

Supporting Information

Zero Liquid Discharge of Ultrahigh Salinity Brines with Temperature Swing Solvent Extraction

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MATERIALS AND METHODS

Assessment of Energy Consumption. Specific energy requirement, defined as the energy required to achieve TSSE-ZLD of a cubic meter of brine, was evaluated as a function of brine to solvent ratio. The brine feed is simulated by 5.0 M NaCl solution and the low and high temperatures, T_L and T_H , utilized are 5 and 70 °C, respectively, i.e., temperature swing of 65 °C. The heat energy required to raise the temperature of the water-laden solvent from $T_L = 5$ °C to $T_H = 70$ °C was calculated with specific heat capacity data (1.16 for water and 0.62 Whkg⁻¹K⁻¹ for solvent, approximating with DIPA), assuming additivity and neglecting non-ideal effects of the mixture. The energy input to drive TSSE-ZLD is then determined by assuming the thermal recovery efficiency of 90%, i.e., temperature difference across the heat exchanger of Figure 4 is 6.5 °C.

Theoretical Minimum Energy for Zero-Liquid Discharge of Saline Feeds.

Theoretical minimum energy demand for ZLD is equivalent to the Gibbs free energy of separation. Here, a simplified scenario is considered, with NaCl solution as the saline feed and 100% salt removal, i.e., pure water and pure NaCl solids as products. Hence, the Gibbs free energy of separation is the difference between the sum of Gibbs free energy of the final pure components and the Gibbs free energy of the initial mixture, minus the enthalpy of solution, ΔH_{sol} . The Gibbs free energy of separation per mole of the mixture, ΔG_{sep} , which corresponds to the theoretical minimum energy required to achieve ZLD of a mole of the saline feed, $E_{min,ZLD}$, is therefore

$$\Delta G_{sep} = \phi_s G_s + \phi_w G_w - G_M \quad (S1)$$

where G is molar Gibbs free energy, ϕ is mole fraction relative to total system, and subscripts s, w, and M denote pure salt, pure water, and mixture, respectively. Note that $\phi_s + \phi_w = 1$.

In a solution containing two or more species, the partial molar Gibbs energy of species i , \bar{G}_i , describes the free energy per mole of the individual species in solution.¹

$$\bar{G}_i = G_i(T, P) + \Delta H_{mix} + RT \ln(\gamma_i x_i) \quad (S2)$$

where $G_i(T, P)$ is the molar Gibbs energy of pure species i at temperature T and pressure P , R is the gas constant, ΔH_{mix} is the enthalpy of mixing, and x_i is the mole fraction of species i in solution.

The activity coefficient, γ_i , is incorporated to account for the behavior of non-ideal solutions and can be determined as a function of the temperature, pressure, and solution composition. The total molar Gibbs free energy of the solution, G , is a measure of the thermodynamic potential of one mole of the solution and is the sum of the weighted contribution of the individual species.²

$$G = \sum x_i \bar{G}_i = \sum x_i G_i + \sum x_i \Delta H_{mix} + RT \sum x_i \ln(\gamma_i x_i) \quad (S3)$$

Following eq S3, the total molar Gibbs free energy of an NaCl solution is expressed as:

$$G_M = x_s G_s + x_w G_w + x_s \Delta H_{sol} + RT [x_s \ln \gamma_s x_s + x_w \ln \gamma_w x_w] \quad (S4)$$

The enthalpy of solution, ΔH_{sol} , accounts for the endothermic breaking of bonds between the solute (here, the ionic bonds within the NaCl crystal lattice), the endothermic breaking of intermolecular bonds between solvent (i.e., hydrogen bonds in water), and the exothermic formation of solvent-solute attractions (that is, water-ions interactions). For the specific scenario considered here, $\phi_s = x_s$ and $\phi_w = x_w$. Inserting eq S4 into eq S1 yields an expression for the molar Gibbs free energy of ZLD separation, based on the compositions and activity coefficients of salt and water in the initial NaCl feed.

$$\Delta G_{sep} = -x_s \Delta H_{sol} - RT [x_s \ln \gamma_s x_s + x_w \ln \gamma_w x_w] \quad (S5)$$

Using the correlation model developed by Pitzer, ΔH_{sol} of 3.88 kJ/mol, and the appropriate molar volume conversion,³⁻⁵ $E_{min,ZLD}$ is determined to be 14.9 kWh/m³ for 5.0 M NaCl solution.

