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Review of solar-enabled desalination and implications for zero-liquid-discharge applications

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Abstract

The production of freshwater from desalinating abundant saline water on the planet is increasingly considered a climate change adaptation measure. Yet, there are challenges associated with the high cost, intensive energy demand, and environmental implications of desalination. Effective integration of solar energy generation and freshwater production can address both issues. This review article highlights recent key advances in such integration achieved in a joint-research university-national laboratory partnership under the auspices of the United States Department of Energy and parallel efforts worldwide. First, an overview of current and emerging desalination technologies and associated pretreatment, brine treatment, and valorization technologies that together can result in zero-liquid-discharge systems is presented, and their technological readiness levels are evaluated. Then, advanced modeling techniques and new software platforms that enable optimization of solar-desalination applications with the dual objective of cost and environmental impact minimization are discussed.

1. Introduction

In the face of climate change and pressing water scarcity, many municipalities in the United States are increasingly considering the production of freshwater from the desalination of alternative water sources such as wastewater, brackish water, and seawater (Gude and Fthenakis 2020, Xu *et al* 2022, Lugo *et al* 2023). In addition to providing a source of clean drinking water, desalination is employed by oil and gas (O&G) industries (Jiang *et al* 2022a, Delanka-Pedige *et al* 2023) and for cooling operations in power stations (Plata *et al* 2022). Desalination can be performed through thermal or membrane filtration techniques. Thermal technologies use both heat for evaporation and electricity for pumping water, while pressure-driven membrane technologies use electricity that is converted to mechanical energy, to overcome osmotic pressure and separate the dissolved solids from the saline water. As solar energy is abundant in arid areas where the production of freshwater is needed, powering desalination with solar electricity or solar thermal energy makes a lot of sense.

To meet drinking water standards and consumer requirements, and improve desalination outcomes, additional treatment is often required before (pre-treatment) and after (post-treatment) the main desalination process. Pre-treatment may include a wide variety of approaches depending on the key fouling and scaling constituents present in the source water; a very common approach involves the addition of chemicals to prevent scaling, biofouling, and corrosion. More specifically, pre-treatment of the feed water is required to reduce the concentration of microorganisms, suspended and colloidal particles, and dissolved organic and inorganic pollutants to acceptable levels for the subsequent process. Commercially available pre-treatment methods include physical technologies such as sedimentation and filtration; biological

methods such as membrane bioreactors and biofilters; chemical methods such as softening, coagulation, and disinfection (Abdel-Fatah and Al Bazedi 2020). Post-treatment may be necessary to demineralize and stabilize the distillate or permeate by increasing the pH and hardness content and it may also include disinfection of product water before distribution as a drinking water supply.

Depending on desalination technologies and source water quality, 10% to 50% of feed water will become concentrate (or brine), restricted by water recovery due to fouling and scaling potential of brackish water and wastewater, or pressure limitation of membrane elements during seawater desalination. Brine management is considered a significant challenge for implementing desalination technologies, especially in inland locations. Many desalination projects could not proceed due to limited brine disposal options such as a lack of suitable receiving bodies for surface water discharge, sewer discharge, land application, and deep well injection; and restrictions due to environmental regulations and/or permitting. These barriers can be overcome by the use of zero-liquid-discharge (ZLD) technology. In a ZLD process, desalination brine is further concentrated into solids or dense slurries that can be transported offsite for disposal or recycling, thus achieving complete (or near complete) elimination of liquid waste from a desalination facility (Alspach and Juby 2018). Conventional ZLD processes have high life cycle costs, which are largely attributed to substantial specific energy demand due to thermal brine concentrators and crystallizers. The ZLD costs can be reduced by using high recovery desalination technologies to minimize brine volume and using solar energy to heat brine concentrators and crystallizers.

Depending on the source water chemistry, desalination brine may contain valuable minerals that can be extracted and create revenues from commercial product sales. Selective chemical precipitation, precision extraction, and crystallization will be needed to produce high-purity chemical products, which have significant energy requirements. Therefore, developing solar-enabled innovative technologies to improve water recovery, reduce brine volume, and achieve ZLD and brine valorization is critical to overcoming the barriers to implementing desalination technologies.

2. Desalination status in the United States

There are approximately 700 desalination plants in the US and most of them are for brackish water sources (Mickley 2018). Fewer than 15 plants use seawater, including the Carlsbad Seawater Desalination Plant in San Diego, California, which is the biggest in North America, producing 50 million gallons per day (MGD), thus 189 270 m³ d⁻¹ of freshwater (Quon *et al* 2022).

The United States Geological Survey (USGS) publishes reports that list data on brackish water resources (Stanton *et al* 2017, USGS Produced Waters Geochemical Database). Gude and Maganti (2021) estimated that about 3 billion gallons of saline groundwater were used every day in the United States, corresponding to roughly 3.7% of the nation's total groundwater use. An estimated 95% of that use occurred in eight states: Alaska, California, Hawaii, Louisiana, Oklahoma, Texas, Utah, and Wyoming (Xu *et al* 2022). Due to the large volume of saline water sources in the sunny regions of the U.S., there is potential for using solar energy and sustainably increasing the brackish water desalination in these regions. For example, the volume of groundwater in aquifers in New Mexico is estimated to be 20-billion-acre feet (ac-ft); however, 75% of the groundwater is too saline (10 000–35 000 ppm) to be used without desalination (NGWA 2013, Kang *et al* 2019). In Texas, there is approximately 2.7 billion ac-ft of brackish groundwater in the aquifers (TWDB 2004). More than 100 public water supply systems in Texas already use brackish groundwater sources in their supply, operating relatively small desalination units. The brackish water desalination plant in El Paso is the country's largest municipal inland desalination plant, producing 27.5 MGD of freshwater. As the underground freshwater resources are strained by climate change, interest in exploring alternative water sources is renewed (Kang and Jackson 2016).

