



# Assessment of desalination technologies for treatment of a highly saline brine from a potential CO<sub>2</sub> storage site



Ruth Kaplan<sup>a</sup>, Darryl Mamrosh<sup>b</sup>, Hafiz H. Salih<sup>a</sup>, Seyed A. Dastgheib<sup>a,\*</sup>

<sup>a</sup> Illinois State Geological Survey, University of Illinois, 615 East Peabody Drive, Champaign, IL 61820, USA

<sup>b</sup> Trimeric Corporation, PO Box 826, Buda, TX 78610, USA

## HIGHLIGHTS

- Geological CO<sub>2</sub> sequestration may generate significant volumes of highly saline brine.
- Existing and emerging high-TDS desalination technologies are critically evaluated.
- Evaporators are identified as the most suitable existing technology.
- Mt. Simon brine treatment by multi-effect evaporation is modeled by Aspen simulation.
- Near-ZLD treatment of Mt. Simon brine requires 246 kWh thermal energy per m<sup>3</sup> of recovered water.

## ARTICLE INFO

### Article history:

Received 2 August 2016

Received in revised form 7 October 2016

Accepted 7 November 2016

Available online 12 November 2016

### Keywords:

Desalination

Brine extraction

CO<sub>2</sub> sequestration

Brine treatment

Mt. Simon sandstone

## ABSTRACT

Brine extraction is a promising strategy for the management of increased reservoir pressure, resulting from carbon dioxide (CO<sub>2</sub>) injection in deep saline reservoirs. The extracted brines usually have high concentrations of total dissolved solids (TDS) and various contaminants, and require proper disposal or treatment. In this article, first by conducting a critical review, we evaluate the applicability, limits, and advantages or challenges of various commercially available and emerging desalination technologies that can potentially be employed to treat the highly saline brine (with TDS values > 70,000 ppm) and those that are applicable to a ~200,000 ppm TDS brine extracted from the Mt. Simon Sandstone, a potential CO<sub>2</sub> storage site in Illinois, USA. Based on the side-by-side comparison of technologies, evaporators are selected as the most suitable existing technology for treating Mt. Simon brine. Process simulations are then conducted for a conceptual design for desalination of 454 m<sup>3</sup>/h (2000 gpm) pretreated brine for near-zero liquid discharge by multi-effect evaporators. The thermal energy demand is estimated at 246 kWh per m<sup>3</sup> of recovered water, of which 212 kWh/m<sup>3</sup> is required for multiple-effect evaporation and the remainder for salt drying. The process also requires additional electrical power of ~2 kWh/m<sup>3</sup>.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) captured from industrial sources can be permanently stored by geological sequestration in deep saline reservoirs. According to a scenario published by the International Energy Agency,

Klapperich et al. reported that by 2050, global geologic storage of 9.12 billion metric tons of CO<sub>2</sub> per year will be required to meet CO<sub>2</sub> emission reduction goals [1]. The U.S. Department of Energy has identified deep saline reservoirs as the largest potential sinks for CO<sub>2</sub> storage in the United States. The total CO<sub>2</sub> storage capacity in major saline reservoirs, estimated by the U.S. Department of Energy carbon sequestration partnerships, is at least 2300 billion metric tons and possibly as high as about 22,000 billion tons [2].

Large-scale geological CO<sub>2</sub> sequestration may result in increasing the reservoir pressure beyond a level that is allowable by safety standards or potential regulations. Brine extraction is considered a promising strategy for managing increased reservoir pressure [3–5]. Significant volumes of brine may be extracted if geological CO<sub>2</sub> sequestration in deep brine reservoirs is implemented at industrial scales. Assuming that each metric ton of injected CO<sub>2</sub> displaces 1.25 m<sup>3</sup> of reservoir fluid, Klapperich et al. estimate that up to 31.2 million m<sup>3</sup> of brine

**Abbreviations:** CO<sub>2</sub>, carbon dioxide; ED, electrodialysis; EDR, electrodialysis reversal; ENRTL, Electrolyte, Non-Random Two Liquid; FO, forward osmosis; GE, General Electric; gpm, gallons per minute; HD, humidification–dehumidification; kWh<sub>elec</sub>, kilowatt hour electrical; kWh<sub>elec equiv</sub>, kilowatt hour electrical equivalent; kWh<sub>th</sub>, kilowatt hour thermal; LMTD, logarithmic mean temperature difference; MD, membrane distillation; MED, multiple-effect distillation; MEE, multiple-effect evaporation; MJ<sub>th</sub>, megajoules thermal; MSF, multiple-stage flash; MVC, mechanical vapor compression; ppm, parts per million (mg/L); ppmw, parts per million weight (mg/kg); RO, reverse osmosis; TDS, total dissolved solids; wt%, weight percent; ZLD, zero-liquid discharge.

\* Corresponding author.

E-mail address: [seyed@illinois.edu](mailto:seyed@illinois.edu) (S.A. Dastgheib).

**Table 1**

Comparison of selected water quality parameters of Mt. Simon brine with selected water quality parameters of seawater and brackish water.

Brine/water	TDS (ppm)	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Sr <sup>2+</sup> (mg/L)	Na <sup>+</sup> (mg/L)	Cl <sup>−</sup> (mg/L)	SO <sub>4</sub> <sup>2−</sup> (mg/L)	Alkalinity as CaCO <sub>3</sub> (mg/L)	pH	Data source
Mt. Simon brine	197,000	22,000	1500	791	48,000	120,000	360	55	7.0	<sup>b</sup>
Seawater at Doha Research Plant	47,000	570	1700	NR <sup>a</sup>	12,300	24,000	3400	175	8.2	[14]
Brackish water at Kantor Desalination Plant	3890	196	146	NR	1014	1970	251	305	6.9	[15]

TDS was estimated by summation of all cations and anions.

<sup>a</sup> NR: not reported but expected to be negligible.<sup>b</sup> Obtained from the Illinois State Geological Survey Geochemistry team based on previously described methods [12,13].

might be extracted globally each day, although extraction rates may be limited by site-specific factors [1]. Breunig et al. estimate that 2 m<sup>3</sup> of brine will be extracted for every metric ton of CO<sub>2</sub> injected, and that a single CO<sub>2</sub> injection site might receive 8.9 million metric tons of CO<sub>2</sub> per year, resulting in about 48,000 m<sup>3</sup>/day of brine extraction [3]. The extracted brines usually have high concentrations of total dissolved solids (TDS), suspended solids, and various contaminants and require proper disposal or treatment. Veil et al. reported the distribution of different water quality parameters of 34,000 brine samples collected from basins that are considered potential targets for CO<sub>2</sub> sequestration [6]. They found that, of 52 formations sampled, 58% of geological formation brines had a median TDS concentration of at least 50,000 ppm, and 23% exhibited salinities > 100,000 ppm [6].

The high-TDS extracted brine cannot be discharged to the environment or applied for beneficial uses without proper treatment. The disposal of extracted brine by deep well injection into other formations might not be an option for many CO<sub>2</sub> sequestration sites for several reasons, including the availability of proper geological formations, the high volume of extracted brine, the high cost or other challenges of brine transportation, required pretreatments before brine injection, and environmental regulations. Therefore, treatment of extracted high-TDS brine might be the only practical option for some sequestration sites.

Highly concentrated salt brine effluents are also generated from a variety of sources, including seawater desalination processes, cooling tower blowdown, mine tailing leachate, and produced water from fossil fuel production. The International Desalination Association reported that, as of 2015, there were >18,000 desalination plants worldwide, with a total production capacity of >86 million m<sup>3</sup>/day of fresh water [7], about 59% of which comes from seawater desalination [8]. The waste brine effluents from seawater desalination plants are major current sources of high-TDS brine. For instance, the desalination of seawater by reverse osmosis (RO) produces brine concentrates that are typically 65,000 to 85,000 ppm of TDS [9]. A simple assumption of 50% water recovery for seawater desalination plants suggests a brine flow rate of ~51 million m<sup>3</sup>/day from worldwide seawater desalination plants. Produced water from oilfields, natural gas, and coalbed methane also generates large quantities of high-TDS brine [10]. For example, the produced water resulting from global oil and gas production is around 250 million barrels per day (~40 million m<sup>3</sup>/day) [11].

It is apparent that treatment of brines is increasingly necessary, both for the successful implementation of CO<sub>2</sub> sequestration and for the reduction of waste in other industries. High-TDS brine treatment creates a challenge in water treatment because conventional seawater desalination methods are not designed for feed water streams higher than 50,000 ppm of TDS. In this article, we evaluate the applicability, limits, and advantages or challenges of various desalination technologies that can potentially be employed to treat the highly saline brine (with TDS values >70,000 ppm) and those that are applicable to a ~200,000 ppm TDS brine extracted from the Mt. Simon Sandstone, a potential CO<sub>2</sub> storage site in Illinois, USA. We performed a side-by-side comparison of desalination technologies and selected multi-effect evaporation (MEE) as the most suitable existing technology for treating Mt. Simon brine. We performed process simulations for treatment of Mt. Simon brine for near-zero liquid discharge (ZLD) treatment for 88% water recovery by MEE. We performed material balance for a 454 m<sup>3</sup>/h (2000 gpm)

brine input unit and determined stream compositions, energy requirements, and other process specifications.

## 2. The challenge of high-TDS brine desalination

Concentrations of major salts (e.g., salts of Na, Ca, and Mg) are significantly higher in high-TDS brines compared with those in seawater. The high salt content of brine creates specific treatment challenges, such as scaling, fouling, corrosion, and high energy consumption. Scaling and fouling are common problems in desalination processes. Scales are formed when mostly divalent (e.g., Ca, Mg, Sr) species are transformed from soluble to insoluble forms that result from changes in solution chemistry (e.g., pH and composition change) or process conditions (e.g., temperature) during the desalination process. Scales and other suspended solids may precipitate on the equipment surface or separation devices (e.g., membranes) and impede the desalination process by reducing the heat transfer rate in thermal desalination systems or reducing the mass transfer rate through membrane-based systems. Brines extracted from potential CO<sub>2</sub> sequestration sites may have high concentrations of TDS, scale-forming species, and suspended solids. As an example, the composition of a high-TDS brine extracted from the Mt. Simon Sandstone in Illinois, USA, is compared with typical seawater and brackish water, which are the feed streams to conventional desalination plants (Table 1).

The cumulative concentrations of scale-forming cations, mainly Ca, Mg, and Sr, in the Mt. Simon brine are one order of magnitude higher than those of other water samples listed in Table 1. The major divalent anion, sulfate, can form scales with divalent cations under appropriate precipitation conditions. Concentration of total suspended solids in the Mt. Simon brine was measured at our laboratory according to standard method 2540C [16] and is about 2800 ppm, which is up to two orders of magnitude higher than typical values for seawater or brackish water. As an example, concentrations of total suspended solids for selected seawater and brackish water samples is reported as 5–20 ppm [17,18] and 24–144 ppm [19], respectively. Mt. Simon brine may require vigorous pretreatments for the removal of suspended solids and scale-forming species. The pH of sampled Mt. Simon brine is similar to other water sources for desalination. However, we observed that upon extended exposure to air the pH decreased to ~5.5 due to oxidation reactions.

