Low-Energy Water Recovery from Subsurface Brines

DOE Award No. DE-FE0024074

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Crosscutting Research & Rare Earth Elements Portfolio Review
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Project Overview & Objectives

- **DOE Award No. DE-FE0024074**
- **Total project value**: 937,500$
  - DOE Share: 750,000$ (80%)
  - Cost Share: 187,500$ (20%)
- **Period of Performance**:

  Sep. 2015 to Feb. 2017 (18mos.)
- **Project Team**:
  - RTI International (Prime recipient)
  - Tampa Electric Company (TECO)

- **Project Objectives**:
  - Develop of a low-cost, low-energy treatment process using a non-aqueous solvent (NAS) extraction to recover water from deep aquifer brine
    1) Identify candidate solvents that can absorb water in one condition and release in another condition
    2) Test different solvents and/or mixture of solvents for optimum water uptake and release to maximize water recovery from 180,000 ppm TDS brine
    3) Develop optimum conditions to maximize the kinetics of the process
    4) Test water quality and if necessary, develop downstream process to satisfy potable water standard
    5) Develop strategies to optimize the overall process and perform techno-economic assessment for scale up

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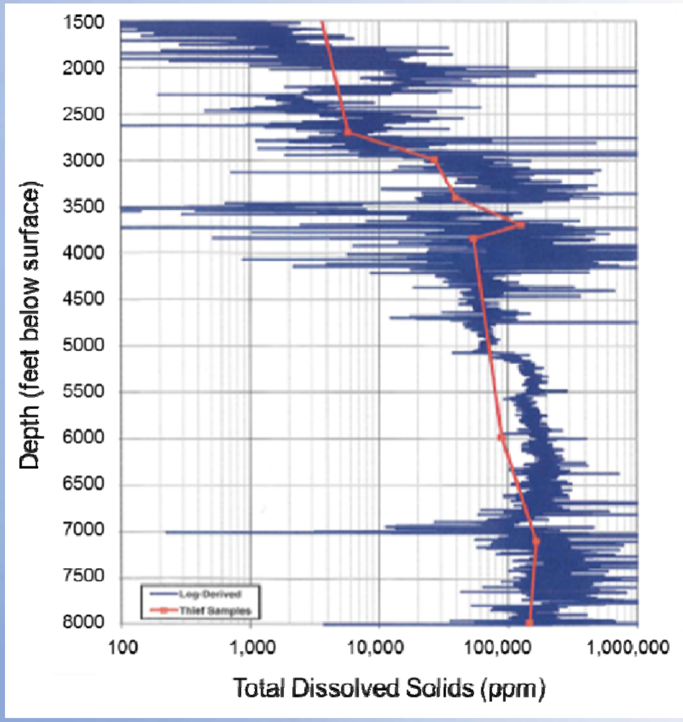
Project Background – Deep-well CO_2 Injection

- Deep-well CO2 injection can create pressure build-up in the subsurface aquifer. A portion of ground water should be extracted to relieve the pressure.
- The ground water (brine) may contain very high total dissolved solids (TDS) concentration, in the range of 180,000 ppm
- These dissolved contaminants that make up TDS are generally some of the most difficult constituents to remove.
- The values for TDS with increasing depth from a well water sample are shown in the figure
- Because TDS removal remains an issue across the industry, The impact of developing a technology to treat these wastewaters would extend beyond power plant and fossil fuel-based industries



Subsurface plot showing the increasing TDS concentration in water with depth at TECO CO_2 site

Existing Water Management Practices and Treatment Technologies

Current Water Management Practices

- Approximately 2 billion tons of CO2 are emitted annually from power plants in the U.S.
- 3.2 billion m^3/yr (~2,300 MGD) gallons of brine will be produced to store this amount of CO_2 in injection wells.
- In unconventional resource extraction, most high concentration brines generated in the U.S. are currently disposed of in Class II deep injection disposal wells, which often require a long distance transportation (>100 miles)
- Existing technologies provide limited disposal and treatment options for high-TDS waters.
- Therefore, there is a significant need to develop a low-cost, reliable approach to enable treatment for reuse of these high-TDS wastewaters.

Existing Treatment Technologies

- Reverse osmosis (RO), which uses hydraulic pressure to force pure water through a semi-permeable membrane when the TDS is lower than 60,000 mg/L
- Chemical precipitation methods such as lime softening or ettringite precipitation will remove a large portion of divalent salts.
- Thermal processes (evaporation and crystallization) can potentially treat such high-TDS water with appropriate pretreatment and achieve the goal of producing potable water.

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Solvent-Based Water Extraction

- Solvent-based extraction can potentially provide a moderate temperature (low energy), membrane-free approach to treat high TDS brines
- The solvent-based water extraction system would eliminate or reduce many of the operational challenges that current technologies face during high TDS water treatment, since a water/solvent system would be simpler to operate, provide greater reliability, and reduce equipment costs.
- Reducing the energy requirement to absorb/release water in each cycle is necessary to move this technology toward the commercial scale.