3. Overview of desalination technologies with potential for solar energy integration

Desalination processes, in principle, can be classified as phase change, non-phase change, and hybrid processes (Gude *et al* 2010, Chen *et al* 2020). Phase change processes involve vaporization of the feed water to produce salt-free products. Feed water is heated to produce vapor leaving the salts behind on the heated surface. The freshwater vapor is then condensed in cooling tubes (evaporating surface in the next stage) producing freshwater. Technologies based on phase change processes, also called thermal desalination technologies, include solar stills (SS), multi-effect distillation (MED), and multi-stage flash distillation (MSF). Since MSF is a bulk distillation process needing high-temperature steam, we limit the current discussion to SS and MED, which are more amenable to solar energy utilization. MED process can be

Technology	Application	Thermal energy (kWh _t m^{-3})	Electricity (kWh m ⁻³)
RO	Brackish & seawater	_	1.5–2.5 brackish
			3–5 seawater
MED	Seawater	45-320	1.5–3
MED-TVC	Seawater	45-128	8-15
MD ^c	Seawater	50-300	1.5-2.1
Batch-MD ^{a,d}	Seawater, high salinity water/ brine concentration	90–173	0.4-0.6
OARO ^{b,e}	Seawater, high salinity water/brine concentration	—	5–13

Table 1. Specific energy consumption of various desalination processes.

^a Demonstrated in a pilot plant, not commercial scales.

^b Only R&D scale; ranges dependent on the salinity of the feed water (20 -125 g l⁻¹ feed salinity).

^c Andrés-Mañas et al (2020).

^d Zhang et al (2022).

^e Atia *et al* (2021).

designed to operate in either low temperature (\sim 50 °C–70 °C) or moderate temperature (\sim 90 °C) when coupled with a thermal vapor compressor (TVC).

Non-phase change processes involve the separation of dissolved salts from the feed water by applying mechanical pressure or voltage gradients. In pressure-driven systems (e.g. reverse osmosis (RO)), a semi-permeable membrane barrier is used to separate the dissolved solids to allow water to permeate through the membrane. In voltage-driven processes (e.g. electrodialysis—ED), voltage is applied across two electrodes to create an electric field and electrical charges that allow for ionic separation from the feed water through charged ion exchange membranes. Hybrid processes integrate the operating principles of phase change and non-phase change separation techniques in a single unit, in the form of novel materials, or in sequential steps to produce freshwater. The most promising hybrid processes are membrane distillation (MD) and RO combined with forward osmosis (FO).

Currently, the energy needed in desalination processes is supplied by burning fossil fuels in thermal desalination plants or using grid electricity, which is mostly powered by fossil fuels, in membrane-based technologies. The energy required for unit freshwater product is expressed as 'specific energy consumption' (SEC) and can be categorized as specific thermal energy consumption (STEC) with units of MJ m⁻³ or kWhthermal m⁻³, and specific electric energy consumption (SEEC) with unit of kWh m⁻³. The large range of values of STEC and SEEC shown in table 1 reflects small and large, and old and modern plants. As shown, RO is less energy intensive than thermal processes in producing freshwater from brackish and seawater, but thermal processes have an advantage in treating high salinity feed water and producing completely demineralized water, as that is needed for hydrogen production via electrolysis (Ginsberg *et al* 2021).

4. Solar energy generation systems for powering desalination

Solar energy can provide electricity to power RO and pumping in desalination systems and/or thermal energy to power thermal desalination systems. Solar electricity can be provided by photovoltaics (PV) or concentrating solar power (CSP) plants, and thermal energy can be provided by solar collectors, solar steam generators (SSG), and CSP plants. In our days, electricity from PV is less expensive than electricity from CSP and the former is the preferred technology for powering RO and pumping in desalination systems. Solar collectors are a relatively low-cost technology for small-scale thermal desalination technologies that can be drawn with low-temperature (<80 °C) thermal energy, such as LT-MED and MD. SSGs can power thermal desalination with higher temperature demand, such MED-TVC, while CSP plants are suited for cogeneration of steam and electricity. Recent advances in conventional SSGs include the Sunvapor system comprising CSP structured with wood framing and a high reflectivity metal laminate, integrated with phase-change material thermal-energy storage at 150 °C–250 °C (figure 1). This technology replaces expensive steel assemblies with wood, 'improving both the optical and structural functions of the collector without compromising heat generation' and is expected to cut the cost of the CSP parabolic trough solar steam generation by as much as 50% (DOE SETO 2019).