Table S1. Solution properties of actual RO concentrate from the San Luis plant, CA, which desalinates irrigation drainage water from the San Joaquin Valley, and the brine concentrated by thermal evaporation and adjusted with saturated NaCl solution, employed for TSSE-ZLD experiments.

| | pH | conductivity (mS/cm) | TDS (g/L) | TOC (g/L) |
|-----------------------|------|-------------------------|--------------|--------------|
| RO Concentrate | 7.75 | 38.4 | 36.6 | 0.31 |
| Concentrated Brine | 7.55 | 242.7 | 295.4 | 0.42 |

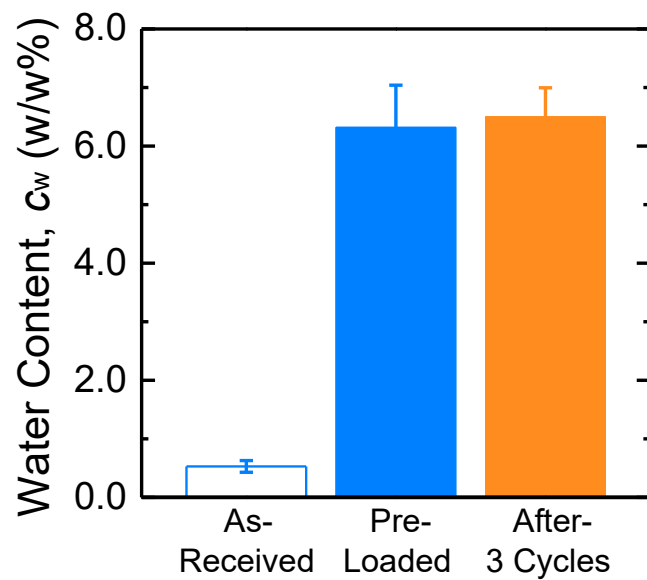


Figure S1. Water content in as-received DIPA solvent, solvent preloaded with DI water for the experiment with repeated TSSE cycles, and solvent after three repeated cycles of TSSE-ZLD.

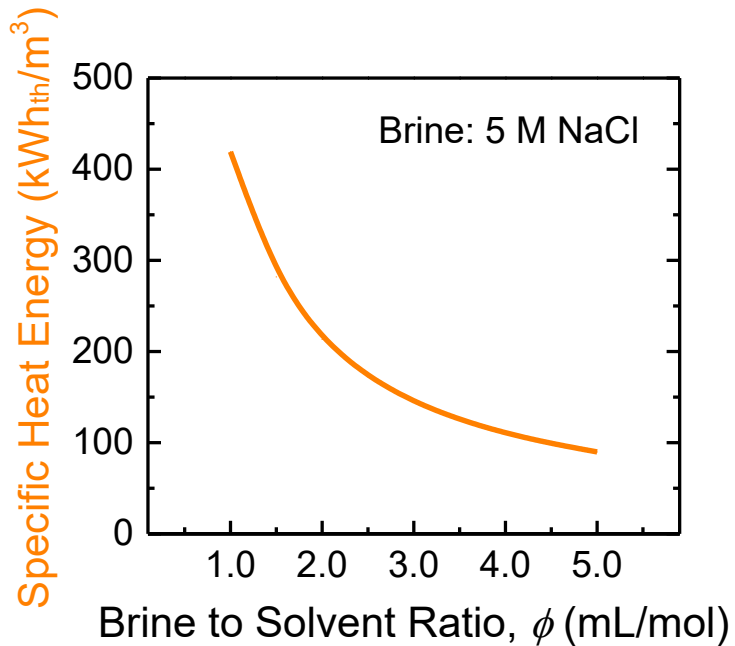


Figure S2. Specific heat energy for ZLD treatment of a cubic meter of hypersaline brine (simulated with a NaCl solution of 5.0 M or 292,000 ppm TDS) by TSSE, as a function of brine to solvent ratio. Thermal recovery efficiency is assumed to be 90% and temperature swing is from $T_L = 5\text{ }^\circ\text{C}$ to $T_H = 70\text{ }^\circ\text{C}$.

References

1. Smith, J. M.; Van Ness, H. C.; Abbott, M. M., *Introduction to chemical engineering thermodynamics*. 7th ed.; McGraw-Hill: Boston, 2005; p xviii, 817 p.
2. Yip, N. Y.; Elimelech, M., Thermodynamic and Energy Efficiency Analysis of Power Generation from Natural Salinity Gradients by Pressure Retarded Osmosis. *Environ Sci Technol* **2012**, *46*, (9), 5230-5239.
3. Pitzer, K. S.; Peiper, J. C.; Busey, R. H., Thermodynamic Properties of Aqueous Sodium-Chloride Solutions. *J Phys Chem Ref Data* **1984**, *13*, (1), 1-102.
4. Sandler, S. I., *Chemical and engineering thermodynamics*. 2nd ed.; Wiley: New York, 1989; p xxiii, 622 p., 2 p. of plates.
5. *CRC handbook of chemistry and physics*. 100th ed.; CRC press: 2019.