Management and dewatering of brines extracted from geologic carbon storage sites

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Abstract

Subsurface pressure management is a significant challenge in geologic CO_2 storage. Elevated pressure generated from the injection of supercritical CO_2 can be managed by the withdrawal of brine from saline formations before or during CO_2 injection; however, management of the extracted brines is non-trivial because they may have high concentrations of dissolved solids and other contaminants. Dewatering a brine can reduce the volume needing disposal; in addition, water separated from the brine can be a source of usable low salinity water. This review will summarize the composition of brines extracted from select domestic geologic CO_2 storage sites, will calculate the minimum of work of dewatering, and will provide a critical review of developed and developing desalination/dewatering technologies that could be applied to brines extracted from saline formations before or during geologic CO_2 storage operations. Herein are also highlighted, when appropriate, the similarities and the differences between dewatering brines produced from oil/gas operations and brines extracted from geologic CO_2 storage. Since a source of steam or natural gas is likely unavailable/unsuitable for dewatering brines extracted during CO_2 storage, the ideal treatment processes should have a high electrical efficiency and, if possible, should be able to take advantage of the inherent elevated temperature of these brines.

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1. Introduction

To continue making use of abundant fossil fuels while simultaneously preventing increased greenhouse gas emissions, there will need to be widespread adoption of CO_2 capture, which is the separation and compression of CO_2 from anthropogenic sources. Following the CO_2 capture step is the geologic CO_2 storage (GCS) step, which is the disposition of CO_2 into those selected subsurface storage formations that present no risk of significant release over geologic time scales (Holloway, 2005; IPCC, 2005; Pires et al., 2011; Varre et al., 2015). The formations available for GCS include: offshore/onshore saline formations, depleted oil and gas wells, and unmineable coal seams (Bachu et al., 2007; Gibson-Poole et al., 2006; IPCC, 2005). Of these, saline formations represent the overwhelming majority of GCS storage capacity with optimistic estimates of CO_2 storage in saline formations suggesting a total CO_2 storage capacity equivalent to at least several decades at current global CO_2 emission rates (Damen et al., 2006; Gale, 2004; Goodman et al., 2011; Potdar and Vishal, 2016). Saline formations are subsurface formations whose available porosity is saturated by saline brine. The ideal saline formation for GCS would be at a depth greater than 800 m such that CO_2 injected within would be in a supercritical state, would be highly permeable so as to minimize the number of injection wells needed, and would be capped by a low permeability seal such as clay or shale (Bachu, 2000; Birkholzer et al., 2009; Holloway, 1997; Holloway, 2005; IPCC, 2005; Rochelle et al., 1999).

1.1. Brine extraction for GCS risk management

Quantifying the risks associated with CO_2 injection into underground geologic formations has been an active focus area for studies on GCS (Buscheck et al., 2016; Damen et al., 2006; Li and Liu, 2016; Michael et al., 2009; Pawar et al., 2013). In addition to studying the geochemical interactions between aqueous CO_2 moieties and supercritical CO_2 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 (Birkholzer and Zhou, 2009; Buscheck et al., 2016; Buscheck et al., 2011; Cihan et al., 2015; Gaus, 2010; IPCC, 2005). Excess formation pressure can cause seismic events and/or drive CO_2 leakage through pre-existing wells in the formation or natural faults with the potential to hydraulically fracture the formation seals (Lee et al., 2016; Varre et al., 2015). Accumulation of subsurface pressure might require lower rates of CO_2 injection and possibly reduce a formation's CO_2 capacity. One mitigation strategy is to extract brine from a saline formation before and/or during CO_2 injection, reducing reservoir pressure and allowing for higher rates of CO_2 injection (Buscheck et al., 2016; Buscheck et al., 2011; Cihan et al., 2015; IEAGHG, 2012). The optimal extraction ratio, which is the volume of brine extracted for pressure management normalized by the volume of CO_2 injected, is largely formation dependent. Open and highly porous formations will permit a lower extraction ratio than formations that are closed, have low porosity, or are close to active faults. Because these formations present a greater risk to overpressure, they require a higher extraction ratio (Bourcier et al., 2011; IEAGHG, 2012; IPCC, 2005). In the case of a deep sandstone formation near active faults with a CO_2 injection rate of 5 Mt/yr, the volume of extracted brine was estimated to be 38-67% of the volume of injected supercritical CO_2. This value was developed from an optimization of extraction well placement

and extraction ratio to prevent the escape of CO_2 through the extraction wells and maintain formation pressure below 1 MPa (Cihan et al., 2015).

