Electrified Solar Zero Liquid Discharge: Exploring the Potential of PV-ZLD in the US

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Abstract

Current brine management strategies are based on the disposal of brine in nearby aquifers, representing a loss in potential water and mineral resources. Zero liquid discharge (ZLD) is a possible strategy to reduce brine rejection while increasing resource recovery from desalination plants. However, treatment of high-salinity brine through ZLD substantially increases the energy consumption and carbon footprint of a desalination plant. The predominant strategy to reduce the energy consumption and carbon footprint of ZLD is through the use of a hybrid desalination technology that integrates with renewable energy. Here, we built a thermodynamic model of the most mature electrified hybrid technology for ZLD powered by photovoltaics (PV). The PV-ZLD system is comprised of a reverse osmosis system coupled with mechanical vapor compression and crystallization. By coupling the thermodynamic model with a computational model, we are able to examine the potential size and geographic distribution of ZLD plants in Arizona, California, Florida, and Texas (e.g., the top four states that produce desalination brine). A multi-objective optimization framework determines the potential plant size considering the location and a number of operational variables. The objective function aims to maximize the thermodynamic performance of the ZLD system and minimize the cost of water and environmental impacts. Texas has the lowest levelized cost of water (1.2 to 1.7 $/m^3) which is largely attributed to the state having available backup power. California is the most effective at using solar energy to power ZLD plants (above 90%), but the state also has the largest projected

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land area requirements. The massive adoption of large-scale PV-ZLD systems depends on the inclusion of efficient preconcentration subsystems that decrease the energy requirements of the brine concentration process, the reduction in CAPEX for PV systems, and the development of a low-cost and low-carbon intensity electric grid. Treating all brine produced in Arizona, California, Florida, and Texas could allow the production of an additional 963 million gallons of freshwater per day.

1 Synopsis

We evaluate the potential of PV-ZLD to treat desalination brine produced in Arizona, California, Florida, and Texas. The feasibility of PV-ZLD is found to depend more significantly on the cost of the energy received from the grid and the regional solar potential. Large-scale PV-ZLD systems have the potential to recover almost 1 billion gallons per day of freshwater if efficient preconcentration subsystems are included, CAPEX is reduced for PV systems, and a low-cost and low-carbon electricity grid is available.
Introduction

Every day, the desalination industry in the contiguous US rejects about 2 billion gallons of brine (or 7.8 million cubic meters). California, Florida, Texas, and Arizona are responsible for rejecting approximately 70% of the total desalination brine in the contiguous United States. The approximate percentage of brine produced in each state is 27%, 26%, 15%, and 3% (Figures S1 and S2). For plants close to the coast, direct discharge of brine to the sea is the most commonly used brine management system. For the inland areas, the predominant means of disposal is deep-well injection\(^1,2\). Both management strategies have several negative social and environmental impacts\(^3,4,5\). Without consolidated brine management, there are also logistical challenges. The disposal of water transported away from a desalination site is an energy-intensive and counterproductive process that loses valuable water. The use of desalination brine as an anthropogenic stream with high salinity in the production of power from the salinity gradient is an alternative for brine management. However, new technologies are needed to prevent membrane contamination and reduce costs to achieve large-scale applicability\(^6,7\).

Zero liquid discharge (ZLD) has recently gained interest as a strategy to completely recover water from desalination brine\(^8\). The main challenge in developing a ZLD industry is the enormous energy consumption of the available technologies. This increases proportionally to the brine-treated concentration\(^8,9\). The expansion of the treatment of high-salinity brine through desalination or reuse requires improvement of materials and processes with the aim of reducing capital and operating costs\(^10\). New technologies have emerged to improve this, such as forward osmosis, solvent extraction, and new evaporative methods that use renewable energy. However, none had large-scale commercial applications\(^11,12,13,14,15,16,17\).

The minimum energy required to separate all salts from brine in the United States is equal to 7.8 TWh (Figure S3). This is equivalent to 0.8% of the total electricity (consumption) in the industrial sector in the United States during 2021, according to the Energy Information Administration (EIA)\(^18\). Since the thermodynamic minimum is unrealistic to attain, the actual minimum energy requirement is closer to double this value. In ZLD, the process with the greatest potential for improvement is the brine concentration\(^10\). Here, the brine reaches the saturation point in terms of solubility.

Without considering a technological breakthrough for saturating the brine in one step, the best strategy for decreasing the energy requirements of ZLD is the hybridization of different
technologies based on operation salinity limits. Hybridization reduces the total specific energy consumption by combining the most efficient technologies for a particular feeding salinity in series. There are numerous alternative hybrid methods based on membranes to concentrate brine, but none is in the commercial state. The use of osmotically assisted reverse osmosis (OARO) and low salt rejection reverse osmosis (LSRRO) systems can decrease the specific energy consumption by 50% compared to traditional brine concentration systems. However, membrane-based methods for the treatment of high-salinity brine had particular challenges related to fouling, which restricts water flux. Combining freeze desalination, membrane distillation, and crystallization can reach ZLD levels and use renewable energy as an energy source. However, energy consumption is greater than RO-based systems. The use of electrodialysis, combined with traditional membrane processes, has shown a potential to concentrate brine with lower energy requirements than conventional systems. Today, the most mature technologies for ZLD are electricity-driven, combining reverse osmosis with mechanical vapor compressors and crystallizers. As more brine with high salinity is treated, the system will require more energy, putting additional stress on the grid. Here, the integration of ZLD with solar energy is a strategy that may alleviate dependence on the current grid. However, the optimal size of the solar field depends on the expected energy consumption of the ZLD plant, which depends on the flow and concentration of brine. Using a dilution for high concentration brine from the desalination industry (up to two times greater than seawater) is a potential strategy that can decrease the energy requirements and costs of a ZLD system. Here, the high-concentration brine mix with the low-concentration feed to reduce the overall concentration of the rejected flow. Dilution is used in brine rejection methods to reduce the environmental risk associated with rejection from water surfaces. However, we hypothesize that there is potential for treating this diluted stream to produce additional freshwater.