Steam can also be created via SSG technology. Application of this complex technology is typically limited by high manufacturing cost and stability, but a recent adaptation by Yaping *et al* (2024) showed high efficiency and stability in both laboratory and pilot settings. The fabric-based SSG is a commercial hydrophilic superfine polypropylene fiber conventionally weaved around a water-repellent polyethylene foam that showed approximately 96% solar absorption at wavelengths 400–2500 nm. Steam is generated via



gradients in surface tension (Marangoni effect) created by temperature gradients along the yarn, leading to a peak generation of $1.4 \text{ kg m}^{-2} \text{ h}^{-1}$. Salt is driven out of the bulk water matrix via both thermal and salinity gradients along the length of the yarn. Researchers expect aspects of this technology could be further analyzed and fine-tuned to improve efficiency. Though not yet tested for SSs, it has the potential for an all-in-one solar energy generation and water desalination system (Yaping *et al* 2024).

Currently, the largest operating renewable-energy-driven desalination plant is the CSP with MED Sundrop Farms plant in Australia, with 1,200 m³ d⁻¹. The biggest proposed projects are the 30 000 m³ d⁻¹ —expandable to 60 000 m³ d⁻¹ PV-RO plant in Metito, Saudi Arabia, and a 227 232 m³ d⁻¹ PV-RO in Chile (Molina 2018). Desalination processes such as MD may find wide applications for solar and geothermal energy utilization for desalination. However, at this point, the large cost of solar thermal energy hinders the commercial viability of solar MD when PV-RO is feasible, so the niche for solar MD in desalination is mostly brine concentration (Zaragoza *et al* 2018).

5. Solar desalination with ZLD potential

5.1. SS desalination

A SS operates by solar energy heating and evaporating saline water, producing vapor and condensing the vapor to produce freshwater. A slanted transparent cover of a water basin allows for sunlight absorption, evaporation, and condensation (figure 2). The first large SS system was constructed in Las Salinas, Chile, in 1872. It was constructed of wood frame covered by a sheet of glass and used saltpeter mine effluent water of high salinity with a total dissolved solids (TDS) concentration of 140 000 mg l⁻¹. It had 64 bays with a total surface area of 4450 m² producing 22.7 m³ of freshwater per day under the sunny skies of Las Salinas. It served the needs of the mining community there for 40 years till the mining site was decommissioned. This application exemplified SS as a viable solution with advantages in cost, simplicity, and implementation especially in remote areas that have limited access to electricity (Rufuss *et al* 2016).

However, SS implementation is limited by large evaporation area requirements, low energy efficiency, and low product yield. These limitations are largely due to the very slow nature of the evaporation process, losses associated with the greenhouse effect inside SSs, and reduction of evaporation rate as the salt concentration increases. However, due to its simplicity and ease of operation, this technology can play a significant role in addressing global water scarcity in high-solar insolation regions and has also a potential for low-cost brine concentration in ZLD applications (Mashaly *et al* 2016).

Solar energy harvesting can be enhanced in SS desalination using four key approaches: (i) concentrating solar energy using solar concentrators such as mirrors and lens; (ii) enhancing energy transfer to water by increasing evaporation surface area using wicks or dispersed solid media; (iii) improving condensation using glass cover cooling mechanisms or altering glass wettability; and (iv) by storing excess or unused energy in a thermal storage medium for use during non-sunlight hours (Gude and Fthenakis, 2020). For example, the Fresnel lens could boost the daily yield and thermal efficiency by 467% (from 1.62 to 9.22 l m⁻²) and 84.7% (from 11.1% to 20.5%), respectively (Mu *et al* 2019). When an SS was connected with a hybrid PV/thermal collector, the daily product yield increased from 1.42 to 5.38 l m⁻² (Kumar and Tiwari 2008).

There is a wide range of costs for SS depending on the various enhancements used. The assessment of various designs revealed the most economical option using the double-slope, single-basin with a flat plate collector would cost 7.8 m^{-3} of product water for small systems (Katekar and Deshmukh 2021). A



10 000 m² SS could meet the freshwater needs of small rural communities at a cost below \$7.71 m⁻³, with potential investment options to reduce production costs to less than \$1.75 per m³ (Hota *et al* 2022).

Overall, the findings from these studies suggest that the SS product yields can be improved in general, but the cost-effectiveness of the integrated configuration should be evaluated in detail.

5.2. Multi-effect desalination (MED)

MED recovers and recycles thermal energy in a number of stages, which are called 'effects' (figure 3). MED is a commonly used evaporative technology for producing high quality distillate from seawater. The system is composed of a series of effects with gradually decreasing temperature and pressure (figure 3). Each effect in MED contains a horizontal tube bundle heat exchanger. Feedwater is sprayed at the top of the tube bundle and flows down the outside of the tubes due to gravity. At the first effect, external steam is used to supply energy to the MED process. The heating steam is introduced inside the tubes where the steam condenses into distillate. The seawater outside the tubes receives the latent condensation heat and partially evaporates, creating vapor that moves to the inside of the tubes of the next effect. As the feedwater flows down the tube bundle and evaporates, the remaining seawater is concentrated, resulting in brine accumulating at the bottom of the cell. The vapor generated by evaporation is at a lower temperature than the initial heating steam, but it can still be used as heating media for the next effect, where evaporation and condensation occur at a lower operating pressure. The decreasing pressure from one cell to the next also drives the flow of brine and distillate to each successive cell, where the brine will flash and release additional amounts of vapor at the lower pressure. This cascade of condensing vapor into distillate and evaporating the solution to generate more vapor continues until the generated vapor is condensed in the last effect by transferring the heat in the condenser to the cooling water (seawater). A portion of the heated seawater exiting the final condenser tubes becomes the makeup water for evaporating effects while the remainder is discharged to the sea. Brine is collected from the last effect of the evaporator and discharged while the distillate is collected from the final condenser (Al-Shammiri and Safar 1999).