While brine extraction can be used to manage a formation's pressure, a required 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 are 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 reduced volume and 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; Buscheck et al., 2016). A schematic of a potential GCS operation is shown in Figure 1.

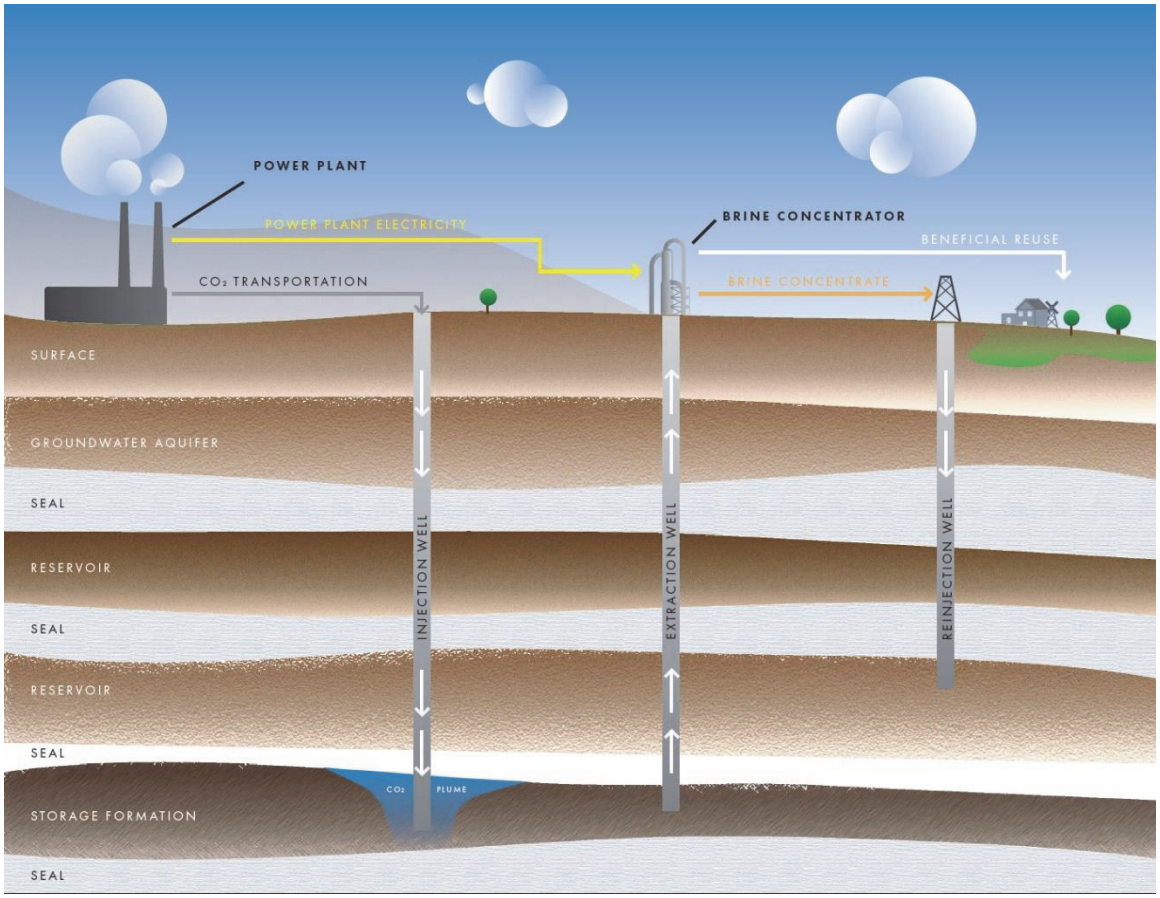


Figure 1. Schematic illustrating GCS operations. Image courtesy of Jacob Howell.
Note: Geology not to scale.

