portfolio Review, April 21st 2016, Pittsburgh, PA**

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# What Is RTI International


RTI is an independent, nonprofit institute that provides research, development, and technical services to government and commercial clients worldwide.

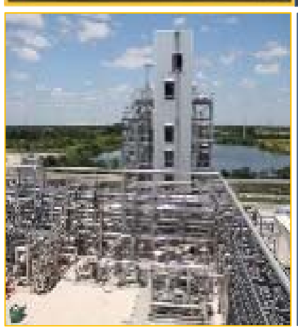
Our mission is to improve the human condition by turning knowledge into practice.

# Energy Technology Development with RTI

- RTI develops advanced process technologies in partnership with leaders in energy
- From concept to large scale demonstration

Industrial Water

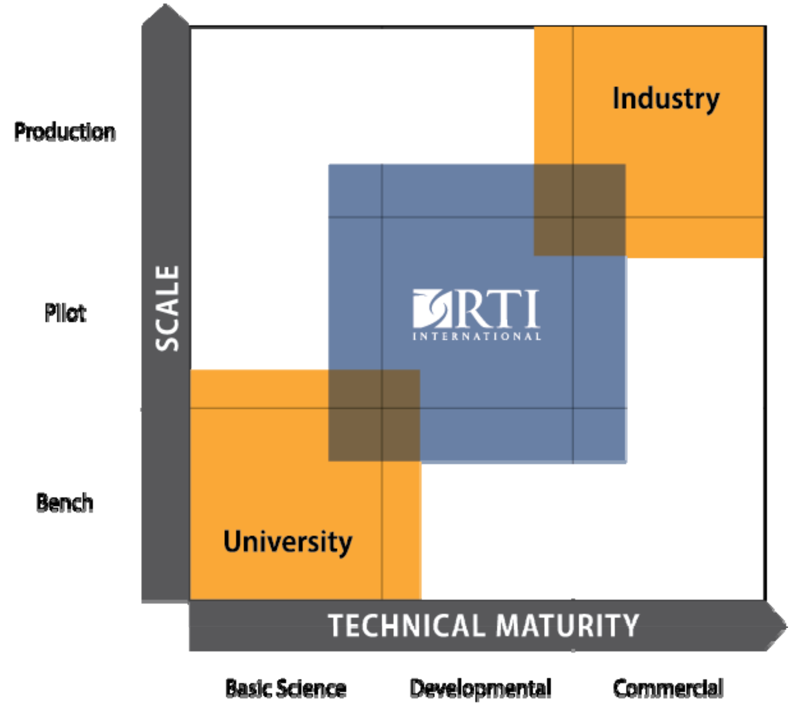
Carbon Capture



Syngas / Clean Coal

Biomass Conversion

Emerging Technologies




GM
PHILLIPS 66
AEROJET ROCKETDYNE A GenCorp Company
Masdar A MUBADALA COMPANY
SINTEF
BASF The Chemical Company
CLARIANT
ADM
THE LINDE GROUP
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U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
BIOENERGY TECHNOLOGIES OFFICE
CCEMC
arpa·e
GASSNOVA

# Water-Related Energy Use in U.S.

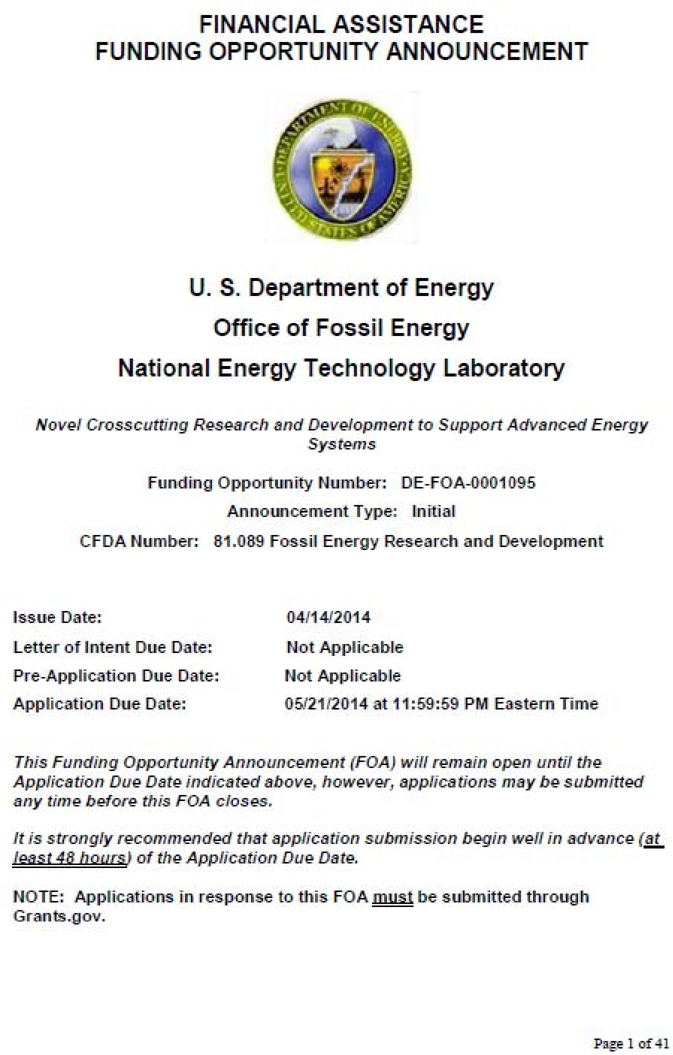
Source: <https://www.nasa.gov/mission_pages/NPP/news/earth-at-night.html>

Source: <http://solutions.borderstates.com/
what-is-the-future-of-mercury-vapor-lamps>>

http://info.waterdesignbuild.com/blog/bid/240179/New-Data-on-Biogas-Production-at-U-S-Wastewater-Treatment-Plants

- In 2010, 69 TWh/yr of electricity is consumed in US as water-related energy (water distribution, water and wastewater treatment).
- This is higher than (but comparable) to electricity consumption of ~51 TWh/yr for all U.S. public roadway lighting (street lights, highway etc.)

# Project Overview



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.

