Desalination of brines produced from the geologic storage of carbon dioxide

August 2016
Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference therein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed therein do not necessarily state or reflect those of the United States Government or any agency thereof.

Cover Illustration: Schematic illustrating geologic carbon dioxide storage operations. Please note the geology is not to scale.

Suggested Citation: J.T. Arena; J.C. Jain; C.L. Lopano; J.A. Hakala; N.S. Siefert. Desalination of brines produced from the geologic storage of carbon dioxide; NETL-PUB-20717; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: City, ST, 2016.

An electronic version of this report can be found at: http://www.netl.doe.gov/research/on-site-research/publications/featured-technical-reports

An electronic version of this report has been uploaded to the Office of Science, Technology, and Industry website at: http://www.osti.gov/bridge.
Desalination of brines produced from the geologic storage of carbon dioxide

Jason T. Arena¹,², Jinesh C. Jain¹,³, Christina L. Lopano¹, J. Alexandra Hakala¹, Nicholas S. Siefert¹,*

¹National Energy Technology Laboratory U.S. DOE, Pittsburgh, PA
²Oak Ridge Institute for Science and Education (ORISE), Pittsburgh, PA
³AECOM Corporation, Pittsburgh, PA

NETL-PUB-20717

August 2016

NETL Contacts:
Nicholas S. Siefert, Principal Investigator & Task Portfolio Lead for Water-Energy Nexus

nicholas.siefert@netl.doe.gov
This page intentionally left blank.
# Table of Contents

Disclaimer ..................................................................................................................... 2  
Table of Contents ........................................................................................................... I  
List of Figures ............................................................................................................. III  
List of Tables .............................................................................................................. III  
Acroynms, Abbreviations, and Symbols .................................................................... IV  
Acknowledgments....................................................................................................... VI  
Executive Summary ...................................................................................................... 1  
1. Introduction .............................................................................................................. 5  
1.1. Risks and risk management associated with GCS ............................................. 6  
2. Brine Composition ................................................................................................. 7  
2.1. U.S. sources of high TDS brines associated with GCS ................................... 7  
3. Thermodynamics of brine desalination ................................................................. 9  
4. Dewatering/desalination technology .......................................................... 14  
4.1. Evaporative processes .................................................................................... 14  
4.1.1. Multi-effect distillation ........................................................................... 15  
4.1.2. Multi-stage flash distillation ................................................................ 15  
4.1.3. Vapor compression distillation ............................................................ 16  
4.2. Membrane processes and technology ........................................................... 17  
4.2.1. Hydraulic pressure driven membrane separations ................................... 18  
4.2.2. Vapor pressure driven membrane separations ........................................... 19  
4.2.3. Osmotic pressure driven membrane separations ....................................... 20  
4.2.4. Electrochemical membrane separations .................................................... 21  
4.3. Hybrid processes ............................................................................................ 22  
4.3.1. Combined separation processes .............................................................. 22  
4.3.1.1. Multi effect distillation-mechanical vapor compression .................... 22  
4.3.1.2. Forward osmosis with draw solution REGeneration ......................... 23  
4.3.2. Combined driving force processes .......................................................... 25  
4.3.2.1. Assisted forward osmosis ................................................................. 25  
4.3.2.2. Osmotically assisted reverse osmosis .................................................. 25  
4.3.2.2.1. Transport in OARO ...................................................................... 25  
4.3.2.2.2. OARO process description .......................................................... 28
4.3.2.2.3. Differences between OARO and thermolytic FO ....................................................... 28
4.4. Concentrate management ........................................................................................... 29
4.4.1. Reinjection ................................................................................................................. 30
4.4.2. Evaporation ponds .................................................................................................. 30
4.4.3. Crystallizers ............................................................................................................. 30
5. Conclusions .................................................................................................................. 31
6. References .................................................................................................................... 31
List of Figures

Figure 1. Schematic illustrating GCS operations. ................................................................. 7

Figure 2. a) Composition of four brines produced from GCS-relevant formations. b) Geographic location of the four brines produced from GCS-relevant formations, adapted from Michael et al. (2010). ...................................................................................... 8

Figure 3. Composition of four brines produced from GCS-relevant formations, grouped by ionic component. ................................................................................................................................. 9

Figure 5. Boiling point temperatures of sodium chloride solutions calculated assuming an ideal solution or from osmotic coefficients compiled by Hamer and Wu (1972). ............ 10

Figure 6. Osmotic pressures of sodium chloride solutions calculated either assuming an ideal solution or using osmotic coefficients compiled by Hamer and Wu (1972) at 25°C. .... 11

Figure 7. Minimum work required to produce 1 m³ of pure water as a function of the water recovery fraction for five different inlet sodium chloride concentrations (\(\dot{w}_\text{min}/\dot{v}_p\)). ... 12

Figure 8. Minimum work required to produce a m³ of pure water (\(\dot{w}_\text{min}/\dot{v}_p\)), minimum work of dewatering per m³ of inlet brine (\(\dot{w}_\text{min}/\dot{v}_b\)), remaining brine concentration, and solid weight fraction for a 2 mol/L sodium chloride solution as a function of the water recovery fraction. ........................................ 13

Figure 9. Principle of the MED process. ........................................................................... 15

Figure 10. Principle of the MSF process. ......................................................................... 16

Figure 11. Principle of a) mechanical vapor compression and b) thermal vapor compression distillation processes. ........................................................................................................... 17

Figure 12. Streams common to a membrane separation. .................................................. 19

Figure 13. Streams common to a FO process. ................................................................. 21

Figure 14. Principle of an electrodialysis process. ......................................................... 22

Figure 14. Multi effect distillation‒mechanical vapor compression hybrid operating principle. .............................................................................................................................. 23

Figure 15. Flow diagram of a thermolytic FO brine concentrator using a draw soltion of ammonia and carbon dioxide. ................................................................. 24

Figure 16. Streams of an OARO process. ....................................................................... 25

Figure 17. Simulated flux from an osmotically assisted reverse osmosis process using Hydration Technology Innovations woven supported cellulose triacetate forward osmosis membrane. .................................................... 27

Figure 18. Principle of an osmotically assisted reverse osmosis process. ...................... 28

List of Tables

Table 1. Transport parameters for a woven supported cellulose triacetate membrane (She et al. 2012) ................................................................. 27
## Acronyms, Abbreviations, and Symbols

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFO</td>
<td>Assisted forward osmosis</td>
</tr>
<tr>
<td>ED</td>
<td>Electrodialysis</td>
</tr>
<tr>
<td>GCS</td>
<td>Geologic carbon dioxide storage</td>
</tr>
<tr>
<td>FO</td>
<td>Forward osmosis</td>
</tr>
<tr>
<td>MED</td>
<td>Multi effect distillation</td>
</tr>
<tr>
<td>MED-MVC</td>
<td>Multi effect distillation with mechanical vapor compression</td>
</tr>
<tr>
<td>MD</td>
<td>Membrane distillation</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>MSF</td>
<td>Multi stage flash distillation</td>
</tr>
<tr>
<td>MVC</td>
<td>Mechanical vapor compression</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>OARO</td>
<td>Osmotically assisted reverse osmosis</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>TVC</td>
<td>Thermal vapor compression</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids, $\frac{g}{L}$</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>$a_w$</td>
<td>Activity of water</td>
</tr>
<tr>
<td>$c_{f,b}$</td>
<td>Feed molar concentration in the bulk, $\frac{mol}{L}$</td>
</tr>
<tr>
<td>$c_{f,m}$</td>
<td>Feed molar concentration at the membrane, $\frac{mol}{L}$</td>
</tr>
<tr>
<td>$c_i$</td>
<td>Molar concentration of component i, $\frac{mol}{L}$</td>
</tr>
<tr>
<td>$c_{s,b}$</td>
<td>Sweep molar concentration in the bulk, $\frac{mol}{L}$</td>
</tr>
<tr>
<td>$c_{s,m}$</td>
<td>Seep molar concentration at the membrane, $\frac{mol}{L}$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Permeate molar concentration, $\frac{\text{mol}}{\text{L}}$</td>
</tr>
<tr>
<td>$m_i$</td>
<td>Molal concentration of component $i$, $\frac{\text{mol}}{\text{kg}}$</td>
</tr>
<tr>
<td>$p_w$</td>
<td>Vapor pressure of water, bar</td>
</tr>
<tr>
<td>$p_{\text{solution}}$</td>
<td>Vapor pressure of solution, bar</td>
</tr>
<tr>
<td>$v_w$</td>
<td>Molar volume of water, $\frac{\text{L}}{\text{mol}}$, @ 25°C</td>
</tr>
<tr>
<td>$A$</td>
<td>Water permeance of a membrane, $\frac{\text{L}}{\text{m}^2 \cdot \text{h} \cdot \text{bar}}$</td>
</tr>
<tr>
<td>$B$</td>
<td>Solute permeability of a membrane, $\frac{\text{L}}{\text{m}^2 \cdot \text{h}}$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient of solute in water, $\frac{\text{m}^2}{\text{s}}$</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Molecular weight of water, 18.02 $\frac{\text{g}}{\text{mol}}$</td>
</tr>
<tr>
<td>$P_f$</td>
<td>Feed hydraulic pressure, bar</td>
</tr>
<tr>
<td>$P_s$</td>
<td>Sweep hydraulic pressure, bar</td>
</tr>
<tr>
<td>$R$</td>
<td>Ideal gas constant, 0.08314 $\frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}}$</td>
</tr>
<tr>
<td>$S$</td>
<td>Structural Parameter, m</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute Temperature, K</td>
</tr>
<tr>
<td>$\dot{w}_{\text{min}}/\dot{v}_p$</td>
<td>Minimum work of separation per volume of produced water, $\frac{\text{kWh}}{\text{m}^3}$</td>
</tr>
<tr>
<td>$\dot{w}_{\text{min}}/\dot{v}_b$</td>
<td>Minimum work of dewatering per volume of original brine, $\frac{\text{kWh}}{\text{m}^3}$</td>
</tr>
<tr>
<td>$\delta_f$</td>
<td>Feed external boundary layer thickness, m</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Conversion factor, $3.6 \cdot 10^6 \frac{\text{L} \cdot \text{s}}{\text{m}^3 \cdot \text{h}}$</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Osmotic coefficient</td>
</tr>
<tr>
<td>$\pi$</td>
<td>Osmotic pressure, bar</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of Water, 0.9970 $\frac{\text{kg}}{\text{L}}$, @ 25°C</td>
</tr>
</tbody>
</table>
Acknowledgments

