# Low-Energy Water Recovery from Subsurface Brines

## 2017 Crosscutting Research Portfolio Review - March 23rd, 2017

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# PROJECT GOALS AND OBJECTIVES

## Project Goal:

**Develop of a low-cost, low-energy treatment process using a non-aqueous solvent (NAS) extraction to recover water from deep aquifer brine**

**Project Objectives:**

- Identify candidate solvents that can absorb water in one condition and release in another condition
- Test different solvents and/or mixture of solvents for optimum water uptake and release to maximize water recovery from 180,000 ppm TDS brine
- Develop optimum conditions to maximize the kinetics of the process
- Test water quality and if necessary, develop downstream process to satisfy potable water standard
- Develop strategies to optimize the overall process and perform techno-economic assessment for scale up

## Milestone Schedule

| Milestone | Description | Planned Completion Date | Verification Method |
|---|---|---|---|
| 1 | Identification of at least one candidate solvent formulation that has the ability to recover water in a single pass from high-TDS wastewater. | 6/30/2017 | Experimental data showing that at least 3% clean water recovery can be achieved. |
| 2 | Design of a multi-stage, semi-continuous treatment process train. | 7/31/2017 | Modeling data showing that the design can produce a mass flow rate of 1 gal/day. |
| 3 | Production of potable water with the use of post treatment. | 8/31/2017 | Experimental data showing that recovered water contains <500 ppm TDS. |

# PRESENTATION OUTLINE

1. Background

2. Results

3. Summary or Results

4. Future work

# BACKGROUND

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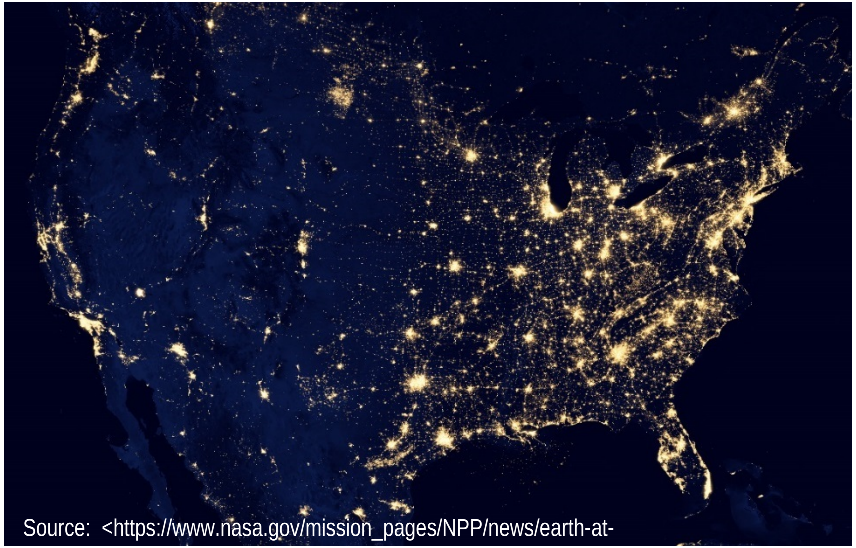
RTI International is an independent, nonprofit research institute dedicated to improving the human condition. We combine scientific rigor and technical expertise in social and laboratory sciences, engineering, and international development to deliver solutions to the critical needs of clients worldwide.