As shown in table 1, it uses more energy than RO for seawater desalination but nevertheless is preferred in regions where the seawater quality is inconsistent due to algal blooms and elevated seasonal temperatures. Also, it can be less expensive than RO if low-cost thermal energy is available from solar, geothermal, and waste sources.

As the desalination product in thermal processes is dependent on the total temperature difference (i.e. seawater temperature and the top brine temperature), increasing the top brine temperatures and modifying the process operating conditions can enhance energy efficiency and productivity. The energy efficiency of MED can be improved by combining the process with a TVC. A portion of the vapor generated in an intermediate or the last effect of the MED unit is recompressed in the TVC (steam ejector) to reduce the heat loss and to be reused as an energy source for the first effect. In this way, energy efficiency is increased through the reduction of the amount of steam required to drive the distillation process, and the specific power consumption is also reduced by decreasing the cooling requirements of the condenser at the end of the process circuit.







Coupling MED with solar thermal energy is being investigated, both experimentally and analytically, at the Solar Desalination Unit of the Plataforma Solar de Almeria (PSA) and other facilities (figure 4). The PSA pilots include flat-plate solar collectors, CSP parabolic trough units, and thermal storage units connected with a 14-effect MED pilot plant (Chorak *et al* 2017). Flat-plate static solar collectors can drive an LT-MED process of relatively small size. However, large MED plants would require a large field of solar collectors and many interconnections that would create unfavorable economics affected by capital and operating expenditures (Alhaj and Al-Ghamdi 2019). CSP on the other hand, requires a much smaller footprint for desalination. (Mohammadi *et al* 2019, Soomro and Kim 2018). We also note that the economics of cogeneration are more favorable for large CSP capacities.

5.3. Membrane distillation (MD)

MD is a thermally-driven separation process, in which only vapor molecules transfer through a microporous hydrophobic (non-wetting) membrane. The driving force in the MD process is the vapor pressure difference induced by a temperature difference across the hydrophobic membrane between a hot feedwater and a colder permeable side (figure 5). Mass transfer in MD is controlled by three basic mechanisms, which are Knudsen diffusion, Poiseuille flow (viscous flow) and molecular diffusion. This gives rise to several types of resistance to mass transfer resulting from transfer of momentum to the supported membrane (viscous), collision of molecules with other molecules (molecular resistance) or with the membrane itself (Knudsen resistance (Alkhudhiri *et al* 2012). In MD, the treated water does not have to reach the boiling point, which means that low grade waste heat (e.g. 60 °C–70 °C) or heat from solar collector, can be used.

MD has been well studied at laboratory and pilot scales, and technological improvements have been reported recently (Zaragoza *et al* 2014, Ruiz-Aguire *et al* 2019). However, commercial implementation of MD has not been achieved yet, primarily due to the high energy consumption and membrane development challenges. Most of the energy needed is in the form of thermal energy, which makes it a suitable candidate for solar collector and CSP thermal applications (figure 6).







Even more, MD has the potential to facilitate ZLD operations as a brine management technology when integrated with RO, which is currently the most economical desalination method. Commercial MD systems with increased thermal efficiency could utilize either multi-effects or modules with spiral membranes and heat recovery. The challenge is in minimizing heat transfer/heat losses while maximizing mass transfer along the membranes.

MD possesses unique potential for providing a low-cost alternative for small-scale applications. Though initial designs were energy-prohibitive, recent investigations at the PSA show that vacuum-assisted air gap MD technology could reduce SEC to levels that the technology becomes cost competitive, e.g. below 50 kWht m⁻³ (Andrés-Mañas *et al* 2018, Zaragoza *et al* 2018). However, RO is still cheaper in desalinating brackish and seawater so the applications for MD are high salinity waters and high-brine concentration cases where thermal technologies have an inherent advantage over RO, especially for achieving ZLD using solar thermal energy.

5.4. Forward osmosis (FO)

FO is a two-stage desalination process where water is extracted from saline feed water through a semipermeable, hydrophilic membrane into a more concentrated draw solution (DS) with a higher osmotic pressure (figure 7). This results in concentration of the feed solution and dilution of the DS. The second stage is the regeneration/reconcentration step where the draw agent is recovered by extracting water from the DS. Depending on the nature of the DS, thermal processes (McCutcheon *et al* 2005), pressure-driven membrane separation (McCutcheon *et al* 2005, Bandara *et al* 2022), magnetic separation (Ge *et al* 2011), and



MD (Ge *et al* 2012), have been employed to recover the draw agents for reuse/recycling while generating product water for beneficial use. Regeneration of DS is the most expensive and energy-intensive step in the FO process, which determines the economics of implementing FO technologies (Lugo *et al* 2023). Overall, the energy requirement of the DS regeneration surpasses the energy saving from pumping in FO because the majority of these downstream techniques such as thermal evaporation, RO, and MD, consume large amounts of energy, primarily electricity. Hence, it is of utmost importance to develop an appropriate DS that provides high osmosis pressure, minimum reverse flux, and efficient separation and recovery of water with a minimum energy demand (Amjad *et al* 2018, Abounahia *et al* 2023).