This work was completed as part of National Energy Technology Laboratory (NETL) research for the U.S. Department of Energy’s (DOE) Fossil Energy (FE) program. Support for Jason Arena was provided by an appointment to the National Energy Technology Laboratory Research Participation Program, sponsored by the U.S. Department of Energy and administered by the Oak Ridge Institute for Science and Education.
EXECUTIVE SUMMARY

Geologic carbon dioxide sequestration (GCS) will play a crucial role in limiting anthropogenic greenhouse gas emissions. GCS is the practice of capturing carbon dioxide (CO₂) from industrial sources and storing it in subsurface geologic formations, such as saline formations. These saline formations are typified by a porous interconnected rock strata, saturated with saline brine at a depth of >800 m. Because of the large volumes available, storage of CO₂ into deep saline formations with caprock seals and far from exiting faults will be key for long term reductions of anthropogenic CO₂ emissions. The high pressure injection of CO₂ into the subsurface can cause an increase in subsurface pressure. Open and highly porous formations can have CO₂ injected without causing a significant rise in formation pressure; however, closed or low porosity formations are more sensitive to the subsurface injection of CO₂ with regard to subsurface pressure. Such formations would ideally be located near existing fossil fuel power plants or other industrial emitters of CO₂ who would require GCS. In order to reduce the risk of induced seismic activity near minor fault structures, formation pressure management is needed. This will require the extraction of brines from the formation and these brines could be extracted prior to or during GCS. This extraction will maintain or reduce the subsurface pressure and enhance CO₂ storage capacity. The extracted brine can be dewatered/desalinated, becoming both a source of usable water and a concentrated brine which could be either reinjected into a nearby formation, crystallized, or discharged into an evaporation pond. The Department of Energy Office of Fossil Energy’s commitment to studying formation pressure management in GCS has been demonstrated with the recent awarding of $30,000,000 for two Brine Extraction Storage Test (BEST) projects, whose main goal is to develop and validate strategies for managing formation pressure through brine (Martin 2016). A secondary goal of these projects is to develop and demonstrate processes to extract usable water from these high salinity produced brines.

BRINE COMPOSITION AND DEWATERING

GCS produced brines can have large variations in total dissolved solids (TDS). A quantitative evaluation of four GCS-relevant brines, showed that GCS produced brines can have a TDS between 100 g/L and 250 g/L. This salinity is significantly higher than sea water (35 g/L), for which most desalination technologies have been developed and optimized. For example, in conventional reverse osmosis (RO), the maximum concentration of a solution that can be dewatered at 50% water recovery (i.e. a reduction in brine volume of 50%) is about 45 g/L TDS. This limitation will impede the application of conventional RO for a significant volume reduction of high salinity produced brines, leaving evaporative processes as the only commercially available means by which a produced brine can be dewatered.

A constraint in the selection of a process to economically dewater GCS produced brines is that extraction wells could be 5‒50 km from the power plant generating the CO₂ needing sequestration. This means that while electricity could cost-effectively be transported from the power plant to dewater the brine, this distance is such that high quality steam cannot be cost-effectively transported from the power plant to the well where the GCS brines are extracted. In addition, because the goal of GCS is to significantly reduce the greenhouse gases emissions, combusting fossil fuels like natural gas to provide the thermal energy for dewatering/desalination of the brine is counter-productive. As such, thermal evaporation technologies are likely not applicable unless the brine can be cost effectively transported to/from the power plant. While it appears that process
that rely on electricity (MVC, OARO) and/or that rely on the elevated temperature of these brines
(MD) will be more applicable to this application, for completeness we reviewed those process that
rely only on electricity, those process that rely mainly on thermal input, and those processes that
rely on both electricity and thermal input.

EVAPORATIVE PROCESSES AND TECHNOLOGY

Evaporative processes mimic the natural water cycle by evaporating water from a brine,
separating the steam, and condensing the water vapor to recover pure water. Characteristically,
evaporative processes consist of 1) a source of useful work, such as an external heat source and/or
electricity, 2) heat exchangers for the heating/evaporation of seawater, 3) a condenser for water
vapor, and 4) a collector for the condensate. A number of evaporative processes have been
commercialized, including multi effect distillation (MED), multi stage flash distillation (MSF),
and mechanical vapor compression (MVC). The primary drawback of all evaporative processes is
water’s large heat of vaporization, 40.7 kJ/mol\textsubscript{H2O} at 100°C (Smith et al. 2005, Semiat 2008). While
much of the heat of vaporization is recovered during condensation, there is significant
irreversibility from the temperature gradient between the hot and cold sides of a heat exchanger.
Irreversibility associated with the large transfer of thermal energy across a temperature gradient
means the typical efficiency of evaporative processes is around 10% or less (Nafey et al. 2008,
Mistry et al. 2011). Here, efficiency is defined as the minimal amount of useful work required for
a reversible process divided by the actual amount of useful work consumed in the process. Many
evaporative processes are designed to use steam as a source of useful work, but as stated
previously, steam may not be available near sources of produced brines.

When only electricity is available as the source of useful work to dewater the produced brines,
the current standard in high salinity brine dewatering is mechanical vapor compression (MVC).
MVC uses a compressor to extract and pressurize steam from a brine within an evaporator. The
extracted steam is condensed to pure water via heat exchange with the incoming brine. A drawback
to MVC is its low efficiency (<10%). The low efficiency is mostly due to the irreversibility from
temperature gradients across the heat exchangers. At 10% efficiency, the power consumption to
dewater a 120 g/L brine can be substantial at 50% water recovery and quite large at 100% water
recovery. For example, at 50% water recovery, the minimum work of dewatering is 2.0 kWh per
m\textsuperscript{3} of original brine and, at 100% water recovery and generation of crystal salt, the minimum work
of dewatering is 6.6 kWh per m\textsuperscript{3} of original brine. So, at 10% efficiency, these numbers convert
to 20 kWh and 66 kWh per m\textsuperscript{3} of original brine. To put these numbers in perspective, the NETL
baseline for coal-fired power plants producing around 550 MW of net power will need to capture
around 600,000 kg/h of CO\textsubscript{2} (Black 2013). Assuming that the amount of produced saline brine is
equal to 50% of the volume of the sequestered supercritical CO\textsubscript{2}, then the actual power
consumption of a 10% efficiency process would be 7.5 MW (1%) for a 50% water recovery process
and 25 MW (4.5%) for a 100% water recovery process that generates pure water and crystal salt.
Therefore, one can see that, in order to minimize the energy penalty on the power plant, one should
design a process with an efficiency >10% and avoid generating crystal salt, unless there is an
economic driving force for generating the crystal salt. Since membrane processes that rely on high
pressure pumps typically have efficiencies closer to 30%, membrane processes could significantly
reduce the amount of power consumed compared with evaporative processes, such as MVC.
MEMBRANE PROCESSES AND TECHNOLOGY

Membranes are discrete barriers that allow for the selective permeation of chemical species (Shirazi et al. 2010). A number of membrane processes have been developed that can be used to dewater a solution and could be categorized by the driving forces for water flow across the membrane be they osmotic pressure, vapor pressure, voltage, and/or hydraulic pressure. Osmotic pressure driven processes, elsewhere referred to as forward osmosis, osmotically driven membrane processes, or engineered osmosis, are processes that use the natural osmosis phenomena as a means of dilution/concentration for two solutions separated by a membrane. Vapor pressure processes, like membrane distillation and pervaporation, could dewater solutions having high TDS but have not yet seen large scale adoption. Voltage driven electrochemical separations like electrodialysis are efficient for deionizing brackish water that has a salinity up to ~5 g/L but suffers from increase voltage and current usage at higher salinities. Hydraulic pressure driven processes rely on the hydraulic pressure of a solution or suspension to drive water flow across a membrane. These processes are classified by the size of a dissolved or suspended solutes they remove, including microfiltration, ultrafiltration, nanofiltration and reverse osmosis (RO). Of these, only reverse osmosis is capable of dewatering brine having dissolved salts which dissociate into two monovalent ions. Examples of these would be salt having cations of sodium, potassium, or ammonium and anions of chloride, bromide, nitrate, or bicarbonate.

Due to the aforementioned concentration limitations of RO, with respect to water recovery, special emphasis will be given in this report to a new membrane process that expands the operating conditions for RO so it can dewater high concentration solutions of sodium chloride. This technology, called osmotically assisted reverse osmosis (OARO) or cascade RO, is being developed to expand the allowable operating conditions for reverse osmosis processes for dewatering high salinity brines (Wohlert 2012). OARO operates by the serial dilution of a saline sweep solution. This sweep solution has a salinity lower than the brine and is diluted from brine being dewatered by reverse osmosis. The sweep solution is on the permeate side of a membrane and flows counter-current to the produced brine with a near constant concentration gradient between the feed and sweep solutions. The diluted sweep solution can then be dewatered in subsequent OARO stages and returned to its initial concentration. A complete process will have a sufficient number of OARO stages to dilute the sweep solution until it can be desalinated by a final RO stage. Discussion of the OARO process in this report will highlight where future research at NETL can strive to significantly reduce the electricity consumed when generating usable water from the high salinity brines produced during GCS.

CONCLUSIONS

A number of factors are discussed in this report, many commercially-available dewatering processes are not applicable to GCS brines. For example, RO and ED are best suited to salinities less than seawater. Also, MSF, MED, and thermolytic FO require steam or low grade thermal energy to be the source of useful work to dewater a brine, and thermal energy will likely not be available near either the brine extraction well or brine injection well. Electricity from the power plant will be the only likely source of useful work to dewater the brine, and electricity consumption to dewater the brine will ultimately be subtracted from the electricity generated at the power plant. This subtraction is also crucial when calculating key environmental parameters, such as kg CO₂ emitted per kWh of net electricity generated.
When electricity is the only available source of useful work to dewater the produced brines, the current standard in high salinity brine dewatering is mechanical vapor compression (MVC). A drawback to MVC is low efficiency (<10%), meaning 10 times the minimum electrical work to desalinate the brine is needed. This parasitic power loss could be decreased the development and deployment of more efficient advanced membrane processes, such as the novel OARO process. The novelty of the OARO process requires further development to identify optimal membranes and perform a detailed economic analysis of an OARO process to compare against an MVC process concentrating a brine of identical salinity.

