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

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List of Acronyms

BBL	Barrel
COD	Chemical oxygen demand
CNT	Carbon Nanotubes
DCMD	Direct contact membrane distillation
ECMD	Electrically Conductive Membrane Distillation
gpd	Gallons per day (gal/day)
gpm	Gallons per minute (gal/min)
J_W	Water flux [$L/(m^2 \cdot h)$] in forward osmosis or membrane distillation
L/min	Liters per minute
LMH	Liters per square meter per hour [$L/(m^2 \cdot h)$]
MD	Membrane distillation
MF	Microfiltration
PFD	Process flow diagram
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
R^2	Coefficient of determination
RO	Reverse osmosis
TDS	Total dissolved solids
TFC	Thin film composite
VOCs	Volatile organic compounds

Executive Summary

The high total dissolved solids (TDS) levels in the wastewater quality generated from unconventional oil and gas development make the current state-of-the art approach to water treatment/disposal untenable. Our proposed membrane technology approach addresses the two major challenges associated with this water: 1) the membrane distillation process removes the high TDS content, which is often 8 times higher than that of seawater, and 2) our novel membrane coating prevents the formation of scale that would otherwise pose a significant operational hurdle. This is accomplished through next-generation electrically conductive membranes that mitigate fouling beyond what is currently possible, and allow for the flexibility to treat to the water to levels desirable for multiple reuse options, thus reducing fresh water withdrawal, all the way to direct disposal into the environment.

The overall project objective was to demonstrate the efficacy of membrane distillation (MD) as a cost-savings technology to treat concentrated brines (such as, but not limited to, produced waters generated from fossil fuel extraction) that have high levels of TDS for beneficial water reuse in power production and other industrial operations as well as agricultural and municipal water uses. In addition, a novel fouling-resistant nanocomposite membrane was developed to reduce the need for chemicals to address membrane scaling due to the precipitation of divalent ions in high-TDS waters and improve overall MD performance via an electrically conductive membrane distillation process (ECMD). This anti-fouling membrane technology platform is based on incorporating carbon nanotubes (CNTs) into the surface layer of existing, commercially available MD membranes. The CNTs impart electrical conductivity to the membrane surface to prevent membrane scaling and fouling when an electrical potential is applied.

In this work, a CNT based surface coating was implemented to produce a novel fouling-resistant nanocomposite membrane that reduces scaling due to the precipitation of divalent ions on the membrane surface. Depending on the feedwater and voltage conditions, the ECMD improved fouling resistance as demonstrated by maintaining the relative flux above 0.8 [Relative Flux = Flux(t)/Flux(t=0)] for at least twice as long when compared to the relative flux of a non-conductive membrane during the treatment of highly scaling water. The ECMD system was shown to prevent scaling of calcium sulfate and calcium chloride species as well as reduce the onset of membrane scaling for a real produced water with a feed TDS ~ 190,000mg/L. In advancing the ECMD technologies from lab/bench-scale to pilot-scale evaluation, valuable lessons were learned. Modeling results show that the charge repulsion effect is minimally impacted by temperature and ion concentration, although differences in scaling inhibition behavior were observed for the real wastewater when compared the synthetic solutions. A techno-economic and environmental analyses of the ECMD water treatment processes utilizing these electrically conductive membranes suggests that this approach can provide cost savings relative to MD treatment without the charged surface coating.

This project demonstrated the technical feasibility of the ECMD process by taking water high scaling potential and increasing the processing time for water recovery by a factor of two relative to a non-electrically conductive coating. This technology shows promise as a solution for high TDS wastewaters and warrants further evaluation at a wider range of operating conditions and different wastewaters.

1. INTRODUCTION

Energy and water are mutually dependent, and wastewater often containing high levels of dissolved salts, heavy metals, and minerals is generated throughout the fossil fuel lifecycle: extraction (produced waters, coal wash wastewater), power generation (flue gas desulphurization blowdown), and disposal (coal ash storage ponds). These dissolved contaminants that make up total dissolved solids (TDS) are generally some of the most difficult constituents to remove during treatment. Although a technical challenge, these waters represent a significant opportunity as an untapped resource for water reuse. For example, each fracturing operation requires 1 to 8 million gallons of water, typically supplied from nearby surface waters, area municipalities, or trucked from outside regions. A portion of this water is returned as flowback water, along with additional water over time (referred to as produced water). The actual amount of water needed is region-dependent, with the Barnett, Bakken, and Marcellus basins reporting average water requirements per well of 4.6, 3.0, and 5.6 million gallons, respectively. Production is often stimulated by refracturing a well every 3–4 years. A single well may be hydraulically fractured up to 10 times, each time requiring 25% more water than the amount used in the previous fracture.[1] This presents a significant technical and environmental problem on two fronts: water availability and water treatment/disposal.

Membrane Distillation (MD) is a promising technology that can treat water with very high TDS that are commonly encountered in industrial processes, such as oil and gas production and has garnered attention for potential application in the water and wastewater industries for desalination and water reuse.[1-4] The high TDS levels in concentrated brines (often 8 times higher than that of seawater) make the current state-of-the art approaches to water treatment untenable. MD has an advantage over thermal evaporation in that the materials of construction do not have to be exotic alloys. Another key advantage of MD is that it is not limited by feed-solution osmotic backpressure, making it ideal for treatment of high TDS wastewaters. Additionally, the product water leaving the MD unit will be extremely high quality and directly suitable for reuse. However, like other membrane processes, MD suffers from scaling and fouling of the membrane surface, increasing energy requirements for water production and limiting the overall effectiveness of the process. We address this issue by coating the membrane with carbon nanotubes (CNTs) to develop an electrically conductive surface that prevents organic, inorganic, and biological fouling. Our approach, illustrated in **Figure 1**, addresses the two major challenges associated with these waters: 1) the membrane distillation process removes the high TDS content and produces high quality effluent suitable for beneficial reuse, and 2) the charged CNT membrane coating prevents the formation of scale that would otherwise pose a significant operational hurdle.

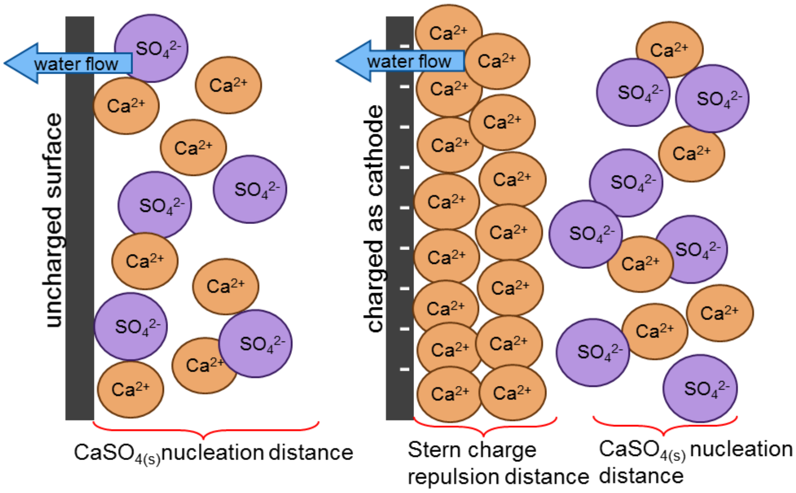


Figure 1. Conceptual illustration of the charged membrane surface coating with CNTs and under an applied voltage.