Integrating FO desalination systems with renewable energy has been widely considered as one of the sustainable solutions that can mitigate the challenge of high energy demand. For example, Trevi Systems in California developed thermally responsive organic DS that can be separated and recovered by thermal energy sources such as solar ponds or CSP systems (Thilmany 2022).

FO is evolving as a promising technology for desalinating/cleaning high-concentration waters produced from O&G extraction (McGinnis *et al* 2013, Coday *et al* 2014). Some produced water, such as in the Marcellus, Bakken, Barnett, and Permian Basins, may have TDS concentrations >100 000 mg l^{-1} and cannot be treated with conventional RO (McGinnis *et al* 2013, Coday *et al* 2014, Jiang *et al* 2021, Jiang *et al* 2022a, 2022b). In this case, the brine is typically disposed of, at a high cost, by transportation away from the site when disposal wells are unavailable. The characteristics of this market (high salinity water, typically isolated, off-grid, with high brine disposal costs) justify a higher treatment cost using FO coupled with a solar thermal DS separation process.

5.5. RO desalination

RO separates freshwater from a pressurized saline solution using a semi-permeable, salt-rejecting membrane. By applying a hydraulic pressure greater than the osmotic pressure differential across the membrane, water molecules pass through the membrane resulting in a freshwater product (permeate), while the larger salt molecules are retained on the feed side of the membrane resulting in an increased salinity solution (brine). The brine passes through a mechanical energy recovery device before being discharged. Most of the energy required in RO is in the form of electricity to pump up the pressure in the vessel; for seawater desalination pressures of up 100 bar are required to overcome the osmotic pressure differential between seawater and fresh water. In addition, energy is consumed in pretreatment processes the need of which may be more critical in membrane than in distillation technologies (Fritzmann *et al* 2007).

Depending on the cost of electricity, energy costs for seawater RO desalination can account for up to 60% of the final product water costs and the recovery ratio is about 40%–60%. Desalination of brackish water can result in recovery ratios as high as 80% for salinity less than 10 g l^{-1} , limited by membrane fouling and scaling propensity. Due to the high-pressure requirement, conventional RO is ineffective in high-salinity waters. However, enhanced RO technologies based on designs that enable the reduction of relative osmotic pressure between the two sides of membranes (Atia *et al* 2021) have shown promise in laboratory and small pilot scale.

Depending on the requirements for product water quality, RO processes can involve one or two passes through membranes. For producing the highly demineralized water needed for water electrolysis, a 3-pass system or a 2-pass with an ion-exchange system is needed (Ginsberg *et al* 2021).

8

Low-cost solar electricity can significantly reduce RO operating costs. The PV industry has accomplished phenomenal cost reductions through improving efficiency in the stages of manufacturing and deployment. Currently, PV systems have the lowest levelized cost of electricity (LCOE) in arid areas of high solar irradiation that need to expand the capacity of water desalination. The performance of PV powered RO desalination systems has been demonstrated in several pilot and small systems of less than 100 m³ d⁻¹ (Gude and Fthenakis 2020). Designs include autonomous systems with and without batteries operating in island grids (Karavas *et al* 2019). Also, recent studies pointed to the feasibility of PV-based systems that can handle some of the variability of solar energy resources (Dimitriou *et al* 2017, Kyriakarakos *et al* 2017, Atia and Fthenakis 2019).

5.6. Hybridizations

Desalination process hybridizations can be motivated by various objectives: (i) increasing water recovery; (ii) reducing energy consumption or enhancing energy recovery; (iii) maximizing the use of renewable energy; (iv) minimizing concentrate volumes; and (v) achieving ZLD. Utilizing osmotic processes such as FO for pretreatment is an attractive alternative as several combinations of FO with MD and RO processes can be envisioned. Altmann *et al* (2019) estimated the energy and exergy of hybridizations of RO, FO, and MED in power-water cogeneration schemes powered by CSP-parabolic trough systems and determined that hybridizations can help reduce energy requirements. Among the examined systems, hybridization of RO + FO, showed a potential for the lowest STEC, followed by FO + MED, RO + MED, and RO + MED-TVC.

Another study (Ghaffour *et al* 2019), examined the potential of MD to hybridize with other desalination technologies, and they reported that RO matches well with MD because MD can alleviate RO limitations when treating concentrated feeds. However, chemical additives used in RO can compromise MD efficiency. According to these authors, the highest impact of hybridization seems to lie mostly in MED/MSF-MD systems. Indeed, the significant amount of waste heat from the thermal processes associated with relatively hot brines allows running MD at a relatively low cost.