This work integrates the previously mentioned strategies (hybridization and brine dilution) and evaluates the potential of hybridization as a sustainable application in the contiguous United States to treat brine rather than reject it. This work aims to identify the optimal size of distributed electrified PV-ZLD plants in the four main brine producer states (Arizona, Texas, California, and Florida). The potential of a solar-driven ZLD must be analyzed by combining different performance metrics and parameters, which usually are location-dependent. Geospatial information must be integrated into the analysis. The consideration of multiple criteria allows us to avoid being misled in decision making. Considering multi-criteria or locations implies the
processing of a large amount of data. Machine learning algorithms help integrate computational simulations and geospatial data in the multi-objective optimization framework\textsuperscript{29}. A multi-objective optimization framework determines the potential size considering the location and operational variables, maximizing the thermodynamic performance of the ZLD system while minimizing the cost of water produced and the environmental impact. The Pareto-optimal size for every state is used as a threshold for implementing a spatially constrained clustering algorithm that determines the number of required plants in the studied regions. This work also explores the benefits in performance and costs of using high-pressure reverse osmosis (HPRO) as preconcentration.

**Methodology**

This work evaluates an electrified hybridized system for zero liquid discharge (see Figure S4). The system produces freshwater and solid salts as its outputs. The energy is supplied by a photovoltaic system that uses the grid as a backup. In the United States, connecting devices directly to the electricity grid has been shown to be a competitive alternative to using fully renewable systems that rely on battery storage, due to the current cost of battery technologies\textsuperscript{30}. The development of a computational model aims to estimate relevant metrics for designing and installing the system in a specific location.

**Computational model of the electrified zero liquid discharge system**

In the pre-concentration stage, the effluent brine (composed by mixing brine from different desalination plants) is the feedwater entering the intake pump. The first pressure exchanger (PX1), mixes 60\% of the feedwater with the remaining feedwater before entering the first RO module (RM1). The second pressure exchanger (PX2), mixes 60\% of the brine of the first RO module with the remaining brine before entering the second RO module (RM2). In the RO module, the flow is divided equally to flow into several units composed of 43 pressure vessels with seven membrane elements each. The brine from the second RO module flows into the pressure exchangers as the high-pressure fluid and the regenerators (R1 and R1) as low-temperature fluid. Each unit treats 2000 m\textsuperscript{3}/h (12.7 MGD). In the concentration step, the brine enters the evaporator. Here, the vapor from the compressor transfers heat to drive the evaporation process. The condensed vapor mixes with the permeate of the RO modules.
producing freshwater. Saturated brine (260 g/kg of concentration) leaves the evaporator/condenser and is transferred to the crystallizer. A heater uses the vapor produced in the crystallizer to increase the temperature of the saturated brine before entering the crystallizer. In this device, part of the brine evaporates, producing a high-concentration slurry where crystal salts are formed. The vapor, compressed into the heater, condenses and produces freshwater. Crystals separate from the slurry in the separator, producing solid salts. The remaining slurry flows through the recirculation pump to mix with the incoming brine to repeat the cycle. The power requirements in this system are the energy consumption from pumping and compressing in the concentration and crystallization steps. A photovoltaic system without battery storage but grid energy backup supplies the required power to the system. The size of the photovoltaic is a variable in the optimization process.

The computational model, developed in the Engineering Equation Solver software\textsuperscript{31}, solves for energy and mass balances providing second law efficiency, power consumption, freshwater and salt produced as a function of input brine flow (m\textsuperscript{3}/h), and concentration (g/kg). Correlations and data from literature regarding thermo-physical and thermodynamics properties of brine complement EES in-built functions for estimating the required parameters\textsuperscript{32,33,34,35,36,37,38}. Furthermore, the correlations available in the literature provide the capital cost for every studied composing the studied system (see supplemental methodology section). The relevant economic metrics obtained are the annualized capital cost for the preconcentration (RO), concentration (MVC), and crystallization (BCr) subsystems.

**Development of a surrogate model using machine learning**

The EES software employs a modified version of Newton’s method, which involves numerically evaluating the Jacobian matrix in every iteration\textsuperscript{31}. However, due to the large resource requirement in each iteration, the software is unsuitable for optimization with large search spaces. Additionally, the software does not implement efficient multi-objective optimization algorithms. Supervised learning algorithms can overcome these limitations to predict the performance of the ZLD system based on computational simulation results. For training, Artificial Neural Networks (ANN) and k-nearest neighbors (kNN) regression are evaluated (see supplemental methods for details about the training process and hyperparameter definition). The computational model provides 50580 points for training. Based on the flow and concentration of the brine, the fitted functions predict the power consumption, the freshwater produced, and
annualized capital cost individualized for the RO, MVC, and BCr subsystems. These functions allow us to estimate second-law efficiency ($\eta_{II,ZLD}$) and levelized cost of water (LCOW).

