# Supporting Information

to

“Energy efficient vortex-enhanced water evaporation technology for concentrated brine management: Theory and process simulation evaluation”

## Section A – Equations

### A.1 Calculation of pure water vapor pressure

For pure water, the saturated vapor pressure, , can be calculated as a function of temperature, *T* (°C), using the following expression:

 Equation A-1

The coefficients are from ChemCAD version 8 (Chemstations, Houston, TX).

### A.2 Calculation of water vapor pressure **with** dissolved NaCl

For water containing NaCl, the following expression for water vapor pressure was developed based on NaCl-solution properties between 40 and 110 °C given by Clarke and Glew[1]:

 Equation A-2

Where: is the mole fraction of NaCl in the solution

* The molecular weights are 58.442 and 18.015 g/mol for NaCl and water, respectively

 the relative temperature difference from 110 °C and *T* is in °C

### A.3 Calculation of salt mole fraction from weight fraction in salt-water mixture

The mole fraction of NaCl is calculated from the weight fraction of salt () in a binary NaCl/water mixture as:

 Equation A-3

In the case of a slurry of NaCl in water, the vapor pressure of water is the same as that above a saturated solution of NaCl. The mole fraction to be used in the vapor pressure expression is that of NaCl at saturation at the given temperature.

### A.4 Solubility of NaCl in water as a function of temperature

The solubility of NaCl in water is temperature dependent. Yaws' Critical Property Data for Chemical Engineers and Chemists[2] provides the following relationship between temperature and NaCl solubility between 0 and 100 °C:

 Equation A‑4

Where is solubility in g-salt/100 g-solution. The weight fraction of salt in the salt-saturated liquid phase at a particular temperature will be :

 Equation A‑5

Accordingly, the solubility of NaCl in water is a weight fraction of 0.26402 at 20 °C and rises to only 0.28050 at 100 °C, corresponding to NaCl mole fractions of 0.09957 and 0.10728, respectively.

The density of NaCl crystals is assumed to be 2.17 g/mL per the same reference[2].

### A.5 Humidity Ratio

Applying the ideal gas law to water and air in a water-air mixture yields the following expressions for the partial pressure of water () and air ():

 Equation A-6

 Equation A-7

Where:

 = partial pressure of species in an air-water mixture (kPa)

 = mass of species in an air-water mixture (kg)

 = molecular weight of species

(18.015 and 28.951 kg/kmol for water and dry air, respectively, from ChemCAD v8)

 = system volume (m3)

 = gas constant (8.314 m3·kPa/kmol·K)

 = system temperature (K)

The total pressure of the system () is the sum of the partial pressures of air and water:

 Equation A-8

The humidity ratio () is defined as the mass ratio of water to dry air in a humidified air sample. Using Equations A-6, A-7, and A-8, the humidity ratio can be calculated from partial pressures and total pressure as:

 Equation A-9

Solving for yields (Equation 4 in the body of the paper):

 Equation A-10

## Section B – Process Simulation Description

Schematic diagram of CHEMCAD simulation is shown in Figure B1.

Additional process assumptions:

* Heat exchangers
	+ Mode: countercurrent
	+ Cooling water to HX4: supplied at 20°C, flow adjusted so that it is discharged at 40°C
	+ Pressure drops in the heat exchangers were those predicted by the heat exchanger vendor
	+ HX1 was designed to heat air returning to the Pod to 80 °C, the actual performance of HX1 will depend on the process flows and temperatures for a given scenario
	+ Heat exchanger parameters *U* and *A*:
		- HX1: *U* = 60.47 W/m2·K, *A* = 0.2644 m2
		- HX2: *U* = 176.13 W/m2·K, *A* = 49.82 m2
		- HX3: *U* = 273.74 W/m2·K, *A* = 3.636 m2
		- HX4: *U* = 255.11 W/m2·K, *A* = calculated
			* The area calculated by the vendor for HX4 was 0.758 m2, but specifying *U*, *A*, and cooling water parameters for HX4 caused an error in the simulation. Since the air outlet temperature from HX4 is specified, the heat being transferred will be unaffected by allowing the area to be variable.
	+ HX2 was simulated with 10 heat transfer zones and 10 shell-side passes. The log-mean temperature difference for HX2 was calculated as the weighted average of the log-mean difference over the 10 zones using the fraction of the heat transferred in each zone as the weighting factor. Otherwise, the desuperheating portion of HX2 would exaggerate the log-mean temperature difference for the amount of heat that was transferred in that section. For the baseline case, the temperatures of the evaporator and condenser streams, as a function of the enthalpy transferred, are shown in Figure B3. As noted in the caption, the temperature difference between the two streams is smaller in the middle of the heat exchanger than at either end.
* Pressure drops in piping and separators are assumed to be zero.
* In the TOP™ process, air is recirculated inside the process. In order to stabilize the simulation, air was introduced as a feed stream (#8 in Figure B1) to the Pod and discharged as a product stream (#88) after being heated in HX1. The properties of stream #8 were manually adjusted to match those of #88 and the simulation was rerun. This iteration continued until the flow, temperature, and pressure of stream #88 differed from that of #8 by less than 1%.
* Similarly, in the TOP™ process, a portion of the overflow from the Hydrocyclone is recycled to the Pod. This was managed in the simulation by having a Concentrate Recycle feed stream (#12) and a Hydrocyclone Overflow product stream (#24). Process parameters were manually adjusted between simulation runs until the properties of stream #24 differed from that of #12 by less than 1%.
* Additional note about thermodynamic model: the results of the baseline scenario with the eNRTL and Pitzer models were within 0.3% of each other, indicating that they both arrived at similar simulation outcomes.