The salinity of Mt. Simon brine or similar high-TDS brines is also significantly higher than the salinity of seawater. Therefore, Mt. Simon brine can be more corrosive to many commonly-used metals. Special corrosion-resistant materials, such as nickel alloys or corrosion-resistant coating, may be needed for pumps, heat exchangers, pipes, or other parts of the desalination systems. Existing seawater desalination processes may need to be significantly upgraded to be compatible with the high-TDS brines.

Even if the technical issues associated with high-TDS brine desalination are resolved, costs may be prohibitive. In addition to higher pretreatment costs and capital costs for corrosion-resistant equipment, energy costs will be much higher for high-TDS brine desalination facilities than for seawater desalination. The theoretical thermodynamic minimum energy consumption for desalination, which sets a baseline for energy efficiency, is dependent on the concentration of the feed

and product streams [20]. For seawater with 35,000 ppm of TDS at 25 °C and with 50% water recovery, the minimum energy for desalination is about 1.06 kWh/m<sup>3</sup> [21,22]. Thiel et al. explored Gibbs free energy of mixing (the difference in free energy between the feed and product streams, equivalent to the least work of separation) for various feed waters and recovery ratios. They concluded that, at 50% recovery, the minimum work of separation for a highly saline brine of approximately 18.3 wt% NaCl is about 9 kWh/m<sup>3</sup>, almost an order of magnitude higher than for seawater [23]. Thus, even a highly efficient high-TDS desalination process will still exhibit much higher energy costs than a low-TDS desalination process.

### 3. Overview of desalination technologies and their suitability for treatment of highly saline brine

Prevalent commercial desalination technologies are mainly designed for seawater and brackish water (TDS of <10,000 ppm) desalination. In most cases, a highly saline brine feed does not fall within the design parameters. We focus our discussion on brief descriptions of

different desalination processes and relevant research related to highly saline brine treatment.

The majority of desalination plants employ RO, multiple-stage flash (MSF), multiple-effect distillation (MED), and electrodialysis (ED). Water desalination by RO is favored over that by MED and MSF because of its lower energy consumption, typically 3.5 to 6.0 kWh<sub>elec</sub>/m<sup>3</sup> for seawater desalination and 0.5 to 3.1 kWh<sub>elec</sub>/m<sup>3</sup> for brackish water [8,24–28], compared to typical reported energy consumption ranging from 10 to 28 kWh<sub>elec equiv</sub>/m<sup>3</sup> for MSF [20,26,27,29] and from 5.5 to 20 kWh<sub>elec equiv</sub>/m<sup>3</sup> for MED [20,26,27,29–31]. Energy requirement is one of the leading factors in selection of desalination technologies. To compare total energy consumption of various processes, thermal energy consumption can be converted to the electrical equivalent by multiplying an approximate electrical power generation efficiency of about 30% [20]. Water recovery for single-stage seawater RO desalination is typically 40% to 60% and is 75% to 90% for brackish water [9,32]. Despite its commercial success, salinity limitations of RO render it impractical for hypersaline (highly saline) water treatment. The osmotic pressure of a solution is directly proportional to its concentration. Standard membranes and membrane modules can handle pressures up to

**Table 2**

Reported process parameters for brine concentrators and crystallizers that might be used in zero liquid discharge processes.

Process	Inlets and outlets	Energy requirements	Source
Single stage MVC modeled by Thiel et al.	Feed: 15 wt% TDS. Concentrate: 26 wt% TDS.	~27 kWh <sub>elec</sub> /m <sup>3</sup>	Thiel et al. [23]
3-effect MED modeled by Thiel et al.	Feed: 15 wt% TDS. Concentrate: 26 wt% TDS.	~250 kWh <sub>th</sub> /m <sup>3</sup> and ~2 kWh <sub>elec</sub> /m <sup>3</sup>	Thiel et al. [23]
212 resources, mechanical vapor recompression process	Feed: Marcellus Shale produced water and frac flowback, TDS often 150,000 + ppm Concentrate: 300,000 + ppm of TDS	Not reported	212 Resources [80]
GE ZLD system, case study: 920 MW coal-fired baseload power plant system with 1 large evaporator with extra-long heat transfer tubes (20 m instead of 15 m) and 2 crystallizers	Feed: treating 140 m <sup>3</sup> /h of cooling tower blowdown, ~3600 ppm of TDS	18 kWh <sub>elec</sub> /m <sup>3</sup> feed for the evaporator with the extra-long tubes, but a typical energy requirement for the evaporator would be about 25 kWh <sub>elec</sub> /m <sup>3</sup> of feed	GE Water & Process Technologies [81]
GE ZLD system: 95% water recovery by brine concentrator; remaining slurry sent to a solar pond, crystallizer, or spray dryer	Feed: industrial wastewater	The brine concentrator uses ~13–23 kWh <sub>elec</sub> /m <sup>3</sup> of feed. Energy requirements for the crystallizer are not stated	GE Water & Process Technologies [82]
Ambient technologies, vapor compression evaporation	Feed: 12,000 ppm of TDS brine from brackish water RO Permeate: <10 ppm of TDS Concentrate: 210,000 ppm of TDS	Not reported	Awerbuch and Weekes [74]
Resources conservation company, vapor compression evaporation <sup>a</sup>	Feed: 9084 ppm of TDS brine from brackish water RO Permeate: 10 ppm of TDS. Concentrate: 206,676 ppm of TDS	Not reported	Awerbuch and Weekes [74]
Single-stage or 3-stage brine concentrator with thermal vapor compression followed by a crystallizer	Feed: brine from a seawater distillation process	Estimated ~46–48.7 kWh/m <sup>3</sup> of work required	El-Sayed mathematical modeling, reported by Ahmad and Williams [28]
Mechanical evaporators as brine concentrators	Feed: 30,000–150,000 ppm of TDS. Concentrate: 200,000–300,000 ppm of TDS	20.8–36.5 kWh <sub>elec</sub> /m <sup>3</sup>	2012 Global Water Intelligence Report, reported by Zuback et al. [76].
Thermal crystallizer	Feed: residual liquid from brine concentrator, as concentrated as possible. Outlet: solid by-product	Energy requirement not stated, but generalized to be 5 times higher than that of a mechanical evaporator	2012 Global Water Intelligence Report, reported by Zuback et al. [76].
Brine concentrator	Feed: varied. Concentrate: 167,000–358,000 ppm of TDS	19.8–25.1 kWh <sub>elec</sub> /m <sup>3</sup>	WaterReuse Foundation [83]
Vapor compression crystallizer	Feed: concentrated brine	52–66 kWh <sub>elec</sub> /m <sup>3</sup>	WaterReuse Foundation [83]

<sup>a</sup> Note: GE purchased Resources Conservation Company in 2005.

**Table 3**

Pretreatment technologies based on information provided by Igunnu and Chen, Fakhru'l-Razi et al., and Guerra et al. [10,11,85].

Pretreatment	Target contaminant(s)	Process notes	Applicability to Mt. Simon brine
<i>Chemical</i>			
Coagulation and flocculation	Colloidal particles	Coagulant forms colloidal particles and flocculent promotes the collection of those particles into flocs.	Needed
Softening	Scale-forming contaminants including calcium, and other metals.	Addition of calcium hydroxide to cause precipitation of scale-forming contaminants, especially calcium. Addition of sodium hydroxide to increase silica solubility and reduce scaling. Other chemicals may be used.	Needed
Chemical oxidation	Organic chemical and particulate removal, COD, BOD, and some inorganics including iron, manganese, and sulfur.	An oxidant (usually ozone, peroxide, permanganate, oxygen, or chlorine) is mixed in.	Not needed because level of organics is low.
pH adjustment	Not applicable	pH adjustment by acid/base addition may be required for some processes.	Possibly
<i>Physical</i>			
Media/gravity filtration	Suspended solids, oil and grease	Use sand, gravel anthracite, walnut shell, or other filtration medium. Process not affected by salinity.	Yes; after initial coagulation and lime softening.
Hydrocyclone	Hydrocarbons including dispersed oil and grease; removes 5 $\mu\text{m}$ – 15 $\mu\text{m}$ particles but cannot remove soluble oils.	Separates oil from water based on density, can also separate solids.	Might be applicable for removal of fine solids.
Flotation	Organic chemicals and particulates including natural organic matter, oil and grease.	Gas, mechanical shear propellers are used to generate bubbles which collect particulates.	Not needed because no oil and grease are present.
Adsorption	Mostly dissolved organics, but heavy metals, iron, and manganese adsorption is also possible.	Mainly organoclays and activated carbon used for adsorption of organics. May use zeolites and activated alumina adsorbents for metals. Process is best used as a polishing step because the adsorbent can be easily overloaded and regeneration can be costly.	Might not be needed because level of organics is low.
Clarifier or settling pond	Suspended solids/large particulates	A clarifier is a sloped-bottom tank or basin used to separate liquid from suspended solid particles. Solid particulates may also be separated by gravity settling in a pond or basin.	Might be necessary after coagulation.
Air stripping	Volatile organic compounds.	Air is brought into contact with the water in a packed column and contaminants are transferred to the gas phase.	Not needed because the brine does not expect to contain volatile organic compounds.
Ion exchange	Scaling and fouling contaminants	Water softening by ion exchange resin. Resin will require regeneration.	Not applicable for high-TDS feed.
<i>Biological</i>			
Biological aerated filters	Oil, suspended solids, ammonia, nitrogen, chemical oxygen demand, biological oxygen demand, iron, manganese, heavy metals, dissolved and soluble organics, and hydrogen sulfide.	A permeable media facilitates the biochemical oxidation/removal of organic constituents.	Not applicable for high-TDS feed.
Membrane bioreactors	COD, oil, and gas.	Bench and pilot scale studies for oil and gas removal.	Not needed because no oil and grease are present.

1200 psi, appropriate for seawater RO and specialized membrane modules may handle pressures up to 1500 psi [5]. Aines et al. suggest that advanced RO processes might be applied to a feed of up to 105,000 ppm of TDS with 10% water recovery [5]. In addition to the practical pressure limits associated with RO membranes and the module hardware, operation of the membranes at these high pressures would result in the need to pump the feed brine to these high pressures, increasing the energy requirement for the separation. These practical limitations result in the feed salinity of current RO processes being limited to about 55,000 to 70,000 ppm of TDS [33,34].

One innovative technology that might be applicable to highly saline brines is slurry precipitation and recycling RO (SPARRO), in which seed crystals are introduced to induce solids precipitation on the seed crystals instead of on the membrane. This would reduce scaling issues associated with high-TDS feed waters, although pressure limitations might still limit the applicability of RO to highly saline brines. The process has been tested at a pilot scale [35].

Electrodialysis and electrodialysis reversal (EDR) are voltage-driven membrane processes that are popular in industry for brackish water desalination. Electrodialysis as a treatment option for

highly saline brines is an emerging technology. Ahmad and Williams predicted that it would be technically possible to treat high-TDS brine with ED, but that the process would be highly energy consumptive. They estimated the energy required to desalinate a 70,000 ppm of TDS brine by ED to be 49.7 kWh<sub>elec</sub>/m<sup>3</sup> and the energy required for a 250,000 ppm of TDS feed to be 175.7 kWh<sub>elec</sub>/m<sup>3</sup>, which is not lower than the energy demand of evaporators. They also suggested that, although scaling might limit the flux for ED, membrane scaling would not be as problematic with ED as for RO [28].