# It takes a lot of energy to treat and move water



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

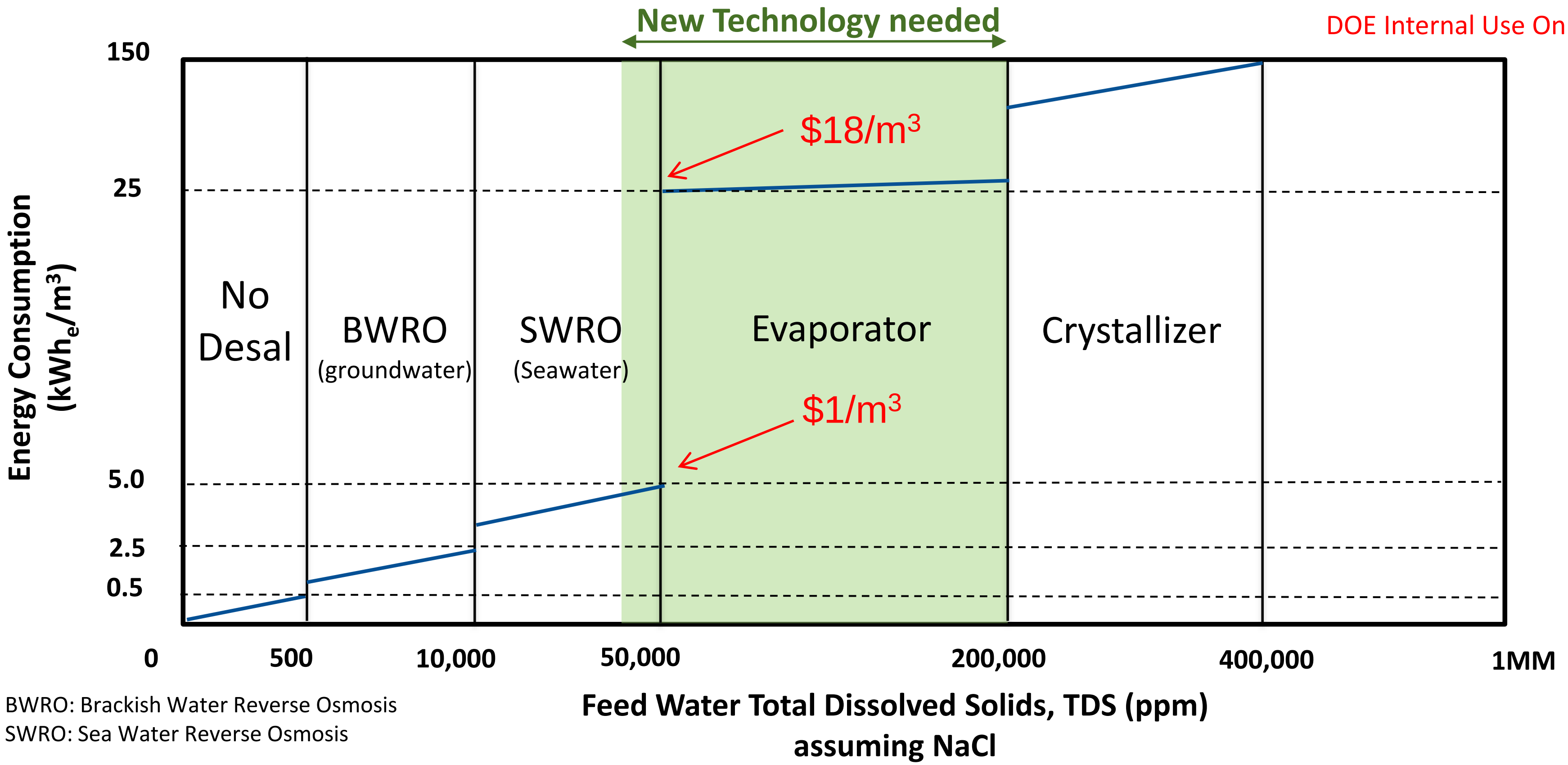
Source: <http://solutions.borderstates.com/what-is-the-future-of-mercury-vapor-lamps>>

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

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

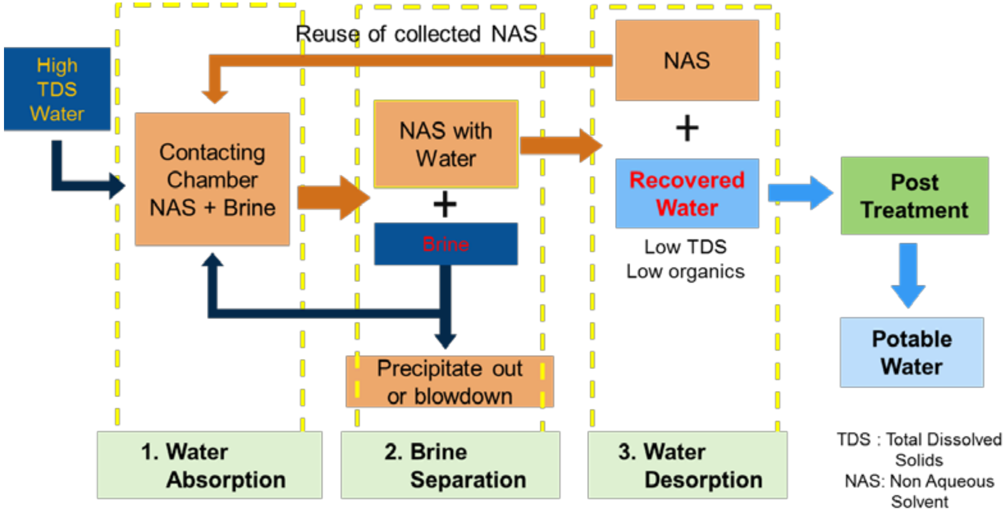
# Problem Area…






BWRO: Brackish Water Reverse Osmosis
SWRO: Sea Water Reverse Osmosis

# Low-Energy Water Recovery from Subsurface Brines




**Solvent Desalination process without membrane or evaporation/condensation**

**Low-cost, low-energy treatment process using non-aqueous solvent (NAS) extraction to recover water from deep aquifer brine**

## Technology Status

- Identified solvents that can recover more than 5% water with more than 90% salt rejection
- Water recovery can be improved by lowering absorbing temperature and salt rejection can be enhanced by increasing desorbing temperature
- Water recovery can be multiplied with minimal salt rejection decrease by repeating the absorb/desorb process

## Impact

Solvent absorbs only water, rejects salt, and desorbs pure water by changing conditions (e.g., temperature or $CO_2$).

