Advanced Supercritical Water-Based Process Concepts for Treatment and Beneficial Reuse of Brine in Oil/Gas Production

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ABSTRACT

Produced water generated from oil/gas reservoirs is a cost burden for oil/gas producers, with over 21 billion barrels of the waste generated in 2019. Average disposal costs range from \$4.00-\$8.00·bbl^{-1}, with up to \$20·bbl^{-1} spent on transportation alone. Dissolved solids content is a contributing factor which limits economical treatment options for this waste stream. This work proposes a novel technique that can handle high salinity waste, employing favorable properties past the critical point of water. In this study, process simulation of two supercritical water desalination (SCWD) scenarios was completed. Zero liquid discharge (ZLD) and brine

concentration operating scenarios were compared, weighing the associated economics and benefits for each case. The results were shown to be economically feasible for brines with a high dissolved solids content, ranging from \$3.49 to \$17.28·bbl^{-1} in an expanded sensitivity analysis.

1 Introduction

U.S. energy demand is expected to increase through 2050, despite increases to energy efficiency [1]. To meet growing U.S. energy demand, natural gas production is expected to grow along with associated produced water generation [2–5]. Produced water composition varies widely depending upon reservoir geology and well age [6]. Produced water may contain high salinities (measured as "total dissolved solids", or TDS), dissolved organic components and naturally occurring radioactive material (NORM), complicating treatment. Water recovery becomes more challenging with increasing brine salinity; traditional desalination methods, such as reverse osmosis (RO) and mechanical vapor compression (MVC) experience lower recoveries and higher operation costs when treating high salinity brines due to osmotic pressure limitations or inefficiency [7–12]. In addition, fouling is a particular challenge for membrane technologies treating solutions with high carbonate, sulfate or organic contents [13].

High salinity produced waters are generated from conventional and unconventional resources [6], but have become more prevalent as of late. In particular, produced water generated by unconventional reservoirs within the Appalachian Basin [14] contain very high salinities, organic material and sometimes NORM, requiring alternative desalination methods. Currently, most produced water treatment research has been conducted at lower salinity ranges, less than 75,000 mg·L^{-1} [10,11,15–20]. Produced water desalination techniques which have been considered include membranes (RO and forward osmosis (FO) as well as membrane distillation), multi-stage flash and multi-effect distillation, and MVC [9–11,15,20,21]. RO technology is unable to achieve appreciable recovery when processing salinities past that of seawater [8,9,13]. Other desalination techniques have been modeled to treat produced water containing up to 160,000 mg·L^{-1} [10]; however, experimental or operational results supporting these studies are limited [11,18,21]. Among the techniques being developed for high salinity produced waters, supercritical water desalination (SCWD) is capable of producing a clean water product in conjunction with a concentrated brine [14,22] or solid salt product [14,23–26]. Techno-economic analyses have been completed for supercritical water desalination to estimate the affiliated treatment cost [27,28]; these analyses concluded the technique was similar in cost to existing produced water management methods, including injection disposal with associated transportation [27], but were conducted without experimental validation.

This current study reconciles these differences with a simulation based upon reported experimental results from a prototype Joule-heated desalination system [14,22], treating produced water at the supercritical condition. Beyond this point, water's dielectric constant shifts, allowing for creation of a non-polar phase within the desalinator vessel [29]. This permits the production of a low TDS vapor, the density of which is modulated by the operating pressure [22]. Two produced water treatment scenarios are considered in this study. In the first case, produced water is minimally pretreated followed by SCWD to generate clean water and a concentrated brine solution which may be reused as a drilling fluid [30]. In the second case, substantial pretreatment is added to remove problematic components (Ba^{2+}, Sr^{2+}, NORM, etc.), before SCWD generates a clean water and solid salt product, hereafter referred to as zero liquid discharge (ZLD). Sensitivity analyses are also conducted to determine the impact of salinity and water recovery on desalination system costs, as well as other factors, such as capacity, consumables, electrode efficiency and dissolved solid concentrations.

2 Methodologies

2.1 Process Model

The SCWD process was simulated with Aspen Plus v.10 software using the electrolyte non-random two liquid (ELECNRTL) model to estimate fluid thermodynamic properties. The Aspen simulation was used to estimate material and energy balances for the process, except for the desalinator. However, the ELECNRTL model has significant error when used to simulate brines past water's critical point; thus, it was necessary to supplement this portion of the simulation with operational data made available by Ogden [22]. Desalinator power requirements were simulated based upon prior experimental results using FORTRAN code in a user-defined operation block [14,22]. The specific water recovery was a user-defined input which defined the ratio of vapor to liquid mass flow rate driven by desalinator power consumption. In addition, simulation stream temperatures exiting the desalinator (estimated by ELECNRTL) were corrected based on experimental data [22].

The inlet brine salinity of 176.3 $g{\cdot}L^{-1}$ was selected based upon previous prototype testing with field-derived produced water [14]. Details of the brine composition are provided in Table 1. Additional compositions are provided which are used in a sensitivity analysis. The presence of divalent cations in the default brine are expected to escalate treatment cost associated with additional chemical pretreatment. Thus, three compositions are considered which reduce the impact of key divalent ions; Composition A excluded Sr^{2+}, Composition B excluded Mg^{2+} and Composition C has a higher Na^+ content weighting, thereby reducing the concentration of all other ions. All three compositions are normalized to contain identical TDS levels; this is also shown in Table 1.

Table 1: The default brine salinity used in the Aspen process model and alternative salinities considered.

Constituent Salt ($mg{\cdot}L^{-1}$)	Default Salinity	Comp. A	Comp. B	Comp. C
Na^{+}	35,115	35,847	37,896	52,673
Sr^{2+}	1,988	0	2,145	968
Ca^{2+}	25,167	25.692	27,160	12,260
K^{+}	421	430	454	205
Mg^{2+}	3302	3,371	0	1,609
Cl^{-}	110,298	110,953	108,636	108,577
Total	176,292	176,292	176,292	176,292

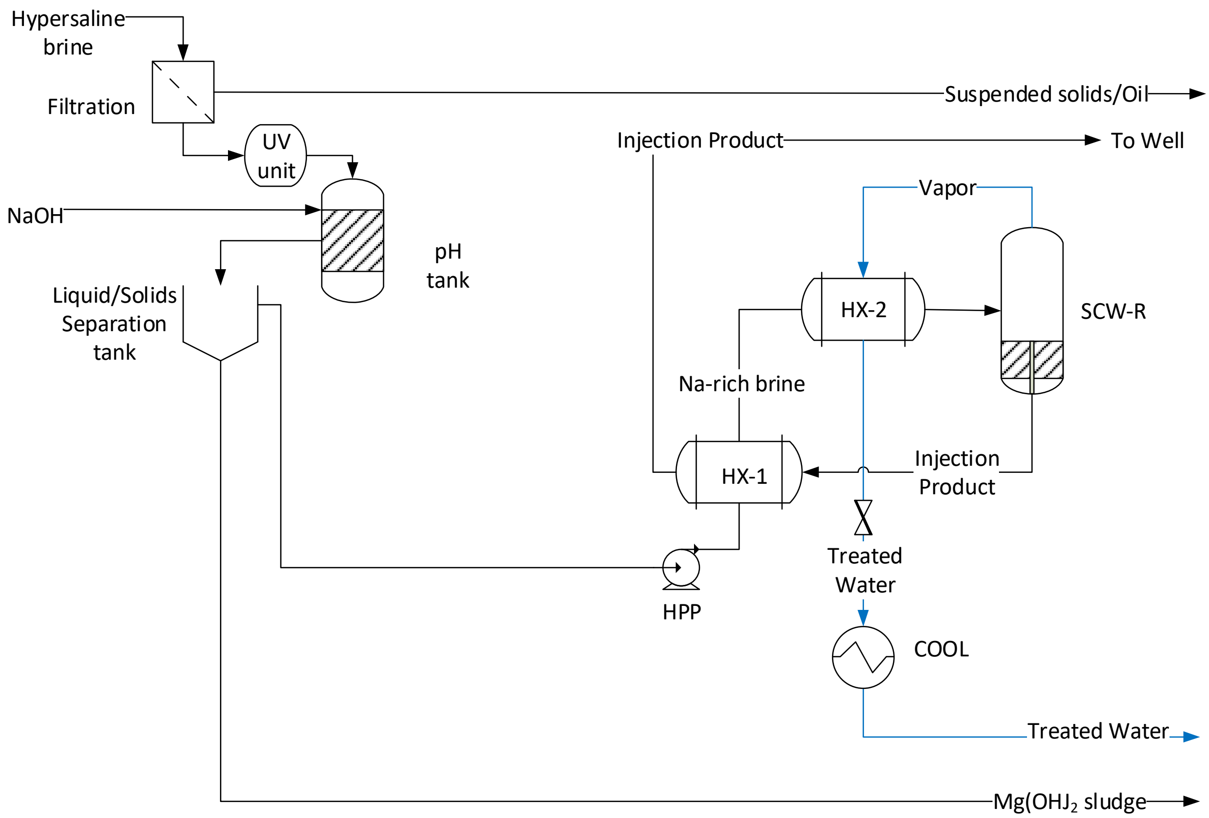
Process flow diagrams for both cases are shown in Figure 1. Prior to chemical treatment, sand filtration and UV systems are used to remove suspended solids and bacteria; this is not modeled in Aspen. A combination of mixing tanks and hydrocyclones are used for chemical precipitation in both the ZLD and brine concentration cases; in the ZLD case, three tanks/hydrocyclones are necessary to remove strontium (as $SrSO_4$), magnesium (as $Mg(OH)_2$) and calcium (as $CaCO_3$) before treatment in the desalinator. This is to avoid equipment scaling [27,28] or generation of a hazardous bulk salt product [27]. The water chemistry for the three reactions are as given [31,32]:

$$\mathrm{Sr^{2+}(aq) + SO_4^{2-}(aq) \leftrightarrow SrSO_4(s)} \qquad (1)$$

$$\mathrm{Mg^{2+}(aq) + 2OH^{-}\,(aq) \leftrightarrow Mg(OH)_2(s)} \qquad (2)$$

$$\mathrm{Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrow CaCO_3\,(s)} \qquad (3)$$

In the brine concentration case, only magnesium is removed (as $Mg(OH)_2$) to meet drilling fluid standards [30,33]. NORM removal is considered in the ZLD case, to avoid radioactive material in the final salt product. The NORM removal unit reduces the radioactive concentration in the brine (measured in picocuries per liter, or $pCi{\cdot}L^{-1}$) [34]. The waste products discussed here are given additional attention in Appendix A. A high pressure pump is used to increase fluid pressure between 230 and 280 bar; a single heat exchanger is used in the ZLD case, whereas two heat exchangers are used for heat recovery in the brine concentration case. All high temperature equipment (heat exchangers, desalinator and flash vessels) are crafted from Hastelloy C-276 alloy for corrosion protection; this has been shown to be successful in experiments [14,22] as well as in isolated corrosion tests [35]. The preheater and flash vessel blocks are used in tandem to estimate energy requirements for the desalinator electrode; the flash vessel is used to estimate recovery ratios, while the aforementioned FORTRAN code is used to account for brine heat of vaporization [22]. The liquid effluent is charged to an additional heat exchanger to recover thermal energy in the brine concentration case; in the ZLD case, two flash vessels in series (operating at 10 and 1 bar, respectively) are used to remove the remaining water to generate solid salt [14,23]. In the ZLD case, all vapor streams (desalinator plus downstream flash vessels) are mixed before entering the cooling water heat exchanger (labeled COOL in Figure 1); this heat exchanger is solely used to liquefy the desalinator vapor outlet in the brine concentration case.


