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Review: Water recovery from brines and salt-saturated solutions: operability and thermodynamic efficiency considerations for desalination technologies

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Abstract

BACKGROUND—When water is recovered from a saline source, a brine concentrate stream is produced. Management of the brine stream can be problematic, particularly in inland regions. An alternative to brine disposal is recovery of water and possibly salts from the concentrate.

RESULTS—This review provides an overview of desalination technologies and discusses the thermodynamic efficiencies and operational issues associated with the various technologies particularly with regard to high salinity streams.

CONCLUSION—Due to the high osmotic pressures of the brine concentrates, reverse osmosis, the most common desalination technology, is impractical. Mechanical vapor compression which, like reverse osmosis, utilizes mechanical work to operate, is reported to have the highest thermodynamic efficiency of the desalination technologies for treatment of salt-saturated brines. Thermally-driven processes, such as flash evaporation and distillation, are technically able to process saturated salt solutions, but suffer from low thermodynamic efficiencies. This inefficiency could be offset if an inexpensive source of waste or renewable heat could be used. Overarching issues posed by high salinity solutions include corrosion and the formation of scales/precipitates. These issues limit the materials, conditions, and unit operation designs that can be used.

Keywords

desalination; brine management; membrane distillation; pervaporation; zero liquid discharge

Overview of Desalination Technologies

Reverse osmosis (RO) is an energy- and cost-effective technology for producing potable water from brackish and saline water sources.^{1–7} As illustrated in Figure 1, in RO the feed saline solution is pressurized and directed to the feed side of a permselective membrane that rejects salt ions while allowing water to permeate to the low pressure permeate side of the membrane. The applied pressure gradient must overcome the difference in osmotic pressure between the feed (Π_f) and permeate liquids (Π_p). The brine concentrate rejected by the

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membrane passes through an energy recovery device after exiting the membrane unit. The recovered energy is used to partially pressurize the feed stream, thereby reducing the energy required to pressurize the feed liquid.

Prior to the development of RO technology, the most common means of desalinating saltwater was with a thermally-driven technology, typically flash evaporation or distillation generally implemented as multi-stage flash (MSF) and multiple effect distillation (MED), depicted in Figures 2 and 3, respectively. In MSF, the feed saline solution is preheated using condensing vapors from the flash units and eventually raised to the maximum process temperature with a higher temperature heat source, such as steam. The hot feed is then passed through flash units of successively lower vapor pressure and temperature wherein a portion of the water in the feed is evaporated and condensing against the feed solution in the feed preheat exchangers. The condensed water vapor is the desalinated product while the brine reject is the liquid leaving the final flash unit in the series. MED is similar to MSF, except condensation of the overhead vapor is carried out in heat exchange with the liquid in the next distillation effect unit in the sequence. In addition, the higher temperature heat source in MED is used to heat the liquid in the first effect chamber rather than the feed to that first effect as in MSF. Because of these differences, more water is evaporated in a typical distillation effect than in a flash unit.

Mechanical vapor compression (MVC), illustrated in Figure 4, is similar to MED in that the vapor generated in the evaporation unit is condensed in heat exchange with liquid inside an evaporation unit, however in MVC the water vapor generated in the evaporation unit is compressed and then condensed in heat exchange with the same evaporation unit that generated the vapor rather than the next unit in the sequence. In MED and MSF, the water vapor from a distillation or flash unit cannot condense at the temperature of that unit due to the difference in the dew point (condensation temperature) of the vapor and the bubble point (boiling temperature) of the saline solution. Compressing the vapor raises the pressure of the vapor thereby increasing the temperature at which the vapor will condense, making it possible to recover the heat of condensation back into the same unit. In this way, a single MVC unit could be used to desalinate water. Just as with MED and MSF, a series of MVC units operating at successively lower temperatures and pressures is usually more efficient than a single MVC unit.

Several alternatives to the conventional thermal processes (MED, MSF, MVC) and pressure-driven RO have been developed including electrodialysis (ED), forward osmosis (FO), membrane distillation (MD), pervaporation (PV), and humidification-dehumidification (HDH). ED, illustrated in Figure 5, utilizes an applied electrical voltage gradient to drive anions and cations in opposite directions. Alternating cation and anion exchange membranes create alternating regions of depletion and accumulation of the ions, yielding two sets of streams: one consists of partially deionized product water streams and the other is the brine concentrate streams. FO, like RO, is controlled by an osmotic pressure gradient between the feed-side and permeate-side of a water permselective membrane. However, in FO, illustrated in Figure 6, the permeate-side liquid is a high osmotic pressure solution that draws water (hence the name “draw solution”) from the lower osmotic pressure saline feed solution, thereby concentrating the feed while diluting the draw solution. In a regeneration unit, the

diluted draw solution is separated into a product water stream and a reconcentrated draw solution stream for reuse. The regeneration step requires some combination of heat and mechanical work to carry out the separation. Although osmotic pressure is involved in FO, no applied liquid pressure is used in a standard FO step to transport water through the membrane. Pressure-assisted FO (or “pressure assisted osmosis”), wherein pressure is applied to the feed in FO, has been proposed to process more highly concentrated saline feed streams.^{8, 9}

Membrane distillation (MD) covers a variety of processes utilizing a porous, non-wetted membrane to transport water based on the vapor pressure gradient between the feed solution and the permeate water product. The distinctions are based on the design of the permeate side of the membrane unit, including direct contact (DCMD), air gap (AGMD), vacuum (VMD), and permeate gap (PGMD).¹⁰ DCMD, shown in Figure 7, is the most developed and studied MD process for desalination. In DCMD, the feed saline solution is heated prior to contacting the microporous membrane. Water evaporates from the warmer saline source stream, moving as vapor through the open pores of the membrane, and then condenses into a cooler purified water permeate stream that is in direct contact with the other side of the membrane. In this case, the driving force is the difference in water vapor pressure between the salt solution at one temperature and purified water at a lower temperature. As noted in Figure 7, heat must be added to the feed stream and removed from the permeate stream in order to establish and maintain a vapor pressure driving force. Instead of having the receiving stream in direct contact with the porous membrane as in DCMD, the reduced water partial pressure on the purified water side of the membrane can be achieved using a condenser and vacuum pump system separated from the membrane. Such a process would be referred to as “vacuum membrane distillation” (VMD) if the membrane were porous or “pervaporation” (PV) if a non-porous coating were present. The PV process is depicted in Figure 8.