1.2. Comparison to oil/gas produced brines

Brines produced from oil/gas development, which have a similar composition to the brines extracted during GCS operations, have recently received considerable attention (AQWATEC, 2009; Coday et al., 2014; Igunnu and Chen, 2012; Shaffer et al., 2013; Thiel et al., 2015). Both

oil/gas and GCS brines, while highly variable in their concentration of dissolved solids, can contain high concentrations of dissolved solids equal to many times the concentration of seawater (Bourcier et al., 2011; Fakhru'l-Razi et al., 2009; Igunnu and Chen, 2012). Besides dissolved solids, there are differences both in the concentration of minor species and in the treatment options available. For example, brines produced during oil/gas development contain dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids (i.e. formation solids, corrosion and scale products, bacteria, waxes and asphaltenes), and dissolved gases (Fakhru'l-Razi et al., 2009). The presence of hydrocarbons within oil/gas produced brines can make dewatering them more challenging than the treatment of a similar TDS brines extracted during CGS operations because non-polar organic compounds, such as hydrocarbons, have a high propensity to foul membranes used for the treatment and/or the dewatering of oil/gas produced brines (Coday et al., 2014; Rana and Matsuura, 2010; Shaffer et al., 2013). Unlike oil/gas producing formations, GCS formations are regarded as typically bearing little hydrocarbons; however, there may be low levels of organics present in the form of oils from the subterranean strata (Wolery et al., 2009).

More significant than the slight differences in composition are the operational differences between oil/gas produced brines and GCS extracted brines. First, there are differences in scale/timing that must be considered. A typical oil/gas well has a varying flow of brine production and salinity that changes as the well ages (Barbot et al., 2013; Igunnu and Chen, 2012; Thiel et al., 2015). Requiring additional consideration is the management of flowback water, which is produced during the drilling and subsequent hydraulic fracturing of a gas well (Barbot et al., 2013; Coday et al., 2015; Miller et al., 2013; Thiel et al., 2015). Contrastingly, brine extraction at a GCS site would be more stable and correspond to the rate of CO_2 injection and formation characteristics. Second, oil/gas produced brines are coupled with the production of a potential energy source that could be used to drive dewatering processes; currently, CO_2 emissions from the combustion of the oil/gas to drive the brine/water separation are not regulated by the U.S. EPA. Unlike with oil/gas produced brines, there is an impetus for minimizing CO_2 emissions from GCS brine management because these emissions would be in addition to the CO_2 emitted from the power plant. There is also a requirement to minimize electricity consumption during brine treatment because this electricity consumption should be subtracted from the power plant's electrical production for calculating environmental parameters, such as CO_2 emissions per net electricity produced.

2. High TDS Brines associated with U.S. GCS operations

Saline formation waters can vary widely in their composition, but at the depths suitable for GCS, these brines typically have a total dissolved solids (TDS) ranging from 10– 400 g/L (Blondes et al., 2016; Bourcier et al., 2011). Brine within a saline formation is primarily composed of water and sodium chloride, which are also the primary components of seawater. Some saline formation brines may also contain significant concentrations of either calcium or sulfate (Aines et al., 2011). While nearly insoluble in water, the solubility of sulfate salts having divalent cations, such as calcium, strontium, barium, and radium are affected by brine salinity, temperature, and pressure (Howell et al., 1992; Ostroff and Metler, 1966; Raju and Atkinson, 1988, 1989, 1990). Divalent cation sulfate salts, even at low concentrations, have the propensity

to form chemical fouling or scale on the wetted surfaces of equipment that is used to dewater the brines (Aines et al., 2011; Budhiraja and Fares, 2008; El Din et al., 2002; Shirazi et al., 2010).

