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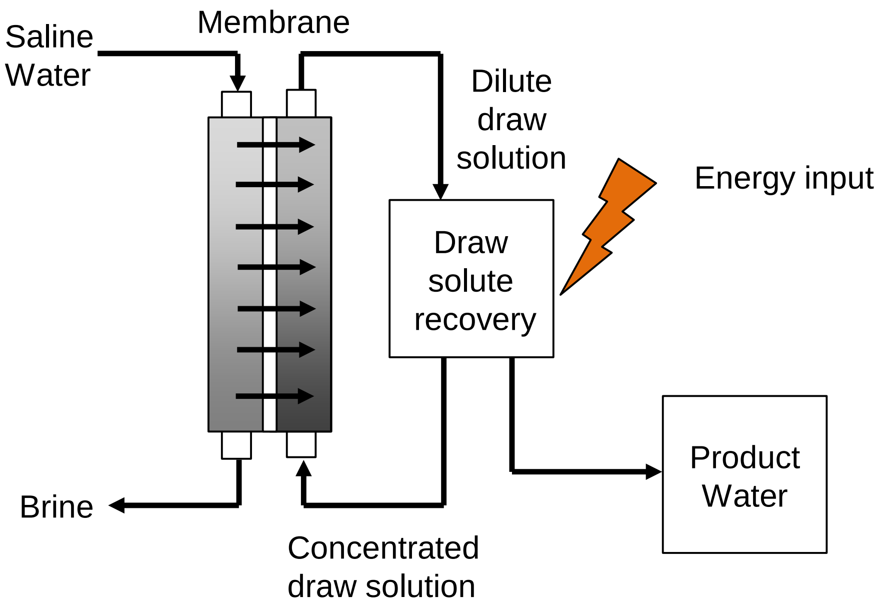

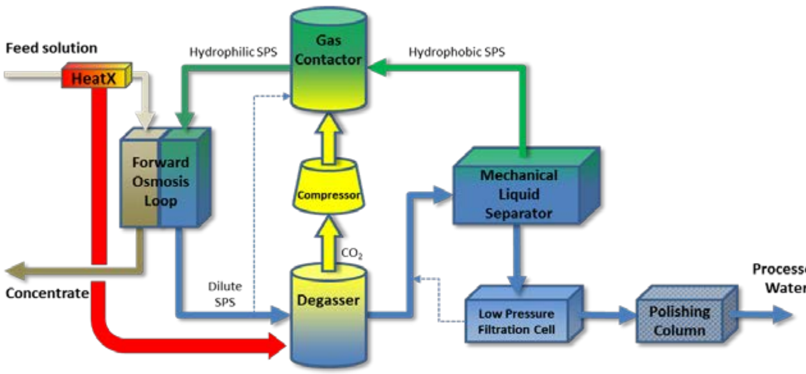

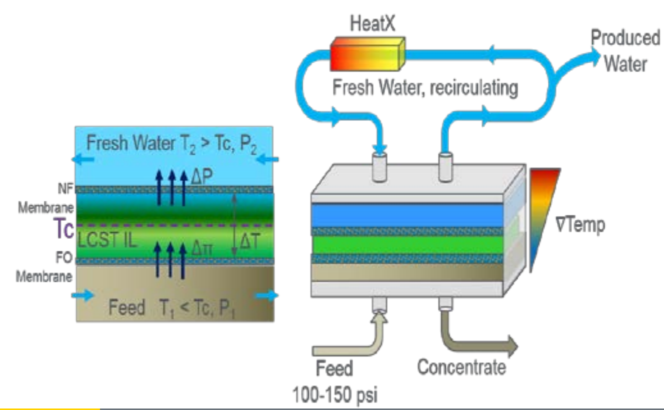

Low Energy, Low Cost Forward Osmosis for Water Treatment using Geothermal Heat

Project Officer: Josh Mengers

Total Project Funding: $2,947,000 ($1519K INL; $1428K LBL)

November 14, 2017

Dan Wendt & Aaron Wilson (INL)
Robert Kostecki & Nic Spycher (LBNL)
Aaron Wilson, presenter
Idaho National Laboratory & Lawrence Berkeley National Laboratory

Track 1: SALT General R&D

Desalination via Forward Osmosis

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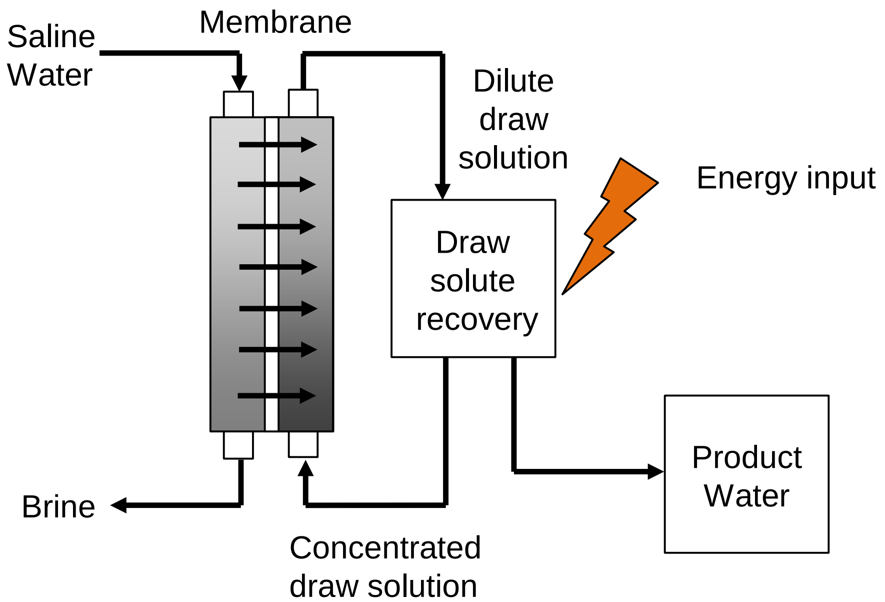
Forward Osmosis:

- A semi-permeable membrane-based water treatment process
- Spontaneous (no energy input) flux of water from the feed to the draw stream
- Primary process energy requirements delivered during draw solute recovery
  - Reverse Osmosis
  - Distillation
  - **Thermal solute separation**



INL project investigating FO desalination using thermolytic solutes (Switchable Polarity Solvents (SPS))

- 1-cyclohexylpiperdine (CHP): A second generation SPS developed at INL
- Low-grade heat input induces phase separation of solute and recovered water
- Immiscible solute and water subsequently separated using gravity separation (decanter) or related processes

LBNL project investigating FO desalination using Lower Critical Solution Temperature (LCST) Ionic Liquids (IL)

- LCST IL have advantages and process requirements related to SPS.