Solvent Formulation	Rich Loading[1]	Lean Loading[2]	Heat of Reaction[3]	Specific Heat Capacity[4]	Density[5]	Rich Water Content[6]	Lean Water Content[6]
3-FPEA/OFP	0.36	0.08	67	1.49	1.38	8.5	2.25
2-FPEA/OFP	0.35	0.06	64.2	1.28	1.38	8.8	1.8
3-FNMBA/NFHp	0.41	0.09	68.7	1.42	1.28	6.8	2.7
4-FNMBA/NFHp	0.4	0.09	71.7	1.44	1.28	10.2	4.25

[1]moles CO_2/mole amine @ 30C, [2]moles CO_2/mole amine @80C, [3]kJ/mole CO_2 @ 80C, [4]J/kG*C, [5]g/mL, [6]wt%

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Project Vision

CO2 Solvent System Advantages:

- Low capital cost:

  Low material cost: the system does not require high pressures or temperatures

  Simple structure: the process occurs in contacting vessels, not in reaction piping line or tower

  Therefore, the capital cost of a prospective full-scale system will be low

- Low operating cost:

  A simple pressure equilibrium changes can be used to trigger water uptake/release (the water-bonding mechanism is hydrogen bonding of water to the carbamate formed with CO_2).

  The fully developed will use minimal to no thermal energy for water removal.

  The water will require little to no pre-treatment before treatment.

- High quality effluent:

  The process will also yield high-quality product water because the water absorption is based on hydrogen bonding of water molecules to the (carbonated and thus) protonated end of the NAS.

- Easy to scale-up:

  Because this method is based on mixing two phases and is conducted in a large vessel, there will be no issue with scale-up

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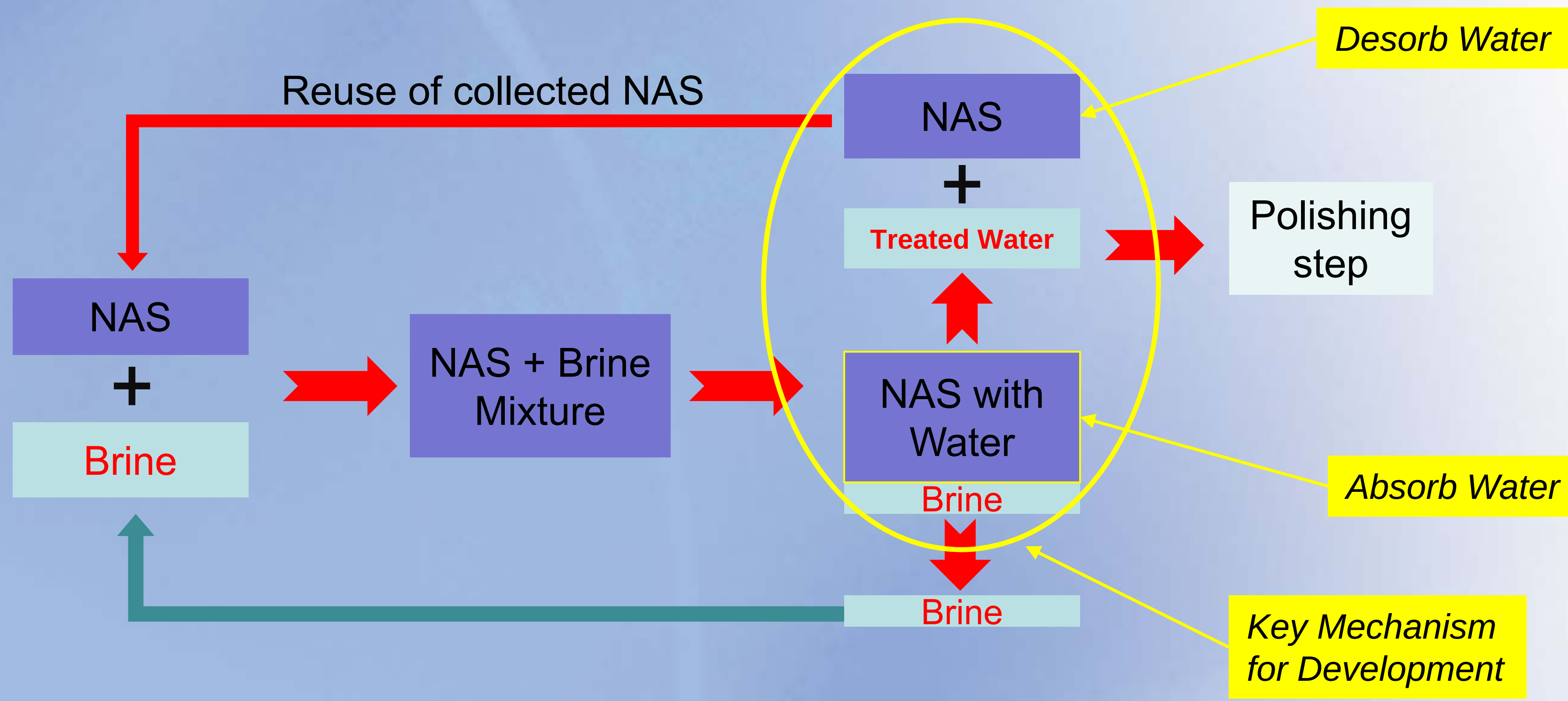
Solvent Extraction vs. Conventional Technologies