The second law efficiency is a function of the specific energy consumption of the system and the minimum required energy for separating the salts from the water as follows

$$\eta_{II} = \frac{SEC_{\text{real}}}{SEC_{\text{min}}}$$  \hspace{1cm} (1)

where $SEC_{\text{real}}$ is the ratio between the power consumption and the freshwater produced (predicted using kNN) and $SEC_{\text{min}}$ is the minimum energy required as a function of the Gibbs free energy of the inlets and outflows$^{39,40}$. For brine concentration systems, $SEC_{\text{min}}$ estimations considers a finite recovery ($rr > 0$)$^{41}$.

$$SEC_{\text{min}} = \frac{R \cdot T_f}{M_w} \left[ \ln \left( \frac{1}{a_{w,f}} \right) + b_w \cdot M_w \cdot \ln \left( \frac{a_{s,p}}{a_{s,f}} \right) \right]$$  \hspace{1cm} (2)

where $R$ is the universal gas constant, $T_f$ the feed temperature, $M_w$ is the molar mass of water, $b_w$ the molality of the inlet (feed) brine, $a_{w,f}$ the activity of the inlet brine, $a_{s,p}$ the activity of the salt in a saturated solution and $a_{s,f}$ the activity of the salt in the feed brine.

The levelized cost of water considers the size of the PV field (which is a direct function of the power consumption), the total freshwater production, and the annualized capital cost as follows

$$LCOW = \frac{TAC_{PV} + TAC_{RO} \cdot 1.03 + TAC_{MVC} + TAC_{BCr}}{m_{\text{fresh,system}} \cdot \text{hours} \cdot 365 \cdot f_c}$$  \hspace{1cm} (3)

where $TAC_{PV}$, $TAC_{RO}$, $TAC_{MVC}$, and $TAC_{BCr}$ are the total annualized cost of the PV field, RO, MVC, and BCr subsystems. The factor of 1.03 represents a conservative difference between a traditional RO system and one working as high-pressure reverse osmosis (HPRO) where the upper pressure increases to 120 bar$^{42}$. $f_c$ is the capacity factor of the system assumed as 0.9.

The total annualized cost is the summation of the annual operational cost (TOC) and the annualized capital cost (ACC and predicted using kNN for the RO and MVC subsystems and ANN for the BCr) as follows

$$TAC = ACC + TOC$$  \hspace{1cm} (4)
\[ ACC = CC \cdot CRF \]  

where \( CRF \) is the capital recovery factor used to annualize the total capital cost of the system, which is equal to the sum of the purchase cost of each device. The annualized capital cost per device are corrected to the year 2021 using the CEPCI correction factor (see supplemental methodology section)\(^{43,44}\)

\[ CRF = \frac{i \cdot (1 + i)^{LF}}{(1 + i)^{LF} - 1} \]  

where \( i \) is the interest rate assumed as 0.05 and \( LF \) the lifetime of the plant, assumed as 20 years. The CAPEX and OPEX for the solar field are 1549 \$/kWp and 14 \$/kWp/year\(^{45,46}\). The total annualized cost for the PV field also considers the land annualized cost (see supplemental methods section).

**Multi-objective optimization**

This work considers two multi-objective optimization problems. In the first problem, second-law maximization and levelized cost of water minimization are the objectives. In the second problem, second-law efficiency maximization, levelized cost of water, and \( CO_2 \) emissions minimization are the objectives. In both problems, the goal is to identify the potential size of PV-ZLD plants from the Pareto-solution set minimizing cost, environmental impact, and maximizing thermodynamic performance through second-law efficiency. The \( CO_2 \) emissions depend on the power consumed, the size of the photovoltaic field, and the carbon intensity of the grid as follows

\[ CO_2,emit = Carbon_{intensity} \cdot W_{grid} = Carbon_{intensity} \cdot (W_{system} - W_{PV}) \]  

where \( W_{grid} \) is the total power provided by the grid and is equal to the difference between the total power required by the ZLD system (\( W_{system} \), predicted with kNN) and the contribution of the PV field (\( W_{PV} \)). For simplicity, the operation of the photovoltaic field is assumed to be carbon-free.

In the developed multi-objective optimization problems, the variables are the brine feed flow entering the ZLD system, the concentration, the nominal size of the PV field, and the daily PV yield in the studied region (see supplemental methods). The PV yield is a geospatial variable.
that indicates the potential power yield (kWh/kWp) that a PV system reaches in a determined region. This PV yield is a function of the optimal inclination angle, temperature and global tilted irradiation (GTI)\(^45\). The consideration of this variable aims to include in the analysis a geospatial variable that constrains the nominal PV field size to potential real values based on the solar potential of the region studied. The studied system uses the grid as a backup option, i.e, the grid supplies the energy that the PV field does not. Therefore, as constraints in this multi-objective optimization problem, the solar contribution (defined as the ratio between the power supplied by the PV field and the total power required) must vary between 0 and 1. A value of 0 indicates a system operating only with grid energy, while a value of 1 indicates that the systems operates without the grid support (therefore the PV systems must provide all the required energy during day time). The multi-objective optimization framework developed, available in pymoo library on Python\(^47\), uses as solving algorithm the non-sorted genetic algorithm II (NSGA-II). This algorithm has capacities for fast solve multiple objectives problems\(^48,49\).

**Spatially-constrained clustering**

The results of the multi-objective optimization, applied in the four regions of interest, provide Pareto fronts and the design space distribution, which allows for selecting a potential size for the PV-ZLD plant. The selected brine flow is the desired capacity of the PV-ZLD plant. The number of required plants per region is determined using the Max-P algorithm. This clustering algorithm groups the current desalination plants in the regions of interest\(^50\). Every cluster is assigned to one PV-ZLD plant. The selected algorithm allows spatially constrained clustering that aggregates areas (polygons) into an unknown number of homogeneous regions ensuring the satisfaction of a minimum threshold value defined from an attribute (in this case, the summation of the brine flow from all the desalination plants belonging to the cluster)\(^51\).