Figure B1. Schematic diagram of CHEMCAD process flowsheet for TOP1000™ system.



Figure B2. Results of baseline scenario simulation.



Figure B3. Temperature profiles for the evaporator-side stream (Stream 9 in red) and the condenser-side stream (Stream 3333 in blue) in HX2 for the baseline case (Scenario 6 in Table 1). Each of the 10 zones represents 10% of the enthalpy change. Note that the temperature difference between the two streams is smaller for the majority of the heat exchanged than it is at either end of the heat exchanger.

## Section C. Details of Total Energy Calculation for Conventional Brine Concentrator (BC) – Crystallizer (CRYS) System

When a CRYS unit follows a BC unit, the volume of feed liquid treated by the CRYS is only a fraction of the brine fed to the BC. Thus, the total energy required to treat a volume of brine through a combined BC-CRYS system will be that of the BC plus that of a CRYS treating only the volume of concentrate from the BC. According to Mickley, typical MVR BC systems require 22.5 kWh per m3 of brine feed while a typical vapor compression forced convection CRYS system requires 62 kWh per m3 of feed to the CRYS[3]. In previous reports by the same author, the energy usage for BC and CRYS units have been reported in terms of a range for each that is about ±10% of the above values[4, 5]. For example, if the concentrate produced by the BC is 40% of the initial brine volume fed to the BC, the total energy of the combined BC-CRYS would be 47.3 kWh/m3-brine (22.5 kWh/m3-brine for the BC plus 0.4×62 kWh/m3-feed for the CRYS).

Energy calculations were made for combined BC-CRYS systems yielding a final Concentrate of either 100% solids (ZLD) or a 55 wt% solids slurry out. The performance of conventional BC-CRYS combined systems will be described in terms consistent with the TOP1000™ simulation results, using “Influent” and “Concentrate” to denote the brine feed and final concentrate streams to/from the overall system. Lowercase “concentrate” denotes a stream enriched in salt.

### ZLD BC-CRYS

For example, assuming the concentrate from the BC unit is a 26.4 wt% NaCl-saturated solution (like that generated in TOP1000™ Scenarios 7, 8, and 9), the volume of saturated solution fed to the crystallizer would be 0.237, 0.527, and 0.809 m3 per m3 of brine treated by the BC for Influent concentrations of 7.15, 15, and 22 wt% NaCl, respectively. As a result, the combined conventional BC-CRYS technologies would require 37.2, 55.2, and 72.7 kWh/m3-Influent, respectively, for those same Influent brine concentrations. In the case of the 22 wt% NaCl Influent, the BC might not be necessary, with brine fed directly to the CRYS. In that case, the CRYS alone would only require 62 kWh/m3-Influent instead of 72.7 kWh/m3-Influent for the combined BC-CRYS. By comparison, the TOP1000™ system is estimated to require 74.7, 77.2, and 77.5 kWh/m3 for ZLD production of salt and water from the 7.15, 15, and 22 wt% Influent brines.