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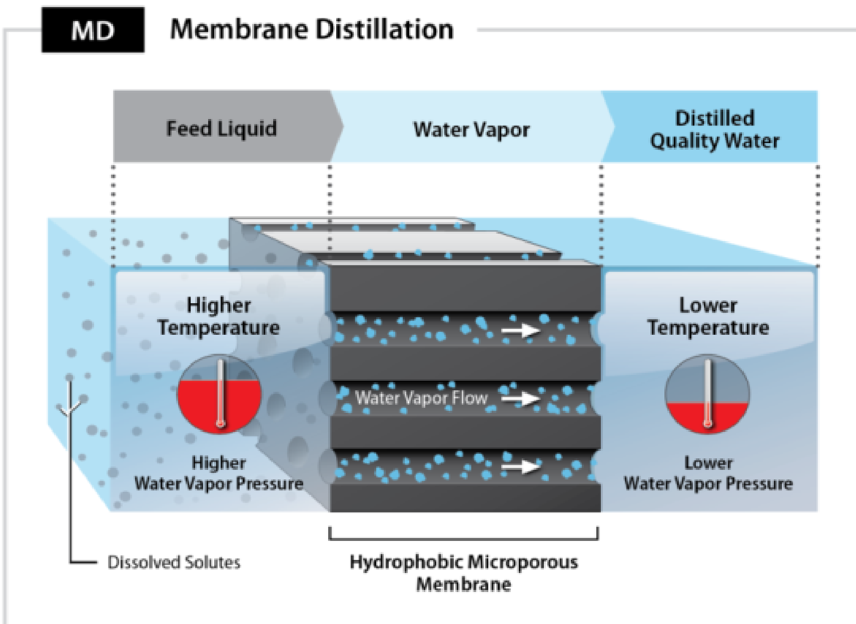
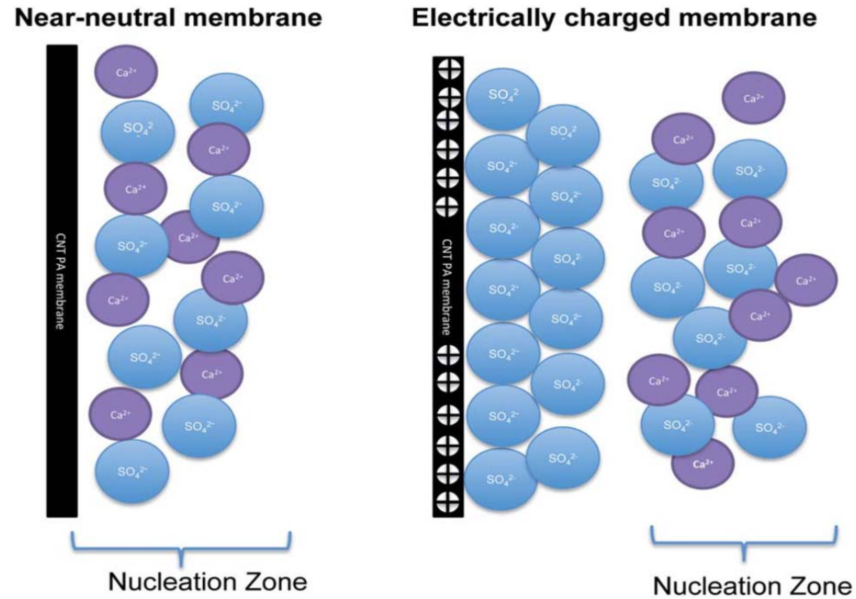
- **DOE Award No. DE-FE0024074**
- **Total project value**: $625,000
  - DOE Share: $500,000 (80%)
  - Cost Share: $125,000 (20%)
- **Period of Performance**: 10/1/2014 to 9/30/2016 (24 mos.)
- **Project Team**:
  - RTI International (Prime Recipient)
  - University of California, Riverside
  - Veolia Water
- **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.

# Project Team

| Team Member | Role |
|---|---|
| RTI International | ▪ Prime Recipient<br>▪ MD membrane benchmarking and performance evaluation<br>▪ Bench-scale parametric studies and performance testing of MD membranes with synthetic and real high-TDS wastewaters<br>▪ Process modeling, development, and integration<br>▪ Techno-economic process analyses |
| University of California, Riverside | ▪ University partner<br>▪ Electrically conductive membrane development<br>▪ Membrane characterization and optimization |
| Veolia Water | ▪ Industrial partner [>$29B revenue (2013)]<br>▪ World's No. 1 water services provider [Operating in 120+ countries]<br>▪ Access to real wastewaters to validate process performance<br>▪ Engineering, economic, and market expertise in water solutions technology and application |