Finally, it should be pointed out that these produced brines will likely still be at elevated temperatures (30°C – 75°C) at the surface, and there is the potential to decrease the amount of electricity consumed during brine-water separation by taking advantage of this elevated temperature compared with the temperature of the environment. This appears to be another area for future research & develop.
1. **INTRODUCTION**

To continue using abundant, energy-dense fossil fuels while simultaneously preventing increased greenhouse gas emissions, primarily carbon dioxide (CO₂), there will need to be widespread adoption of CO₂ capture and geologic CO₂ storage (GCS). CO₂ capture and GCS consists of separating CO₂ from industrial/electrical power generation gas streams, compressing the CO₂, transporting the CO₂, and disposing the compressed CO₂ into a selected subsurface storage formation (IPCC 2005, Pires et al. 2011). The formations available for GCS are divided into various categories, including offshore/onshore saline formations, depleted oil and gas wells, and unmineable coal seams (IPCC 2005, Gibson-Poole et al. 2006, Bachu et al. 2007). At minimum, CO₂ stored as part of GCS should not be at risk of significant release or escape in the next century, and ideally be stored for longer geologic time scales (Holloway 2005, Varre et al. 2015). The mechanisms for long term storage and ultimate geochemical fate of CO₂ depends on the reservoir temperature, pressure, brine salinity, rock mineralogy, fluid injection rates, and time-scale of geological storage (Holloway 2005, Bachu et al. 2007, Gaus 2010, Lemieux 2011). One crucial target for GCS is the depth of the reservoir and the state of CO₂ within the reservoir following injection. At shallow depths (<800 m), CO₂ exists in the gas phase. This is considered unfeasible for GCS because of the low density of gaseous CO₂. Ideally, a storage formation for GCS would be at a depth where CO₂ exists in a supercritical state, in which CO₂ still expands to fill all available volume but has a “liquid” like density of 700 – 900 kg/m³ (Rochelle et al. 1999, Bachu 2000, Holloway 2005, Das et al. 2014). One exception to the need for CO₂ to be in the supercritical state exists for the case of CO₂ sequestration in unmineable coal seams. Here, CO₂ storage occurs by the preferential adsorption of CO₂ onto the surface of coal displacing adsorbed methane (Gunter et al. 1997, Gale 2004, Pashin 2016).

Of the potential formations for GCS, saline formations represent the overwhelming majority of GCS storage capacity (Gale 2004, Goodman et al. 2011, Potdar and Vishal 2016). Saline formations are subsurface formations whose available porosity is saturated by saline waters, and some of these formations could potentially store significant amounts of CO₂, making them primary sites for GCS. Optimistic estimates of CO₂ storage in saline formations suggest a total CO₂ storage capacity equivalent to at least several decades at current global CO₂ emission rates (Gale 2004, Damen et al. 2006, Potdar and Vishal 2016). The ideal saline formation for GCS would be sufficiently deep such that CO₂ injected within would be in a supercritical state, be highly permeable so as to minimize the number of injection wells needed, and be capped by a low permeability seal such as clay or shale (Holloway 1997, IPCC 2005, Birkholzer et al. 2009).

To minimize parasitic losses associated with CO₂ transportation, the storage formation should ideally be in close proximity to one or more CO₂ sources (i.e. power plants or other industrial sources) (IPCC 2005, Bachu 2008, Ettehadatavakkol 2016). If transportation is required to move the CO₂ from the source to the injection reservoir, the use of CO₂ pipeline is preferred to reduce parasitic losses. The required proximity of source to storage adds an additional facet to GCS site selection where not only geologic but also geographic considerations are needed to achieve maximum efficiency of a GCS operation.
1.1. **RISKS AND RISK MANAGEMENT ASSOCIATED WITH GCS**

Quantifying the risks associated with CO₂ injection into underground geologic formations has been an active focus area for studies on GCS (Damen et al. 2006, Michael et al. 2009, Pawar et al. 2013, Li and Liu 2016). In addition to the complexity of geochemical interactions between aqueous CO₂ moieties and supercritical CO₂ with the formation’s structure and mineralogy, a growing area of research in this field is the management of brine displacement and subsequent subsurface pressure build-up within both the storage formation and any overlying formations (IPCC 2005, Birkholzer and Zhou 2009, Gaus 2010, Buscheck et al. 2011, Cihan et al. 2015). Recently, the U.S. Department of Energy announced the winners of two $15,000,000 awards to study formation pressure management, plume movement, and brine extraction (Martin 2016). The rate of subsurface pressure accumulation will influence the rate of CO₂ injection, requiring a lower rate of injection, and possibly reduce a formation’s CO₂ capacity. Excess formation pressure can cause seismic events and/or drive CO₂ leakage through pre-existing wells into the formation, natural faults, or hydraulic fracturing of the formation seals (Varre et al. 2015, Lee et al. 2016). One mitigation strategy is to extract brine from a saline formation before and/or during CO₂ injection, reducing reservoir pressure and allowing for higher rates of CO₂ injection (Buscheck et al. 2011, IEAGHG 2012). The amount of brine produced from CO₂ injection is largely formation dependent. For example, when supercritical CO₂ is sequestered in porous, permeable, and/or open formations, the volume of produced brine is likely small compared with the volume of injected supercritical CO₂; however, in closed formations or in formations close to active faults, a significant amount of brine withdrawal will be required for pressure management (IPCC 2005, Bourcier et al. 2011, IEAGHG 2012). For example, the optimal volume of displaced brine was estimated to be between 30% and 60% of the volume of the injected supercritical in a deep sandstone formation near active faults (Cihan et al. 2015).

While brine extraction can be applied to formation pressure management, a dependent next step is the disposition of the produced brine. Typically, these brines are sufficiently saline such that they cannot be used for domestic, industrial or agricultural purposes (Bourcier et al. 2011, Veil et al. 2011). In the disposition of these brines, isolation from formations used for industrial, agricultural, and drinking water is paramount; therefore, disposal into surface waters is not a viable option (Birkholzer and Zhou 2009, Lemieux 2011). One possible solution is to dewater these brines, such that the brine, now having a higher concentration of dissolved solutes, can be reinjected with a net reduction in subsurface volume. The product water should be of sufficient quality that it could be used for industrial or agricultural purposes or discharged into surface waters (Aines et al. 2011, Bourcier et al. 2011). A schematic of a potential GCS operation is shown in Figure 1.
2. BRINE COMPOSITION

Saline formation waters can vary widely in their composition, but can have a total dissolved solids (TDS) ranging from 10–400 g/L (Blondes et al. 2016). The primary component of many of these saline formations water is sodium chloride, also the primary component of seawater. Additionally, in some saline formations a brine may contain significant concentrations of either calcium or sulfate (Aines et al. 2011). Sulfate salts having divalent cations, such as calcium, strontium, barium, and radium, are nearly insoluble in water. If divalent sulfate salts are present in a produced brine, they would be present at very low concentrations; however, if present, these salts do have propensity to form inorganic scale on the wetted surfaces of equipment that would be used to dewater them (El Din et al. 2002, Budhiraja and Fares 2008, Shirazi et al. 2010, Aines et al. 2011).

2.1. U.S. SOURCES OF HIGH TDS BRINES ASSOCIATED WITH GCS

Produced brines are typically highly variable in composition with brines produced from GCS being no exception (Blondes et al. 2016). A number of “pilot,” “demonstration,” and “commercial”
GCS operations have been undertaken at locations within the continental United States (Michael et al. 2010). The brine chemistry from four sandstone formations that are either a part of GCS operations or under consideration are used for comparison (Sass et al. 1998, Knauss et al. 2005, Dilmore et al. 2008, Lu et al. 2012). As shown in Figure 2 and Figure 3, the majority of ionic components are sodium, chloride, and calcium; however, as with other produced waters, there can be large variety in composition with some brines having significant quantities of magnesium, strontium, and/or sulfate. Also, these brines are quite saline, having salinities 3–6 times greater than seawater, which has approximately 35 g/L (0.6 mol/L) sodium chloride.

![Figure 2. a) Composition of four brines produced from GCS-relevant formations. b) Geographic location of the four brines produced from GCS-relevant formations, adapted from Michael et al. (2010). Data from Lu et al. (2012), Sass et al. (1998), Knauss et al. (2005), and Dilmore et al. (2008) for the Lower Tuscaloosa, Mt. Simon, Frio, and Oriskany formations respectively.](image-url)
3. THERMODYNAMICS OF BRINE DESALINATION

Dissolved solutes in an aqueous solution depress the activity of water. The activity of water is an intrinsic property of a solution, and the activity of water in a solution decreases with an increase in the concentration of dissolved, suspended or emulsified solutes. A solution having water activity less than one will have an increased boiling point temperature, via a reduction in the vapor pressure of water, and an osmotic pressure (Hamer and Wu 1972, Smith et al. 2005). By affecting the activity of water, dissolved solutes influence the amount of useful work that is required to extract pure water from it. In fact, the osmotic pressure of a solution is related to the Gibbs free energy of mixing or the minimum amount of useful work (kWh/m³) required to dewater a saline brine in the limit of zero water recovery (Elimelech and Phillip 2011, Mistry and Lienhard 2013). The water recovery is the quantity of water extracted from a solution, expressed as a fraction or percentage of the water in the permeate compared with the water in the initial brine (Bourcier et al. 2011, Mistry and Lienhard 2013). The minimum work required to dewater a brine is independent of the operating principles of the separation process (i.e. evaporative, membrane, electrochemical, etc.), and instead assumes perfect reversibility of a ‘black box’ process (Mistry et al. 2011, Mistry and Lienhard 2013). The minimum work of desalination increases with initial brine concentration because the increasing salinity of a brine causes both an increase in a solution’s boiling point (for evaporative processes) and osmotic pressure (for membrane process). The energy cost to dewater a brine is affected because an increased boiling point means that thermal energy of either a higher quality or quantity is required, and an increased osmotic pressure means that additional hydraulic pressure is needed to overcome the osmotic pressure, requiring more pumping power.
The vapor pressure of a solution is the partial pressure of gas phase of a chemical species over the surface of liquid phase of that same chemical species. The vapor pressure of water over an aqueous solution is directly related to the activity of water in that solution, shown by Eq. (1) (Hamer and Wu 1972). The activity of water for an ideal solution can be calculated using the molar concentrations of solutes in solution and molar volume of water by Eq. (2) or for well characterized solutions using the osmotic coefficient and molal concentrations of solutes in solution by Eq. (3).

\[
a_w = \frac{p_{\text{solution}}}{p_w}
\]

\[
a_w \approx \exp\left(-v_w \sum_{i=w} c_i\right)
\]

\[
a_w = \exp\left(-\varphi M_w \sum_{i=w} m_i\right)
\]

Figure 4. Boiling point temperatures of sodium chloride solutions calculated assuming an ideal solution or from osmotic coefficients compiled by Hamer and Wu (1972). Also shown are the osmotic pressures of four produced brines that are a part of GCS operations or under consideration using the activity of water calculated in Geochemist’s Workbench v9 with the thermo_phrpitz database. Vertical green line represents the approximate concentration of seawater.