Can handle higher TDS (Total Dissolved Solids) content (e.g., 180,000 ppm)

Minimum pretreatment required

Low energy requires not using evaporation/condensation

# 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 industrial activities in the U.S. calls for development of a novel solution that requires low energy and low capital cost.

# 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 would 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 to minimize post-treatment polishing of final treated effluent
- Small temperature change required for solubility variation
  - Energy input required to swing between water absorption/desorption needs to be minimal.
- Low vapor pressure (low volatility):
  - To minimize solvent replacement rate 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.

# Project Vision

**Solvent Desalination 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).

  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:

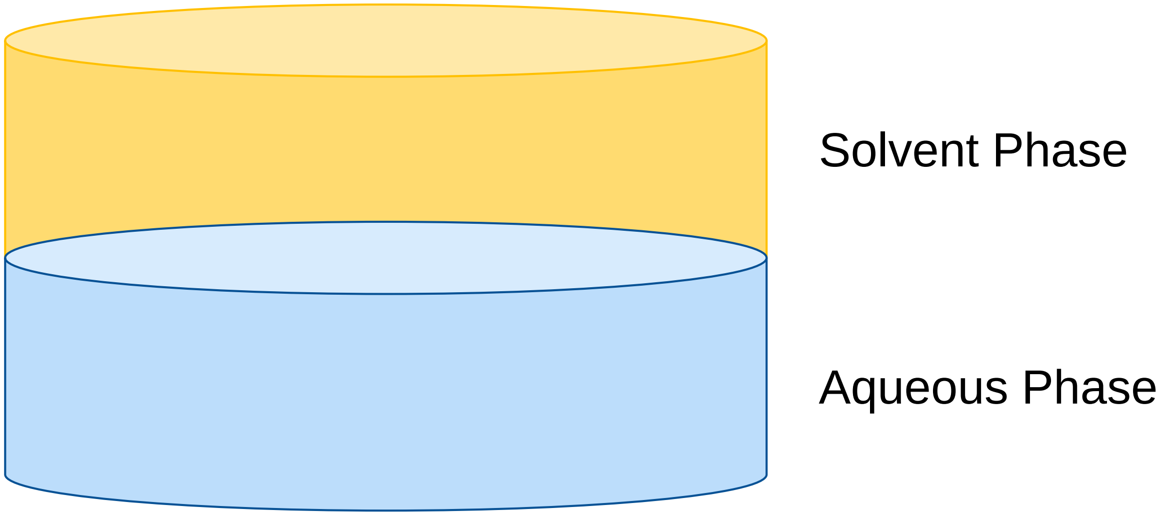
  The process will also yield high-quality product water because the water absorption is based on hydrogen bonding of water molecules to the (carbonated and thus) protonated end of the NAS.