Like PV and VMD, Humidification-Dehumidification (HDH), illustrated in Figure 9, utilizes the difference between the water vapor pressure of a heated feed solution and that of a vapor permeate stream to transport water across a membrane (porous or non-porous) and recovers the water product in a separate condenser. However, in HDH, the vapor phase is an air stream that is recirculated from the membrane unit, where it is humidified with water permeating the membrane from the heated feed solution, to the condenser heat exchanger, where it is dehumidified by condensing the added water vapor. The condensation is achieved by transferring heat from the warm, humid air to the cool inlet feed liquid.

Each of the aforementioned desalination technologies generates a low salinity product water and a brine concentrate. The treatment and disposal of the brine concentrate from desalination operations, particularly RO systems, is garnering more attention as this means of desalination is applied in more and different locations.^{11–19} Brine disposal methods include discharge to the environment or further treatment to recover additional water or even salts.^{11–22} For inland arid locations that lack ready access to a saline receiving body, the disposal options are limited and additional means of concentrating the brine or even zero liquid discharge (ZLD) are considered.

Minimum separation energy

One challenge faced by any technology used to further concentrate the brine is the thermodynamic work necessary to drive the separation increases with increasing salt concentration. The minimum work (w_{min}) required to accomplish a separation is equal to the negative of the Gibbs Free Energy of mixing (Δg_{mix}^*);^{5, 23–25}

$$w_{min} = -\Delta g_{mix}^* = \Delta h_{mix} - T_0 \Delta s_{mix} \quad (1)$$

Where h_{mix} is the heat of mixing, s_{mix} is the entropy of mixing, and T_0 is the temperature. The minimum work to separate a mixture of n components into pure streams of each (illustrated in Figure 10a for a binary mixture) per mole of the feed mixture is calculated as:

$$w_{min} = -T_0 R \sum_{i=1}^n x_i \ln(\gamma_i x_i) \quad (2)$$

Where γ_i and x_i are the activity coefficient and mole fraction, respectively, of component i in the feed to the separation unit and R is the gas constant (8.314 J/mol·K). The product ($\gamma_i x_i$) is the activity (a_i) of the component. For ideal binary mixtures of compounds A and B (i.e. $\gamma_i = 1$) Equation 2 simplifies to:

$$w_{min} = -T_0 R [x_A \ln x_A + (1-x_A) \ln(1-x_A)] \quad (3)$$

The relationship in Equation 3 is plotted as the lower curve in Figure 11. This curve represents the minimum work per mole of the initial mixture (i.e. moles of “A” + moles of “B”). Since this is assumed an ideal mixture, the maximum in the curve occurs for an equimolar mixture. If only “A” is the desired product, the minimum work per mole of “A” recovered is determined by dividing Equation 3 by the mole fraction of “A,” yielding the top curve in Figure 11. In this case, the significance of attempting to recover a compound from a dilute solution is evident, since the minimum work rises rapidly as the concentration of “A” is reduced, particularly below $x_A = 0.1$.

In most separation processes, two impure streams, a reject stream and a product stream, are produced rather than pure streams of components A and B . As a result, the minimum rate of work required to perform an imperfect separation, $\dot{W}_{min}$ (J/s), assuming ideal solutions, is:

$$\dot{W}_{min} = -T_0 R \left[\dot{N}_f (x_{Af} \ln x_{Af} + x_{Bf} \ln x_{Bf}) - \dot{N}_r (x_{Ar} \ln x_{Ar} + x_{Br} \ln x_{Br}) - \dot{N}_p (x_{Ap} \ln x_{Ap} + x_{Bp} \ln x_{Bp}) \right] \quad (4)$$

Where f , r , and p in a subscript designates the feed, reject, or product stream, respectively. $\dot{N}_j$ is the total molar flow rate of species in stream j . Equation 4 can be rewritten as:⁵

$$\dot{W}_{min} = T_0 R \left[\dot{N}_r \left(x_{Ar} \ln \frac{x_{Ar}}{x_{Af}} + x_{Br} \ln \frac{x_{Br}}{x_{Bf}} \right) + \dot{N}_p \left(x_{Ap} \ln \frac{x_{Ap}}{x_{Af}} + x_{Bp} \ln \frac{x_{Bp}}{x_{Bf}} \right) \right] \quad (5)$$

Dividing both sides by $\dot{N}_p$ yields the minimum rate of work per mole of product. For desalination of NaCl solutions, where essentially pure water and a salt-enriched brine reject stream are produced from a binary salt/water mixture, the minimum work required per mole of water recovered can be calculated as:⁴

$$w_{min} = \phi T_0 R x_{sf} \left[\frac{x_{sr}}{x_{sr} - x_{sf}} \right] \ln \left(\frac{x_{sr}}{x_{sf}} \right) \quad (6)$$