# Project Concept: Electrically Conductive Membranes + Membrane Distillation = ECMD




Increasing TDS concentration & scaling potential

No desalination

Brackish RO

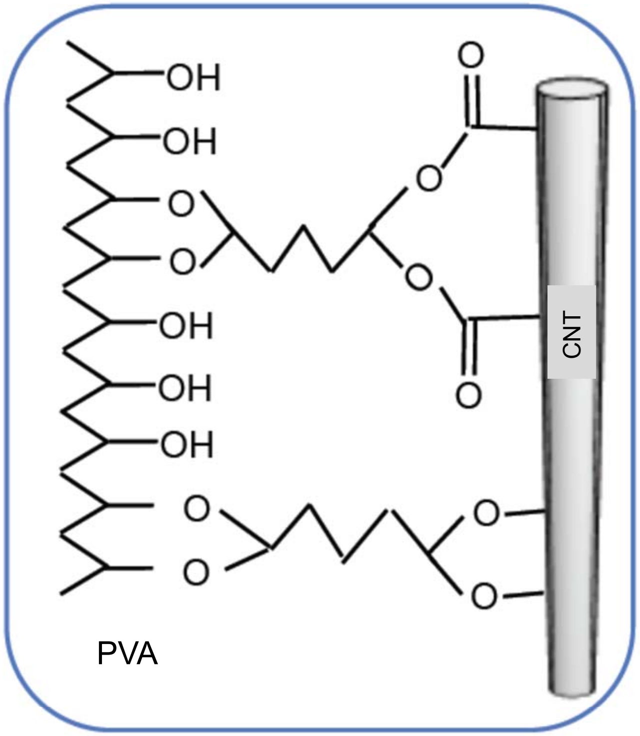
Seawater RO

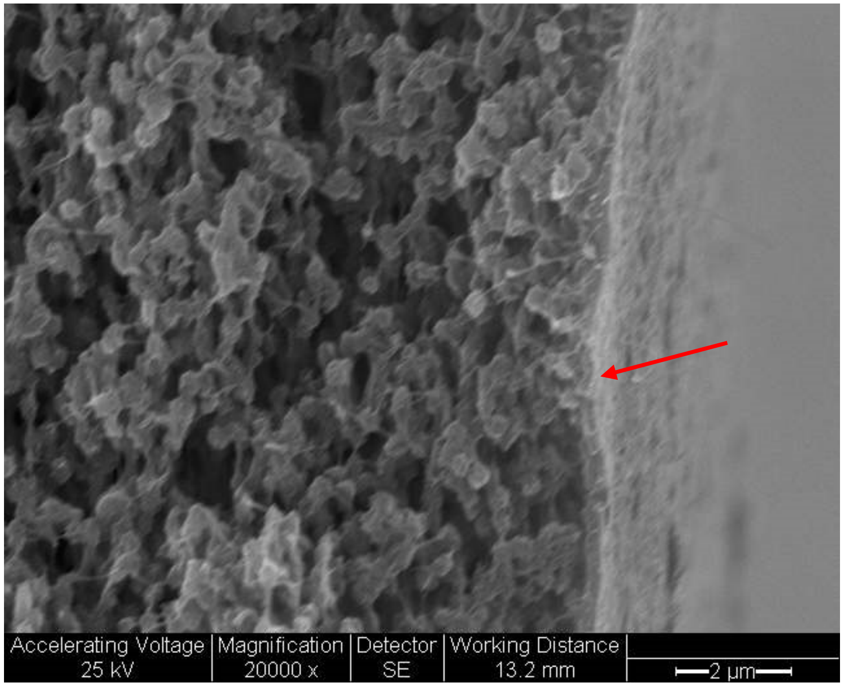
Evaporation

Crystallization

**Membrane Distillation (MD)**

# Grafting Carbon Nanotubes (CNTs) to MD Membranes

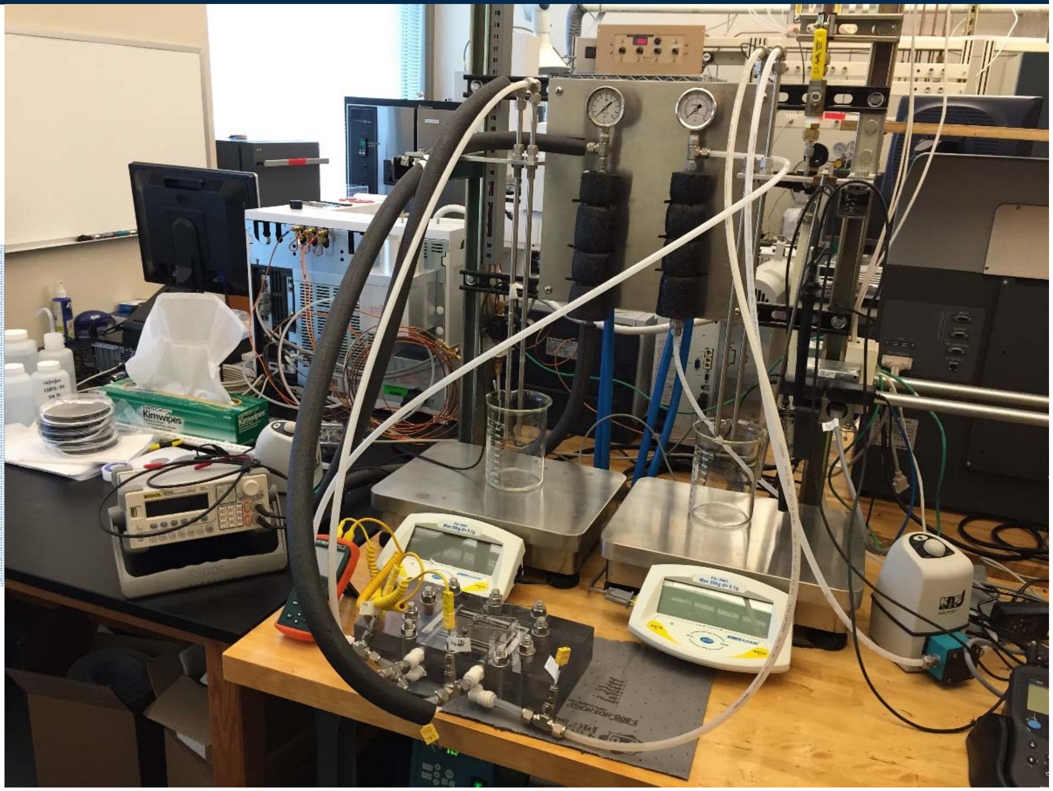


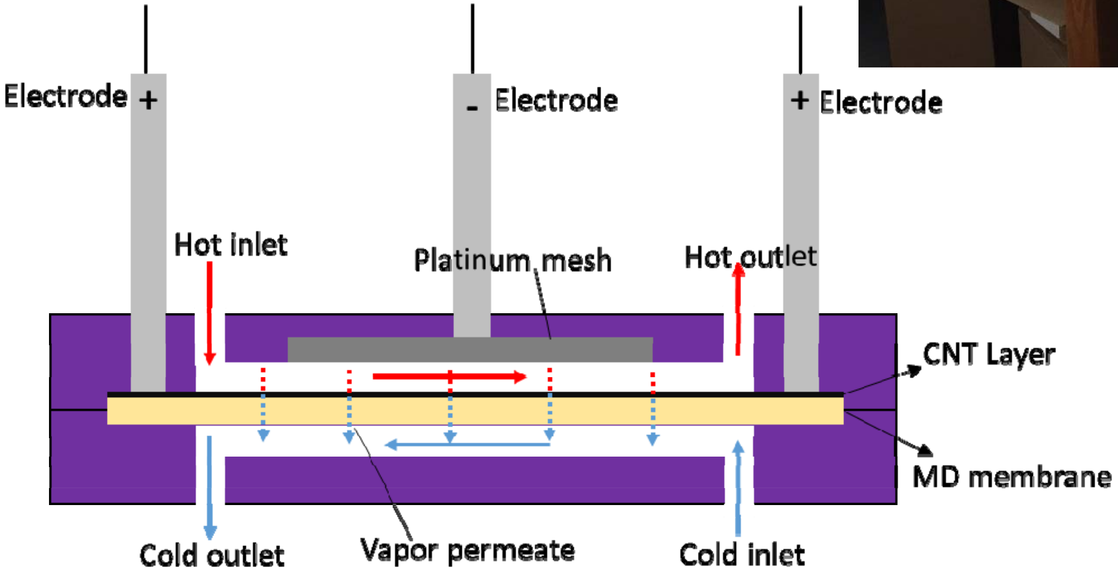




- Modification via CNT-OH and polyvinyl alcohol (PVA) cross-linked to polyvinylidene fluoride (PVDF) MD membrane.
- Membranes are permanently bonded between the carboxyl groups on the CNTs and the hydroxyl groups on PVA. Goal is to leave original membrane permeability intact.
- Polytetrafluoroethylene (PTFE) membranes not cross-linked, but pressure deposited to surface and held together via Van der Waal forces.
- Membranes with CNT coating have measured sheet resistances: ~6200 Ω/sq (cross-linked) and ~5900 Ω/sq (pressure deposited). Newer formulations are as low as **600 Ω/sq**.

