# Low-Energy Water Recovery from Subsurface Brines

## Final Technical Report

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by

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# List of Acronyms

| | |
|---|---|
| cm/s | Centimeters per second |
| COD | Chemical oxygen demand |
| FO | Forward osmosis |
| FTIR | Fourier-transform infrared spectroscopy |
| GOR | Gained output ratio |
| gpd | gallons per day (gal/day) |
| gpm | gallons per minute (gal/min) |
| $kWh_e$ | electric kWh |
| $kWh_{th}$ | thermal kWh |
| LCOW | Levelized cost of water |
| L/min | Liters per minute |
| MED | Multi-effect distillation |
| MMBTU | One million british thermal units |
| MSF | Multi-stage flash distillation |
| NAS | Non Aqueous solvent |
| NF | NanoFiltration |
| PFD | Process flow diagram |
| RO | Reverse osmosis |
| TDS | Total dissolved solids |
| TE | Techno-Economic |
| TOC | Total Organic Carbon |

# Executive Summary

Thermal evaporation such as multi-stage flash distillation (MSF) or multi-effect distillation (MED) and reverse osmosis (RO) membrane processes are the current technologies that dominate the desalination market. Membrane processes are generally lower cost compared to thermal technologies, but their ability to produce water is limited to the total dissolved solids (TDS) levels of 60,000 ppm in the feed water. Thermal processes can treat high TDS (TDS>60,000 ppm) but they are very energy-intensive technologies. Chemical precipitation processes also can be used for high TDS brines, but they require a significant amount of chemicals and generates huge amounts of solid waste. Therefore, the development of cost effective desalination technology for high TDS brine would provide a transformative technology alternative for both the deep-well injection and gas & oil production industries which commonly produce brine with TDS in excess of 180,000 ppm. A novel non-aqueous phase solvent (NAS) desalination process was proposed and developed in this research project. The NAS desalination process uses less energy than thermal processes, doesn't require any additional chemicals for precipitation, and can be utilized to treat high TDS brine.

In this project, our experimental work determined that water solubility changes and selective absorption are the key characteristics of NAS technology for successful desalination. Three NAS desalination mechanisms were investigated: (1) $CO_2$ switchable, (2) high-temp absorption to low-temp desorption (thermally switchable), and (3) low-temp absorption to high-temp desorption (thermally switchable). Among these mechanisms, thermally switchable (low-temp absorption to high-temp desorption) showed the highest water recovery and relatively high salt rejection. A test procedure for semi-continuous, bench scale NAS desalination process was also developed and used to assess performance under a range of conditions.

Experimental testing showed several amine solvents to be suitable candidates for desalination (>90% salt rejection and >5% water recovery). One solvent showed more than 10% water recovery and higher than 94% salt rejection. Several chemistry modifications were applied to those high performing solvents with the goal of improving desalination potency: $CO_2$ addition, mixing with other solvents, polymer addition, and fatty acid addition. Lowering the water absorbing temperature was shown to significantly increase the water recovery. It was also demonstrated that desorbing water from solvent at high temperature minimized the residual solvent in the product water. Computational simulations of the NAS desalination mechanisms were studied via Molecular Dynamic Simulations (MDS). The MDS results showed agreement with experimental results, which suggests this simulation tool can reduce both labor and time costs for screening of future candidate solvents.

This project demonstrated the technical feasibility of a NAS approach for the desalination of high TDS brine (180,000 ppm) and provided key insight into the relationship between different solvent chemistries and overall desalination performance. The semi-continuous NAS desalination tests showed that the solvent salt rejection occurs during the water absorbing step. The test results were used to develop a conceptual process flow diagram (PFD) for future continuous pilot plant testing, which will be vital in the continued development of this technology. A techno-economic analysis was performed and showed that the temperature swing difference and water recovery are the key cost drivers of NAS desalination. In summary, the results at this stage indicate that the NAS desalination approach is a promising technology for high TDS saline water treatment and may provide economic benefit in comparison with thermal technologies.

# 1. INTRODUCTION

Deep-well $CO_2$ injection can create a pressure build-up in subsurface aquifers [1]. To relieve this pressure, it is necessary to extract a portion of the groundwater (brine) from the deep well [2]. The brine may contain a very high TDS concentration, in the range of 180,000 ppm. Wastewaters containing high levels of dissolved salts, heavy metals, and minerals are generated throughout the fossil fuel life cycle, such as during extraction (produced waters, coal wash wastewater), power generation (flue gas desulfurization blowdown), and disposal (water from $CO_2$ subsurface storage, coal ash storage ponds). The dissolved contaminants that make up the high TDS are generally some of the most difficult constituents to remove in any water treatment processes. Figure 1 shows the values for TDS with increasing depth from a well water sample at the TECO site obtained by RTI. In addition to TDS values, we have access to data showing a comprehensive assessment of the major and minor constituents (ions, metals, radionuclides, etc.) present in the deep well brine. Although a technical challenge, these waters represent a significant opportunity as an untapped resource for water reuse, which would significantly change the water balance associated with power plant activity. In addition, since 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.

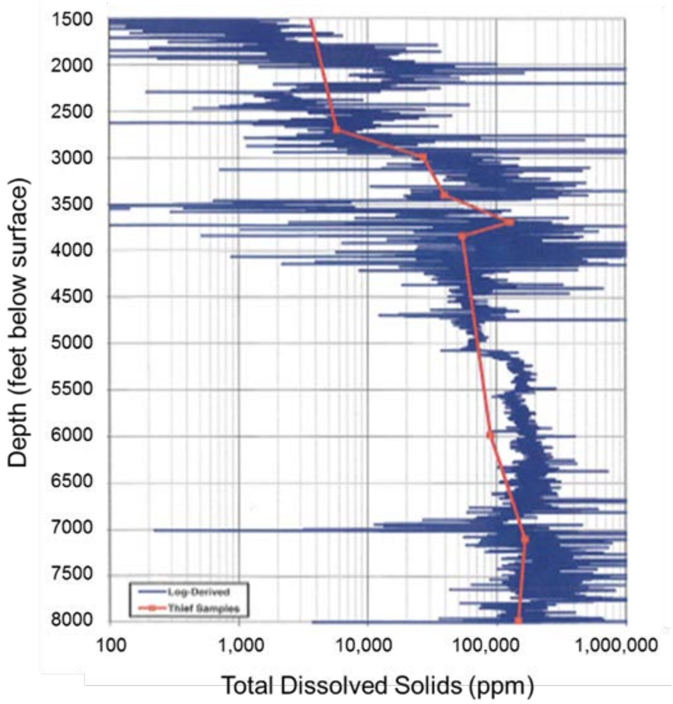


**Figure 1.** Subsurface plot showing the increasing TDS concentration in water with depth at TECO $CO_2$ site.

The overall project objective was to demonstrate the efficacy of NAS as a cost-saving technology to treat concentrated brines. These brines include, but are not limited to, the produced waters generated from $CO_2$ subsurface storage in deep saline aquifers or from energy extraction. Low-cost and low-energy water recovery from these brines will allow beneficial water reuse in power production or other industrial operations, as well as in agricultural and municipal water uses. The selection of NAS was the key activity of this project to meet the low capital and operational costs that will ensure that a solvent-based water extraction technology outperforms current desalination methods. Ideal characteristics of NAS are that the solvents have high water recovery, low vapor pressure, low degradation rates, require small or minimal temperature changes for regeneration/product water recovery, and finally are environmentally safe.

Management of concentrated brines depends on the production region, disposal options, economics, and treatability. Large volumes of these brines will be generated as the practice of subsurface carbon storage grows. For every ton of $CO_2$ sequestered in deep injection wells, between 0.8 and 1.5 $m^3$ (200 and 400 gal) of brine will be returned that requires treatment prior to discharge or reuse. Approximately 2 billion tons of $CO_2$ are emitted annually from power plants in the U.S. [3]. The corresponding brine volume produced from subsurface storage of this emitted $CO_2$ could be as high as 3.2 billion $m^3$/yr (~2.3 billion gallons per day) depending on geological features of the injection well. In unconventional resource extraction, generated wastewater is not treated to levels that would allow for safe discharge; most high-concentration brines generated in the U.S. are currently disposed of in Class II deep-injection disposal wells that often require the water to be transported over 100 miles from the extraction site [4]. Other high-TDS wastewaters such as coal wash wastewater and coal fly-ash are held indefinitely in surface ponds. Existing technologies provide limited disposal and treatment options for high-TDS waters. Thus, there is a significant need to develop a low-cost, reliable approach to enable treatment for reuse of these high-TDS wastewaters.

Although several technological approaches exist to remove TDS from wastewater, they all have drawbacks that limit their applicability at the high-TDS levels present in water generated from deep-well brines. The current state-of-the-art technology for removing highly soluble dissolved salts is RO, which uses hydraulic pressure to force pure water through a semi-permeable membrane. However, RO is limited to feed water having an upper limit of approximately 60,000 mg/L TDS, well below the higher concentrations in many brines (>180,000 mg/L TDS). Chemical precipitation can be utilized in cases where divalent ions are the dominant species present in the wastewater. Methods such as lime softening or ettringite precipitation will remove a large portion of divalent salts. However, these methods typically require large quantities of chemicals and generate large volumes of sludge that require further treatment/disposal. Another drawback of these approaches is that they are ineffective at reducing TDS in brines containing significant concentrations of monovalent ions (Na and Cl), characteristic of many deep aquifer brines. Thermal processes (evaporation and crystallization) can treat such high-TDS water with appropriate pretreatment and achieve the goal of producing potable water, but the capital cost will be significant due to the exotic alloys required to withstand the corrosive effects of heat and chemicals on the materials of construction. Additionally, this approach would likely require high concentrations of NaOH and anti-foaming agents to stabilize the pH and reduce foaming, which would impair the final distillate quality. Such chemical additions can significantly increase the operating cost of thermal treatment, which is generally very high to begin with. No new technologies have been developed on the commercial scale within the last few decades to handle such high-TDS wastewater, and the increase in these waters generated from $CO_2$ 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.

Therefore, the development of a novel solvent desalination process that can handle the TDS brine (>180,000 mg/L) is the main objective of this research project and specific technical objectives are

(i) Identification of candidate solvents;

(ii) Characterization and evaluation of solvent capabilities with respect to water recovery from brine;

(iii) Establishment and successful demonstration of bench-scale treatment process train for the production of potable water;

(iv) Development of an implementation plan for pilot-scale treatment system.

# 2. BACKGROUND

## Solvent desalination technologies

The use of solvents to extract pure water from saline solutions was first explored in the 1950s [5]. Solvent-based extraction can potentially provide a moderate temperature (low energy), membrane-free approach to treat high TDS brines [6]. An effective solvent for extracting pure water from brine must have the properties that allow pure water to be dissolved in it while rejecting soluble salt, and the solvent itself must not be soluble in water under certain controllable conditions. Researchers have found medium to long chained carboxylic acids, primary/secondary/tertiary amines, and glycerol ethers and amino-ethers possess this unique ability [7]. In most of these approaches, water solubility in the solvent is a function of temperature. Raising or lowering the temperature of the solvent/brine mixture facilitates water transport into or out of the solvent. Once dissolution is complete, the water-rich phase can then be decanted and the process is reversed to recover pure water. Others have demonstrated that solvents such as decanoic and octanoic acids extract pure water from high-concentration saline solutions with a bench-scale system. Although promising, the moderate water content delta of < 3% within the solvent may provide a challenge for economic scale-up. Triethylamine has also been shown to be an effective solvent for extracting pure water from saline solutions [5]. For triethylamine, water is more miscible at low temperatures and becomes immiscible as temperature increases. However, this solvent poorly rejects salt as the water recovery increases. Experiments conducted with polyethylene glycol-polypropylene glycol (UCON™) polymer have shown this polymer has the ability to absorb water and reject soluble salts. The polymer can dissolve water at low temperatures, and water is recovered by raising temperature. Adding heat causes the polymer chain to reconfigure and become hydrophobic, which leads to the precipitation of water.

The design and implantation of a 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.

However, a key challenge with the approaches listed above are that they require significant thermal and electrical energy during both the heating and cooling steps; reducing the energy requirement to absorb/release water in each cycle is necessary to move this technology toward the commercial scale. Table 1 compares currently available TDS removal technologies with a potential full-scale solvent extraction approach.

**Table 1.** Available TDS Removal Technologies Compared with Proposed NAS Technology for High-TDS Waters.

| 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 |

***Ideal Solvent Properties.*** To meet the low capital and operational costs that will ensure that a solvent-based water extraction technology does outperform current state-of-the-art methods, the NAS needs to be selected using the following criteria:

- Environmentally safe: In case there is any spill or human contact, the NAS should be reasonably safe. If there is any extreme toxicity, it would not be a candidate for this process.
- High water recovery: RTI has found vastly different water absorption rate for different solvents. An NAS with the highest water uptake and complete discharge is ideal.
- Small temperature change required for solubility variation: The energy input required to swing between water absorption/desorption needs to be closely studied and minimized. RTI’s process has the potential to require much less energy than thermal evaporators and crystallizers, but estimations for water/solvent-based treatment at the large scale are currently unavailable and need to be conducted.
- Low vapor pressure (low volatility): To minimize the replacement rate of the NAS and prevent atmospheric release of organics, it is necessary to select solvents with low vapor pressures.
- Low degradation rate (low maintenance): Degradation by temperature, chemical conditions, sunlight, or biological attack will increase the operational cost and the cost of replacement chemicals. Chemicals with low replacement rate under repeated absorption-desorption will be studied and selected.