Hypersaline brine
Filtration
Suspended solids/Oil
UV unit
Injection Product
To Well
NaOH
pH tank
Vapor
Liquid/Solids Separation tank
HX-2
SCW-R
Na-rich brine
HX-1
Injection Product
Treated Water
HPP
COOL
Treated Water
Mg(OHJ$_2$ sludge

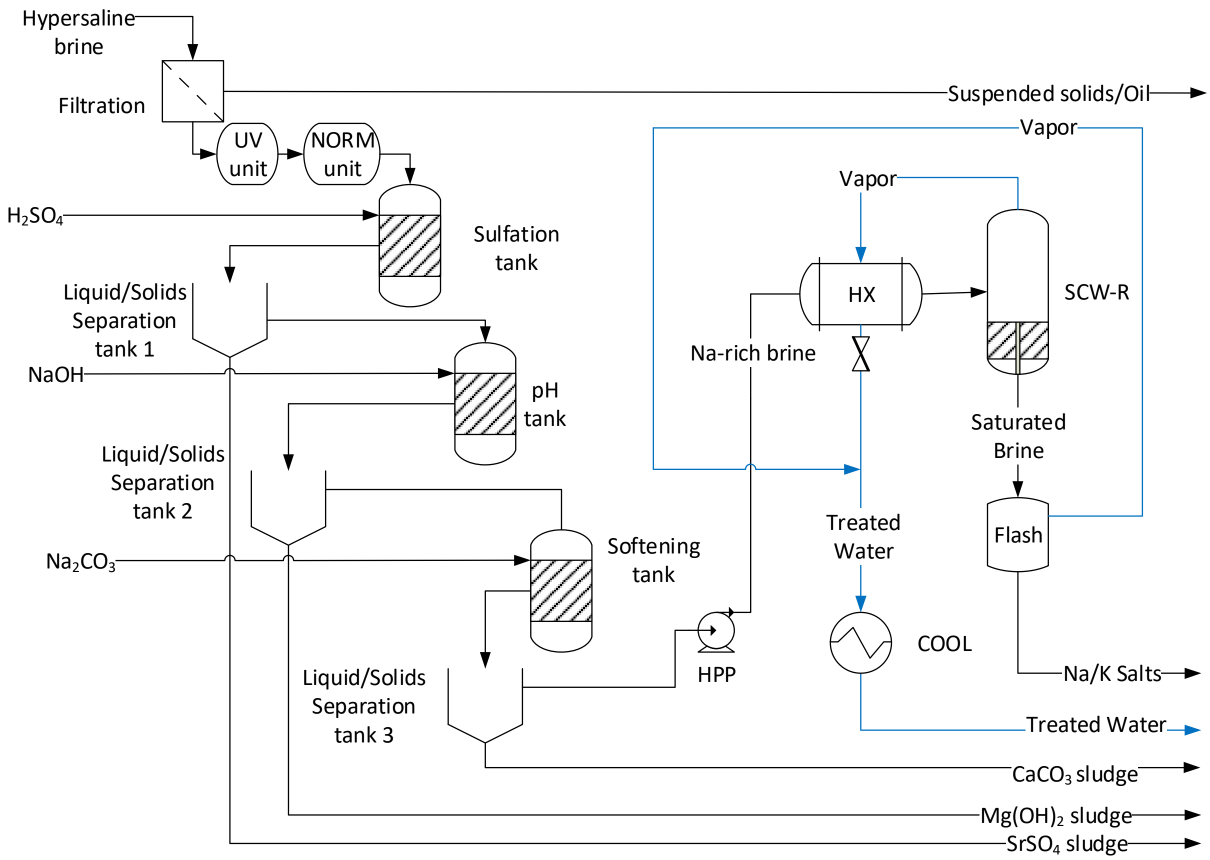


Figure 1: Process flow diagrams of the simulation used to estimate desalination process variables for brine concentration (above) and ZLD (below).

2.2 Cost Analysis

Two costing scenarios are considered for each operating scenario in this study. In the brine concentration case, brine product is sold as ten-pound brine for drilling operations as an alternative to well re-injection [30]. In the ZLD case, the chloride product is sold as rock salt [36,37] as an alternative to disposing the chlorides as non-hazardous waste [32].

The results of the Aspen process model for the SCWD process were subsequently analyzed from a cost perspective using a combination of methods outlined by Turton [38] and vendor quotes for specialized equipment [27,32], corrected to 2018 dollars using the Chemical Engineering Plant Cost Index [39]. A process treatment cost ($\$\cdot bbl^{-1}$) was developed to be used in comparison with other desalination techniques as well as for economic optimization. The treatment cost consists of both capital (equipment) and operating (utilities, raw materials, waste disposal and labor) costs. Parameters used in the study are provided in Table 2 and explained subsequently.

Table 2: Default values and sensitivity ranges used in SCWD process cost analyses.

Variable	Default	Range	Units	Source
Salinity	176.3	75-270	$g \cdot L^{-1}$	14
Pressure	250	230-280	bar	22
Recovery Ratio (per mass)	0.5	0.4-0.8	-	
Cost of re-injection	-	0.5-2.5	$\$ \cdot bbl^{-1}$	40
Electrolysis Losses	44	0-44%	%	22
Flow Rate	100	10-500	gpm	
Power Source	Natural Gas	WV, US Average	-	27,41
Cost of NG	3.0	-	$\$ \cdot MMBtu^{-1}$	42
NG Efficiency	30	-	%	27
Hazardous Waste Cost	250	0-2,000	$\$ \cdot ton^{-1}$	27
Non-Hazardous Waste Cost	33	0-100	$\$ \cdot ton^{-1}$	27
Cooling water	0.354	-	$\$ \cdot GJ^{-1}$	28,38
NORM in feed	5,000	0-10,000	$pCi \cdot L^{-1}$	34
Equipment Lifetime	9.5	-	Years	
Capacity Factor	0.9	-		
Interest Rate	5%	-	yr^{-1}	
Transportation costs for brine	0	0-20	$\$ \cdot bbl^{-1}$	
Ion Removal	Sr, Mg, Ca	Sr, Mg (keep Ca)	-	
Brine sale price	2.15	-	$\$ \cdot bbl^{-1}$	30,43
Rock salt sale price	72.24	-	$\$ \cdot ton^{-1}$	44,45
Cost of Materials				
H_2SO_4	110	55-220	$\$ \cdot ton^{-1}$	46
NaOH	640	320-1280	$\$ \cdot ton^{-1}$	47
Na_2CO_3	222	111-444	$\$ \cdot ton^{-1}$	48
Clinoptilolite	108	-	$\$ \cdot ton^{-1}$	27

The pressure of 250 bar is the midrange pressure used in prior experiments [14,22]. Other pressures evaluated experimentally are 230 and 280 bar; this is considered in the sensitivity analysis below.

The recovery ratio is determined on a per mass basis per Equation 4 – this is for ease of use in future calculations as well as a reference for prior data [14,22]. Here, $\dot{\mathrm{m}}_{\mathrm{v}}$ is the mass flow rate of the vapor and $\dot{\mathrm{m}}_{\mathrm{i}}$ is the mass flow rate of the inlet to the desalinator block.

$$\text{Water Recovery } (per\ mass) = \frac{\dot{\mathrm{m}}_{\mathrm{v}}}{\dot{\mathrm{m}}_{\mathrm{i}}} \tag{4}$$

Equipment costs were estimated using methods outlined in Turton [38] or estimated vendor quotes from 2014 [32] corrected to 2018 values [39]. Capital cost was subsequently annualized at a 5% interest rate with a 9.5 year equipment lifetime. The electrolysis losses (defined as "electrochemical power loss" in the experimental data [22]) were calculated based on low- and high-voltage tests in the desalination system, and were used to explain the large discrepancy in the experimental data vs. the theoretical limitations. Because of the voltages employed in the system (8 VAC), it is expected that some electrolysis will occur due to the high voltages, temperatures and overall conductivity of the fluid. However, it is noted no gaseous products (H_2, O_2) have been detected during any experiments. Based on the existing supercritical water desalination design, the energetic losses from electrolysis are expected to be 44% [22] at an operating voltage of 8 VAC; electrolysis losses decrease at lower applied voltages but also require varying reactor volumes, these factors are explored in the sensitivity analyses.

The costs of labor were provided using the Bureau of Labor Statistics for wastewater treatment operators in the Parkersburg-West Virginia area [49] as of May 2018. It is assumed this process will require two operators for continuous operation (ten total operators for 24-hour operation).

Raw materials costs were gathered from various industry sources for sulfuric acid [46], sodium hydroxide [47], and sodium carbonate [48]; these values were from 2018-2019 and are used as is. In addition, clinoptilolite zeolite was necessary for the removal of NORM; wholesale prices for this zeolite were gathered from Zhao and industry sources [50,51] for a cost per ton of zeolite.

Disposal costs for various product streams were dependent upon composition. Sulfate precipitates generated in the ZLD case, for example, were assumed to be hazardous waste, as was the spent zeolite used for NORM removal (in both cases). Chloride and hydroxide salts were assumed to be non-hazardous in the ZLD case. The sodium and potassium chloride salt produced at the end of the ZLD case was alternatively considered as a revenue generating product to assess economic outputs based upon current rock salt pricing [44,45]. For convenience, these products are tabulated in the supplementary information in Appendix A. The estimates for the disposal of hazardous and non-hazardous waste have been considered in prior techno-economic analyses on this front [27]; $250 per ton was used for the disposal of hazardous waste, while $33 per ton was used for the disposal of non-hazardous waste.

Utility costs were estimated using a mobile natural gas generator from a vendor quote from prior work [32] scaled to 2018 values [39]. The spot price of natural gas was used to calculate utility costs (around $3 per MMBtu [42]) and a 30% conversion efficiency (converting natural gas into electrical power) was used. Industrial electrical sources exist as an alternative to using a natural gas generator for this process; however, the remote nature of fracturing wells coupled with current low natural gas pricing make this a reasonable option. Cooling water was used to condense vapor from the desalinator unit; these costs were roughly estimated from Turton [38].

Sensitivity ranges in Table 2 were selected based on available information for specific variables that may impact the overall produced water remediation cost. For example, a salinity range of 75 to 270 $g \cdot L^{-1}$ was assessed to reflect produced water composition [6] and operating pressure was varied from 230 to 280 bar based on prior experimental data [22].

3. Results and discussion

Operating cases considering treatment cost per barrel for 100 GPM waste throughput are shown in Table 5. In the ZLD cases, rock salt is generated and disposed via landfill or sold, resulting in nearly full recovery of water entering the system. In the brine generation cases, a ten-pound brine is generated and disposed via reinjection or sold, resulting in limited solids generation and lower volume of clean water product. Capital costs for the brine concentration cases is marginally greater than the ZLD cases (11.4%) due to the additional heat recovery equipment. Capital costs associated with additional hydrocyclones and separators required for ZLD operation are limited in comparison to the additional heat exchanger necessary for brine concentration. Brine concentration treatment costs are lower in comparison to the respective ZLD disposal (37.5%) and sales cases (31.1%). The lowest overall treatment cost was found for the brine concentration sales case ($4.75); although the utilities costs are comparable (contributing $2.46·bbl^{-1} in the ZLD case and $2.59·bbl^{-1} in the brine concentration case), the disposal and raw materials cost of the ZLD case is substantially larger than the brine concentration case, contributing an additional $5.31·bbl^{-1} for ZLD vs. only $1.14·bbl^{-1} for brine concentration. Itemized cost breakdowns of each individual component have been reported for previous techno-economic analyses of supercritical water treatment of produced water [27,28]; these itemizations for each capital and operating component for the default cases reported here are provided in Appendix B.

Table 3: Default ZLD and brine concentration cases considered, including capital costs, mineral product and cost per barrel.