**Results**

**Multi-objective optimization per state**

Multi-objective optimization allows for a deep exploration of this trade-off and allows us to identify an optimal design size for a PV-ZLD plant in different states in the United States. The selected states: California, Texas, Florida, and Arizona are chosen because these states produce 70% of the total brine production in the country and represent regions with many desalination
plants and each state has problems with water scarcity (Figure S19). The Pareto front shows how increasing the second law efficiency of the system also increases the LCOW of the system; therefore, there is a trade-off between economic and thermodynamic performance (Figure 1). California presents the largest trade-off, where increasing efficiency from 0.14 to 0.2 results in an increase in LCOW of 15% (from 2.2 to 2.7 $/m^3$). In terms of second-law efficiency, there is no difference from the other states studied. Increasing the efficiency in Texas from 0.14 to 0.2 results in an increase in LCOW of 13% (from 1.21 to 1.37 $/m^3$). For Arizona and Florida, an increase in efficiency in the same range resulted in an increase in LCOW of 14% and 12%. Increasing efficiency to the maximum value per state resulted in an increase in LCOW by 5%, 22%, 17%, and 16% for California, Texas, Arizona, and Florida.

![Figure 1: Pareto front for the LCOW and second-law efficiency for the four studied states (California, Arizona, Texas, and Florida).](https://doi.org/10.26434/chemrxiv-2023-j902p)

California has a higher cost for all second-law efficiency values ranging from 2.3 to 2.7 $/m^3$. This is explained by the high price of the grid electricity when compared with the other three locations (0.138 $/kWh$ for the industrial electricity price\(^5\)) and the high cost of the land (Figure S14b). The plant capacity in the set of solutions for the system located in this region varies in two main ranges; from 3 to 4 MGD and 12 to 13 MGD, with the majority of solutions in the last range (91%) and the remaining in the first range (Figure S17 and Figure S20b). The concentration fluctuates throughout the study range, but for small-capacity ZLD plants, the
concentration is greater than 43 g/kg. The PV yield in the solution set is in the upper bound of 5.94 kWh/kWp per day (or 2168 kWh/kWp per year) during the optimization process, indicating a preference for locations with large solar potential (Figure S20a and Figure S14c). From the geospatial data for the PV potential in the region, only a small central area of this state is suitable for the installation of the system (Figure S14c). The high price of energy from the grid in California makes the implementation of larger PV systems between 10 MW and 30 MW plants attractive (Figure S20c). Throughout the set of solutions, the solar contribution of the photovoltaic field is above 80% indicating potential grid independence to treat the desalination brine in this region (Figure 2). A decrease in CAPEX for solar technologies may contribute to a decrease in LCOW in California. California is a region where PV-ZLD can operate almost independently of the grid when considering the central area as a potential location for low or medium capacity PV-ZLD plants (2 MGD or 13 MGD). The system can operate with large capacities, but is not competitive in cost with other regions. Although the LCOW is larger than surface discharge technologies, it is comparable to deep-well injection and land applications.

Texas is the state where the LCOW is the lowest for all second-law efficiency values ranging from 1.2 to 1.7 $/m^3$. This is explained mainly by the low price of the energy grid in this region compared to the other three locations (0.056 $/kWh for the industrial electricity price\textsuperscript{53}). The plant capacity in the set of solutions for the system located in this region varies in three main ranges; from 2 to 4 MGD, 13 to 14 MGD, and 25 to 27 MGD, with the majority of points in the last range (85%) and similar points in the first and second range with 8% and 7% (Figure S17 and Figure S21b). The concentration fluctuates throughout the range, but for small-capacity ZLD plants, the concentration is higher than 47 g / kg (Figure S17 and Figure S21b). The PV yield in the solution set fluctuates between 5.2 kWh/kWp per day (or 1989 kWh/kWp per year) and the maximum potential (Figure S21a and Figure S16c). From the geospatial data for the PV potential in the region, the west area of this state is suitable for the installation of the system (Figure S16c). The low price of the energy of the grid in Texas makes the implementation of small photovoltaic systems with an average capacity of 5 MW attractive (Figure S21c). Throughout the set of solutions, the solar contribution of the PV field fluctuates between 0.06 and 0.9, and the majority of solutions between 0.06 and 0.14 (Figure 2). However, this indicates that the existence of low potential grid independence for treating desalination brine in this region is subject to the selected solution set, unlike California. From the solution set, the subset with large solar contribution has the smallest plant capacity (Figure S21). Texas
is a region where PV-ZLD can operate with low grid support when considering the west area as a potential location for low-capacity PV-ZLD (2 MGD). The system can operate with large capacities, with a competitive cost (below 1.4 $/m³), but with a lower second-law efficiency.