## Group 1: $CO_2$ Switchable solvent

RTI has developed NAS that are mixtures of various hydrophobic amines and hydrophobic diluents that participate in several reactions with $CO_2$. When $CO_2$ is added to the solvent with amine, one reaction pathway generates a carbamate group as shown in Figure 2.

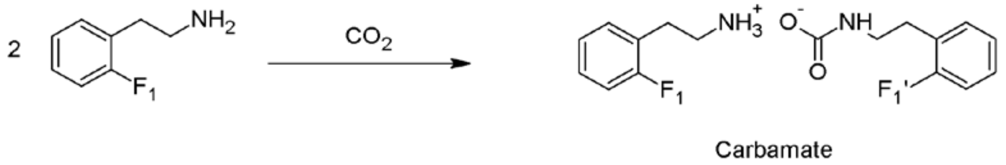


**Figure 2.** Reaction pathway showing $CO_2$ uptake by NAS to form carbamate group.

The above pathway shows 2-fluorophenethylamine (2-FPEA), but a wide range of potential solvent diluent combinations might prove effective. The solvents that RTI has investigated have $CO_2$ loadings that are equivalent to aqueous amine solvents on a molar basis, but are higher on a volume basis. When combined with hydrophobic, non-aqueous diluents with low volatility, such as fluorinated alcohols, homogeneous mixtures are formed. These mixtures have $CO_2$ vapor-liquid equilibrium loadings at relevant temperatures that make them extremely attractive for $CO_2$ capture applications, and in turn, we predict the same effectiveness for water extraction applications as well. Figure 3 shows the NMR spectrum that confirms the incorporation of $CO_2$ capture mechanism after reaction with the solvent 2-FPEA. Although these solvents are specifically tailored to prevent water absorption, results have shown that water content increases in the solvent phase as $CO_2$ concentration increases. Table 2 shows the increase in water content within the NAS as $CO_2$ concentration increases.

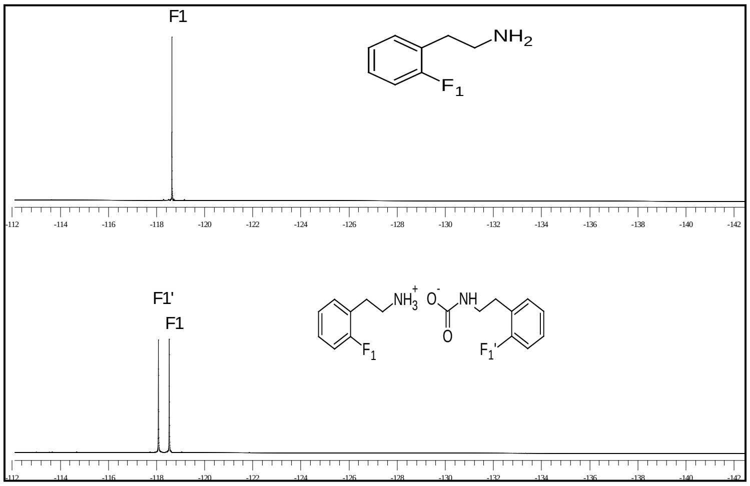


**Figure 3.** Fluorine NMR spectra of 2-FPEA before (top) and after (bottom) reaction with $CO_2$, showing the formation of the carbamate, which we hypothesize is the structure responsible for water uptake.

**Table 2.** Measured $CO_2$ Loadings and Corresponding Water Content for Various NAS (amine/diluent) Combinations Measured by RTI.

| 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%

These solvents absorb 5 to 10% more water when they are rich in absorbed $CO_2$ than when they have been regenerated to a lean $CO_2$ state by nitrogen purging and/or heating. The water absorbed in the $CO_2$-rich state is observed as a desorbed separate phase in the regenerated solvent upon cooling. We hypothesize that this water absorption is due to hydrogen bonding with the carbamate group formed with the captured $CO_2$, as shown in Figure 4. The postulated hydrogen bonding arrangement agrees well with the experimentally observed change in magnitude of the water content of the NAS when the solvent goes from $CO_2$-lean to $CO_2$-rich.

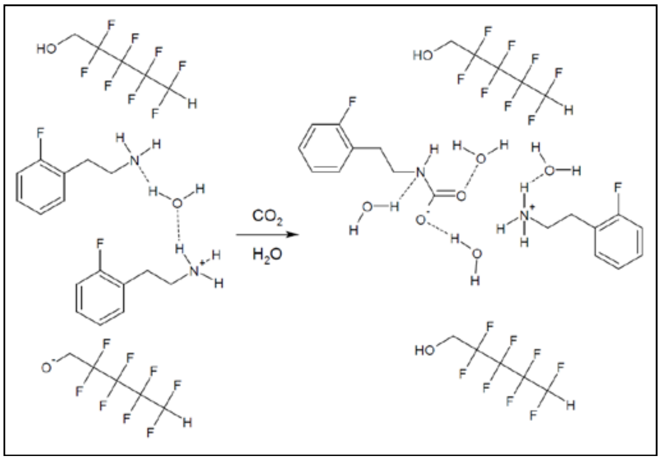


**Figure 4.** Structures suggesting a plausible hydrogen bonding upon the addition of $CO_2$ to the NAS.

Although a challenge in $CO_2$ capture technology, this phenomena can potentially be used to tailor a water/solvent extraction system that maximizes water uptake while requiring low energy during the release/regeneration step. Recent results support the mechanistic theory that water content is released along with $CO_2$. In addition, the solvents have other physical properties such as low specific heats (typical $C_p < 1.4\ J\cdot g^{-1}\cdot K^{-1}$) and reaction heats ($\Delta H_{abs}$) that we believe will lower the energy required for regeneration relative to other solvent-based water extraction combinations. The solvents have also shown stability during multiple cycles, so a system can be designed with a high reuse rate for both the solvent and the $CO_2$. We note that the solvent mixtures presented in Table 2 are specifically designed to limit water absorption by incorporating a hydrophobic diluent, and the change in water content between the lean and rich phases with these formulations is measured as high as 10 to 15%, which is better than those reported for other water/solvent systems. Our initial work with these solvent systems suggests that the water content can be precisely controlled via the $CO_2$ content within the solvent.

### Group 2: High Temperature salt rejection/low temperature water recovery

Another interesting class of solvents are carboxylic acids, whose amphipathic properties facilitate hydrogen bonding and organic/aqueous layer separation. In their publication “Exceptional Ion Rejection Ability of Directional Solvent for Non-Membrane Desalination,” the authors found that decanoic acid can reject all major salt ions in seawater with very high rejection rates (98-99%), similar to those of the best RO membranes [8]. The authors also used MD simulations to calculate the solvation free energy of all these major ions including $Na^+$, $Ca^{2+}$, $K^+$, $SO_4^{2-}$, $Br^-$, and $Cl^-$; they calculated that ions have much more negative free energies when dissolved in water rather than in decanoic acid. This suggests the ions are more thermodynamically stable when staying in the water phase rather than the organic phase and that recovered water is essentially free of salt [8].

### Group 3: Low Temperature salt rejection/high temperature water recovery

Due to the myriad of organic solvents available, it is difficult to identify an “ideal” solvent, meaning one that is substantially better than others in all of the desirable categories. However, studies concerning the solubility of brines and numerous organics have been conducted over the course of the last fifty years. An essential characteristic of a solvent candidate is that it has a heteroatom(s) that is not sterically hindered in order to facilitate water absorption/desorption. Amines make great solvent candidates due to the hydrogen bonding ability of their nitrogen atom(s). All amines up to four carbons are miscible, up to the boiling temperature of the amine; however, amines with a higher number of carbons (8-12) show low solubility in water but a high solubility of water in amine. For a given molecular weight, there is no difference in the solubility of primary, secondary, and tertiary amines [9]. However, there is an increase in the temperature sensitivity of solubility in going from primary to tertiary amines; in addition, tertiary amines and highly-branched secondary amines containing 5 or 6 carbon atoms in each instance have the best solubility curves [10].

Unsurprisingly, due to a large number of heteroatoms, fatty acids (i.e. soybean oil) and some long-chain polymers (i.e. UCON, a polyalkylene glycol) are able to facilitate this desalination process. RTI International has tested UCON polymer in different percentages by volume with another candidate solvent, and discovered that a greater percentage of polymer allows for greater water recovery, but higher organic contamination and decreased salt rejection in the recovered water.

# 3. EXPERIMENTAL METHODS

## Solvent screening test

Various candidate solvents were separated into three groups based on their property change triggers such as $CO_2$ and temperature change. Group 1 solvents ($CO_2$ switchable solvent) absorb water when the solvent is saturated with $CO_2$ and desorb water when the $CO_2$ is removed from solvent. Group 2 solvents (thermally switchable solvent) absorb water when the temperature is high (> 80°C) and desorb water when the temperature is low (20°C or 40°C). And Group 3 solvents are also thermally switchable solvent but the water absorption and desorption condition is reversed with those of Group 3 solvents. The characteristics are summarized in Table 3.

**Table 3.** Characteristics of each Solvent group.

| Solvent Group | Water Absorption | Brine Separation | Water Desorption |
|---|---|---|---|
| **Group 1 Solvent ($CO_2$ Switchable)** | $CO_2$ Purging | Gravitational | $N_2$ purging, High Temp (80 °C) |
| **Group 2 Solvent (Thermally switchable)** | High Temp (80 °C) | Gravitational | Low Temp (25 °C) |
| **Group 3 Solvent (Thermally switchable)** | Low Temp (4–25 °C) | Gravitational | High Temp (80 °C) |

The test procedure was designed based on the water absorption/desorption mechanism of each group.

### *Group 1 ($CO_2$ switchable solvent) test plan*

The Group 1 solvents were tested according to the procedure below:

1) Purging of solvent with $CO_2$ for 30 minutes at 40 °C
2) Mixing of $CO_2$-saturated solvent with aqueous NaCl solution (0.5 M or 3 M) (25 – 40 °C)
3) Equilibration of $CO_2$-saturated solvent/salt solution mixture to allow absorption of water from the salt solution into the solvent
4) Purging of the water-bearing solvent with $N_2$ (80 °C) to desorb $CO_2$ and separate product water from the solvent phase

The multi-sample purging station shown in Figure 5 has a built-in heating block and was used to bubble $CO_2$ and $N_2$ into the Group 1 solvents. Candidates of the Group 1 solvent were selected from a literature review.

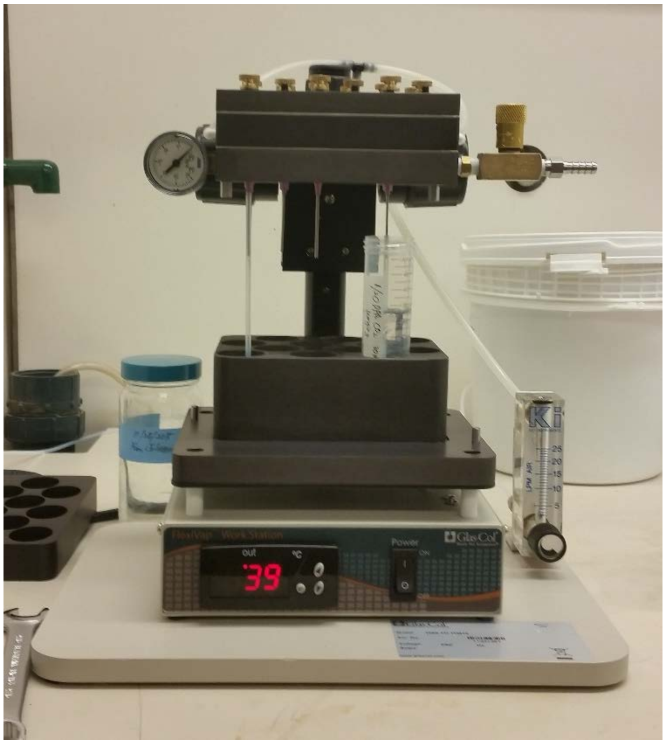


**Figure 5.** Gas purging station for screening of $CO_2$-switchable solvents (Group 1).

### Group 2 (Thermally switchable solvent-high temp absorption) test plan

The Group 2 solvents absorb water at a higher temperature (e.g., 80 °C) and release (desorbs) water at a lower temperature (e.g., 20 °C or 40 °C). Depending on the solvent characteristics, $CO_2$ purging could also be applied during heating. After heating and adding NaCl solution into the solvent, the mixture was placed on a stirrer plate to facilitate water uptake into the solvent phase. The water-bearing solvent phase was recovered from the mixture and cooled down to room temperature. The recovered solvent phase was then centrifuged to actively phase-separate and collect the product water droplets from the cooled solvent.