The overall project objective is to demonstrate the efficacy of membrane distillation (MD) as a cost savings technology to treat produced water generated from fossil fuel extraction that has high levels of TDS. In addition, we aim to develop a novel fouling-resistant nanocomposite membrane to reduce the need for chemicals to address membrane scaling due to the precipitation of divalent ions in the produced water and improve overall MD performance, via an electrically conductive membrane distillation process (ECMD). This anti-fouling membrane technology platform is based on incorporating carbon nanotubes (CNTs) into the surface layer of existing, commercially available MD membranes. The CNTs confer electrical conductivity to the membrane surface so that an electrical potential can be applied to remove and prevent membrane scaling and fouling. Specific technical objectives are:

- Demonstration of MD to recover at least 50% of wastewater with a concentration of 180,000 mg/L TDS
- The development of electrically conductive MD membranes having improved fouling resistance of at least 35% relative to the corresponding baseline nonconductive membranes when tested with real flowback/produced waters
- The development of experimentally validated models that can predict the separation performance achievable with the new conductive membrane types
- Techno-economic and environmental analyses of the MD water treatment processes utilizing these electrically conductive membranes

2. BACKGROUND

High TDS Water Quality

The quality of the water that comes from a well as flowback and produced water is dependent on the source water used in the fracking operation, constituents of the fracking fluids, the geochemistry of the host material, and the age of the well. In general, the purpose of the production fluid is to enhance the effectiveness of the fracking operation by introducing proppants to support the fractures, friction reducers, and scale and bacterial growth inhibitors. The volumetric composition of a typical fracking fluid is comprised of 90.6% water, 8.96% proppant, and 0.44% production chemicals. Typified by high concentrations of suspended and dissolved constituents, the wastewaters have limited disposal and treatment options using existing technologies. Between 10%–40% of the water used during hydraulic fracturing is returned as flowback water. In addition, produced water continues for the life of the well, and although smaller in volume than flowback water, it is typically of poorer quality due to higher salinity (often many times that of seawater) and may contain a variety of heavy metals, scalants, radioactive elements, particles, large concentration of unusual salts, and exotic microbes.[4] Water produced from gas deposits often contain large amounts of benzene and other toxic volatile chemicals that can be difficult to safely remove from water using conventional approaches, and has been shown to be have an overall toxicity 10 times that of comparable produced water from oil operations.[5] High TDS, primarily in the form of sodium chloride, poses the biggest problem in terms of treatability and reuse opportunities. Membrane technology has been demonstrated to be an effective treatment method for energy-related wastewater.[6-8] Currently available technologies such as dissolved air floatation, microfiltration, and ultrafiltration are well suited to remove the particles, oils, and dissolved organics present in flowback and produced wastewater that may otherwise have a tendency to foul the MD membrane surface. However, the formation of scale due to the precipitation of divalent salts and minerals on the MD membrane that potentially leads to flux decline and membrane deterioration must be adequately addressed by any proposed MD process. ***Table 1*** summarizes the high concentrations of divalent ions that have been measured in flowback and produced waters generated during resource extraction, as well as the precipitate that may foul the membrane during treatment.

Table 1. Maximum ion concentrations found in oil and gas produced wastewater with potential for membrane scaling.

Scaling Ion Present in Wastewater	Max Concentration (mg/L)	Potential Precipitate of Concern
Barium (Ba^{2+})	850	$BaSO_4$
Strontium (Sr^{2+})	6,250	$SrSO_4$
Sulfate ($SO4^{2-}$)	15,000	$BaSO_4$, $SrSO_4$, $CaSO_4$
Bicarbonate (HCO_3^-)	15,000	$CaCO_3$, $MgCO_3$
Calcium (Ca^{2+})	74,000	$CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$
Magnesium ((Mg^{2+})	47,000	$MgCO_3$

Source: Guerra et. al.[4]

Both this flowback water and the water produced over the well lifetime must be properly managed. Current management and treatment options do not offer a viable and sustainable solution to the water disposal problems associated with unconventional natural gas development. Although water produced during resource extraction contains a myriad of contaminants, the various organics, oils, and suspended solids can be readily and effectively treated using existing commercial technologies. The true barrier to treating the water at levels suitable for reuse lie in the high levels of TDS, which can be greater than 400,000 mg/L.

Current Management Practices

Management of wastewater generated from the production of unconventional gas resources is dependent on production region, disposal options, economics, and treatability. A management strategy common in some areas is the practice of storing the flowback on-site in large impoundments and reusing small volumes diluted with freshwater in additional fracking operations. However, issues associated with this practice include offensive odor problems should the water go anaerobic, volatilization of organic constituents that may be of human health concern (e.g., benzene, toluene, xylene, etc.), and concerns over storing large amounts of potentially hazardous material in Earthen structures that could be vulnerable to leaks and overflows during precipitation events. As the number of unconventional wells increases, the total volume of flowback and produced water will far exceed the available capacity, rendering this management approach a non-viable option. Most flowback and produced waters generated in the U.S. are currently disposed in Class II deep injection disposal wells. However, as unconventional gas production increases, this disposal method will be capacity-limited (see **Figure 2**). U.S. oil and gas producers reuse less than 1% of the 21 billion barrels of wastewater generated each year. There is a significant need and opportunity to develop a low cost, reliable approach to enable water reuse in this industry.

Existing Treatment Technologies

There are several technological approaches to treat the conventional pollutants associated with oil and gas production wastewaters. Chemical/physical process operations typically used to treat industrial wastewaters are suitable for the removal of oils and greases, suspended solids, and many trace metals. Although membrane processes Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO) are potentially promising for the treatment of flowback/produced waters, none of these existing membrane approaches are viable for the treatment of high TDS wastewater. For example, the current state-of-the-art technology for removing highly soluble dissolved salts is RO, which utilizes hydraulic pressure to force pure water through a semi-permeable membrane and has an upper limit of approximately 40,000 mg/L TDS, well below the higher concentrations in many produced waters (>200,000 mg/L TDS). The only proven technology that can adequately treat wastewater with extremely high TDS concentrations is thermal distillation, such as AltelaRain®. However, high capital and operating costs (>$5/bbl water), combined with limited mobile applications, have hindered broad use of this technology. **There exists a need for a low-cost, effective treatment technology for the removal of high TDS constituents present in oil and gas production wastewaters that produces effluents suitable for direct discharge, recycle, or beneficial reuse**. One approach for high-TDS water treatment is to employ the emerging technology membrane distillation (MD). Presented in **Table 2** is a detailed comparison of currently available TDS removal technologies compared to utilizing a technical approach involving low-pressure FO/MD.

Table 2. Available TDS Removal Technologies Compared to Proposed MD Technology for High-TDS Waters.