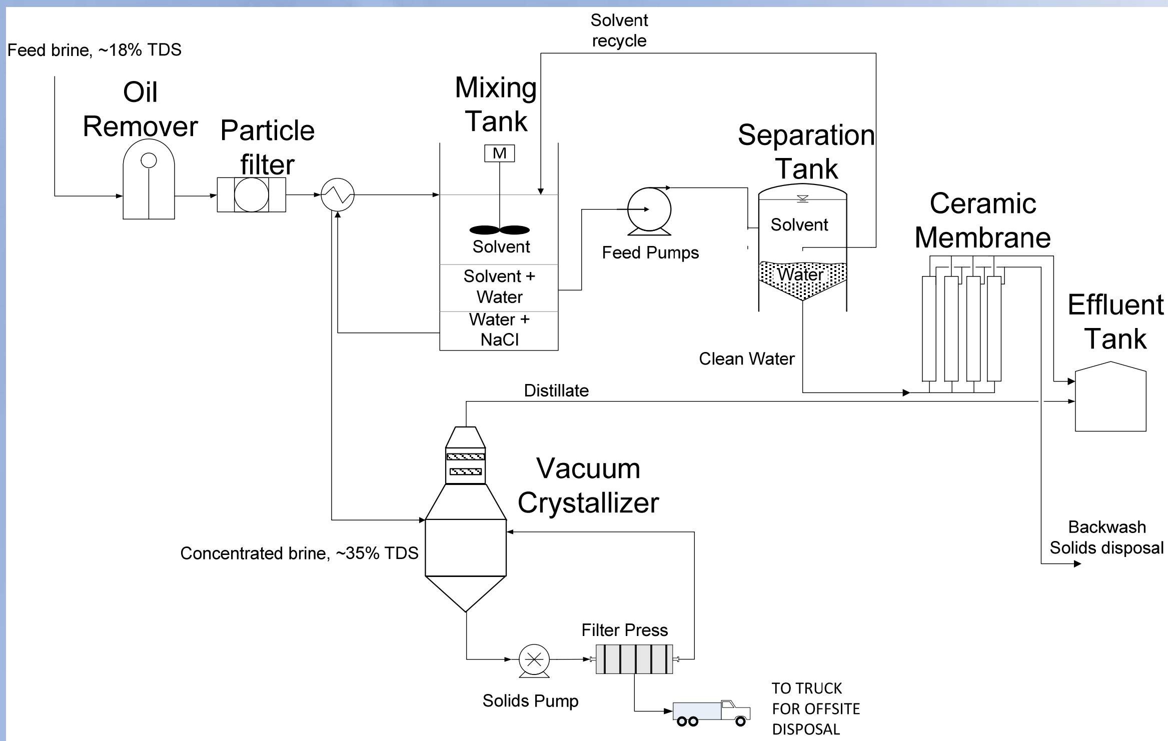
Characteristic	Ion Exchange	Reverse Osmosis	Electrodialysis Reversal	Evaporation/ Crystallization	Water/Solvent Extraction
Energy cost	Low	Moderate	High	High	Low/moderate
Electricity usage vs. TDS	Low	Increase	High increase	Increase	Low
Plant/unit size	Modular	Modular	Modular	Large	Variable
Pretreatment requirement	Filtration	Extensive	Filtration	Chemical/pH	Minimal
Capital expenditure	Low	Medium	Medium	Very high	Low
Suitable for 180,000 mg/L TDS wastewater?	No	No	No	Yes	Yes

- No new technologies have been developed on the commercial scale within the last few decades to handle such high-TDS wastewater
- The increase in these waters generated from CO2 capture and extraction of fossil energy in the U.S. calls for development of a novel solution that requires low energy and low capital cost.