### Group 3 (Thermally switchable solvent-low temp absorption) test plan

The water solubility behavior of the third group solvent (Group 3) are the opposite of those of Group 2 solvents. Group 3 solvents absorb water at a lower temperature (e.g., 20-25 °C) and release water at a higher temperature (e.g., 80 °C). After a Group 3 solvent was mixed with NaCl solution at room temperature on a stirrer plate, the separation of the water-rich and solvent-rich phases were allowed to separate by gravity. The water-bearing solvent phase was then removed from the mixture and heated in an oven. After 30 minutes of heating, the product water released from the solvent was collected for water-quality analysis. The mixing temperature (water absorbing temperature) was varied up to 4°C to increase the amount of water absorbed. And the water desorbing temperature was also changed to test the water separation performance and residual solvent in the recovered water.

## Post treatment test

An experimental setup was prepared to test potential post treatment options. A membrane test unit (Sterlitech, Sepa CF Med/High Foulant cell Assembly, 316SS, 75 Mil) and a pump were installed to test various types of membranes. Both NF and RO membranes were utilized, and the set-up is shown in Figure 6.

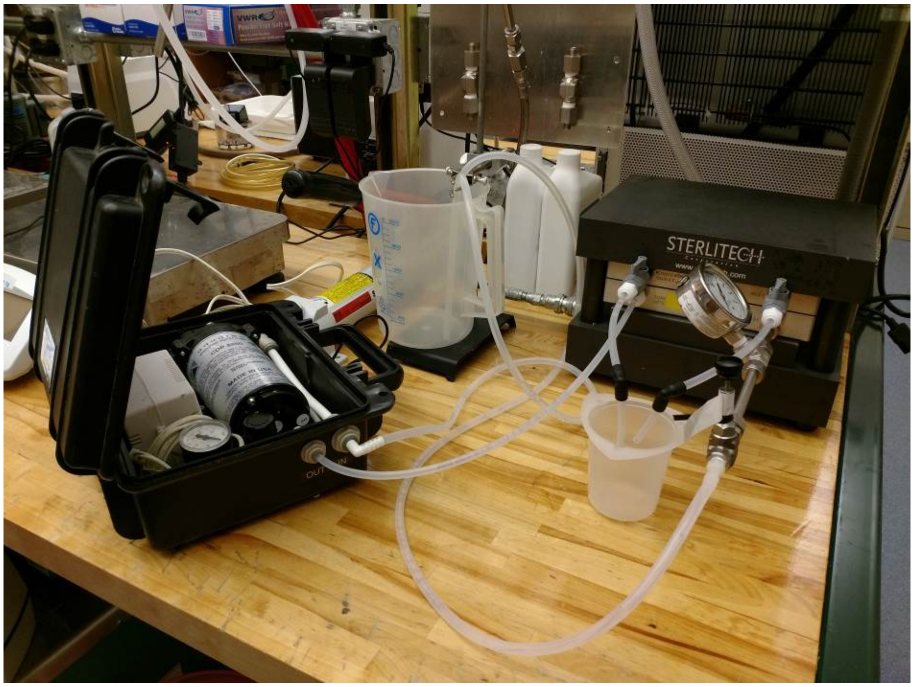


**Figure 6.** SEPA cell test set-up

## Water quality analysis

To confirm the desalination performance, water quality was measured such as pH, Chemical oxygen demand (COD), and various ions such as $Na^+$, $Cl^-$, $Ca^{2+}$ and $Mg^{2+}$. pH was measured using litmus paper in small volume tests, and with a Hach gel-filled pH electrode for larger volume test. Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, TOC-Vcph). The COD was measured using Hach TNT 822 kit with spectrophotometer (Hach, DR6000). Ion concentration was measured using Ion Chromatograph (Thermo-Dionex, ICS3000).

# 4. RESULTS AND DISCUSSION

## Screening for solvent desalination mechanism

***Group 1 solvents***. Several amine solvents were tested as Group 1 solvent candidates, which were miscible with NaCl solution after purging with $CO_2$; however, some solvents did not mix with the salt solution upon $CO_2$ purging. Solvents that were completely miscible with the brine exhibited zero salt rejection since the salt also mixed with solvent completely. These solvents were omitted from further testing. A Group 1 solvent generated a solid precipitate upon mixing with NaCl solution, but FTIR (Fourier-transform infrared spectroscopy) analysis showed that the precipitate was not NaCl salt. The precipitation after centrifuge and FTIR results are shown in Figure 7.

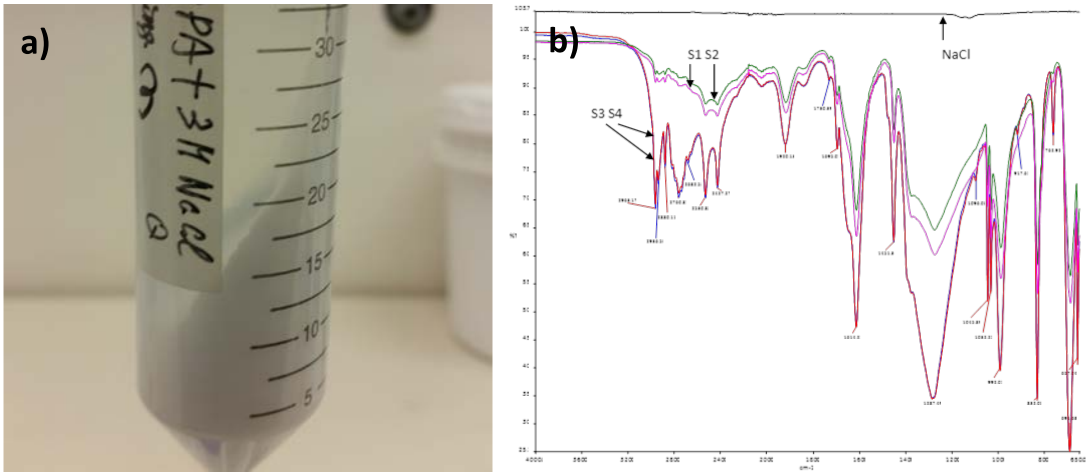


**Figure 7.** (a) Precipitation after centrifuge and (b) FTIR result of the precipitation.

A mixture of two amine solvents (2-Fluorophenethylamine (2FPA) and 2,2,3,3-Tetra fluoro-1-propanol (TFP)) from Group 1 yielded a high water recovery of more than 30%, but the product water was found to have a high organic content (COD > 575,000 ppm) because of solvent dissolution into the recovered water. This solvent exhibited low salt rejection (36%). The data for this solvent is shown in Figure 9.

***Group 2 solvents***. The Group 2 solvents identified absorb water at a higher temperature (e.g., 80 °C) and releases (desorbs) water at a lower temperature (e.g., 20 °C or 40 °C). Depending on solvent characteristics, $CO_2$ purging could also be applied during heating. After heating and adding NaCl solution into the solvent, the mixture was placed on a stirrer plate to facilitate water uptake into the solvent phase. The water-bearing solvent phase was recovered from the mixture and cooled down to room temperature. The recovered solvent phase was then centrifuged to actively phase-separate and collect the product water droplets from the cooled solvent. The separated water droplet is shown in Figure 8.

**Figure 8.** Product water in Group 2 solvent test.

One Group 2 solvent showed high salt rejection (>99 %) but very low water recovery (1.4–2 %) with 0.5 M NaCl solution. To enhance water uptake into the solvent phase, several alcohols were selected as co-solvents to combine with the Group 2 solvents. Screening tests with these Group 2/alcohol solvent combinations were conducted, but none showed any water recovery in experimental tests.

***Group 3 solvents***. The water solubility behavior of the Group 3 solvents is the opposite of that of Group 2 solvents. Group 3 solvents absorb water at a lower temperature (e.g., 20 – 25 °C) and release water at a higher temperature (e.g., 80 °C). After mixing Group 3 solvents with NaCl solution at room temperature on a stirrer plate, the water-rich and solvent-rich phases were allowed to separate by gravity. The water-bearing solvent phase was then removed from the mixture and heated in an oven. After 30 min of heating, the product water released from the solvent was collected for water quality analysis. When the solvent volume was more than 500 mL, a 2-hour heating time was used instead of 30 minutes. A polymeric solvent test demonstrated high rejection of divalent ions (e.g., $Mg^{2+}$, $SO_4^{2-}$) but minimal rejection of monovalent ions (e.g., $Na^+$, $Cl^-$). The performance of each group solvent in terms of their water recovery and salt rejection is summarized in Figure 9. Based on this test results, several Group 3 solvents were selected for further testing.

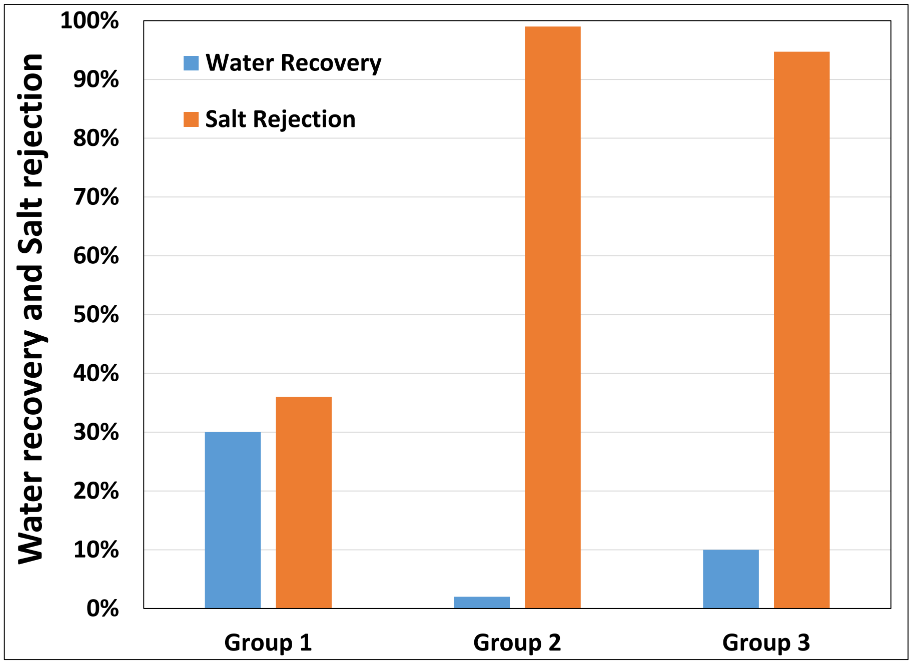


**Figure 9.** Water recovery and salt rejection performance of each group of solvents.

## Solvents test

***Single Solvent Test*** Group 3 solvents, which employ the low-temperature water absorbing mechanism, showed the best combination of high water recovery and salt rejection in initial screening tests. More detailed experiments were conducted to find the optimal solvent or combination of solvents. Based on these tests, Solvent A and Solvent C displayed promising desalination properties and were thus downselected for further evaluation.

The desalination performance of all the amine solvents (A-N) in Group 3 are presented in Figure 10. Synthetic brine solution (0.5 M NaCl) was used and temperature was changed from 23 °C (water absorption) to 80°C (water desorption), except for Solvent G and H, which required a temperature of 40 ºC since these solvents became very viscous liquids (jelly-like) with the salt solution at room temperature (22 ºC). The water separation temperature of 80 ºC was kept the same for G and H. Solvents G and H showed very high water recovery (50 – 59 %) and low COD in the produced water (less than 10,000 ppm), which meant that the solvent content remaining in the produced water was very low. However, there was no salt rejection in either of those solvent tests and the salt concentration in the produced water was increased for all three times repeated tests.

Five solvents showed more than 90% salt rejection and one, Solvent A, showed high water recovery performance (10%). Solvent E showed decent water recovery (7.5%) and high salt rejection performance, but the residual COD of product water was too high to be selected for further test. Solvent C also showed decent water recovery (5%), very high salt rejection (98%) and low residual solvent in the product water (COD < 17,000ppm) so was also selected as further test solvent. Solvent N also showed very high salt rejection and low residual solvent in the product water but the water recovery was too low to be used for high TDS brine (180,000 ppm).