Characteristic	Ion Exchange	Reverse Osmosis	Electrodialysis Reversal	Thermal Distillation	Membrane Distillation
Energy cost	Low	Moderate	High	High	Moderate
Energy usage vs. TDS	Low	Increase	High increase	Independent	Low
Applicability to	All water types	Moderate TDS	High TDS	High TDS	All water types
Plant/unit size	Modular	Modular	Modular	Large	Modular
Pretreatment requirement	Filtration	Extensive	Filtration	Minimal	Filtration
Final water TDS	200–500 mg/L	200–500 mg/L	200–1,000 mg/L	<10 mg/L	<10 mg/L
Suitable for 180,000 mg/L TDS wastewater?	No	No	No	Yes	Yes

Electrically Conductive Membranes to Mitigate Scale in MD

Current membrane modification approaches to reducing fouling include increasing surface hydrophilicity, reducing surface charge, and reducing surface roughness.[9] However, these approaches yield only incremental improvement in membrane performance, and do not address the long-term flux decline and reduced membrane lifespan associated with repeated fouling. Some of the previously reported membrane modifications require complicated and costly post-fabrication steps, such as oxygen plasma etching or surface doping, that are not easily integrated into the standard membrane fabrication process. In addition, some of these modifications are material specific, and cannot be applied to all membrane materials. Our approach towards anti-fouling via incorporation of carbon nanotubes (CNT) with membranes to develop and electrically conductive surface prevents, organic, inorganic, and biological fouling, and can be easily applied in any membrane application. Furthermore, the physical nature of our anti-fouling method does not require regular recharging of the membrane, and is independent of the fouling species involved, so long as they are charged. Charged species make up the bulk of fouling materials, including scaling divalent ions in water, and we therefore expect our approach to yield superior results.

The application of an electrical potential to the membrane surface has the potential of significantly improving the treatment of flowback and produced waters by simultaneously addressing the fouling issues associated with each of the scaling constituents present in the water. The membranes maintain the transport properties that make them useful in separation processes, but have the additional advantage of being electrically conducting. Electrical conductivity is imparted to the membrane surface by covalently bonding functionalized carbon nanotubes into the polymeric membrane material, forming a true nanocomposite. The conductive properties of the membrane depend on forming a percolating network of carbon nanotubes within the polymer composite. Typical conductivity values range between 400 – 1,200 S/m, depending on the amount of CNT used.[10] This falls within the semiconducting range and allows the application of a tunable, externally provided, electric potential to the membrane surface.

3. EXPERIMENTAL METHODS

Modeling of Scaling Inhibition

Poisson-Boltzmann for Concentration as Function of Distance

Modeling efforts focused predicting the ion concentration layers as function of distance from the charged membrane surface. Although the Poisson-Boltzmann equation is typically used for such problems since our system operates at voltages above 200mV, the modified Poisson-Boltzmann (MPB) equation is valid. The first expression describes the potential as a function of distance from the membrane surface:

$$\frac{d\psi}{dx} = \left(2 \int -\frac{1}{\epsilon} \frac{eN_a \sum_i z_i c_i^{\infty} \exp\left(-\frac{z_i e\psi}{k_b T}\right)}{1+\sum_i \frac{c_i^{\infty}}{c_i^{max}}\left[\exp\left(-\frac{z_i e\psi}{k_b T}\right)-1\right]+C} d\psi \right)^{\frac{1}{2}} \qquad \text{(eq. 1)}$$

The ion concentration as a function of distance from the membrane surface is:

$$\frac{c_i^{\infty} \exp\left(-\frac{z_i e\psi}{k_b T}\right)}{1+\sum_i \frac{c_i^{\infty}}{c_i^{max}}\left[\exp\left(-\frac{z_i e\psi}{k_b T}\right)-1\right]} \qquad \text{(eq. 2)}$$

Where:

ψ = electrical potential; z = valence of ions; e = elementary charge; N_a = Avogadro's number;

T = Temperature; c = ion concentration; k = Boltzmann constant.

The equation above is set to solve for a position of a given potential away from a charged surface, so to calculate the complete potential profile away from the surface we have to solve on distance point at a time, but integrating from surface potential, to a known potential away from the surface. If we are solving for surface potential of 1500mV, we integrate from 1500- 1490, and then 1500-1480 etc. The integral solution gives a point where the potential is located.

2.1 OLI Software Modeling

Scaling potential of the solutions was measure using based on the electrolyte thermodynamics software from OLI Systems, Inc. (Cedar Knolls, NJ). Major ion concentrations were measured using a Thermo Dionex ICS3000 ICP-MS (ThermoFisher, Waltham, MA, USA). The ion concentrations and solution pH were input into the software to determine scaling potential.

Materials and Methods

Electrode Modified Cross-Flow Cell

A custom designed polycarbonate cross-flow filtration unit was used to measure both membrane flux and salt rejection and was used for all experiments. The filtration unit was designed with built-in insulated titanium electrodes that delivered electric charge to both the membrane surface as well as the counterelectrode plate at the top of the cell. Membrane performance was evaluated using a bench scale polycarbonate plate-and-frame ECMD test cell containing a flat sheet membrane module. **Figure 2** shows a graphical illustration of the ECMD cell, electrode ports, and the CNT bound MD membrane. The active membrane area was fixed at 75 cm^2. Anchored to the top of the cell are electrode ports constructed out of titanium. Titanium was chosen to minimize the potential of corrosion in a high TDS environment. A RIGOL DG1022 Waveform Generator (Beijing, China) was used to provide DC voltage to the electrodes. The conductive membrane itself served as the anode, while an interchangeable metal plate and/or mesh and plate served as the cathode.

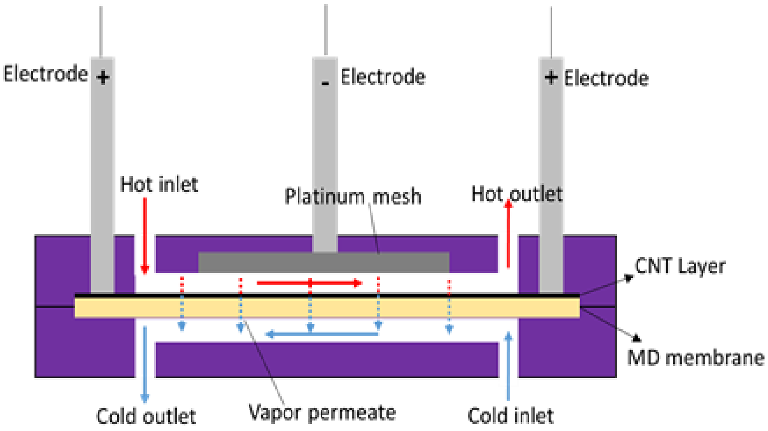


Figure 2. Schematic of ECMD Test Cell

In each of the tests, 2 L of deionized water was used as the permeate stream, while the selected feed stock was either 2 or 3 L. Both the feed and permeate waters were recirculated in counter current fashion in order to promote mixing to ensure a uniform temperature and salinity gradient. The cross flow velocity of both the feed and permeate streams were controlled with booster pump controllers. The feed stream was pumped with an Aquatec Pressure Boost Pump CDP880 (1-1.90 L/minute, Canonsburg, PA, USA) while the permeate stream was pumped with a KNF Lab Liquiport 1.300 NFXX pump (0.5-3 L/minute, Trenton, NJ, USA). Both pumps were set at the maximum flow rate. The permeate and feed streams were temperature controlled by Lab Companion RW-0525G (Jeio Tech, Seoul, South Korea) refrigerated and heating circulators (20 °C and 40-70 °C, respectively). The temperature of the influent and effluent feed and permeate streams were measured using thermocouples attached to the tubing. Both the mass of the feed and permeate tanks were measured over time using ADAM PGL20001 (Oxford, CT, USA) scales; the mass of permeate recovered over time allowed for flux calculations. The electrical conductivity of the permeate tank was measured over time with a HACH HQ40d (Loveland, CO, USA) conductivity probe in order to calculate ion rejection and to serve as an indication of membrane punctures, based on the assumption that any loss in membrane integrity would negatively impact ion rejection. Both conductivity and mass were logged continuously using each instrument's respective software packages until water recovery ceased.