The water vapor pressure depression of an aqueous solution by reduced water activity translates to an increase of a solution’s boiling point temperature, which is the temperature where the vapor pressure is equivalent to atmosphere pressure (1.013 bar). Shown in Figure 4 are the boiling points of a sodium chloride solution as a function of concentration. Two curves are shown where the first assumes an ideal solution and the second accounts for solution non-ideality from osmotic coefficients compiled by Hamer and Wu (1972). Figure 4 also shows the boiling points for the four produced CGS brines discussed previously, using water activities calculated in Geochemist’s
Workbench v9 (Aqueous Solutions LLC, Champaign, IL, USA) with the thermo_phrqpitz database.

The osmotic pressure of a solution is the potential of a solution to draw pure solvent into it if the solution were separated from pure solvent by perfectly selective semi-permeable membrane (Wilson and Stewart 2013). Osmotic pressure is commonly calculated using the van’t Hoff equation which assumes an ideal solution with concentrations expressed in molarity as shown in Eq. (4) (Cath et al. 2006, Wilson and Stewart 2013). A more accurate calculation of the osmotic pressure can be performed from the activity of water, or, for well characterized solutions, the osmotic pressure of a solution can be calculated from the osmotic coefficient and solute concentration expressed in molality as shown in Eq. (5) (Hamer and Wu 1972). The effect of solute concentration on the osmotic pressure of a solution is shown in Figure 5.

\[
\pi \approx \sum_{i \in W} c_i RT 
\]

\[
\pi = -\frac{RT}{\nu_w} \ln(a_w) = \varphi \sum_{i \in W} m_i \rho_w RT 
\]

Figure 5. Osmotic pressures of sodium chloride solutions calculated either assuming an ideal solution or using osmotic coefficients compiled by Hamer and Wu (1972) at 25°C. Also, shown are the osmotic pressures of four produced brines that are a part of GCS operations or under consideration using the activity of water calculated by Geochemist’s Workbench v9 with the thermo_phrqpitz database. Vertical green line represents the approximate concentration of seawater.

In addition to decreasing the water activity of a solution, an increase in the solute concentration of a produced CGS brine from dewatering can cause moderately soluble salts to precipitate. Precipitation can affect both evaporative and membrane processes. In an evaporative process, solids can form on heat transfer surfaces, decreasing heat transfer coefficients (Abdul-Latif et al. 1988); meanwhile, in membrane processes, solids on a membrane will decrease external mass
transfer coefficients, increase pressure drop, and increase a membrane’s thermal resistance (Shirazi et al. 2010, Warsinger et al. 2015).

As mentioned previously, the minimum work required to dewater a brine is dependent on two primary attributes: 1) the concentration of solutes within the initial brine and 2) the water recovery (Semiat 2008, Elimelech and Phillip 2011, Mistry and Lienhard 2013, Mazlan et al. 2016). Shown in Figure 6 is the minimum useful work of separation (\(\dot{w}_{\text{min}}/\dot{v}_p\)) for five brines of different inlet sodium chloride concentrations (2 g/L, 35 g/L, 61 g/L, 96 g/L, and 117 g/L), as a function of water recovery fraction. Here, the interconnectedness of salt concentration, osmotic pressure, and minimum useful work of separation can be seen from the fact that the 96 g/L brine requires roughly 3 times more work than does a 35 g/L brine. Shown in Figure 7, for the case of a 2 mol/L (117 g/L) inlet sodium chloride brine, is the minimum useful work of separation per volume of pure water (\(\dot{w}_{\text{min}}/\dot{v}_p\)) and the minimum useful work of dewatering per volume of inlet brine (\(\dot{w}_{\text{min}}/\dot{v}_b\)) as a function of water recovery fraction. This figure includes high values of water recoveries in which halite precipitates out of the solution as crystals. This figure also includes the molarity of the concentrated brine and the weight fraction of halite (i.e. the mass precipitated sodium chloride divided by the initial mass of aqueous sodium chloride). The NRTL electrolyte equation of state within AspenPlus V8.4 (Aspen Technology Inc., Bedford, MA, USA) was used to model an ideal reversible process and calculate the Gibbs free energy of the three streams required to estimate the minimum useful work to dewater a brine, as a function of water recovery.

**Figure 6.** Minimum work required to produce 1 m³ of pure water as a function of the water recovery fraction for five different inlet sodium chloride concentrations (\(\dot{w}_{\text{min}}/\dot{v}_p\)). Calculations were done at 20°C using the NRTL electrolyte equation of state with AspenPlus V8.4.

*Note: that the last point on each curve is maximum water recovery fraction before halite forms.*
Figure 7. Minimum work required to produce a m³ of pure water ($\dot{w}_{\text{min}}/\dot{V}_p$), minimum work of dewatering per m³ of inlet brine ($\dot{w}_{\text{min}}/\dot{V}_b$), remaining brine concentration, and solid weight fraction for a 2 mol/L sodium chloride solution as a function of the water recovery fraction. Calculations were done at 20°C using the NRTL electrolyte equation of state with AspenPlus V8.4.

Note: 2 mol/L sodium chloride = 117 g/L sodium chloride

For brine extraction to reduce formation pressure, it would generally be desirable that the produced brine be as concentrated as possible before final disposition. Increasing the concentration of the rententate brine means decreasing the total volume that would ultimately be disposed of; however, as shown Figure 6 and Figure 7, there are unavoidable useful work requirements associated with concentrating the brine to reduce the volume that must be disposed of. As shown in Figure 7, the minimum amount of useful work increases significantly if there is production of salt crystals in the process. For the case of the 117 g/L brine at 50% recovery, the minimum power consumption would be approximately 2.0 kWh/m³ of original brine produced. This equates to a power consumption of approximately 0.75 MW, when assuming that the volume of produced brine is equal to 50% of the volume of the 600,000 kg/h of sequestered supercritical CO₂ captured from a 550 MW power plant (Black 2013). When generating dry salt at 100% water recovery, the minimum work required per m³ of original brine increases by over three fold, from 2.0 kWh/m³ to 6.6 kWh/m³ of original brine produced, yielding a minimum power consumption of 2.5 MW from the 550 MW power plant. This is the case for a hypothetical process with no irreversible generation of entropy, but as we will see shortly, the actual amount of power consumption in commercially-available desalination processes is often ten times larger than the theoretical minimum.
4. DEWATERING/DESALINATION TECHNOLOGY

4.1. EVAPORATIVE PROCESSES

Historically, desalination of saline waters has relied upon evaporative processes, which mimic the natural water cycle by evaporating water from a brine, separating the steam, and condensing the water vapor to recover pure water. Evaporative separation processes were the platform of choice for water desalination until the maturation of reverse osmosis (Lonsdale 1982, Greenlee et al. 2009, Fane et al. 2011), and in some regions evaporative processes continue to be preferred for desalination due to a reduced sensitivity of the technology to inlet water conditions with respect to product quality and pretreatment requirements.

Characteristically, an evaporative process consist of a source of useful work be it an external heat source and/or electricity, heat exchangers for the heating/evaporation of seawater, a condenser for water vapor, and a collector for the condensate. A number of evaporative processes have been commercialized for the desalination of seawater, including multi effect distillation (MED), multi stage flash distillation (MSF), and vapor compression distillation. The primary drawback of an evaporative process is water’s large heat of vaporization, 40.7 kJ/mol\textsubscript{H2O} at 100°C (Smith et al. 2005, Semiat 2008). While much of the heat of vaporization is recovered during condensation, there is significant irreversibility from the temperature gradient between the hot and cold sides of a heat exchanger. Large quantities of thermal energy are transferred from the condensing vapor to the evaporating brine (~630 kWh/m\textsuperscript{3}liq\textsubscript{H2O}) and even small temperature gradients can cause significant irreversible generation of entropy. Because of this irreversibility, a 5°C temperature gradient across the heat exchanger requires the actual work consumption to be at least 7 kWh/m\textsuperscript{3} above the minimum useful work needed to separate pure water from a brine. Losses due to irreversibility associated with the large transfer of thermal energy across a temperature gradient is the main reason why the typical efficiency of evaporative processes is around 10% or less (Nafey et al. 2008, Mistry et al. 2011). Here, efficiency is defined as the minimal amount of useful work required for a reversible process divided by the actual amount of useful work consumed in the process. This means that, for a 10% efficient process, the values for useful work consumption go from 2.0 kWh/m\textsuperscript{3} or 6.6 kWh/m\textsuperscript{3} of original brine produced to 20 kWh/m\textsuperscript{3} or 66 kWh/m\textsuperscript{3} of original brine produced. And hence the power consumption would be 7.5 MW for the 50% water recovery case and would be 25 MW for the 100% water recovery case, which are respectively 1.4% and 4.5% of the power generated at the coal-fired CCS power plant. Although the efficiency can be maximized through the use of heat exchangers with large heat transfer coefficients, the temperature gradient across a heat exchanger can increase significantly when scaling occurs on the heat exchanger surface.