Table C.1 Effect of feed brine concentration and BC-concentrate concentration on the total energy of a BC-CRYS system per unit of brine Influent fed to the BC unit in ZLD operation (i.e., all concentrate from the BC is treated by the CRYS unit).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Brine (wt% NaCl) | BC-concentrate (wt% NaCl) | BC-concentrate volume (m3 per m3 of brine) | BC energy (kWh/m3-brine) | CRYS energy(kWh/m3-brine) | Total BC-CRYS energy (kWh/m3-Influent) | TOP1000™ predicted energy (kWh/m3-Influent) |
| 7.15 | 15 | 0.451 | 22.5 | 28.0 | 50.5 | 74.7 |
| 15 | " | 1 | - | 62.0 | 62.0 | 77.2 |
| 7.15 | 22 | 0.293 | 22.5 | 18.2 | 40.7 | 74.7 |
| 15 | " | 0.651 | 22.5 | 40.4 | 62.9 | 77.2 |
| 22 | " | 1 | - | 62.0 | 62.0 | 77.5 |
| 7.15 | 26.4 | 0.237 | 22.5 | 14.7 | 37.2 | 74.7 |
| 15 | " | 0.527 | 22.5 | 32.7 | 55.2 | 77.2 |
| 22 | " | 0.809 | 22.5 | 50.2 | 72.7 | 77.5 |

### 55 wt% Solids Slurry BC-CRYS

For the 55 wt% solids Slurry Concentrate, the energy calculations for the BC-CRYS unit were made assuming the BC unit treats the entire Influent to 15, 22, or 26.4 wt% concentration and the CRYS unit treats a sufficient portion of the resultant BC-concentrate to remove the necessary amount of water for slurry formation. The liquid portion of the slurry is assumed to be saturated in NaCl at 26.4 wt% (at 20 °C). A 7.15 wt% Influent can be concentrated in the BC up to 15, 22, or 26.4 wt%. A 15 wt% Influent could be processed directly in the CRYS or concentrated up to 22 or 26.4 wt% in the BC before being processed in the CRYS. A 22 wt% Influent could be processed directly in the CRYS or concentrated up to 26.4 wt% in the BC before being processed in the CRYS.

The final 55 wt% solids slurry contains 66.88 wt% NaCl, 55 wt% in solid form and 11.88 wt% NaCl dissolved in the liquid phase. Thus, of the mass of NaCl in the 55 wt% solids slurry, 17.76% of it is in the saturated solution and 82.24% is in solid form. The formula for determining the fraction of the BC-concentrate, *R*, that must be processed by the CRYS unit to arrive at a final Concentrate with a total weight fraction of NaCl of (0.6688 for 55 wt% solids) is:

 Equation C-1

Where is the weight fraction of NaCl in the BC-concentrate.

If the BC-concentrate is 26.4 wt% NaCl, then each m3 of BC-concentrate contains 316.0 kg NaCl. Since the solution is already saturated, the 82.24% of the BC-concentrate must be processed through the CRYS to yield the 55 wt% solids Slurry Concentrate.

If, however, the BC-concentrate is 22 wt% NaCl, then each m3 of BC-concentrate contains 255.6 kg and a larger portion of the BC-concentrate must be dried in the CRYS to yield the 55 wt% solids Slurry Concentrate since the concentration of the liquid portion of the slurry is higher than that of the BC-concentrate. As a result, 86.03% of the BC-concentrate must be processed by the CRYS unit.

Similarly, if the BC-concentrate is 15 wt% NaCl, then each m3 of BC-concentrate contains 166.4 kg of salt and water. To yield a 55 wt% solids Slurry Concentrate from a BC-CRYS system, an even larger portion of the 15 wt% NaCl BC-concentrate must be dried compared to a 22 wt% NaCl BC-concentrate. As a result, 91.26% of the 15 wt% NaCl BC-concentrate must be processed by the CRYS unit.

The total BC-CRYS energy per unit of Influent brine to a hypothetical BC-CRYS system producing 55 wt% solids NaCl Slurry Concentrate was calculated and is shown in Table C.2 for the same scenarios as for ZLD in Table C.1. The BC-concentrate concentrate volume per unit of Influent are the same as for the ZLD scenario, but the CRYS unit for the 55 wt% solids case only processes a fraction of the BC-concentrate volume instead of the entire volume. A column has been added showing the fraction of the BC-concentrate processed by the CRYS unit. The CRYS energy is then calculated based on the reduced volume of BC-concentrate processed per unit of Influent brine and the assumed CRYS energy usage of 62 kWh/m3-CRYS-feed.