Produced Waters from Oil & Gas Production

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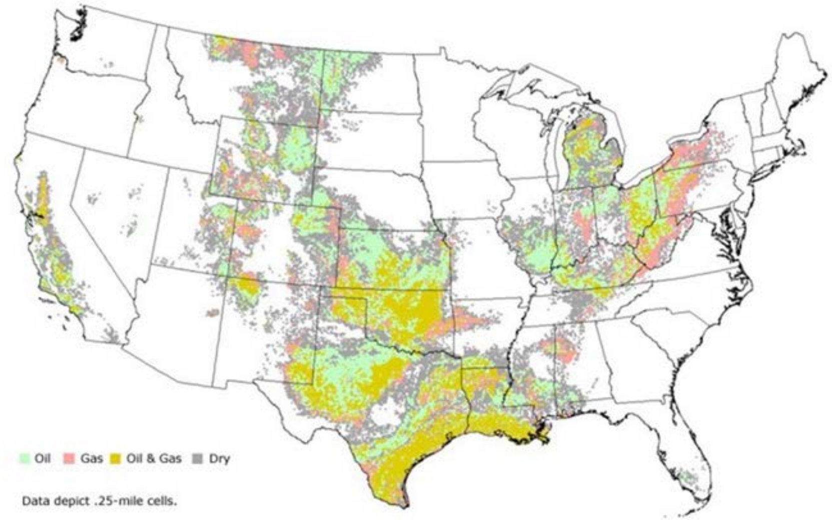
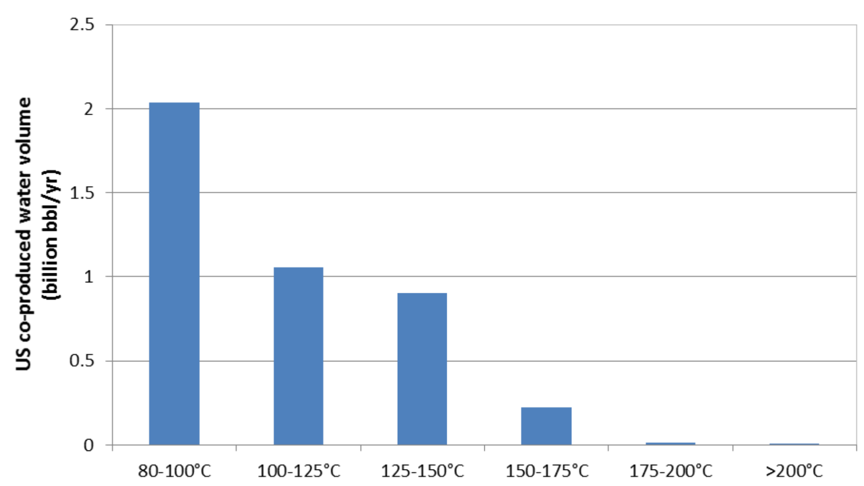
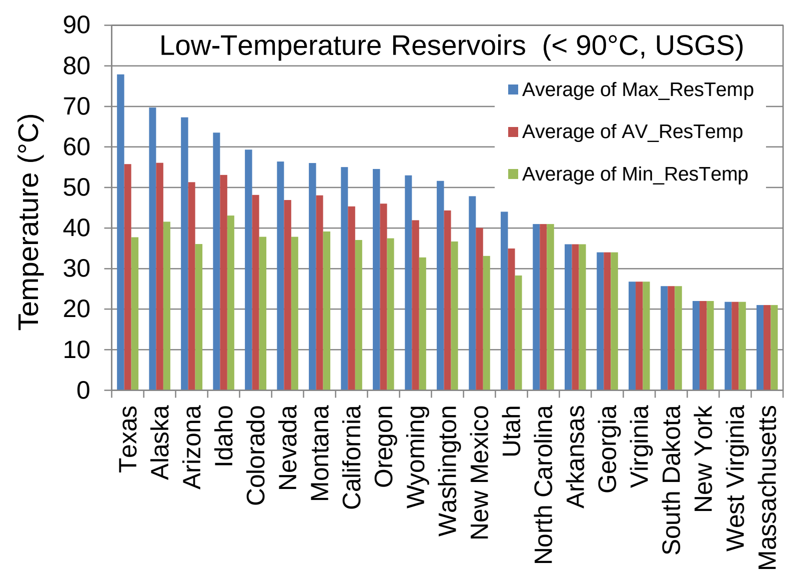




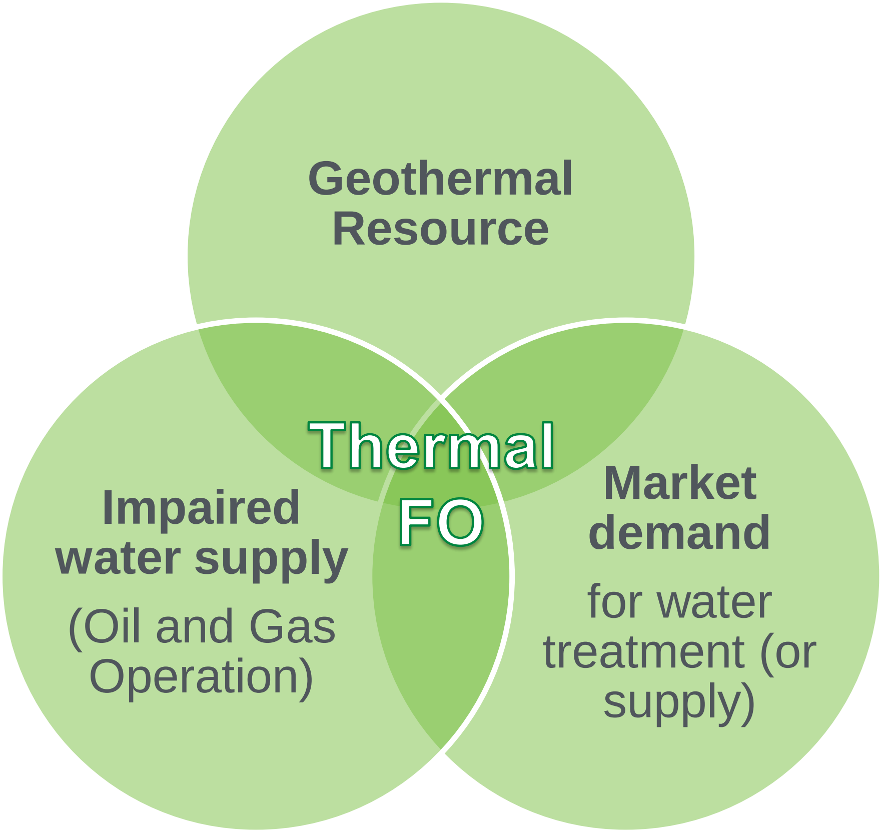
- 20 to 30 billion bbl/yr of co-produced water from U.S. oil & gas production operations (~4 billion bbl/yr have temperature >80°C)
- Majority of produced water is disposed of via injection at a typical cost of ~$1/bbl ($6.3/m³). Cost effective treatment could:
  - Reduce volume requiring disposal
  - Decrease environmental risks including spills and induced seismicity
  - Provide additional water source for beneficial uses



Relevance to Industry Needs and GTO Objectives

Project Objective: To advance forward osmosis (FO) technology to enable low-cost water treatment for applications using low-temperature geothermal resources

- Many geothermal resources are too low in temperature for electricity generation but could provide energy for water treatment
  - **Impaired Water Source** Greater than 20 billion bbl of produced water per year is associated with oil & gas production operations
  - **Market Demand** O&G wastewater typically disposed of via injection at a cost of $1/bbl or greater; disposal associated with environmental risks including spills and earthquakes
  - **Geothermal Resource** Approximately 4 billion bbl of O&G wastewater has a temperature ≥ 80°C, a temperature which is suitable to drive SPS FO.
- Development of novel low temperature, low cost desalination technologies could result in
  - Utilization of low-temperature geothermal resources unsuitable for efficient power generation
  - Diversification of geothermal energy use by expansion into new industry and market sectors (oil & gas / wastewater treatment)