- 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

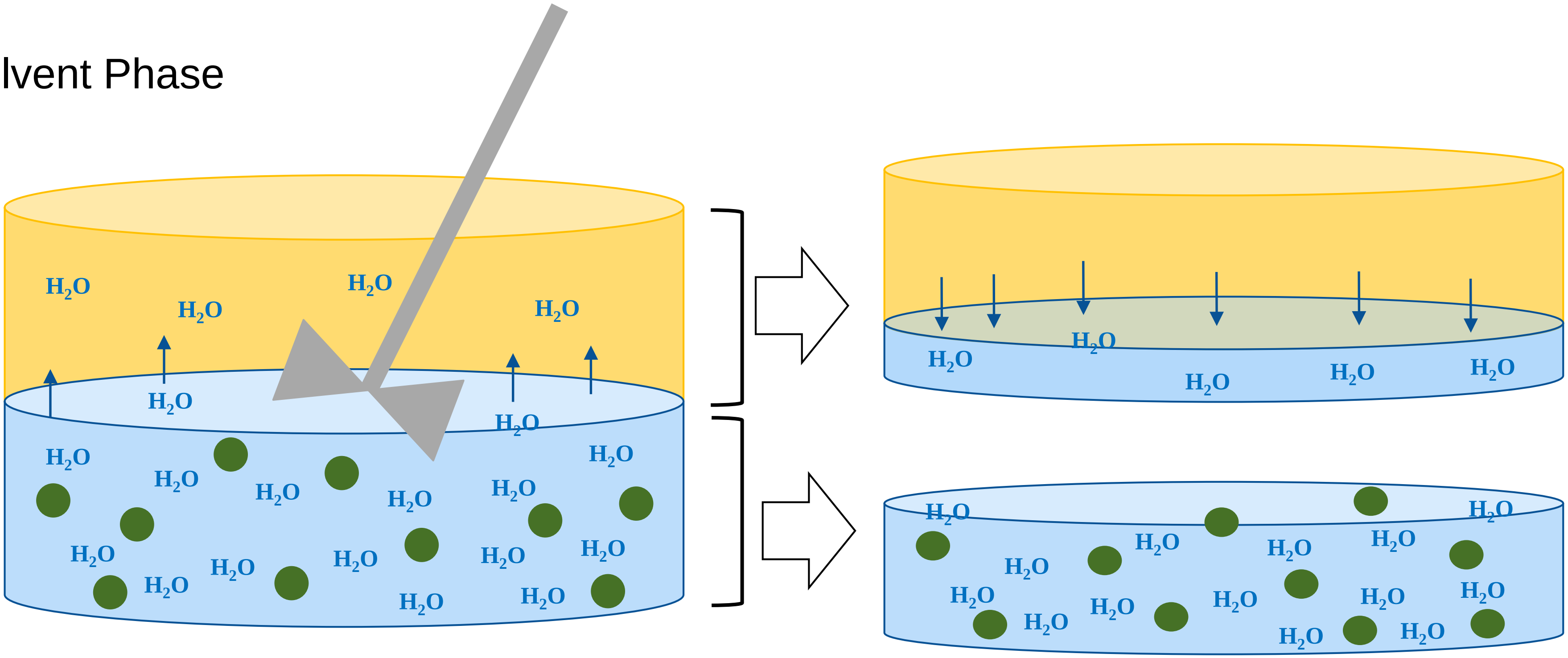
# RESULTS

# Non-Aqueous Solvent



# Separation of Water and Salt

Solvent Phase

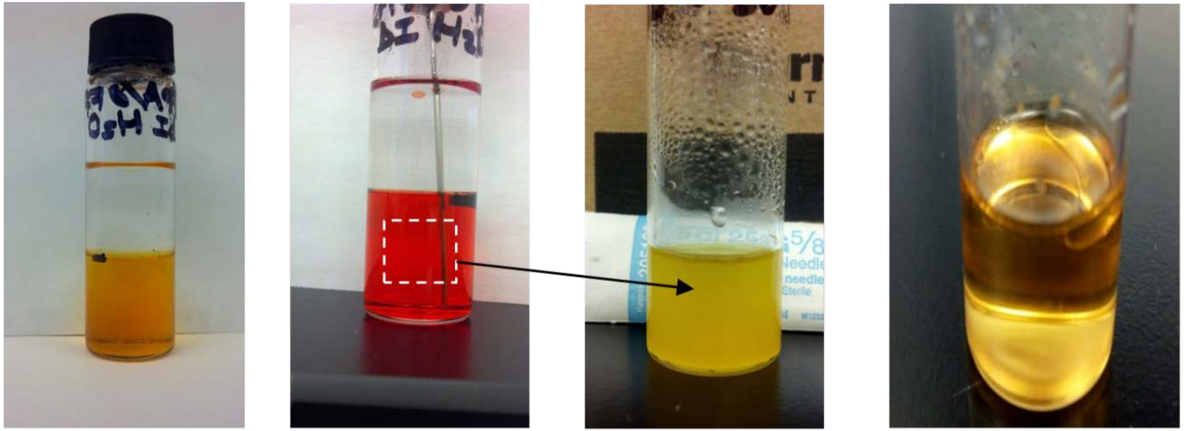



Aqueous Phase

● Salts (Na, Cl)