	ZLD (Disposal)	**ZLD (Sales)**	**Brine Concentration (Disposal)**	**Brine Concentration (Sales)**
Produced Water Inlet Flow (GPM)	100	100	100	100
Capital Cost ($M)	3.1	3.2	3.5	3.5
Mineral Product (tons·day^{-1})	134.2	134.2	4.1	4.1
NORM (tons·day^{-1})	1.8	1.8	0	0
Sulfates (tons·day^{-1})	2.0	2.0	0	0
Hydroxides (tons·day^{-1})	3.2	3.2	4.1	4.1
Carbonates (tons·day^{-1})	31.9	31.9	0	0
Chlorides (tons·day^{-1})	95.3	95.3	0	0
Clean Water Product (GPM)	92.3	92.3	51.8	51.8
Brine Product (GPM)	0	0	48.3	48.3
Treatment Cost ($·bbl^{-1})	10.19	6.89	6.37	4.75

A detailed cost breakdown for the ZLD (solids disposal) and brine concentration (re-injection) cases are provided in Figure 2. The predominant cost for ZLD is the cost of raw materials (sodium carbonate, sodium hydroxide, sulfuric acid and clinoptilolite); these become dominant when significant pretreatment is needed to generate a reusable chloride product, accounting for \$3.78·bbl^{-1}. Cost of solids waste disposal is also large in this case. The resultant NORM and strontium sulfates are hazardous material; in spite of their relatively low production (a combined 3.8 tons per day), their disposal costs still contribute approximately \$0.28·bbl^{-1}. Additionally, large amounts of calcium carbonate (31.9 tons per day) and sodium and potassium chloride (95.3 tons per day) are generated, substantially increasing solids waste disposal (\$0.90·bbl^{-1}). With hydroxides included, non-hazardous waste produced via ZLD totals around 130.4 tons per day, dwarfing the combined 3.8 tons per day of hazardous material. Utilities costs are dominant in the brine concentration case, due to lower pretreatment requirements. Re-injection accounts for a large portion of brine concentration cost, totaling between $0.22·bbl^{-1} and $1.11·bbl^{-1}. If this liquid is sold as drilling fluid, significant cost savings result ($0.95·bbl^{-1}), not including cost of re-injection ($0.22-$1.11·bbl^{-1}). Capital costs and labor costs are low in comparison to other operational costs in either case, as seen in Table 5 and Appendix B (labor costs account for $0.24·bbl^{-1}).

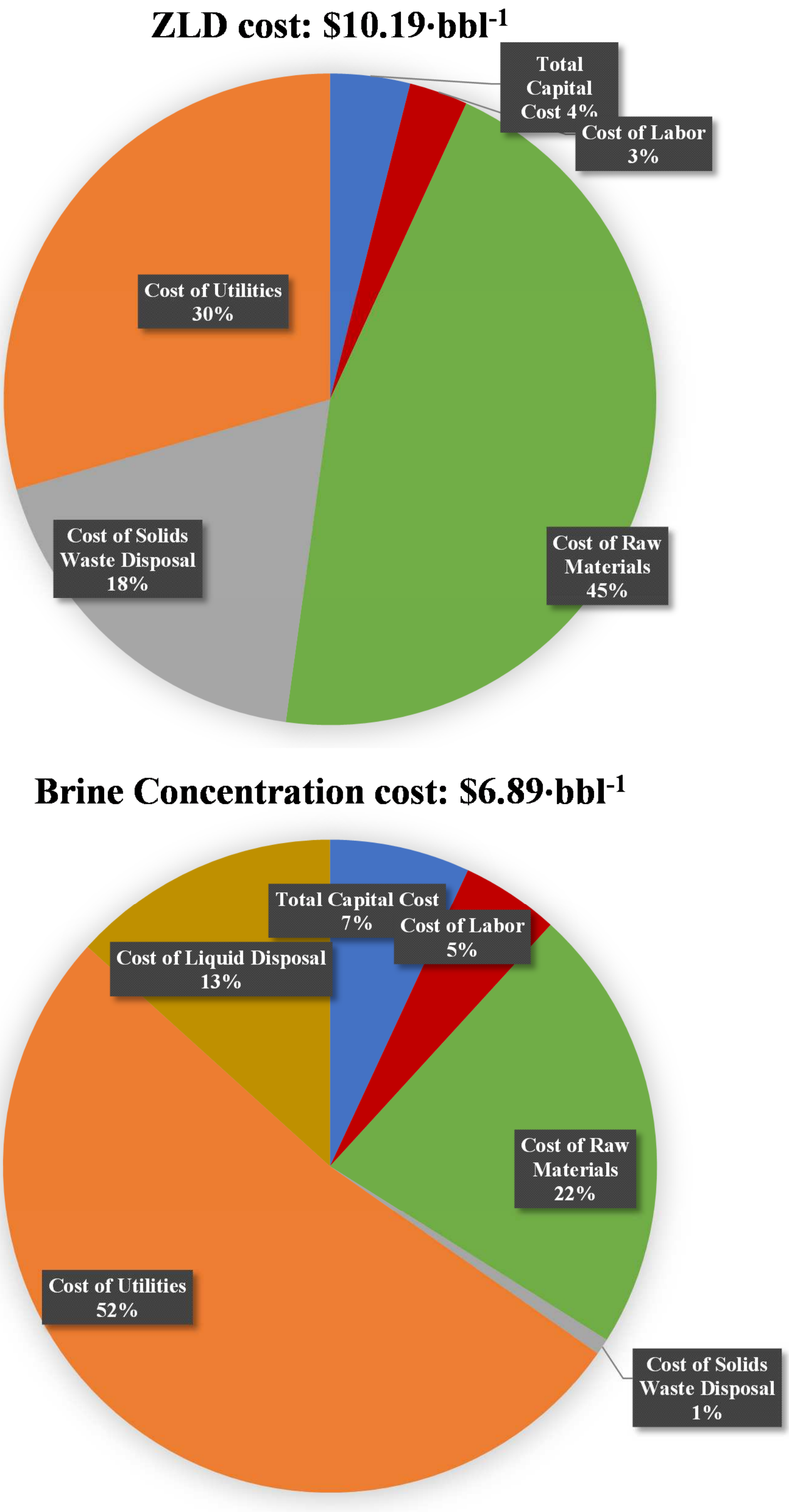


Figure 2: Disposal case cost breakdowns for the ZLD (above) and brine concentration (below) cases.

3.1. Recovery Ratio

The impact of clean water recovery on treatment case costs ($\$\cdot bbl^{-1}$) was evaluated at the default salinity and pressure values of 176.3 $g\cdot L^{-1}$ and 250 bar, respectively [14,22]. Results for the brine concentration and ZLD cases are shown in Figure 3 and Figure 4, respectively. For the concentration case, two re-injection costs and a single revenue generation case were considered. The impact of recovery ratio is dependent on the cost of re-injection; higher re-injection costs prioritize larger recoveries, whereas a lower re-injection cost is economical at lower recoveries. In either case the impact is minimal; increasing recovery ratio of 0.4 to 0.6 increases treatment costs from \$5.86 to $\$6.07\cdot bbl^{-1}$ (for lower re-injection costs) and decreases from \$6.98 to $\$6.74\cdot bbl^{-1}$ (for higher re-injection costs). Desalinator power consumption increases with water recovery, while generating less waste for re-injection. Power consumption increases cost by $\$0.39\cdot bbl^{-1}$ and savings due to lower re-injection costs amount from $\$0.11\cdot bbl^{-1}$ to $\$0.55\cdot bbl^{-1}$. Other impacts are minimal – the capital cost of the system shifts slightly in favor of higher recoveries due to a smaller liquid effluent heat exchanger, corresponding to $\$0.04\cdot bbl^{-1}$ of savings. For creating a drilling fluid, an increase in brine volume is beneficial, as further water recovery will only increase costs. As expected, increasing water recovery from 0.4 to 0.6 leads to an increase of $\$0.79\cdot bbl^{-1}$ for the drilling fluid resale case. For the ZLD case, an increased vapor product can be used for further thermal recovery in the heat exchanger used to heat inlet flow. If the brine is flashed or re-injected rather than processed to produce clean vapor, the energy consumed to achieve operating conditions is effectively wasted – the total cost of utilities decreases by $\$0.40\cdot bbl^{-1}$ with an increase in mass recovery ratio from 0.4 to 0.6.

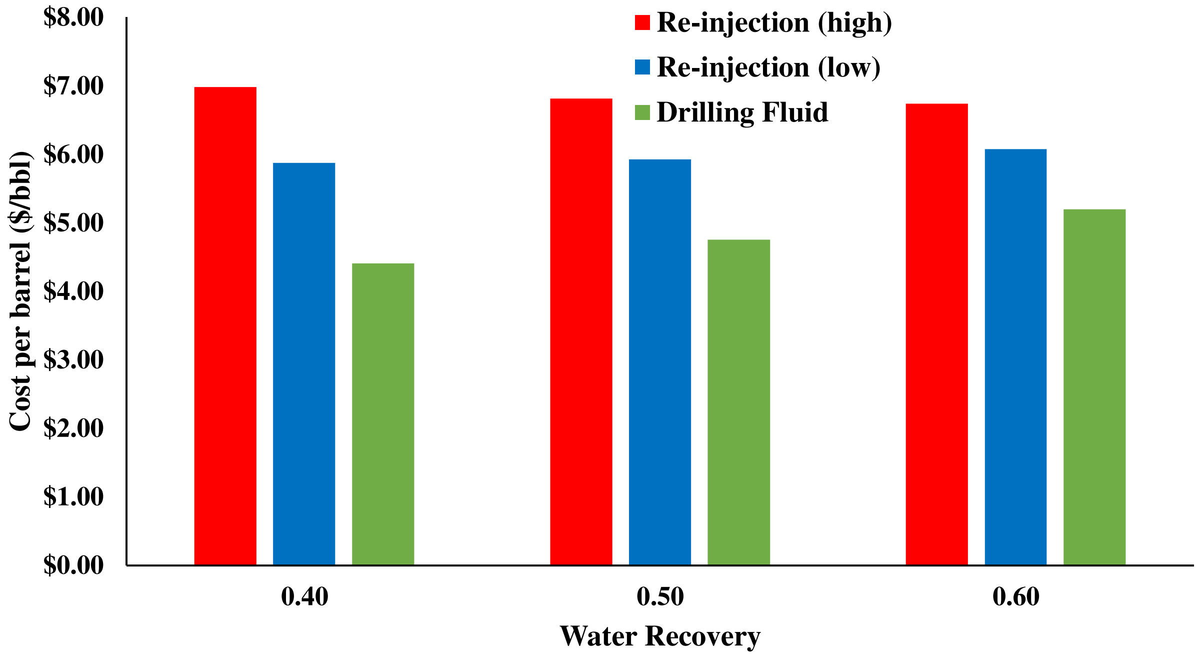


Figure 3: Brine product case process treatment costs ($\$\cdot bbl^{-1}$) with increasing water recovery, 176.3 $g\cdot L^{-1}$ inlet salinity (at default composition) and 250 bar operating pressure.