# 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





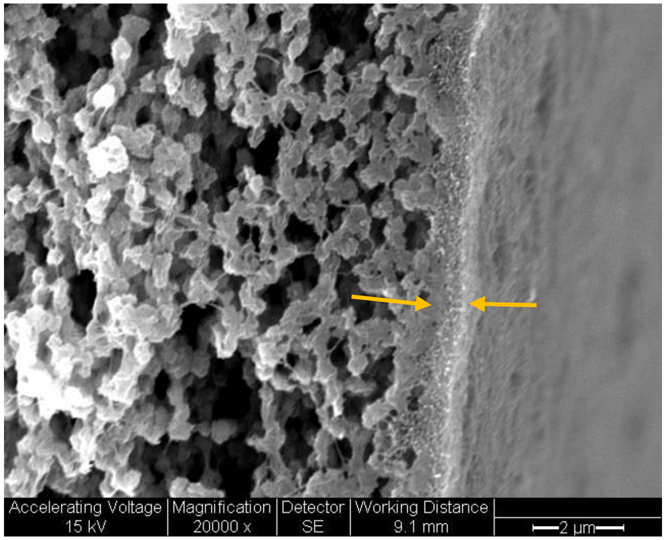
# Baseline MD & ECMD Membrane Performance (1M NaCl)

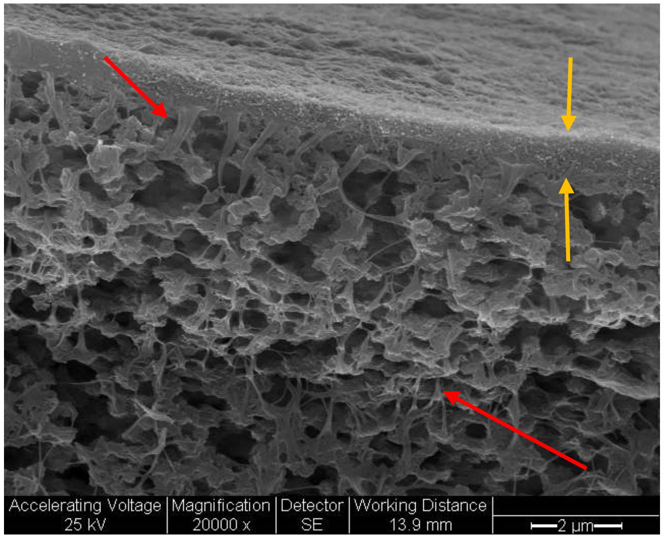
| Feed Temp (ºC) | PVDF 0.22μm | | CNT-PVDF 0.22μm | | PVDF 0.45μm | | CNT-PVDF 0.45μm | |
|---|---|---|---|---|---|---|---|---|
| | Flux (LMH) | Rejection (%) | Flux (LMH) | Rejection (%) | Flux (LMH) | Rejection (%) | Flux (LMH) | Rejection (%) |
| 50 | 12.0 | 99.98 | 11.4 | 99.99 | 19.0 | 99.97 | 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=20ºC)

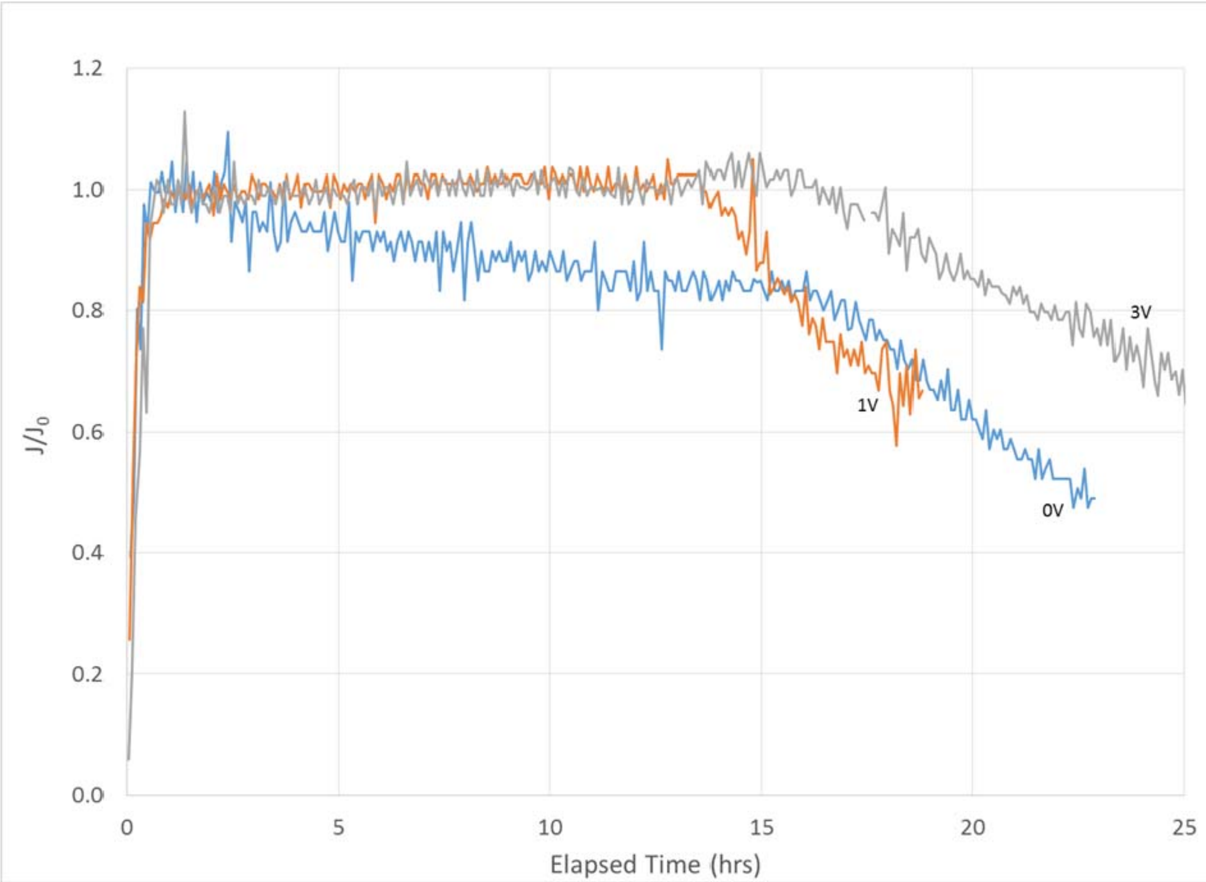
CNT coating slightly decreases flux
Salt rejection is maintained.

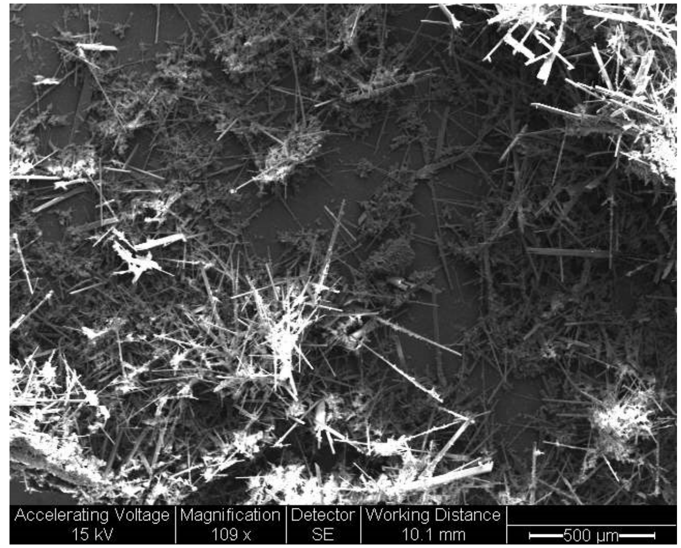
!!!CNT coating entered pores and allowed liquid to pass through