# 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.



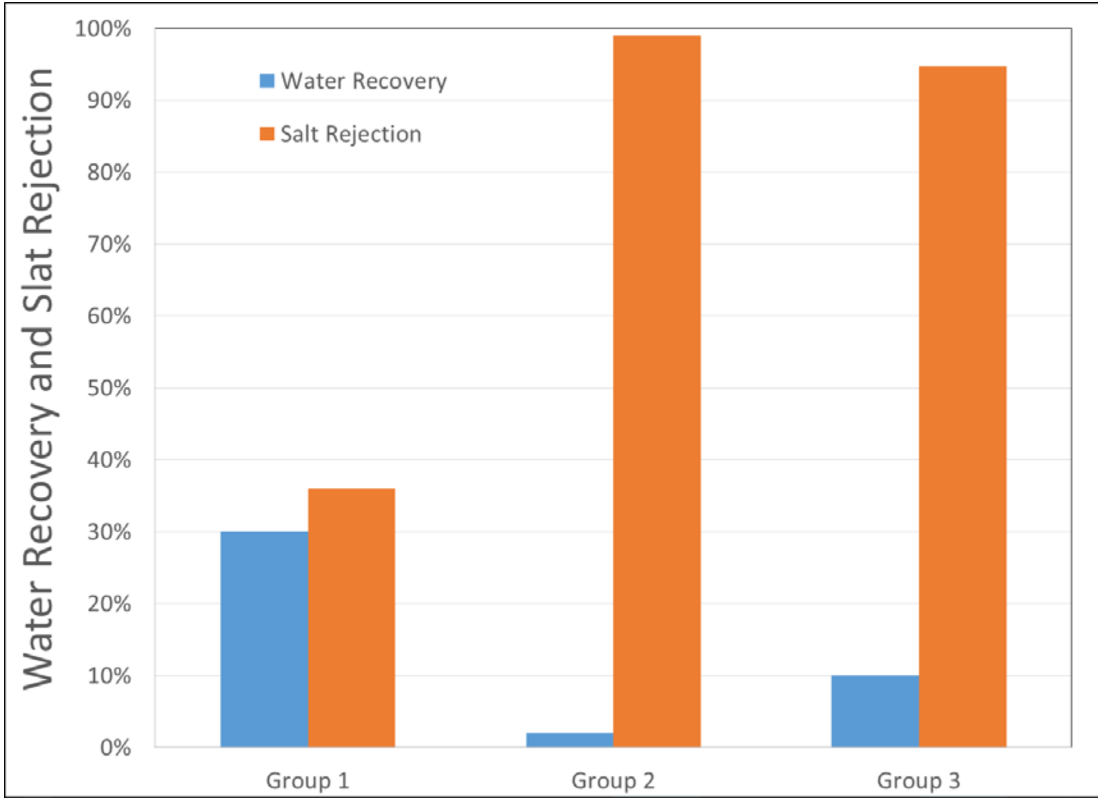
Water + Solvent | After $CO_2$ purge | $CO_2$ removal | Water layer formed

# Test Solvent Groups by Water Adsorption/Desorption Mechanisms

1. Gas-Switchable Solvents
   - Solvent purged with Gas for 30 min at 40 ºC
   - Gas laden solvent mixed with aqueous NaCl solution (0.5 M or 3 M) (25–40 ºC)
   - Water-bearing solvent purged with $N_2$ (80 ºC) to desorb Gas and separate product water from the solvent phase
2. High-Temperature Water-Absorbing Solvents
   - Water absorbed at higher temperature (e.g., 80 ºC) and released (desorbed) at lower temperature (e.g., 20 ºC or 40 ºC)
3. Low-Temperature Water-Absorbing Solvents
   - Water absorbed at lower temperature (e.g., 20-25 ºC) and released at higher temperature (e.g., 80 ºC)

| Solvent Group | Water Absorption | Brine Separation | Water Desorption |
|---|---|---|---|
| Group 1 Solvent (Gas Switchable) | Gas Purging | Gravitational | $N_2$ purging, High Temp (80 °C) |
| Group 2 Solvent (Fatty Acid) | High Temp (80 °C) | Gravitational | Low Temp (25 °C) |
| Group 3 Solvent (Amine, Polymer) | Low Temp (4–25 °C) | Gravitational | High Temp (80 °C) |

# Water Recovery and Salt Rejection of each Group

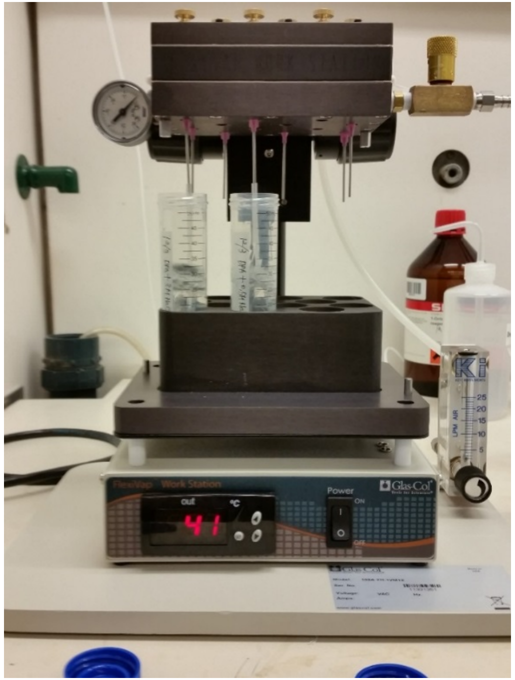



- Group 2 Solvents showed highest salt rejection (99%) but poor water recovery (2%).
- Group 1 Solvents showed highest water recovery (30%) and poor salt removal performance (36%).
- **Group 3 Solvents showed good water recovery (10%) and high salt rejection (95%).**