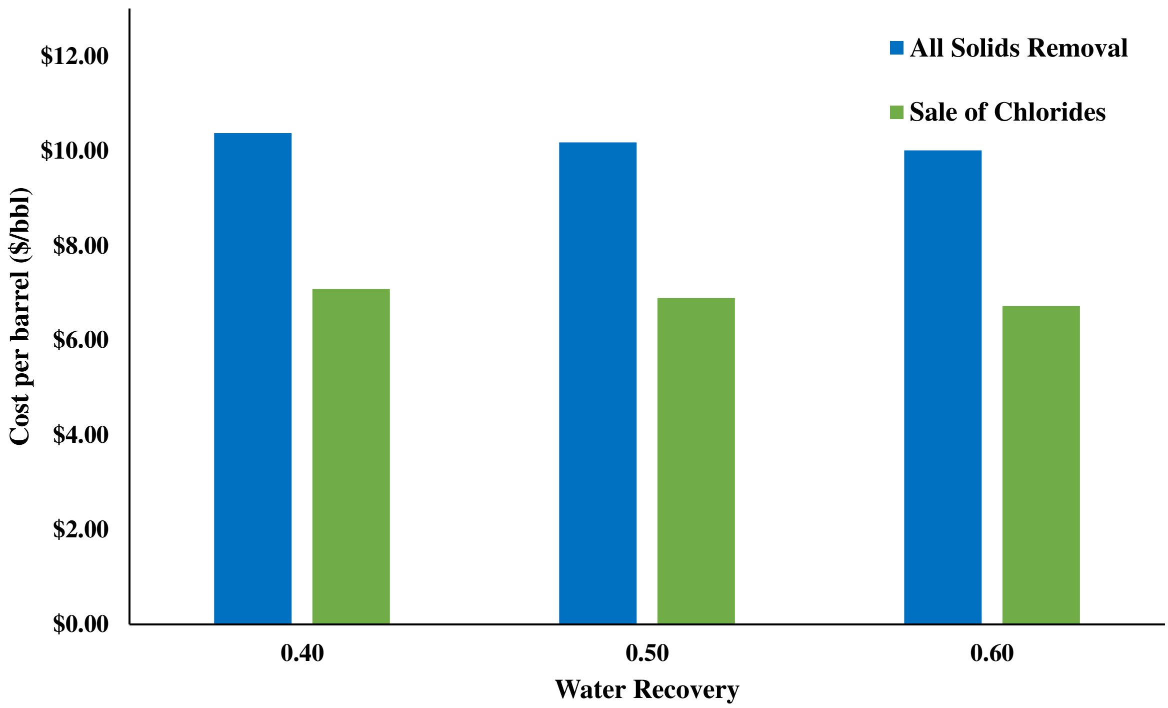


Figure 4: ZLD case process treatment costs ($\$\cdot bbl^{-1}$) with increasing water recovery, 176.3 $g\cdot L^{-1}$ inlet salinity (at default composition) and 250 bar operating pressure.

3.2. Inlet Brine Salinity

To evaluate process performance with a wide variety of feedstocks, the inlet salinity was varied between 75 and 270 $g\cdot L^{-1}$ (keeping the anion/cation ratios constant for this case). Brine concentration and ZLD case results with salinity are shown in Figure 5 and Figure 6, respectively. Based upon estimates using sodium chloride and water solutions [52], a higher salinity brine is expected to have a lower specific heat, resulting in lower desalinator power consumption. However, a lower brine specific heat can also inhibit heat recovery. With a constant water recovery of 0.4, increasing inlet salinity from 75 to 270 $g\cdot L^{-1}$ decreases the inlet temperature to the desalinator from 306 to 258 °C thereby increasing desalinator power requirements from 6,949 kW to 12,890 kW, an increase of $\$1.42\cdot bbl^{-1}$. Additionally, a higher salinity brine will require greater pretreatment chemical consumption (sulfuric acid, sodium hydroxide and sodium carbonate); for ZLD, this cost (raw materials + solids disposal) increases from $\$2.34\cdot bbl^{-1}$ to $\$8.07\cdot bbl^{-1}$. The case of producing a drilling fluid is buffered by higher salinities producing larger quantities of drilling fluid product. The brine savings increases from $\$0.51\cdot bbl^{-1}$ at 75 $g\cdot L^{-1}$ to $\$1.86\cdot bbl^{-1}$ at 270 $g\cdot L^{-1}$. It should be noted this limiting case is only shown to complete the trend; a salinity of 270 $g\cdot L^{-1}$ would be easier to simply remove magnesium and sell directly as ten-pound brine. In direct comparison, the ZLD case becomes more expensive relative to the brine concentration case with increasing salinity due to upfront treatment costs necessary for removal of solids; ZLD and brine concentration costs differ by $\$1.36\cdot bbl^{-1}$ at 75 $g\cdot L^{-1}$ and $\$5.79\cdot bbl^{-1}$ at 270 $g\cdot L^{-1}$ for the disposal cases (comparing solids disposal to re-injection) and $0.82·bbl^{-1} at 75 g·L^{-1} and $2.69·bbl^{-1} at 270 g·L^{-1} for the value-added product (drilling fluid or rock salt) cases.

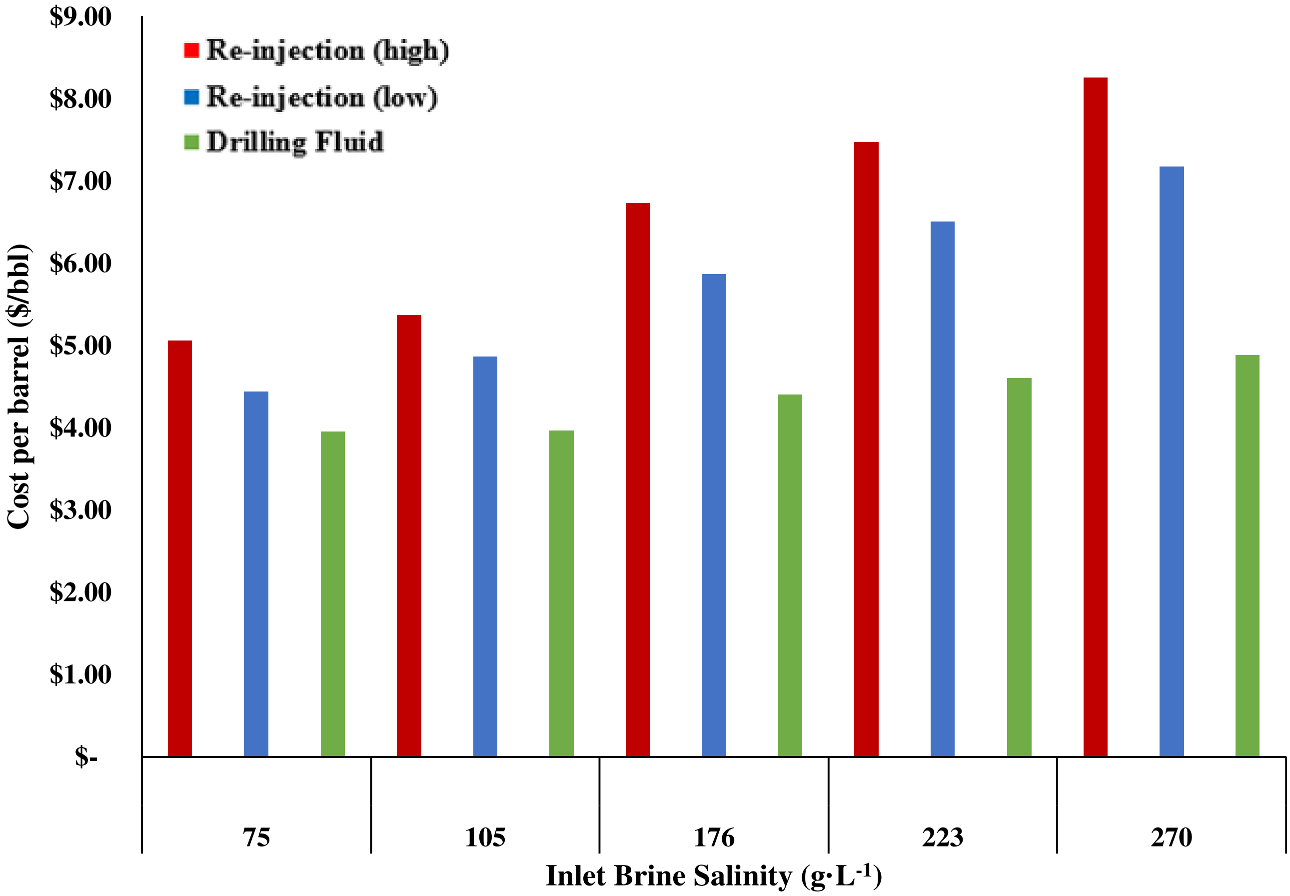


Figure 5: Cost of desalination ($·bbl^{-1}) for increasing salinity for the brine concentration case at 250 bar. For each salinity, the recovery ratio which produces the most favorable cost per barrel is shown.

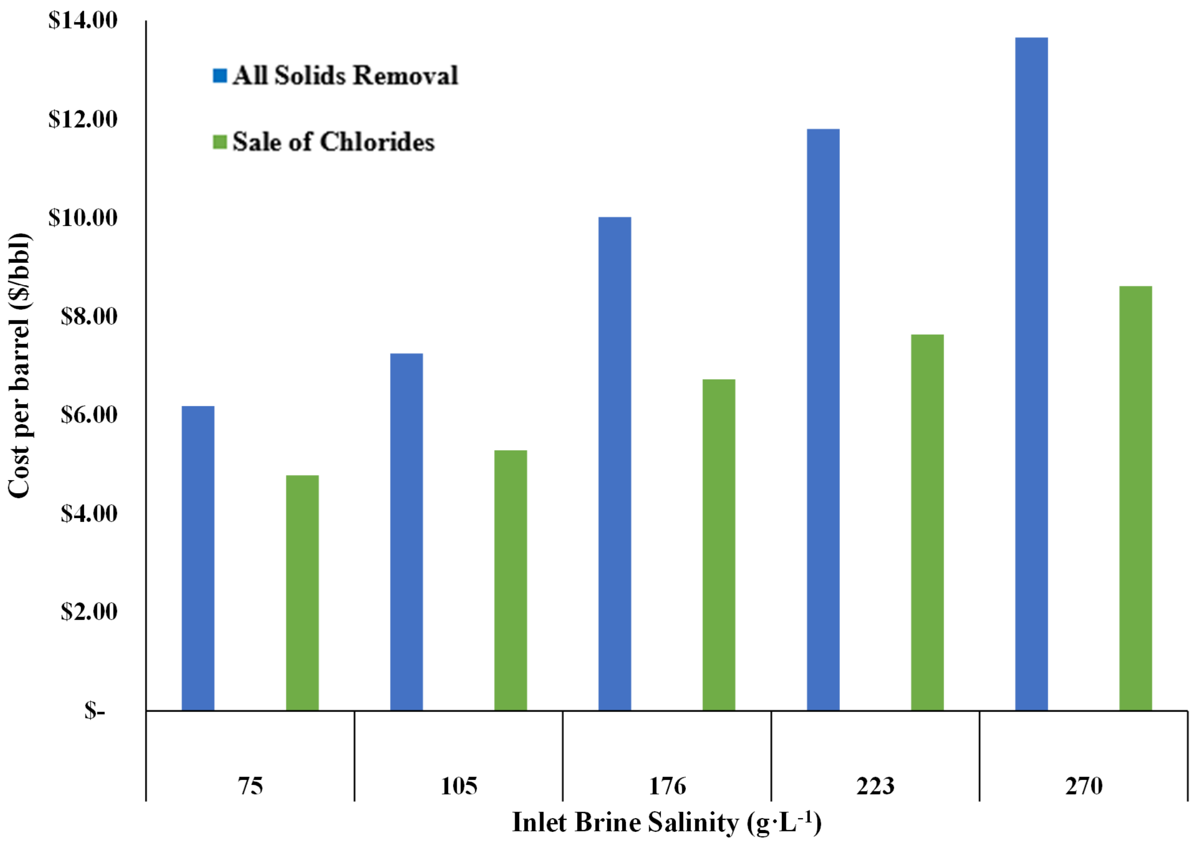


Figure 6: The cost of desalination ($\$\cdot bbl^{-1}$) for increasing salinity for the ZLD case at 250 bar. For each salinity, the recovery ratio which produces the most favorable cost per barrel is shown.

3.3 Pressure

Prior experiments [14,22] provided insight as to the impact of operational pressure on the overall process. Higher desalinator temperatures are necessary with operating pressure to create a clean vapor product; the vapor-liquid equilibrium temperature, T_{vle}, increases with increasing pressure [22]. However, the energy required to generate clean vapor is lower once the appropriate equilibrium temperature is achieved – this is true in binary mixtures of sodium chloride and water [52] and verified using experimental brine data [22]. Table 4 contains these values for the operating pressures studied; note the stark differences in ΔH_{Vap} and T_{vle} as a function of pressure.