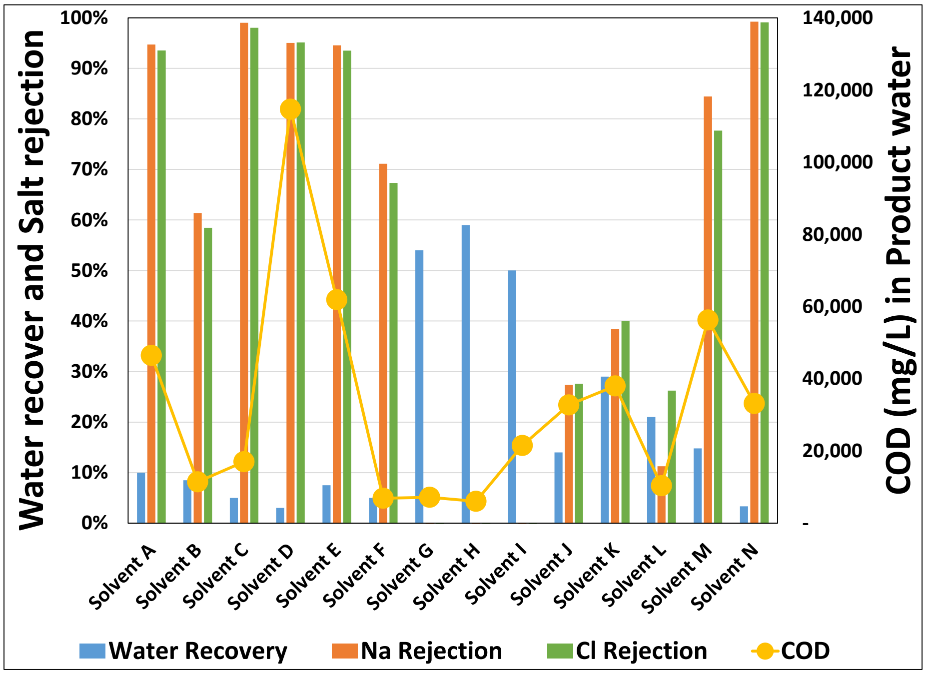


**Figure 10.** Desalination performance of Group 3 solvents.

***Solvent additives for performance improvement*** To improve the solvent desalination performance (water recovery, salt rejection and residual solvent), several approaches were conducted such as mixing two solvents, $CO_2$ addition, and temperature change. The improvement methods and related results are presented below.

As discussed above, several low-temperature water-absorbing solvents exhibited high water recovery and salt rejection in initial screening tests. More detailed experiments were conducted showed that three amine solvents – Solvent A, Solvent B and Solvent C – displayed promising desalination properties (see Figure 10) and were thus downselected for further evaluation. Solvent A had the highest water recovery, and Solvent C had the highest salt rejection. The lowest COD content was found in the product water recovered from Solvent B.

To further increase water recovery and salt rejection and lower COD in the product water, different two-solvent combinations of the three selected amine solvents were prepared and tested. These results are presented in Figure 11. The Solvent A–Solvent B combination showed the highest water recovery and the lowest COD but had the lowest salt rejection relative to the other solvent combinations.

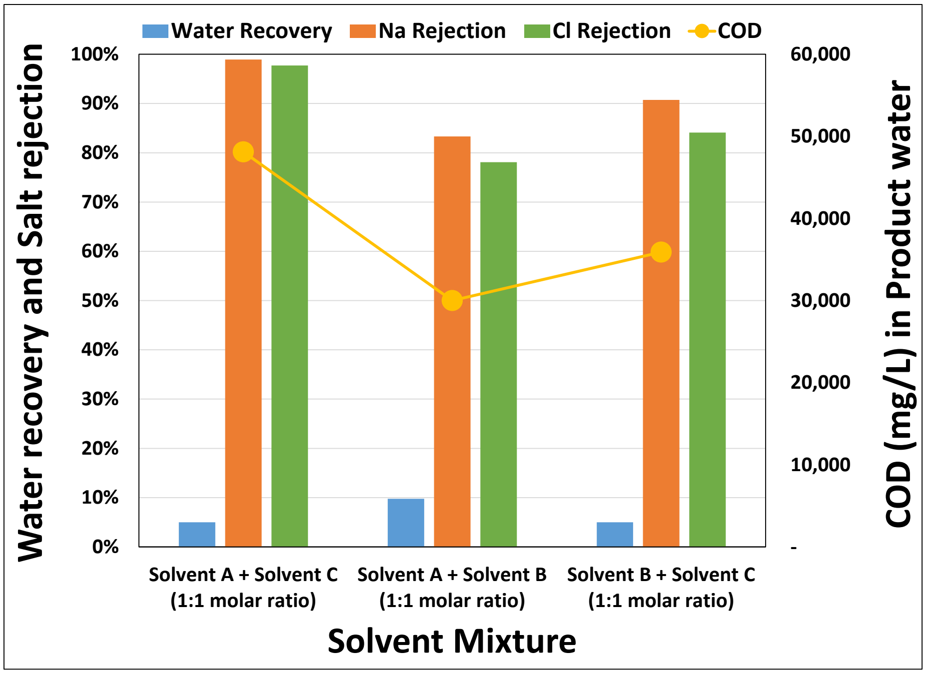


**Figure 11.** Desalination performance of solvent mixtures.

Solvents that showed high salt rejection from previous tests were mixed with Solvent G to improve overall salt rejection performance. Solvent A (94% salt rejection) and Solvent C (98% salt rejection) were mixed with Solvent G and tested using a 0.5 M NaCl solution at varying compositions of each solvent. The results from this experiment are presented in Figure 12  and 13. Solvent C showed the highest salt rejection in the previous test; therefore, it was expected that it could improve the salt rejection of Solvent G by adding more than 40% of total volume. However, Solvent C actually decreased the water recovery performance of the solvent mixture and increased the COD in the produced water significantly (40,000 ppm at 80% Solvent C + 20% Solvent G).

Solvent A increased overall water recovery of the solvent mixture and lowered the COD in the produced water significantly as seen in Figure 12. The water recovery was about 64% with 5% Solvent A and 95% Solvent G. Furthermore, the salt rejection was not increased by mixing the two solvents. The Solvent A and Solvent G mixture can be used as a draw solution for a Forward Osmosis (FO) system, but the COD in the produced water could be a potential obstacle for FO applications. Solvent H was also mixed with Solvent C and tested (data is not shown), but there was no improvement in neither water recovery nor salt rejection.

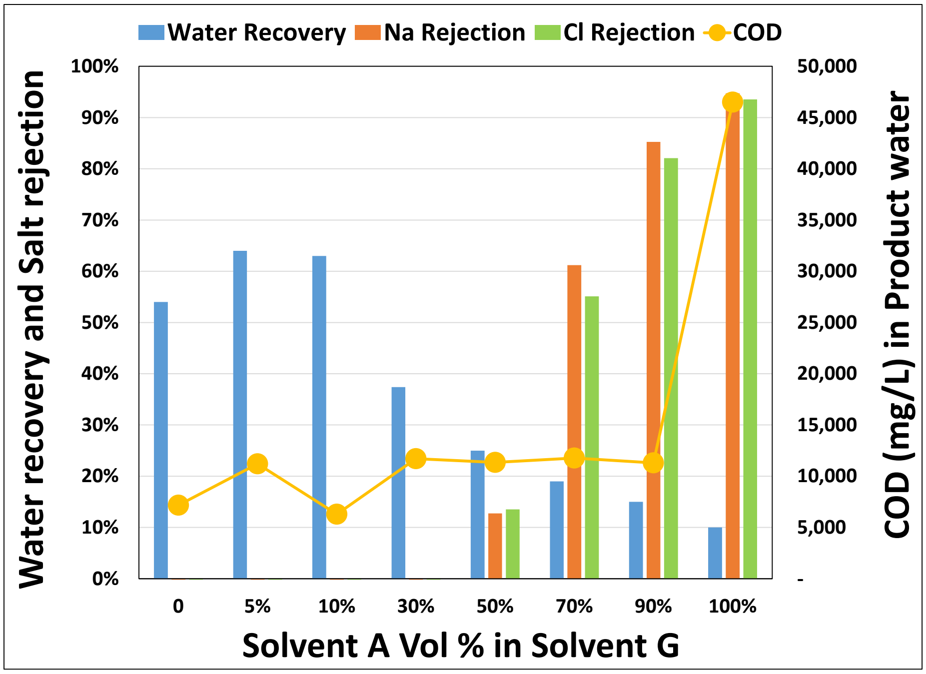


**Figure 12**. Test Results of Solvent A and Solvent G mixture.

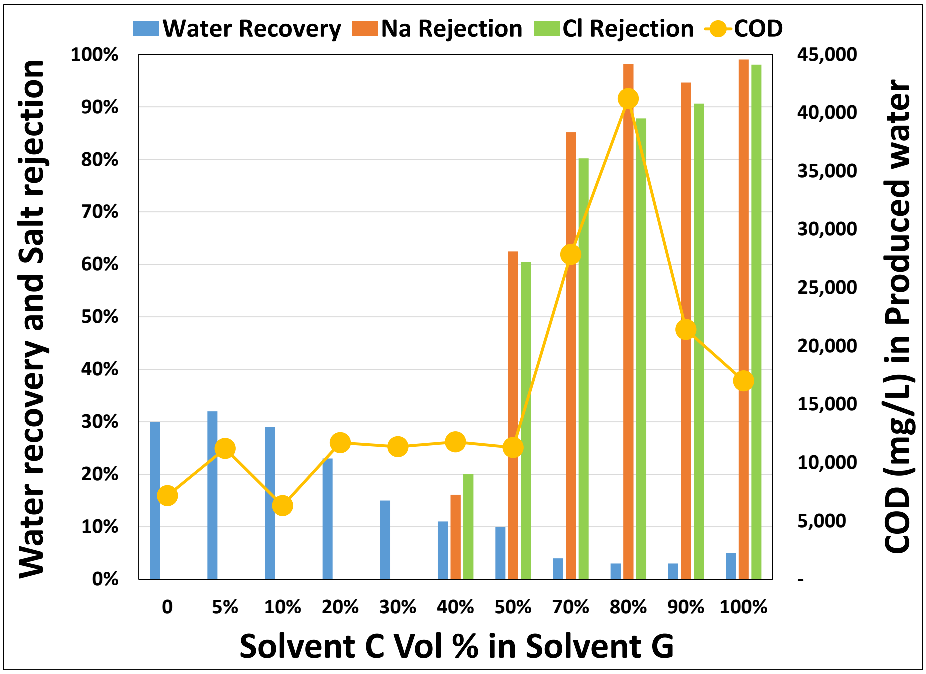


**Figure 13.** Test Results of Solvent C and Solvent G mixture.

$CO_2$ addition was also conducted in order to enhance the water recovery for Solvents A, B and C. Solvents saturated with $CO_2$ were prepared by purging with $CO_2$ for 30 minutes to determine the effect of $CO_2$ on solvent desalination performance. It was found that, while the measured water recovery did increase, the addition of $CO_2$ into the solvents resulted in decreased salt rejection and increased COD in the produced water. As a representative example, Figure 14 summarizes the $CO_2$ effect on the desalination performance of Solvent A. The water recovery achieved was as high as 25% when the portion of $CO_2$-saturated Solvent A was 25 % (v/v). However, the associated salt rejection was very poor (<40%), and the COD content in the product water significantly increased to 385,000 ppm.

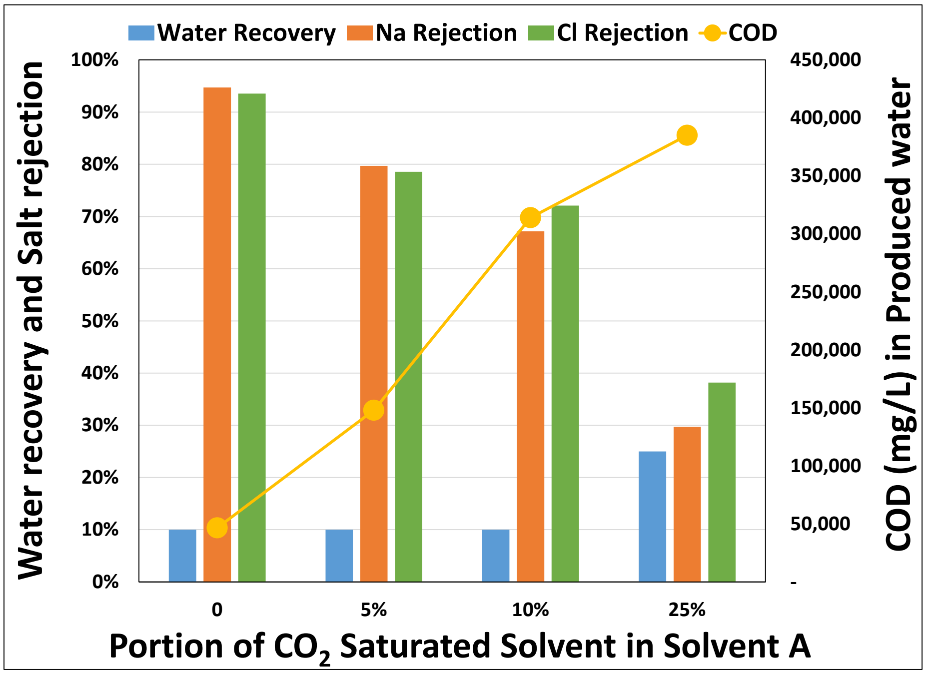


**Figure 14.** $CO_2$ effect on the desalination performance of Solvent A.

Another attempt to increase water recovery and lower COD in the product water was made via addition of alcohol, fatty acid, or low-molecular-weight glycol polymer to the solvents. Although the addition of alcohol and fatty acid proved non-beneficial, the combination of Solvent B and polymer had interesting results. As shown in Figure 15, when the polymer content in the Solvent B–polymer mixture was 10%, the COD of product water was less than 10,000 ppm, the salt rejection was ~60%, and the water recovery was ~10%. From preliminary data collected before this project, the polymer additive used could reject divalent ions and desorb water with a slight increase in temperature. With regard to post-treatment, low COD of the product water recovered from a NAS-based process is desirable to reduce the load on a post-treatment step. However, for a viable NAS-based desalination process, salt rejection must be much higher.