Scaling is the formation of inorganic precipitates on wetted process surfaces. For heat exchangers, scaling reduces the heat transfer coefficient, requiring a larger temperature gradient and leading to additional irreversible entropy generation. In an evaporative desalination process, scaling occurs via three paths: 1) solutes that have an inverse temperature solubility relationship, 2) supersaturation of a solute from water removal during distillation, or 3) thermal decomposition of bicarbonate salts (El Din et al. 2002, Budhiraja and Fares 2008). Two bicarbonate salts of concern would be magnesium bicarbonate and calcium bicarbonate because the decomposition of the bicarbonate anion would form scales of magnesium hydroxide and calcium carbonate respectively (El Din et al. 2002). One further issue associated with evaporative technologies is
corrosion. Corrosion may be increasingly problematic for highly saline brines because elevated temperatures needed to drive evaporative processes will increase corrosion rates of wetted metal surfaces; however, the proper selection of process materials can lead to long lifespan without significant impact to capital costs (Sommariva et al. 1999, Sommariva et al. 2001).

4.1.1. MULTIPLE-EFFECT DISTILLATION

Multi-effect distillation (MED) is the oldest process used for the desalination of seawater with development beginning in the middle of the nineteenth century and the first land based MED facility constructed in Saudi Arabia in 1930 (Al-Shammiri and Safar 1999, Reddy and Ghaffour 2007). A MED process uses an external steam source to evaporate water from a saline solution in the first effect. Steam condensed in the first effect is returned to the boiler, while steam generated in the first effect is used to evaporate water from the second effect. Steam generated in the second effect is used to evaporate water in the third effect and so forth. This sequence of steam generation and transmission continues until there is an insufficient temperature gradient (heat flux) in the generated steam to heat up and evaporate the incoming seawater. The steam condensed in each stage after the first is collected, becoming the product water from the process. A diagram of the MED process is shown in Figure 8 (Darwish et al. 2006).

![Figure 8. Principle of the MED process. Redrawn from Darwish et al. (2006).](image)

4.1.2. MULTI-STAGE FLASH DISTILLATION

The multi-stage flash (MSF) distillation process is currently the dominant evaporative process used in the desalination of seawater. MSF was developed in the late 1950s with the first installed desalination plant becoming operational in Kuwait in 1957 (El-Dessouky et al. 1995, Reddy and Ghaffour 2007). In a MSF process, a saline solution is heated and flows into a chamber at progressively lower pressures. In the chamber, a portion of the brine flashes into steam. The flashed steam passes through a mist eliminator, condenses to pure water, and is recovered as the product water. The product water often requires remineralization as part of its post-treatment because its TDS (2–10 mg/L) is too low for potable water (Khawaji et al. 2008). MSF remains the dominant technology for the desalination of seawater because many MSF plants have outlived their design lifetime; however, MSF’s market share for new construction has decreased considerably due to a competition from more energy efficient membrane technologies and improvements in the MED
Desalination of GCS Brines

In general, the MSF and MED processes share common features amongst the two processes with the largest differences arising from the physical construction of these processes. For example, the MED process has more heat transfer area, permitting lower top brine temperatures than the MSF process and higher efficiency; however, a drawback to the MED process is the higher propensity to scaling because water evaporation occurs directly on heat exchange surfaces rather than in the bulk as in MSF (Ghaffour et al. 2013, Mistry and Lienhard 2013). Both MED and MSF processes require an external heat source, such as steam. Most likely, a GCS brine extraction well would not be in close enough proximity to a power plant for there to be a steam supply available. Traditionally, the steam for MED/MSF is generated from the combustion of fossil fuels, such as natural gas; however, the CO₂ emissions from the combustion of these fossil fuels would ultimately be assigned to the power plant at which CO₂ captured occurred. As such, there is likely limited applicability of MED and MED processes to the dewatering/desalination of produced GCS brines.

4.1.3. VAPOR COMPRESSION DISTILLATION

Vapor compression distillation operates by creating a pressure difference between the hot (pure water/steam) and the cool (saline brine) sides of a heat exchange surface (Al-Sahali and Ettouney 2007). The vapor/steam compression increases the temperature and pressure to drive the evaporation of water from a brine. Vapor compression can be done thermally by a steam ejector, thermal vapor compression (TVC), or mechanically by a compressor, mechanical vapor compression (MVC) (Miller 2003). Vapor compression distillation has been employed in desalination of seawater, dewatering of RO concentrate, and dewatering produced brines (Miller 2003, Shaffer et al. 2015). The evaporator of a vapor compression process operates similarly to MED processes; however, vapor compression processes operate with only a single effect. In the effect, water vapor from a preheated brine would be withdrawn and compressed, increasing its pressure and temperature. The compressed steam flows into a heat exchanger forming additional water vapor within the effect as the steam condenses. Water vapor formed within the effect then

Figure 9. Principle of the MSF process.
Redrawn from El-Dessouky et al. (1995) and El-Dessouky et al. (1998).
goes to the steam ejector or compressor. The outgoing product water and rejected brine are used to preheat fresh seawater going into the process.

Of the three main evaporative processes, MVC is unique in that the useful work required for evaporation is not derived from an external heat source, as in MSF and MED, but by a mechanical compressor. This unique aspect allows MVC to operate when a high quality steam source is unavailable, making it a viable technology that could be mounted onto a mobile platform and transported to a brine extraction well or other produced water source with compressor operation done by electricity only (Igunnu and Chen 2012, Shaffer et al. 2013). The electricity to drive the MVC process can come from either from local solar power and/or from the power plant at which the CO₂ was originally captured. For this reason, MVC is likely to be of greater interest than TVC, MED, or MSF in GCS applications.

![Diagram of process](image)

**Figure 10. Principle of a) mechanical vapor compression and b) thermal vapor compression distillation processes.**

Redrawn from Miller (2003).

### 4.2. MEMBRANE PROCESSES AND TECHNOLOGY

Membrane technology can be applied to achieve the goal of brine management where, depending on the membrane employed, they can be used both to dewater GCS brines and/or remove suspended solids as a precursor to brine dewatering. Membranes are discrete barriers that allow for the selective permeation of chemical species (Shirazi et al. 2010). There are three streams common to membrane processes. These streams are called: 1) the feed, 2) the permeate, and 3) the retentate. The feed solution is the input to a membrane separation; the permeate is the solution that crosses the membrane from the feed; and the retentate is the concentrated feed solution containing some water with dissolved, suspended or emulsified solutes that do not cross the membrane (Van der Bruggen and Vandecasteele 2002, Wang et al. 2011). In most membrane processes, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, the permeate is a new stream the comprises only the material that crosses the membrane; however, in some membrane processes, such as forward osmosis, direct contact membrane distillation, and osmotically assisted reverse osmosis, the permeate that crosses the membrane is mixed with a solution that flows along the permeate side of a membrane (Lonsdale 1982, Alkhudhiri et al. 2012, Van der Bruggen and Luis 2015).
The flow rate or flux of a chemical species permeating a membrane depends on all of the relevant potential gradients across the membrane. Depending on the process, relevant potentials can include the chemical potential, mechanical potential, and/or the electrical potential. Typically, though, the flux of liquid water across a membrane is driven by the difference between transmembrane osmotic and hydraulic pressures (Cath et al. 2006, Greenlee et al. 2009). And the flux of water vapor is typically driven by the transmembrane vapor pressure (Shao and Huang 2007, Mistry et al. 2011, Alkhudhiri et al. 2012). The flux of dissolved solutes is driven by either the concentration gradient of the solutes, the convective flow of a solution, or in the case of electrochemical separations, by the voltage difference between an anode and a cathode across a membrane stack (Strathmann 2010).

Membranes used in water treatment can be symmetric or asymmetric as well as porous or dense. Symmetric membranes have a uniform cross section with both faces of a membrane being similar. Asymmetric membranes have a distinct gradation in features throughout their cross-section having a distinct selective layer that defines a membrane’s selectivity and contributes a majority of the pressure drop through the structure (McCUTCHEON et al. 2006, Chen et al. 2011). Porous membranes have interconnected pores throughout and remove chemical species by a physical interaction between the membrane and a feed solution/suspension. Dense membranes have no visible pores and separate chemical species by the solution-diffusion, where a chemical species crosses a membrane by partitioning into it, diffusing through it, and partitioning out of it (Wijmans and Baker 1995, Paul 2004, Fane et al. 2011). Dense membranes which are also asymmetric typically have a very thin dense layer supported by underlying porous layers which enables high selectivity and minimal transport resistance.

4.2.1. HYDRAULIC PRESSURE DRIVEN MEMBRANE SEPARATIONS

There are four established hydraulic pressure driven membrane separation techniques including microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF) (Lonsdale 1982, Chen et al. 2011, Fane et al. 2011). Figure 11 shows the stream common to a hydraulic pressure driven membrane process. MF and UF use porous membranes for removal of suspended solids by size exclusion and are not selective to dissolve solutes. This means that they are unsuitable for the desalination of brines; however, they are effective technologies for the removal of emulsified organics and suspended solids (Fane et al. 2011). Depending on produced water quality, MF and/or UF may likely be needed for the pretreatment of these brines.

NF and RO are pressure driven membrane desalination technologies that use dense membranes for water softening and desalination. NF membranes are typically effective at removing divalent salts, while RO membranes are capable of removing all dissolved salts within a solution, making RO applicable to the desalination of sea water (Dow , Lonsdale 1982, Chen et al. 2011). RO has more recently received attention for its expanded application to the concentration of CGS brines (Aines et al. 2011, Bourcier et al. 2011). In NF and RO, a hydraulic pressure is applied to a saline feed solution in excess of the osmotic pressure difference across the semi-permeable membrane. An osmotic pressure is only exerted across a membrane by solutes to which the membrane is impermeable (Lee et al. 1981). As shown in Figure 5, when the concentration of solutes increases in solution, so does the osmotic pressure of that solution.
RO is called such because the applied hydraulic pressure is greater than the feed solution’s osmotic pressure and so the flow of water occurs in the opposite direction of natural osmosis. RO has become widely accepted as a desalination technology for both seawater and brackish waters, having benefited greatly from technological improvements in the past thirty years, leading to great reductions in the amount of useful work required to dewater a brine (Greenlee et al. 2009, Elimelech and Phillip 2011). RO membranes typically operate at pressures less than 82.8 bar (1200 psi) (Dow, Bourcier et al. 2011). This upper limit on operational pressures hinder the maximum recovery that can be achieved when concentrating high salinity brines, which are generally more concentrated and, as shown in Figure 5, have higher osmotic pressures than seawater. The salinity of some brines is sufficiently high such that any further concentration is not possible with RO (Aines et al. 2011).