Arizona follows Texas as the state with the second lowest LCOW for all second-law efficiency values ranging from 1.33 to 1.76 $/m³. The price of the energy grid (0.063 $ / kWh for the price of industrial electricity⁵⁴) explains these results and marks a trend that indicates that the LCOW is directly dependent on the price of the electricity in the grid. The plant capacity in the set of solutions for the system located in this region varies in three main ranges; from 2 to 5 MGD, 13 to 14 MGD and 25 to 26 MGD, with the majority of solutions (70%) in the last range and similar points in the first and second range with 10% and 9% (Figure S17 and Figure S22b). The concentration fluctuates throughout the range, but for small-capacity ZLD plants, the concentration is above 45 g/kg (Figure S17 and Figure S22b). The PV yield in the solution set fluctuates in the majority between 5.25 kWh/kWp per day (or 1916 kWh/kWp per year) and the maximum potential (Figure S22a and Figure S13c). From the geospatial data for the PV potential in the region, the northwest and southern portions of this state are suitable for the installation of the system (Figure S13c). The low price of electricity from the grid in Arizona makes the implementation of small PV systems with an average capacity of 5 MW attractive (Figure S22c). Throughout the set of solutions, the solar contribution of the photovoltaic field fluctuates between 0.06 and 0.92, with the majority of solutions between 0.06 and 0.14 (Figure 2). However, this indicates that the existence of potential grid independence for treating desalination brine in this region is subject to the selected solution set, unlike California and similar to Texas. From the solution set, the subset with a large solar contribution has the smallest plant capacity (Figure S22). Arizona is a region where PV-ZLD can operate with low grid support when considering the south and northeast areas as potential locations for low-capacity PV-ZLD (2 MGD). In other areas, the system can operate with large capacities, with a competitive cost (below 1.5 $/m³), but with a lower second-law efficiency.

Florida follows California as the state with the second largest LCOW for all second-law efficiency values ranging from 1.6 to 2 $/m³. The energy grid price (0.081 $/kWh for the industrial electricity price⁵⁵) explains these results following the trend of the states mentioned above, indicating that the LCOW is directly dependent on the price of the electricity from the grid. The plant capacity in the set of solutions for the system located in this region varies in three main ranges; from 2 to 4 MGD, 13 to 14 MGD and 25 to 27 MGD, with the majority (54%) of
the points in the last range followed by the second range with 40% (Figure S17 and Figure S23b).

The concentration fluctuates throughout the study range, but for small-capacity ZLD plants, the concentration is above 45 g/kg (Figure S17 and Figure S23b). The PV yield in the solution set fluctuates between 4.6 kWh/kWp per day (or 1679 kWh/kWp per year) and the maximum potential, indicating that the location of PV-ZLD does not depend on the largest solar potential areas (Figure S23a and Figure S15c). From the geospatial data for PV potential in the region, the area on the southwest coast is suitable for the installation of the system (Figure S15c). The price of grid energy in Florida makes the implementation of small to medium photovoltaic systems with capacities between 5 and 10 MW attractive (Figure S23c). Throughout the set of solutions, the solar contribution of the photovoltaic field fluctuates between 0.07 and 0.99, and the majority of solutions are between 0.07 and 0.22 (Figure 2). However, this indicates that the potential independence of the grid for treating desalination brine in this region is subject to the selected set of solutions. From the solution set, the subset with a large solar contribution has the smallest plant capacity (Figure S23). The cost and efficiency of these plants increase as the concentration of the inlet brine increases from 46 to 49 g/kg. Florida is a region where PV-ZLD can operate with low grid support when considering the Southwest Coast area as a potential location for low-capacity PV-ZLD (2.7 MGD). In other areas, the system can operate with large capacities, with a competitive cost but lower second-law efficiency.

Figure 2: Solar contribution of the PV field to the PV-ZLD plants in the solution set. A value of 1 indicates a plant driven 100% by solar energy while 0 indicates a plant driven completely by grid energy.
The influence of CO\textsubscript{2} emissions

The multi-objective optimization framework in this work allows for identifying the potential size for PV-ZLD plants when considering the minimization of cost and maximization of efficiency. These two metrics are of interest from an economic and thermodynamic point of view. The addition of the minimization of CO\textsubscript{2} emissions as an objective incorporates an environmental metric of interest. The Pareto front shows how increasing the second-law efficiency of the system also increases the LCOW of the system, as in the previous case. However, for the same second-law efficiency, the levelized cost of water can increase due to the influence of the third objective (Figure S24a). Similarly, there is a trend to decrease the levelized cost of water while increasing CO\textsubscript{2} emissions for Texas, Arizona, and Florida (Figure S24b). California is an exception since in this region the solar contribution is greater and the system is not dependent on the grid (Figure S26). The inverse relation between cost and CO\textsubscript{2} emissions is due to the large CAPEX associated with the implementation of a PV system in the studied regions. For example, installing PV-ZLD with a low contribution from the grid in Texas allows us to treat the brine with a LCOW of 1.6 $/m^3$. Increasing the contribution of the grid to the system allows the LCOW to decrease to 1.2 $/m^3$, but increases 10 times the CO\textsubscript{2} emissions per year.

California’s LCOW has a marginal change when including CO\textsubscript{2} emissions as an objective, ranging now from 2.3 to 2.83 $/m^3$ (Figure S27d). The remaining states LCOW also have a marginal change when including CO\textsubscript{2} emissions as objective ranging now from, 1.3 to 1.8, 1.6 to 2.1, and 1.2 to 1.7 $/m^3$ for Texas, Arizona, and Florida (figures S28d, S29d, and S30d).

From an economic point of view (red line in Figure S31a), California benefits from installing large capacity PV-ZLD plants (30 MW and 13 MGD) that treat low salinity brine (25 g/kg) with a solar contribution greater than 94%. From a thermodynamic point of view (blue line in Figure S31a), California benefits from installing small capacity PV-ZLD plants (5 MW and 2.3 MGD) that treat high salinity brine (49 g/kg) with a solar contribution of 93%. From an environmental point of view (green line in Figure S31a), California benefits from installing medium capacity PV-ZLD plants (14 MW and 5.7 MGD) that treat brine at seawater levels (38 g / kg) with full contribution from the PV field.