Membrane Surface Modification

Both polyvinyldienylefluoride (PVDF) (0.22 and 0.45 μm) and polytetraflouroethlyle (PTFE) (0.22 μm) membranes were used as starting MD membrane for coating with CNT. Two types of fabrication methods were used to coat the two MD membranes used. The first was CNTs in a polyvinyl alcohol (PVA) matrix to create a polymerized "skin" layer on top of the porous. The second was pressure deposition of an aqueous suspension of CNT onto the membrane surface without any reaction to bind them the surface. The CNT is held to the surface via Van der Waals forces. Carbon nanotubes purchased from CHASM (VC 101, Chasmtek, Canton, MA, USA). For the PVA method, a ratio of 2:3 CNT ink to DI H20 was used. For the pressure deposition approach a 0.1 g/L solution of the CHASM ink was prepared in isopropyl alcohol and applied in a 2:3 ratio with deionized water. The solutions were carefully poured into the filtration system housing the membranes, and N_2 gas gently pressurized (~5psi) the cell in order to compact the CNT layer to the membrane. Once all excess liquid was removed from the vessel, nitrogen was applied for an additional 5 minutes in order to facilitate final binding of the CNT layer via Van der Waals forces. After, the membrane was removed from the cell and gently washed with DI H20 in order to remove excess surfactant. Finally, the membranes were dried in a binder oven at 90 °C for 30 minutes; a circular weight was applied to the outer edge of the membrane to prevent curling. Coating resistance was measured using a 4-point connection approach with Keithley 2440 SourceMeter (Tektronix, Beaverton OR, USA). A sweeping voltage of 0.01-1V was applied to the membrane to produce I-V curves; the inverse of the slope was calculated to obtain resistance.

Feed Solution Preparation

A variety of synthetic feed solutions and produced oil field water provided by Veolia were tested in the ECMD. The synthetic salt solutions were chosen to mimic high salinity waters and/or to encourage $CaSO_4$ and $CaCO_3$ formation, primary scalants that form on the membrane surface and significantly reduce performance. The tested solutions included:

- 1M NaCl
- Na2CO3 (1000 mg/L), KCl (800 mg/L), CaCl2 (800 mg/L), and MgCl2 (452 mg/L)
- 180,000 mg/L NaCl
- NaSO4 (1.91 g/L), MgSO4 (1.75 g/L), and CaCl2*2H2O (2.41 g/L)
- Veolia produced oil field water (TDS 190,000 – 200,000 ppm)

The high TDS wastewater provided by industrial partner Veolia was characterized via ICP-MS. In initial tests, the Veolia produced water was used as it had been provided; however, this caused the membrane to almost immediately foul due to the very high TDS and larger molecules (organics, colloids) in solution. To circumvent this problem the water was filtered with a 1.0 µm glass fiber filter prior to feeding.

4. RESULTS AND DISCUSSION

CNT Coating Results

The coatings method A is pressure deposited surface coating, with the CNT held in place by Van der Waals forces, while the second method created a polymerized "skin" layer on top of the porous membrane surface. **Figure 3** shows the SEM image of the CNT-coated PVDF membranes for methods A and B. The resistivity of the CNT coated membranes was measured at 0.3 kΩ/cm for method A and 1.7 kΩ/cm for method B. The dried membranes were cut to fit the ECMD test cell.

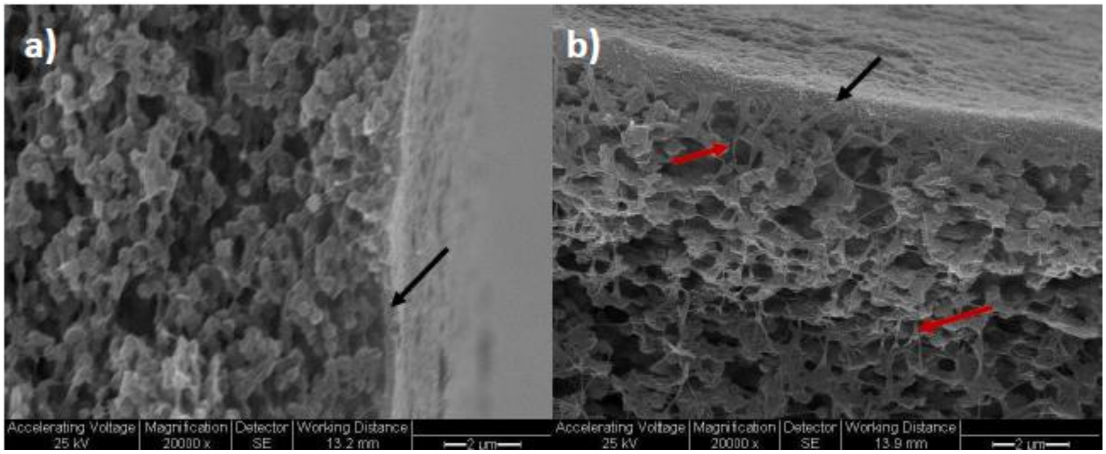


Figure 3. SEM images of the CNT-coated PVDF ECMD membranes using (a) coating method A and (b) method B. The black arrows indicate the polymerized CNT surface layer of the membrane. Resistance measurements along the surface were between 0.95 and 1.0 kohm/cm for both coating methods, falling within the semi-conductive range. It is clear that the CNT binding methods presented here do not damage the internal porosity of the PDVF membrane.

The CHASM ink coatings used throughout the project used for the real wastewater treatment. The ink provided a coating with resistivity of 0.28 kΩ/cm, which was similar to the performance provided by the UCR approach. The CNT is held to the surface via Van der Waals forces. The resistivity of the CNT coated membranes was measured to be between 0.9~1.0 kΩ/cm, for both methods. This falls within the semi-conductive range. **Table 3** compares the water/salt selectivity measured for the various membranes.

Table 3. Applied and observed voltage during ECMD operation. Feed water tested 1M NaCl. T_{hot}^{in} setpoint ~60ºC, T_{cold}^{in} ~20ºC. Membrane as the anode.

MD Performance Results		**Voltage [V] (applied/observed)**	
PTFE CNT	PVDF CNT	PTFE CNT	PVDF CNT
Flux: 12.4 l/m²/hr	Flux:10.5 l/m²/hr	0.5/0.46	0.5/0.48
		1.5/1.46	1.5/1.45
Salt Rejection: >99.9%	Salt Rejection: >99.9%	2.5/2.38	2.5/2.41
		3.5/3.40	3.5/3.31

Modeling Results

ECMD Modeling of Ion Charge

The modeling approach allows us to understand how charge impacts ion concentration near the membrane surface. **Figure 4** is an example of output from the model showing ion concentrations at different water temperatures. The figure demonstrates that the charged surface that acts as a barrier to ions decreases with temperature, but that this effect is minimal (~3A from 40ºC to 80ºC) and unlikely to have much of an inhibitory effect on the effectiveness. This is a useful finding, since MD performance and efficiency increases with temperature, we can conclude that this approach to scaling mitigation will have applicability at all likely ranges of MD operation.