Subsurface brines are highly variable in composition, with brines extracted from GCS operation being no exception (Blondes et al.; Bourcier et al., 2011; Fakhru'l-Razi et al., 2009). In this review article, focus will be given to the brine chemistry of four selected sandstone formations that have been both well analyzed and are either a part of GCS operations or have been considered as candidates for GCS within the eastern half of the United States (Dilmore et al., 2008; Knauss et al., 2005; Lu et al., 2012; Michael et al., 2010; Sass et al., 1998; US-DOE-NETL, 2010). These brines are also likely indicative of other high salinity brines that will be encountered with widespread application of GCS within this geographic region; the four brines assessed in this review were extracted from the following formations: the Lower Tuscaloosa formation (Franklin County, Mississippi, USA) (Lu et al., 2012), the Mt. Simon formation (Decatur, Illinois, USA) (Sass et al., 1998), the Frio formation (Liberty County, Texas, USA) (Knauss et al., 2005), and the Oriskany formation (Indiana County, Pennsylvania, USA) (Dilmore et al., 2008).

As shown in Figure 2 and Figure 3, the majority components within the four brines are sodium, chloride, and calcium; however, there is variability in other ionic components, with some brines having significant quantities of magnesium, strontium, and/or sulfate. These brines are also quite saline, having salinities 3− 6 times greater than seawater, which varies globally but is approximately 35 g/L (0.6 mol/L) sodium chloride. In addition to the considerable salinity of these brines, another problematic aspect of their composition is revealed when mineral equilibria are calculated. Here, the mineral equilibria of these brines was calculated using Geochemist's Workbench v9 (Aqueous Solutions LLC, Champaign, IL, USA) with the thermo_phrqpitz database; details relating to the mineral equilibria for these for these brines as calculated can be found in the supplementary material. Analysis of the mineral equilibria reveals that two of these four brines have divalent salts at concentrations above their respective solubility limit. Specifically, the Mt. Simon brine is saturated with gypsum ($CaSO_4 \cdot 2H_2O$) and the Oriskany brine is saturated by calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and aragonite ($CaCO_3$). This indicates that, for brines such as these, additional pretreatment, pH control, and/or antiscalant(s) will be needed to mitigate the scaling that would occur from an increase in the concentration of low solubility salts as water is removed from these brines. One detail regarding the composition of these GCS brines as well as other that is notably missing from these brine data is an analysis of the rare-earth elements comprising these brines. The limited information of rare earth element composition of GCS brines was previously noted by Breunig et al. (2013). Higher than nominal concentrations of rare earth elements, such as those which have been noted for geothermal brines, may provide economic incentive for recovering rare earth elements from extracted GCS brines (Haas et al., 1995; Noack et al., 2014).