Where “ S ” in a subscript designates the mole fraction of NaCl in a solution and is ϕ the dissociation factor with a value between 1 and 2, assumed to be 2 for sodium chloride.⁴ The dissociation factor accounts for the fact that aqueous solutions of NaCl actually contain three species (Na^+ , Cl^- and water) instead of just two. For the production of pure NaCl and pure water from a NaCl feed solution containing an NaCl concentration of x_{sf} , the minimum work per mole of feed mixture (including Na^+ , Cl^- and water) can be calculated from Equation 2 as:

$$w_{min} = -T_0 R \left[x_{+f} \ln x_{+f} + x_{-f} \ln x_{-f} + x_{w\pm f} \ln x_{w\pm f} \right] \quad (7)$$

Where the mole fraction of Na^+ ions (x_{+f}), Cl^- ions (x_{-f}), and of water in the ionic feed solution ($x_{w\pm f}$) are calculated as:

$$x_{+f} = x_{-f} = \frac{x_{sf}}{1 + x_{sf}} \quad (8)$$

$$x_{w\pm f} = 1 - x_{+f} + x_{-f} = 1 - \left(\frac{2x_{sf}}{1 + x_{sf}} \right) \quad (9)$$

Thus, Equation 7 becomes:

$$w_{min} = -T_0 R \left[2x_{+f} \ln x_{+f} + (1 - 2x_{+f}) \ln (1 - 2x_{+f}) \right] \quad (10)$$

Water recovery, Y_W , here defined as the fraction of water in the feed that is recovered in the product, is calculated from these concentrations as:

$$Y_W = \frac{1}{(1-x_{sf})} \left[1 - \frac{x_{sf}}{x_{sr}} \right] \quad (11)$$

For the first drop of water removed from the feed solution (i.e. $x_{sr} \approx x_{sf}$ and $Y_W = 0$), the minimum work per mole of pure water recovered is calculated as:⁴

$$w_{min} = \phi T_0 R x_{sf} \quad (12)$$

The minimum work for small recovery can be estimated from the osmotic pressure of the solution (Π) and molar volume of water (V) as:⁴

$$w_{min} \cong \Pi V \quad (13)$$

Similarly, the minimum work for small recovery can be estimated based on the ratio of the vapor pressure of pure water (p_w^{sat}) to that of water in the salt solution (p_w^x):⁴

$$w_{min} \cong T_0 R \ln \left(\frac{p_w^{sat}}{p_w^x} \right) \quad (14)$$

The minimum theoretical work per mass of pure water recovered from aqueous NaCl as a function of the NaCl mole fraction is shown in Figure 12 for a temperature of 25 °C and in Figure 13 for 80 °C. In these calculations, all of the separation work has been allocated to the water product. The lower curve in these graphs represents the minimum work to produce the first drop of water from the feed solution (i.e. $Y_W = 0$). The top curve represents the minimum work required to separate the feed solution into pure salt and pure water output streams (i.e. $Y_W = 1$). The curves between these extremes each represent a different constant concentration of salt in the brine reject stream, ranging from a typical RO brine reject (7 wt. % NaCl, $x_{sr} = 0.0227$) to a brine saturated with NaCl (26.4 wt.% NaCl, $x_{sr} = 0.0998$ at 25 °C).

A few observations can be made from Figures 12 and 13. First, for a fixed brine reject stream concentration (following one of the curves), the minimum energy of separation increases as the concentration of salt in the feed solution increases. Second, as the brine reject stream concentration increases for a constant feed concentration (moving vertically from one curve to another), so does the minimum energy per unit of water recovered in the product stream. Neither of these observations is unexpected, but they serve to highlight the degree to which water removal from a more concentrated brine feed stream requires more

energy than from typical seawater. From Figure 12, the minimum work per mass of water recovered when the feed is a typical seawater (approximated as 3.5 wt.% NaCl, $x_{Sf}=0.0111$) for the first drop of water is 3.05 kJ/kg-water while the work required to concentrate the seawater up to the typical RO brine reject stream (7 wt.% NaCl, $x_{Sr}=0.0227$) is 4.28 kJ/kg-water. If the RO brine reject stream was the feed, the first drop of water would require 6.25 kJ/kg-water while the work to concentrate the RO brine reject up to the saturation concentration of NaCl would be 12.0 kJ/kg-water.

Thermodynamic efficiency of desalination technologies

The above analysis was for the theoretical minimum work. The actual work or energy required to produce pure water from a salt solution will be higher, sometimes much higher, depending on the efficiency of the desalination units. For example, the latest commercial seawater reverse osmosis (SWRO) membrane units require about 2 kWh-electricity/m³-water for 50% recovery or about 7.1 kJ of electrical energy per kg of water produced, 65% higher than the theoretical minimum in Figure 12.^{1, 26} The average efficiency of the fossil-fuel powered electrical power grid results in 0.37 units of electrical energy delivered per unit of higher heating value (HHV) of primary energy source consumed (average for US fossil fuel-powered grid in 2011).^{27, 28} As a result, commercial SWRO units require 19.2 kJ-primary energy per kg-water produced. The intake, pretreatment, post-treatment, and brine discharge stages of a SWRO plant are estimated to require an additional 3.6–7.2 kJ-electricity/kg-water (kJ-elec/kg-water).²⁶

Thermally-driven desalination units require significantly more energy than those using mechanical work. One of the reasons for this is the theoretical minimum heat required to separate a mixture, q_{min} (J/mol), is calculated from the minimum work as follows:^{3, 29}

$$q_{min}=w_{min}\left(1-\frac{T_0}{T}\right)^{-1} \quad (15)$$

Where T is the temperature of the heat source and T_0 is ambient temperature, both in Kelvin. If the heat source is at 100 °C and ambient temperature is 25 °C, the q_{min} is 5.0 times greater than w_{min} . Thus, for a feed of 3.5 wt.% NaCl and a brine reject of 7.0 wt.% NaCl, with w_{min} of 4.28 kJ/kg-water, q_{min} would be 21.4 kJ-heat/kg-water.