5.7. Energy storage in desalination systems

Due to the relative ease of storing thermal energy (i.e. by storing hot fluids or other materials) solar thermal energy is a unique complement to other forms of variable renewable (e.g. PV and wind). While daily thermal energy storage (TES) allows desalination plants to operate continually, seasonal variations still need to be considered when assessing the economic advantages of solar thermal desalination. Desalination technologies that utilize thermal energy and thus require TES for uninterrupted process operation include LT-MED, MED-TVC, and MD. TES can enable continuous operation and higher reliability. Phase change and non-phase change storage materials can be utilized to capture extra energy for storage and its later usage. Application of storage materials depends on the temperature needs. Water is the most commonly used non-phase change material and is suitable for low-temperature applications. Mineral salts (e.g. NaNO₃, MgCl₂, and Na₂CO₃), oils, and paraffin can be used for both low-temperature and high-temperature desalination. Another category of storage materials is thermochemical materials which are CaO, MgO, MgSO₄, silica gel, and zeolite. In cogeneration (water-power) schemes, molten salts, water, and high-temperature oils are used (Gude 2015, Jamil *et al* 2023).

5.8. Need for ZLD

While desalination plants produce freshwater, they also generate large quantities of brines as a waste product that must be managed properly. For coastal plants, the brine is commonly discharged into the sea, potentially impacting aquatic ecosystems and wildlife (Xu *et al* 2013). Typical inland brine disposal methods include co-mingling with treated municipal wastewater sewer discharge, evaporation ponds, deep-well injection, and land disposal applications (Mickley 2018). Sewer disposal is limited to municipal wastewater and brackish water desalination brines because high salinity can inhibit biological treatment in a wastewater treatment plant and affect the beneficial reuse of reclaimed water. Deep well injection consists of injecting brines into saline water aquifers 500–1500 m deep but poses risks to adjacent aquifers used for drinking water purposes. Land application includes spray irrigation on salt-tolerant plants but is limited to small volumes of brines to avoid soil salinization and depends on seasonal demand and land availability.

Concentrate management is a major challenge for implementing and expanding water desalination and reuse, especially in arid and semi-arid inland areas. Developing innovative technologies to reduce the concentrate volume for disposal and potentially achieve ZLD, is of utmost importance to address such challenges in a technically feasible, cost-effective, energy-efficient, and environmentally sustainable manner. As climate change intensifies the need for desalination and brine disposal is increasing, and particular interest is given to technologies that can achieve ZLD driven by solar thermal energy (USDOE 2017). A summary of

Table 2. Desalination brine management options.

Method	Cost (\$ m ⁻³) ^a	Energy (kWh m^{-3})	Application Criteria
Surface discharge	0.05-0.30	_	Location
Evaporation pond	1.18 - 10.04	_	Location, brine properties
Sewage discharge	0.32-0.66		Location
Deep-well injection	0.54-2.65	_	Hydrogeology
Landfill disposal	0.74-1.95	—	Location, hydrogeology
ZLD via Brine Concentrator (BC) & Crystallizer (BCr)	0.66–26.41 ^b	16–26 (for BC) 52–70 (for BCr) ^c	Brine properties

^a Panagopoulos et al (2019).

^b Ziolkowska and Reyes (2017).

^c Panagopoulos *et al* (2020).



these options is shown in table 2. The conventional ZLD approach includes the combination of thermal brine concentrators and crystallizers and can treat concentrates of almost any quality (Date *et al* 2022). The primary limitations of conventional ZLD include high specific energy requirements and costs (Alspach and Juby 2018). Table 2 shows the costs for ZLD vary between 0.66 and 26.41 \$ m⁻³, which are largely attributed to the high energy requirements of 16–26 kWh m⁻³ for brine concentrators and 52–70 kWh m⁻³ for thermal crystallizers. As a result, currently there are limited applications of ZLD processes.

Improving water recovery and minimizing concentrate volume can significantly reduce the ZLD costs. For example, Irwin Water Works Desalination Plant in California uses electrodialysis reversal (EDR) to treat brackish water for drinking and achieves ZLD. The water recovery of the EDR process is 92%, and the concentrate volume is further reduced to 0.1%–2% using a series of air stripping, lime softening, microfiltration, RO, ion exchange, and a mechanical evaporator. The waste residual is sent to evaporation ponds, where the solids are removed to a permitted landfill (Xu *et al* 2022). The total cost to build this 6.0 MGD (22 712 m³ d⁻¹) desalination plant in 2016 was \$100.1 million, of which \$51 million was for water treatment and \$49.1 million for brine management. The water cost was estimated \$1.50 m⁻³ and SEC 3.5 kWh m⁻³ for the Irwin facility (Xu *et al* 2022)

As ZLD further increases the energy burden of desalination, solar has become the perfect candidate for sustainable desalination (Fthenakis 2017). A schematic of a solar-driven system is shown in figure 8.

5.9. Brine valorization

With the increase in water recovery, the concentrations of valuable minerals also increase in desalination brine, especially in a ZLD process. In the United States, there are several desalination plants that integrate resource recovery with ZLD. For example, Eureka Resources operates multiple centralized produced water treatment facilities in the Marcellus Basin to generate multiple qualities of effluent water and recover valuable minerals. Advanced desalination treatment involves mechanical vapor recompression (MVR) distillation and MVR crystallization with ZLD. Marketable chemicals including high purity sodium chloride, lithium products, and calcium chloride are recovered from produced water brine generated during the desalination processes. The crystallization costs are approximately 68.75 m^{-3} with the potential to reduce to approximately 43.75 m^{-3} with integrated, commercially viable resources (Cooper *et al* 2022).