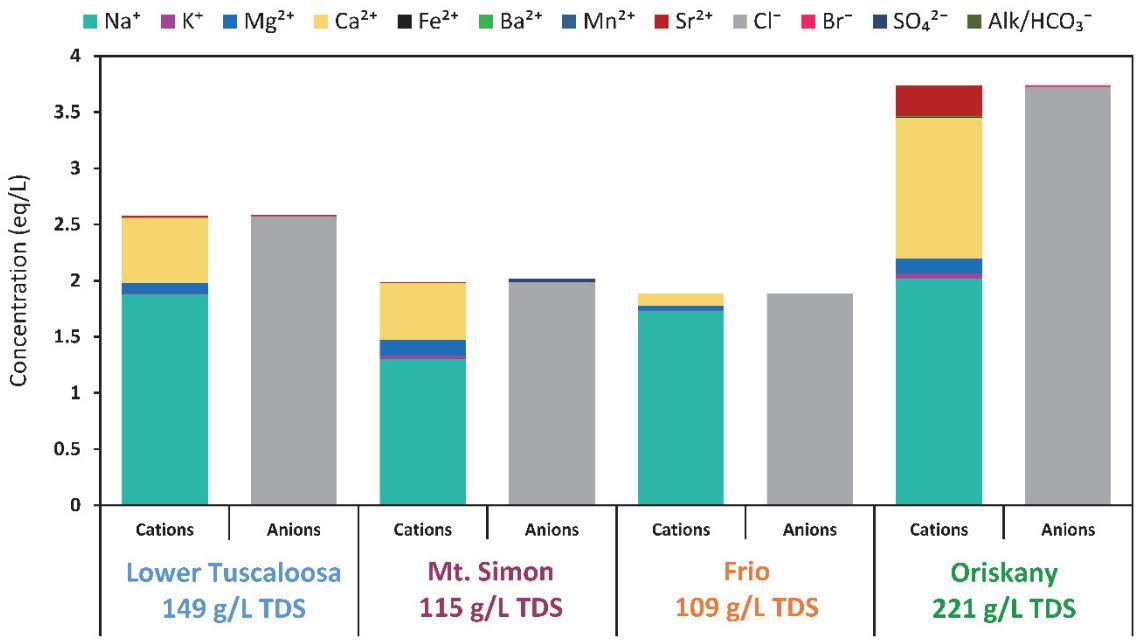


Figure 2. Composition (eq/ L) of four brines extracted from GCS-relevant formations in the US assuming complete disocciation. A more detailed report of ion speciation as calculated by Geochemist's Workbench v9 can be found with supplemental material. Data from Lu et al. (2012), Sass et al. (1998), Knauss et al. (2005), and Dilmore et al. (2008) for the Lower Tuscaloosa formation (Franklin County, MS), Mt. Simon formation (Decatur, IL), Frio formation (Liberty County, TX), and Oriskany formation (Indiana County, PA), respectively.

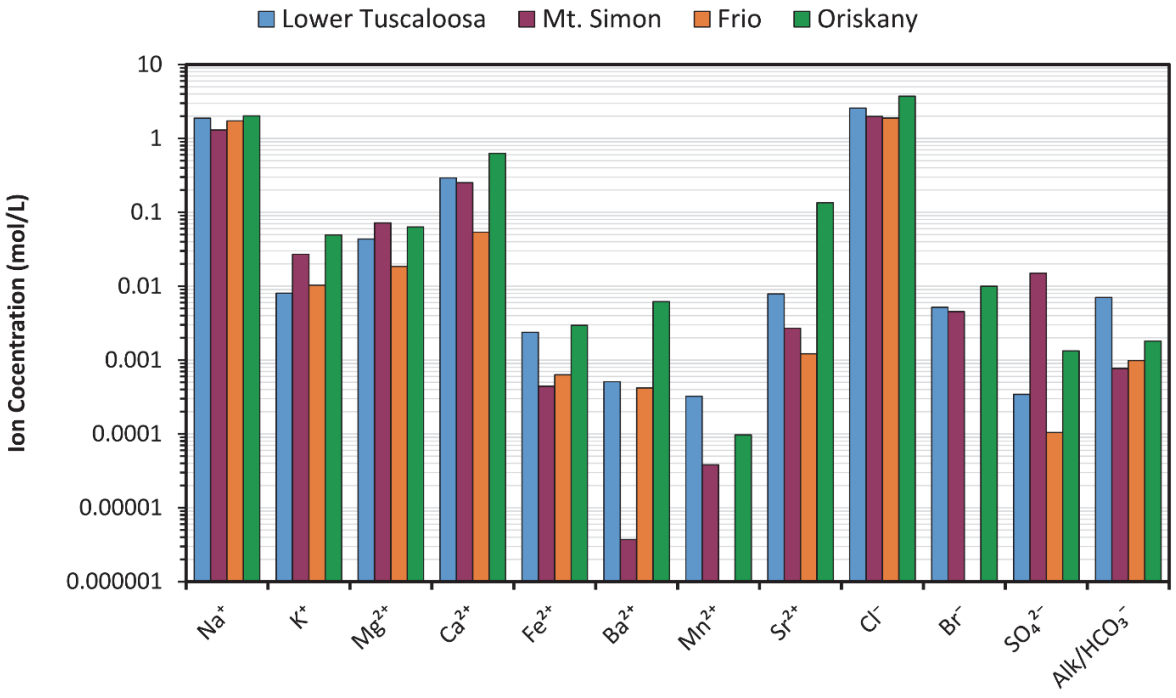


Figure 3. Composition of four brines produced from GCS-relevant formations, grouped by component and assuming complete dissociation. A more detailed report of ion speciation as calculated by Geochemist's Workbench v9 can be found with supplemental material. Data from Lu et al. (2012), Sass et al. (1998),

Knauss et al. (2005), and Dilmore et al. (2008) for the Lower Tuscaloosa, Mt. Simon, Frio, and Oriskany formations, respectively.