From an economic point of view (red line in Figure S31b), Texas benefits from installing large capacity PV-ZLD plants (5 MW and 26 MGD) treating low salinity brine (25 g/kg) with a large dependence on the grid (8% of the solar contribution). From a thermodynamic point of view (blue line in Figure S31b), Texas benefits from installing small-capacity PV-ZLD plants...
(5 MW and 2 MGD) that treat large salinity brine (50 g / kg) with a large solar contribution (91%). From an environmental point of view (green line in Figure S31b), Texas benefits from installing medium-capacity PV-ZLD plants (7 MW and 3 MGD) that treat salt brine at seawater levels (30 g / kg) with a large solar contribution (99%).

From an economic point of view (red line in Figure S31c), Arizona benefits from installing large capacity PV-ZLD plants (5 MW and 26 MGD) that treat low salinity brine (25 g/kg) with a large grid dependence (9% of the solar contribution). From a thermodynamic point of view (blue line in Figure S31c), Arizona benefits from installing small capacity PV-ZLD plants (5 MW and 2 MGD) treating high salinity brine (50 g/kg) with a large solar contribution (84%). From an environmental point of view (green line in Figure S31c), Arizona benefits from installing medium capacity PV-ZLD plants (8 MW and 3 MGD) that treat salt brine of seawater levels of salinity (43 g / kg) with a large solar contribution (99%).

From an economic point of view (red line in Figure S31d), Florida benefits from installing large capacity PV-ZLD plants (5 MW and 26 MGD) that treat low salinity brine (25 g/kg) with a large grid dependence (8% of the solar contribution). From a thermodynamic point of view (blue line in Figure S31d), Florida benefits from installing small-capacity PV-ZLD plants (6 MW and 3.7 MGD) treating large salinity brine (49 g / kg) with a large solar contribution (62%). From an environmental point of view (green line in Figure S31d), Florida benefits from installing medium-capacity PV-ZLD plants (20 MW and 7.7 MGD) that treat high salinity brine (49 g / kg) with a large solar contribution (99%).

Including CO$_2$ emissions as the third objective allows the addition of environmental parameters that affect the optimization process. This also allows for including a new parameter from the grid (carbon intensity) in the analysis. The negligible change in the LCOW from the Pareto front, suggests that the grid carbon intensity is not as relevant as the grid electricity price, however, influences the increase of the solar contribution in the Pareto optimal solution set for Texas, Arizona, and Florida.

**Selection of number of required PV-ZLD**

From the Pareto optimal solution set in this problem, the selection of a singular solution depends on the preference of decision-makers between thermodynamic, economic, or environmental performance and the requirements of brine treatment (flow and concentration). When there is no preference available, knee solutions are attractive to study. In the knee region of a Pareto front,
a solution improves a determined goal with a small degradation of other objectives, compared to solutions located far from the knee along the front\textsuperscript{56}. This section explores the influence of selecting a solution set from the knee region in every studied state. The brine feed flow, the concentration of the brine, the yield of the photovoltaic field, and the nominal size of the photovoltaic field compose the solution set in this work. The pymoo library contains an in-build method for estimating high trade-off points (knee region)\textsuperscript{47,56}. The brine feed flow from the high trade-off points for every state represents the threshold in a spatially constrained clustering. This threshold will establish the minimum capacity a PV-ZLD plant must have to treat the incoming brine from real desalination plants in the state of interest. This method allows for the creation of homogeneous groups in terms of the capacity of the PV-ZLD plant to treat brine.

California has 19 Pareto-optimal solutions in different knee regions when considering two objectives (Figure S32a and Table S2). A small plant (4 MGD) or a large plant (MGD) can treat brine with a concentration of 45 g/kg. For treating brine with a lower concentration, the best option is a larger capacity plant (13 MGD). The small ZLD plant has the maximum second-law efficiency, but also an increased LCOW compared to the larger ZLD plants. Due to the concentration range, 13 MGD is the threshold value used in spatially restricted clustering. Based on this value, a total of 26 PV-ZLD plants in California can treat the total brine produced by desalination plants in this state (Figure 3a and Table S10). Each plant treats an average of 15 MGD (minimum of 13 MGD and maximum of 22 MGD) with a concentration of 34 g/kg (minimum 23 and maximum 57 g/kg). The brine from the desalination plants belonging to the same group mixes before entering the plant. This process decreases the total concentration because of the dilution produced during the mixing of high-concentration brine with low-concentration brine. Treatment of the entire brine produced in California allows recovering 368 MGD of freshwater and 48404 tons of salt per day (Table S10).

For a three-objective analysis, considering the reduction of CO\textsubscript{2} emissions, California has 14 Pareto-optimal solutions in different regions of the knees (Figure S33a and Table S6). A small plant (2 MGD) or a large plant (13 MGD) can treat brine with a concentration of 45 g/kg, but a plant of capacity equal to 2 MGD can treat brine with up to 49 g/kg concentration. For treating brine with a lower concentration, the best option is a large capacity plant (13 MGD) from an economic point of view and a small capacity plant (3 MGD) from a thermodynamic point of view. Again, 13 MGD is the threshold value used in the spatially constrained clustering, since
it is possible to treat a higher concentration brine and decrease the required number of PV-ZLD plants. With the same minimum threshold of 13 MGD during clustering, as the case with two objectives (Figure 3b and Table S11), every plant treats an average of 15 MGD (minimum of 13 MGD and maximum of 22 MGD) with a concentration of 34 g/kg (minimum 23 and maximum 55 g/kg). The small difference is due to the decimal approximation for the threshold value.