# Scaling Resistance for Calcium Sulfide, CNT-PVDF




Feed = $CaSO_4$ scaling solution:

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

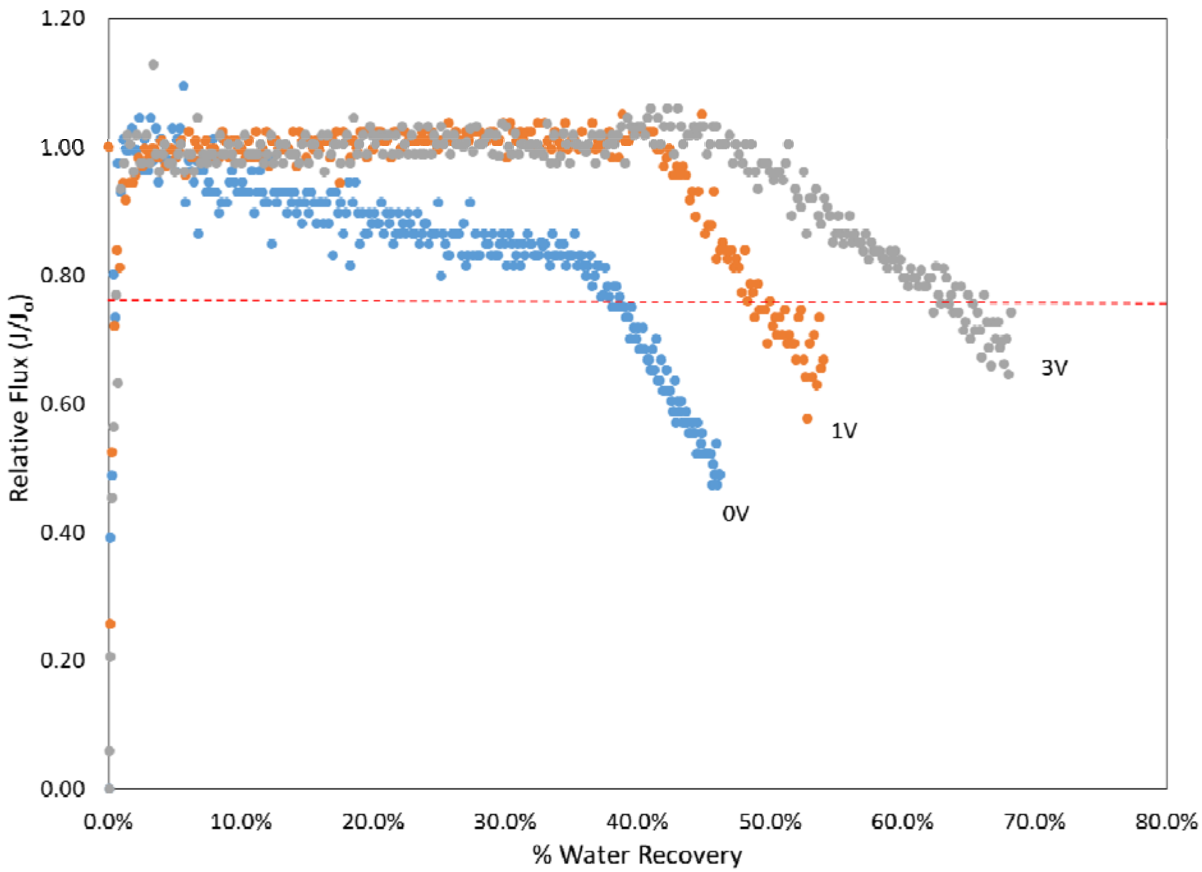
$T_f$ = 60°C

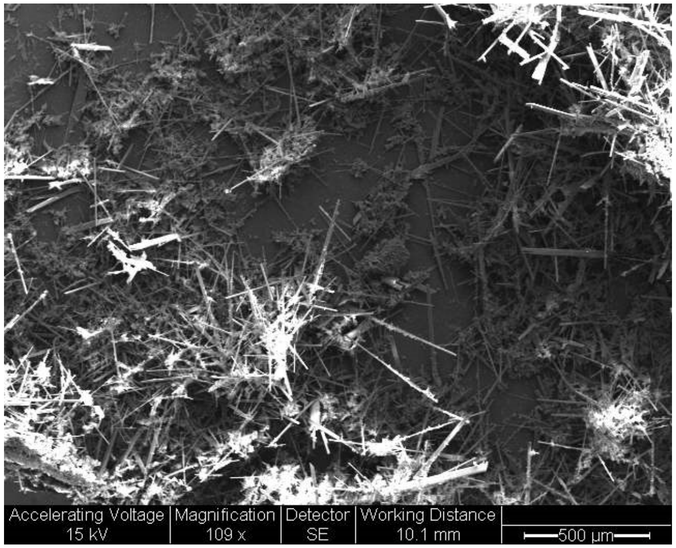
$T_p$ = 20°C

Average salt rejection >99.99%

Membrane as cathode for all tests

# Scaling Resistance for Calcium Sulfide, CNT-PVDF




Feed = $CaSO_4$ scaling solution:

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

$T_f$ = 60°C

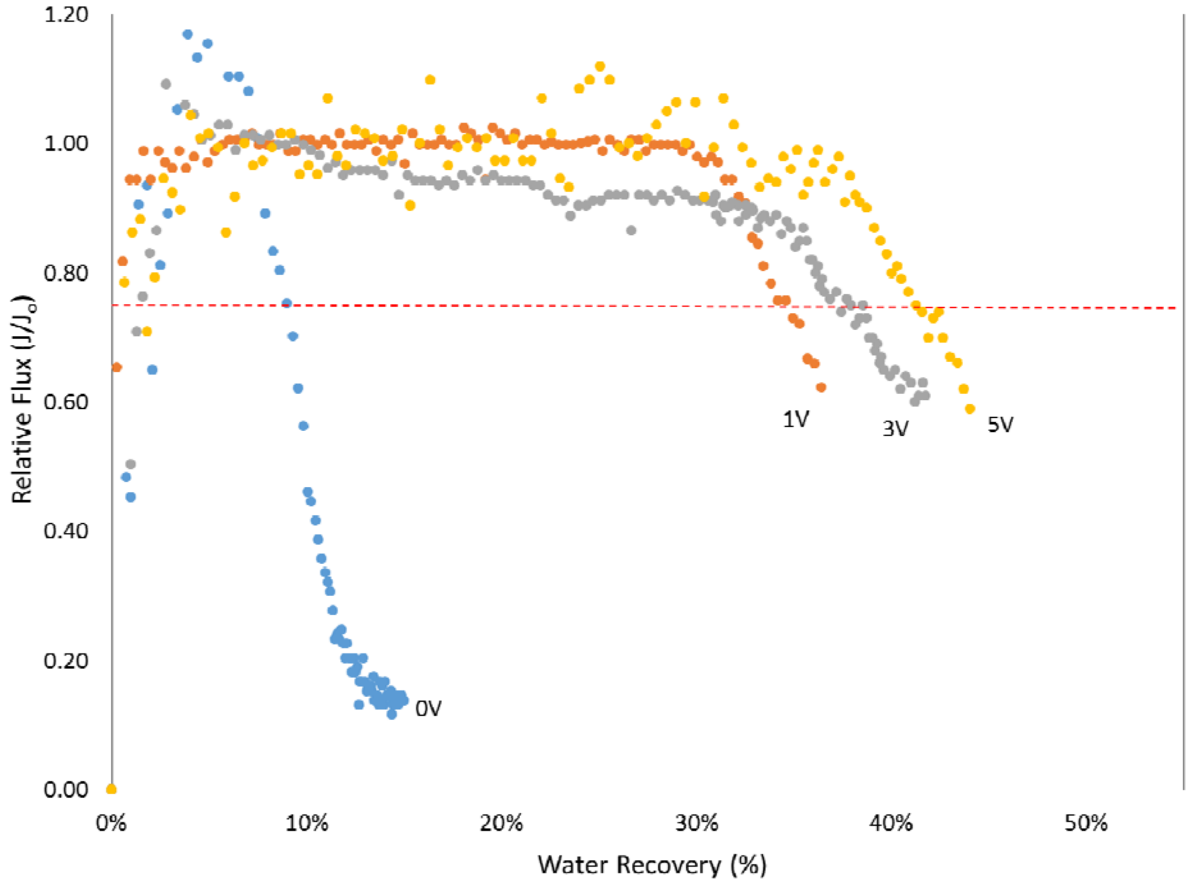
$T_p$ = 20°C

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 Sulfide, CNT-PTFE




Feed = $CaSO_4$ scaling solution:

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

$T_f$ = 60$^o$C
$T_p$ = 20$^o$C
Average salt rejection >99.99%

| Membrane | Feed T ($^o$C) | EC voltage | Time (min) | Volume recovered (%) |
|---|---|---|---|---|
| CNT-PTFE | 60 | 0V | 110 | 10% |
| CNT-PTFE | 60 | 1V | 378 | 35% |
| CNT-PTFE | 60 | 3V | 401 | 37% |
| CNT-PTFE | 60 | 5V | 439 | 41% |

To reach 75% relative flux

# Modeling Ion Concentrations Along ECMD Surface

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

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

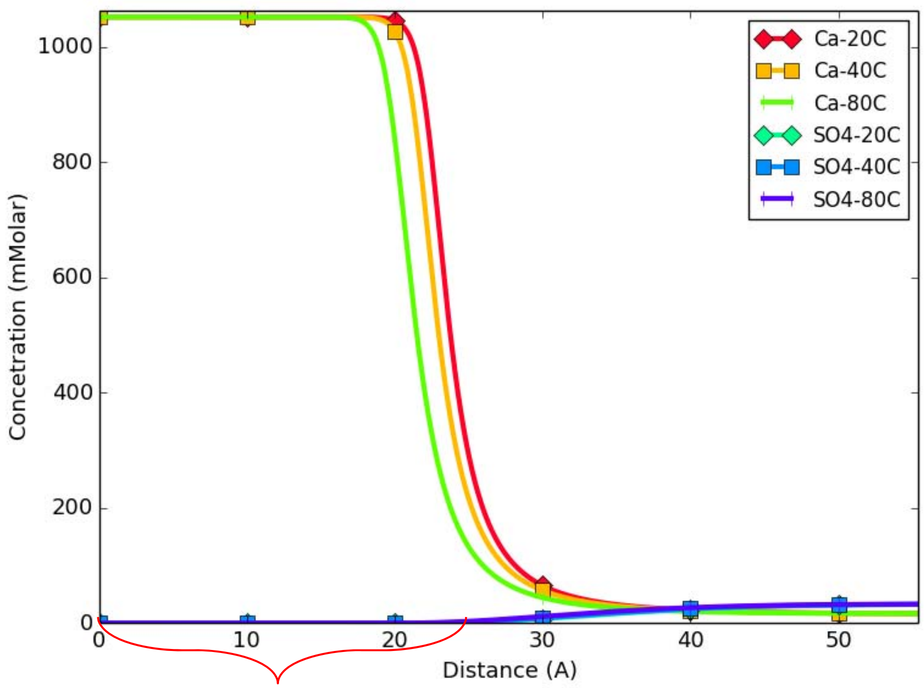
Potential as function of distance from the membrane surface

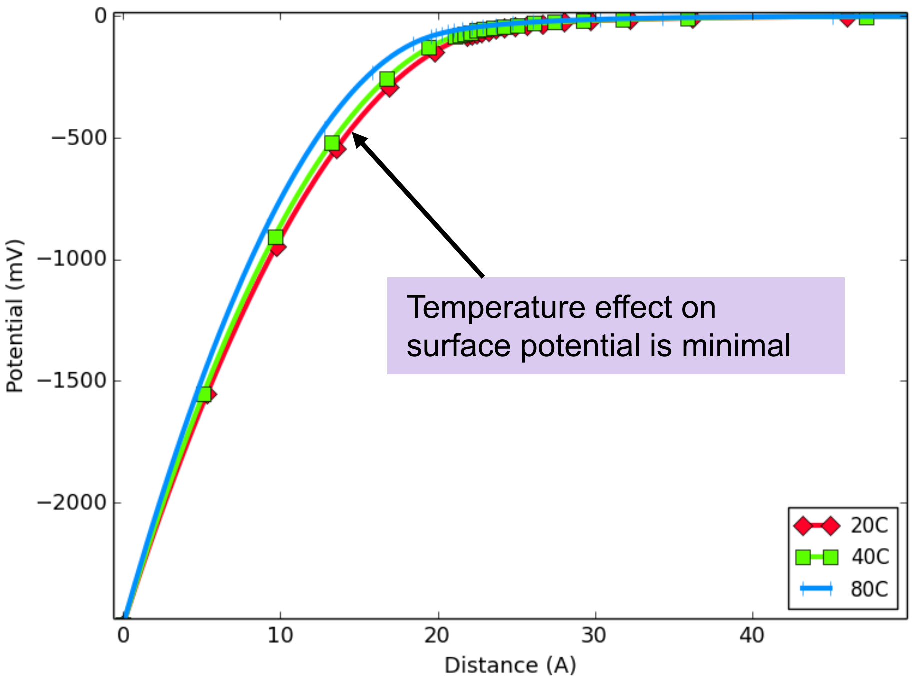
$$c_i = \frac{c_i^\infty \exp\left(-\frac{z_i e\psi}{kT}\right)}{1 + \sum_{i=1}^{m} \frac{c_i^\infty}{c_i^{max}} \left[\exp\left(-\frac{z_i e\psi}{kT}\right) - 1\right]}$$