Here, the "enthalpy of vaporization" denotes the amount of energy required to produce a low TDS vapor from the inlet brine, once the appropriate T_{vle} has been achieved [22].

Table 4: Enthalpies of vaporization, vapor-liquid equilibrium temperatures and pump power requirements as a function of pressure.

Pressure (bar)	ΔH_{Vap} **(kJ·kg^{-1})**	**T_{VLE} (°C)**	**Pump Power (kW)**
230	420	380.1	168.1
250	290	387.8	181.7
280	180	398.4	204.8

The re-injection case shown in Figure 7 presents treatment cost estimates at varying operating salinity combinations. For all cases and salinities, it is more expensive per barrel to create a clean vapor at 230 bar in comparison to 250 bar. This cost discrepancy increases with salinity, \$0.16·bbl^{-1} at 75 g·L^{-1}, \$0.41·bbl^{-1} at 176.3 g·L^{-1}, and \$0.60·bbl^{-1} at 270 g·L^{-1} for the re-injection cases. Thus, the benefit of lower pump power consumption (168 kW vs 182 kW) and lower T_{vle} (380.1 vs 387.8 °C) do not outweigh increased desalinator power requirement. At a recovery ratio of 0.5 and inlet salinity of 176.3 g·L^{-1}, desalinator power decreases from 11,895 kW to 10,512 kW when moving from 230 to 250 bar for the re-injection cases shown, contributing \$0.33·bbl^{-1} difference between the two cases. Note the vapor produced at 230 bar possesses a lower TDS (622.3 mg·L^{-1}) than at 250 bar (1167.7 mg·L^{-1}) [14]; thus, it may be preferential to operate at a pressure just above water's critical point in spite of the larger utility requirements depending upon operational strategy. 280 bar requires an even higher T_{vle} but corresponds to a lower energy requirement for clean vapor production [22]. The cost per barrel trend past 250 bar, however, is not as large at 75 g·L^{-1}, resulting in a \$0.04·bbl^{-1} difference, increasing to \$0.29·bbl^{-1} at 176.3 g·L^{-1}, and \$0.41·bbl^{-1} at 270 g·L^{-1}. This is another result of decreasing desalinator power as seen in Table 4. At 176.3 g·L^{-1}, for example, the decreased desalinator power requirements corresponded to a decrease of \$0.21·bbl^{-1} for comparable recovery ratios.

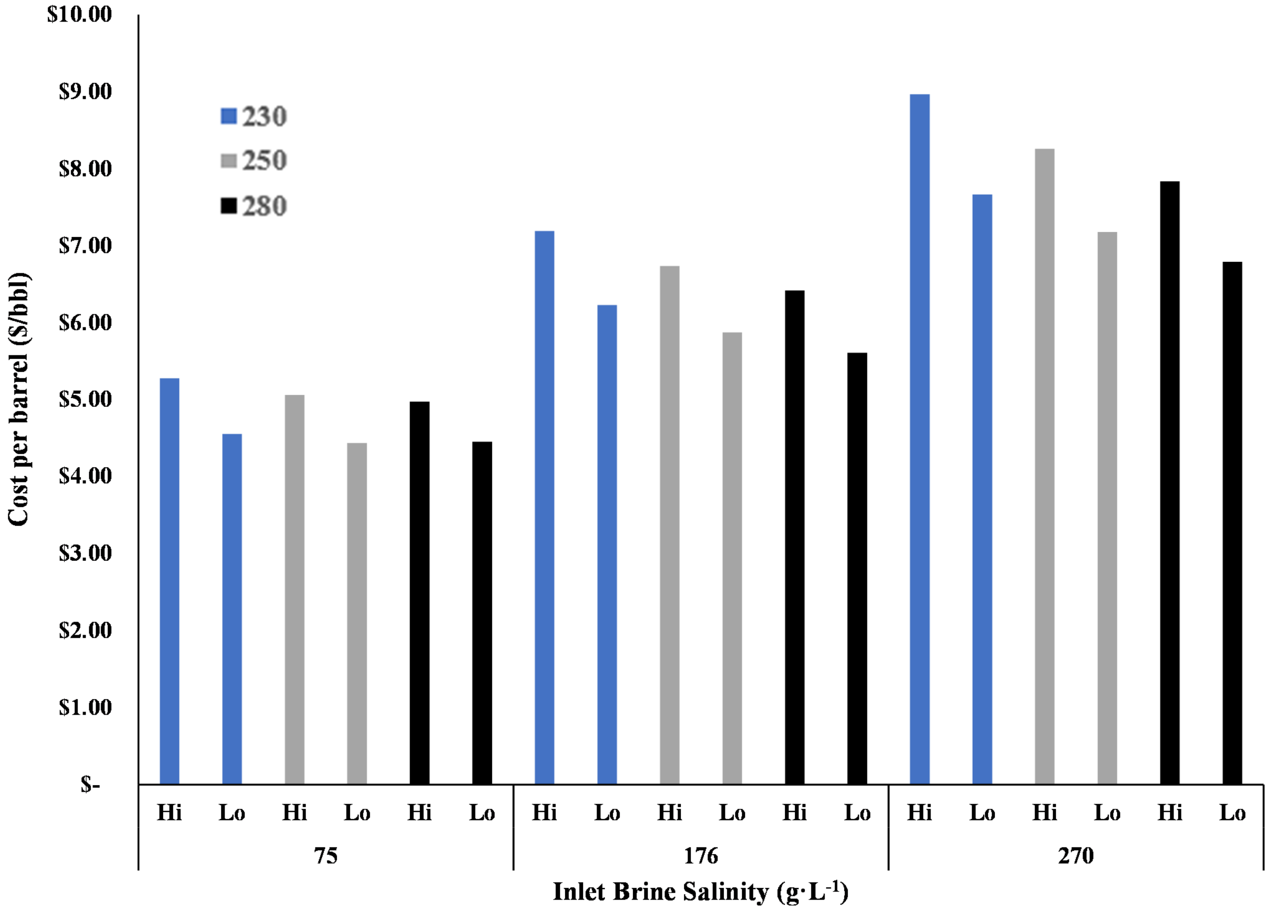


Figure 7: Brine concentration case costs with re-injection with salinity and pressure. For all salinities, the optimum recovery ratio is shown.

3.4 Process Cost Sensitivity Analyses

For all other process variables considered, cost ranges are given and compared to the default in Table 6 and Table 7. These costs are based on the high and low values for each variable as detailed in Table 2. For these cases, the salinity, water recovery and pressure are fixed at 176.3 $g \cdot L^{-1}$, 0.5, and 250 bar, respectively. Operating costs are highly sensitive to process capacity (flow rate). Treating brine with a considerably smaller system (10 GPM) will be more expensive per barrel than a much larger system due to increased capital cost weighting. Electrolysis losses are limited according to Driesner [52]; thus, only two reactor designs for differing voltages are considered. Because of this limitation, alternative reactor designs result in minimal savings ($\$0.11 \cdot bbl^{-1}$). Given energetic requirements, power sourcing has an obvious effect on process treatment costs, adding an additional $\$2.40 \cdot bbl^{-1}$ if switching from natural gas to average U.S. power cost. Solid waste disposal and chemical consumption costs have a much larger impact on ZLD operating costs. Non-hazardous waste disposal has a large impact (increasing costs by up to ~$\$2.80 \cdot bbl^{-1}$), while sodium carbonate consumption also has a significant impact (increasing costs by up to $\$2.90 \cdot bbl^{-1}$). Likewise, the ion concentration has a similarly large impact on the ZLD case – a high sodium brine (such as that found in the Permian Basin) [6] would be far easier to treat in this case using ZLD removing the need for extensive divalent cation pretreatment. If all of the final chloride product could be sold, the default case is $\$4.45 \cdot bbl^{-1}$, which could imply a greater degree of success for this process in geographic locations where produced water is lower in calcium content. Additionally, if only chloride salts are present, the calcium does not require removal. Removing the need for sodium carbonate leads to massive savings in material costs. NORM has minimal impact – although the waste is considered hazardous, the amount produced (even with a 10,000 $pCi \cdot L^{-1}$ brine) is considerably lower than the amount of sulfides, carbonates and chlorides produced via ZLD. Note that NORM removal is not considered for brine concentration, as it is assumed not to meaningfully impact re-injection or drilling fluid use. Finally, transportation has a significant impact on the brine concentration case. At $\$5 \cdot bbl^{-1}$, the sale of rock salt and removal of solid wastes (ZLD cases) become more lucrative than simply re-injecting or selling leftover brine, while at $\$15 \cdot bbl^{-1}$ or greater, processing the brine is more cost effective than re-injection. This solidifies the importance of minimizing brine production in cases of remote geographic locations, where transportation costs are higher. Note, this transportation cost is not considered in the ZLD case, where costs of disposal factor in transportation.

Table 5: Brine concentration cases sensitivity analysis results.

Brine Concentration					
Default Value: 176.3 $g \cdot L^{-1}$ salinity, 250 Bar Pressure, 0.5 water recovery					
Average treatment cost with re-injection (default):	$ 6.37		Average treatment cost with drilling fluid sale (default):	$ 4.75	
Variable	Low $	High $	Variable	Low $	High $
Electrolysis Losses	$ 6.26	$ 6.37	Electrolysis Losses	$ 4.64	$ 4.75
Flow Rate	$ 5.65	$ 13.30	Flow Rate	$ 4.03	$ 11.69
Power Source	$ 6.37	$ 8.72	Power Source	$ 4.75	$ 7.11
Non-Hazardous Waste Cost	$ 6.32	$ 6.46	Non-Hazardous Waste Cost	$ 4.71	$ 4.84
Transportation Costs	$ 6.37	$ 15.21	Transportation Costs	$ 4.75	$ 13.60
Ion Concentration	$ 5.12	$ 6.43	Ion Concentration	$ 3.49	$ 4.81
NaOH Cost	$ 5.75	$ 7.61	NaOH Cost	$ 4.13	$ 5.99

Table 6: Zero liquid discharge (ZLD) cases sensitivity analyses results.

Zero Liquid Discharge					
Default Value: 176.3 $g \cdot L^{-1}$ inlet salinity, 250 bar operating pressure, 0.5 water recovery					
Average treatment cost with solids removal (default):	$ 10.19		Average treatment cost with chloride salt sale (default):	$ 6.89	
Variable	Low $	High $	Variable	Low $	High $
Electrolysis Losses	$ 10.08	$ 10.19	Electrolysis Losses	$ 6.78	$ 6.89
Flow Rate	$ 9.45	$ 17.28	Flow Rate	$ 6.15	$ 14.05
Power Source	$ 10.19	$ 12.40	Power Source	$ 6.89	$ 9.11
Non-Hazardous Waste Cost	$ 8.78	$ 13.05	Non-Hazardous Waste Cost	$ 6.51	$ 7.66
Hazardous Waste Cost	$ 9.88	$ 12.37	Hazardous Waste Cost	$ 6.58	$ 9.08
NORM Cost	$ 10.00	$ 10.35	NORM Cost	$ 6.71	$ 7.06

Ion Concentration	$ 7.69	$ 10.19	Ion Concentration	$ 4.45	$ 6.89
Ion Removal	$ 7.10	$ 10.19	Ion Removal	$ 3.90	$ 6.89
H2SO4 Cost	$ 10.15	$ 10.27	H2SO4 Cost	$ 6.87	$ 6.94
NaOH Cost	$ 9.57	$ 11.43	NaOH Cost	$ 6.27	$ 8.13
Na2CO3 Cost	$ 8.73	$ 13.10	Na2CO3 Cost	$ 5.44	$ 9.80

The impact of each variable on brine concentration and ZLD cases is shown in Figure 8, with cost differences relative to the default. In spite of the sensitivity to key variables (flow rate, ion concentrations, chemical pricing), this process mostly falls within range of other competitive desalination and treatment processes under \$8·bbl^{-1} [27].