RO requires hydraulic pressure to operate, so the process is limited by the mechanical stability of a semi-permeable membrane when a hydraulic pressure is applied to it. Excessive pressure on a membrane may result in rupture or collapse of the membrane. This inherent hydraulic pressure limitation means that, if a brine produced from GCS operations is only slightly more saline than seawater, then the solution can only be reduced in volume a small amount before the osmotic pressure is equivalent to the applied hydraulic pressure (Greenlee et al. 2009, Aines et al. 2011). At this point, the net driving force across reverse osmosis membrane is zero; therefore, water will cease to permeate across the membrane (Lonsdale 1982).

4.2.2. **VAPOR PRESSURE DRIVEN MEMBRANE SEPARATIONS**

Vapor pressure driven membrane processes, such as membrane distillation (MD) and pervaporation, are driven by differences in the partial pressure of water vapor. While differences in the vapor pressure of water exist between solutions of differing salinity, these separation processes commonly have a feed solution that is heated to a temperature less than its boiling point, typically 40-70°C. The elevated vapor pressure of the heated water drives the permeation of water vapor across the membrane (Kuznetsov et al. 2007). MD and pervaporation are commonly differentiated by differences in the properties of the membrane employed. MD membranes are porous and hydrophobic with water vapor diffusing through unwetted pores (Alkhudhiri et al. 2012); while, pervaporation membranes are dense and can be tailored to have a high selective for water vapor (Shao and Huang 2007). Pervaporation membranes designed for desalination are hydrophilic and have an affinity for water (Zwijnenberg et al. 2005, Liang et al. 2014).
Despite differences in membrane properties, there is significant commonality between the configurations of MD and pervaporation processes. In most embodiments, the side of the membrane that does not contact the feed solution is in contact with an air stream or a gap that serves as the carrier or medium for diffusion to a condenser. If the air gap is stagnant, water vapor needs to diffuse through the air gap to a condenser within the membrane module (Zwijnenberg et al. 2005, Alkhudhiri et al. 2012). Alternatively, the air stream can be flowing or under vacuum carrying water vapor that permeates a membrane to a condenser outside of the membrane module (Quiñones-Bolaños et al. 2005, Alkhudhiri et al. 2012, Liang et al. 2014).

Another configuration not usually employed for pervaporation but commonly used for MD is direct contact. Here, the membrane mediates vapor transport directly from a warmer feed solution to the cooler permeate solution. This application gives the shortest distance of water diffusion since water vapor from the feed solution will condense into the distillate. A drawback to a direct contact application is that heat conduction through the membrane can cool the feed and warm the permeate, lowering the rate of water flux across the membrane (Alkhudhiri et al. 2012).

One challenge of the MD process is membrane wetting (Franken et al. 1987, Alkhudhiri et al. 2012). When a membrane in an MD process wets out, liquid enters into the membrane pores causing cross-over of feed solution into the permeate stream. In the case of direct contact MD, feed solution cross-over will decrease permeate quality. The propensity of MD membranes to wet-out is affected by: 1) the pore sizes of the membrane, 2) the materials of membrane construction, and 3) the composition of the feed solution. In particular, MD membranes used for desalination are not selective to volatile organics, and even worse, the presence of volatile organics may lower the surface tension of an aqueous feed solution, which promotes pore wetting and can in turn lead to low permeate quality (Franken et al. 1987).

One advantage of the MD process is that the elevated temperature of these brines can be used a driving force for brine-water separation. Depending on the depth, the temperatures of these brines are typically between 30°C and 75°C (Sass et al. 1998, Knauss et al. 2005, Dilmore et al. 2008, Lu et al. 2012). This elevated temperature can be used a driving force for brine-water separation provided that the thermal energy that passes through the membrane can be effectively dissipated to the environment. For example, the amount of useful work inherent to a 50°C brine with respect to a 20°C environment is approximately 1.7 kWh per m³ of the hot brine. As seen in Figure 7, this value is on the same order of magnitude as the minimum work of dewatering, and this means that the elevated temperature of these brines can help to decrease overall electricity consumption.

4.2.3. OSMOTIC PRESSURE DRIVEN MEMBRANE SEPARATIONS

Forward osmosis (FO) is a membrane technology where water flux is driven by an osmotic pressure differences between two solutions separated by a semi-permeable membrane. In FO, a draw solution, osmotic pressure higher than the feed solution being dewatered, will typically flow on the permeate side which has an of a membrane. The streams common to a FO process are shown in Figure 12. Draw solutions are prepared from a selected draw solute that, when in solution, can be either directly used after dilution or easily regenerated (Cath et al. 2006, Achilli et al. 2010, Qasim et al. 2015). Two advantages cited by proponents of FO processes are its superior resistance to fouling and its potential for a reduction in the energy costs of desalination by pairing it with a draw solute that can be recovered in a high efficiency process (McGinnis and Elimelech 2007, Lee et al. 2010, Mi and Elimelech 2010;2013, Mazlan et al. 2016).
In FO a lower osmotic pressure feed solution is dewatered by a higher osmotic pressure draw solution. Permeate that crosses the membrane is mixed with and dilutes the draw solution. Dashed line represents the semi-permeable membrane.

One important consideration unique to FO processes is that, unlike other membrane separations, water that crosses a membrane in FO is mixed with and dilutes the draw solution (Van der Bruggen and Luis 2015). It is not directly converted to a low salinity water, meaning that a single standalone FO stage would be incapable of continuous operation for the conversion of a saline water to freshwater. Some applications of FO, such as fertigation or emergency hydration, use draw solutions, such as sugars or fertilizers, that do not require recovery because a diluted draw solution is the desired product (Cath et al. 2006, Hoover et al. 2011, Qasim et al. 2015). Given the large volumetric flow rates potentially associated with GCS, there will be limited application for non-regenerative FO, such as fertigation; therefore, a FO process will need to be coupled with a draw solution regeneration process requiring the consumption of useful work, be it thermal, mechanical, and/or electrical (Mazlan et al. 2016).

4.2.4. ELECTROCHEMICAL MEMBRANE SEPARATIONS

In addition to vapor pressure and hydrostatic pressure driven membrane separations, a saline brine can be deionized electrochemically. This technique, called electrodialysis (ED) and shown in Figure 13, uses a cathode, an alternating arrangement of cation and anion exchange membranes, and an anode to separate ions from a solution (Miller 2003, Strathmann 2010). A voltage across the electrodes drives the migration of anion and cations through the anion and cation exchange membranes. This creates two alternating product streams: 1) an ion enriched concentrate and 2) an ion depleted diluate (Strathmann 2010). One advantage possessed by ED, and similar to evaporative processes, are lower requirements for pretreatment due to a higher tolerance of the process to suspended solids; however, this is offset by an increase in stack resistance with increasing ion concentrations that greatly increases the useful work needed to separate dissolved ions from water. The tradeoff between ED and RO has been observed experimentally with brackish waters having 2.7 g/L and 5.3 g/L TDS. ED was observed as being a more efficient option for a 2.7 g/L feed, while RO was more efficient for a 5.3 g/L feed (Walha et al. 2007). Since ED uses only electricity as the source of useful work to deionized a brine, conventional ED would be relevant to the concentration of those GCS produced brines that have low salinity; however, since CGS produced brines typically have high salinities, conventional ED is likely not viable without significant reduction in the amount of electricity consumed.
4.3. HYBRID PROCESSES

A hybrid process would combine different membrane and evaporative separations to synergize advantages and mitigate disadvantages amongst available technologies to desalinate high TDS brines. Most continuous FO processes could be considered hybrid technologies in that they employ both a forward osmosis stage and separate stages to recover draw solutes and/or concentrate the draw solution. Here, hybrid processes are grouped into two loosely connected categories: 1) combined separation process and 2) combined drive force processes. For example, a combined separation process is one which would synergize multi-separation processes in series to improve overall thermal efficiency or to take advantage of different types of useful work in different stages. Combined drive force processes are those that use multiple driving forces within the same stage, i.e. osmotic pressure and hydraulic pressure to extract water from a feed solution.

4.3.1. COMBINED SEPARATION PROCESSES

4.3.1.1. MULTI EFFECT DISTILLATION-MECHANICAL VAPOR COMPRESSION

Multi effect distillation-mechanical vapor compression (MED-MVC) hybrid technology combines elements of MVC and MED to both increase the thermal efficiency of MVC by the addition of additional effects and operate MED without an external steam source. As shown in Figure 14, the MED-MVC process operates similarly to MED; however, water vapor produced in the last effect goes to a compressor and serves as the high temperature and pressure steam for the first effect (El-Dessouky et al. 2000). Since, like MVC, the MED-MVC process is driven by a compressor, it would be capable of operating when electricity is the only utility available. The addition of heat transfer area allows the MED-MVC hybrid to operate with a low top brine temperature and offers higher performance efficiency compared to a standalone MVC process (Al-Juwayhel et al. 1997, Nafey et al. 2008). One limitation to the MED-MVC process is that, while additional effects can increase the efficiency of this process significantly, the capital costs of those
added evaporators can make the total levelized cost of the product water higher than would be the case for a single effect MVC process (Nafey et al. 2008).

![Figure 14. Multi effect distillation–mechanical vapor compression hybrid operating principle. Redrawn from El-Dessouky et al. (2000).](image)

4.3.1.2. **FORWARD OSMOSIS WITH DRAW SOLUTION REGENERATION**

A continuous FO process that includes steps for draw solution regeneration can also be considered a hybrid process. In these processes, a FO first stage is used to dewater the feed solution and dilute the draw solution. Subsequent stages are used to regenerate the diluted draw solution by the removal of water or the recovery of draw solutes. The specific process(es) used for draw solution concentration is/are dependent on the draw solute selected. An ideal draw solute for FO should meet the following criteria: 1) the solute is water soluble or can be made water soluble, 2) it must have a higher osmotic pressure than the feed solution, 3) the reverse diffusion across the membrane is minimal, 4) the dilute solution can be regenerated back to the concentrated draw solution, 5) it is safe to handle, and 6) the cost is low enough to ensure an economic viability of the FO process (Achilli et al. 2010).