# Group 1  Results (gas switchable solvents)

- Gas purging and heating station was used to supply and remove gas from the solvent.
- The test kit can control the temperature of the solvent
- Some solvent became gel form with gas supply

| No | Solvent | Water recovery | Na+ rejection | Cl- rejection | Test Brine |
|---|---|---|---|---|---|
| 1 | 2FPA + OFP | 2% | 5.1% | 0% | 3M NaCl |
| 2 | 2FPA + TFP | 8.5% | 32.3% | 0% | 3M NaCl |
| 3 | 2FPA + 1-Octanol | 0% | 0% | 0% | 0.5M NaCl |
| 4 | N,N,N'-Tributylpentanamidine | 1.25% | 16% | -65% | 0.5M NaCl |
| 5 | N-Methybenzylamine | 0% | 0% | 0% | 0.5M NaCl |
| 6 | NMBA + 1-Octanol | 15.38% | -100% | -63% | 0.5M NaCl |
| 6 | n-ethylbenzylamine | 0% | 0% | 0% | 0.5M NaCl |
| 7 | n-benzylbutylamine | 0% | 0% | 0% | 0.5M NaCl |



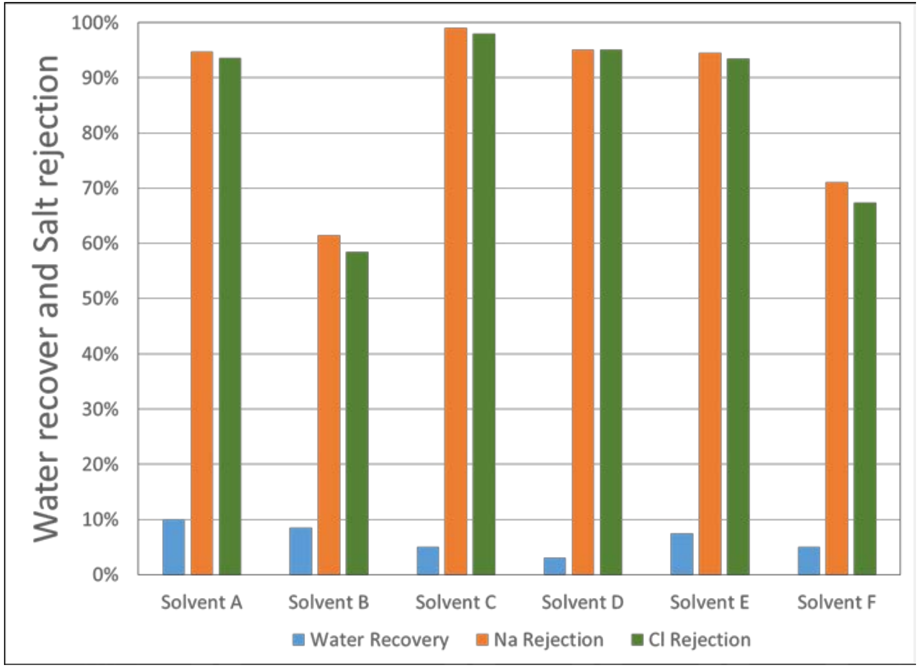
**Multi port gas purging/heating test kit**

# Group 2 Results (High-Temperature Water-Absorbing Solvents)

- Absorbing water at high temperature (80°C) and desorbing at low temperature (fatty acid).
- Significant time to cool down brine & solvent mixture
- Centrifuge to aggregate and precipitate fine water droplet.
- High salt rejection with low water recovery

| No | Solvent | Water recovery | Na+ rejection | Cl- rejection | Test Brine |
|---|---|---|---|---|---|
| 1 | Octanoic Acid | 0.7 – 0.9% | 99.9% | N/A | 3M NaCl |
| 2 | Octanoic Acid | 1.4 – 2% | 97.6% | 99.9999% | 0.5M NaCl |
| 3 | Decanoic Acid | 0.5 – 0.6% | 90% | 90% | 1M NaCl |
| 4 | Lauric Acid | 0% | 0% | 0% | 0.5M NaCl |
| 5 | Linoleic Acid | 0% | 0% | 0% | 0.5M NaCl |
| 6 | Oleic Acid | 0% | 0% | 0% | 1M NaCl |