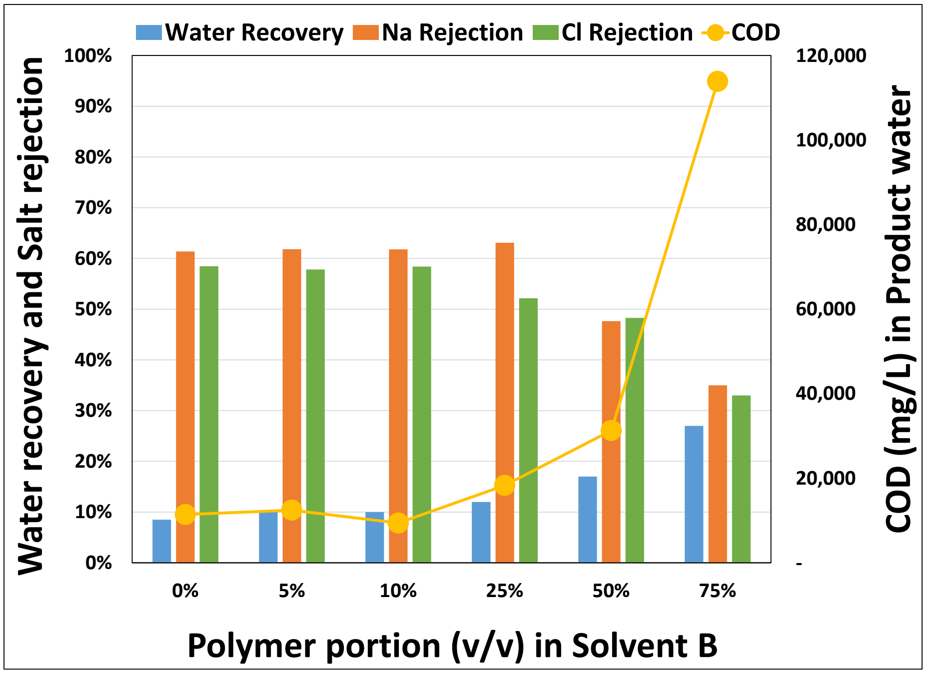


**Figure 15.** Desalination performance of Solvent B–Polymer combination.

The salt rejection mechanism of the solvent desalination process has not yet been proven. Therefore, to test the effect of ion specification on the salt rejection performance, various salt ions such as potassium chloride (KCl) and ammonium chloride ($NH_4Cl$) were tested and compared with that of sodium chloride (NaCl).

Solvent A, B, and C were used for the test and the results are shown in Figure 16-18. The Van der Waals radius of Potassium is 280 pm ($280 \times 10^{-12}$m) and that of sodium is 227pm ($227 \times 10^{-12}$m). Ammonium ions consist of one nitrogen atom and four hydrogen atoms. And both solvent A and C have a linear structure, but Solvent B has one branch in the molecular structure.

The KCl solution increased water recovery of Solvent A and B and decreased water recovery of Solvent C. Salt rejection was increased in Solvent B test and decreased in Solvent A. Solvent B showed negative salt rejection for the $NH_4Cl$ solution. Solvent A water recovery was increased for the $NH_4Cl$ solution test.

No distinct trends could be found in the testing procedures this quarter, but the tests will be continued because the understanding of the solvent desalination mechanism can expedite the solvent identification process.

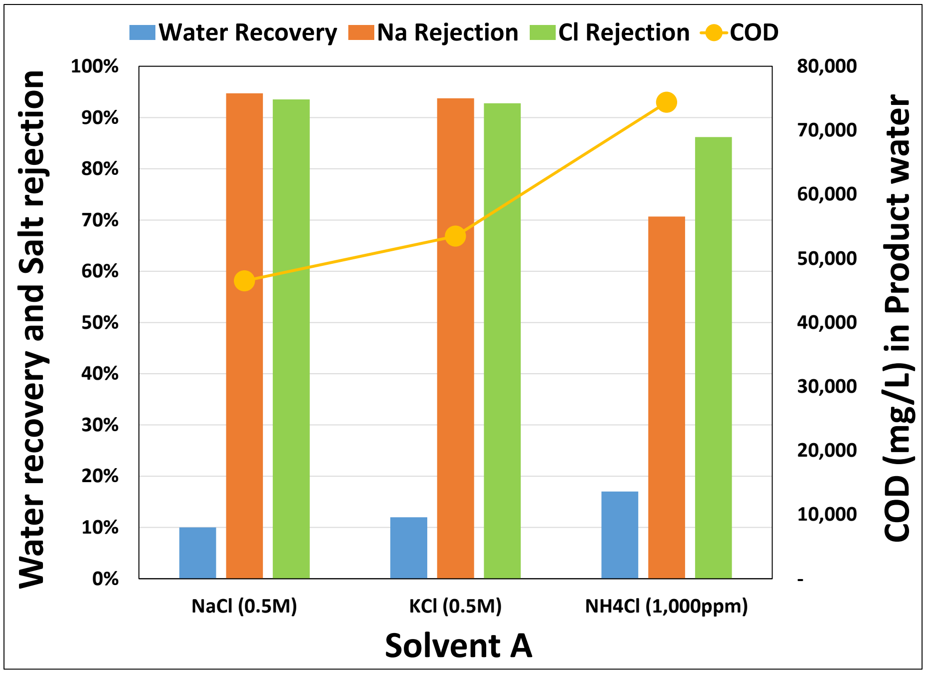


**Figure 16.** Solvent A salt rejection performance on various ions.

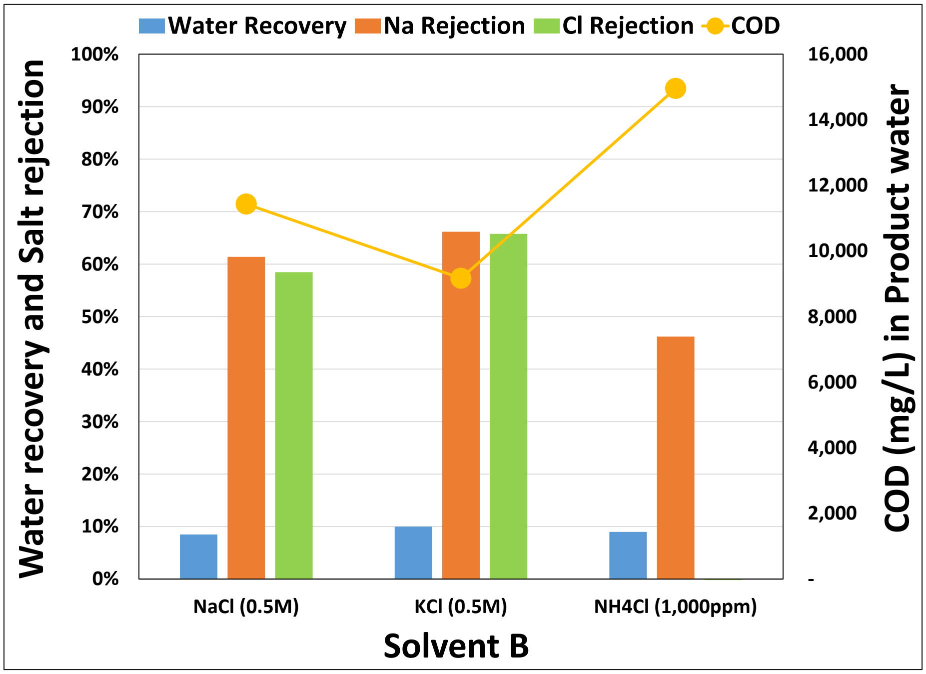


**Figure 17.** Solvent B salt rejection performance on various ions.

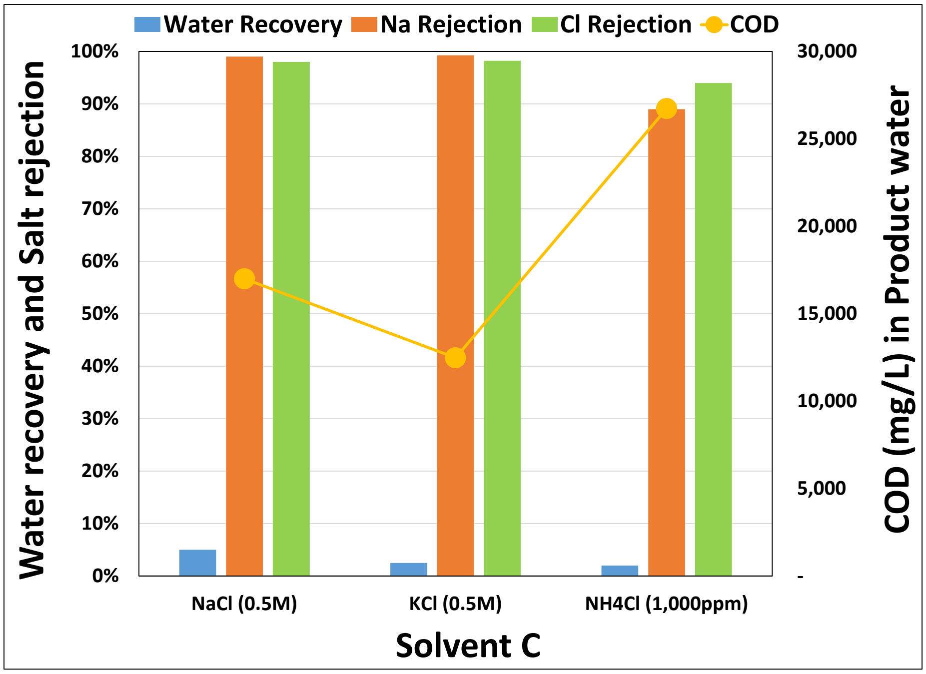


**Figure 18.** Solvent C salt rejection performance on various ions.

The effect of salt concentration in brine was investigated. Solvent A was used as a test solvent and the brine concentration varied from 0.5 M (29,220 mg/L) to 3.1 M (180,000 mg/L). 750 mL of solvent and brine were used for testing to enhance the separation efficiency. Measured water recoveries, salt rejections and CODs in produced water of various brine concentrations are presented in Figure 19. The water recovery decreased as the brine concentration increased. For brine concentration of 3.1M, the water recovery was 2.7%. Prior results demonstrated that decreasing the mixing temperature could improve the water recovery. Therefore, the mixing temperature was reduced to 4 °C to improve the water recovery. The results for increased water recovery (5.3%) at 4 °C mixing temperature is also included in Figure 19. Water content in the solvent and organic content in the water were also measured to understand the exchange between water and solvent. The results are presented in Figure 20. The water content in the residual solvent (after desorption process) was not affected by the brine concentration change. However, the water content in the solvent just after the brine and solvent mixing was significantly affected by the brine concentration. This implied that the water adsorption rate in the initial mixing stage can be the limiting factor for the overall water production efficiency of the solvent desalination process. The organic concentration in the water can be used to measure the quantity of dissolved solvent in the water since there are no organics in the brine.