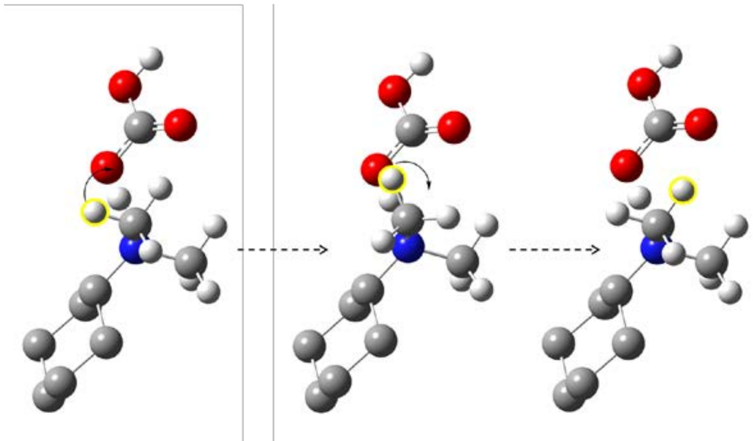


Methods/Approach

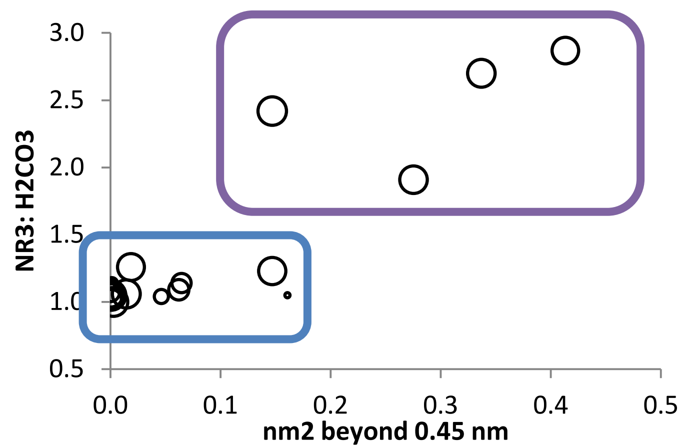
Approach: Early Stage Applied Research required for Scale-up

Systematic testing of significant process variables to optimize component performance and determine system limits while constantly updating a preliminary engineering design basis (technoeconomic model)

- Capitalized on previous fundamental work
  - Previous INL LDRD Supported research which systematically varied structural features of tertiary amines and compared results to for both empirical and computational analysis to identify 1-cyclohexylpipiridine (CHP) as an optimal switchable polarity solvent for SPS FO.
- Use of small but industrially relevant components (modules vs. coupons) when possible.
- Target continuous operation (vs batch operation)
- Collaborate with National Labs (INL plus LBNL) and Industrial Partners (Porifera) whenever possible.

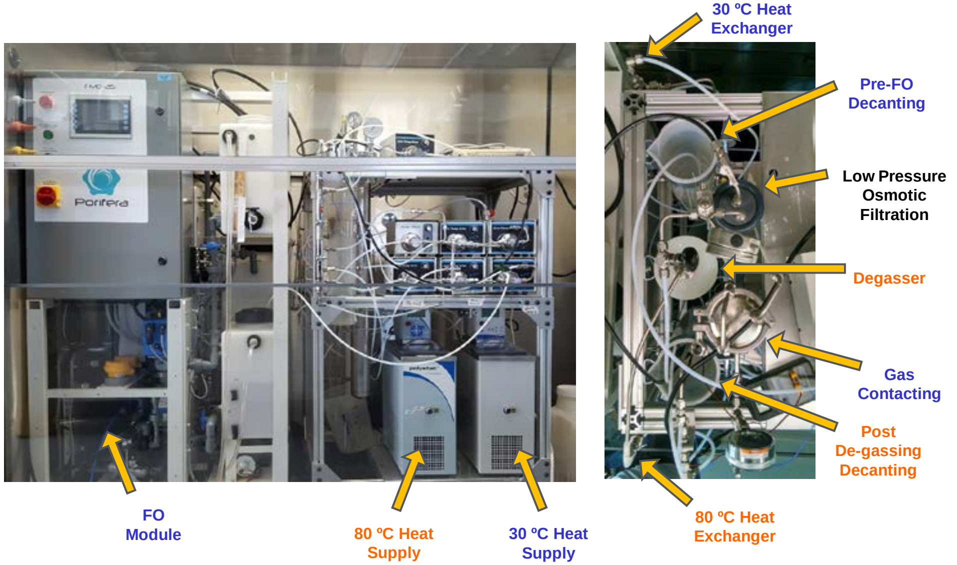


DFT Potential Energy Scan



Technical Accomplishments and Progress

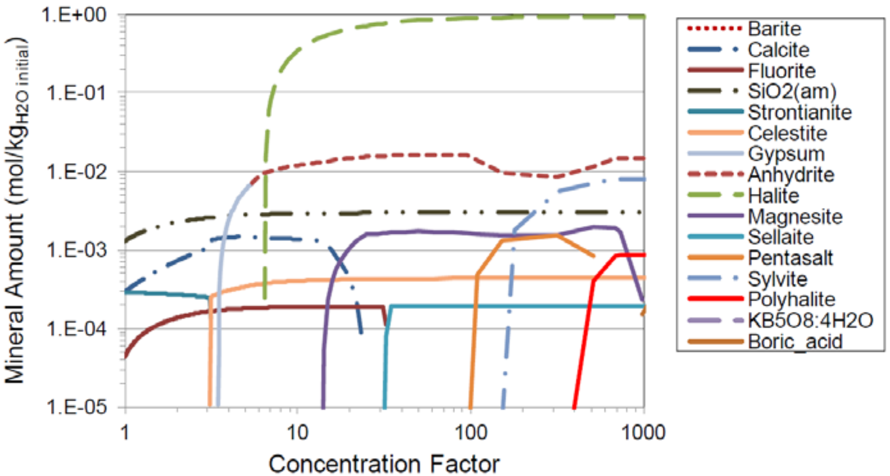
- Development of Membrane Gas Contactor
  - Resulted in a patent application and drafted paper
  - Applicable to all SPS applications
  - Takes draw solution generation from days to ~1 hour
- Pressure Driven Removal of Trace Amines
  - Generalizable to all thermally sensitive draw solutes
  - Resulted in a published paper
- Identification of thermodynamic limits of thermal removal of draw solution
  - Treatment relevant all thermolytic draw
  - Paper drafted
- Fully integrated SPS FO System
  - First of its kind
- Preliminary SPS FO Engineering Design Basis
  - Documented in a GRC Transactions paper
  - Essential to guiding where research should focus
- Fundamental Studies of Thermoresponsive IL-H_2O Solutions
- Preliminary energy and mass flow model of the geothermal fluid heat-driven FO-IL concept
  - Developed an empirically-derived function to estimate water flux as a function of brine and IL concentrations, and IL composition
- Resource Assessment
- Modeling of Geochemical Impacts
- Presentations
  - Professional meetings, Lab Day on the Hill, and The White House



Task 1.4 Milestone. Testing of integrated system with SPS and SPS process components.