# Group 3 Results (Low-Temperature Water-Absorbing Solvents) 1/2

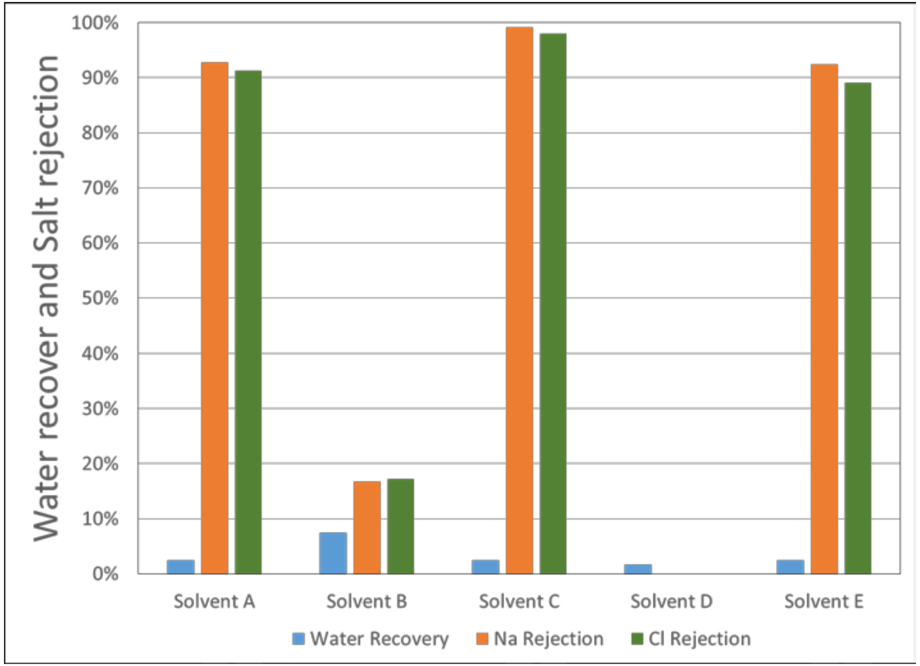



- 20mL Brine (0.5M NaCl) and 20mL solvent were used for test.

$$\text{Water recovery} = \frac{\text{(recovered water vol.)}}{\text{(solvent vol.)}}$$

- Some solvents showed high salt rejection (>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.

# Group 3 Results (Low-Temperature Water-Absorbing Solvents) 2/2

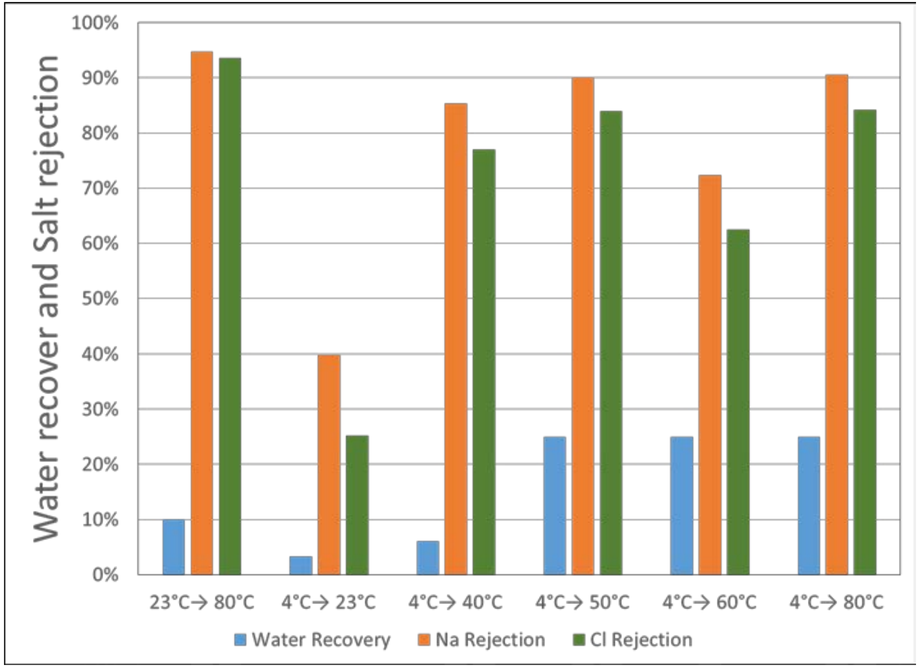



- 20mL Brine (3M NaCl) and 20mL solvent were used for test.

$$\text{Water recovery} = \frac{\text{(recovered water vol.)}}{\text{(solvent vol.)}}$$

- Some solvents showed high salt rejection (>90%) but water recovery lowered compared with that of 0.5M NaCl brine test (2.5 – 7.5 %).
- Solvent B showed high water recovery but salt rejection was low
- Solvent D showed small water recovery (1.7%)

# Temperature Effect of Solvent A (Group 3)




- Solvent A was tested
- Absorption temperature lowered to 4°C and desorption temperature varied from 23°C to 80°C
- 0.5M NaCl was used as Brine (Feed)
- Low absorption temperature increases water recovery.
- High temperature desorption increased salt rejection.

# SUMMARY OF RESULTS

# Summary of Result

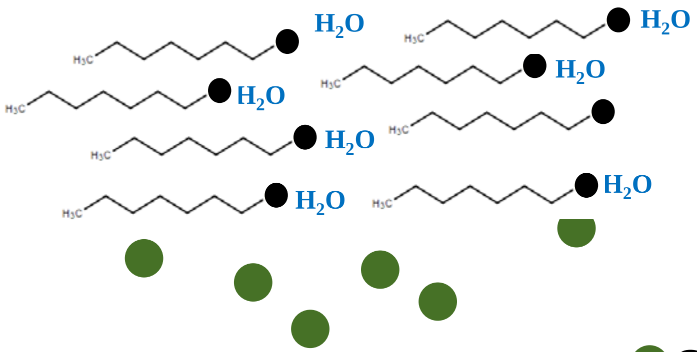
- Three mechanisms were developed for NAS desalination process
- Solvents that can recover 10% water and reject salt 90% were identified
- By repeating process 10 times, the water recovery can increase to 50%
- Low temperature can increase water recover and high temperate can increase salt rejection
- A Process Flow Diagram was developed for a large scale testing