Ion concentration as function of distance from the membrane surface

**Where:**
$\psi$ = 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 Along ECMD Surface



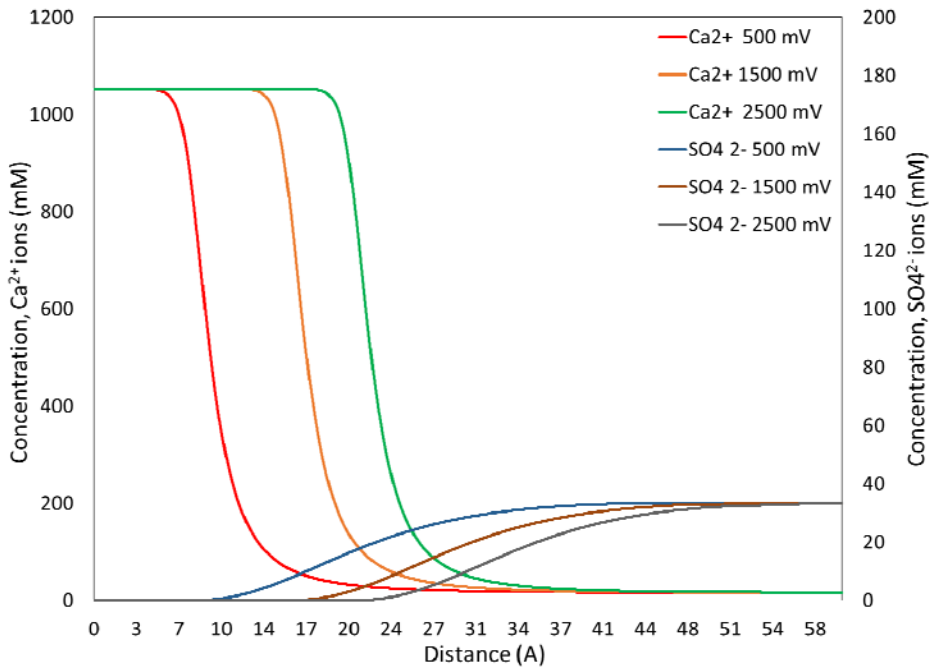



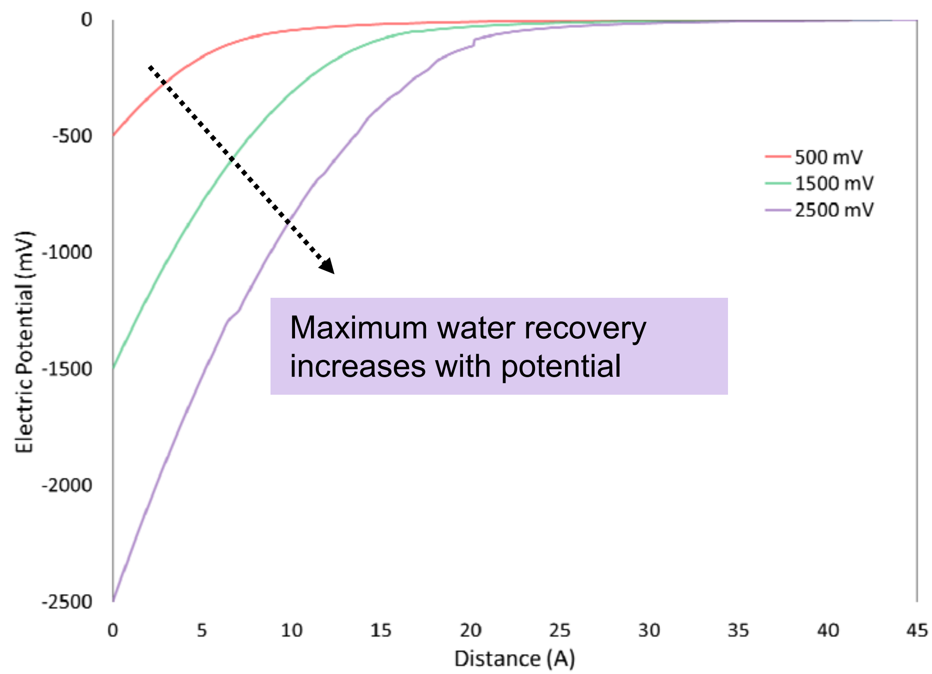

Temperature effect on surface potential is minimal

Charged surface generates high concentration of cations that “push” away anions and delay scale formation on membrane surface

# Modeling Ion Concentrations Along ECMD Surface

Feed Temperature = 60$^{o}$C

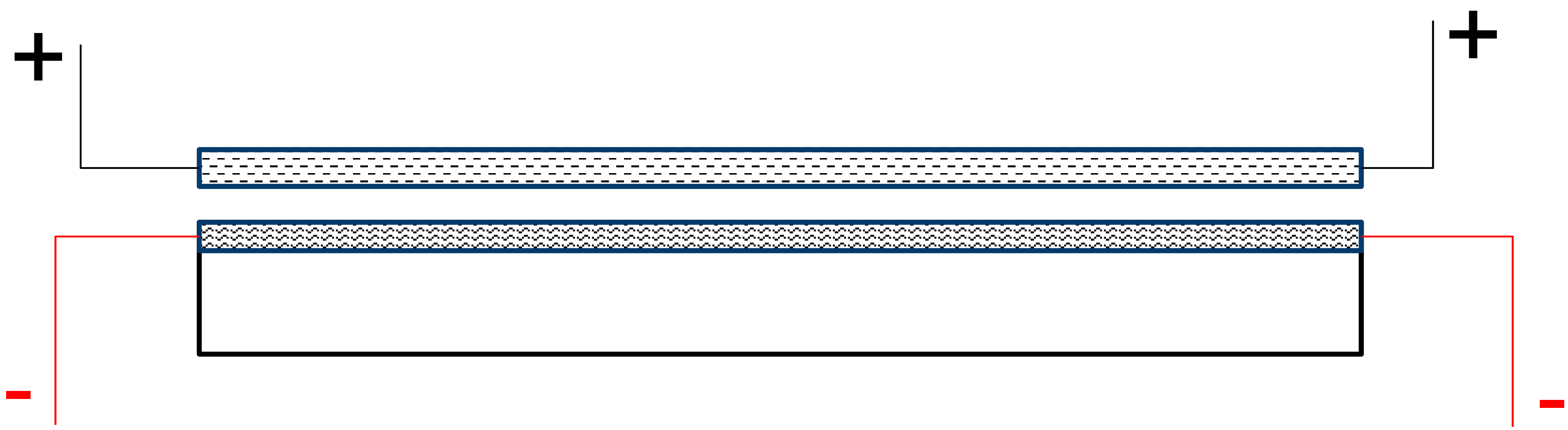



Increasing surface charge increases the thickness of the ion layer along the surface, with a corresponding decrease in the rate of scaling for a given concentration.