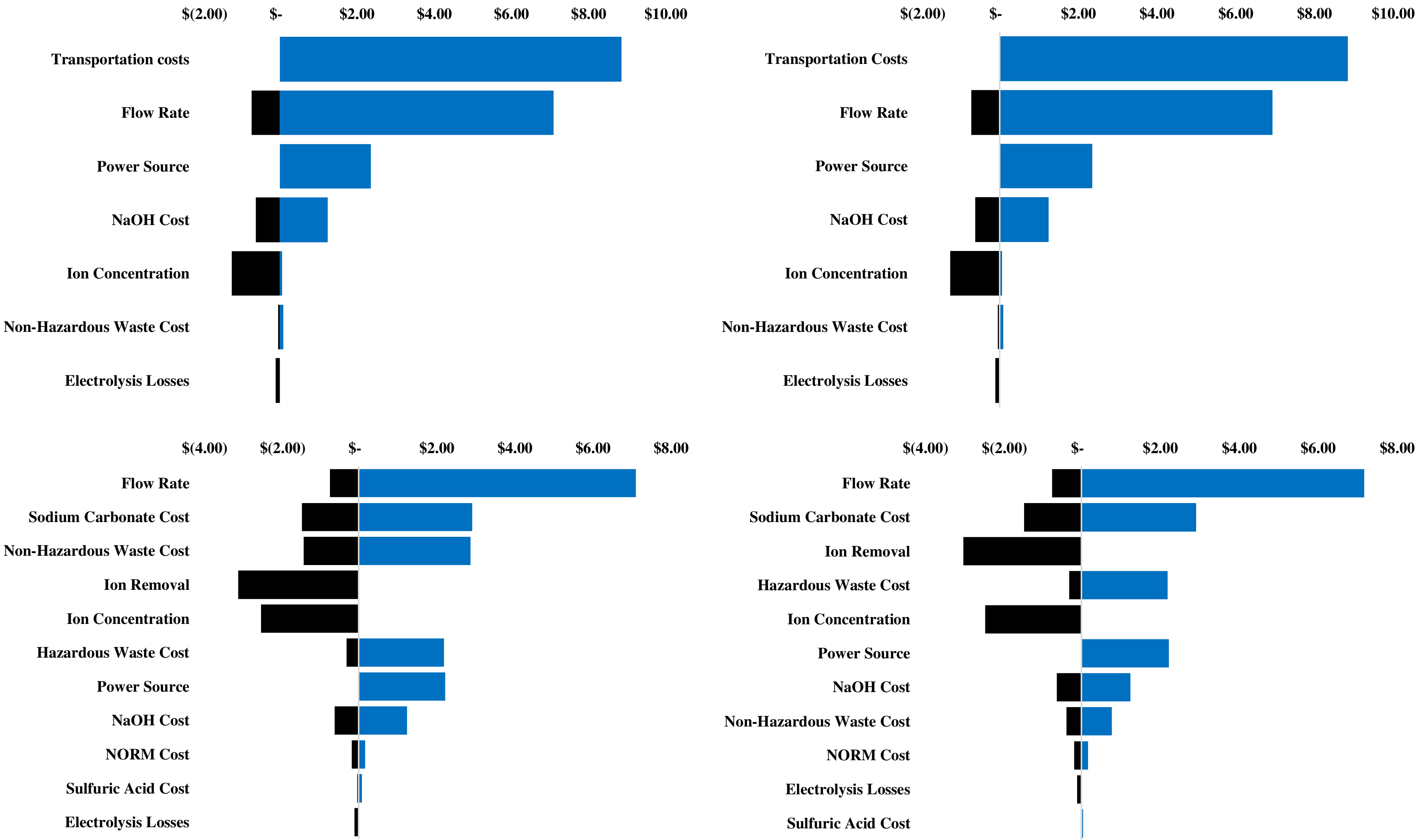


Figure 8: Case sensitivity charts: re-injection (upper-left), drilling fluid (upper-right), solids removal (lower-left) and sale of chlorides (lower-right). The color of the bar denotes the impact on the default case.

3.5 Comparison with conventional technologies

There are numerous technologies potentially available for produced water remediation at lower salinities[10]; however, most of these techniques have only been tested at salinities similar to seawater[11,15–18]. The currently accepted commercial technology for high salinity brine concentration and zero liquid discharge is an evaporator/crystallizer technique; for this technique, SaltWorks[53] makes their energetics for treatment readily available. The comparison between this technique and the SCWD cases considered is shown in Table 7. For this comparison, all salinities, recoveries and pressures were considered to create a range of energetics requirements; however, the flow rate was fixed at 100 GPM. Additional analyses have been completed using a pretreatment step with MVC prior to crystallization in literature [54]; for this analysis, the SaltWorks crystallizer is considered as a single-step process.

Table 7: A comparison between the energetics of the SaltWorks crystallizer and the SCWD process described herein. All energetics units are in $kWh \cdot bbl^{-1}$ for a flow rate of 100 GPM.

	Saltworks	**SCWD**
Brine Concentration	52.9	48.6 - 109.0
ZLD	55.3	48.7 - 116.8

Conclusions

The purpose of this study was to assess produced water treatment costs of the experimentally evaluated Joule-heated desalination system over a variety of process conditions. The process was simulated in Aspen Plus v.10 with user-defined models based upon prior experimental data for the application. Projected produced water treatment costs range from $\$3.49 \cdot bbl^{-1}$ to $\$17.28 \cdot bbl^{-1}$. Treatment costs were highly dependent on process capacity, cost of transportation, cost of sodium carbonate (as a pretreatment chemical) and power sourcing. Additionally, sensitivity to produced water composition was considered; high sodium content brines are less costly to treat than brines high in divalent ions (such as Ca^{2+}, Sr^{2+} and Mg^{2+}) which require chemical pretreatment. The future direction of this research will consider the ability to process high TDS content brine in remote regions where transportation costs are unusually high or re-injection capacity is low. Further, experimental studies to determine specific heat for various produced water compositions will be completed.

Author Contributions

The manuscript was written through contributions of the authors. The authors have given approval to the final version of the manuscript.

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ADDITIONAL INFORMATION

Appendix A: Products formed

Table S1: The products formed from each case.

Brine Concentration	**Zero Liquid Discharge**
Suspended solids/oil	Suspended solids/oil
Hydroxides (Magnesium)	Hydroxides (Magnesium and Calcium)
Clean water	Sulfates (Barium and Strontium)
Concentrated brine (all ions save Magnesium)	Carbonates (Calcium and Strontium)
Drilling Fluid	NORM (adsorbed onto clinoptilolite)
	Clean water
	Chloride product (sodium, potassium, calcium)
	Rock Salt

Appendix B: Individual cost breakdown

Table S2: Bare module cost factors used for ZLD case equipment costing [38]. Equipment cost based upon vendor quotes features the appropriate citation.

Equip	A	P	K1	K2	K3	C1	C2	C3	B1	B2	Fm
SCWD											
(as pressure vessel)	0.248	300	3.4974	0.4485	0.1074	-	-	-	2.25	1.82	4.8
(control valves) [32]	-	-	-	-	-	-	-	-	-	-	-
(electrode cost) [55]	-	-	-	-	-	-	-	-	-	-	-
HX	40.7	300	3.9912	0.0668	0.243	-0.4045	0.1859	0	1.74	1.55	3.7
Sulf											
(hydrocyclone) [32]	-	-	-	-	-	-	-	-	-	-	-
(holding tank) [56]	-	-	-	-	-	-	-	-	-	-	-
(pump)	4.08	3.40	3.3892	0.0536	0.1538	-0.3935	0.3957	-0.00226	1.89	1.35	2.5
Soft											
(hydrocyclone) [32]	-	-	-	-	-	-	-	-	-	-	-
(holding tank) [56]	-	-	-	-	-	-	-	-	-	-	-
(pump)	4.08	3.40	3.3892	0.0536	0.1538	-0.3935	0.3957	-0.00226	1.89	1.35	2.5
Hydro											
(hydrocyclone) [32]	-	-	-	-	-	-	-	-	-	-	-
(holding tank) [56]	-	-	-	-	-	-	-	-	-	-	-
(pump)	2.93	3.40	3.3892	0.0536	0.1538	-0.3935	0.3957	-0.00226	1.89	1.35	2.5
HP Pump [32]	-	-	-	-	-	-	-	-	-	-	-
Flash											
10 Bar	1.62	9	3.5565	0.3776	0.0905	-	-	-	1.49	1.52	4.8
1 Bar	0.62	0	3.4974	0.4485	0.1074	-	-	-	2.25	1.82	4.8
(flash control valves) [32]	-	-	-	-	-	-	-	-	-	-	-
NORM											
(as pressure vessel)	2.70	3.40	3.5565	0.3776	0.0905	-	-	-	1.49	1.52	1.7
(tower packing)	0.804	3.40	2.4493	0.9744	0.0055	-	-	-	-	-	4.1
(pump)	4.08	3.40	3.3892	0.0536	0.1538	-0.3935	0.3957	-0.00226	1.89	1.35	2.5
Sand											
(sand filter) [32]	-	-	-	-	-	-	-	-	-	-	-
(pump)	4.08	3.40	3.3892	0.0536	0.1538	-0.3935	0.3957	-0.00226	1.89	1.35	2.5
UV [32]	-	-	-	-	-	-	-	-	-	-	-
Generator [32]	-	-	-	-	-	-	-	-	-	-	-
Cool	86.8	1	4.3247	-0.303	0.1634	0.03881	-0.11272	0.08183	1.63	1.66	1

The design of the supercritical water desalination system itself bypassed Aspen Plus entirely; instead, the existing reactor design [22] was scaled appropriately to a much larger vessel volume. The vessel itself was costed as a pressure vessel comprised of a high Ni-alloy with a maximum pressure rating of 300 barg. Once the required inner volume was found, the scaled height and diameter of the system were used in conjunction with ASME boiler and pressure vessel codes [57] to determine vessel thickness. These equations are listed here:

$$t = \frac{PR}{SE-0.6P}, \frac{PR}{2SE+0.4P} \qquad \text{(S1)}$$

In Equation S1, P is the pressure rating (chosen as 300 barg), R is the radius (in inches), S is the ultimate tensile strength of the material (chosen as 98,800 psi based on Haynes International documentation for HC-276 [58]) and E is the joint efficiency (chosen as 0.9). The larger of the two thicknesses was used to determine the vessel thickness as an appropriate safety measure. Assuming the existing reactor design can successfully treat 300 $mL \cdot min^{-1}$, the reactor volume necessary for treating 100 GPM would have to be roughly 0.25 m^3. The authors believe that the existing design can handle higher throughputs - this constraint is merely a limitation of the pump used in the existing design. As the higher throughput is not yet confirmed, this conservative estimate is used to scale the existing design.

The electrode was scaled in a similar manner along with the outer vessel, shifting the length and diameter of the electrode to appropriately reflect the new height and inner diameter of the outer vessel. Using this method, the volume of the electrode was found to be 0.024 m^3, roughly 1/10th of the volume of the vessel itself. Costing the electrode was done merely by taking the expected mass of HC-276 in the electrode (using the density value found from Haynes International [58]) and costing it appropriately per kilogram. The range for HC-276 was found to be $25-80 per kilogram [55]; the high value of $80 per kilogram was used for costing the electrode.

The existing system uses two control valves to modulate both the vapor and liquid flow rates depending on pressure and resistance requirements within the system. Quotes for these control valves were furnished in 2014 [32] and were scaled appropriately to 2018 values. With these three costs combined, the total C_{BM} for the SCWD system was found to be $249,000.