Note: y-axis is logarithmic scale.

3. Brine pretreatment

As shown in Figure 4, a requisite first step for dewatering a brine or desalinating seawater is the pretreatment of the saline brine to mitigate conditions that will lead to rapid deterioration in the performance of downstream processes (Alawadhi, 1997). There are four types of fouling that can adversely impact the performance of a brine dewatering processes: physical fouling, biological fouling, organic fouling, and chemical fouling (Fritzmann et al., 2007; Matin et al., 2011; Mi and Elimelech, 2010b; Sagle and Freeman, 2004; Sutzkover-Gutman and Hasson, 2010; Valavala et al., 2011). Physical fouling is the deposition of particulate matter by convective flow (Fritzmann et al., 2007; Shirazi et al., 2010). Biological fouling or simply biofouling is the adhesion and growth of microorganisms that have become strongly associated with a surface (Fritzmann et al., 2007; Matin et al., 2011). Organic fouling is the adsorption of organic material such as oil, proteins, alginate, or humic substances that cause a rapid decline in membrane productivity (Mi and Elimelech, 2008, 2010b; Sutzkover-Gutman and Hasson, 2010). Chemical fouling or scaling is the formation of inorganic precipitates on wetted surfaces in a dewatering process (Sheikholeslami, 2000; Shirazi et al., 2010). These fouling mechanisms impact many of the different dewatering processes; so pretreatment in a desalination/dewatering process will be needed to mitigate fouling induced increases in process heat/mass transfer resistances and system downtime for maintenance (Ettouney et al., 2002; Valavala et al., 2011; Vedavyasan, 2007). The level of pretreatment required prior to a dewatering process is inextricably linked to the quality of the brine to be dewatered with pretreatment tailored to the specific water chemistry of the brine for mitigation of the brine's fouling characteristics. Even if no brine dewatering process is used, a degree of pretreatment may be needed before reinjection to remove fine solids, organics, or scale forming ions that can reduce permeability in the disposal formation and potentially lead to well damage (Castillo et al., 2015; Cihan et al., 2015; Kharaka et al., 1997; Su et al., 2012).

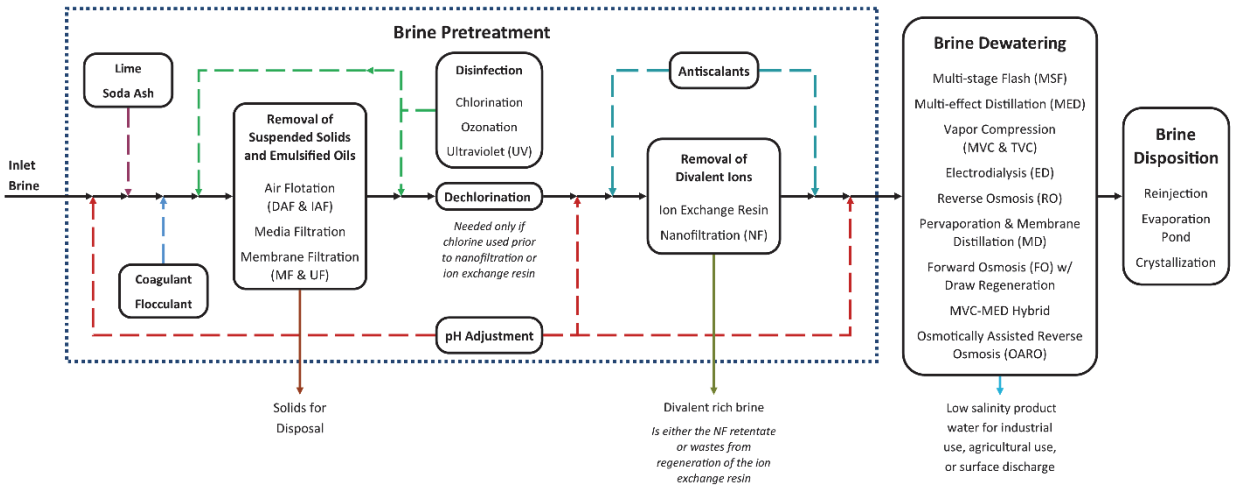


Figure 4. Flow diagram of a generalized brine dewatering process integrated with pretreatment and disposition of the brine. Dashed lines represents possible chemical additions to the brine. Due to oxidative instability, dechlorination is needed for some ion exchange resins and most nanofiltration/reverse osmosis

membranes used downstream of chlorination.