Texas has five Pareto-optimal solutions in different knee regions when considering two objectives (Figure S32b and Table S3). The capacity ranges from 5 to 26 MGD, indicating that this region is feasible for installing small and large PV-ZLD plants. The concentration for small and medium plants (5 and 14 MGD) is 49 g/kg. For larger plants (26 MGD), the concentration is 35, 45 or 49 g/kg. This indicates that Texas benefits when installing large-capacity plants capable of treating brine with a concentration greater than 45 g/kg. Due to the concentration range, 26 MGD is the threshold value used in the spatially constrained clustering. Based on this value, a total of 7 PV-ZLD plants in Texas can treat the total brine produced by the desalination plants in this state (Figure 4a and Figure S12). Each plant treats an average of 30 MGD (minimum of 26 and maximum of 35 MGD) with a concentration of 29 g/kg (minimum of 13 and maximum of 42 g/kg). Treating the whole brine produced in Texas allows recovering 202 MGD of freshwater and 22955 tons of salt per day (Table S12).

For a three-objective analysis, Texas has 20 Pareto-optimal solutions in different knee regions (Figure S33b and Table S7). The capacity ranges from small sizes (2 to 4 MD), medium (13
to 15), to large (26 MGD), indicating that this region is feasible for installing small and large PV-ZLD plants. The concentration ranges from 30 to 50 g/kg, while for larger plants it ranges from 40 to 50 g/kg. In terms of LCOW, larger plants produce freshwater at a 10% lower value, but CO₂ emissions increase 33 times (from 0.29 to 9.68 tons per year on average). 26 MGD is the threshold value used in the spatially constrained clustering, in an attempt to install the lowest number of plants with the lowest cost. With the same minimum threshold during the clustering, the number of clusters remains in the case with two objectives (Figure 4b and Table S13). Each plant treats an average of 30 MGD (minimum of 27 MGD and maximum of 35 MGD) with a concentration of 28 g/kg (minimum of 14 and maximum of 39 g/kg). The small difference is due to the decimal approximation of the threshold value.

Arizona has 14 Pareto-optimal solutions in different knee regions when considering two objectives (Figure S32c and Table S4). The capacity ranges from 2 to 26 MGD indicating that this region is feasible for installing small and large PV-ZLD plants. The concentration for small and medium plants (2 to 14 MGD) ranges from 45 to 50 g/kg. For larger plants (26 MGD), the concentration is 30, 35, 40, 45 or 49 g/kg. This indicates that Arizona benefits when installing large capacity plants capable of treating brine with concentrations ranging from 25 to 44 g/kg. The size of the photovoltaic field is 5 MW. Due to the low number of desalination plants and therefore the brine rejected that needed treatment, using the maximum capacity (26 MGD) as the threshold results in only one group to treat all the brine produced in Arizona. In this context, the plants receive brine with a concentration of 30 g/kg based on the mixing between all brine streams rejected by the desalination plants. However, the unique plant capacity is larger...
than the value at the high trade-off point, so, for Arizona, the new threshold value selected is 14 MGD. Based on this value, 3 PV-ZLD plants can treat the total brine produced in this state (Figure 5a and Table S14). Each plant treats an average of 15 MGD (minimum 14 MGD and maximum 16 MGD) with a concentration of 30 g/kg (minimum of 25 g/kg and maximum of 35 g/kg). It is possible to recover 43 MGD of freshwater from Arizona brine and 4967 tons of salt per day (Table S14).

For a three-objective analysis, Arizona has 11 Pareto-optimal solutions in different knee regions (Figure S33c and Table S8). The capacity ranges from 3 to 27 MGD indicating that this region is feasible for installing small and large PV-ZLD plants. The concentration for small and medium plants (3 and 14 MGD) ranges from 25 to 47 g/kg. For larger plants (26 to 27 MGD) the concentration is 25, 39, 44 or 45 g/kg. This indicates that Arizona benefits when installing large capacity plants capable of treating brine with concentrations ranging from 25 to 44 g/kg. The size of the photovoltaic field ranges from 8 MW to 29 MW indicating potential independence from the grid. The selected threshold value is 14 MGD to avoid installing only one plant. The number of PV plants is the same as the case of two objectives (Figure 5b and Table S15).

Florida has eight Pareto-optimal solutions in different knee regions when considering two objectives (Figure S32d and Table S5). The capacity ranges from 3 to 26 MGD indicating that this region is feasible for installing small and large PV-ZLD plants. The concentration...
for small and medium plants (5 and 14 MGD) is 45 and 49 g/kg. For larger plants (26 MGD) the concentration is 30, 35, 40 or 45 g/kg. This indicates that Florida benefits when installing large capacity plants capable of treating brine with a concentration above 30 g/kg. The size of the photovoltaic field is 5 MW indicating a larger dependence on the grid. Due to the concentration range, 26 MGD is the threshold value used in spatially constrained clustering. Based on this value, a total of 11 PV-ZLD plants in Florida can treat the total brine produced by desalination plants in this state (Figure 6a and Table S16). Each plant treats an average of 32 MGD (minimum of 26 and maximum of 43 MGD) of brine with a concentration of 28 g/kg (minimum of 15 and maximum of 39 g/kg). Treatment of the entire brine produced in Florida allows 350 MGD of freshwater to be recovered and 37842 tons of salt per day (Table S16).

For a three-objective analysis, Florida has 14 Pareto-optimal solutions in different knee regions (Figure S33d and Table S9). The capacity ranges from small sizes (3 to 4 MD), medium (13 to 14), to large (26 MGD), indicating that this region is feasible for installing small and large PV-ZLD plants. The concentration ranges from 32 to 49 g/kg, while for larger plants it ranges from 33 to 45 g/kg. In terms of LCOW, large plants produce freshwater at a 4% lower value, but CO₂ emissions increase 8.75 times (from 0.96 to 8.4 tons per year on average). 26 MGD is the threshold value used in the spatially constrained clustering, in an attempt to install the lowest number of plants with the lowest cost. With the same minimum threshold during the clustering, the number of clusters remains in the case with two objectives (Figure 6b and Table S17). Each plant treats an average of 3 MGD (minimum 26 MGD and maximum 44 MGD) with a concentration of 28 g / kg (minimum 14 and maximum 39 g / kg). The small difference is due to the decimal approximation of the threshold value.