As with work-driven SWRO, the actual energy required for thermally-driven desalination is higher than the minimum. For example, with no heat recovery, evaporating water requires 2260 kJ-heat/kg-water, 2 orders of magnitude higher than the minimum heat requirement. For this reason, thermally-driven desalination processes, like distillation and flash evaporation, operate with multiple effects wherein the heat is reused several times through sequential condensation and evaporation steps. For example, a once-through multistage flash (MSF-OT) unit with 24 stages is estimated to require 0.24 kg of steam per kg of water produced³⁰, or about 540 kJ-heat/kg-water. This is still 25 times the minimum heat required.

This leads to the definition of a “Second Law Efficiency” or “exergetic efficiency” (η_{II}) for the generic steady state separation process depicted in Figure 10b as the ratio of the minimum work to the actual work:³¹

$$\eta_{II} = \frac{w_{min}}{LW + w_{min}} \quad (16)$$

Where LW is the lost work, or destroyed exergy, defined as:

$$LW = \sum_{\substack{\text{streams,} \\ \text{heat,} \\ \text{work} \\ \text{in}}} \left[\dot{N} (h - T_0 s) + \dot{Q} \left(1 - \frac{T_0}{T_s} \right) + \dot{W} \right] - \sum_{\substack{\text{streams,} \\ \text{heat,} \\ \text{work} \\ \text{out}}} \left[\dot{N} (h - T_0 s) + \dot{Q} \left(1 - \frac{T_0}{T_s} \right) + \dot{W} \right] \quad (17)$$

Where h and s are the enthalpy and entropy of a stream, respectively, T_0 and T_s the temperature of the reference surroundings and heat source (or sink), respectively. The Second Law Efficiency reported by Mistry *et al.* for several desalination processes producing water from seawater are shown in Table 1.³⁰

While these efficiencies depend on a number of design and operating factors and so are specific to the conditions assumed in the reference, they illustrate the thermodynamic advantage for reverse osmosis, here with an η_{II} of 31.9%. The next highest efficiency was calculated for MVC evaporation wherein mechanical work is used to compress the water vapor generated in an evaporator such that it can be condensed at a temperature sufficient to return the heat released during condensation back into the hot brine. Thus, the processes with the top two efficiencies rely on mechanical work. The remaining four processes are thermally-driven and have efficiencies ranging from 1.0 to 5.9%.

Thiel *et al.* extended the Second Law Efficiency analysis for desalination technologies to a broader range of feed salinities – up to the saturation limit of NaCl.¹¹ The general ranking of the technologies in efficiency was the same as in Table 1. For most of the salinity range, the efficiency of all technologies increased. However, at very high salinities, greater than 20 wt. % NaCl, the Second Law Efficiency of RO processes decreased allowing MVC to overtake it at saturation conditions. Nevertheless, the highest efficiency of 63% was calculated for a 2-stage RO system operating on a feed containing 20 wt.% NaCl. The Second Law Efficiencies for the technologies analyzed in the article with a near saturated feed (25 wt.%) are listed in Table 2.

The energy consumption, both heat and work, per unit water produced for the technologies analyzed by Thiel *et al.* for a 15 wt.% NaCl feed ($x_{Sr} = 0.0516$) and an NaCl-saturated brine reject stream (26.4 wt.% NaCl, $x_{Sr} = 0.0998$ at 25 °C) are shown in Figure 14.¹¹ As

indicated in Figure 12, the minimum work for these conditions would be 19.4 kJ-work/kg-water. According to Thiel *et al.*, hypothetical 2- and 1-stage RO systems use the least amount of energy, requiring 40 and 51 kJ-elec/kg-water, respectively.¹¹ These RO systems were followed in increasing energy usage by 2- and 1-stage MVC systems, using 68 and 95 kJ-elec/kg-water, respectively. The thermally-driven processes (MED, HDH, PGMD, and FO) are estimated to require significantly more energy, ranging from 868 kJ-heat/kg-water (plus 12 kJ-elec/kg-water) for a 3-effect MED system to 2210 kJ-heat/kg-water (plus 10 kJ-elec/kg-water) for an FO system. Thus, even accounting for the inefficiency of electricity generation, the work-driven processes are predicted to use markedly less energy than the thermally-driven processes to concentrate a 15% NaCl brine to saturation.

Thermodynamic efficiency does not directly translate into economic or operational viability. In situations where useful waste heat is available at a low cost of capture/transfer, thermally-driven processes may have an economic advantage.³² In addition, there may be operating conditions that prevent use of certain technologies. Such is the case for high salinity brines. As the salt concentration increases, the osmotic pressure increases relatively linearly while the vapor pressure of water is only modestly effected. This difference is shown in Figure 15 for osmotic pressure at 25 °C and vapor pressure at 80 °C for seawater with a salinity up to 12 wt.%.^{33–35} Thus, very high feed pressures are required to operate RO systems as salinity increases, while the operating pressures and driving forces in evaporative processes only change modestly. According to Figure 15, the minimum pressure required to express water from a 7 wt.% salinity seawater by RO is 5.5 MPa (54 atm or 800 psi). The osmotic pressure of a 7 wt.% NaCl is somewhat higher, about 6.0 MPa. The maximum pressure rating for standard SWRO membranes ranges from 6.9 to 8.3 MPa¹¹, thereby limiting the maximum salinity of seawater brine to 8.5 to 9.8 wt.% and NaCl solutions to 7.7 to 9.2 wt.%, about one-third the solubility limit of NaCl. As noted by Thiel *et al.*, in addition to simple mechanical issues, the thin film composite (TFC) membranes used in SWRO modules experience structural compaction at high pressures resulting in reduced permeability which translates to higher required membrane area.¹¹ Future advances in membrane, modules, and flowsheet design will likely extend the pressure range of RO systems allowing operation with higher salinity feeds. However, the use of RO systems at salt concentrations over 10 wt.% is currently not practical.