Technical Accomplishments and Progress: Geochemical Resource and Impacts

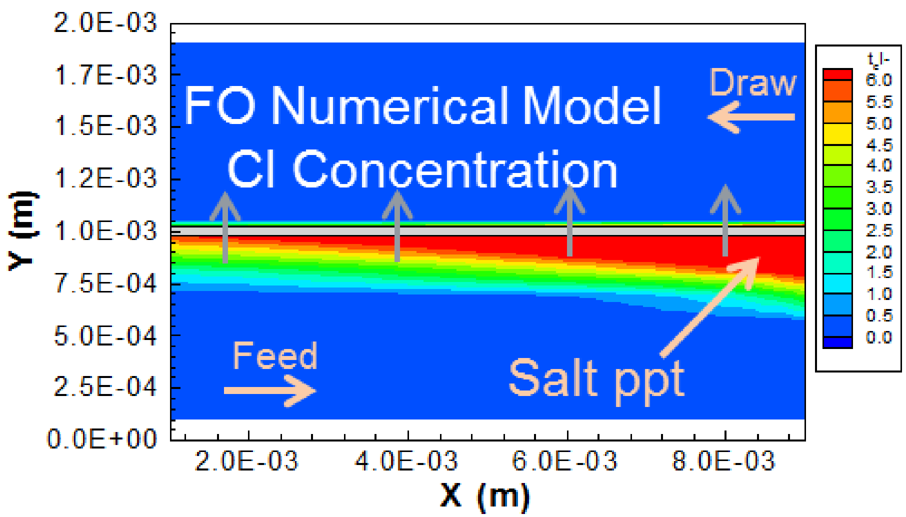
- Resource Assessment
  - Merging of various U.S. databases
  - Water quality, salinity, temperature, geol formation
  - GIS data integration (desal "favorability index")



TDS ~59,600 mg/L, low Ca (relative to HCO_3, SO_4)

Modeling of Geochemical Impacts

- Development of TOUGHREACT-Brine
- Scaling and deleterious chemical interactions (front- and back-end of desalination)
- Disposal of waste solutions



Technical Accomplishments and Progress: FO Processes

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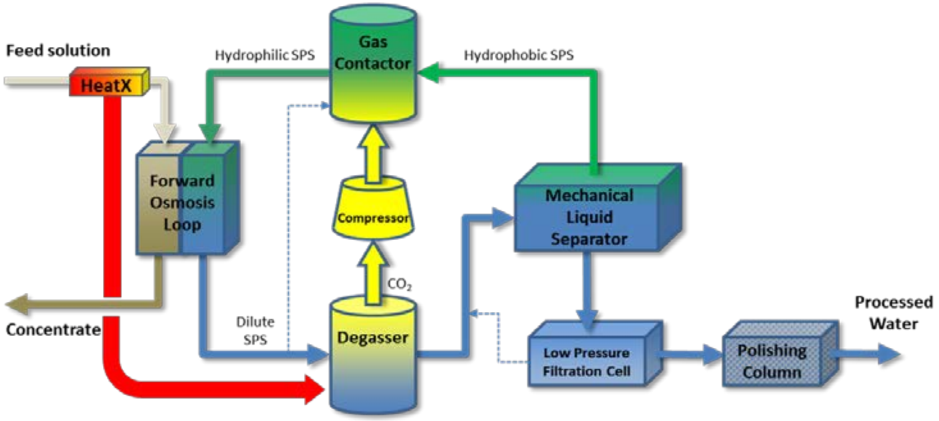
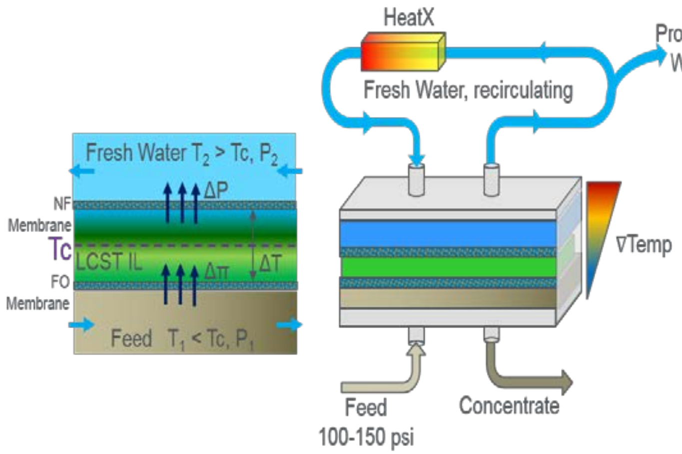
Switchable Polarity Solvent (Thermolytic Solute) Driven FO

- Intrinsically fouling resistant technology that can treat high salinity brines
- High water recovery possible using SPS FO (~90% demonstrated in lab testing of produced water samples)
- FO process thermal energy can be obtained from low-grade heat sources (process operates at T≤80°C)
- Heat input provided through sensible heat transfer (process steam not required)
- Low pressure operation in main process loop, moderate pressure polishing filtration operations
- SPS FO process is well-suited for produced water treatment applications



Thermoresponsive Ionic Liquid-H_2O LCST Driven FO

- Concentrated ionic liquid generates high osmotic P
- Waste heat driven liquid-liquid separation at higher T
- Separated aqueous phase requires reduced P-driven NF
- Novel design aimed at achieving forward osmosis and draw solute regeneration in a single step, and requiring minimal volume of ionic liquid



Technical Accomplishments and Progress: Fundamental Studies of IL-H_2O Solutions

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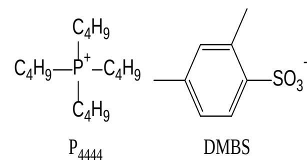
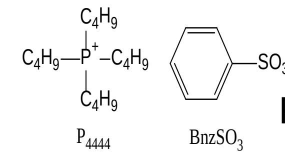
- Chemical modification on anion (Ar.-CH_3 → Ar.-H) results in fully miscible solution vs temperature, and different aggregation behavior
- Raman spectroscopy shows substantial changes in water hydrogen bonding network across phase diagram
- System studied with dynamic light scattering, ion aggregates grow in size leading up to Tc
- Results and temperature dependent NMR experiments are being integrated and drafted for publication.