**The importance of the preconcentration step**

Clustering of different desalination plants into a distributed network of PV-ZLD plants benefits the operation of the studied system due to the potential mixing of brine from different plants. The main benefit is the possibility of diluting the incoming brine, reducing the concentration of the feed flow into the ZLD system. The decrease in the concentration makes the use of a membrane-based system (HPRO in this work) as a preconcentration step. In southern California, it is common to use brine disposal lines to transport brine to wastewater facilities for further disposal into the ocean. The design of a competitive alternative to surface discharge can encourage the design of brine mixing pipe systems to transport the brine to strategically
Two objectives

Three objectives

Figure 6: Cluster distribution for the required PV-ZLD plants based on spatially constrained clustering in Florida using the Max-P algorithm. The desalination plants clustered by color provides brine to a PV-ZLD plant. The multi-objective optimization provides the minimum threshold value for a) 2 and b) 3 objectives. The centroid (hexagon) represents the center of mass of every cluster for better visualization.

Located ZLD plants. There is recognition of the crucial impact of the preconcentration step in the goal of making ZLD a substitute for discharge methods. Without it, in this work, for treating the same brine (feed flow and concentration), the capital cost of the concentration increases 2 times on average (Figure S34b). This is due to the increase in the feed flow inside the subsystem, which increases the heat transfer area and compressor size. The cost difference of the crystallization subsystem is negligible (2% lower on average without preconcentration step) mainly due to a reduced flow entering the system (Figure S34d). With a preconcentration step, less brine flows into concentration and crystallization.

The trade-off between second-law efficiency and levelized water cost remains, but the levelized cost range increases, while the second-law efficiency range decreases compared to the case with preconcentration (Figure S35a). The maximum second-law efficiency reachable of the system without preconcentration is 41% lower than the maximum second-law efficiency obtained by optimization of the system with preconcentration (Figure S35a and Figure 1). The LCOW increases 41%, 44%, 46% and 61% for the multi-objective optimization results in Texas, Arizona, Florida, and California when the system does not consider preconcentration (from a minimum of 1.7 $/m^3$ in Texas to up to 4 $/m^3$ in California compared to 1.3 $/m^3$ and 2.7 $/m^3$ for the same conditions, when using preconcentrator). Regarding the size of the plants. There is a wide range of sizes (from 10 MGD to 35 MGD) compared to a preconcentration system (Figure S35b). Texas and Arizona’s size trend to the maximum, while California and Florida to the minimum. This difference in size influences the solar contribution in every state.
For Arizona and Texas, the cost of the low energy grid incentives a small PV field (Figure S39c and Figure S37c) with a solar contribution lower than 20%. The higher power consumption of a system without preconcentration decreases the potential of renewable-driven ZLD in these states (Figure S34f). On the other hand, Florida and California had a greater solar contribution, explained mainly due to their higher energy grid cost compared to the previous states (Figure S35). In these states, the PV field size trends to the maximum (Figure S36c and Figure S38c). The increase in solar contribution is directly related to the increase in the required solar area (S40). For both cases (with and without an HPRO system operating as preconcentrator), an increase in solar contribution implies the need of producing all the power required during the day as this study does not consider battery backup option. Therefore, the investment in the solar field is larger compared to the locations where the grid is a viable backup option (Texas and Arizona).

The inclusion of a preconcentration system (in this work, a HPRO system), allows a reduction in the total cost and power consumption. This reduction also increases the potential of the solar contribution to the studied system. The reduction of energy consumption due to the implementation of efficient systems benefits the sustainable growth of the ZLD industry.

Zero liquid discharge is a growing strategy for treating brine from desalination. Through the combination of computational thermodynamic models and machine learning, it is possible to predict the performance of a PV-ZLD system on the basis of the characteristics of the brine (total flow and concentration). This work evaluated the potential strategy for identifying and implementing PV-ZLD plants in a distributed brine work in four states.

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Author Contributions


Declaration of Interests

There are no conflicts of interest to declare.

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Figure Legends

1. Pareto front for the LCOW and second-law efficiency for the four studied states (California, Arizona, Texas, and Florida).

2. Solar contribution of the PV field to the PV-ZLD plants in the solution set. A value of 1 indicates a plant driven 100% by solar energy while 0 indicates a plant driven completely by grid energy.

3. Number of required PV-ZLD plants based on spatially constrained clustering in California using the Max-P algorithm\(^\text{(51)}\). The multi-objective optimization provides the minimum threshold value for a) 2 objectives and b) 3 objectives. The centroid (hexagon) represents the center of mass of every cluster for better visualization.

4. Number of required PV-ZLD plants based on spatially constrained clustering in Texas using the Max-P algorithm\(^\text{(51)}\). The multi-objective optimization provides the minimum threshold value for a) 2 objectives and b) 3 objectives.

5. Number of required PV-ZLD plants based on spatially constrained clustering in Arizona using the Max-P algorithm\(^\text{(51)}\). The multi-objective optimization provides the minimum threshold value for a) 2 objectives and b) 3 objectives.

6. Number of required PV-ZLD plants based on spatially constrained clustering in Florida using the Max-P algorithm\(^\text{(51)}\). The multi-objective optimization provides the minimum threshold value for a) 2 objectives and b) 3 objectives.