A wide variety of draw solutes have been investigated for FO, including sugars, inorganic salts, magnetic nanoparticles, polyelectrolytes, 2-methylimidazole-based compounds, temperature sensitive water soluble polymers, switchable polarity solvents, and thermolytic salts (McCutcheon et al. 2005, Yen et al. 2010, Luo et al. 2014, Qasim et al. 2015). Sugars, inorganic salts, and polyelectrolytes can be recovered by various pressure driven membrane separations or membrane distillation. Magnetic nanoparticles can be recovered through either a magnetic separation or UF. Switchable polarity solvents use a non-polar tertiary amine that when mixed with water and sparged with carbon dioxide forms a water soluble tertiary ammonium salt and can be separated by removal of dissolve carbon dioxide that causes the tertiary amine to revert to its non-polar state (Stone et al. 2013, Orme and Wilson 2015, Reimund et al. 2016). Thermolytic salts are made from anions and cations formed from water soluble gases, such as ammonia or trimethylamine and carbon dioxide, that when heated causes dissolved solutes to come out of solution as gases (McCutcheon et al. 2005, Boo et al. 2015).

The energy consumption of FO dewatering is mainly determined by these additional separation steps that ultimately extract water from and regenerate the diluted draw solution. The energy requirements of the secondary process appear to be generally less than or equivalent to
conventional alternatives such as RO or evaporation (McGinnis and Elimelech 2007, Mazlan et al. 2016). One notable draw solution, which has promised a reduced minimum amount of work over both evaporative processes and RO is based upon the thermolytic draw solution of ammonia and carbon dioxide. The ammonia-carbon dioxide FO process that promises reduced energy consumption is not currently viable as the continuous 2-step process originally envisioned from the incompatibility between the draw solution and available membrane chemistries. The ammonia-carbon dioxide draw solution is alkaline which cause accelerated hydrolysis in cellulose acetate membrane and facilitates cation exchange across thin film composite membranes (Vos et al. 1966, Arena et al. 2014, Arena et al. 2015a, Arena et al. 2015b).

Figure 15. Flow diagram of a thermolytic FO brine concentrator using a draw solution of ammonia and carbon dioxide.
Redraw from McGinnis et al. (2013).

FO using a thermolytic draw solute is capable of treating high salinity waters that would be impossible to treat by conventional RO process. One pilot study using a thermolytic draw solution of ammonia and carbon dioxide has shown a produced water brine could be concentrated up to 180 g/L TDS operating with an average water recovery of about 64% (McGinnis et al. 2013). A flow diagram for this process is shown in Figure 15. For comparison, evaporative brine concentrators used in similar applications typically treat water of similar salinity (between 70-80 g/L TDS) by concentrating it to 200-230 g/L TDS, a similar degree of concentration to that observed for this FO process.
4.3.2. **COMBINED DRIVING FORCE PROCESSES**

4.3.2.1. **ASSISTED FORWARD OSMOSIS**

Assisted forward osmosis (AFO) is a combined driving force hybrid FO process that uses a small hydraulic pressure applied to the feed to augment the osmotic pressure difference being exerted by the draw solution offering improvements in the water flux across a membrane (Blandin et al. 2013, Coday et al. 2013).

4.3.2.2. **OSMOTICALLY ASSISTED REVERSE OSMOSIS**

The AFO process uses a slightly pressurized feed solution and concentrated draw solution to enhance the rate of water transport across a semi-permeable membrane; however, water flux remains most significantly influenced by the osmotic pressure difference between the feed and draw solution. In considering enhancements to water flux in FO, the most significant amount of useful work required by an FO process will reside in regeneration of the draw solution. As an alternative to AFO, rather than use osmotic pressure as the primary driving force for water flux hydraulic pressure could be the primary driving force for water flux. In a typical RO process, water flux is against the osmotic pressure difference across the membrane that is dependent on the selectivity of that membrane; however, the osmotic pressure difference across the membrane can be adjusted by circulating a less saline sweep solution on the permeate side of a membrane. The salinity and associated osmotic pressure of this sweep solution lowers the bulk osmotic pressure difference across a semi-permeable membrane (Karode et al. 2000, Lakerveld et al. 2010, Wohlert 2012). This osmotically assisted reverse osmosis (OARO) is not a process of direct desalination but one of dilution by stages arranged in series.

![Figure 16. Streams of an OARO process](image)

Here a lower osmotic sweep solution is diluted by a higher osmotic pressure feed solution under applied hydraulic pressure. The hydraulic pressure is greater than the osmotic pressure difference between the two solutions, driving water flux from the feed solution into the sweep. Dashed line represents the semi-permeable membrane.

The OARO process would allow for a gradual stepping down of the osmotic pressure using a hydraulic pressures comparable to those typically employed within a RO process (Wohlert 2012). The streams of an OARO process are shown in Figure 16. Here, attention is given to the multi-stage OARO process because it appears to be quite applicable to and relevant for dewatering of GCS produced brines.
4.3.2.2.1. TRANSPORT IN OARO

Limitations on water flux in OARO differs from RO. The presence of the sweep solution and resulting interaction between solute concentration and osmotic pressure introduces competition between convection and diffusion of solutes in both the feed and sweep solutions. This behavior is akin to the internal concentration polarization that encountered in FO when a membrane’s selective layer is in contact with the feed solution (Tiraferri et al. 2011); however, in OARO, hydraulic, and not osmotic, pressure is the primary driving force for the flow of water across the membrane as such the positive direction for water flux is the same as RO, against the osmotic pressure difference. The water and solute flux across a membrane in OARO are defined by Eq. (6) and Eq. (7).

\[
J_w = A \cdot \left[ \left(p_{ \text{f} } - p_{ \text{s} } \right) - \pi(c_{ \text{f},m}) - \pi(c_{ \text{s},m}) \right]
\]  
(6)

\[
J_s = B \cdot \left( c_{ \text{f},m} - c_{ \text{s},m} \right)
\]  
(7)

Movement of water and solutes across a membrane in OARO will greatly influence the concentration of solutes at the membrane arising from a competition between the convective flow of solution and diffusion of solutes against it. The convection/diffusion of solutes and the non-linearity of the osmotic pressure of a sodium chloride solution at high concentration (i.e. >3 mol/L) means that the salt concentration of both the feed and sweep solutions at the membrane must be known. The concentrations of the feed and sweep solutions at the membrane are defined by Eq. (8) and Eq. (9).

\[
c_{ \text{f},m} = c_{ \text{f},b} \cdot \exp \left( \frac{J_w \cdot \delta_f}{D \cdot \kappa} \right) + \frac{B}{J_w} \cdot \left\{ c_{ \text{f},b} \cdot \exp \left( \frac{J_w \cdot \delta_f}{D \cdot \kappa} \right) - c_{ \text{s},b} \cdot \exp \left( -\frac{J_w \cdot \delta_f}{D \cdot \kappa} \right) \right\} \cdot \left[ 1 - \exp \left( -\frac{J_w \cdot \delta_f}{D \cdot \kappa} \right) \right]
\]  
(8)

\[
c_{ \text{s},m} = c_{ \text{s},b} \cdot \exp \left( -\frac{J_w \cdot \delta_f}{D \cdot \kappa} \right) + \frac{B}{J_w} \cdot \left\{ c_{ \text{f},b} \cdot \exp \left( \frac{J_w \cdot \delta_f}{D \cdot \kappa} \right) - c_{ \text{s},b} \cdot \exp \left( -\frac{J_w \cdot \delta_f}{D \cdot \kappa} \right) \right\} \cdot \left[ 1 - \exp \left( -\frac{J_w \cdot \delta_f}{D \cdot \kappa} \right) \right]
\]  
(9)

Given that the membrane’s transport parameters (A, B, and S) are known, then \( c_{ \text{f},m}, c_{ \text{s},m}, J_w, \) and \( J_s \) can be calculated from Eq. (6), Eq. (7), Eq. (8), and Eq. (9). The membrane’s transport parameters are temperature dependent and, possibly, pressure dependent; therefore, they ultimately must be measured experimentally. Literature values by She et al. (2012) have been used to represent a baseline membrane, which was characterized under conditions similar to those that would be seen in OARO dewatering of a GCS brine. The model transport properties of this membrane and expected water flux are shown in Table 1 and Figure 17 respectively.
Table 1. Transport parameters for a woven supported cellulose triacetate membrane (She et al. 2012).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.3672</td>
</tr>
<tr>
<td>B</td>
<td>0.27684</td>
</tr>
<tr>
<td>S</td>
<td>( 10.415 \left( \frac{P_f - P_s}{1 \text{ bar}} \right) + 714.39 ) ( \times 10^{-6} ) m</td>
</tr>
</tbody>
</table>

Figure 17. Simulated flux from an osmotically assisted reverse osmosis process using Hydration Technology Innovations woven supported cellulose triacetate forward osmosis membrane. Assumptions constant water permeance (A) and salt permeability (B). Effective structural parameter is assumed to be linearly responsive with applied transmembrane pressure. External boundary layer thickness (\( \delta_f \)) is 50 \( \mu \text{m} \). Operating temperature is 25°C. The membrane's transport properties are shown in Table 1 (She et al. 2012).