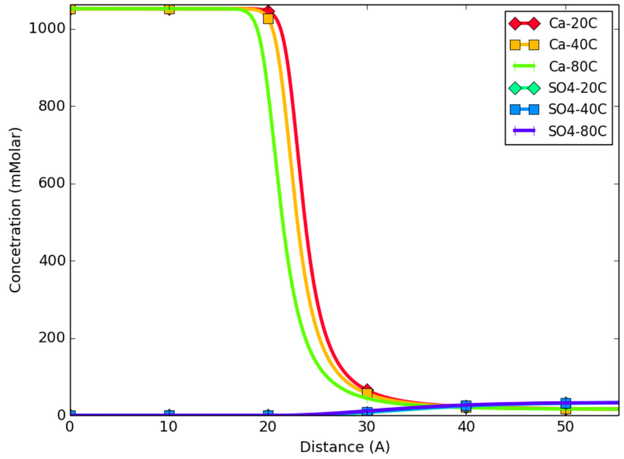


Figure 4. Ion concentration as a function of distance from charged membrane surface for water temperatures 20, 40, and 80ºC

Figure 4 shows the ion concentration of calcium and sulfate ions calculated as a function of distance from the membrane while **Figure 5** shows the corresponding surface potential for calcium and sulfate ions for different applied voltages. The results suggest that higher voltage will lead to greater surface charge and should also lead to decreased ion concentrations near the surface.

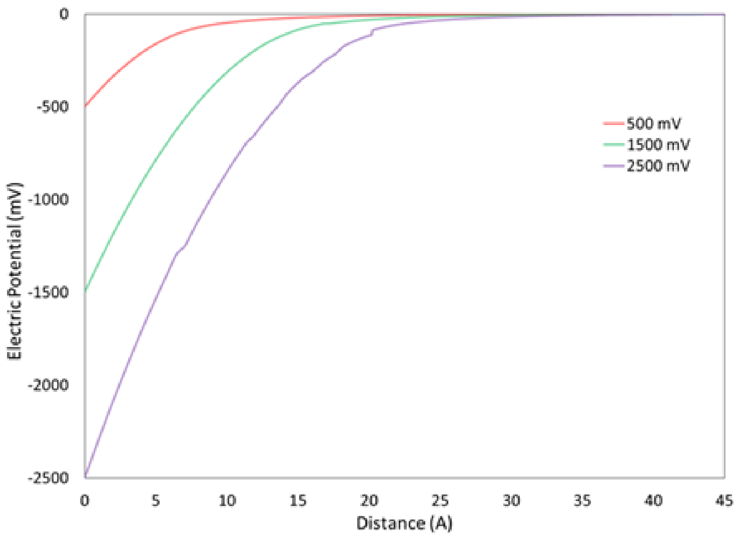


Figure 5. Surface potential of charged membrane surface as function of distance from the charged surface for applied voltages of 0.5, 1.5, and 2.5V

Based on ICP-MS analysis of ion concentration in the produced water, Veolia ran OLI's aqueous electrolyte thermodynamic framework model to determine the speciation of the water and identify likely scaling species. The software was run for two scenarios, first one at feed concentration of 180,000 mg/L, and the other at 50% water recovery, which corresponds to a feed concentration of 360,000 mg/L total dissolved solids. The results for both analyses are presented in **Table 4**.

Table 4. OLI software modeling results for complex real produced water used to identify potential scaling species. Temperature = 60ºC and pH = 5.5.

Species in water	**Scaling Tendency for Produced water Concentration = 180,000 mg/L**	**Scaling Tendency for Produced water Concentration = 360,000 mg/L**
BaSO4 (Barite)	1.0000	1.00000
SrSO4 (Celestine/Celestite)	1.0000	1.00000
Fe(OH)3 (Bernalite)	1.0000	1.00000
H2O	0.758818	0.528493
SiO2 (Lechatelierite)	0.10656	0.131120
NaCl (Halite)	0.012323	0.0516195
NaCl*2H2O (hydrohalite)	0.012023	0.0241227

Na2SO4 (Thenardite)	1.10e-3	7.75961e-3
MgSO4*6H2O (Hexahydrite)	-	1.55983e-3
KCl (Sylvite)	7.73e-4	1.55135e-3
MgSO4*7H2O (Epsomite)	1.12e-3	1.38799e-3
MgSO4*5H2O (Pentahydrite)	3.17e-4	1.21202e-3
Na2SO4	5.10e-5	7.12882e-4
MgSO4*4H2O (Starkeyite)	1.03e-4	7.02735e-4
Na2SO4*10H2O (Mirabilite)	6.12e-3	6.49557e-4
MgSO4*H2O (Kieserite)	3.12e-5	5.20088e-4
MgSO4*12H2O	-	9.44676e-5
Mg(OH)2 (Brucite)	-	1.77197e-6
SrCL2*6H2O	-	1.00955e-6
BaCl2*2H2O	-	1.24431e-7
BaCl2*H2O	-	5.05870e-8
BaCl2*1/2H2O	-	4.34553e-8
NaFeO2	-	4.55190e-11

According the OLI results, any sold species with a scaling tendency of 1 suggests that it will precipitate (scale) under the test conditions. This suggest that at both the starting concentration and the final concentration (at 50% water recovery), the same three scaling species, Bernalite ($Fe(OH)_3$, Celestine $SrSO_4$, and Barite $BaSO_4$ will be the dominant constituents of the scale formed on the membrane surface.

ECMD Scaling Inhibition Performance

Testing with Synthetic Wastewater

The impact of the electrical coating was measured by monitoring membrane flux as a function of time to determine permeability decline. Scaling experiments were conducted using the PTFE membrane coated with CNT using the pressure deposition method. The synthetic solution contained concentrations of 0.0134M Na_2SO_4, 0.02M $MgSO_4$, and 0.0164M $CaCl_2$. This solution was designed to have concentrations that will precipitate $CaSO_4$ on the membrane surface as water is removed. **Figure 6** shows the comparative results from experimental runs both without and with voltage applied across the ECMD cell.

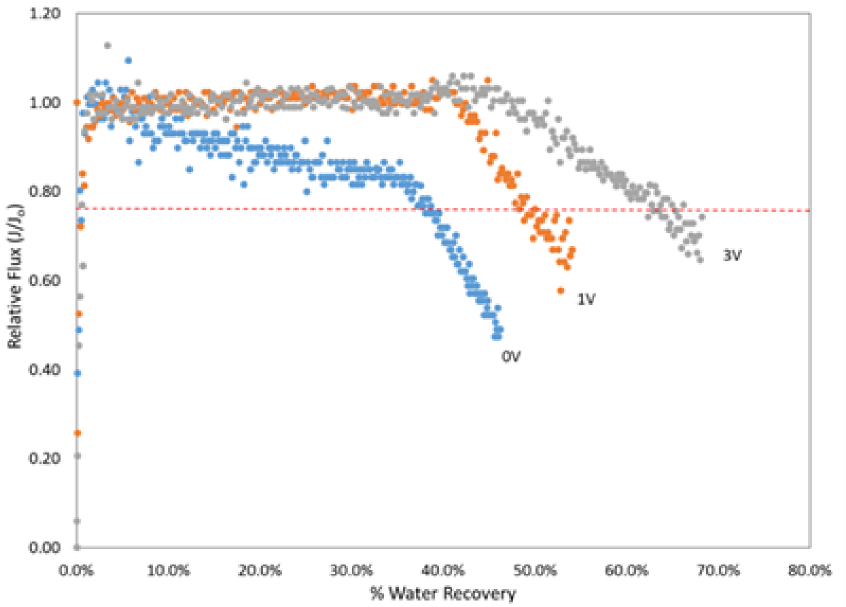


Figure 6. Relative flux as function of time for both MD (0V) and ECMD (1V, 3V, 5V) membranes as cathode) treatment of $CaSO_4$ scaling solution. Feed temperature inlet = 60ºC, permeate temperature inlet = 20ºC. Average salt rejection for the tests > 99.9%.