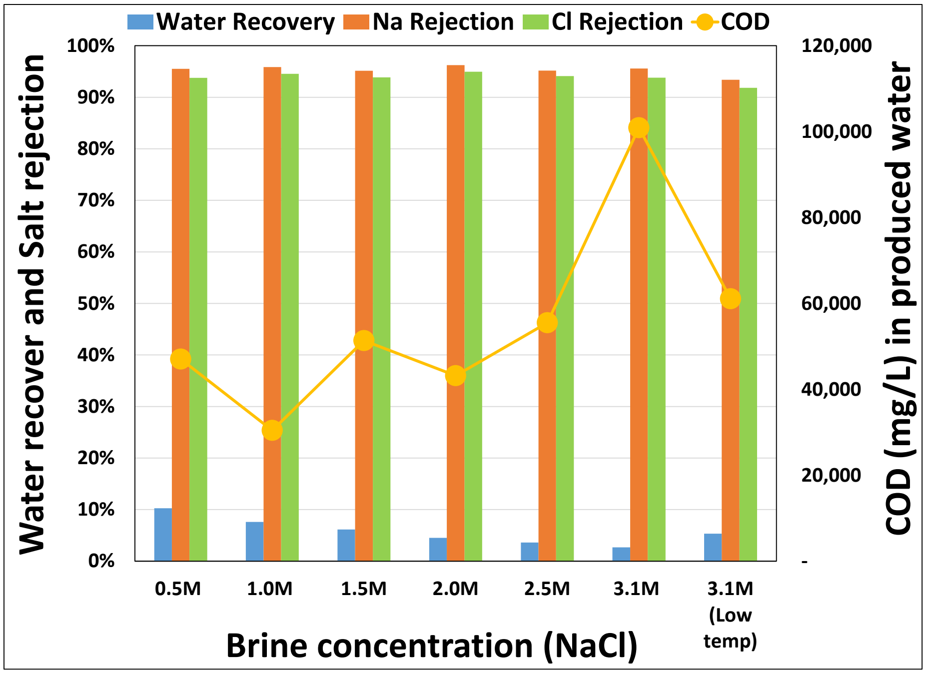


**Figure 19.** Test of the effect of brine concentration on desalination performance.

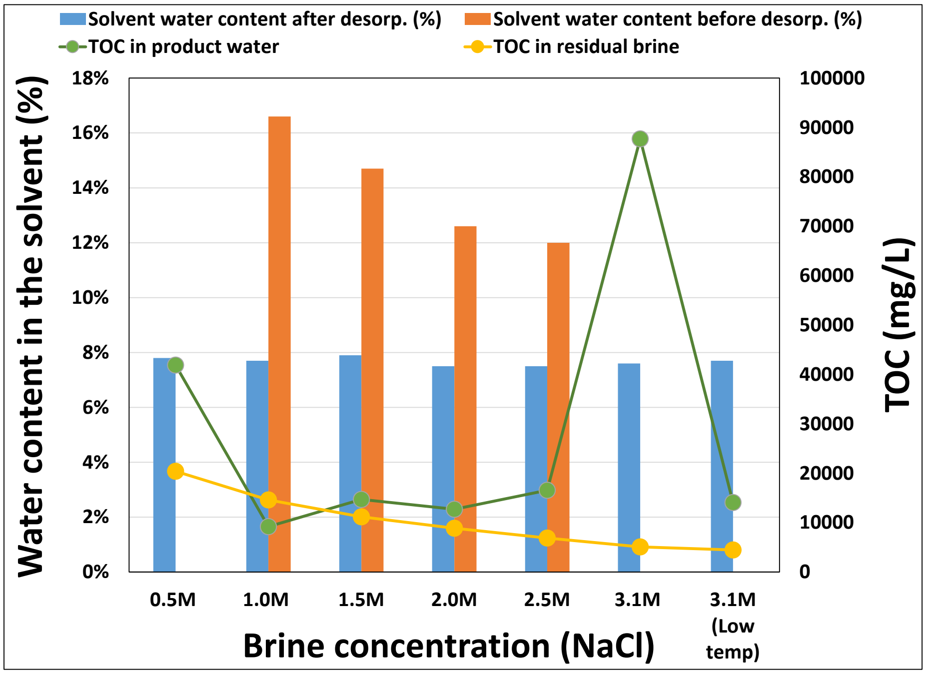


**Figure 20.** Water content and TOC in various brine concentrations.

High salt concentration inhibits the COD measurement so total organic carbon (TOC) was measured to estimate dissolved solvent in the brine. In this experiment, the brine samples were taken after solvent was removed from the solvent/brine mixture. The TOC in the brine sample was measured to estimate how much solvent moved to the brine during solvent/brine mixing. TOCs in the product water from solvent were also measured. The results implied that the brine TOC concentration decreased as the brine concentration increased. The trend of TOC in the product water was not consistent with the trend of TOC in the brine. The TOC in the produced water was highest when the brine concentration was the highest (3.1M). However, the TOC measured in the product water from the low temperature mixing condition was low. Therefore, more testing is required to understand this relationship.

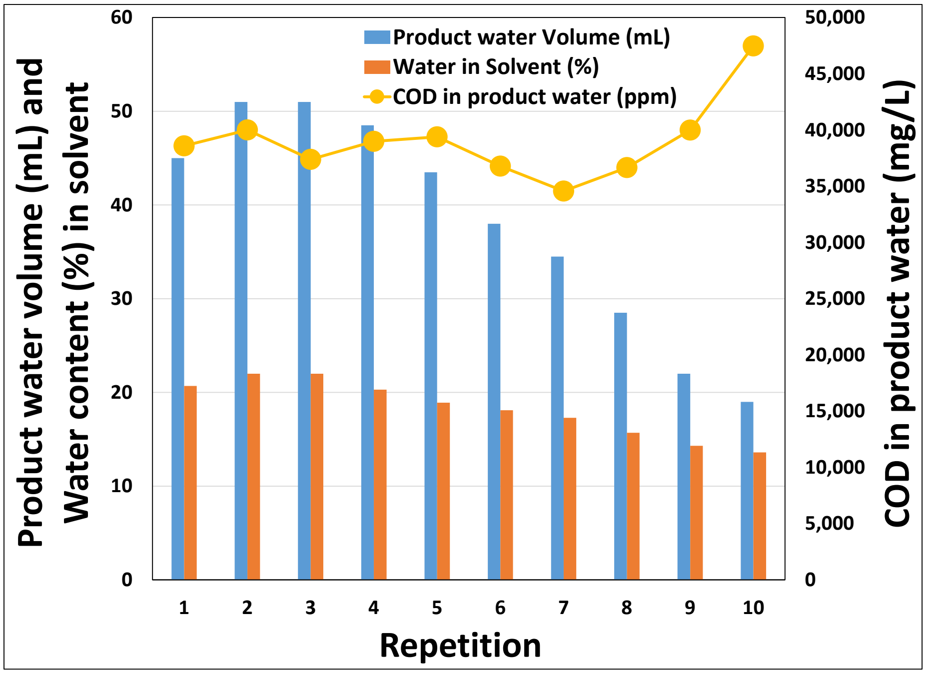


**Figure 21.** Product water quality and water content in the solvent.

***Bench-scale semi-continuous test*** Bench-scale experiments to analyze the salt and residual solvent movement in a semi-continuous process were also conducted to assess performance of the solvent after multiple absorption/desorption cycles. In these tests, 500 mL of 0.5M NaCl brine was used as test brine and was mixed with 500 mL of Solvent A. Solvent A showed the best performance in our testing period in terms of water recovery, salt rejection and residual COD in the product water. The water recovery process (water adsorption and extraction recovery) was repeated without any replenishment of either brine or solvent. The process was repeated 10 times and the product water quality and water content in the solvent phase is shown in Figure 21. The $Na^+$ and $Cl^-$ concentration in brine, product water and solvent are shown in Figure 22 and Figure 23. The overall salt rejection is shown in Figure 23. The water recovery efficiency was sharply reduced after the 5th repetition attempt and the COD in the product water increased after the 8th attempt. The overall water recovery after the 10th attempt was about 381 mL, which accounts for 76% of the initial brine volume. By increasing the brine's salt concentration, the salt concentration in the product water also increased. However, the overall salt rejection efficiency is not affected by the high salt concentration in the brine. The interesting finding in this experiment is that the salt concentration in the solvent was minimal. This means that salt rejection happens during adsorption when water migrates into the solvent phase.

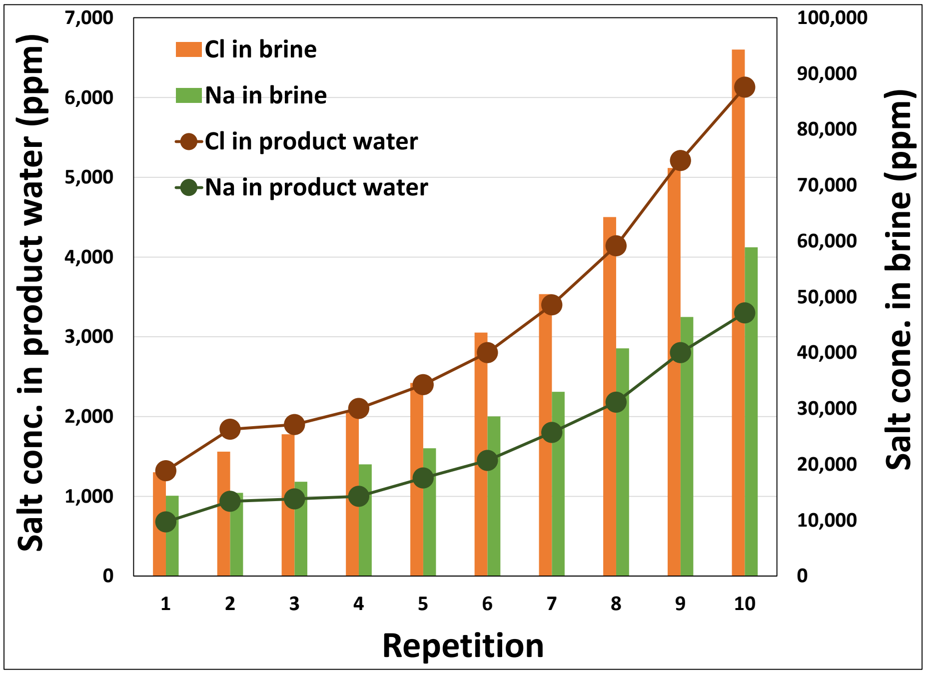


**Figure 22.** $Na^+$ and $Cl^-$ concentration in brine and product water.

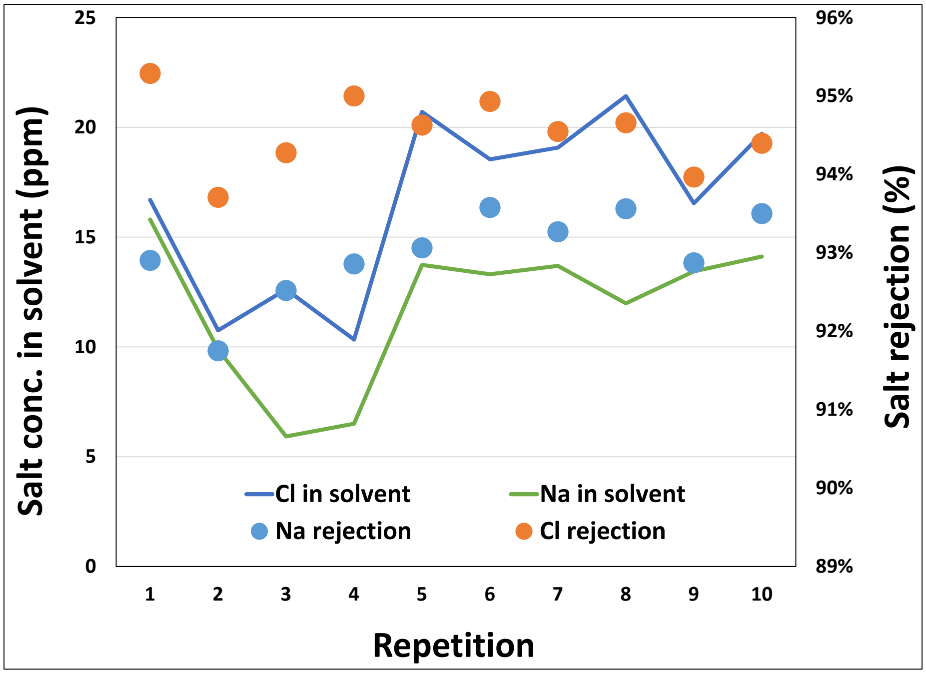


**Figure 23.** $Na^+$ and $Cl^-$ concentration in solvent and overall salt rejection.

## Rational Directional Solvent Design for Water Desalination Using All-Atom Molecular Dynamics Simulations

***Introduction*** Clean water scarcity is a mounting problem wherein access to clean and safe drinking water is denied to 783 million people worldwide [11]. As a result, nearly 80% of illnesses in developing countries can be linked to poor water sanitation [12] and nearly 1 out of every 5 deaths under the age of 5 can be attributed to water related disease [13]. As the world's population continues to grow, water scarcity and access to clean and reliable water sources will become increasingly dire. Current commercial methods of water desalination such as seawater reverse osmosis (SWRO) has achieved filtration rates of 2 to 20 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ [14] and additional mechanisms of salt rejection such as water desalination through functionalized nanoporous graphene [15] and directional solvent desalination [16] are currently being explored.

This research is concerned with the latter: designing a small organic solvent that will selectively reject salt while absorbing recoverable pure water. Characteristics such as molecular weight, linearity, and degree of shielding on the electronegative moiety inform the viability of a potential solvent molecule as a simultaneous water acceptor and ion rejector. The work outlined below is concerned with the rational design of the target solvent molecule from information obtained using all-atom molecular dynamics simulations. It is the aim of this research that correlations can be drawn from the previously mentioned characteristics to a solvent molecule's water purification performance so that an optimal solvent molecule geometry and chemistry can be elucidated to avoid spurious and costly testing in the lab.