In addition to the energy required, the recovery of water and salts from brine concentrate streams presents a number of technical challenges. Two particular problems are scale/precipitate formation and corrosion.^{36–38} The former can lead to the failure of equipment, decline in production, and/or increased maintenance. The latter may result in equipment failure and increased maintenance. Antiscalants are commonly added to avoid scale formation while corrosion inhibitors may be added and corrosion resistant materials employed to limit material corrosion.¹² Any antiscalant or corrosion inhibitor compound that is added in a desalination operation will usually end up in the brine concentrate stream. If the objective of the brine treatment process is to ultimately precipitate the salts, antiscalants added upstream may complicate the process.

Brine concentrate management and Zero Liquid Discharge

Several recent publications and reports have focused on brine concentrate management in terms of additional water recovery with some including salt recovery and/or ZLD.^{11–16, 20, 22, 39–55}, including general reviews/overviews of brine treatment technologies^{11–16, 20, 39–44}, reviews of ZLD options^{16, 44}, an analysis of ED for salt recovery⁵⁵, and MD paired with a crystallization process (termed “membrane distillation crystallizer” or “MDC”).^{22, 45–54} In one, a 2006 report prepared for the U.S. Department of the Interior Bureau of Reclamation (BoR), Mickley and Associates identified the six most frequently practiced disposal methods for RO brine concentrate streams.⁴⁰ In decreasing frequency, the methods were: surface water discharge, sewer discharge, deep well injection, evaporation ponds, spray irrigation, and ZLD.⁴⁰ The ZLD technologies were single- and multi-effect evaporators, vapor compression evaporator systems (“Brine Concentrators”), crystallizers, and spray dryers.⁴⁰ Except for spray dryers, these ZLD technologies enable additional water recovery in addition to salt recovery. A subsequent 2009 BoR report on inland brine concentrate treatment and disposal highlighted brine volume reduction technologies (“liquid-residual-producing processes”) and ZLD systems, further separating the technologies into those currently available and those under development (as of 2009).¹⁴ The technologies highlighted in the 2009 BoR report and in several of the other brine management documents are summarized below.^{13–15, 40, 42, 56}

1. Brine Volume Reduction Technologies (methods for extracting additional water up to or beyond the salt saturation concentration):
 - 1a Available now:
 - 1a.1 ED/ED Reversal (EDR).
 - 1a.2 RO systems tolerant of scale/precipitate solids (like vibrating membrane units).
 - 1a.3 Precipitative softening combined with RO, scale-forming ions are intentionally precipitated out before further water recovery by RO.
 - 1a.4 Enhanced membrane system that uses ion exchange softening to remove scale-forming ions to extend the water recovery range of RO.
 - 1a.5 Brine concentrator consisting of mechanical evaporation (like MVC system) or thermal evaporation (such as MSF or MED).
 - 1a.6 Natural Treatment Systems involving halophytes or constructed wetlands.
 - 1b Under development:
 - 1b.1 FO
 - 1b.2 Two-pass Nanofiltration

- 1b.3** MD
 - 1b.4** Advanced Rejected Recovery of Water
 - 1b.5** Dewvaporation (an HDH technology)
 - 1b.6** Capacitive Deionization
 - 1b.7** Liquid-liquid extraction
 - 2.** ZLD/Crystallization Technologies (for water and salt recovery from salt-saturated feeds):
 - 2a** Available now:
 - 2a.1** Mechanical and thermal evaporative crystallizers
 - 2a.2** Cooling crystallization
 - 2a.3** Freezing with water removed as a solid from ice/brine slurry
 - 2a.4** Evaporation ponds (no water recovery)
 - 2a.5** Spray Dryers (no water recovery)
 - 2b** Under development:
 - 2b.1** Wind-aided intensified evaporation (no water recovery)
 - 2b.2** Dewvaporation (aka HDH)
 - 2b.3** Salt solidification and sequestration
 - 2b.4** Slurry Precipitation and RO

Although several technologies are available for both volume reduction and crystallization, the capital and operating costs, as well as the energy required, of the available technologies, and many of those under development, are seen as prohibitive. As a result, the BoR is launching a grand challenge in the fall of 2016 to stimulate new brine concentrate management options for inland RO operations.¹⁷

In order to reduce capital expenses (CAPEX), operating expenses (OPEX), and primary energy usage, a number of technology characteristics would be beneficial:

- 1.** Able to operate using solar thermal energy or low grade waste heat
- 2.** Utilizes inexpensive materials of construction wherever possible (or at least avoids using expensive corrosion-resistant metals)
- 3.** Not affected by the formation of scale or precipitates (or at least is easily cleaned/regenerated)
- 4.** Limits use of rotating equipment, such as compressors and pumps, that require more frequent repair
- 5.** Requires small temperature changes to operate
- 6.** Recovers salts in salable form(s)

Example. Multiple effect membrane evaporation concentrators and crystallizers with mechanical vapor compression

Based on the thermodynamic efficiency of multi-effect and MVC systems for brine concentrations, a multi-effect membrane evaporation system with permeate vapor compression and condensation is considered here as an example brine concentration/crystallization process. The membrane unit could utilize either a porous membrane (i.e. VMD) or a non-porous membrane (i.e. PV). An example flow diagram for a two-effect membrane evaporation MVC (ME-MVC) system is shown in Figure 16. In this example, the permeate water vapor from a membrane evaporation unit in one effect is compressed and condensed in heat exchange with the saline solution in that same effect. An alternative design would be to condense the vapor from one effect in heat exchange with a subsequent lower temperature effect, this would reduce the compression ratio required, although another heat source would be required to provide the heat for the first effect.