# FUTURE WORKS

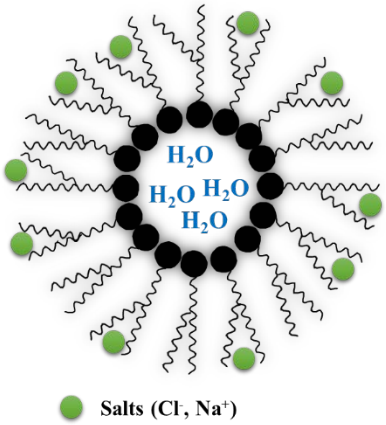
# Salt Rejection mechanism – Steric Effects?

## Questions

- Linear vs Micelle structure?
- Na and Cl bound $H_2O$ molecules, do they act similar to water?
- Which is more efficient, if we have a choice?



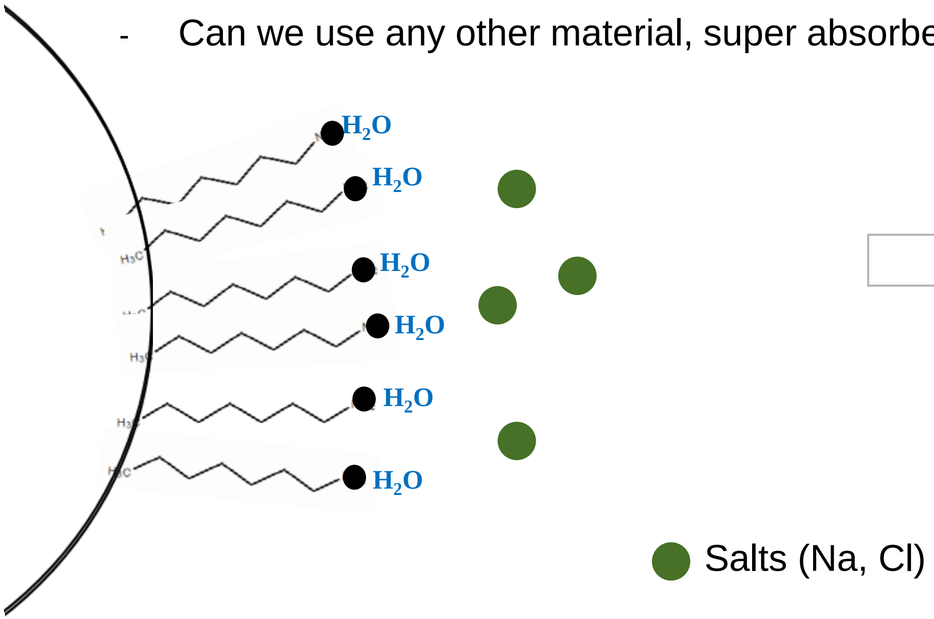

Salts (Na, Cl)

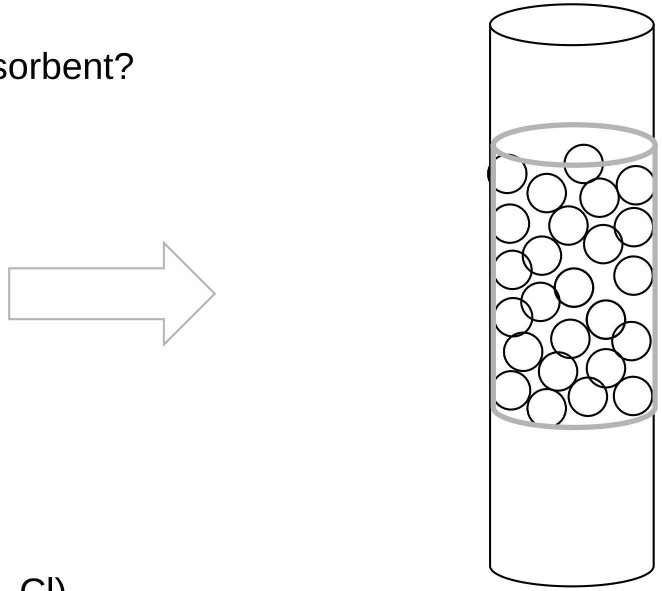


# Functionalization on a media?

**Questions**

- Can (liquid) solvent be functionalized? Or do we need in solid form?
- Does this work on micelle hypothesis?
- Can we use any other material, super absorbent?



Capture water on the surface while rejecting salt

Operate in a column reactor to prevent the loss of solvents

# 500-GPD Pilot FO/MD Unit


RTI Mobile Water Lab

# Acknowledgement

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# Thank You!

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