3.1. Disinfection

Disinfection of a saline brine may be a necessary pretreatment step prior to brine dewatering in order to deactivate any halophilic thermophilic anaerobes living within a brine (Canganella and Wiegel, 2014). Some bacteria are capable of living in oxygen deficient environments (anaerobic), in saline environments (halophilic), in nutrient deficient environments (oligotrophic), and at elevated temperatures (thermophilic) (Canganella and Wiegel, 2014; Ollivier et al., 1994; Willis et al., 1975). As these brines are significantly more deficient in organic matter than surface waters, the amount of microorganisms living in GCS brines are expected to be relatively low (Wolery et al., 2009); however, a number of different metabolic paths exist that would allow anaerobic halophiles to live within GCS brine and their presence in the brine may be indicated by metabolic byproducts that can include alcohol, organic acids, and hydrogen sulfide (Ollivier et al., 1994). Detailed analyses of microbial ecology in GCS brines is an important characteristic, deserving further study because colony forming microorganisms will impact the brine pretreatment approaches.

The most common disinfection approach is by chlorinating a saline brine. Chlorination does increase the total dissolved solids within a saline brine, and, if used before a reverse osmosis or nanofiltration membrane, the brine must be dechlorinated prior to membrane contact. Dechlorination is especially important when using thin film composite membranes having an aromatic polyamide or polypiperamide chemistry because amide bonds are vulnerable to chemical degradation in the presence of chlorine (Greenlee et al., 2009; Matin et al., 2011; Younos, 2005). Additionally, dechlorination may also be required prior to strong base cation exchange resin as the quaternary ammonium groups are vulnerable to oxidation (Neagu et al., 2000). Alternative disinfection strategies would include the use of ozonation or UV disinfection on a brine. Ozonation carries with it many of the disadvantages that chlorination does, as it will also degrade amide bonds and has shown the tendency to promote biofouling from the breakdown of higher molecular weight organic matter. One benefit of ozonation is the reduced formation of disinfection byproducts (Matin et al., 2011). Apart from chemical additions for disinfection, UV disinfection is another method for deactivation of microorganisms that can contribute to biofouling. The effectiveness of UV disinfection is reduced in waters that have high concentrations of humic substances, as humic substances strongly absorb the 254 nm wavelength used for UV disinfection (Edzwald and Haarhoff, 2011; Matin et al., 2011). Because saline formations targeted GCS are generally regarded to have minimal amount of organics present (Wolery et al., 2009), interference by humic substances will most likely not impact application of UV disinfection.

3.2. Removal of suspended solids and oils

One critical objective in the pretreatment of a brine fed to a dewatering process is the removal of suspended solids, emulsified oils, and microorganisms, as these all contribute to fouling within a dewatering process. Part of suspended solids removal may entail the addition of coagulant to promote the aggregation and settling of solid matter out of the solution to be dewatered. Commonly added coagulants are salts of aluminum or iron, including iron (III) chloride, iron (II) sulfate, aluminum chloride, aluminum sulfate, and aluminum potassium sulfate

(alum), as well as low molecular-weight (<500,000 kDa) cationic polymers such as dimethyldiallylammonium chloride or polyamines (Edzwald and Haarhoff, 2011; Greenlee et al., 2009; Tatsi et al., 2003; Valavala et al., 2011; Younos, 2005). Coagulants aggregate colloids by neutralizing negative surface charges, which allows aqueous colloidal and particulate matter to stick together. In general, iron or polymer coagulants are preferred to aluminum coagulants because of aluminum's higher solubility in a saline brine with a propensity to be carried beyond steps that remove the suspended solids and onto a dewatering process where the aluminum can concentrate and cause fouling, such as the formation of aluminum silicate (Dow; Edzwald and Haarhoff, 2011; Gabelich et al., 2007; Greenlee et al., 2009; Shih et al., 2006). Care should be exercised if a coagulant is required because the addition of inorganic salts will increase the concentration of an ionic species that could promote the inorganic fouling of a dewatering process. To enhance colloid aggregation a flocculant can be added. Flocculants are high molecular weight water soluble polymers with an anionic or non-ionic functionality (Dow; Greenlee et al., 2009).