NAS Desalination Technology Process Flow



Prospective Process Scheme

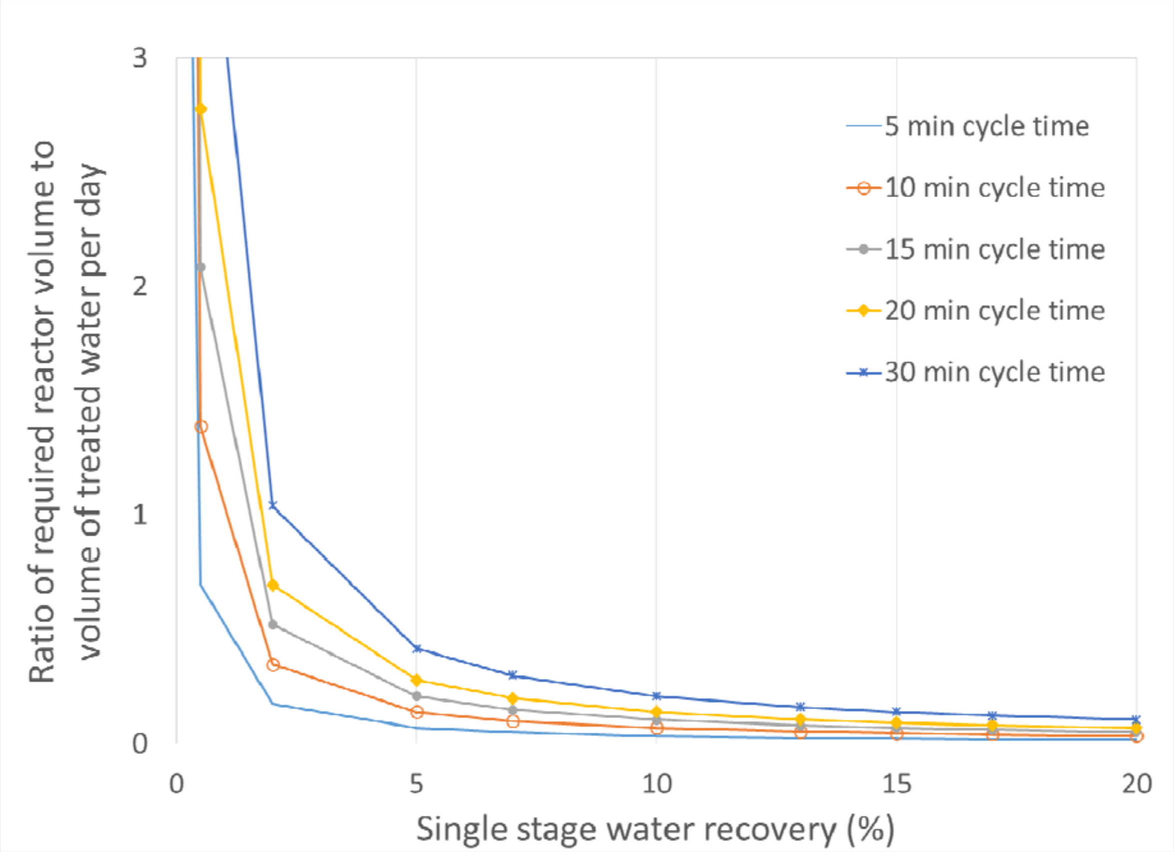


Developed technology can be utilized for ZLD process for high TDS wastewater

Ideal Solvent Properties

- Environmentally safe:
  - In case there is any spill or human contact, the NAS should be reasonably safe.
- **(T1)** High water recovery:
  - NAS with the highest water uptake and complete discharge will be the ideal solvent.
- **(T2)** High salt rejection:
  - NAS with high salt rejection is necessary to significantly reduce TDS.
- **(T3)** Low residual solvent transfer to water phase after separation
  - Necessary for minimal post treatment polishing of final treated effluent.
- Small energy swing required for solubility variation:
  - The energy input required to swing between water absorption/desorption needs to be minimal
- Low vapor pressure (low volatility):