Researchers at the Massachusetts Institute of Technology have investigated ED in stages to treat high-TDS water. A feed consisting of 195,000 ppm of NaCl was treated in a 10-stage ED unit to produce water with only 240 ppm of NaCl. The exact energy requirements were not reported, but the authors suggested that the energy consumption was comparable to that of a mechanical vapor compression (MVC) process for a 40,000 to 90,000 ppm TDS feed. They further suggested that voltage optimization would reduce the costs by 30% to 60% [36]. They also suggested operating ED in conjunction with RO to treat highly saline brines [37].

**Table 4**

Side-by-side comparison of desalination technologies to screen for applicability to brine treatment.

Point of comparison	Membrane				Evaporative concentration		
	Reverse osmosis (RO)	Forward osmosis (FO)	Membrane distillation (MD)	Electrodialysis (ED) & electrodialysis reversal (EDR)	Conventional distillation: multi-effect distillation (MED) & multi-stage flash (MSF)	Standard brine concentrators	Humidification compression
Can brine with TDS > 70,000ppm be treated effectively?	Partial treatment for a maximum feed salinity up to 105,000 ppm of TDS might be possible, based on 1500 psi maximum applied pressure for advanced membrane modules. Inlet TDS < 70,000 ppm is typically recommended.	Might be technically feasible. Finding the best draw solution will be critical, but salt precipitation will still inhibit flux and recovery.	Might be possible if the issues related to salt precipitation and low flux are resolved. Pilot testing indicates feasibility of concentrating brine to near saturation.	ED/EDR might be technically feasible for high TDS. Saltworks advertises an EDR process for feed stream with 80,000 ppm of TDS (resulting brine: 150,000 ppm of TDS). Lab-scale research investigating multi-stage ED for a 195,000 ppm NaCl feed is ongoing.	Present systems are not designed for brine treatment. Partial treatment with corrosion-resistant materials possible for brines in the range of 80,000 to 150,000 ppm. Fouling with solid precipitant will also occur at any reasonable recovery because of solubility limits.	Brine concentration may be increased to near saturation.	Possible after further development.
Characteristics of the brine or salt produced	Concentrated brine.	Concentrated brine.	Concentrated brine.	Concentrated brine.	Concentrated brine.	Concentrated brine near saturation.	Concentrated brine near saturation, possible crystallization of salts.
Expected recovery of treated water (%)	Maximum recovery of 10% for 105,000 ppm TDS feed.	~10–50% or more, depending on feed TDS and salt precipitation issues.	~10–50% or more, depending on feed TDS and salt precipitation issues.	~50% for an 80,000 ppm TDS brine feed.	Possibly ~10–50% with upgraded technologies.	Very high, depending on the feed TDS.	Unknown; further research required.
Advantages	Less energy intensive technology.	Less energy intensive technology.	Can utilize low quality heat sources.	Unknown.	Technology is readily available and might be further upgraded to handle high-TDS brines.	Established technology capable of handling high-TDS brines. Energy requirements may be reduced with MVC. Thermal evaporative processes tend to be energy intensive.	Low-grade heat sources and solar energy can be used.
Challenges	Standard membrane modules fail for highly saline brines with TDS > 70,000 ppm. Only partial treatment is possible.	Operating issues include undesired precipitation of salts leading to membrane fouling and low water recovery. Draw solution recovery will also be challenging.	Low water recovery and other operating issues associated with membrane processes for high-TDS feeds.	Highly energy consumptive because ED energy requirement increases with increasing feed salinity, although some researchers claim it will be competitive with MVC evaporation. Commercially available for brackish water.	Expensive materials of construction will be required to prevent corrosion for high-TDS feeds. Process requires a high energy input.	Expensive equipment may be required to minimize corrosion. High-TDS liquid waste will still require further treatment or disposal.	Further research required before process can be applied industrially. Potential corrosion/scaling of equipment at high TDS.
Technology readiness level	Commercially available technology.	Emerging technology.	Emerging technology.	Commercially available for brackish water.	Commercially available technology.	Commercially available technology.	Emerging technology.
Applicability to Mt. Simon brine	Not applicable at this time. May be feasible after further development of technology.	Likely to be feasible after further development of technology, but technology is not yet available.	Likely to be feasible after further development of technology, but technology is not yet available.	Likely to be feasible after further development of technology, but technology is not yet available.	May be feasible after further development of existing technology.	Applicable to Mt. Simon brine.	Likely to be feasible after further development of technology, but technology is not yet available.
Point of comparison	Evaporative crystallization			Antisolvent crystallization	Refrigerated crystallization	Supercritical desalination	
	Standard evaporative crystallizers	Spray drying	Natural evaporation	Antisolvent addition, with antisolvent recovery by distillation	Fractional freeze crystallization of ice	Supercritical desalination/power cogeneration process	
Can brine with TDS > 70,000ppm be treated effectively?	Technology is specifically developed for high-TDS brine feed.	Technology is specifically developed for high-TDS brine feed, but capacity is limited.	It is applicable, provided sufficient space is available and water recovery is not an issue.	Some literature indicates that this is technically feasible but further research is needed.	Possibly. Further research required.	Applicable to brines with different TDS concentrations.	
Characteristics of	Solid product is filtered	Solid product is	Impure mixed salt	Solid product. Salt will be	Concentrated brine.	Solid salt product will	

(continued on next page)



Table 4 (continued)

Point of comparison	Evaporative crystallization			Antisolvent crystallization	Refrigerated crystallization	Supercritical desalination
	Standard evaporative crystallizers	Spray drying	Natural evaporation	Antisolvent addition, with antisolvent recovery by distillation	Fractional freeze crystallization of ice	Supercritical desalination/power cogeneration process
the brine or salt	out and dried. Salt will be impure. Might improve with pretreatment of brine or specialized crystallizer design.	collected and dried. Salt will be impure. Might improve with pretreatment of brine or specialized design.	sludge would occasionally be dug out from a pond and landfilled (or reprocessed).	impure. Might improve with pretreatment of brine or specialized crystallizer design.		be impure. Might improve with pretreatment or stage-wise salt precipitation.
Expected recovery of treated water (%)	Very high; near complete water recovery.	Water can be recovered if needed.	Water not usually recovered.	Unknown; further research is required.	Further research is required.	Very high; near complete water recovery.
Advantages	Could be used for ZLD or near-ZLD treatment. Well established, commercial technology.	Simple process, which could be ZLD. Commercially proven.	Simple technology.	Relatively simple technological concept.	Theoretically lower energy requirements; less risk of scaling at low temperatures.	Integration with a power plant can result in power generation and high-purity water production in a ZLD system.
Challenges	Energy intensive. Recovery of a salt stream with any value may be difficult.	Highly unlikely to be economically viable at large scale. Recovery of water from outlet gas would be difficult and expensive.	No water recovery, produces a mixed salt sludge. Requires a large land area and is most effective in an arid environment.	Experimental technology. Uncertain whether as much effort went into developing compared with other emerging technologies. Probably poor economics compared with evaporation.	Low product purity; complexity of equipment (difficulties in handling and melting ice).	Emerging technology that is dependent on integration with power plants, so could not be implemented everywhere.
Technology readiness level	Commercially available technology.	Commercially available technology.	Commercially available technology.	Emerging technology.	Emerging technology.	Emerging technology.
Applicability to Mt. Simon brine	Applicable to Mt. Simon brine.	Technically feasible, but not practical due to low capacity of technology.	Technically feasible, but not practical due to land area requirements low rates of evaporation at the potential sequestration site.	Not applicable at this time. May be feasible after further development of technology, but other emerging technologies show more promise.	Not applicable at this time. May be feasible after further development of technology, but other emerging technologies show more promise.	Likely to be feasible after further development of technology, but technology is not yet available for Mt. Simon brine treatment.

Saltworks advertises an advanced EDR process: the ElectroChem™ stack technology with its IonFlux™ ion exchange membranes. The inlet stream concentration is up to 80,000 ppm of TDS and the outlet stream may be as high as 150,000 ppm of TDS [38]. The process may be worth pursuing as a brine concentrator for feeds in which salinity is double that of seawater, although crystallization or some other treatment would still be required for the EDR brine. The salinity limits for this commercial system are still too low for the Mt. Simon brine, which has a salinity of about 200,000 ppm of TDS.

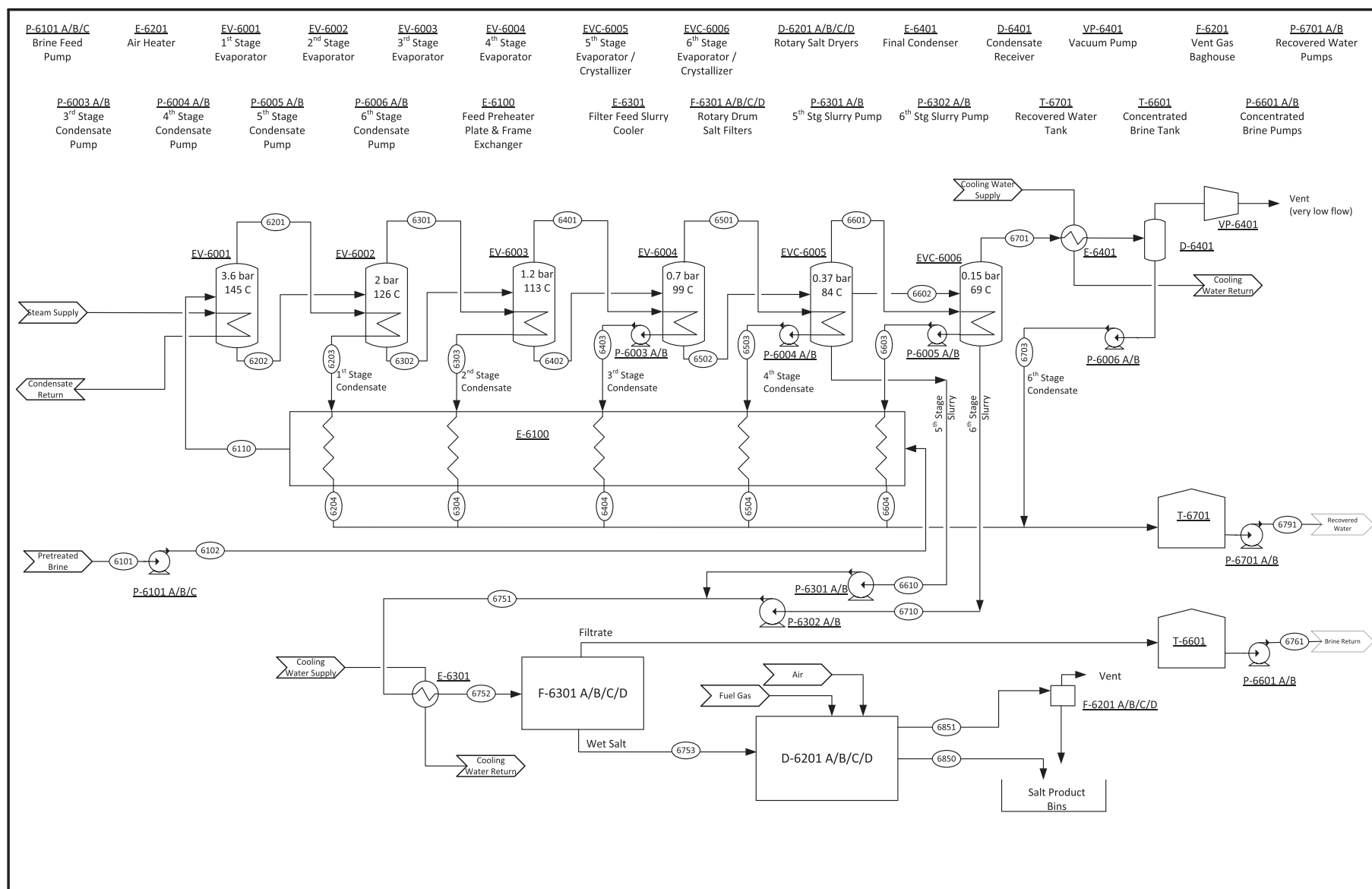
The conventional desalination processes (RO, MSF, MED, and EDR) primarily target brackish water and seawater sources, but various emerging desalination technologies might be suitable for hypersaline feed streams. These include forward osmosis (FO), membrane distillation (MD), humidification compression, fractional freeze crystallization of ice, supercritical desalination processes, and antisolvent addition. Mature, commercially available high-TDS desalination technologies are limited to evaporators including brine concentrators and crystallizers.