# 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

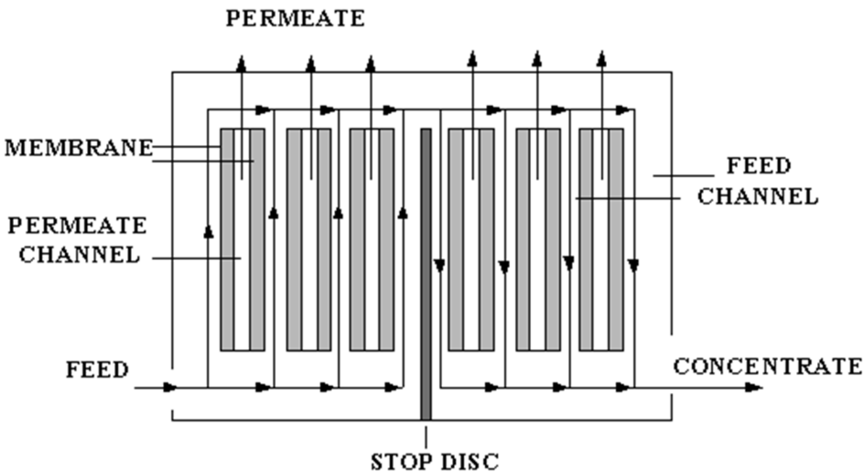


# Full Scale ECMD Module Design Considerations

## Module Configuration

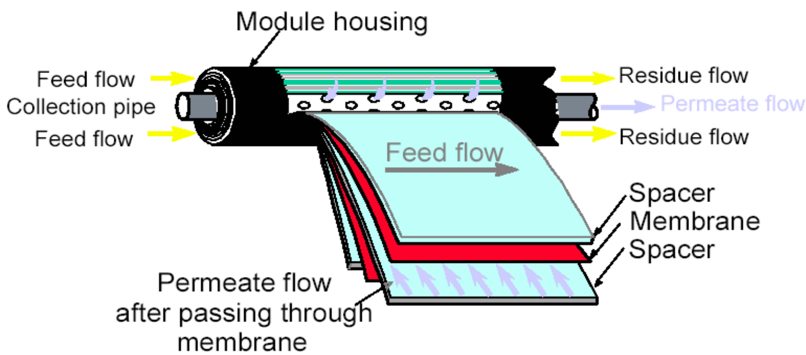
– Packing density/surface area, CNT coating distribution, MD operational mode (VMD, DCMD, AGMD).

- Plate-and-frame module

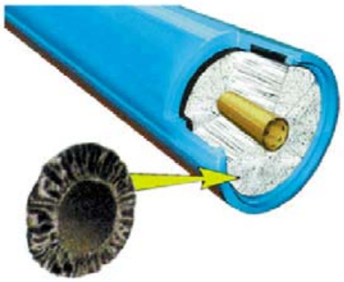



- Tubular module

- Spiral-wound module

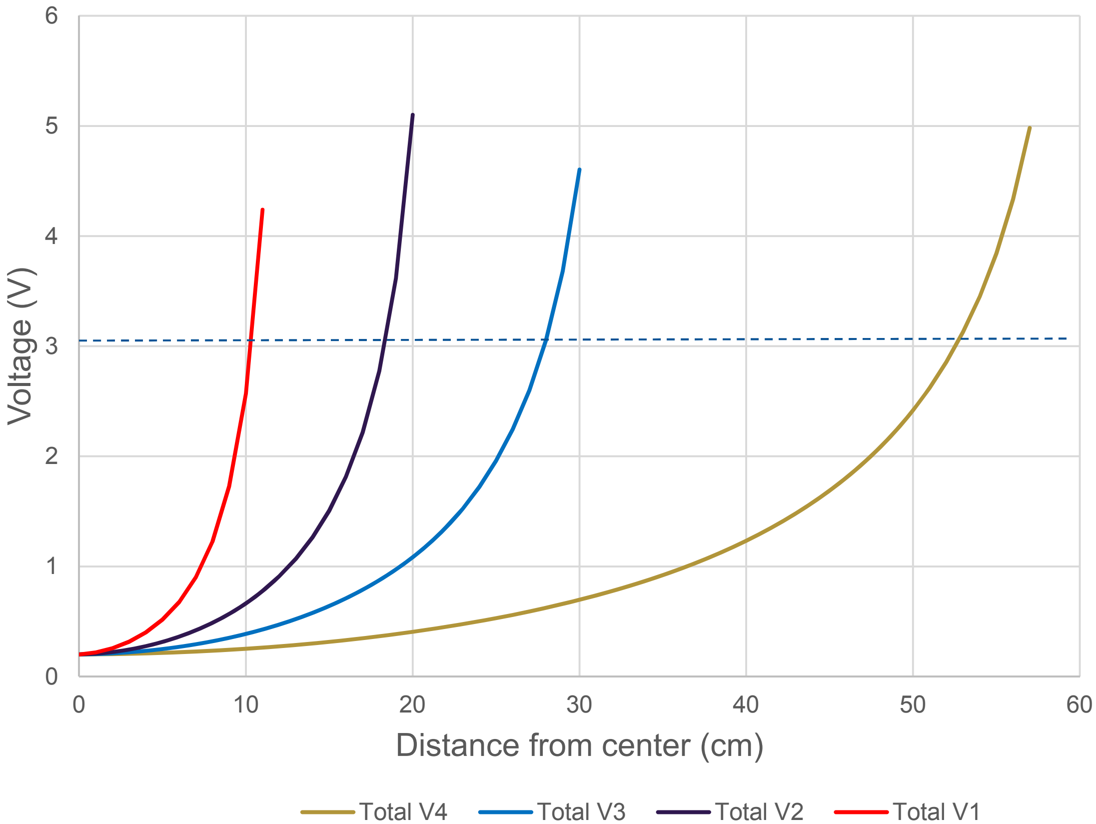



- Hollow-fiber module



# Voltage Distribution at Larger Scale

- 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




0 is center of film between metal electrodes

- Resistance of electrodes have big effect
  - V4 with 100 Ω/square electrodes has more uniform voltage for greater distance than other combinations

# Concluding Remarks & Continuing Work

*** ECMD operation has a repeatable, significant effect increasing water recovery.**

*** Effect of charged surface is minimally impacted by temperature.**

*** The delay/reduction of scaling on membrane is proportional to the applied charge.**

- Scalants remaining: barium sulfate and strontium sulfate
- Testing with real, complex, high TDS WW (from Veolia)
- Modeling of scalant-membrane interaction (in progress)
- Design of prototype module (spiral wound vs. flat sheet stack)
- Preliminary process integration analysis (effect of increased E input vs. operational savings)

# Acknowledgements


- Department of Energy - National Energy Technology Laboratory project manager: Jessica Mullen
- RTI: David Bollinger, Nandita Akunuri, Young Chul Choi
- UC Riverside: Wenyan Duan, Alexander Dudchenko, David Jassby
- Veolia: Shan Young, Herve Buisson

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# More Information

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