  - To minimize the replacement rate of the NAS and prevent atmospheric release of organics.
- Low degradation rate (low maintenance):
  - Chemicals with low replacement rate under repeated absorption-desorption will be studied and selected by minimizing degradation by temperature, chemical conditions, sunlight, or biological attack.

Solvent Properties and Impact on Process Performance



- Water yield is the ratio of purified water to unit weight of the solvent used in a single extraction step and is an important measure of the effectiveness of the water/solvent system
- The combination of the water yield and the time required to perform and complete the extraction step will determine the number of cycles that can be completed in a given time period and will affect the overall system design

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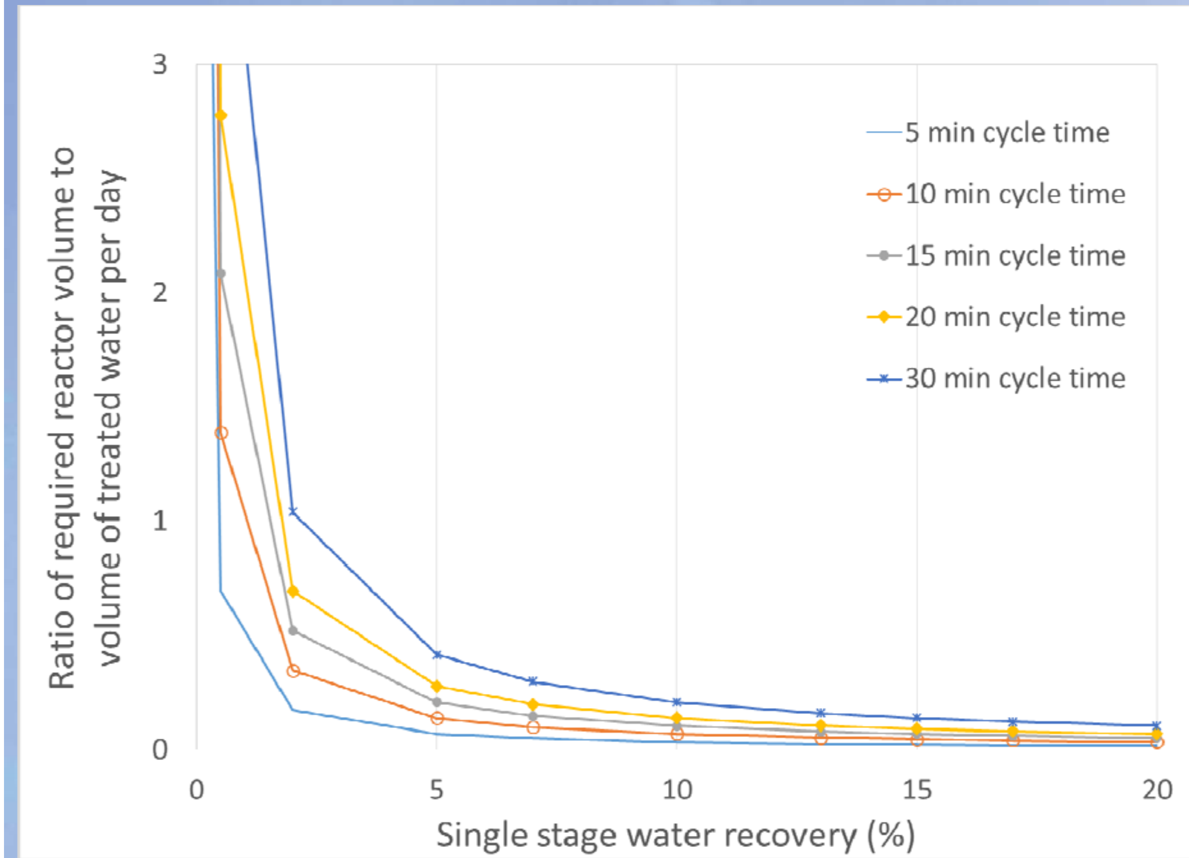
Solvent Properties and Impact on Process Performance