A full minerals recovery facility was constructed to convert the brackish water RO concentrate from the Kay Bailey Hutchinson Desalination Plant in El Paso, Texas, to drinking water, gypsum, hydrochloric acid, and caustic soda (Xu *et al* 2022). The initial investment in this 3 MGD mineral recovery and ZLD plant was \$65 million, the facility will need an additional \$100 million to make it operational by 2025. A recent study

estimated economic values of 13.4 and 29.8 billion euros/year could be expected from extracting valuable elements (sodium, magnesium, calcium, lithium, rubidium, strontium, boron, and gallium) in the brine of over 100 desalination plants in Spain (Del Villar *et al* 2023). Seawater brine generates higher economic values than brackish water concentrate, and two-thirds of the revenues come from two major elements—magnesium and sodium (Del Villar *et al* 2023).

Although the economic analysis showed a potential market for brine valorization, the feasibility of brine mining depends on source water quality. The complexity of operating chemical precipitation and crystallizers, and the high energy demand need to be considered.

6. Current challenges

6.1. Concentrate management and energy consumption issues

One of the key issues related to desalination is the management of the effluent concentrate stream (brine). Current options for concentrate management in inland desalination plants include surface water disposal, deep well injection, evaporation ponds, connections to sewer disposal, and brine concentration followed by crystallization and salt recovery aimed at ZLD. R&D activities in the ZLD area are motivated by the USEPA effluent limitation guidelines (and similar policies in Europe and Asia), as well as by power and O&G sectors in the United States. The management of highly saline waters generated by conventional and unconventional O&G recovery activities presents environmental challenges. For example, the saline water generation rate at O&G well sites in the United States can reach 2.4 billion gallons/day (9 million m³ d⁻¹), with TDS as high as 300 000 mg l⁻¹, and treatment of these effluents is challenging (Groundwater Protection Council).

Innovative technologies that can be used for brine concentration including MD, FO, and enhanced-RO technologies to achieve high recovery and treat hypersaline brine, are under development (Atia *et al* 2021).

6.2. Pre-treatment to tackle fouling and scaling

High TDS waters, such as desalination concentrate and O&G produced water, can cause scaling and fouling in desalination and ZLD systems due to the presence of a wide variety of organic and inorganic constituents that can attach or clog membrane pores. The presence of fouling in membranes is mostly attributed to organics and microorganisms that may attach to the membrane surface and form a biofilm that can clog its pores. In the case of scaling, the most common inorganic scale-forming chemicals are calcium carbonate $(CaCO_3)$, calcium sulfate $(CaSO_4)$, and silica (SiO_2) . The mechanisms involved in both fouling and scaling of membrane-based desalination processes include particulate fouling, concentration polarization, pore blocking, cake formation, inorganic precipitation, organic adsorption, and biological fouling (Guo et al 2012). Both scaling and fouling pose a significant challenge for treatment facilities due to deteriorated system performance along with increased energy consumption and costs (Guo et al 2012, Xu et al 2013). Providing an effective pretreatment is essential for successful ZLD applications since the main objective is to extend the lifetime as well as to enable effective and consistent performance of the downstream desalination units through the removal of the constituents responsible for the fouling and scaling in the system. The main goal of a pretreatment application should be to reduce the different fouling and scaling constituents of predominance to effectively operate subsequent treatment systems without any potential operational limitations due to the input water source. Some of the pretreatment units that can be considered in ZLD involve chemical softening, chemical coagulation, ion-exchange, granular activated carbon, electrocoagulation, oxidation, and disinfection (Yaqub et al 2022). The selection of an adequate pretreatment approach depends on the types of organic and inorganic constituents present in the stream as well as the desalination technologies since some membranes are much more susceptible to fouling and scaling than thermal distillation. Thus, data on the feed water chemistry, removal requirements, and limitations are needed for the design of pretreatment process for effective ZLD applications.

6.3. Cost reduction challenges

The recent drastic reductions in the LCOE catalyze cost reductions in fresh-water production via desalination of brackish and seawater; in addition, it creates strong feedback for further cost reductions as the growth of solar desalination markets creates economics of scale and incentives for developing technologies that can handle solar variability. In addition to lowering costs, using solar energy to displace fossil fuels and associated greenhouse gas emissions may eventually result in carbon credits driving price reductions.

Development of operating strategies that will increase the variable renewable energy contribution to desalination, will minimize greenhouse gas emissions while taking the maximum benefit from inexpensive abundant solar energy. For example, while conventional desalination plants consume power at a constant rate, new plant designs that facilitate variable operation may allow for time-shifting of energy use, demand

response, utilization of over-generation by solar and wind power, and other functions. These functions would enhance the ability of the desalination/reuse system to serve an evolving electricity system.

In addition, combinations of PV with CSP with thermal storage, geothermal and/or wind resources can power desalination at the minimum possible costs and life-cycle emissions.