Table C.2 Effect of feed brine concentration and BC-concentrate concentration on the total energy of a BC-CRYS system per unit of brine fed to the BC unit for a system producing 55 wt% solids slurry (i.e., only a portion of the BC-concentrate is treated by the CRYS unit).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Brine (wt% NaCl) | BC-concentrate (wt% NaCl) | BC-concentrate volume (m3 per m3 of brine) | BC energy (kWh/m3-brine) | CRYS feed volume\*(m3 per m3 of BC conc) | CRYS energy(kWh/m3-brine) | Total BC-CRYS energy (kWh/m3-Influent) | TOP1000™ predicted energy (kWh/m3-Influent) |
| 7.15 | 15 | 0.451 | 22.5 | 0.913 | 25.5 | 48.0 | 71.3 |
| 15 | " | 1 | - | 0.913 | 56.6 | 56.6 | 70.6 |
|  |  |  |  |  |  |  |  |
| 7.15 | 22 | 0.293 | 22.5 | 0.860 | 15.6 | 38.1 | 71.3 |
| 15 | " | 0.651 | 22.5 | 0.860 | 34.7 | 57.2 | 70.6 |
| 22 | " | 1 | - | 0.860 | 53.3 | 53.3 | 67.2 |
|  |  |  |  |  |  |  |  |
| 7.15 | 26.4 | 0.237 | 22.5 | 0.822 | 12.1 | 34.6 | 71.3 |
| 15 | " | 0.527 | 22.5 | 0.822 | 26.9 | 49.4 | 70.6 |
| 22 | " | 0.809 | 22.5 | 0.822 | 41.2 | 63.7 | 67.2 |

\*This represents the fraction of the BC-concentrate from the BC unit that must be converted to solid NaCl to result in a final slurry containing 55 wt% solids slurry with the liquid portion being 26.4 wt% NaCl solution (at 20 °C).

Table C.3 Properties of various process streams for calculation of brine concentrate volume reduction, all at 20 °C\*.

|  |  |  |  |
| --- | --- | --- | --- |
| Nature of Stream | Density(kg/m3) | Weight fraction NaCl | NaCl concentration (kg/m3) |
| Water | 997.8 | 0 | 0 |
| 7.15 wt% NaCl | 1050 | 0.0715 | 75 |
| 15 wt% NaCl | 1109 | 0.1500 | 166.4 |
| 22 wt% NaCl | 1162 | 0.2200 | 255.6 |
| 26.4 wt% NaCl | 1197 | 0.2640 | 316.0 |
| Solid NaCl | 2162 | 1 | 2162 |
| 55 wt% solids slurry | 1586 | 0.6688 | 1061 |

\*As calculated with CHEMCAD.