- Water yields <2% will require that the tank volume be sized by more than a factor of 1.5 of the total volume to be treated
  - *For example, if a site requires treating 1 million gallons of brine each day, even a solvent that extracts and releases water within 10 min would require a reactor volume of ~1.5 million gallons*
- There is a clear point of diminishing returns, where increasing the water yield and/or reactor volume provides minimal improvements in process size

Test Solvent Groups by Water Adsorption/Desorption Mechanisms

1. CO_2-Switchable Solvents
   - Purging of solvent with CO_2 for 30 min at 40 ^oC
   - Mixing of CO_2-laden solvent with aqueous NaCl solution (0.5 M or 3 M) (25 – 40 ^oC)
   - Equilibration of CO_2-laden solvent/salt solution mixture to allow absorption of water from the salt solution into the solvent
   - Purging of the water-bearing solvent with N_2 (80 ^oC) to desorb CO_2 and separate product water from the solvent phase
2. High-Temperature Water-Absorbing Solvents
   - Absorbs water at a higher temperature (e.g., 80 ^oC) and releases (desorbs) water at a lower temperature (e.g., 20 ^oC or 40 ^oC) with our without CO_2
3. Low-Temperature Water-Absorbing Solvents
   - Absorbs water at a lower temperature (e.g., 20-25 ^oC) and releases water at a higher temperature (e.g., 80 ^oC)

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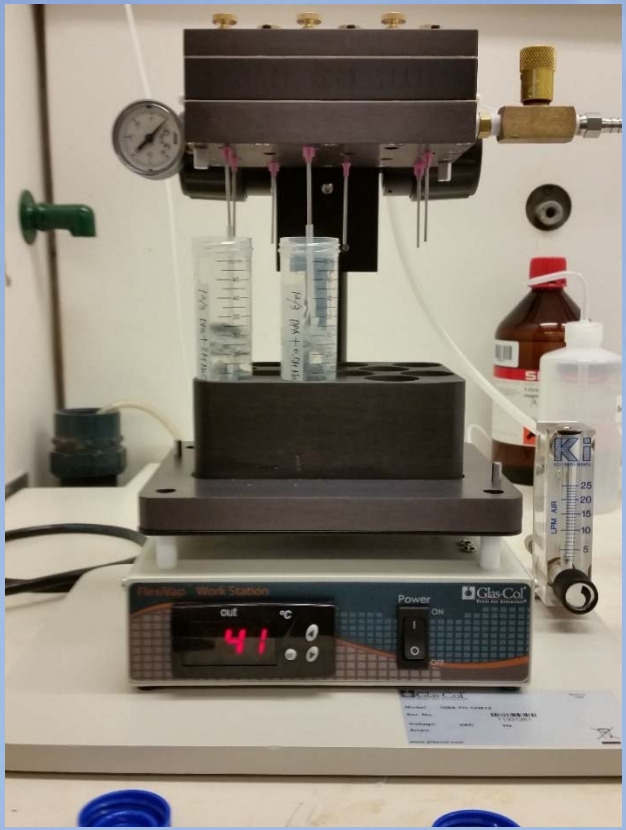
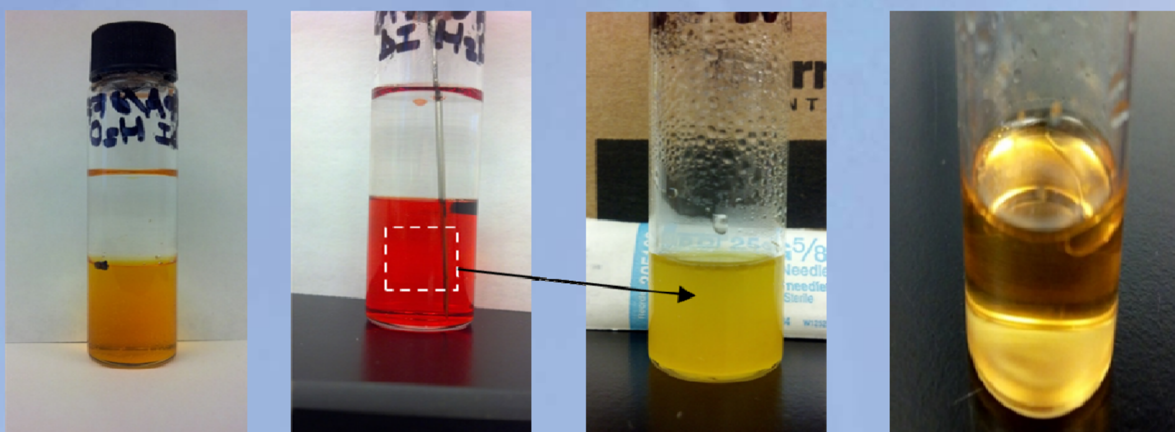
Multi port gas purging/heating test kit