***Methods*** All-atom molecular dynamics simulates nanoscale phenomena by iteratively solving Newton's classical equations of motion for a system of potentially millions of atoms. In these systems, individual atoms are treated as hard spheres joined by flexible, unbreakable bonds. Initial positions and velocities for each atom in the system are specified and a coordinate dependent potential energy function $V(r^N)$ is chosen. For this system, we adopt the widely used General AMBER force field (GAFF) [17]:

$$V(r^N) = \sum_{\text{bonds}} k_b(l-l_0)^2 + \sum_{\text{angles}} k_a(\theta-\theta_0)^2$$

$$+ \sum_{\text{torsions}} \sum_{n} \frac{1}{2} V_n[1+\cos(n\omega-\gamma)] + \sum_{j=1}^{N-1} \sum_{i=j+1}^{N} f_{ij}\left\{\epsilon_{ij}\left[\left(\frac{r_{0ij}}{r_{ij}}\right)^{12} - 2\left(\frac{r_{0ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}\right\}$$

In this function, the first summation represents the energy contribution from the oscillation of covalent bonds. The second summation represents the energy contribution from the vibration of the angles between three bonded atoms. The third (double) summation represents the energy contribution from the twisting of torsional angles between four bonded atoms. Finally, the last (double) summation represents the energy contribution from non-bonded interactions in two components: a 12-6 Leonard-Jones van der Waal's energy (first term) and an electrostatic Coulombic energy (second term). Together, these energy terms constitute the total potential energy for each molecule in the system. Once this potential energy is known, the force acting on each atom in the system can be calculated from the relation $F = -\nabla V(r^N)$. This force, together with the specified initial positions and velocities, is sufficient to calculate the positions and velocities of each atom one time step (2 fs) in the future. This technique is performed iteratively until the system has evolved for 100 total nanoseconds. All simulations are performed using the molecular dynamics package AMBER, all visualizations are performed in the software VMD [18], and analyses are performed using in-house Python scripts.

***System setup*** Each system is modeled inside a box of side length between 70 to 80 Å with periodic boundary conditions in all three dimensions. The boxes are filled with 1,000 solvent molecules, and a variable number of water molecules and sodium and chloride ions. The number of water molecules is on the order of 8,000 and the number of ions is on the order of 75 each. Modulating the number of water and ions in each systems ensures that system is at a consistent solvent and ion concentration across all solvents. Initially, the molecules are randomly and uniformly distributed throughout the box and evolve over time into an equilibrium state (Figure 24).

In this research, eighteen solvents have been simulated exhibiting varying degrees of branching, shielding of the electronegative moiety, and molecular weight.

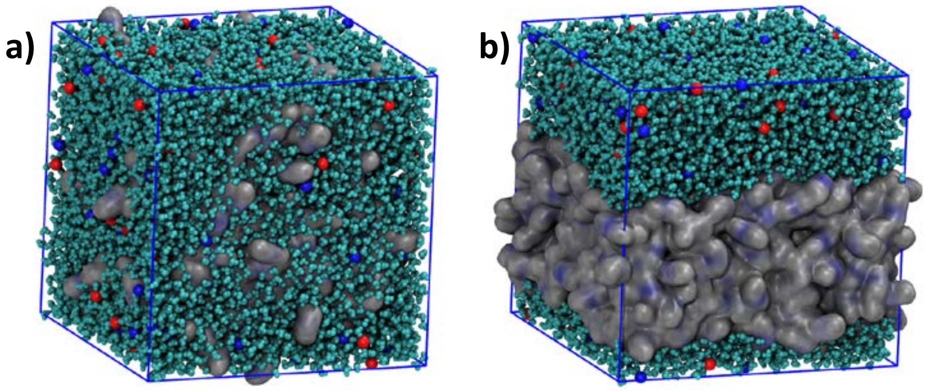
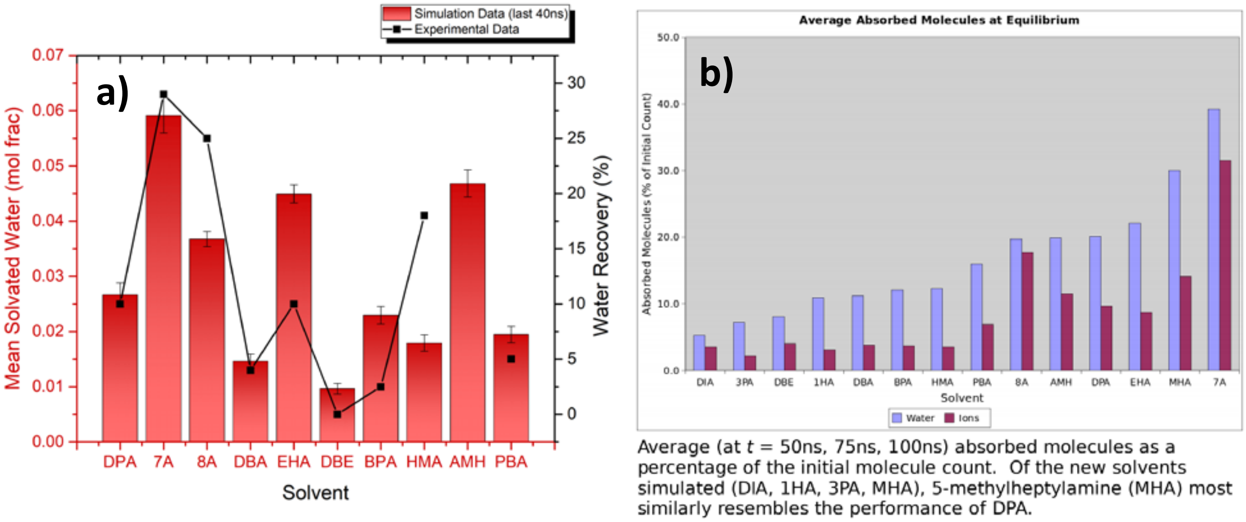


**Figure 24.** Initial (a) and final (b) configurations for a solvent in water simulation. Solvent molecules are grey\blue surface, water molecules are cyan, and ions are solid red/blue spheres. After 100 ns, an

amorphous monolayer structure has formed inside which some water molecules have been captured while ions remain in the water bulk.



Average (at *t* = 50ns, 75ns, 100ns) absorbed molecules as a percentage of the initial molecule count. Of the new solvents simulated (DIA, 1HA, 3PA, MHA), 5-methylheptylamine (MHA) most similarly resembles the performance of DPA.

**Figure 25.** (b) Majority agreement in mean solvated water from experiment and simulation data for ten solvents. (a) Analysis of captured water (blue) and ions (magenta) for fourteen solvents as a percentage of total water/ion molecules.

***<u>Results</u>*** Regarding ion rejection, preliminary analysis of these simulations show majority agreement with experimental results with most solvents. A separate analysis of captured water molecules and captured ions illustrates the relative performance of solvents as ions rejecters and water acceptors (Figure 25).

Qualitative trends have been intuited from these results. For example, solvent molecules with unshielded moieties tend to self-assemble into bilayers, trapping large quantities of both water and ions between layers of solvent while solvents with more shielded moieties assemble into monolayers which are more prone to reject ions. Some highly branched solvents resist assembling into layered structures, creating captured regions of both water and ions within a solvent network (Figure 26).

Molecular geometry and chemistry have shown to have a strong impact on the self-assembly of small-molecular weight solvents in water which impacts with water-recovery and salt-rejection performance. While strong predictions on the performance of a given chemistry are not yet possible, promising solvents exhibit low branching and shielded electronegative moieties.

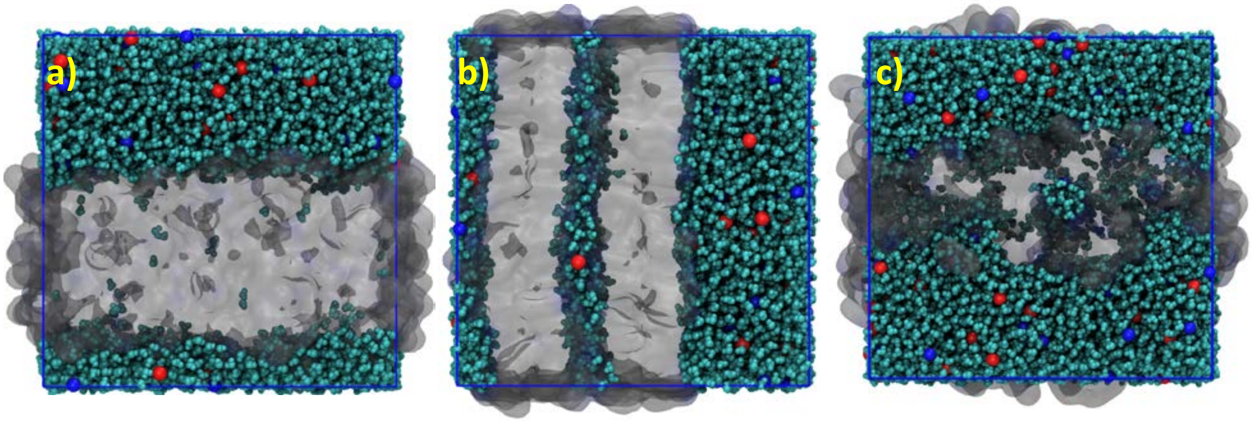


**Figure 26.** Various modes of self-assembly for three different solvents at equilibrium. Solvents that assemble into bilayers (b) and networks (c) tend to trap both water and ions and thus exhibit high water recovery but low salt rejection which is congruent with experimental data. Solvent is shown as a transparent gray surface, water is cyan, and ions are solid red/blue spheres.

## Solvent Desalination Process Development

The overall solvent desalination process can be categorized into three main parts: water absorption, brine separation and water desorption. NAS is mixed with high TDS brine to transfer water from the brine phase into the solvent phase. Intense mixing can break down solvent and water into micro droplets in order to increase contacting layer of solvent and water. Based on experimental results, salt rejection occurs in this stage. After the water absorption stage, the water-laden solvent is separated from brine by gravitation, which equilibrates in 5 – 10 minutes. In water desorption stage, high heat decreases water’s solubility in solvent and precipitation ensues. The precipitated water is separated from solvent by gravitation as well. The product water from the last separation stage will go through post treatment step as a polishing step. The conceptual solvent desalination process is presented in Figure 27.

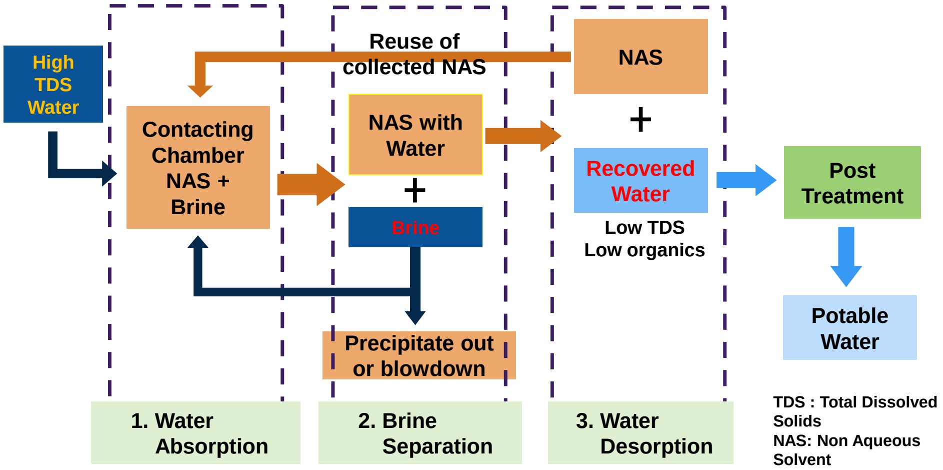


**Figure 27.** Conceptual NAS desalination process.

A PFD was prepared in this project for a potential pilot plant using NAS for desalination. Based on the solvent test results, the brine and solvents are mixed in an in-line mixer and are moved to a solvent separation tank. The solvent will absorb water and increase in volume. This portion of solvent with pure water drawn in will be separated and then pass through a heat exchanger which will heat up the mixture and induce phase separation. With gravity, the treated water is separated from the solvent and collected as the final product water. A membrane system with one heat exchanger was added at the post treatment step to contribute to additional purification. The heat exchanger was installed to lower the product water temperature (< 40 °C) to protect the membrane. Another three heat exchangers were added for solvent heating and cooling. The PFD is shown in Figure 28. This PFD can be utilized to design a continuous large scale system for pilot plant testing.