As shown in Figure 17, by using a single OARO stage and by applying a hydrostatic pressure difference across the membrane of at least 52 bar, one could dewater a solution having a concentration of 330 g/L sodium chloride (403 bar osmotic pressure) using a sweep solution having 300 g/L sodium chloride (349 bar osmotic pressure). Water flux across the membrane at these conditions is predicted to be low; however, the water flux across the membrane is heavily dependent on the S parameter. The S parameter is a measure of the effective thickness of an asymmetric membranes porous support through which solute must diffuse through to exert an osmotic pressure across the membrane. As shown in Eq. (8) and Eq. (9), the S parameter affects the exponential decay of the concentration of the sweep solution at the membrane. The S parameter used to simulate the performance shown in Figure 17 is assumed to increase linearly with applied hydraulic pressure and was extrapolated from experimental data (She et al. 2012). One area of immediate future work will be the characterization of commercial membranes at multiple applied hydraulic pressures to evaluate the S parameter of membranes and gather data to evaluate their transport properties at applied hydraulic pressures anticipated for OARO.
4.3.2.2.2. **OARO PROCESS DESCRIPTION**

Figure 18 shows one possible configuration of an OARO process (Note: that the value of inlet and outlet brine composition were chosen somewhat arbitrarily, and the number of stages was chosen in order to convey the process as simply as possible). Multiple-stage OARO can handle brines of varying inlet and outlet concentration. As shown, this process contains multiple OARO stages followed by a final RO stage. In the first OARO stage of this example, a 90 g/L sodium chloride solution at a high hydraulic pressure (~70 bar) would flow counter-current to a saline sweep solution having an inlet concentration of 120 g/L sodium chloride. With counter-current flow under steady-state conditions, the concentration difference between the feed and sweep solutions should remain approximately constant over the length of a membrane module. This means membrane performance and surface area would largely dictate the recovery of the OARO stage. In this particular case, the feed solution was chosen to have an outlet concentration of 150 g/L and the sweep solution would have an outlet concentration of 60 g/L, having been diluted by dewatering the 90 g/L solution. The 60 g/L diluted sweep solution would then be pressurized and fed into the second OARO stage where as the feed solution it would flow counter current to a sweep solution having an inlet concentration of 90 g/L. The 60 g/L will be concentrated to 120 g/L while the 90 g/L solution is diluted to 30 g/L. The 30 g/L solution is now sufficiently dilute so that it may be concentrated in a final RO stage. Rather than being discharged as in seawater desalination, the retentate from the RO stage is circulated back to the prior OARO stage as a 90 g/L solution for dilution. This three stage OARO-RO process shown in Figure 18 could operate continuously concentrating the 90 g/L brine to a 150 g/L brine with only electricity needed to be supplied to the pumps. Additional components not shown in Figure 18 that would be included in an assembled OARO process are 1) the pumps and 2) the pressure exchangers, which would be necessary for energy recovery of the high pressure streams in the OARO process.

![Figure 18. Principle of an osmotically assisted reverse osmosis process.](image)

4.3.2.2.3. **DIFFERENCES BETWEEN OARO AND THERMOLYTIC FO**

OARO differs from the thermolytic FO brine concentrator in the compositions and pressures of the feed and sweep/draw solutions. While these processes both use a final RO step as a component, the rationale for its inclusion is greatly divergent for these two processes. Firstly, the draw solution
in thermolytic FO would need to be as highly concentrated as possible to maximize the osmotic pressure difference across the membrane to have high water flux. This means that there will be two substantial concentration gradients across a membrane in a thermolytic FO process employed for the dewatering of high salinity brines—one for the majority component of the brine, likely sodium chloride, and one for the majority component of the draw solution, either ammonium bicarbonate, ammonium carbamate, or some ratio of the two (Arena et al. 2015b). The bidirectional permeation of feed and draw solutes means that, for thermolytic FO, feed solutes will diffuse into the draw solution and draw solutes will diffuse into the feed solution.

Draw solute flux is problematic in FO because of the economic value of the draw solutes requires high recovery of draw solutes from both the draw and feed solutions. Additionally, the dissimilar solutes in the draw and feed solutions may also interact with one another as in the case of cation exchange which has been observed occurring across thin film composite membranes under alkaline conditions (Arena et al. 2014, Arena et al. 2015a, Arena et al. 2015b). This results in a separation of cation/anion pairs for salts present in both the feed and draw solutions; thereby, creating salts, such as sodium bicarbonate and ammonium chloride, that cannot be readily removed from the draw and feed solution by stripping off the salts. In addition to improve product water quality, the final RO step of the osmotic brine concentrator is to balance cation/anion pairing of the draw solutes to maximize ammonia and CO₂ recovery (McGinnis et al. 2013, Arena et al. 2015b).

In OARO, the final RO stage is a necessary step for the combined regeneration of the final OARO stage sweep solution and to extract the water from the process. The sweep solutions in each stage of the OARO would likely just be the retentate stream from the preceding stage, with perhaps a bleed/make-up stream to maintain steady-state. In either case, the sweep will be predominately made up of the same salts in the original brine, just at slightly lower concentrations than on the feed side. This means that only concentration gradients existing across the membrane are from the feed solution into the sweep solution. This means no reverse solute flux should occur from the sweep to the feed. Also, because solute flux across the membrane is a function of the difference in the solute concentrations across the membrane, there is a reduced driving force for permeation of sodium chloride across the membrane. Consider a case with the feed solution has a concentration of 180 g/L sodium chloride, or the approximate outlet concentration from a thermolytic FO brine concentrator. In an OARO process, a sweep solution of say 150 g/L sodium chloride will be on the opposite side of a membrane. Considering concentration polarization, the OARO concentrator will have as concentration difference between the sweep and feed solutions of ~60 g/L. The FO brine concentrator, assuming a water flux similar to that reported by McGinnis et al., would have a concentration difference between the draw and feed solution of ~185 g/L. The larger concentration difference mean that a larger quantity of salt would cross the membrane.

4.4. CONCENTRATE MANAGEMENT

Processes that dewater a GCS brine will most likely not concentrate these brines to past saturation of dissolve species. This will result in a residual solution of extremely high salinity that requires final disposition. As such, there are a few options for final disposal of the concentrated brine.
4.4.1. **REINJECTION**

Subsurface reinjection of brine is a low cost option for the disposal of both oil/gas produced brines and the concentrated brine produced at inland brackish water desalination plants (Shaffer et al. 2013, Xu et al. 2013). Here, a brine will be injected into a well below drinking water resources commonly at depths of 305–2440 m (1000–8000 ft) (Mickley and Associates 2006, Xu et al. 2013). Brine reinjection is a widely considered technique for the final disposition of GCS produced brines (Buscheck et al. 2011, IEAGHG 2012).

4.4.2. **EVAPORATION PONDS**

If GCS is done at a saline formation in an arid environment with inexpensive land, disposition of the produced brine via an evaporation pond may be viable (Mickley and Associates 2006, Xu et al. 2013). An evaporation pond is a dug pit with an impermeable liner to which the brine concentrate would be discharged. The brine would be furthered dewatered by natural evaporation (Ahmed et al. 2000, Pérez-González et al. 2012). In addition to the considerable land requirement of evaporation ponds, water evaporating from their surface is lost to the environment and evaporation ponds may require removal of precipitated solids (Ahmed et al. 2000, Mickley and Associates 2006).

4.4.3. **CRYSTALLIZERS**

Crystallizers are the only option if a solid product is desired for disposal or sale. For crystallizers to be viable, the brine should be concentrated to near saturation prior to being fed into the crystallizer. Though, because crystallizers evaporate all of the water present within a brine, they have considerable energy requirements and a potentially large carbon footprint (Xu et al. 2013, Morillo et al. 2014). As shown in Figure 7, the minimum useful work consumed per m³ of original brine increases over three fold for 100% water recovery compared to 50% recovery. This large increase in useful work consumption should only be considered if there is considerable local demand for solid salt. When making crystals, the composition of the brine being dewatered important is because, for process economics, salt for sale should not require additional purification. Should GCS in saline formations become an industrial scale reality, the sale price of salt might be greatly diminished damaging the economics of crystallizing GCS brines (Xu et al. 2013). For example, if all of the 1360 billion kg of CO₂ per year were captured at U.S. coal-fired power plants and the supercritical CO₂ were sequestrated underground, if a 120 g/L brine was produced with a volume equal to 50% of the volume of all of the sequestered supercritical CO₂, and if all of this brine were converted into crystal and fresh water, then there would be the generation to roughly 100 million metric tonne of crystal salt per year due to GCS operations, which a significantly greater than currently consumption rates of salt in the U.S. of roughly 44 million metric tonne of salt per year (Bolen 2015). Hence, for GCS applications, crystallizers are likely to be pursued in only a few cases.
5. CONCLUSIONS

Because of their large available volumes, deep saline formations will be key to long term reduction in CO₂ emissions from fossil fueled power plants. To mitigate the risk of induced seismic activity in formations with lower porosity/permeability, formation pressure management will require the extraction of brine from the formation. While also increasing formation capacity for CO₂ storage, the extracted brines can be dewatered as source of usable water in water scarce regions. The brine concentrate can be reinjected into a nearby formation, crystallized, or discharged into an evaporation pond.

While GCS produced brines can have large variations in TDS, in this report we present a quantitative evaluation of four GCS-relevant brines, which have a TDS between 100 g/L and 250 g/L. While sodium chloride is the main solute in these brines, some have significant concentrations of calcium, magnesium, and strontium or sulfate. Also, the salinity of GCS brines is significantly higher than seawater (35 g/L) for which most desalination processes have been optimized.

Due to a number of factors discussed in the report, many commercially-available dewatering processes are not applicable to GCS brines. For example, RO and ED are best suited to salinities less than seawater. Also, MSF, MED, and thermolytic FO require steam or low grade thermal energy to be the source of useful work to dewater a brine, and thermal energy will likely not be available near either the brine extraction well or brine injection well. Other than taking advantage of the elevated temperature of these brines, electricity from the power plant will likely be the only source of external useful work available to dewater the brine. Importantly, this external electrical consumption should ultimately be subtracted from the electricity generated at the power plant when conducting techno-economic assessment of PCC-CCS and IGCC-CCS power plant. For example, including this power consumption at the CO₂ sequestration site is crucial when calculating key environmental parameters, such as kgCO₂ emitted per kWh of net electricity.

When electricity is the only available source of useful work to dewater the produced brines, the current standard in high salinity brine dewatering is mechanical vapor compression (MVC). MVC uses an electrically-driven compressor to extract steam from a brine fed to an evaporator. Ultimately, the extracted steam is condensed to pure water via heat exchange with the incoming brine. A drawback to MVC is its low efficiency (<10%). Given this low efficiency, there is significant driving force for research and development of more efficient advanced membrane processes, such as the novel OARO process as well as novel MD processes that take advantage of the elevated temperature of these brines.

6. REFERENCES


Desalination of GCS Brines


Gale, J., Geological storage of co 2: What do we know, where are the gaps and what more needs to be done? Energy 2004, 29 (9), 1329-1338.


Stone, M. L.; Rae, C.; Stewart, F. F.; Wilson, A. D., Switchable polarity solvents as draw solutes for forward osmosis. *Desalination* 2013, 312, 124-129.