- Multi gas purging center
- Heating block can control the temperature of each solvent
- CO_2 purging for switchable solvent test
- N_2 purging to remove CO_2 in the solvent
- Other gas purging/heating process

Solvent-Based Water Extraction



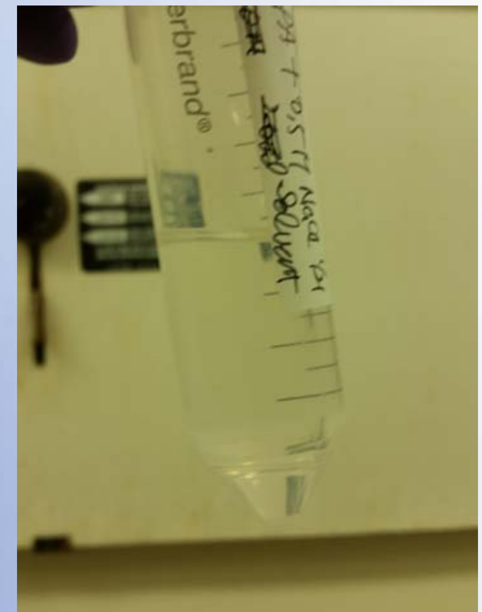
Water + Solvent

After CO_2 purge

CO_2 removal

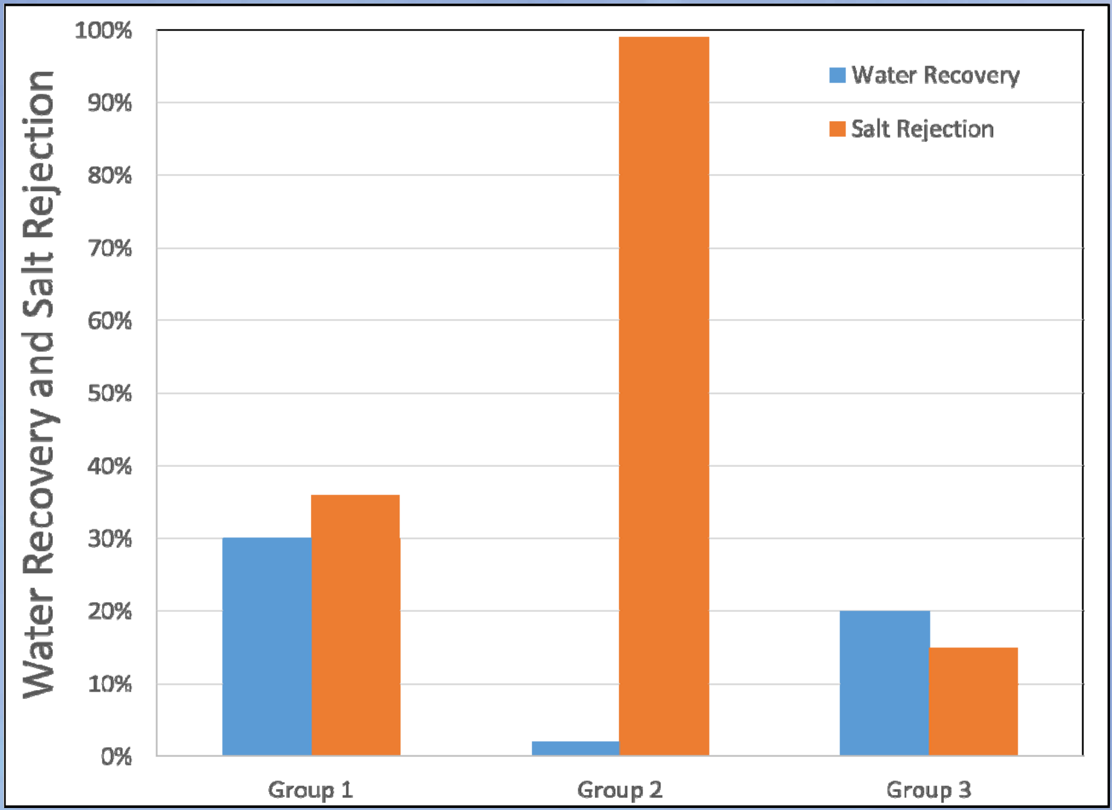
Water layer formed

CO2 trigger



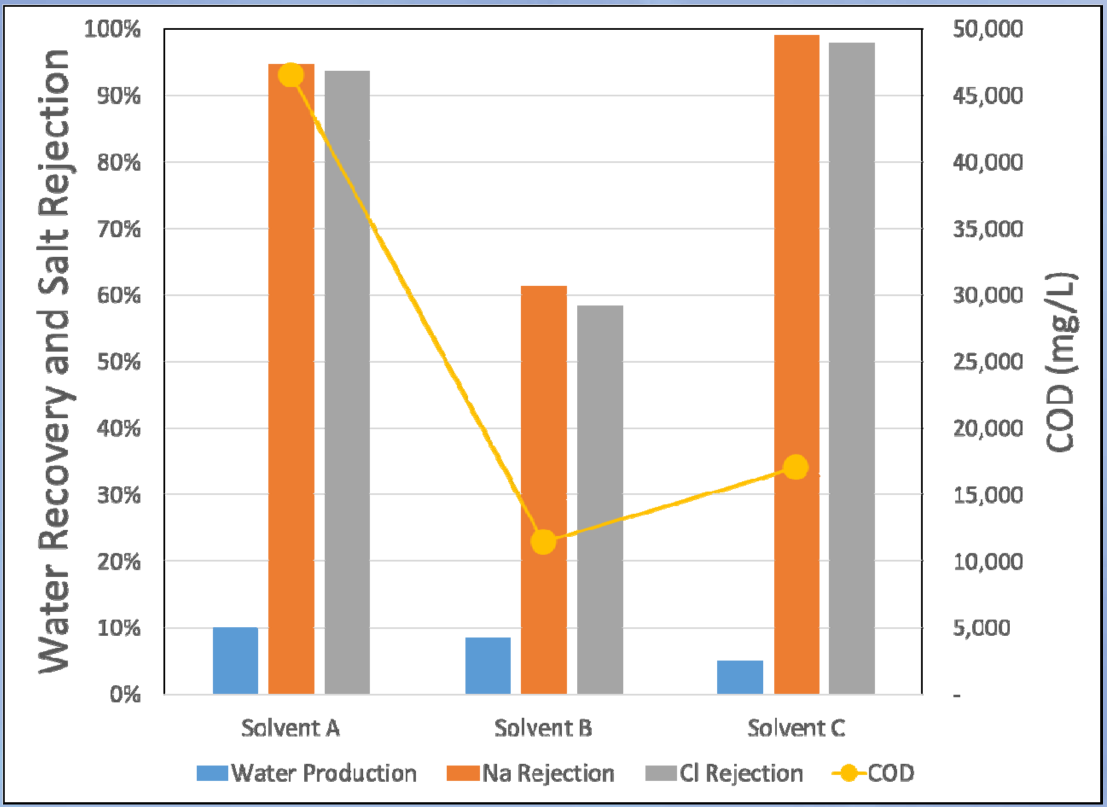
Temperature trigger

Water recovery and Salt rejection of each Group (preliminary)



- Group 2 solvents showed highest salt rejection (99%) but poor water recovery (2%)
- Group 1 solvents showed highest water recovery (30%) and poor salt removal performance (36%)

Group 3 solvent performance



- Some solvents from Group 3 showed high salt rejection (more than 90%) and decent water production (5 – 10 %)
- High salt rejection solvent (Solvent C) showed poor water recovery
- Solvent A showed high water recovery and high salt rejection but COD was high