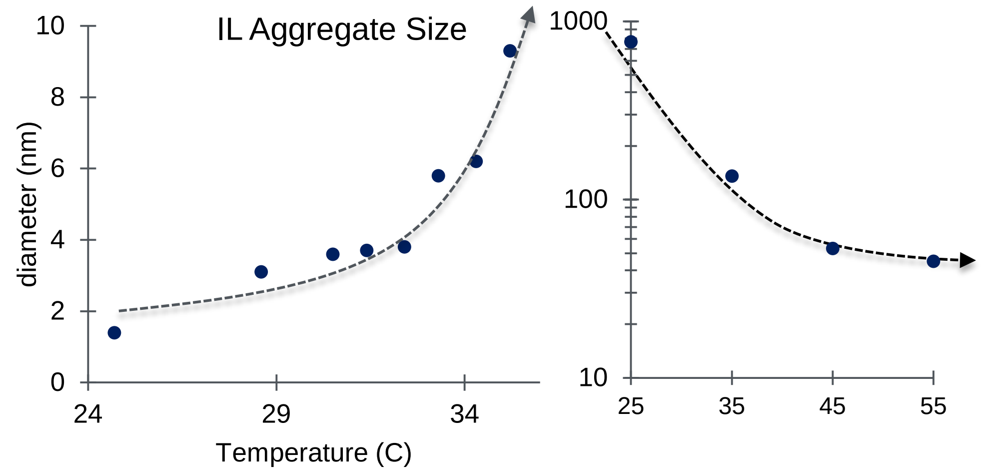
50wt.%

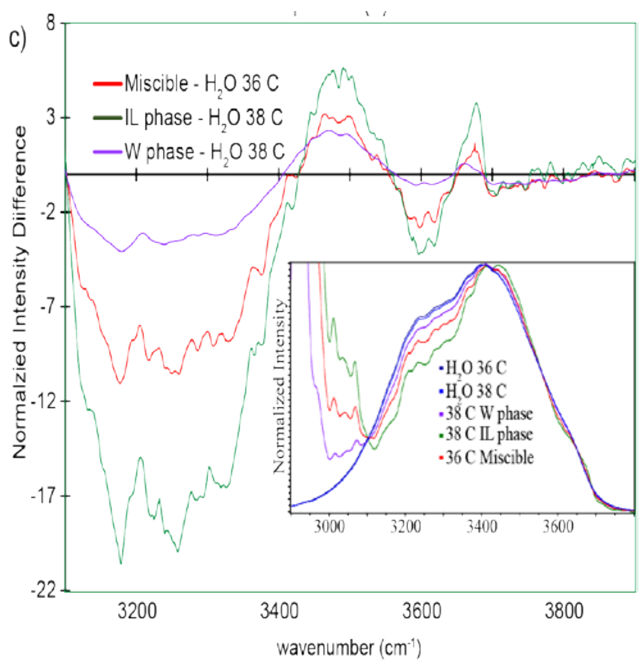
LCST ~ 36 C

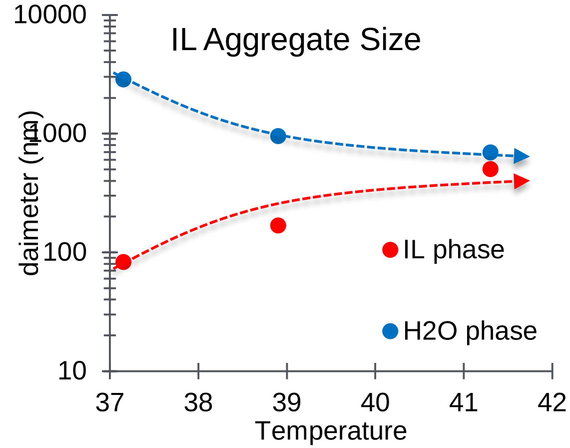


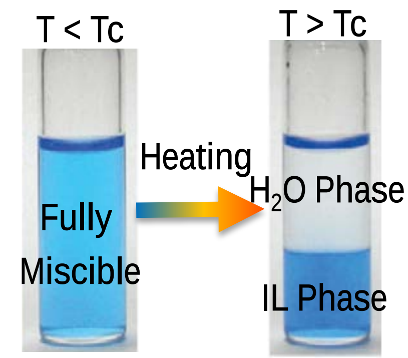
50wt.%

Fully Miscible









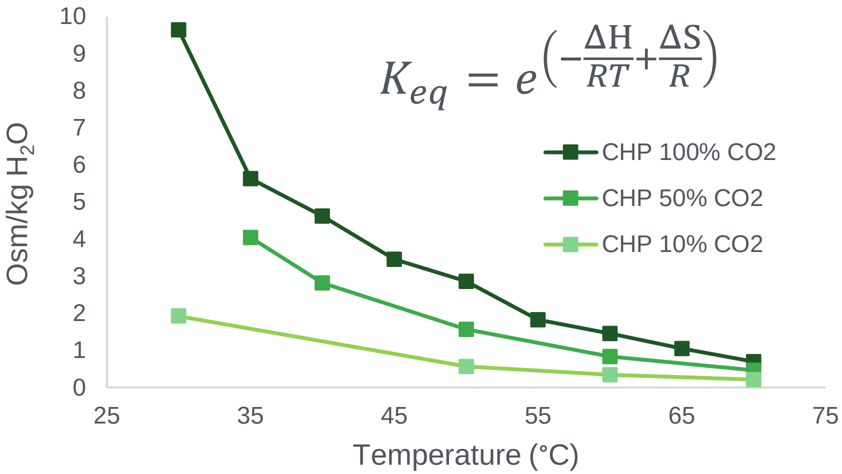
Recovery of CHP from diluted draw stream through application of heat to drive bicarbonate decomposition reaction

Determination of Thermodynamic Limit

- All “thermal” draw solutes (such as SPS and LCST IL) are expected to be governed by thermodynamics which are relatively low order (i.e. First order in CO_2 concentration).

$$-RTln\left(K_{eq}\right) = \Delta G = \Delta H - T\Delta S$$

$$K_{eq} = e^{\left(-\frac{\Delta H}{RT}+\frac{\Delta S}{R}\right)}$$



Work Conducted by Pedro M Da Silva and Julie A Nguyen through the Science Undergraduate Laboratory Internships (SULI) program

Optimization of the Process Kinetics

Improved the process
- Modest Vacuum (~4 psi)
- Regulation of Temperature (target 80°C)
- A well-designed conventional column is targeted

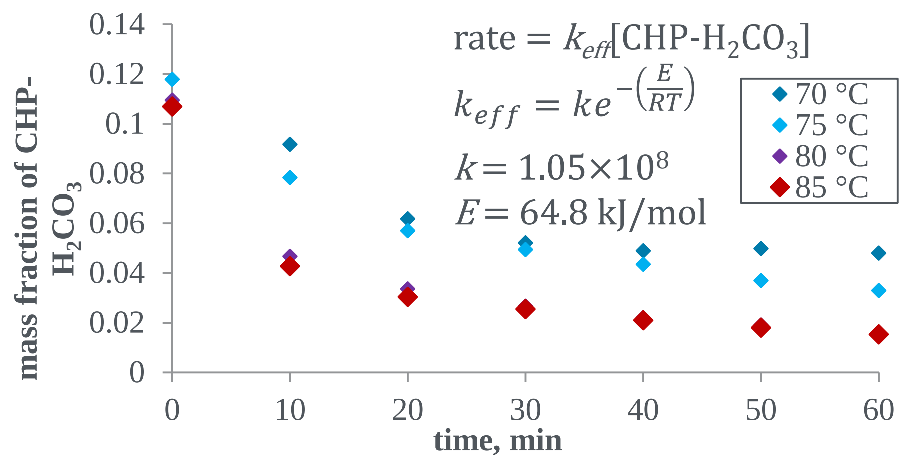
No improvement to process (based on studies so far)
- Packing Material
- Use of Spray nozzles
- Membrane Degasser

$$\text{rate} = k_{eff}[\text{CHP-}H_2CO_3]$$

$$k_{eff} = ke^{-\left(\frac{E}{RT}\right)}$$

$$k = 1.05\times10^{8}$$

$$E = 64.8\ \text{kJ/mol}$$



$$\underbrace{CHPH^{+}(aq) + HCO_3^{-}(aq)}_{\text{miscible}} \rightleftharpoons \underbrace{CHP(org) + CO_2(g) + H_2O}_{\text{immiscible}}$$

Technical Accomplishments and Progress: Gas Contactor

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Mixing and reaction of organic, aqueous, and CO_2 phases to form aqueous solution of 1-cyclohexylpiperdinium bicarbonate

$$\underbrace{CHP(org) + CO_2(g) + H_2O}_{\text{immiscible}} \rightleftharpoons \underbrace{CHPH^{+}(aq) + HCO_3^{-}(aq)}_{\text{miscible}}$$