Unlike an RO process, in forward or direct osmosis, no pressure is applied to the membrane. Instead, a draw solution with a higher osmotic pressure than the feed solution is used to draw clean water out of the saline feed solution and across the membrane. Technically, FO is feasible for highly saline solutions depending on the availability of suitable draw solutions. Various salinity ranges have been reported, up to at least 175,000 ppm of TDS [39]. In one laboratory study, 5 M fructose was used as the draw solution for 1 M or 2 M NaCl (~58,000 to 117,000 ppm of NaCl). Water recoveries of 56.8% and 38.5% were achieved for the 1 M and 2 M NaCl solutions, respectively. The water flux was significantly lower for the 2 M feed solution (4.0 L/m<sup>2</sup>/h) than for the 1 M feed (8.2 L/m<sup>2</sup>/h) [40,41].

From an energetic standpoint, FO is a promising desalination technology, but the commercialization potential will ultimately depend on the energy required in the draw solution recovery step. The ideal draw solution will have to be an inexpensive, stable, and nontoxic solution with high osmotic pressure, and must be recoverable by a simple process [42].

One promising draw solution is ammonia/carbon dioxide (NH<sub>3</sub>/CO<sub>2</sub>). Oasys Water's Membrane Brine Concentrator uses NH<sub>3</sub>/CO<sub>2</sub> as a draw solution to treat wastewater in the Permian basin [43,44]. The average feed salinity is 103,000 ppm, with an average product concentration of 737 ppm and a brine by-product concentration of 241,000 ppm [43,44]. A pilot demonstration of the technology yielded concentrate of about 180,000 ppm of TDS when the feed solution salinity was about 73,000 ppm. Thermal energy consumption in that case, including NH<sub>3</sub>/CO<sub>2</sub> draw solution regeneration, was reported to be about 275 kWh<sub>th</sub>/m<sup>3</sup> (~83 kWh<sub>elec</sub> equiv./m<sup>3</sup>), with water recovery of 64% and a rather low flux of 2.6 L/m<sup>2</sup>-h [45]. However, some authors argue that the energy consumption of this process is too high for practical applications and that the presence of residual ammonia in the treated water renders it unfit for use as drinking water [46].

Membrane distillation is a promising emerging technology that combines some of the features of thermal and membrane processes. The process is based on a vapor pressure gradient across a hydrophobic membrane. The first MD plant (a small plant with a capacity of only 10 m<sup>3</sup>/day) for seawater desalination was commissioned by Aquaver in February 2014 [47]. Aquaver's vacuum MD process was tested on synthetic seawater and on samples with salinities up to 175,000 ppm of TDS [48]. Membrane distillation may be a viable option for highly saline brine desalination because, theoretically, there is no limitation on the salinity of the feed solution and brines up to 300,000 ppm of TDS,



**Fig. 1.** Process flow diagram for near-zero liquid discharge treatment of Mt. Simon brine by a multi-effect evaporation system.





Stream no.	6601	6602	6603	6610	6701	6703	6751	6752	6761	6791	6850	6851
Temp., C	83.5	83.5	74.2	83.5	68.5	53.7	72.4	50.0	45.0	46.3	150.0	150.0
Pres., bar	0.37	0.61	2.00	0.61	0.14	2.00	3.00	3.00	3.00	3.00	1.01	1.01
Mass flow, Kg/h	73,807	176,038	73,807	42,495	77,117	77,246	141,416	141,416	75,431	373,768	60,210	15,755
Vap. fract.	1	0	0	0	1	0	0	0	0	0	0	1
Liq. fract.	0	0.99428	1	0.66116	0	1	0.81204	0.80811	0.99915	1	0.02349	0
Solid fract.	0	0.00572	0	0.33884	0	0	0.13287	0.19189	0.00085	0	0.97651	0
Enthalpy Flow, MJ/h	-9.8E+05	-2.3E+06	-1.2E+06	-4.0E+05	-1.0E+06	-1.2E+06	-1.5E+06	-1.5E+06	-9.4E+05	-5.9E+06	-4.3E+05	-7.5E+04
pH		9.5	6.4	9.5		6.6	9.7	10.3	10.5	4.5	9.7	
Component mass fraction												
H <sub>2</sub> O	1.00E+00	6.66E-01	1.00E+00	2.78E-01	1.00E+00	1.00E+00	3.67E-01	3.67E-01	5.93E-01	1.00E+00	2.64E-03	3.66E-01
H <sub>2</sub> S	5.64E-05	2.75E-09	0	1.15E-09	2.61E-05	0	4.58E-10	2.16E-10	2.95E-10	2.05E-04	4.48E-13	3.01E-06
Ca++	0	5.65E-02	0	2.36E-02	0	0	7.73E-02	7.73E-02	1.30E-01	0	3.02E-03	0
CaOH+	0	5.05E-04	0	2.11E-04	0	0	7.24E-04	7.22E-04	1.17E-04	0	2.36E-04	0
H <sub>3</sub> O+	0	3.17E-12	8.36E-09	1.33E-12	0	4.91E-09	5.92E-13	1.31E-13	1.49E-13	6.28E-07	4.89E-15	0
K+	0	8.24E-03	0	3.45E-03	0	0	1.09E-02	7.71E-03	1.14E-02	0	2.46E-05	0
Na+	0	5.70E-02	0	2.38E-02	0	0	8.78E-03	8.08E-03	1.28E-02	0	1.06E-05	0
HS-	0	1.18E-05	0	4.93E-06	0	0	2.38E-06	2.38E-06	3.85E-06	1.09E-06	2.19E-09	0
HSO <sub>4</sub> -	0	4.79E-12	0	2.00E-12	0	0	3.61E-13	4.02E-14	3.83E-14	0	3.00E-13	0
Cl-	0	1.95E-01	0	8.15E-02	0	0	1.60E-01	1.56E-01	2.50E-01	2.05E-11	5.23E-03	0
OH-	0	2.87E-06	7.47E-09	1.20E-06	0	4.39E-09	1.52E-06	1.92E-06	3.27E-06	2.24E-11	1.50E-08	0
Br-	0	1.55E-03	0	6.47E-04	0	0	2.12E-03	2.12E-03	3.43E-03	0	6.83E-04	0
SO <sub>4</sub> --	0	2.36E-04	0	9.89E-05	0	0	2.09E-05	1.69E-05	2.59E-05	0	8.96E-07	0
S--	0	3.28E-08	0	1.37E-08	0	0	3.17E-09	2.04E-09	3.01E-09	2.28E-16	1.84E-10	0
KCl (S)	0	0	0	0	0	0	8.02E-04	6.83E-03	2.00E-03	0	2.07E-02	0
CaCl <sub>2</sub> (S)	0	0	0	0	0	0	0	0	0	0	8.03E-02	0
CaSO <sub>4</sub> . 2H <sub>2</sub> O (S)	0	1.93E-04	0	7.20E-03	0	0	2.95E-03	2.95E-03	2.49E-06	0	6.94E-03	0
NaCl (S)	0	1.56E-02	0	5.81E-01	0	0	3.70E-01	3.72E-01	6.27E-04	0	8.80E-01	0
Air	0	0	0	0	0	0	0	0	0	0	1.05E-08	6.34E-01

or near saturation, may be treated [39,49]. General Electric (GE) and Memsys successfully operated an MD system over a 200 h test period to concentrate a 150,000 ppm of TDS feed up to 230,000 ppm of TDS [40]. Pilot studies by ConocoPhillips Global Water Sustainability Center, Qatar University, and Qatar Electricity & Water Company indicate that ~70,000 ppm TDS brine concentrate from a thermal desalination plant may be desalinated by multi-effect vacuum MD with 52% recovery and a flux of 6.2 L/m<sup>2</sup>/h [50]. Many researchers, e.g. Mericq et al. [51], and Zhang et al. [52], have reported successfully operating MD at bench scale to concentrate wastewater or synthetic brines to near saturation. Sanmartino et al. report concentrating synthetic NaCl brine to supersaturation [53].

Membrane distillation is especially promising when coupled with a crystallizer. Tun and Groth investigated an integrated MD crystallization process to treat RO brine concentrate. The initial brine concentration of 19,200 ppm TDS was increased to 212,899 ppm TDS by MD, with a flux of 3–5 L/m<sup>2</sup>/h, which declined as the solution became more concentrated. When water recovery was about 75–80%, the MD brine was fed to a crystallizer, which facilitates the precipitation of salt crystals. Liquid concentrate from the crystallizer is recirculated back to the MD system, allowing for a total water recovery of up to 95% [49].

In a humidification–dehumidification (HD) process, hot air is brought into contact with saline water, resulting in the extraction of water vapor from the feed solution. The humid air must then be dehumidified by being brought into contact with a cold surface. In the first major variation of the HD process, condensation occurs in a heat exchanger used to preheat the seawater. In the second variation (dewvaporation), evaporation and condensation take place in the same vessel [54]. Humidification–dehumidification desalination requires a large amount of thermal energy (300 to 550 kWh/m<sup>3</sup>) but may be a viable process when a waste heat source or renewable energy source is available [39]. In HD processes, filtration and softening are required to prevent equipment fouling.

A dewvaporation module is commercially available through Altela, Inc [32]. Gradient Technology and Saltworks are examples of vendors that use the HD process. Saltworks Technologies Inc. advertises a thermally driven crystallizer based on a multiple-effect humidified air cycle that has no limit for inlet TDS concentration [55]. Gradient, a startup company that resulted from HD desalination research at Massachusetts Institute of Technology, advertises a carrier gas extraction process specifically designed to treat highly saline brines [56–58].