For large-scale, centralized systems, the coupling of desalination/reuse with solar thermal, PV electricity, geothermal, and grid electricity likely results in the lowest water production cost. One possibility is PV-RO and MED-MD combined in series. The MED-MD can take in RO reject brine, thereby increasing the water recovery. The brine is then transferred to a crystallizer to form salts, precursors to salable products, thus reducing potential environmental impacts and the lowest emissions. For small-scale, decentralized systems, adaptive operational controls need to be implemented to optimize the coupling of variable renewable energy sources with desalination systems. Intermittent desalination plant operation with water storage may be a less expensive option than continuous operation using electricity storage.

7. Solar desalination tools of analysis

Two software packages relevant for solar desalination techno-economic analyses, namely SEDAT and WaterTAP with Renewable Energy and Flexible Load Optimization (WaterTAP-REFLO). SEDAT, 'Solar Energy Desalination Analysis Tool' is an open-source simulation tool for techno-economic evaluation of desalination technologies and selection of regions with the highest potential for using solar energy to power desalination plants. SEDAT uses Dash for integrating various layers of large volumes of GIS data with Python-based models of solar energy generation and desalination plants, power plants, water conveyance networks, natural gas pipeline networks, regulatory data, utility water prices, and fuel prices. It derives time-series of energy generation and water production, with details of plant performance and suggestions for improving the solar-desalination coupling (Fthenakis *et al* 2022).

Water treatment Technoeconomic Assessment Platform (WaterTAP), is an open-source simulation and optimization software for water treatment. At its core, WaterTAP is a library of water treatment technologies that are compatible with the Institute for the Design of Advanced Energy Systems (IDAES) Integrated Platform, an advanced process systems engineering tool developed by the United States Department of Energy (DOE) (Lee et al 2021). Both WaterTAP and IDAES are open-source Python software packages that use equation-oriented solution strategies by representing models in Pyomo, an algebraic programming language environment that can interface with numerous open-source and commercial optimization solvers. The combination of WaterTAP and IDAES provides an advanced computation capability to assemble, simulate, and optimize a water treatment train composed of modular models. These modular models span three categories: 1) unit models—relating equipment performance to its design and operating variables, 2) property models—relating water properties (e.g. density, viscosity, osmotic pressure) to the state variables (e.g. flowrate, concentration, pressure, and temperature), and 3) cost models—relating capital and operating costs to the system design and operating variables. An application of WaterTAP in simulations and cost optimization of low-salt-rejection RO is presented by (Atia et al 2023). Recently, members of this team have expanded the functionality of WaterTAP to include renewable energy and storage models to enable analysis of integrated water treatment and renewable energy systems. This package, dubbed WaterTAP-REFLO includes solar electric and solar thermal (e.g. concentrated solar power) models as well as desalination technologies for treatment of high salinity brines (e.g. LT-MED and MED-TVC). As high salinity brines become more prevalent and increasingly regulated, solar thermal desalination technologies can realize high recoveries and have more potential for minimum- or zero liquid discharge. There is need for robust modeling tools capable of analyzing and optimizing these systems for various outcomes over short- and long time domains.

8. Conclusion

Solar energy generation, which is abundant in arid regions, has become cost competitive with fossil fuel power generation, and it creates great prospects for affordable and sustainable water production through desalination of brackish water, seawater, and other saline waters. The focus of this paper is on thermal desalination technologies that have the highest potential for ZLD applications, and which can be coupled with solar energy systems, namely SSs, solar collector-LT-MED, CSP-MED-TVC, CSP-MD, and CSP-FO.

SSs are appealing for rural and small-scale communities due to their simplicity and capability to handle all types of saline water such as brackish water, seawater, and produced water. While they can be part of a broader water treatment strategy, they often work in tandem with other technologies to achieve ZLD, so that they minimize environmental impact. However, barriers to commercialization include efficiency challenges, high initial costs, maintenance issues, scale-up complexities, and energy storage challenges. Overcoming these obstacles requires ongoing research and development to enhance design, materials, and efficiency, along with government incentives promoting sustainable water solutions and renewable energy. Development of new fabrics that can both absorb solar energy and allow for water evaporation may open possibilities for SS applications. LT-MED's potential to be powered by inexpensive solar collectors also makes it suitable for small systems in rural communities, while CSP-MED-TVC plants are best suited for large plants and co-generation.

MD is an attractive technology for solar-powered decentralized desalination, but it has not yet reached commercial scale. The main barriers are energy consumption and cost; thus, increasing thermal energy efficiency is a pathway towards commercialization. The spiral wound air-gap membrane distillation process allows for internal heat recovery through multiple channels and stands out in terms of SEC when compared with the plate-and-frame type flat sheet MD process. FO is also very promising, especially for high-salinity water desalination and ZLD applications. However, there is a need to develop efficient membranes for both MD and FO.

The costs of ZLD are high and typically involve energy-intensive thermal brine concentrators and crystallizers. Using solar thermal energy to power ZLD processes can significantly reduce the burden on electrical grids and reduce greenhouse gas emissions. In addition, solar energy can also facilitate mineral recovery processes such as chemical precipitation and crystallization enhanced by solar thermal energy, thereby reducing treatment costs.

Data availability statement

No new data were created or analysed in this study.

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