The ZLD case utilizes two flash vessels for the liquid effluent from the SCWD system. The system uses the heat from the steam in the 10 bar flash vessel in order to dry the salt product in the 1 bar flash vessel; this is shown to be thermodynamically viable [14,23] regardless of effluent concentration and is not processed through Aspen. The overall volume of the vessel was estimated using the inlet flow rates with an assumed 5 minutes of holdup time. The diameters of these flash vessels were estimated using the Souders-Brown equation [59] which is used to calculate the maximum vapor velocity based on the difference in liquid and vapor densities:

$$v = k\sqrt{\frac{\rho_L-\rho_V}{\rho_V}} \qquad \text{(S2)}$$

In Equation S2, k is assumed to be 0.0535 for a system lacking a demister pad based on GPSA Engineering Data Book [60] factors. Once the vapor velocity is known, the diameter is determined using the following relation in Equation S3:

$$D = \left(\frac{4}{\pi} * \left(\frac{Q_V}{v}\right)\right)^{0.5} \qquad \text{(S3)}$$

Here, Q_V is the vapor flow rate and D is the required vessel diameter. Using the volume and diameter, the length/height of the flash vessel could also be calculated; the relationship between L and D was used to determine if the vessel should be horizontal or vertical. A table for these values is found below.

Table S3: Values for flash vessel calculations.

Pressure (bar)	10	1
ρ_L (kg·m^{-3})	1200	2160
ρ_V (kg·m^{-3})	5.15	0.590
Q_V (m^3·s^{-1})	0.188	2.34
Q_i (m^3·s^{-1})	5.40 x 10^{-3}	2.08 x 10^{-3}
V (m^3)	1.62	0.622
L (m)	7.03	0.860
D (m)	0.542	0.960

Additionally, a control valve for each flash vessel was required in order to modulate pressure – these are costed identically to the control valves used in the SCWD design above [32].

Using the total cost, an annual interest rate of 5% and a 9.5 year lifetime, the annual payment can be calculated as follows [38]:

$$Annual\ Payment = C_{BM} * \frac{i(1+i)^n}{(1+i)^n - 1}$$

Here, i is the interest rate (0.05) and n is the number of years.

Table S4: ZLD case equipment capital costs, bare module cost (CBM) and total module cost (CTM).

	Total Cost	Cost·yr^{-1}	Annual Payment·yr^{-1}
SCWR	$ 249,000	$ 26,000	$ 34,000
HX	$ 672,000	$ 71,000	$ 91,000
Sulf	$ 27,000	$ 3,000	$ 4,000
Soft	$ 25,000	$ 3,000	$ 3,000
Hydro	$ 27,000	$ 3,000	$ 4,000
Pump	$ 233,000	$ 24,000	$ 31,000
Flash	$ 131,000	$ 14,000	$ 18,000
NORM	$ 59,000	$ 6,000	$ 8,000
Sand	$ 25,000	$ 3,000	$ 3,000
UV	$ 16,000	$ 2,000	$ 2,000
Generator	$ 1,025,000	$ 108,000	$ 138,000
Cool	$ 112,000	$ 12,000	$ 15,000

Total (CBM)	**$ 2,599,000**	**$ 274,000**	**$ 350,000**
Total (CTM)	**$ 3,067,000**	**$ 323,000**	**$ 413,000**

Table S5: Brine concentration case equipment capital costs, bare module cost (CBM) and total module cost (CTM).

	Total Cost	Cost·yr^{-1}	Annual Payment·yr^{-1}
SCWR	$ 249,000	$ 26,000	$ 34,000
HX0	$ 588,000	$ 62,000	$ 79,000
HX1	$ 432,000	$ 45,000	$ 58,000
Hydro	$ 27,000	$ 3,000	$ 4,000
Pump	$ 233,000	$ 24,000	$ 31,000
Sand	$ 25,000	$ 3,000	$3,000
UV	$ 16,000	$ 2,000	$2,000
Generator	$ 1,060,000	$ 112,000	$ 143,000
Cool	$ 108,000	$ 11,000	$ 15,000
Total (CBM)	**$ 2,737,000**	**$ 287,000**	**$ 367,000**
Total (CTM)	**$ 3,215,000**	**$ 338,000**	**$ 433,000**

Table S6: ZLD case operating costs breakdown.

	Typical Range	Value Used	Cost ($·yr^{-1})
Direct Manufacturing Cost			
Raw Materials	-	1	$ 4,732,000
Solid Waste Disposal	-	1	$ 1,919,000
Utilities	-	1	$ 3,077,000
Operating Labor	-	1	$ 303,000
Direct Supervisory and Clerical Labor	(0.1-0.25)COL	0.1	$ 30,000
Maintenance and repairs	(0.02-0.1)FCI	0.1	$ 307,000
Operating Supplies	(0.1-0.2)Maintenance	0.2	$ 61,000
Laboratory Charges	(0.1-0.2)COL	0	$ 0
Patents and Royalties	(0-0.06)COM	0	$ 0
Fixed Manufacturing Costs			
Depreciation	0.1FCI	0	$ 0
Local Taxes and Insurance	(0.014-0.05)FCI	0.032	$ 98,000
Plant Overhead Costs	(0.5-0.7)*(COL+DSCL+MR)	0.5	$ 320,000

General Manufacturing Costs			
Administration costs	0.15*(COL+DSCL+MR)	0.15	$ 96,000
Distribution and selling costs	(0.02-0.2)COM	0.11	$ 1,353,000
Research and Development	0.05COM	0	$ 0
Total Operating Costs			**$ 12,298,000**

Table S7: Brine concentration case operating costs breakdown.

	Typical Range	Value Used	Cost ($\$\cdot yr^{-1}$)
Direct Manufacturing Cost			
Raw Materials	-	1	$ 1,384,000
Solid Waste Disposal	-	1	$ 49,000
Utilities	-	1	$ 3,254,000
Operating Labor	-	1	$ 303,000
Direct Supervisory and Clerical Labor	(0.1-0.25)COL	0.1	$ 30,000
Maintenance and repairs	(0.02-0.1)FCI	0.1	$ 321,000
Operating Supplies	(0.1-0.2)Maintenance	0.2	$ 64,000
Laboratory Charges	(0.1-0.2)COL	0	$ 0
Patents and Royalties	(0-0.06)COM	0	$ 0
Fixed Manufacturing Costs			
Depreciation	0.1FCI	0	$ 0
Local Taxes and Insurance	(0.014-0.05)FCI	0.032	$ 103,000
Plant Overhead Costs	(0.5-0.7)*(COL+DSCL+MR)	0.5	$ 328,000
General Manufacturing Costs			
Administration costs	0.15*(COL+DSCL+MR)	0.15	$ 98,000
Distribution and selling costs	(0.02-0.2)COM	0.11	$ 734,000
Research and Development	0.05COM	0	$ 0
Total Operating Costs			**$ 6,669,000**

Appendix C. Figures of Aspen Simulation

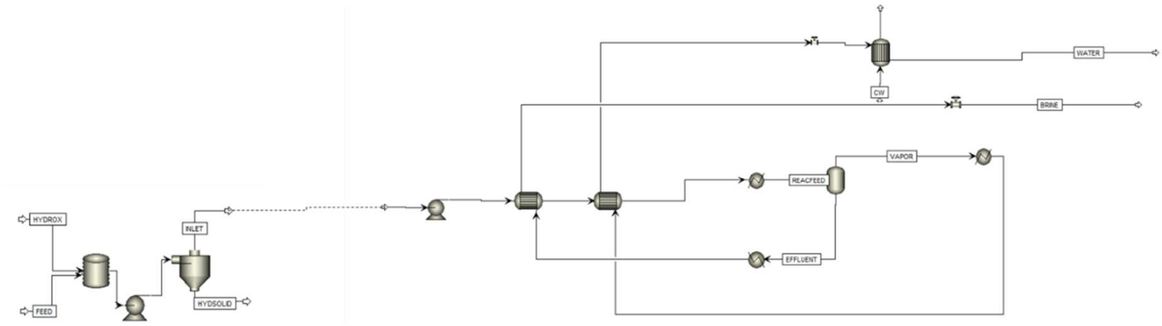

Figure S1: Brine concentration case Aspen Simulation.

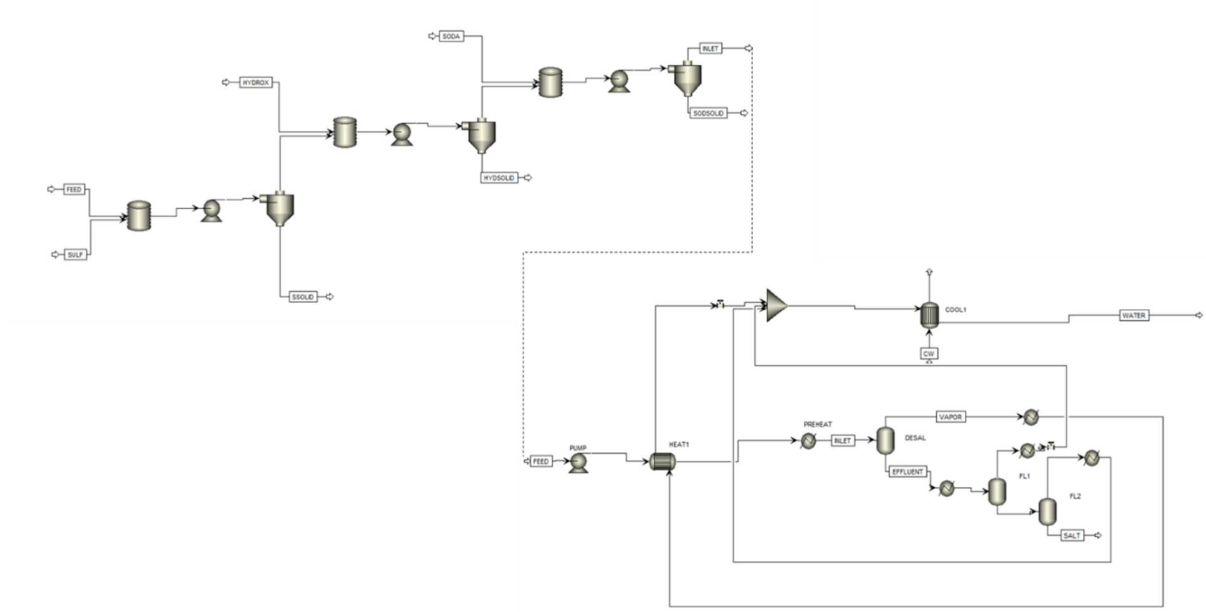

Figure S2: ZLD case Aspen Simulation.