The ME-MVC system would be used to concentrate brine from an RO system and be designed to allow for the precipitation of solids. One potential design for the ME unit would be similar to that of membrane bioreactors (MBRs). In MBRs, porous membrane fibers, tubes, or sheets are immersed in the bioreactor suspension and a vacuum is applied on the other side of the membrane to draw water through the membrane, leaving biosolids behind.⁵⁷ The biosolids are removed from the membrane surface by agitation and/or back-pulsing the filtrate.^{57–59} The agitation could involve mechanically moving the membrane or by scouring the membrane with a gas or with particles in a liquid recirculation. In an ME system, the membrane only allows vapor to pass through the membrane and, therefore, does not allow liquid back-pulsing although gas back-pulsing is possible in VMD. However, all other mechanical means of removing surface solids currently used in MBRs are available in an ME system. Operation of a VMD system of this nature, but without the MVC component, was recently reported by Julian *et al.*⁶⁰ In that study, neither vibration nor aeration of the MD hollow fibers were particularly effective at reducing the steep decline in flux due to crystal formation and blockage of the membrane pores. Thermal treatment of the solution to initiate crystallization was reported to delay the onset of flux decline, suggesting that crystal nucleation methods that do not involve the membrane surface could be beneficial. Crystal nucleation methods, including power ultrasound-assisted crystallization (“sonocrystallization”), might allow for controlled nucleation.^{61, 62} If a PV unit was used for evaporation, the non-porous coating on the PV membrane could be selected such that salt precipitates do not adhere or are easy to remove. Similarly, modification of the surface of MD membrane might be able to reduce crystal attachment or nucleation.

As noted earlier, the driving force for water transport across the membrane in membrane distillation and pervaporation desalination processes is the vapor pressure. As illustrated in Figure 15, the vapor pressure declines modestly with increasing salt concentration. The effect of both temperature and salt concentration on the vapor pressure of NaCl solutions is shown in Figure 17. Clearly, temperature has a much larger effect on vapor pressure than does NaCl concentration. In order to condense the water vapor generated by a salt solution at the same temperature as the salt solution, it must be compressed to a higher pressure.

Because the condensation takes place in a heat exchanger, the condensation temperature must be at a temperature above that of the brine being heated to generate a temperature gradient between the hot condensing side and the cooler brine side of the heat exchange surface. The higher the temperature gradient, the less heat exchanger area that is required and the lower heat exchanger cost contribution to CAPEX. However, the higher temperature gradient is achieved with a higher compression ratio and compressor OPEX and CAPEX. Thus, there will be a tradeoff between compressor costs and heat exchanger costs.

The compressor work ($\dot{W}_{comp}$), in W, required to raise the pressure of a gas stream from p_{in} to p_{out} is:⁶³

$$\dot{W}_{comp} = \frac{z k \dot{N} R T_{in}}{\eta_{comp}(k-1)} \left[\left(\frac{p_{out}}{p_{in}} \right)^{\left(\frac{k-1}{k} \right)} - 1 \right] \quad (18)$$

Where $\dot{N}$ is the molar flow rate (mol/s), T_{in} is the temperature of the inlet vapor, η_{comp} is the adiabatic compressor efficiency, z is the compressibility factor (assumed to be 0.99), and k is the ratio of specific heat of the feed vapor at constant pressure to that at constant volume. For water vapor at 80 to 100 °C, k is about 1.31. The temperature of the compressed vapor (T_{out}) is higher than the inlet vapor temperature due to adiabatic compression and becomes superheated due to compression inefficiencies. The discharge temperature is calculated as:⁶³

$$T_{out} = T_{in} \left(1 + \frac{1}{\eta_{comp}} \left[\left(\frac{p_{out}}{p_{in}} \right)^{\left(\frac{k-1}{k} \right)} - 1 \right] \right) \quad (19)$$

Fortunately, this superheat is recovered in the heat exchange process, although it is not an efficient means of generating heat.

According to Equation 18, the compressor work is a function of the pressure ratio, referred to as the compression ratio, and not directly of each pressure alone. As a result, for the same work, and therefore same pressure ratio, a higher inlet pressure will yield a larger pressure difference (i.e. larger($p_{out} - p_{in}$)). The least work is required by operating at the highest possible pressure when: 1) the inlet pressure has to be below the vapor pressure of the brine in order to create the vapor pressure driving force for membrane transport or 2) when the outlet pressure has to be higher than the vapor pressure of pure water at the temperature of the brine in order to provide a temperature gradient for heat transfer in the vapor condenser. Since both of these conditions are encountered in a ME-MVC system, the lowest compressor work will be required at the highest inlet pressure, which corresponds to the highest possible solution temperature.