In at least one case, HD was integrated with MD hypersaline brine treatment. Minier-Mater et al. developed a pilot system to treat up to 6.3% TDS brine by MD, resulting in brine of up to 10.2% TDS which was then fed to a pilot HD unit which reportedly functioned as a crystallizer. The energy requirement for the MD unit was 260 kWh/m<sup>3</sup> and the energy required by the HD unit was 220 kWh/m<sup>3</sup>, indicating that the process seems to be technically feasible but requires improvement in energy efficiency before scaling up to treat industrial quantities [59].

Freeze–melt desalination processes are based on the principle that some water impurities might be excluded during the formation of ice crystals. A saline solution is subjected to controlled freezing and melting, which can result in the separation of purified water from salts. Multiple freeze–melt cycles can be used. The resulting pure water crystals can be separated from the remaining pockets of saline brine by rinsing, then melted. Advocates of freeze–melt desalination cite the low latent heat of freezing (7 times lower than the latent heat of evaporation) as an indicator of huge potential energy savings compared with traditional evaporative technologies, as well as the lower scaling potential at lower temperatures [60–63]. This emerging technology can be potentially applicable to treatment of high-TDS brine but needs further development to address issues related to equipment and systems for handling ice and separating ice crystals, and correspondingly high capital costs.

Cooling crystallization of salt and multiphase turbo-expansion are both freeze crystallization technologies. A multiphase turbo expander

is presently being developed by GE [64]. Brine is injected into a compressed air stream, and the mixture is then expanded in a turbo-expander capable of handling multiple phases. Quick expansion results in cooling and in the production of salt and ice crystals, which are then separated. This innovative technology claims to be more energy efficient (with predicted energy consumption of under 40 kWh/m<sup>3</sup>) compared with thermal crystallization [64]. Further development of this technology is required before potential application to Mt. Simon brine treatment.

In a supercritical desalination process, the brine is brought to water supercritical conditions (temperature > 374 °C, pressure > 220 bar), at which point the solubility of the salts decreases significantly (e.g., the solubility of NaCl may reduce to ~100 ppm), and salts spontaneously precipitate out by a shock crystallization phenomenon [65,66]. The main advantage of this process is its suitability for treatment of high-TDS brines. Some of the main challenges of this process include the continuous separation of salts, the requirement of special high-pressure/high-temperature and corrosion-resistant equipment, and the high energy demand. Odu et al. developed a pilot scale supercritical water desalination process designed for ZLD treatment of seawater and determined that the energy consumption of the process to produce a water product with 750 ppm of TDS was 450 MJ<sub>th</sub> per m<sup>3</sup> of product water (125 kWh<sub>th</sub>/m<sup>3</sup>) [67]. Supercritical precipitation has also been proposed by other researchers (e.g., Lean et al. [68]; Research Partnership to Secure Energy for America [69]); however, only partial water recovery for highly saline brines by these processes (e.g., for input and output concentrations of 200,000 and 300,000 ppm, respectively) is expected without the addition of a conventional crystallization unit. Furthermore, such an approach might be energetically superior to existing thermal evaporators with an efficient heat integration and recovery system or by integration with a power generation system. Researchers at the University of Illinois at Urbana-Champaign propose using the supercritical steam in a cogeneration process for power production to mitigate energy consumption of supercritical desalination [65]. Using this approach, the input energy will be partially recovered as the electrical power in a water–electricity cogeneration system. Continued research and development is needed to further address the challenges of supercritical water desalination.

Supercritical reactor systems have been developed for wastewater treatment, and in some systems salt removal is accomplished by employing a 2-zone reactor system in which salts precipitate in the upper supercritical zone, and then fall into the lower subcritical zone where they dissolve and are removed as liquid waste [70–72]. In this sort of system, the primary purpose of the system is oxidation of organic materials. The feed salinity is much lower than Mt. Simon brine; while some salts are removed in order to prevent clogging in the system, the process will not be effective for a highly saline feed stream. A means to remove precipitated salts as solids, rather than as a liquid waste stream, must be developed for the successful application of supercritical desalination to high-TDS brines.

In the antisolvent addition process an antisolvent – a chemical that reduces the solubility of the salt solutes – is added to the brine. Antisolvent addition is commonly applied to precipitate salts or organics in specialty chemical production. Zijlema et al. concluded that, compared to evaporative crystallization, antisolvent addition would reduce the energy consumption for NaCl production but would result in high capital costs [73]. The technology might be technically feasible for hypersaline brine treatment, but the operation of such a scheme at a very large scale appears to have no precedent.

Brine concentrators and crystallizers are considered as the common available technology for management of the concentrated brine in a ZLD system. Brine concentrators will typically concentrate a saline feed up to about 200,000 ppm of TDS [74,75], or possibly even higher [76,77], before crystallization. Water recovery depends on feed concentration, but is typically 90–98% [78]. Data on the feed concentration, water recovery, waste stream concentration, and energy consumption of

industrial brine concentrators and crystallizers is limited. Table 2 presents some of the data advertised by manufacturers or reported in the literature for selected processes that might be used in ZLD treatment of brines or industrial wastewater. Many sources indicate that MVC units for seawater desalination may require only 7 to 12 kWh/m<sup>3</sup> of electrical power [29,79], a value much lower than indicated in Table 2. In those cases, MVC is most likely not being used as a brine concentrator but for seawater or brackish water desalination processes, and the concentrate stream probably does not approach saturation.

Spray dryers and evaporation ponds are sometimes used as the final step in a ZLD process. Spray dryers are considered economically practical for use only at a small scale, possibly as the final step for a process with a minimal waste stream remaining or for a very small scale desalination facility. Capacity for spray dryers is < 10 gpm (2.3 m<sup>3</sup>/h) [83]. At one ZLD facility in Florida, GE uses a spray dryer as the final step in the treatment process; the brine is sent to the spray dryer at a rate of 0.45 to 0.9 m<sup>3</sup>/h [81].

Evaporation ponds are another potential option for ZLD treatment but they have very large land requirements, in which the area required by the pond is determined by the evaporation rate, and the feed stream flow rate is limited [32]. Furthermore, this technology is more suitable for areas with dry and hot weather [84].

#### 4. Evaluation of Mt. Simon brine treatment options

Challenging water sources, such as high-TDS produced water from oilfields, are usually managed by disposal, and water extracted during CO<sub>2</sub> sequestration is expected to be handled similarly [1]. However, freshwater generation, the recovery of salts or valuable minerals, and the reduction of adverse effects of wastewater disposal to the environment can be some benefits of pursuing high-TDS brine treatment instead of disposal. Brine treatment usually includes pretreatment and desalination stages. Commercial and emerging water treatment technologies and their potential applicability to high-TDS brine treatment, especially brine from Mt. Simon Sandstone, are evaluated.

##### 4.1. Brine pretreatment

Before desalination, pretreatment is required to remove contaminants such as suspended solids, scale-forming species, and organic impurities that interfere with the desalination process. Pretreatments may be categorized as chemical treatment, physical separation, or biological treatment processes. Table 3 presents the common pretreatment processes for produced water reported by Iggunu and Chen, Fakhru'l-Razi et al., and Guerra et al. [10,11,85], and their relevance to Mt. Simon brine.

The type of required pretreatment depends on the water source. High salinity is generally associated with a high degree of water hardness, so chemical treatment will most likely be required to soften water before high-TDS desalination. Pretreatments that target hydrocarbons are essential for oilfield-produced water, but they are likely not required for Mt. Simon brine. The brine extracted from Mt. Simon Sandstone requires pretreatment to remove a large concentration of suspended solids (i.e., 2800 ppm), which can be achieved by coagulation–flocculation–sedimentation, and media filtration. The large concentration of divalent metal species in Mt. Simon brine (Table 1) may create scaling issues, and scales may be removed by chemical precipitative softening using lime and soda ash.

##### 4.2. Side-by-side comparison of desalination technologies and their potential applicability to highly saline brine treatment

An overview of desalination technologies was presented in Section 3, and energy requirements, capacity, pretreatment and the main desalination requirements, maturity, capital costs, and challenges were considered. Brine concentration or crystallization technologies, as well as

other potential options (spray drying, and natural evaporation) that are commercially available for ZLD processes are also considered. The goal of this side-by-side comparison is to identify the technologies that are most relevant to hypersaline brines generally, and to Mt. Simon brine specifically. Available desalination treatment options, including commercial and emerging technologies, were evaluated and screened for their applicability to highly saline waters. Technologies were evaluated primarily based on salinity limitations and technical feasibility.

The first question addressed in Table 4 is whether a desalination technology can treat highly saline brine with TDS of > 70,000 ppm. If treatment of a highly saline brine is technically feasible, or if further research is required to determine the salinity limitations of a process, then other parameters are evaluated, allowing for an assessment of applicability to Mt. Simon brine at the conclusion of the table.

Table 4 includes a description of process outlets: whether a technology results in a concentrated brine or solid product, characteristics of that brine or solid, and an estimate of the percentage of feed solution that may typically be recovered as product water. An ideal process would minimize the residual brine stream and maximize pure water recovery. The advantages and challenges of applying each process to a high-TDS brine are also reported in Table 4. A desalination method may be theoretically or technically feasible for high-TDS brines but might not presently be appropriate for implementation at an industrial scale because of other issues. These potential issues might include costs, limited data availability, research gaps, and process complexity, among others. Finally, an indication of process maturity and applicability to Mt. Simon brine is provided. The maturity level varies from emerging (laboratory scale or pilot scale) to commercial (industrial scale).

In general, membrane processes exhibit TDS and fouling limitations. The high osmotic pressure of high-salinity brines is a limitation of RO processes because available membrane materials and systems cannot withstand the high pressures needed to overcome high osmotic pressure. For FO, in addition to membrane development, identification of an appropriate draw solution and draw solution recovery processes is also required. Membrane distillation is an evaporative membrane process and might be technically feasible with current membranes and membrane modules, but might be challenging to implement at industrial scales unless scaling, fouling, and other technical issues are further investigated to improve flux at high feed salinity. Electrodialysis reversal might be technically feasible, but it has not been adequately tested for high-TDS feeds.

Brine treatment by brine concentrators is a mature technology, but it exhibits significantly greater energy consumption than the theoretical minimum value, so there is space for a reduction in energy requirements. Current research focuses include the utilization of low-grade heat sources and scaling-reduction techniques, and the development of cogeneration facilities that would reduce energy consumption costs by simultaneous power production at the desalination facility. Humidification compression is an emerging thermal brine concentration technology, and further research is required before it can be implemented at the industrial scale. Corrosion, fouling, and scaling of equipment are more likely with high-TDS feed solutions.

Crystallization processes might be designed to result in significantly less (or even no) liquid waste compared with other technologies, such as membrane processes or evaporative concentrators, which only accomplish recovery of a portion of the water from the feed. As with thermal brine concentration technologies, there is significant room for reduction in energy consumption requirements for thermal crystallizers. Freeze–melt crystallization processes may require low energy consumption, but research gaps include product water quality limitations and efficient salt–ice separation techniques. Crystallization by a supercritical desalination process appears promising, but operation at very high temperatures and pressures can present practical design challenges. Membrane treatment of supercritical steam in the proposed integrated water desalination and power generation process may also be

challenging. This technology needs to be tested at a pilot scale to confirm its performance.