Appendix D: Listing of pertinent streams

D.1. Chemical precipitation

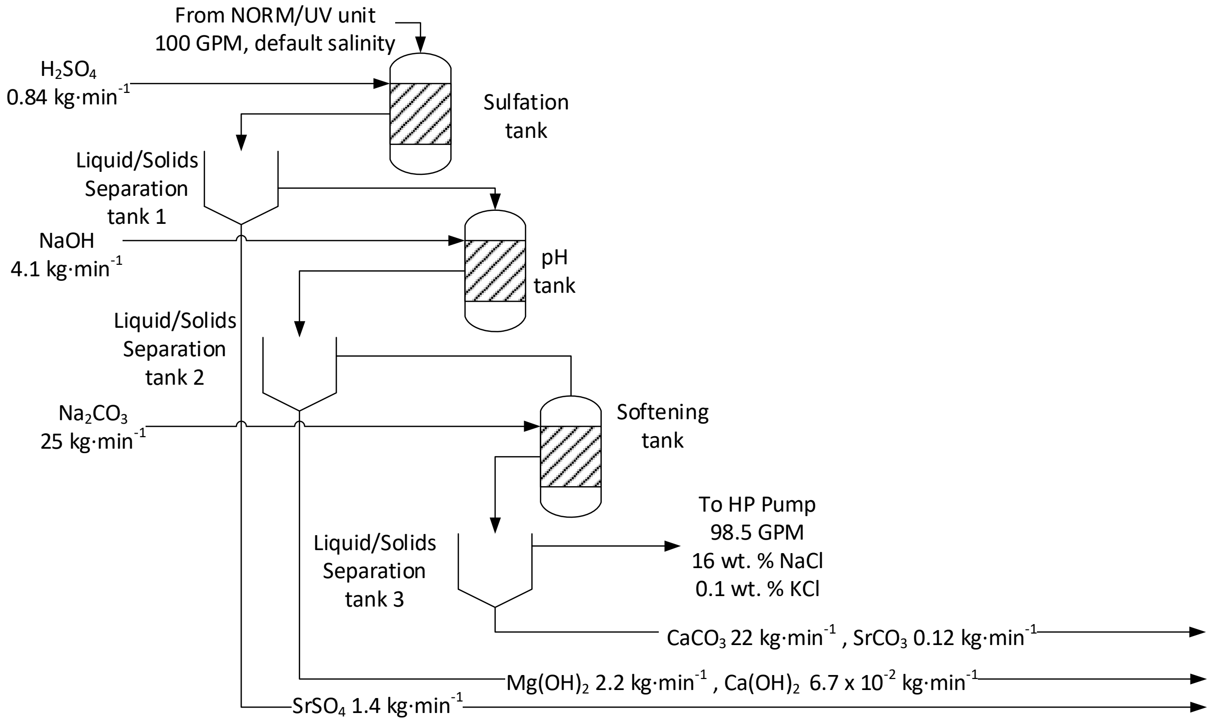

Figure S3: ZLD case precipitation unit material balances.

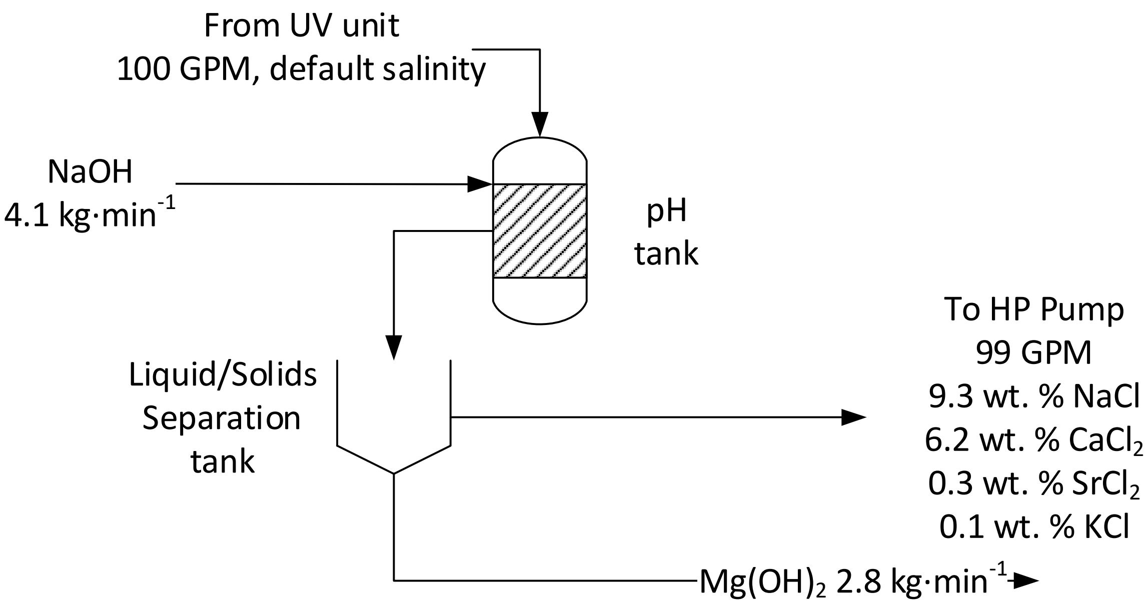

Figure S4: Brine concentration case precipitation unit material balances.

D.2 SCWD system and associated equipment

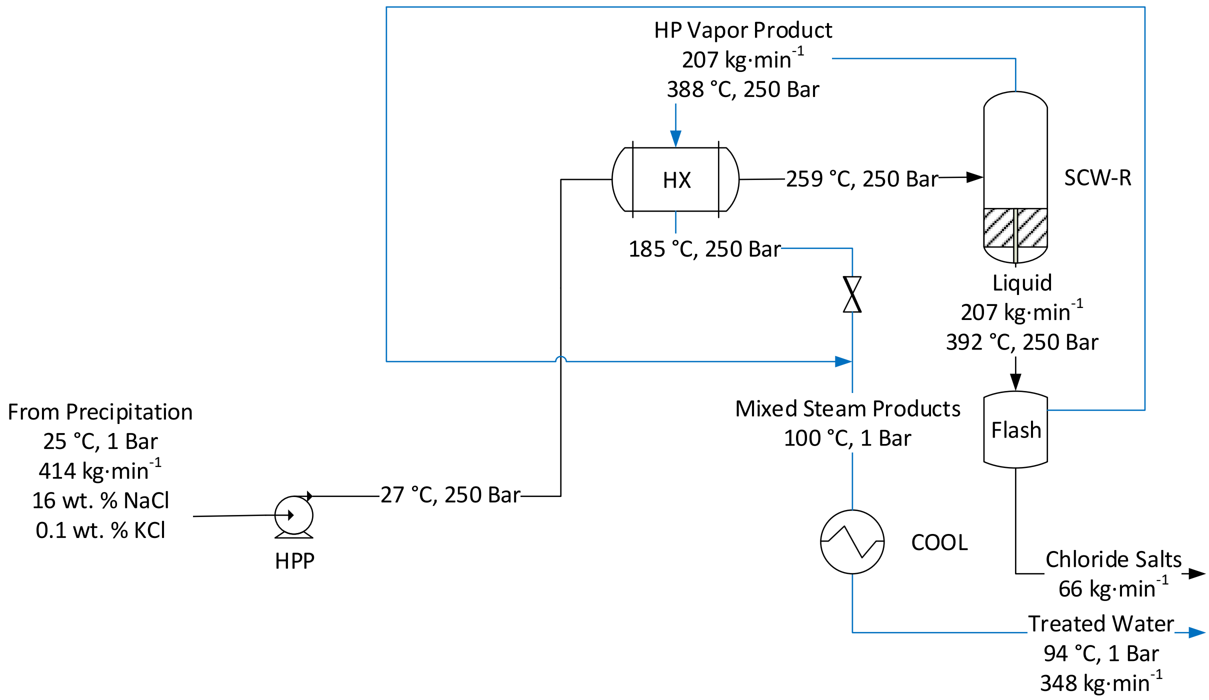

Figure S5: ZLD case high pressure/temperature stream material balances.

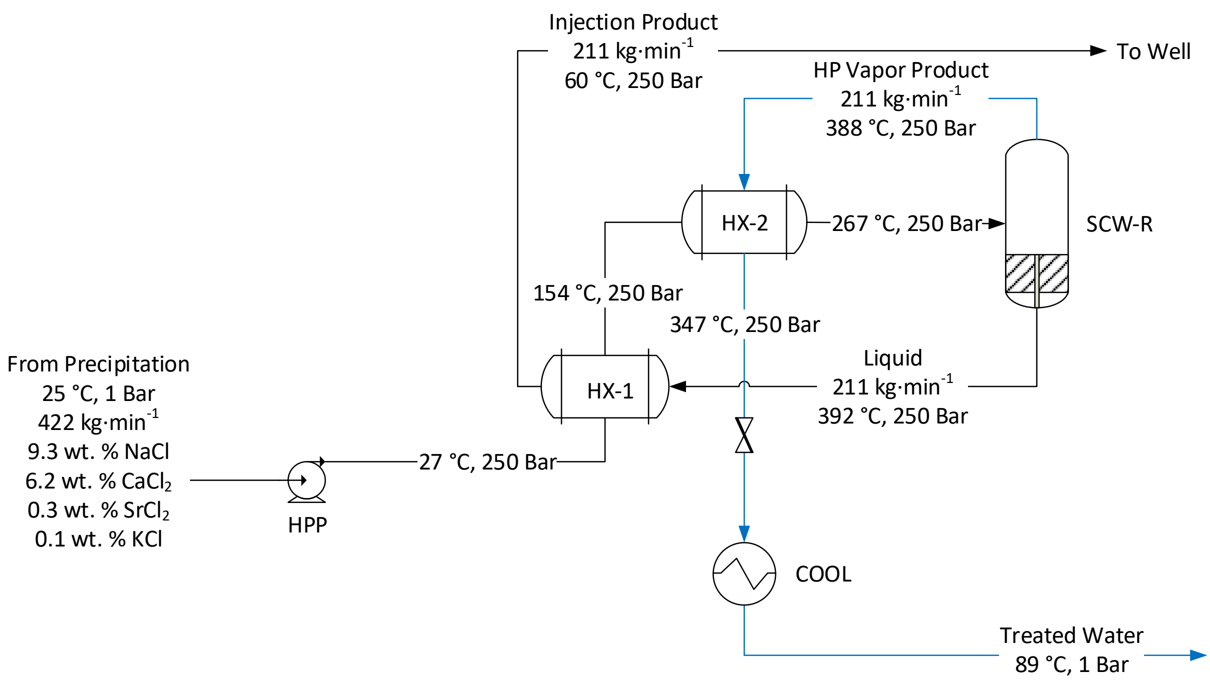

Figure S6: Brine concentration case high pressure/temperature stream material balances.

Appendix E: Cost breakdowns by salinity and pressure

The following tables are meant to demonstrate the shifts in weight for capital, utilities, raw materials, disposal, and labor dependent on the shifts in salinity and pressure for the SCWD system. These are compared to the base case which is also shown in Figure 2.

Table S8: Percentage breakdowns for each cost factor for the ZLD case by salinity and by pressure. The base case numbers are also featured in Figure 2.

		Optimum Recovery Ratio					
		By Salinity, Default Pressure				By Pressure, Default Salinity	
	Base Case	75 g·L^{-1}	105 g·L^{-1}	223 g·L^{-1}	270 g·L^{-1}	230 Bar	280 Bar
Total Capital Cost	**4.0%**	7.6%	6.3%	3.7%	3.2%	4.4%	4.2%
Cost of Labor	**2.9%**	5.1%	4.3%	2.5%	2.1%	2.9%	3.0%
Cost of Raw Materials	**45.3%**	34.2%	39.8%	49.1%	50.8%	44.9%	47.4%
Cost of Solids Disposal	**18.4%**	15.2%	16.9%	19.6%	20.1%	18.2%	19.2%
Cost of Utilities	**29.5%**	37.8%	32.7%	25.1%	23.7%	29.7%	26.2%

Table S9: Percentage breakdowns for each cost factor for the brine concentration case by salinity and by pressure. The base case numbers are also featured in Figure 2.

		Optimum Recovery Ratio					
	Default	By Salinity, Default Pressure				By Pressure, Default Salinity	
	Base Case	75 g·L^{-1}	105 g·L^{-1}	223 g·L^{-1}	270 g·L^{-1}	230 Bar	280 Bar
Total Capital Cost	**6.9%**	9.0%	7.6%	6.1%	5.7%	6.8%	6.8%
Cost of Labor	**4.9%**	6.7%	6.2%	4.3%	3.8%	4.5%	5.1%
Cost of Raw Materials	**22.1%**	13.0%	16.8%	24.7%	26.8%	20.7%	23.3%
Cost of Solids Disposal	**0.8%**	0.5%	0.6%	0.9%	1.0%	0.7%	0.8%
Cost of Utilities	**52.0%**	60.9%	59.3%	52.5%	50.0%	54.8%	53.1%
Cost of Liquid Disposal	**13.3%**	9.9%	9.5%	11.5%	12.7%	12.4%	10.9%