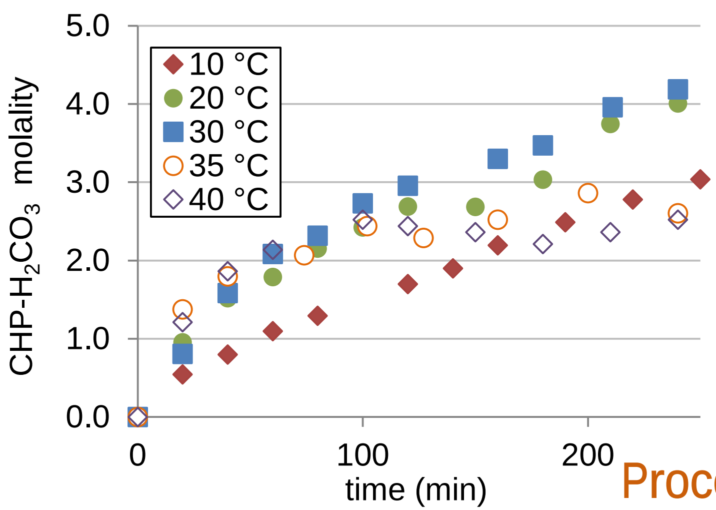
Optimization of the Process Kinetics

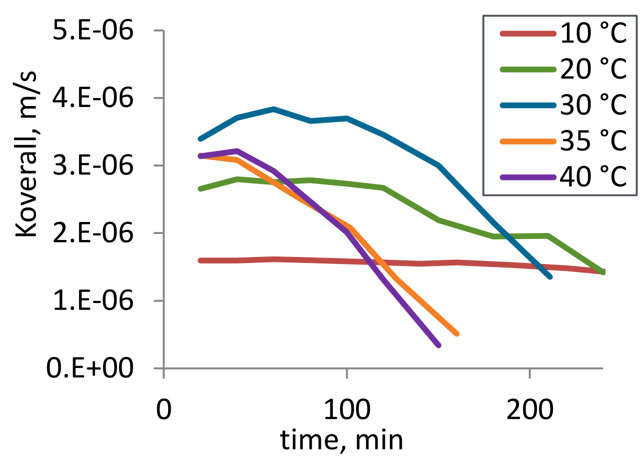
Factors which improved the process

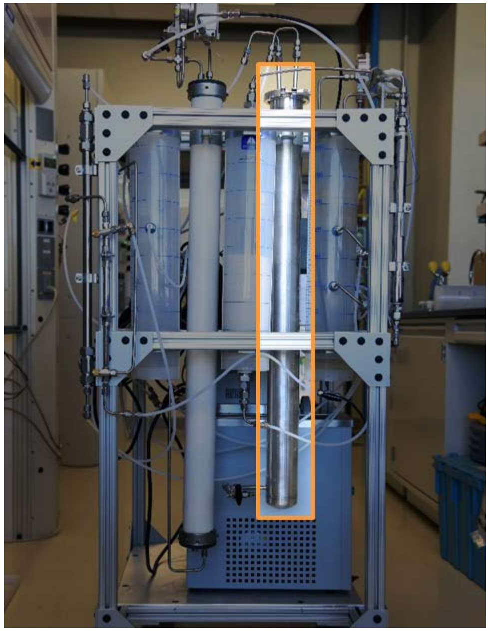
- Use of membrane gas contactors
- Regulation of Temperature (target ~30 °C)
- Fluid pressure
- Flow Rate
- Membrane surface area (too a point)

Challenges

- Determining limiting phenomenon; work is at the boarder of chemical reaction limited and mass transfer limited
  - Do we need more surface area or a catalyst?
- Formation of unreactive third phases







Process time reduced from days to ~1 hour and patent filed

Technical Accomplishments and Progress: Polishing Filtration

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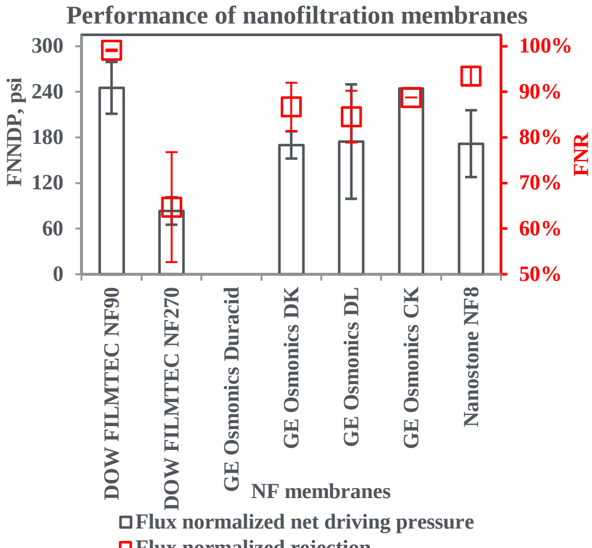
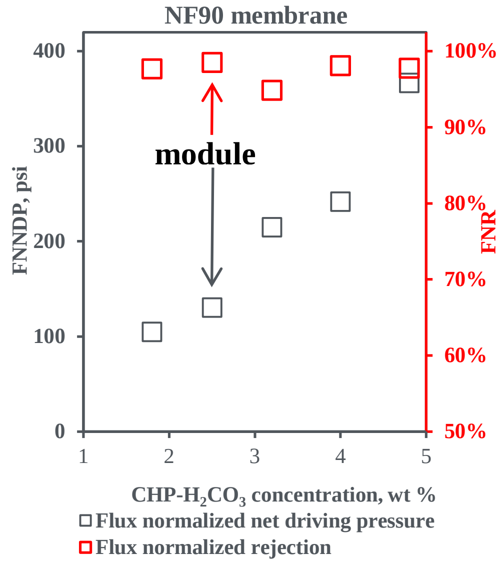
Removal of trace concentrations of CHP from product water stream (material that cannot be removed because of thermodynamic limitations)

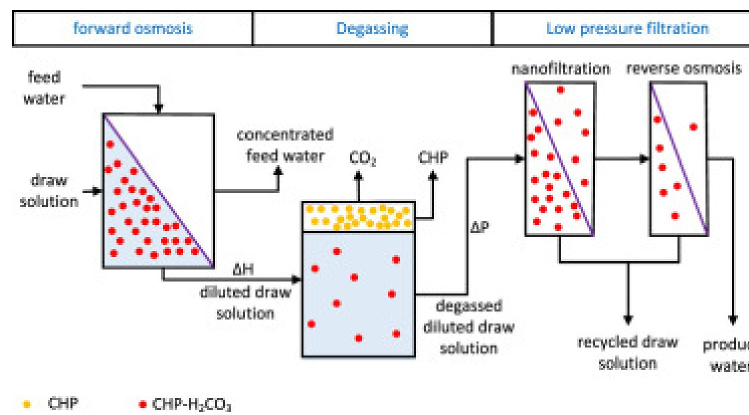
NF and RO membranes were screened for compatibility with tertiary amines

Low flux normalized net driving pressure and high flux normalized rejection were found for select membranes

A double staged system with DOW Filmtec NF90 and TW30 membranes is the proposed configuration







Process generalizable to all “thermal” draw solutes

Research published as:
B. Adhikari, M. G. Jones, C. J. Orme, D. S. Wendt, and A. D. Wilson, "Compatibility study of nanofiltration and reverse osmosis membranes with 1-cyclohexylpiperidenium bicarbonate solutions," *Journal of Membrane Science*, vol. 527, pp. 228-235, 2017.
http://dx.doi.org/10.1016/j.memsci.2016.12.017