The transport of water through the non-porous PV membrane or the porous MD membrane is described by the following expression:

$$\dot{N}_w = A j_w = A \pi_w (p_w^{Feed} - p_w^{Perm}) \quad (20)$$

Where $\dot{N}_w$ (mol/s) is the rate of water vapor transported through membrane area A (m²), j_w is the molar flux of water through the membrane (mol/m²·s), π_w is the permeance of water in the non-porous membrane or the membrane distillation coefficient (mol/m²·s·Pa), and p_w^{Feed} and p_w^{Perm} (Pa) are the partial pressures of water on the feed-side and permeate-side of the membrane, respectively. The difference in the pressures is the membrane water partial pressure driving force. The partial pressure of water on the feed-side of the membrane is calculated as the vapor pressure of water in the saline solution in contact with the membrane. Assuming no permeate-side pressure drop, the inlet pressure of the compressor is equal to the permeate pressure (i.e. $p_{in} \approx p_w^{Perm}$). As noted above, the required outlet pressure of the compressor is dictated by the temperature of condensation required to drive heat transfer, which, in turn, is dictated, by the temperature of the feed-side saline solution, which, in turn, dictates the vapor pressure of water. The membrane area and, therefore, membrane CAPEX, are directly related to the water flux through the membrane. According to Equation 20, for a fixed water vapor flow rate, membrane area and, thus, membrane cost, is minimized when the permeance and/or the partial pressure difference are maximized. Consequently, as with the heat exchangers, there is a trade-off between compressor size and membrane area.

The effect of the membrane water partial pressure driving force and the condenser heat exchanger temperature gradient on the compressor energy per unit water vapor processed is shown in Figure 18 for NaCl-saturated solutions at 50 and 80 °C. These are theoretical calculations based on the equations presented here and the effect of temperature and salt concentration on water vapor pressure from Clarke and Glew.⁶⁴ In the extreme case where both the partial pressure driving force and temperature gradient are zero, the compressor energy is a minimum, 55.3 and 62.4 kJ/kg for 50 and 80 °C, respectively. This difference in the idealized compressor work at the two temperatures is due to the difference in salt solubility (26.8 vs. 27.46 wt.%) and the difference in the vapor pressure relationship with temperature and salt concentration at the two temperatures. As the water partial pressure driving force is increased, the compressor energy required at 50 °C increases more rapidly than does that at 80 °C and surpasses it at low driving forces, below 1 kPa. Thus, operation at the higher temperature is favored for all but the lowest water vapor pressure driving force. Increasing the heat exchanger temperature gradient does increase the compressor work, but not as significantly as the vapor pressure driving force, at least up to a ΔT of 5 °C.

The vapor pressure of NaCl-saturated water at 50 °C is only 9.3 kPa, limiting the maximum possible driving force for water transport to below this value. By contrast, the vapor pressure of NaCl-saturated water at 80 °C is 35.2 kPa, almost four times greater than at 50 °C. Thus, higher operating temperatures result in lower compressor work and greater potential water vapor pressure driving forces, but might require higher cost materials of construction (i.e. metals instead of plastics) and might require a higher value source of auxiliary heat.

A Multiple Effect ME-MVC system, operating at a maximum temperature of about 80 °C, would meet the first three desirable technology characteristics listed earlier: use of lower grade heat, plastic materials of construction, and able to handle precipitates. Due to the use of compressors, any MVC-type system goes against the fourth desirable characteristic of limiting rotating equipment. However, emerging compressor technologies, like the carbon fiber-based woven wheel technology^{65, 66}, promise to greatly reduce the CAPEX and OPEX usually associated with compressors, diminishing the importance of the fourth desirable characteristic. As a thermal process, the ME-MVC system cannot operate effectively at low temperatures, so it cannot meet the fifth desirable technology characteristic of small temperature changes, although it will be better than evaporative processes operating at temperature over 100 °C. Whether ME-MVC meets the sixth characteristic, recovery of salable salts, remains to be demonstrated although previous work on salt recovery from brines suggests it is possible.^{20–22, 48, 51, 53, 55, 67, 68} As a result, an ME-MVC system possesses many of the desired characteristics for a brine concentrate treatment technology, although several aspects require further development and demonstration. In particular, innovative membrane and system designs to prevent the deleterious effect of precipitate formation on or in the pores of the membrane are needed.

Conclusions

The recovery of water and salts from brine concentrate streams is challenging due to the reduction in separation driving force as salt concentration increases and due to the scaling, fouling, and corrosion issues associated with saturated saline solutions. Independent of the separation process considered, the energy required to perform the separation will increase as the salt concentration increases. Processes that rely on mechanical work to drive the separation, such as reverse osmosis and mechanical vapor compression, exhibit higher thermodynamic efficiencies than those reliant on thermal energy, such as distillation or flash evaporation. Unfortunately, the most efficient process for desalinating seawater, reverse osmosis, is currently constrained to sub-saturation salt concentrations due to the pressure limits of the commercially available membranes and modules. For near-saturation salt feed solutions, mechanical vapor compression, combining mechanical work with thermally-driven evaporation, has been predicted to have the highest second law efficiency, even higher than a hypothetical two-stage reverse osmosis process. This paradigm of combining a work-driven process with a thermally-driven process was further illustrated with a discussion of Membrane Evaporation-Mechanical Vapor Compression systems. Due to the added capital and operating costs associated with the separation of brine concentrate streams, brine disposal may continue to be chosen unless location-specific conditions/constraints favor additional water recovery or zero liquid discharge.