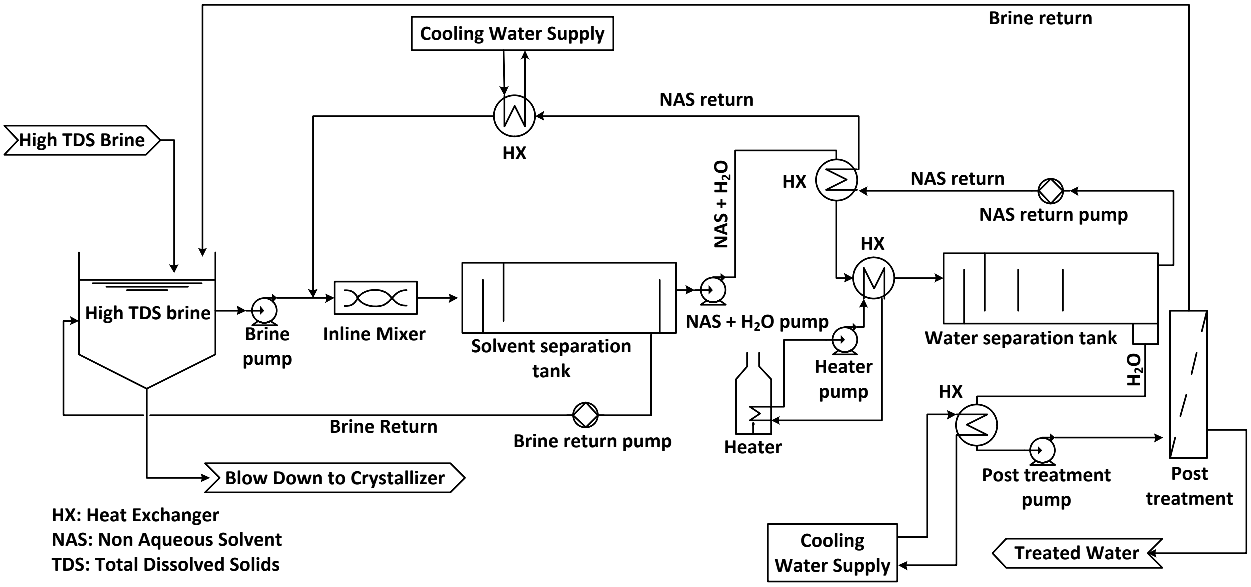


**Figure 28.** Proposed NAS desalination PFD for pilot system.

## Techno-economic assessment

A process techno-economic assessment was conducted to assess the projected economic costs of the solvent-based desalination concept for the treatment of high TDS brines generated from brine extraction. 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 1,000 $m^3$/day of high TDS (180,000 mg/L) wastewater must be produced based on 50% recovery. This is used to develop tank size requirements, pumps sizes, energy requirements and an assessment of the capital and operating requirements for a full-size plant. We project our energy consumption will be about 40 – 60 $kWh_{th}/m^3$ or equivalent of GOR 15 for treating high TDS brine, which is about a 10-fold improvement over current thermal desalting processes. The key parameters that determine NAS economic viability are the salt rejection rate, water recovery, minimum temperature swing, and solvent loss.

***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 4.

**Table 4.** Indirect cost components multiplier.

| Indirect cost component | Factor | |
|---|---|---|
| Construction Overhead | 4% | of Total Direct Capital costs |
| Contingency | 6% | of Total Direct Capital costs |

| | | |
|---|---|---|
| A&E fees; Project Management | 12% | of Total Direct Capital costs |
| Working Capital | 4% | of Total Direct Capital costs |

***__Operating 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
- Solvent Makeup
- Repairs and replacement

***__Key Assumptions__*** The estimation of total costs incurred for a project during its lifetime in operation is essential to evaluate or to compare a process against any other. The total costs incurred on the project in its lifetime can broadly be classified into the total capital costs and total operating costs. The project lifetime was 20 years, and the interest rate was assumed to be 1.6%, based on reported desalination projects. The key capital and operating expenses were assumed for the scenario include:

- Cost of Electricity = 0.12 $\$/kWh_e$
- Cost of Thermal Heating = 0.12 $\$/kWh_{th}$ (based on natural gas price of $3.2/MMBTU)
- Solvent price = $3/gallon
- Solvent desalination cycle time = 15 minutes
- Average salt rejection 99%
- Solvent loss = 15% per year

***__TE Results and Discussion__*** Because this process does not involve high pressures or temperatures, most of the piping can be constructed using PVC instead of super duplex or titanium, which are the standard for thermal desalination plants. Using polymeric material can significantly reduce the levelized cost of water (LCOW). For the current LCOW estimate, we used a 15% loss per year as the basis, which is modeled after a typical membrane replacement rate. The long-term stability of solvents cannot be predicted by modeling and needs to be verified in controlled experiments over time. Also selecting appropriate material for pipes and tanks that are compatible with the NAS is critical. The energy consumption will be very sensitive to the temperature swing necessary for water recovery. For example, for single-stage recovery of 20%, ΔT = 50 °C, the LCOW is $3.51/m3, 90% of which is thermal operating costs; for 20% and 10 °C, the LCOW is $0.91, 69% of which is thermal costs. The impact on the tradeoffs between the high and low temperature swing cases is illustrated below Table 5, which shows a direct comparison for 10 °C and 50 °C temperature swings.

**Table 5.** LCOW comparison between high and low temperature solvent systems designed for 1000 $m^3$/day flow and 50% recovery.

| Operational Parameter | ΔT = 10 ºC | ΔT = 50 ºC |
|---|---|---|
| **Feed Flow ($m^3$/day)** | 2,000 | 2,000 |
| **Recovery (%)** | 50% | 50% |
| **Annual Capital Payment ($/yr)** | $50,655 | $66,533 |
| **Thermal Energy Cost ($/yr)** | $95,434 | $477,169 |
| **All Other Operating Costs ($/yr)** | $58,444 | $58,444 |
| **Solvent use (kg/yr)** | 825 | 4990 |
| **LCOW ($/$m^3$)** | $0.56 | $1.65 |

The preliminary results show that the operational cost of heating the solvent is the main driver of the economic viability for solvent based desalination processes under the solvent cost and loss assumptions used for this analysis. The capital costs account for 25% and 1% of the LCOW for this system, for 10 and 50 °C cases respectively. The reason for the disparity in the two cases is that the thermal energy costs increases from $95k annually, to more than $477k, which is a 385% increase in energy costs from 10 °C to 50 °C. The remaining 28% and 10% at 10 °C and 50 °C, respectively, of the LCOW are due to the other operating costs, which are unlikely to change much based on the assumptions used in the analysis. This analysis illustrates the importance in temperature swing on the economic viability of this technology, and should be a major focus for future development. Even though solvent cost and residual solvent may incur costs, these costs can be addressed through different strategies or by changes in economies of scale, so are less critical drivers at this stage of development. However, future techno-economic assessment should include these factors and refine them as more information is obtained, in addition to key performance metrics such as salt rejection, water absorption, and solvent loss. The results demonstrate that the solvent desalination approach continues to show potential as a cost savings breakthrough technology for high TDS water treatment.

# 5. CONCLUSIONS

The NAS desalination process was shown to be applicable for high salinity brine which the RO process cannot treat. A key outcome of this study is that thermal desalination was achieved without using latent heat to induce phase change (liquid ↔vapor), which is required for all other thermal desalination processes. This shows that the NAS desalination approach has a potential for significant energy savings compared with established thermal desalination technologies. The water solubility temperature swing and selective absorption are key characteristics of NAS that will determine the feasibility of desalination processes using this technology. Three mechanisms were investigated in this study to find optimal NAS for desalination: (1) $CO_2$ gas absorption, (2) high-temp absorption to low-temp desorption (thermally switchable), and (3) low-temp absorption to high-temp desorption (thermally switchable). Among these mechanisms, thermally switchable (low-temp absorption to high-temp desorption) showed the best combination of high water recovery and adequate salt rejection.

The following technical conclusions were made from this project:

- Several amine solvents were identified as suitable candidates for NAS desalination technology (>90% salt rejection and >5% water recovery from 0.5 M NaCl brine). One solvent showed more than 10% water recovery and higher than 94% salt rejection.

- Experimental results showed that chemistry modifications to the solvent (addition of other solvents, polymer compounds, or fatty acids) can enhance the desalination performance in certain cases. However, not all additives were successful, and in some cases, such as mixing two solvents with different desirable performance characteristics (ex. water uptake and salt rejection) decreased the overall desalination performance of both characteristics in the mixture. The complex nature of water uptake, salt rejection, and residual solvent requires further study and performance is not always additive.

- Semi-continuous testing showed that the solvent performance was maintained after repeated cycles, and there was no buildup of salt within the solvent phase. This suggests that the solvent material can be recovered and reused in a larger scale continuous system. Further long term testing will be needed to demonstrate performance over longer time scales.

- Lowering the water absorption temperature increases water recovery significantly and was shown to be a key factor in achieving water recovery >5% for high TDS brine (180,000 ppm). Increasing the water desorption temperature improved water solvent separation.

- The salt rejection was shown to occur in the water absorption step.
- The MDS results showed agreement with experimental results, which shows it can a useful tool in the rapid assessment of different solvent chemical structures.

# 6. RECOMMENDATIONS

We would like to make recommendations as follows:

- MDS was shown to be a very efficient and cost-saving tool for the screening of candidate solvents. Further efforts to improve desalination performance by investigating different solvent chemical structures and functional groups should employ MDS to quickly down select candidates for experimental validation.
- The recovery of solvent from the product water was important to improve product water quality and reduce operating cost. Future testing should include a detailed assessment on technology alternatives for final stage product water polishing and solvent recovery/recycle.
- A key focus for solvent chemistry improvements should be on reducing the temperature difference between water absorption and desorption.
- Future testing should also incorporate water samples with complex contaminant matrices, which will be important in identifying variation in solute rejection.
- It is necessary to conduct much longer-term testing to evaluate the longevity of the solvent. Longer-term testing will also help the advancement of this technology by providing seasonal variation in the feed water conditions.

# References

1. "Extraction of Formation Water From $CO_2$ Storage." (2012). Report No. 2012/12. International Energy Agency (IEA) Environmental Project. November 2012.

2. Buscheck, T.A., Sun Y., Hao Y., Wolery T.J., Bourcier W., Tompson A.F.B., Jones E.D., Friedman S.J., & Ains R.D. (2011). Combining Brine Extraction, Desalination, and Residual-Brine Reinjection with $CO_2$ Storage in Saline Formations: Implications for Pressure Management, Capacity, and Risk Mitigation. *Energy Procedia*, (4) 4283-4290.

3. Annual Energy Outlook 2014. (2014) U.S. Energy Information Administration. Available at: www.eia.gov/forecasts/aeo.

4. Clark, C. E., & Veil, J. A. (2009). *Produced Water Volumes and Management Practices in the United States*: United States Department of Energy, Argonne National Laboratory.

5. C. N. Kimberlin, Jr., et al "Desalination by Solvent Extraction," U.S. Patent: 3,177,139, issued date April 6, 1965.

6. K. Thanapalan & V. Dua. (2011). Using Low-Grade Heat for Solvent Extraction based Efficient Water Desalination. *21st European Symposium on Computer Aided Process Engineering - ESCAPE 21*.

7. A. Bajpayee, T. Luo, A. Muto, and G. Chen, "Very low temperature membrane-free desalination by directional solvent extraction," *Energy & Environmental Science*, vol. 4, p. 1672, 2011.

8. D. Rish, S. Luo, B. Kurtz, and T. Luo, Applied Physics Letters, 2014, 104, 024102

9. M. Stephenson, *J. Chem. Eng. Data*, **1992**, 38, 625-629

10. Davison, R. Smith, W. Hood, D. *Journal of Chemical and Engineering Data.* Vol 5, No. 4, 420-423, **1960**.

11. WHO/UNICEF Joint Monitoring Programme for Water Supply and Sanitation. "Progress on Sanitation and Drinking Water 2010." Available at www.wssinfo.org/

12. United Nations. Statement by Secretary General Koffi Annan. June 2003. http://www.un.org/News/Press/docs/2003/sgsm8707.doc.htm

13. WHO/UNICEF. "Diarrhoea: Why children are still dying and what can be done." 2009. available at http://www.unicef.org/health/index_51412.html.

14. G. Guillen, E.M.V. Hoek, Modeling the impacts of feed spacer geometry on reverse osmosis and nanofiltration prrocesses, Chem. Eng. J. 149 (1-3) (2009) 221-231.

15. Wang, Yunhui, Zhongjin He, Krishna M. Gupta, Qi Shi, and Ruifeng Lu. "Molecular Dynamics Study on Water Desalination through Functionalized Nanoporous Graphene." Carbon 116 (May 2017): 120–27. https://doi.org/10.1016/j.carbon.2017.01.099.

16. Luo, Tengfei, Anurag Bajpayee, and Gang Chen. “Directional Solvent for Membrane-Free Water Desalination-A Molecular Level Study.” Journal of Applied Physics 110, no. 5 (September 1, 2011): 054905. https://doi.org/10.1063/1.3627239.

17. R. Salomon-Ferrer, D.A. Case, R.C. Walker. An overview of the Amber biomolecular simulation package. *WIREs Comput. Mol. Sci.* 3, 198-210 (2013).

18. Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", J. Molec. Graphics, 1996, vol. 14, pp. 33-38.