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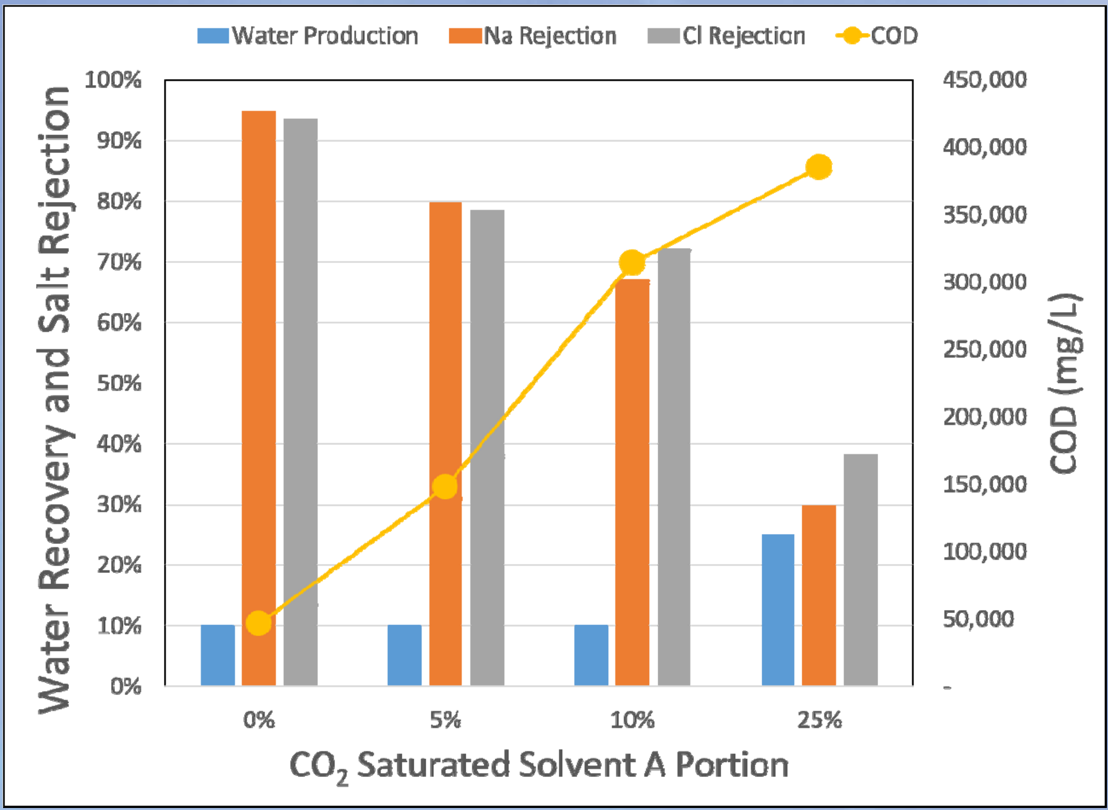
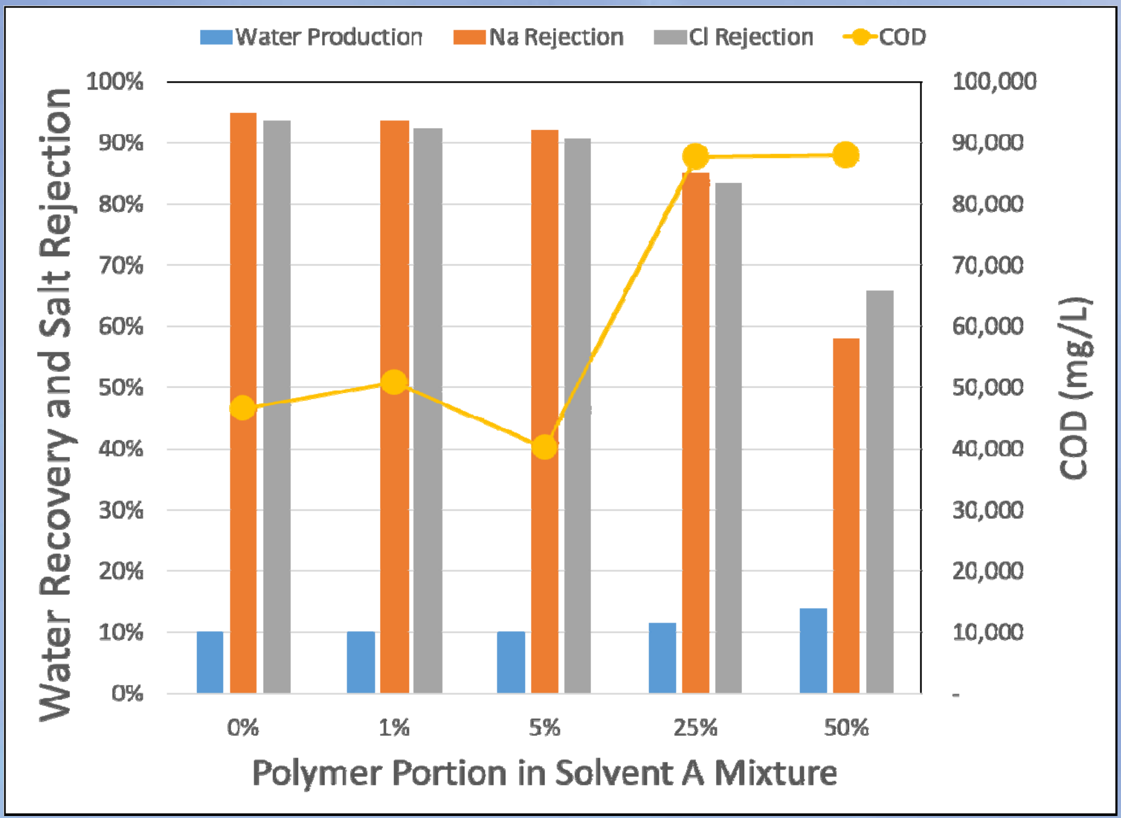
Adding CO_2 to improve water recovery



- CO_2 saturated *solvent A* was added to the raw *solvent A* to increase water recovery
- CO_2 increased water recovery and water quality was more deteriorated (high salt and COD concentration in the produced water)

Adding polymer to improve water recovery



- Polymer was added to the *solvent A* to improve water recovery
- Polymer adding could reduce COD in the treated water but salt rejection lowered

Summary of Results

- Three mechanisms were developed for NAS desalination process
- Water recovery of a solvent can be as high as 30% but salt rejection was very poor
- Salt rejection can be as high as 99% but water recovery was poor (2%)
- Some solvent can produce decent amount of water with low salt concentration but COD was high (more than 10,000 ppm)
- Adding CO2 or other polymer can improve water recovery but decrease salt rejection or increase COD in the water

Future plan for NAS Desalination project

- **New solvent test**
  - From literature and solvent characteristics (pKa or $LogP_{ow}$), new solvents are being selected and tested
  - Different group of solvents are also tested (Group 1 or Group 2)
- **Solvent mixtures**
  - CO_2, Polymer, Alcohol and Fatty Acid are added to the solvent to increase desalination performance (water recovery, salt rejection and low COD in the water)
  - Two more solvent are mixed together to improve the desalination performance
- **NAS desalination process development**
  - Iteration of solvent absorb/desorb process to increase water recovery
  - Test in various temperature conditions for water absorption/desorption
  - Post test to improve treated water quality

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More Information

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