Nomenclature

AGMD	Air gap membrane distillation
CAPEX	Capital expenses
DCMD	Direct contact membrane distillation

ED	Electrodialysis
EDR	Electrodialysis reversal
FO	Forward osmosis
HDH	Humidification-dehumidification
HHV	Higher heating value
MBR	Membrane bioreactor
MD	Membrane distillation
MDC	Membrane distillation crystallizer
MED	Multiple effect distillation
ME-MVC	Membrane evaporation mechanical vapor compression
MSF	Multi-stage flash
MSF-OT	Once-through multi-stage flash
MVC	Mechanical vapor compression
OPEX	Operating expenses
PGMD	Permeate gap membrane distillation
PV	Pervaporation
RO	Reverse osmosis
SWRO	Seawater reverse osmosis
TFC	Thin film composite
VMD	Vacuum membrane distillation
ZLD	Zero liquid discharge
a_i	activity of compound i
A	membrane area, m ²
Δg_{mix}^*	Gibbs Free Energy of mixing, J/mol
h_{mix}	heat of mixing, J/mol
h	enthalpy of a stream, J/mol
j	molar flux through membrane, mol/m ² ·s
k	ratio of constant pressure to constant volume specific heats of a gas
LW	lost work, J/mol

$\dot{N}$	total molar flow rate of species in a stream, mol/s
p	pressure of stream or of component of a stream, Pa
p_W^{sat}	saturated vapor pressure of water at system temperature, Pa
p_W^x	vapor pressure of water in salt solution at system temperature, Pa
q	heat of separation, J/mol
$\dot{Q}$	rate heat supplied or removed, J/s
R	gas constant, 8.314 J/mol·K
s_{mix}	entropy of mixing, J/mol·K
s	entropy of a stream, J/mol·K
T	temperature of system or stream, K
T	temperature gradient, K
T	temperature, K
V	molar volume of water, m ³ /mol
w	work per mole, J/mol
$\dot{W}$	rate work performed, J/s or W
x_i	mole fraction of component i
x_{ij}	mole fraction of component i in stream j
Y	recovery
z	compressibility factor
γ_i	activity coefficient of component i
η	efficiency
π	permeance in non-porous membrane or MD coefficient, mol/m ² ·s·Pa
Π	osmotic pressure of stream, Pa
ϕ	salt dissociation factor
0	Surroundings or ambient
A	generic compound A
B	generic compound B
$comp$	compression or compressor

<i>i</i>	component identifier
<i>in</i>	inlet stream or flow of energy
<i>f</i>	feed stream
<i>min</i>	minimum
<i>out</i>	outlet stream or flow of energy
<i>p</i>	permeate or product stream
<i>r</i>	reject stream
<i>s</i>	source or sink of heat
<i>S</i>	mole fraction of NaCl in the salt solution
+	Na ⁺ ions
–	Cl [–] ions
<i>W</i> _±	water in ionic solution
<i>W</i>	water
Feed	Feed stream
Perm	Permeate stream

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Figure 1.

Reverse osmosis desalination process flow diagram with energy recovery.

Figure 2.
Multi-Stage Flash (MSF) desalination process flow diagram with three stages.

Figure 3.
Multiple Effect Distillation (MED) desalination process flow diagram.

Figure 4. Mechanical Vapor Compression (MVC) desalination process flow diagram with one evaporation stage.

Figure 5.
Electrodialysis (ED) desalination process flow diagram.

Figure 6.
Forward Osmosis (FO) desalination process flow diagram.

Figure 7.
Direct Contact Membrane Distillation (DCMD) desalination process flow diagram.

Figure 8.
Pervaporation (PV) desalination process flow diagram.

Figure 9.
Humidification-Dehumidification (HDH) desalination process flow diagram.

Figure 10.
Theoretical separation of a binary mixture into: a) two pure streams and b) two impure product streams.

Figure 11. Minimum work required to separate an ideal mixture of “A” and “B” into pure product streams at 25 °C according to Equation 3 per mole of the total mixture and per mole of compound “A.”

Figure 12.

Effect of NaCl concentration in the feed streams on the minimum work required at 25 °C to produce water as further functions of the brine reject stream concentration.

Figure 13.
Same as Figure 12, except at 80 °C.

Figure 14.

Energy Consumption calculated for various desalination technologies with feed of 15 wt.% NaCl and brine reject of 26 wt.% NaCl (adapted from Thiel *et al.*¹¹).

Figure 15. Effect of salinity on the osmotic pressure and vapor pressure of seawater^{33–35}

Osmotic pressure is shown with units of bar to be on the same scale as vapor pressure with units of kPa (1 bar = 100 kPa).

Figure 16. Two-effect membrane evaporation-mechanical vapor compression (ME-MVC) desalination process flow diagram.

Figure 17.
Effect of temperature and NaCl concentration on the vapor pressure of water (based on values from Clarke and Glew⁶⁴).

Figure 18.

Effect of the water partial pressure driving force across the membrane and the condenser heat exchanger temperature gradient on the compressor energy per unit water vapor processed for saturated NaCl solutions at 50 and 80 °C (26.80 and 27.46 wt.%) assuming an 80% compressor efficiency.

Table 1

Second Law Efficiencies for several desalination processes operating on seawater listed in order of decreasing efficiency.³⁰

Desalination Process	Second Law Efficiency, η_{II} (%)
Reverse Osmosis (RO)	31.9
Mechanical Vapor Compression (MVC)	8.5
Multi-Effect Distillation (MED)	5.9
Multi-stage Flash (MSF)	2.9
Humidification-Dehumidification (HDH)	2.4
Direct Contact Membrane Distillation (DCMD)	1.0

Table 2

Second Law Efficiencies for several desalination processes operating on a near-saturated feed (25 wt.% NaCl) listed in order of decreasing efficiency.¹¹

Desalination Process	Second Law Efficiency, η_{II} (%)
Mechanical Vapor Compression, 2-stage (MVC-2stage)	43.1
Mechanical Vapor Compression, 1-stage (MVC-1stage)	38.3
Reverse Osmosis, 2-stage (RO-2stage)	37.6
Multi-Effect Distillation, 3-effect (MED)	19.8
Humidification-Dehumidification (HDH)	18.4
Permeate Gap Membrane Distillation (PGMD)	14.8
Forward Osmosis (FO)	6.6