According to the screening of available desalination technologies presented in Table 4, brine desalination by commercially available technologies is presently limited to evaporative concentration and crystallization processes. These will be applicable both to concentrated brines of approximately 70,000 to 100,000 ppm of TDS and to the even more highly concentrated Mt. Simon brine, which exhibits a salinity of ~200,000 ppm (Table 1). Several emerging technologies for brine treatment, including new generation of RO, FO, MD, ED, HD, fractional freeze crystallization of ice, and supercritical desalination, are promising technologies with the potential for application to concentrate feed streams with TDS of 70,000 ppm or more. For high-TDS brines, including the Mt. Simon brine, the applicability of these processes depends on further technology development.

## 5. Conceptual design and process simulation for treatment of Mt. Simon brine

Based on the side-by-side comparison of desalination technologies, we conclude that evaporators are the most suitable existing technology for treating Mt. Simon brine. We perform process simulations for treatment of Mt. Simon brine for near-ZLD treatment to recover 88 wt% of the water by MEE. We assume that the extracted Mt. Simon brine has been pretreated (e.g., by coagulation, sedimentation, and filtration) prior to the desalination stage for removal of suspended solids. We perform material balance for a 454 m<sup>3</sup>/h (2000 gpm) brine input unit and determine stream compositions, energy requirements, and other process specifications. Aspen Plus (Version 8.6) software was used to prepare a process flow diagram, simulate the evaporation and crystallization process, and perform material and energy balance. Results of the simulation were used to estimate energy requirements for the process. The ENRTL (Electrolyte, Non-Random Two Liquid) activity coefficient model was selected in Aspen Plus to represent the thermodynamics of the processes. Mt. Simon brine contains many ionic species (in addition to those listed in Table 1) at low concentrations, and the ENRTL model does not contain predictive solubility (and other thermodynamic) information for all of the salt species that could possibly form. The model focused on the major species present, and those that were most prone to precipitate during the processes. Some minor components, including ions of Fe, Mn, Zn, Li, Sr, and Al, were not included in the simulation because they were present in the Mt. Simon brine at relatively low concentrations, and the complex solubility behavior of the system with these added components would be difficult to model realistically in the software. Fig. 1 shows a process flow diagram of the proposed system to recover majority of the water (~88 wt%) from a pretreated brine stream. A brief description of the main process units and operation conditions of evaporators are also included in Fig. 1. An approximate material balance of the system is shown in Table 5. The process uses a 6-stage MEE system to recover water from the brine. A salt product, consisting primarily of sodium chloride but also containing some calcium chloride, potassium chloride, and calcium sulfate dihydrate is also produced.

Pretreated Mt. Simon brine, containing approximately 20 wt% TDS, is pumped through a plate cross-exchanger (E-6100) at a flow rate of 454 m<sup>3</sup>/h, where it is preheated by water condensate streams from the first 5 MEE stages. The preheated feed is further heated in the first evaporator (EV-6001) by steam (produced by a boiler), evaporating a portion of the water from the brine. The steam produced by the first evaporator is then used to provide heat to the second evaporator, steam produced in the second evaporator is used to provide heat to the third evaporator, and so on. The stream from the last (sixth) evaporator is condensed by cooling water. The key to this process concept is to operate the evaporators at consecutively lower pressures, so that the boiling temperature of the brine (despite it becoming more concentrated in dissolved salts) is reduced from one evaporator to the next; the lower boiling temperature of a second evaporator allows for the steam

from the previous evaporator to transfer heat to the second during condensation.

The first evaporator operates at 3.6 bar and 145 °C, while the sixth evaporator (EV-6006) operates at 0.15 bar and 69 °C. The process flow diagram (Fig. 1) shows the approximate temperature and pressure of each evaporator. The steam produced in each stage (except for the last) is condensed by evaporating brine in the next evaporator in the sequence; the condensed hot water is then further cooled by transferring heat to the feed brine in E-6100. A vacuum pump (VP-6401) provides a vacuum on the final condenser separator drum (D-6401), which allows for the last three evaporator stages to operate under vacuum conditions.

The first four evaporator stages will just concentrate the brine, without precipitation of salts occurring to a significant extent. The brine exiting the 4th stage will be at the solubility limit of salts, and salt precipitation occurs in the 5th and 6th evaporation stages. The design and cost of the first four and last two evaporator units are therefore different in order to accommodate the bulk salt crystallization that occurs.

The recovered water – about 378 m<sup>3</sup>/h – is collected in a storage tank, and pumped to users. In the evaporative crystallizers (EVC-6005, EVC-6006) salts are precipitated as water is evaporated, resulting in the liquid phase being a slurry of solid salt particles and brine. Evaporative crystallizers are equipped with thickening/clarification sections, such that in EVC-6005 a thickened slurry is collected from the bottom of the vessel, while a clarified brine is collected from a different part of the vessel. The clarified liquid from EVC-6005 is fed to EVC-6006. In EVC-6006 it is assumed that the slurry is not thickened, and instead the entire liquid slurry product from this final stage is combined with the thickened slurry from EVC-6005. The combined slurry streams, containing about 40 wt% solids, is cooled and filtered. The solids collected from the filters are then dried.

There are four parallel trains of filtration and drying equipment. Each train consists of a rotary vacuum drum filter (F-6301 A/B/C/D), with the wet solids dumping into a continuous rotary dryer (D-6201 A/B/C/D). The rotary dryer uses direct contact of the wet solids with combustion gases from burning natural gas (note that for simplicity the material balance does not show the combustion gases added to the dryer); extra combustion air can be added to control temperature. The dried solid product is dumped into bins, while the combustion gases from the dryer are sent to a baghouse to filter out entrained solids prior to venting to the atmosphere. Salt is produced at a rate of about 60 MT/h and contains <1 wt% moisture; the dry mass composition of the salt is 89% NaCl, 8.1% CaCl<sub>2</sub>, 2.1% KCl, and 0.7% CaSO<sub>4</sub> dihydrate. All of the minor species in the Mt. Simon brine composition could not be included in the material balance; it is likely that additional small-concentration components (e.g., metals) will also be present in this salt, some of which might be important in the consideration of its disposition.

The filtrate streams from F-6301 A/B/C/D are combined and stored in a tank. This concentrated brine, at a flow rate of about 52 m<sup>3</sup>/h, containing roughly 50 wt% TDS (mostly CaCl<sub>2</sub>), is pumped from the tank for use or disposal; as the brine cools off during storage, it is possible that some additional CaCl<sub>2</sub> may precipitate from solution.

When estimating the energy usage and capital cost of a process in the early phase of design development, a number of assumptions must often be made. These assumptions are typically based on historical experience, information from the literature, and engineering judgment. Key assumptions that affect the design and energy usage of this process are listed below:

- *Steam production efficiency:* A natural-gas-fed boiler is used to generate steam. The thermal efficiency of this unit is assumed to be 80%.
- *Dryer efficiency:* Natural gas is burned to dry the wet salt product. A thermal efficiency of 70% is assumed.
- *Rotating equipment efficiencies:* Equipment efficiencies for pumps, blower, vacuum pump, and electric motor drives were 75%, 72%, 72%, and 98%, respectively.



- *Other power usage:* In addition to the process equipment shown in Fig. 1, another significant electric power load is for the cooling water system (cooling water circulation pumps and cooling tower fans). The cooling water system is estimated to consume over half of the electrical power load of the process.
- *Evaporator/crystallizer train differential temperature:* Stage 1 (EV-601) had a temperature difference – between the boiling brine and condensing steam – of 15 °C. The remaining stages were assumed to have temperature differences of about 6 °C (ranged from 5 to 7 °C).
- *Feed Preheater (E-6100) differential temperature:* Although this exchanger is envisioned to be a single multi-feed plate and frame exchanger, for simplicity of analysis it was modeled as sequential countercurrent exchangers, with logarithmic mean temperature difference (LMTD) of approximately 10 °C.
- *Final condenser (E-6401) differential temperature:* LMTD = 20 °C.
- *Slurry cooler (E-6301) differential temperature:* LMTD = 26 °C.

One issue not addressed directly in this design is hydrogen sulfide. During the distillation process hydrogen sulfide is formed in the brine from soluble sulfide salts, and a portion of the  $H_2S$  is stripped into the vapor (steam) phase. As a result water recovered from each MEE stage is predicted to contain some  $H_2S$ , with the combined recovered water stream containing roughly 205 ppmw of  $H_2S$ , unless measures are taken to prevent it. The  $H_2S$  in the steam can be removed prior to condensing by scrubbing with hot caustic in a packed tower. Another option is to chemically convert  $H_2S$  to a non-volatile product that could be used to prevent the  $H_2S$  problem, including the use of iron redox chemistry to convert the sulfide to sulfur, and other oxidation chemistries.

Results of the energy balance, obtained from the process simulation, are used to determine the energy requirement of the desalination process. The two energy requirements are electrical power and natural gas fuel. The process equipment with the largest power requirements include the rotary salt dryers, the vacuum pump on the final stage crystallizer, the process pumps, the cooling tower system (cooling water pumps, fans), and salt product filters. Total power requirement for the process systems is 718 kW<sub>elec</sub> (~2 kWh per m<sup>3</sup> of recovered water). The electrical power requirement of the salt drying equipment is about 10% of the total power requirement.

The largest overall energy source required for the process is natural gas to provide heat for evaporation of water from the brine. It was assumed that steam would be fed to the first evaporation stage, and this steam would be generated by a package boiler which would use the burning of natural gas as a heat source. Another major use of natural gas is in the salt product dryers; natural gas is burned and fed directly to the rotary dryers, which results in the evaporation of water from the salt. The total natural gas requirement for the process is about 92.8 MW thermal. Since water is recovered at 378 m<sup>3</sup>/h, the total thermal energy usage is 246 kWh per m<sup>3</sup> of recovered water, in which 86% of the thermal energy is required for evaporators and the remaining 14% is needed for drying the salt product. Without salt drying the thermal energy demand of the process is about 212 kWh/m<sup>3</sup> water product.

The most important factor that causes the energy usage for recovering water from this brine via evaporative techniques to be significantly greater than that normally seen when recovering water from brackish or seawater is the high total salt concentration. The boiling temperature of brines generally increases with increasing salt concentration. Therefore, in order to maintain a temperature driving force for heat transfer, the pressure difference between the evaporation and the condensing sides of the evaporator typically must increase with increasing salt content. That factor results in the energy efficiency of water evaporation processes being lower as they treat higher concentration brines.

The energy usage estimated by our process simulation is similar to the value reported by Thiel et al. [23]. Thiel et al. estimated the thermal energy consumption for a 3-stage MED brine concentration process to

be about 250 kWh/m<sup>3</sup>. The process modeled by Thiel et al. assumed a brine outlet concentration of 26 wt% TDS and does not account for the solids drying steps that our process includes. Other values reported in the literature (see Table 2) are based on MVC technology, which is more energy-efficient but has lower capacity limitations than MEE.