The higher surface potential and increased thickness of counter ion layer correspond with increased water recovery values with applied voltage as suggested by the modeling results. These experimental results provide insight in evaluating the tradeoff between reduced membrane scaling and increased energy input to achieve performance results. The test was also repeated for scaling using a calcium carbonate scaling solution. This synthetic solution had initial concentrations of 0.0072 $CaCl_2$, 0.0107M KCl, 0.0047 $MgCl_2$, 0.0094M Na_2CO_3. **Figure 7** shows the results of these experiments with relative flux as a function of water recovery.

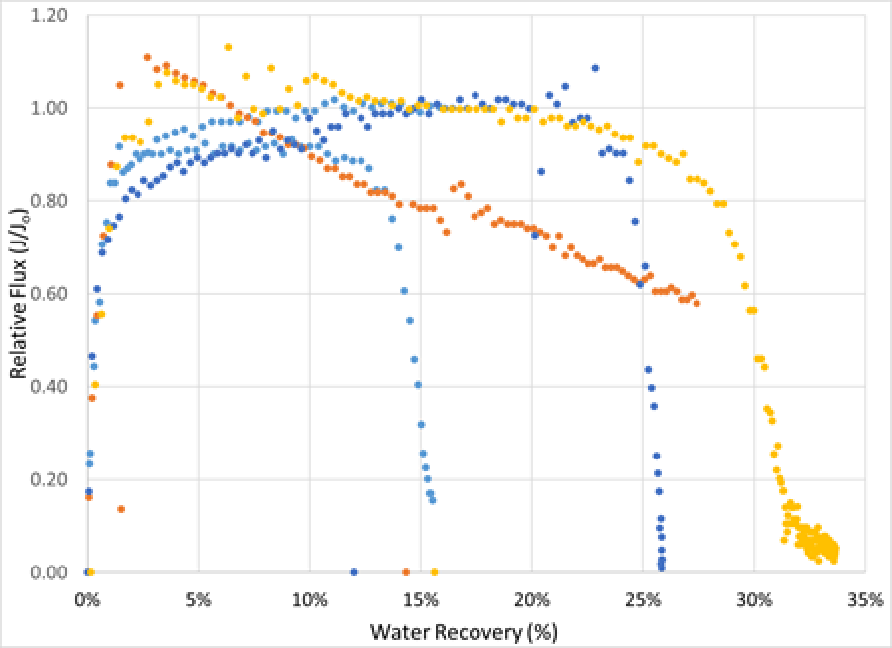


Figure 7. Relative flux as function of time for both MD (0V) and ECMD (1V, 3V, 5V) membranes as cathode) treatment of $CaCO_3$ scaling solution. Feed temperature inlet = 60ºC, permeate temperature inlet = 20ºC. Average salt rejection for the tests > 99.9%.

In this case, we see an improvement in water recovery with increasing applied voltage, with the water recovery reaching 14%, 17%, 25%, and 29% at a relative flux value of 0.75 for voltages 0, 1, 3, and 5. However, the shape of the relative flux curves is not as well defined as with the $CaSO_4$ solution.

Testing with Real Produced Water The scaling experiments were next repeated using real wastewater from an industrial site. The overall TDS of this wastewater was 190,000 mg/L, and a cation scan for a wastewater sample is shown in **Table 5.**

Table 5. Cation scan for high TDS industrial wastewater showing key selected species present in the wastewater sample.

Species	**B**	**Ba**	**Fe**	**Li**	**Mg**	**Na**	**Sr**
Conc. (mg/L)	6.5	201	53	35	2298	41470	2952

The experimental settings used for the real wastewater were the same as for the synthetic water samples. **Figure 8** shows the results summary for relative flux as a function of water recovery with the real water sample.

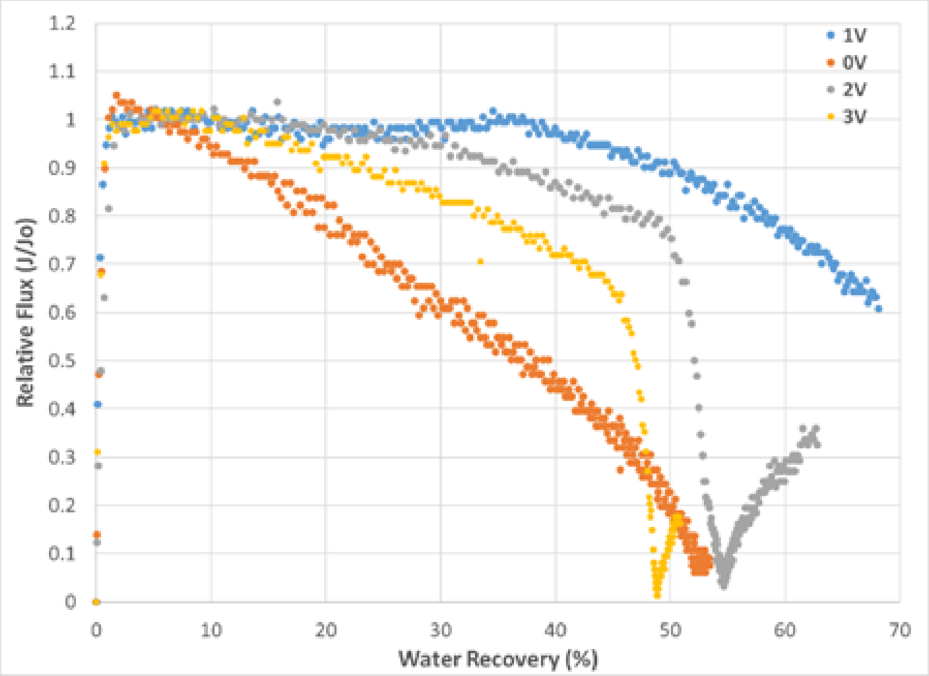
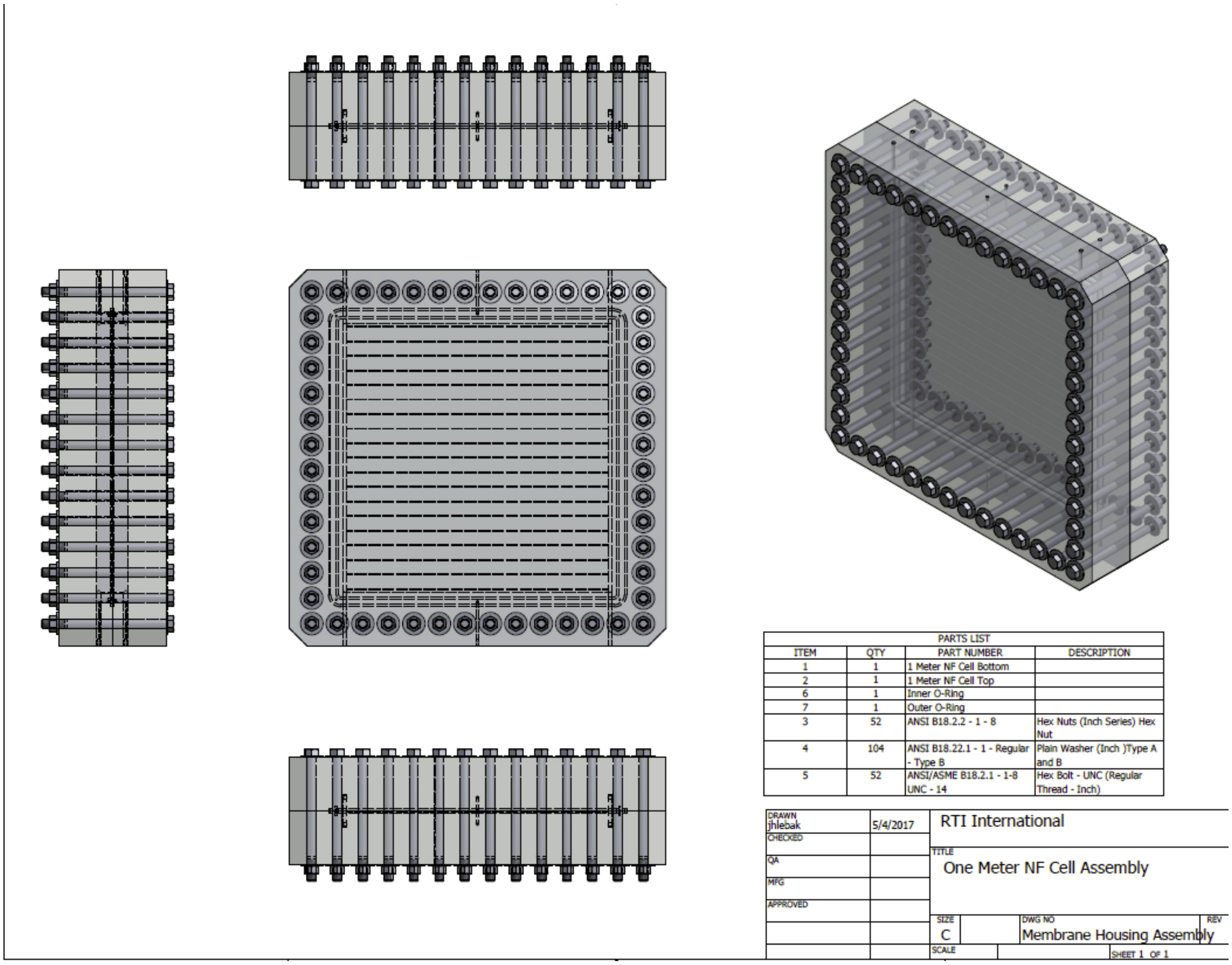