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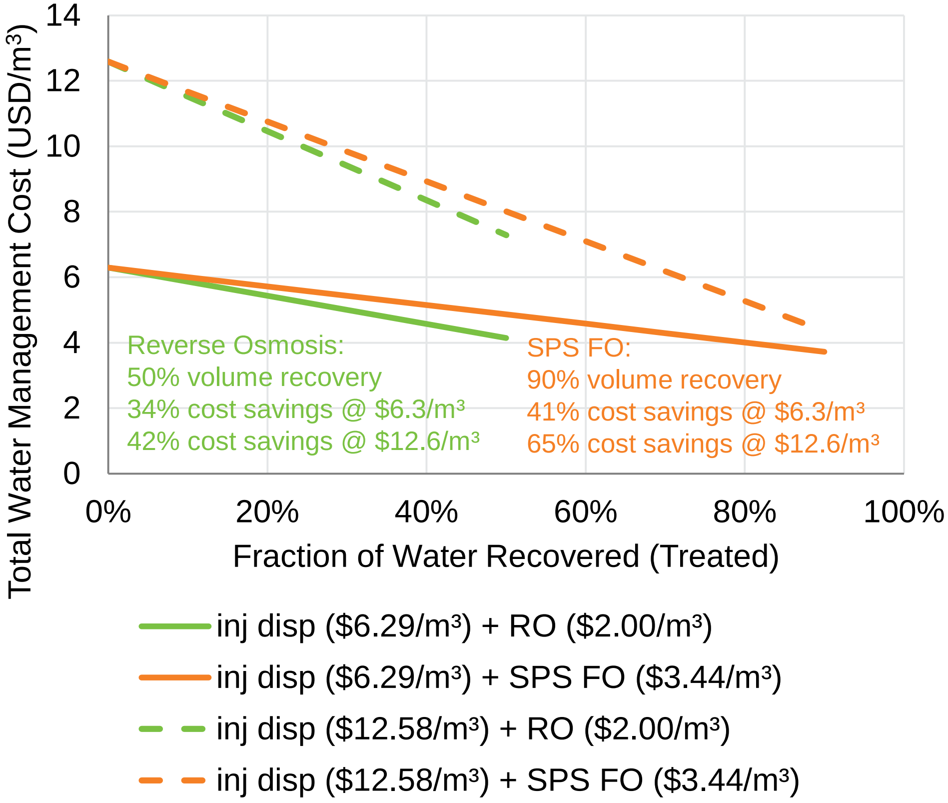
Economic Drive: Aqueous waste minimization

- Waste volume reduction usually ~1,000 more valuable per volume than the value of increasing water supply.
  - Potential for treatment of produced water in lieu of injection
- SPS FO process enables high water recovery, which is a key driver for reducing produced water management costs (treatment & disposal)
- SPS FO treatment results in lower total water management costs (treatment + disposal) than use of RO treatment or injection disposal



- **Task 1.5 & Task 5 Milestone** (1.5) Develop rigorous physical models for predicting process conditions (T, P, composition) of primary process components. Models will utilize previously collected chemical property and kinetic data to determine rates of heat and mass transfer and chemical reaction. & (5) Revise economic model of SPS-FO system.
- Multiple proceeding, presentations, and a publication.

Key Accomplishments and Milestones (INL Only)

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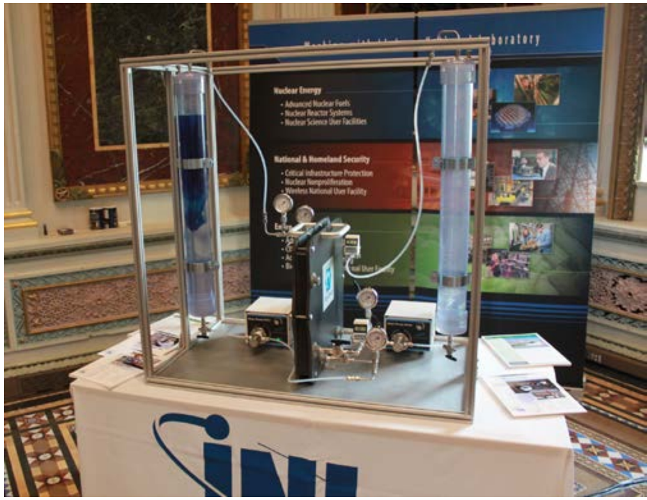
Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Task 1.2 Collect chemical property and kinetic experimental data necessary to complete rigorous process design.	Kinetic data collected during FY16 Q1. Draft manuscript documenting approach and results prepared for future journal submission.	12/31/2015
Task 1.1/1.3 Select system compatible components (polyolefin membranes, fluorinated membranes, metallic membranes, ceramic membranes, module materials, seals, resins, and gaskets.)	Materials compatibility testing performed during FY16 Q1. Chart documenting testing results submitted as Appendix B in milestone report submitted to GTO 12/30/2015.	12/31/2015
Task 2.1 Discuss efforts with oil & gas / geothermal co-produced site providers to test pilot to be built in FY2017.	Discussions have been initiated with multiple oil and gas production operators. Follow up discussions will continue to explore opportunities.	12/31/2015
Task 1.5 Develop models to scale components for various process conditions to identify equipment requirements (e.g. interface area, flow rates, residence time, system volume, temperatures, pressures, and chemical reaction rates)	Models of major process components have been developed in Aspen Plus as well as MS Excel with input informed by experimental data. Models allow computation of major equipment specifications including interface areas, flow rates, and residence times.	3/31/2016
SMART Milestone (Task 1.3/1.5): Select equipment configurations/materials for FO membrane element, gas contactor, osmotic filtration, and stationary phase organic-trace removal material. Osmotic filtration process to be capable of rejecting >98wt% from 1-4 wt% SPS solution at 20 bar or less of hydraulic driving force.	Designated equipment configurations successfully selected. Two-stage NF/RO osmotic filtration process selected capable of >99wt% rejection from 1.5 wt% SPS with 12 bar of hydraulic driving force.	3/31/2016
Task 2.1 Select an oil & gas / geothermal co-produced fluids partner. Draft agreement for pilot testing partnership.	Project personnel have participated in meetings with external collaborators to discuss produced water treatment using SPS FO technology. Feedback has been obtained regarding technical approaches for testing, candidate regional oil & gas production areas with well-suited characteristics for testing, and INL's direct contacts are communicating with industry to identify potentially interested parties.	6/30/2016
SMART Milestone (Task 1.3/1.5): Select equipment configurations/materials for degasser and oil-water separator. Degassing process to be capable of reducing the SPS solution to less than 1.5 wt% with less than 1 hr of residence time at a temperature 80°C or less and pressure greater than 0.25 bar.	Degasser vessel with internal spray nozzles and vertical decanter vessel selected. Integrated degasser/decanter process has demonstrated concentration reduction of SPS solution to ~1.5 wt% in less than 1 hr of residence time at a temperature of 80°C and a pressure of 0.75 bar.	6/30/2016
Task 1.5 Develop rigorous physical models for predicting process conditions (T, P, composition) of primary process components. Models will utilize previously collected chemical property and kinetic data to determine rates of heat and mass transfer and chemical reaction.	Process models have been developed that incorporate experimental data-based models of physical properties, reaction kinetics, reaction enthalpies, and mass transfer coefficients, as applicable. These models have been included in revised versions of the Aspen Plus and Excel models used for evaluating process performance, and have been used to develop a preliminary process design and cost estimate as documented in the Wendt, et al GRC 2016 Annual Meeting paper submission.	6/30/2016
Task 1.4 Testing of integrated system with SPS and SPS process components.	Thermal process components successfully integrated with Porifera FO Unit. Initial testing performed in FY2016 Q4. Additional details provided in Integrated Unit slides.	9/30/2016
Task 2.3 Complete design of SPS-FO prototype system.	Process and economic models revised as part of techno-economic analysis performed for GRC 2016 Annual Meeting. Preliminary SPS-FO process design for an industrial-scale process documented in the Wendt, et al GRC 2016 Annual Meeting paper.	9/30/2016
Task 5 Revise economic model of SPS-FO system.	Process and economic models revised as part of techno-economic analysis performed for GRC 2016 Annual Meeting. Current estimate of SPS-FO water treatment costs for an industrial-scale process documented in the Wendt, et al GRC 2016 Annual Meeting paper.	9/30/2016
Task 1.1: Complete membrane unit and column degasser component optimization testing.	Advanced component testing of membrane unit degasser and column degasser completed. Summary of degasser testing provided in Accomplishments slide.	12/31/2016
Task 1.2: Begin integrated lab-scale testing	Integrated lab-scale test unit fabrication and assembly completed. Initial integrated lab-scale tests have been performed. Some technical issues encountered, but issues have been addressed and integrated unit is ready for testing to be performed in subsequent quarters.	12/31/2016
Go/No-Go Milestone: Proceed if current experimental data and techno-economic analysis supporting an estimated cost of <$3.5/m³ to produce purified water from a 30,000 ppm TDS or 1 Osm/kg solution for a 500 m³/day system.	Milestone successfully met and "Go-Forward" decision reached. **Post milestone direction to perform lab-based R&D to optimize the components in preparation for scale-up rather than proceed with the demonstration scale-up of the SPS-FO process.**	1/31/2017
Task 1.2: Complete integrated lab-scale testing using optimized degasser. Report degasser configuration and performance specifications.	Optimized degasser configuration has been identified and integrated lab-scale tests using selected configuration have been performed. See accompanying slides for configuration and performance specifications.	3/31/2017
Task 1.3: Obtain produced water samples from a candidate test site. Volume of samples must be sufficient to complete testing with SPS FO integrated system.	Produced water samples from Marcellus Shale Formation and samples from various Wyoming sites have been located and transfer/transport to INL is in process.	3/31/2017
Task 1.3: Complete integrated lab-scale testing with produced water sample feed stream.	As directed by GTO, FY17 project efforts have been redirected to focus on further laboratory-based research and development. Therefore integrated lab-scale testing has been rescheduled to follow gas contactor component testing being performed in Q3 and Q4 of FY17.	6/30/2017
Task 2.1: Finalize produced water testing site selection and initiate procedure for documenting scope and terms of collaborative agreement with oil & gas partner.	As directed by GTO, FY17 project efforts have been redirected to focus on further laboratory-based research and development. Research activities have therefore been redirected to investigate fundamental R&D questions related to the SPS-FO process components, with the goals of further refining equipment configurations, de-risking process operations, and quantifying process component performance.	6/30/2017