## 6. Conclusions

Potential utilization of the Mt. Simon Sandstone as a storage site for CO<sub>2</sub> sequestration is likely to involve the extraction of large quantities of highly saline brine, which will require management by disposal or treatment. Desalination of the Mt. Simon brine could potentially reduce adverse environmental impacts of brine disposal while simultaneously increasing fresh water supplies. Solutions for treatment of Mt. Simon brine can also be useful for handling other highly saline brines generated from other sources such as produced water from oil and gas industry or concentrated brine from seawater desalination plants. Through a critical review, we evaluated the applicability, limits, and advantages or challenges of various commercially available and emerging desalination technologies that can potentially be employed to treat the highly saline brine (with TDS values > 70,000 ppm) and those that are applicable to a ~200,000 ppm TDS brine extracted from the Mt. Simon Sandstone. The most promising emerging technologies include ED, FO, MD, HD, supercritical desalination, and freeze-melt technologies that after further development can potentially be used for treatment of high-TDS water. Among these, MD and HD have been tested with pilot scale studies indicating technical feasibility for hypersaline brine desalination. At the laboratory and pilot scale, MD and HD allow for the feed stream to be concentrated near to the saturation point, and HD may even allow for the crystallization of salts. Forward osmosis has not yet been demonstrated to concentrate brine beyond ~200,000 ppm of TDS, but if membranes, membrane modules, draw solutions, and draw solution recovery methods are further developed, it is possible that FO may be applied to higher salinity feeds. Supercritical desalination and freeze-melt processes are both promising because energy requirements may be significantly lower than other technologies, but better separation methods for removing crystals from liquid are required for both of these induced phase change approaches to desalination. Supercritical desalination has the advantage of producing purer products than freeze-melt desalination. Additionally, supercritical desalination processes may be rendered highly energy efficient by integration with a power plant. Continued tracking of the development of all of these technologies is recommended.

Our literature review and technology assessment also revealed that, among commercially available technologies, options are limited to thermal evaporators and crystallizers. We used Aspen Plus software to simulate a process in which 454 m<sup>3</sup>/h of Mt. Simon brine containing ~200,000 ppm of dissolved salts was treated by the MEE process in a near-ZLD system. Pretreated brine is fed to a 6-stage MEE process, with crystallization occurring in the final two stages. About 378 m<sup>3</sup>/h of water is recovered, and the remaining salt sludge is treated by filtration and drying. Energy balance indicates that the thermal energy consumption for the process is extremely high, mostly due to the high energy required for the evaporation of highly saline brine.

From our conceptual design and Aspen simulation results, the near-ZLD process is estimated to consume roughly 246 kWh<sub>th</sub> and 2 kWh<sub>elec</sub> per m<sup>3</sup> of recovered water. Without drying of the salt product, MEE evaporation alone requires 212 kWh<sub>th</sub>/m<sup>3</sup>. This demonstrates a huge potential for reduction in energy consumption, further confirming our recommendation to continue pursuing emerging technologies. The energy demand of currently available technologies is so high that Mt. Simon brine treatment by these technologies may not be economically feasible. Emerging technologies have the potential to significantly reduce desalination costs by lowering the energy demand.



## Acknowledgments

This research was funded by the U.S. Department of Energy, National Energy Technology Laboratory (Cooperative Agreement DE-EE0026136). Any opinions expressed in this paper are those of the authors and do not necessarily reflect the views of the funding agency; therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## References

- [1] R.J. Klapperich, G. Liu, D.J. Stepan, M.D. Jensen, C.D. Orecki, E.N. Steadman, J.A. Harju, D.V. Nakles, IEAGHG investigation of extracted water from CO<sub>2</sub> storage: potential benefits of water extraction and lesson learned, *Energy Procedia* 63 (2014) 7173–7186.
- [2] National Energy Technology Laboratory, National Carbon Sequestration Database and Interactive Viewer. <http://www.netl.doe.gov/research/coal/carbon-storage/natcarb-atlas> (accessed 03/15/16).
- [3] H.M. Breunig, J.T. Birkholzer, A. Borgia, C.M. Oldenburg, P.N. Price, T.E. McKone, Regional evaluation of brine management for geologic carbon sequestration, *Int. J. Greenhouse Gas Control* 14 (2013) 39–48.
- [4] W.L. Bourcier, T.J. Wolery, T. Wolfe, C. Haussmann, T.A. Buscheck, R.D. Aines, A preliminary cost and engineering estimate for desalinating produced formation water associated with carbon dioxide capture and storage, *Int. J. Greenhouse Gas Control* 5 (2011) 1319–1328.
- [5] R.D. Aines, T.J. Wolery, W.L. Bourcier, T. Wolfe, C. Hausmann, Fresh water generation from aquifer-pressured carbon storage: feasibility of treating saline formation waters, 10th International Conference on Greenhouse Gas Control Technologies, Amsterdam, *Energy Procedia*, 4, 2011, pp. 2269–2276.
- [6] J.A. Veil, C.B. Harto, A.T. McNemar, Management of water extracted from carbon sequestration projects: parallels to produced water management, *SPE Americas E&P Health, Safety, Security, and Environmental Conference*, Houston, 21–23, 2011.
- [7] International Desalination Association, Desalination by the Numbers, . <http://idadesal.org/desalination-101/desalination-by-the-numbers/> (accessed 03/15/16).
- [8] S. Miller, H. Shemer, R. Semiat, Energy and environmental issues in desalination, *Desalination* 366 (2015) 2–8.
- [9] N. Voutchkov, Overview of seawater concentrate disposal alternatives, *Desalination* 273 (2011) 205–219.
- [10] E.T. Iggunu, G.Z. Chen, Produced water treatment technologies, *Int. J. Low Carbon Technol.* 9 (2014) 157–177.
- [11] A. Fakhrul-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, *J. Hazard. Mater.* 170 (2009) 530–551.
- [12] D.M. Labotka, S.V. Panno, R.A. Locke, J.T. Freiburg, Isotopic and geochemical characterization of fossil brines of the Cambrian Mt. Simon Sandstone and Ironton-Galesville Formation from the Illinois Basin, USA, *Geochim. Cosmochim. Acta* 165 (2015) 342–360.
- [13] R. Locke, D. Larssen, W. Salden, C. Patterson, J. Kirksey, A. Iranmanesh, B. Wimmer, I. Krapac, Preinjection reservoir fluid characterization at a CCS demonstration site: Illinois Basin – Decatur project, USA, *Energy Procedia* 37 (2013) 6424–6433.
- [14] S. Ebrahim, M. Abdel-Jawad, S. Bou-Hamad, M. Safar, Fifteen years of R&D program in seawater desalination at KISR part I. Pretreatment technologies for RO systems, *Desalination* 135 (2001) 141–153.
- [15] S. Oren, L. Birnhack, O. Lehmann, O. Lahav, A different approach for brackish-water desalination, comprising acidification of the feed-water and CO<sub>2</sub>(aq) reuse for alkalinity, Ca<sup>2+</sup> and Mg<sup>2+</sup> supply in the post treatment stage, *Sep. Purif. Technol.* 89 (2012) 252–260.
- [16] Method 2540C: total dissolved solids dried at 180 °C, in: L.S. Clesceri, A.E. Greenberg, A.D. Eaton (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 20th ed. American Public Health Association, American Water Works Association, and Water Environment Federation 1998, pp. 2–56–2–57.
- [17] J. Xu, G. Ruan, X. Chu, Y. Yao, B. Su, C. Gao, A pilot study of UF pretreatment without any chemicals for SWRO desalination in China, *Desalination* 207 (2007) 216–226.
- [18] N. Prihasto, Q. Liu, S. Kim, Pre-treatment strategies for seawater desalination by reverse osmosis system, *Desalination* 249 (2009) 308–316.
- [19] M.D. Afonso, J.O. Jaber, M.S. Mohsen, Brackish groundwater treatment by reverse osmosis in Jordan, *Desalination* 164 (2004) 157–171.
- [20] A. Al-Karaghoul, L.L. Kazmerski, Energy consumption and water production cost of conventional and renewable-energy-powered desalination processes, *Renew. Sust. Energ. Rev.* 24 (2013) 343–356.
- [21] R. Semiat, J. Sapoznik, D. Hasson, Energy aspects in osmotic processes, *Desalin. Water Treat.* 15 (2010) 228–235.
- [22] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science* 333 (2011) 712–717.
- [23] G.P. Thiel, E.W. Tow, L.D. Banchik, H.W. Chung, J.H.V. Lienhard, Energy consumption in desalinating produced water from shale oil and gas extraction, *Desalination* 366 (2015) 94–112.
- [24] M. Al-Sahali, H. Ettouney, Developments in thermal desalination processes: design, energy, and costing aspects, *Desalination* 214 (2007) 227–240.
- [25] T. Mezher, H. Fath, Z. Abbas, A. Khaled, Techno-economic assessment and environmental impacts of desalination technologies, *Desalination* 266 (2011) 263–273.
- [26] N. Ghaffour, T.M. Missimer, G.L. Amy, Technical review and evaluation of the economics of water desalination: current and future challenges for better water supply sustainability, *Desalination* 309 (2013) 197–207.
- [27] H. Ettouney, M. Wilf, Commercial desalination technologies, in: G. Micale, L. Rizzuti, A. Cipollina (Eds.), *Seawater Desalination: Conventional and Renewable Energy Processes*, Springer, Berlin 2009, pp. 77–107.
- [28] M. Ahmad, P. Williams, Assessment of desalination technologies for high saline brine applications—discussion paper, *Desalin. Water Treat.* 30 (2011) 22–36.
- [29] Energy requirements of desalination processes, in: *Encyclopedia of Desalination and Water Resources*, Eolss Publishers Co. Ltd., Ramsey, Isle of Man, United Kingdom, <http://www.desware.net/Energy-Requirements-Desalination-Processes.aspx> (accessed 11/4/16).
- [30] E. Curcio, G.D. Profio, E. Fontananova, E. Drioli, Membrane technologies for seawater desalination and brackish water treatment, in: A. Basile, A.C.K. Rastogi (Eds.), *Advances in Membrane Technologies for Water Treatment*, Woodhead Publishing, Oxford, United Kingdom 2015, pp. 411–441.
- [31] MED: Multiple effect distillation, . <http://technomaps.veoliawatertechnologies.com/multipleeffectdistillation/en/> (accessed 03/15/16).
- [32] P. Xu, T.Y. Cath, A.P. Robertson, M. Reinhard, J.O. Leckie, J.E. Drewes, Critical review of desalination concentrate management, treatment and beneficial use, *Environ. Eng. Sci.* 30 (2013) 502–514.
- [33] B. Alspach, Produced water and salinity management: the desalination frontier, *J. Am. Water Works Assoc.* 106 (2014) 47–52.
- [34] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, *Water Res.* 43 (2009) 2317–2348.
- [35] G. Juby, A. Zacheis, W. Shih, P. Ravishanker, B. Morazavi, Evaluation and selection of available processes for a zero-liquid discharge system for the Perris, California, ground water basin, *Desalination and Water Purification Research and Development Program Report No. 149*, U.S. Department of the Interior, Bureau of Reclamation, Denver, CO, 2008.
- [36] R.K. McGovern, A.M. Weiner, L. Sun, C.G. Chambers, S.M. Zubair, J.H.V. Lienhard, On the cost of electrodialysis for the desalination of high salinity feeds, *Appl. Energy* 136 (2014) 649–661.
- [37] R. McGovern, S. Zubair, J.H.V. Lienhard, Hybrid electrodialysis reverse osmosis system design and its optimization for treatment of highly saline brines, *IDA J. Desalin. Water Reuse* 6 (2014) 15–23.
- [38] ElectroChem, advanced electrodialysis reversal (EDR), . [http://www.saltworkstech.com/wp-content/uploads/2015/03/Saltworks\\_ElectroChem\\_Product\\_Sheet\\_EN.pdf](http://www.saltworkstech.com/wp-content/uploads/2015/03/Saltworks_ElectroChem_Product_Sheet_EN.pdf) (accessed 03/15/16).
- [39] A. Subramani, J.G. Jacangelo, Emerging desalination technologies for water treatment: a critical review, *Water Res.* 75 (2015) 164–187.
- [40] J. Morillo, J. Usero, D. Rosado, H. El Bakouri, A. Raza, F.J. Bernalola, Comparative study of brine management technologies for desalination plants, *Desalination* 336 (2014) 32–49.
- [41] W. Tang, H.Y. Ng, Concentration of brine by forward osmosis: performance and influence of membrane structure, *Desalination* 224 (2008) 143–153.
- [42] D.L. Shaffer, J.R. Werber, H. Jaramillo, S. Lin, M. Elimelech, Forward osmosis: where are we now? *Desalination* 356 (2015) 271–284.
- [43] N.T. Hancock, M.S. Nowosielski-Slepawron, R.L. McGinnis, High recovery brine treatment using forward osmosis, *AMTA/AWWA Membrane Technology Conference and Exposition 2013*, San Antonio 2013, pp. 1190–1203.
- [44] B.D. Coday, P. Xu, E.G. Beaudry, J. Herron, K. Lampi, N.T. Hancock, T.Y. Cath, The sweet spot of forward osmosis: treatment of produced water, drilling wastewater, and other complex and difficult liquid streams, *Desalination* 333 (2014) 23–35.
- [45] R.L. McGinnis, N.T. Hancock, M. Nowosielski-Slepawron, G.D. McGurgan, Pilot demonstration of the NH<sub>3</sub>/CO<sub>2</sub> forward osmosis desalination process on high salinity brines, *Desalination* 312 (2013) 67–74.
- [46] L. Chekii, S. Phuntsho, J.E. Kim, J. Kim, J.Y. Choi, J. Choi, S. Kim, J.H. Kim, S. Hong, J. Sohn, A comprehensive review of hybrid forward osmosis systems: performance, applications and future prospects, *J. Membr. Sci.* 497 (2016) 430–449.
- [47] E. Drioli, A. Ali, F. Macedonio, Membrane distillation: recent developments and perspectives, *Desalination* 356 (2015) 56–84.
- [48] Aquaver, membrane distillation: a low-cost breakthrough technology for water treatment, . [http://www.aquaver.com/wp-content/uploads/2014/05/Aquaver\\_White-Papers-Industry-Applications.pdf](http://www.aquaver.com/wp-content/uploads/2014/05/Aquaver_White-Papers-Industry-Applications.pdf) (accessed 03/15/16).
- [49] C.M. Tun, A.M. Groth, Sustainable integrated membrane contactor process for water reclamation, sodium sulfate salt and energy recovery from industrial effluent, *Desalination* 283 (2011) 187–192.
- [50] J. Minier-Matar, A. Hussain, A. Janson, F. Benyahia, S. Adham, Field evaluation of membrane distillation technologies for desalination of highly saline brines, *Desalination* 351 (2014) 101–108.
- [51] J.P. Mericq, S. Laborie, C. Cabassud, Vacuum membrane distillation of seawater reverse osmosis brines, *Water Res.* 44 (2010) 5260–5273.
- [52] X. Zhang, Z. Guo, C. Zhang, J. Luan, Exploration and optimization of two-stage vacuum membrane distillation process for the treatment of saline wastewater produced by natural gas exploitation, *Desalination* 385 (2016) 117–125.
- [53] J.A. Sanmartino, M. Khayet, M.C. García-Payo, H. El Bakouri, A. Raza, Desalination and concentration of saline aqueous solutions up to supersaturation by air gap membrane distillation and crystallization fouling, *Desalination* 393 (2016) 39–51.
- [54] Y. Ghalavand, M.S. Hatamipour, A. Rahimi, Humidification compression desalination, *Desalination* 341 (2014) 120–125.
- [55] Saltworks, SaltMaker – evaporator crystallizer – brochure, low temperature crystallizer, . <https://www.environmental-expert.com/downloads/saltmaker-evaporator-crystallizer-brochure-620078> (accessed 03/15/16).