Figure 8. Relative flux as function of time for both MD (0V) and ECMD (1V, 2V, 3V) membranes as cathode) treatment of real high TDS wastewater. Feed temperature inlet = 60°C, permeate temperature inlet = 20°C. Average salt rejection for the tests > 99.9%.

These results again show a clear benefit of an applied charge to the membrane surface in increasing the amount of water recovery before the onset of scaling, but the results do not show the same trend of increasing voltage improving the water recovery. Instead, the highest water recovery is seen at a voltage of 1V, while the water recovery decreases for 2V and decreases further at 3V, with all three voltages showing better recovery than 0V. The reason for this departure is not apparent, although the much higher concentration as well as more complex mixture of ions (as well as organics) could change the behavior of the scale nucleation as the surface at larger voltages. Another notable observation of the results is that when zero flux is reached, there is a minor flux recovery, which suggest some mechanism whereby the pore blockage is reversed.

Preliminary Design of Full-Scale Conductive MD Membrane Module

Work on understanding the implications of increasing membrane surface area to usable scale was a key design constraint of the design of a full-scale module prototype. These results were used to assess the power consumption losses during operation and help to determine the design of the power supply needed on a full-scale module. A detailed design for the full-scale ECMD prototype model was developed and is presented in Figure 9.



PARTS LIST			
ITEM	QTY	PART NUMBER	DESCRIPTION
1	1	1 Meter NF Cell Bottom	
2	1	1 Meter NF Cell Top	
6	1	Inner O-Ring	
7	1	Outer O-Ring	
3	52	ANSI B18.2.2 - 1 - 8	Hex Nuts (Inch Series) Hex Nut
4	104	ANSI B18.22.1 - 1 - Regular - Type B	Plain Washer (Inch)Type A and B
5	52	ANSI/ASME B18.2.1 - 1-8 UNC - 14	Hex Bolt - UNC (Regular Thread - Inch)

Figure 9. Schematic of full-scale ECMD prototype module for design.

The module design uses a flat sheet membrane configuration as opposed the previously targeted spiral wound configuration. The flat sheet was chosen to ensure flow and electrical connection could be integrated into the module, and the only commercially available MD system Memsys^{TM} employs a flat sheet stack. In the design shown in Figure 9, the membranes active area is 1m^2, and channels are created for either hot or cold streams on either side of the membrane face. The electrode contacts are on both sides of the membrane module, so that both the membrane and counter electrode can have the voltage applied. This design basis was used to finalize the final CAD design of the module.

Preliminary Techno-Economic Analysis

A process techno-economic assessment was conducted to assess the potential tradeoffs in increased cost due to the electricity requirements of ECMD as well as the increased material costs for the CNT coating. This comprehensive cost estimate includes thermal energy input and other operating costs and also the construction of basic pumps, pipes, and tanks that will be required for a commercial scale application of this technology. The goal of this analysis is to provide an early evaluation into the tradeoffs between improved performance and increased costs. The design scenario assumes that 1M gallons/day of high TDS wastewater must be treated to achieve 50% recovery. This is used to develop membrane area requirements, energy requirements and an assessment of the capital and operating requirements to compare standard MD to ECMD.

Estimate Quality. The accuracy of a cost estimate is a function of the stage or definition of a project. As a project progresses towards completion the cost estimate becomes more accurate. This progression has been defined by a cost estimate classification system ranging from 5 (>0% to 2% project definition) to 1 (50% to 100% project definition). Based on the current stage of this project, a Class 4 estimate was deemed appropriate and is defined as:

CLASS 4 ESTIMATE (Study or Feasibility)

(Typical level of project definition required: 1% to 15% of full project definition.)

(Accuracy Range: L=-15% to -30%, H=+20% to +50%)

Class 4 estimates are generally prepared based on limited information and subsequently have fairly wide accuracy ranges. They are typically used for project screening, determination of feasibility, concept evaluation, and preliminary budget approval. Class 4 estimates are prepared for a number of purposes, such as but not limited to, detailed strategic planning, business development, project screening at more developed stages, alternative scheme analysis, confirmation of economic and/or technical feasibility, and preliminary budget approval or approval to proceed to next stage.

Capital Costs. The total capital cost is the sum of material equipment costs, the installation cost for the process equipment, and the total indirect capital costs. The total indirect capital costs account for the construction overhead costs, contingency, project management fees, and the working capital required for the project. These were considered to be factors of the total direct costs, and the details are listed in **Table 6**.