Research Collaboration and Technology Transfer

- Industry Engagement:
  - FO membrane manufacturer Porifera has been actively engaged in FO membrane R&D. Porifera supplied this project with the FO system upon which the integrated lab-scale SPS FO process has been built.
  - Discussions with Chevron.



- Current opportunities and efforts to transition technology to the private sector.
  - Outreach activities to oil & gas producers suspended following GTO guidance to forego the field demonstration in favor of further lab research and development
  - Dissemination of research results: 3 publications, 2 proceedings, 7 conference presentations, 1 patent application
- Complimentary projects.
  - FY18 Technology Commercialization Fund (TCF) project investigating integration of SPS FO process with oil & gas production operations (thermal and wastewater treatment),
  - SBIR I,II, and IIB Projects,
  - and FE Project

Future Directions (Primarily INL)

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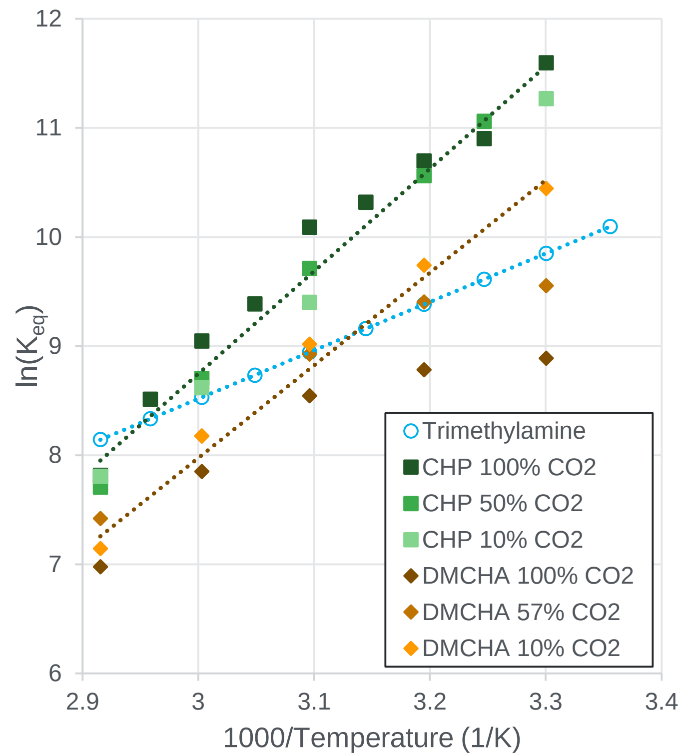
INL Go/No-Go Milestone review result stated "FY18 directed to conduct fundamental applied research to advance the underlying aspect of the technology in preparation for field demonstration"

- Prepare the component process of the SPS-FO system to be scaled up for future field demonstration
  - Process intensification (configuration, equipment, and operating conditions) and optimization
  - Lab scale process integration, instrumentation, and controls
- FY18 project funds limited to carryover; Obtaining future funding for prototype scale testing would allow numerous fundamental research questions to be answered
  - Microfluidic studies to determine the mass transfer and chemical reaction process associate with gas contacting and degassing.
  - Develop a multidimensional (conductivity, torpidity, spectroscopic, and others) method of monitoring SPS concentration.
  - SPS specific membrane studies and advanced membrane studies for FO module , gas contactor, and degassing.
  - Field testing at a scale necessary in advance of larger scale demonstration and/or deployment
- Three manuscripts need to be completed and submitted for publication.
  - Spectroscopic analysis of IL LCST behavior
  - Thermodynamics of thermal draw solutes (van't Hoff plot to right)
  - Generation of tertiary ammonium bicarbonate with membrane gas contacting



Summary Slide

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- SPS-FO and IL-FO water treatment process components have been successfully tested
- SPS-FO water treatment of oil & gas produced water samples has been performed using the lab-scale integrated process

- The results are generalizable to many FO processes
- Economic analysis based on experimental data indicates economic potential for industrial wastewater treatment
  - High recovery, fouling resistance, low process operating temperatures make process well-suited for O&G wastewater treatment
  - Water treatment to reduce wastewater disposal volumes can decrease water management costs, decrease environmental risks (earthquakes, spills), and provide water for beneficial use.

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