- [56] HDH tackles brine disposal challenge, *Water Desalination Report*, 50, 2014, pp. 2–3.
- [57] Gradiant, Carrier Gas Extraction, . <http://gradient.com/technology/carrier-gas-extraction/> (accessed 03/24/16).
- [58] R. Matheson, Toward cheaper water treatment, *MIT News* (July 15, 2015), . <http://news.mit.edu/2015/cheaper-fracking-water-treatment-0716> (accessed 03/24/16).
- [59] J. Minier-Matar, R. Sharma, A. Hussain, A. Janson, S. Adham, Field evaluation of membrane distillation followed by humidification/dehumidification crystallizer for inland desalination of saline groundwater, *Desalination* 398 (2016) 12–21.
- [60] M.V. Rane, Y.S. Padiya, Heat pump operated freeze concentration system with tubular heat exchanger for seawater desalination, *Energy Sustain. Dev.* 15 (2011) 184–191.
- [61] H.F. Wiegandt, R.L. Von Berg, Myths about freeze desalting, *Desalination* 33 (1980) 287–297.
- [62] R. Fujioka, L.P. Wang, G. Dodbiba, T. Fujita, Application of progressive freeze-concentration for desalination, *Desalination* 319 (2013) 33–37.
- [63] P. Gao, Z. Guo, D. Zhang, X. Zhou, G. Zhou, Performance analysis of evaporation–freezing desalination system by humidity differences, *Desalination* 347 (2014) 215–223.
- [64] V. Lissianski, Water desalination using multi-phase turbo-expander, GE Global Research, Munich, Germany, 2015, . [https://www.netl.doe.gov/File%20Library/Events/2015/crosscutting/Crosscutting\\_20150428\\_Poster23\\_GE.pdf](https://www.netl.doe.gov/File%20Library/Events/2015/crosscutting/Crosscutting_20150428_Poster23_GE.pdf) (accessed 03/15/16).
- [65] S.A. Dastgheib, H. Salih, A. Ashraf, H. Lu, S. Nam, An integrated supercritical system for efficient produced water treatment and power generation, *Crosscutting Research & Rare Earth Elements Portfolios Review Meeting*, 2016 (April 18–22).
- [66] F.J. Armellini, J.W. Tester, G.T. Hong, Precipitation of sodium chloride and sodium sulfate in water from sub- to supercritical conditions: 150 to 550 °C, 100 to 300 bar, *J. Supercrit. Fluids* 7 (1994) 147–158.
- [67] S.O. Odu, D.H. Van, S. Metz, S.R.A. Kersten, Design of a process for supercritical water desalination with zero liquid discharge, *Ind. Eng. Chem. Res.* 54 (2015) 5527–5535.
- [68] M.H. Lean, J. Seo, A.R. Volkel, Desalination Using Supercritical Water and Spiral Separation, United States Patent Application Publication, August 16 2012 US 2012/0205320 A1.
- [69] Research partnership to secure energy for America, cost-effective treatment of flowback and produced waters via an integrated precipitative supercritical (IPSC) process, . <http://www.rpsea.org/projects/11122-60/> (accessed 3/6/2015).
- [70] J. Bettinger, P.E. Ferland, E.D. Ferland, W. Killilea, Demonstration of the Modar supercritical water oxidation process, *Waste Management Symposia*, Tucson 1994, pp. 813–818.
- [71] P.A. Marrone, M. Hodes, K.S. Smith, J.W. Tester, Salt precipitation and scale control in supercritical water oxidation—part B: commercial/full-scale applications, *J. Supercrit. Fluids* 29 (2004) 289–312.
- [72] D. Xu, C. Huang, S. Wang, G. Lin, Y. Guo, Salt deposition problems in supercritical water oxidation, *J. Chem. Eng.* 279 (2015) 1010–1022.
- [73] T.G. Zijlema, R.M. Geertman, G. Witkamp, G.M. van Rosmalen, J. de Graauw, Antisolvent crystallization as an alternative to evaporative crystallization for the production of sodium chloride, *Ind. Eng. Chem. Res.* 39 (2000) 1330–1337.
- [74] L. Awerbuch, M.C. Weekes, Disposal of concentrates from brackish water desalting plants by means of evaporation technology, *Desalination* 78 (1990) 71–76.
- [75] D.L. Shaffer, L.H. Arias Chavez, M. Ben-Sasson, S. Romero-Vargas Castrillón, N.Y. Yip, M. Elimelech, Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions, *Environ. Sci. Technol.* 47 (2013) 9569–9583.
- [76] R. Zuback, L. Marchewka, L. Herrmann, Industrial brine concentration using forward osmosis, *Proceedings of the Water Environment Federation, WEFTEC 2014*, Water Environment Federation, Alexandria 2014, pp. 2685–2690.
- [77] P.C. Das, Selection of technology for produced water treatment, *North Africa Technical Conference and Exhibition 2012*, Managing Hydrocarbon Resources in a Changing Environment, NATC 2012, Cairo, 2012, pp. 1122–1128.
- [78] A. Subramani, J.G. Jacangelo, Treatment technologies for reverse osmosis concentrate volume minimization: a review, *Sep. Purif. Technol.* 122 (2014) 472–489.
- [79] O.K. Buros, The ABCs of Desalting, International Desalination Association, Topsfield, MA, 2000.
- [80] 212 Resources, Company overview, . <http://www.212resources.com/company/history.html> (accessed 03/15/16).
- [81] J. Bostjancic, R. Ludlum, Reducing Wastewater to Dryness: Zero Liquid Discharge Case Studies at New Power Plants, 1994. Resources Conservation Company, Bellevue, WA, 1994 (available in the Document Library at [www.gewater.com](http://www.gewater.com), accessed 03/15/16).
- [82] G.E. Water, Process Technologies, Zero Liquid Discharge: Eliminate Liquid Discharge, Recover Valuable Process Water, 2009. GE Water & Process Technologies, Trevose, PA, 2009 (available in the Document Library at [www.gewater.com](http://www.gewater.com), accessed 03/15/16).
- [83] M. Mickley, Survey of High-Recovery and zero Liquid Discharge Technologies for Water Utilities, Water Reuse Foundation, 2008.
- [84] P. Chelme-Ayala, D.W. Smith, M.G. El-Din, Membrane concentrate management options: a comprehensive critical review, *Can. J. Civ. Eng.* 36 (2009) 1107–1119.
- [85] K. Guerra, K. Dahm, S. Dundorf, Oil and Gas Produced Water Management and Beneficial Use in the Western United States, Science and Technology Program Report No. 157, US Department of the Interior, Bureau of Reclamation, Denver, CO, 2011.