Table 6. Indirect cost components multiplier.

Indirect cost component	**Factor of total indirect cost**
Construction Overhead	4%
Contingency	6%

A&E fees; Project Management	12%
Working Capital	4%

Operational Costs. The total cost for operating the processes can be further split based on the cost of utilities required to run the process and the labor costs involved with the project operation. In this study, the operating costs were further split into the following categories

- Electricity
- Labor
- Cleaning Chemicals
- Membrane replacement
- Thermal energy
- Parts repairs and replacement

Key Assumptions. To determine cost savings relative to non-ECMD surface, the system was assumed to require a cleaning event when the relative flux of the system reached 0.75. This requires production to stop and chemical cleaning in place. Chemicals used for each cleaning event include citric acid and sodium hydroxide. Although experimental results showed 2.7 mA/m^2 current density at 3V, we assumed 10-fold increase in power requirements for scale up so used 270 mA/m^2 current density. This corresponded to ~ 20 kWh/day of additional electricity required for 1 MGD system. The additional cost of the carbon nanotubes in the ECMD modules was estimated to be an additional $2.50 per square meter[10].

- Cost of Electricity = 0.12 $\$/kWh_e$
- Cost of Thermal Heating = 0.12 $\$/kWh_{th}$ (based on natural gas price of $3.2/MBtu)
- Flux = 8 liters/m^2-hr (LMH)
- Membrane active area per module = 26.7 m^2
- Average salt rejection 99.9%
- Feed Temperature = 70 ^oC
- Permeate Temperature = 70 ^oC
- Applied voltage for ECMD = 3V

TE Results and Discussion. The impact on the tradeoffs between the regular MD and the ECMD are illustrated in **Table 7**. The preliminary results show that the increased electricity consumption is more than offset by the reduction in required chemical cost. The savings are not limited the reduced chemical usage, as the reduced system size since fewer cleaning events increases the effective processing capacity of the system, which lowers the capital expenditure for membranes. The reduction in scaling needed (and corresponding decrease of acetic acid/sodium hydroxide) to break even from a daily operational cost standpoint is 9%. There are two areas where the cost savings are realized when utilizing ECMD. The first is the operating costs, when water recovery is increased the chemicals required decreases. The second is in the capital costs of the system. The higher water recovery increases the effective processing capacity of the treatment system, which decreases the require system size. For this case cost savings are realized in the form of reduced membrane modules and the added hardware. For this scenario, the ECMD footprint (and associated membrane requirements) were 38% smaller than for the standard MD system, which is more than enough to offset the increased cost of the membranes on a per unit area basis as well as the electricity to charge the surface.

Table 7. Comparison between standard MD and ECMD systems designed for 1 MGD flow and 50% recovery.

Operational Parameter	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

*assuming $2.50/$m^2$ for CNT[10]

Project Accomplishment and Outputs

During the project work, all milestones were met, as shown in Table 8.

Table 8. Project Milestones

Milestone #	Milestone Title or Brief Description	Milestone Completion Date				Milestone Progress Notes
		Original Planned	Revised Planned	Actual Complete	% Complete	
1	Successful demonstration of ECMD membrane	3/31/15	4/30/15	4/21/15	100%	The ECMD test cell was successfully produced high quality effluent under an applied temperature gradient while a voltage was applied across the membrane.
2	Feasibility of MD technology for treating produced waters with total-dissolved-solids concentration of at least 180,000 mg/L	9/30/15	No revision	9/4/2015	100%	Consistent flux for 180,000 mg/L NaCl feed water to MD test system; overall feed water recovery recorded to be 51.2%.
3	Enhanced fouling resistance of conductive MD membranes	6/30/16	5/31/17	6/31/2017	100%	Successful demonstrated of scaling resistance to calcium sulfate species with multiple membrane types. Scaling resistance shown with actual industrial wastewater.
4	Conductive membrane model validation	6/30/16	6/30/17	N/A	100%	Model validated with multiple scalant species based on experimental data.

In addition, research findings were presented at the following conferences and meetings.

- Hendren, Z. D., Jassby, D., Bollinger, D. L., & Duan, W. *Fouling-Resistant Membranes for Treating Concentrated Brines.* Poster presented at NETL 2015 Crosscutting Technology Research Review Meeting, Pittsburgh, PA.

- Hendren, Z. D., Bollinger, D. L., Akunuri, S. N., Choi, Y., Duan, W., Dudchenko, A., & Jassby, D. (2016, March). *Membrane distillation with electrically conductive membranes for scale prevention of divalent salt solutions.* Presented at American Chemical Society Spring Meeting, San Diego, CA.

- Hendren, Z. D., Jassby, D., Bollinger, D. L., & Duan, W. *Fouling-Resistant Membranes for Treating Concentrated Brines. P*resented at NETL 2016 Crosscutting Technology Research Review Meeting, Pittsburgh, PA.

- Lesemann, M., Toy, L. G., Choi, Y., Hendren, Z. D., Hoang, C. Q.,Bollinger, D. L., Akunuri, S. N., Yong, S., & Buisson, H. (2016, May). *Mitigation of Scaling and Fouling in Membrane Distillation Process for Industrial Water Treatment and Reuse*. Presented at 39th Industrial Energy Technology Conference (IETC), New Orleans, LA.

- Hendren, Z. D., Jassby, D., Bollinger, D. L., & Duan, W. (2017, April). *Fouling-Resistant Membranes for Treating Concentrated Brines*. Presented at NETL 2017 Crosscutting Technology Research Review Meeting, Pittsburgh, PA.

5. CONCLUSIONS

The ECMD process is particularly suited to treat high TDS water of approaching 200,000 ppm such as oil field produced water and brine generated from deep-well injection. The ECMD system was shown to prevent scaling of calcium sulfate and calcium chloride species as well as reduce the onset of membrane scaling for a real produced water with a feed TDS ~ 190,000mg/L. In advancing the ECMD technologies from lab/bench-scale to pilot-scale evaluation, valuable lessons were learned. Modeling results show that the charge repulsion effect is minimally impacted by temperature and ion concentration, although differences in scaling inhibition behavior were observed for the real wastewater when compared the synthetic solutions. A preliminary economic comparison also demonstrated that the tradeoffs between the increased electricity and material costs for the ECMD system are favorable in comparison with the standard MD system due to the reduction in chemicals required for cleaning as well as the smaller footprint since afforded by the increased water recovery. To obtain interest from potential field sites, realistic data demonstrating both the membranes' and the technologies' long-term performance efficacies under real wastewater conditions need to be available, even if only at laboratory or bench scale. This technology shows promise as a solution for high TDS wastewaters and warrants further evaluation at a wider range of operating conditions and different wastewaters.

6. RECOMMENDATIONS

We would like to make recommendations as follows

- Different types of industrial and manufacturing process water should be tested to better assess the impact of complex ion matrices on scaling inhibition performance.
- It is also necessary to conduct much longer-term testing to evaluate the longevity of electrical membrane coating. Longer-term testing will also benefit from understanding seasonal variation in the feed water conditions, if present.
- The ECMD technology is a novel combination of water treatment, membrane-based, and thermal processes. It is necessary to communicate the results to broader communities to collect ideas and inputs for future testing and evaluations.
- For MD as a technology, heat and electrical energy minimization needs to be integrated into not only the system design, but also into the details of the membrane module construction.

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