## Section D. Table of Results for Process Parameter Evaluation

Table D.1. Effect of varying process characteristics of baseline scenario. For all simulations: 22 wt% NaCl Influent and 55 wt% solids Slurry Concentrate.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Variance from Baseline Scenario (#6 in Table 1)** | **Blower Energy Per Unit Influent** (kWh/m3) and % Change§ | **Blower Pressure Ratio** | **Influent**(m3/day) [g/s] | **Concentrate**(m3/day) [g/s] | **Product** Water(m3/day) [g/s] | **Blower Energy Per Unit PRODUCT** (kWh/m3) | **HX2 Heat Transferred** (kJ/s) | **Excess Heat Removed in HX4** (kJ/s) |
| D.1 | None | 67.2 | 2.24 | 6.78 [91.2] | 1.61 [29.7] | 5.33 [61.5] | 85.6 | 146.4 | 6.11 |
| D.2 | Blower Efficiency: 10% Increase to 0.847 | 64.5**−4.0%** | 2.33 | 7.08 [95.1] | 1.68 [31.0] | 5.55 [64.1] | 82.1 | 153.0 | 5.54 |
| D.3 | Blower Efficiency: 10% Decrease to 0.693 | 70.4**+4.8%** | 2.14 | 6.47 [87.0] | 1.54 [28.3] | 5.08 [58.6] | 89.8 | 139.3 | 6.68 |
| D.4 | Blower Inlet Pressure: 25% Increase to 79.7 kPa | 66.4**−1.2%** | 2.21 | 6.87 [92.3] | 1.63 [30.0] | 5.39 [62.3] | 84.6 | 148.7 | 5.61 |
| D.5 | Blower Inlet Pressure: 25% Decrease to 47.8 kPa | 68.6**+2.1%** | 2.27 | 6.65 [89.4] | 1.58 [29.2] | 5.22 [60.2] | 87.4 | 142.8 | 6.75 |
| D.6 | Ratio of Influent to Air: 10% Increase | 66.0**−1.8%** | 2.27 | 6.91 [92.9] | 1.64 [30.3] | 5.42 [62.6] | 84.1 | 148.9 | 5.83 |
| D.7 | Ratio of Influent to Air: 50% Increase | 62.6**−6.8%** | 2.34 | 7.28 [97.9] | 1.73 [31.9] | 5.72 [66.0] | 79.7 | 156.4 | 4.98 |
| D.8 | Ratio of Influent to Air: 10% Decrease | 68.7**+2.1%** | 2.21 | 6.64 [89.3] | 1.58 [29.1] | 5.21 [60.2] | 87.5 | 143.6 | 6.43 |
| D.9 | Ratio of Influent to Air: 50% Decrease | 79.7**+19%** | 2.02 | 5.72 [77.0] | 1.36 [25.1] | 4.49 [51.9] | 101.6 | 124.5 | 8.43 |
| D.10 | Blower Power: 10% Increase to 21.9 kW | 69.6**+3.5%** | 2.30 | 7.21 [97.0] | 1.71 [31.6] | 5.66 [65.4] | 88.6 | 155.7 | 7.20 |
| D.11 | Blower Power: 10% Decrease to 17.1 kW | 64.9**−3.5%** | 2.18 | 6.33 [85.1] | 1.50 [27.7] | 4.97 [57.4] | 82.7 | 136.6 | 5.07 |
| D.12 |  of HX2\*: 10% Increase | 65.0**−3.3%** | 2.18 | 7.02 [94.3] | 1.67 [30.7] | 5.51 [63.6] | 82.8 | 151.8 | 5.66 |
| D.13 |  of HX2\*: 50% Increase | 57.8**−14%** | 2.01 | 7.89 [106.0] | 1.87 [34.5] | 6.19 [71.5] | 73.7 | 172.4 | 4.01 |
| D.14 |  of HX2\*: 100% Increase | 52.0**−23%** | 1.88 | 8.77 [117.9] | 2.08 [38.4] | 6.88 [79.5] | 66.2 | 193.4 | 2.32 |
| D.15 |  of HX2\*: 200% Increase | 45.0**−33%** | 1.73 | 10.13 [136.2] | 2.41 [44.4] | 7.95 [91.8] | 57.4 | 225.8 | 0\*\* |
| D.16 |  of HX2\*: 10% Decrease | 69.9**+4.0%** | 2.31 | 6.52 [87.7] | 1.55 [28.6] | 5.12 [59.2] | 89.0 | 140.4 | 6.60 |
| D.17 |  of HX2\*: 50% Decrease | 87.7**+31%** | 2.81 | 5.20 [69.9] | 1.24 [22.8] | 4.08 [47.1] | 111.7 | 109.1 | 9.14 |
| D.18 | Combination: 100% Increase in HX2 and 50% Increase in Influent to Air Ratio | 47.9**−29%** | 1.94 | 9.52 [127.9] | 2.26 [41.7] | 7.47 [86.3] | 61.1 | 209.6 | 0.67 |
| D.19 | Combination: 100% Increas in HX2 and 10% Increase in Blower Efficiency | 49.4**−26%** | 1.93 | 9.24 [124.2] | 2.19 [40.5] | 7.25 [83.7] | 62.9 | 204.2 | 1.43 |

§The % Change is relative to the baseline scenario (entry D.1)

\*A change in the product was simulated as an increase in only.

\*\*No heat was removed in HX4, temperature of air leaving HX3 was 56.4 °C instead of 57 °C in the baseline scenario.

References

[1] E.C.W. Clarke, D.N. Glew, Evaluation of the Thermodynamic Functions for Aqueous Sodium Chloride from Equilibrium and Calorimetric Measurements below 154 °C, Journal of Physical and Chemical Reference Data, 14 (1985) 489-610.

[2] C.L. Yaws, Yaws' Critical Property Data for Chemical Engineers and Chemists. Online version available at: https://app.knovel.com/hotlink/toc/id:kpYCPDCECD/yaws-critical-property/yaws-critical-property, Knovel, 2012: 2013: 2014.

[3] M. Mickley, Emerging Technologies for High Recovery Processing, Desalination and Water Purification Research and Development Program Report No. 208, U.S. Department of the Interior, Bureau of Reclamation, 2021.

[4] M.C. Mickley, Membrane Concentrate Disposal: Practices and Regulation (Second Edition), Desalination and Water Purification Research and Development Program Report No. 123, U.S. Department of the Interior, Bureau of Reclamation, 2006.

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