3.2.1. Air flotation

Induced air flotation (IAF) and dissolved air flotation (DAF) are techniques that promote the removal of small suspended solids or oil droplets that adhere to the surface of rising air bubbles, forming a foam or a froth of impurities on the top of a water's surface, which can be skimmed off (AQWATEC, 2009; Edzwald, 2010; Igunnu and Chen, 2012; Rubio et al., 2002; Valavala et al., 2011). IAF and DAF differ in how air bubbles are introduced into a brine. IAF uses an air sparger combing with mechanical agitation while DAF relies on the depressurization of a brine that had been supersaturated by high pressure air (Rubio et al., 2002). The minimum size of a particulate that can be removed by DAF is 25 μm; however, this can be enhanced by the addition of a coagulant, and particles as small as 3 μm can be removed (AQWATEC, 2009; Igunnu and Chen, 2012). Flotation is often used as a primary means of clarifying a surface water as part of centralized distribution water treatment systems and can be applied for the removal of a variety of materials within a water stream requiring pretreatment, including algae, colloids, particles, proteins, and oils droplets (Edzwald, 2010; Igunnu and Chen, 2012; Rubio et al., 2002). The separation of particles in air flotation can be enhanced by the addition of cationic coagulants because air bubbles naturally have a negative charge, like small suspended particles (Edzwald, 2010); however, care should be taken with air flotation techniques because these brines will be anoxic and the introduction of air into the brine can cause oxidation and/or induce precipitation.

3.2.2. Media and membrane filtration

Filtering a brine prior to dewatering can be done by either granular media filtration or membrane filtration. Media filtration uses various types of media including anthracite, fiber balls, pumice, sand, garnet, gravel, and walnut shells either singularly or in combination (Çakmakce et al., 2008; Greenlee et al., 2009; Igunnu and Chen, 2012; Valavala et al., 2011). In media filtration, particulates down to 0.1 μm in size adsorb onto the surface of the media or other material adsorbs onto the media. Media filtration, preempted by addition of a coagulant and/or flocculant and followed by chlorination for disinfection, is typically considered to be the conventional pretreatment system for seawater desalination (Greenlee et al., 2009; Lattemann et al., 2013). Granular media filters are flexible in their operation and can be operated by gravity

feed while open to the atmosphere or pressurized (Noyes, 1994); however, replacement/regeneration of the media may be necessary for sustained operation.

Membrane filtration has been examined as an alternative to media filters as pretreatment for seawater desalination. These membrane based pretreatment processes are called microfiltration (MF) and ultrafiltration (UF). MF and UF largely differ by the size or molecular weight of particles that they can remove, using porous membranes for the removal of emulsified organics and suspended solids by size exclusion (Fane et al., 2011; Igunnu and Chen, 2012). MF membranes have pore sizes ranging from 0.1 to 10 μm, while UF membranes have pore sizes ranging from 0.001 to 0.1 μm and molecular weight cutoffs of 300-500,000 Da (Chen et al., 2011). MF and UF are not selective to dissolved solutes; therefore, the large osmotic pressures of extracted GCS brines do not affect the required driving pressure for MF and UF processes which are typically 0.7 to 1.7 bar for MF and 1.7 to 10.1 bar for UF (Chen et al., 2011). For management of extracted GCS brines MF and/or UF can be used to remove turbidity and/or suspended solids. One advantage of membrane technologies compared to conventional pre-treatment is the lack of coagulant requirements, which may simplify subsequent pretreatment requirements with regards to antiscalant additions. Comparative studies of membrane pretreatment techniques versus conventional media filtration pretreatment techniques have concluded that the higher quality permeate of membrane filtration allows for improved productivity of the subsequent reverse osmosis stage and reduced space requirements (Pearce, 2007; Valavala et al., 2011; Vedavyasan, 2007).

3.3. Scale mitigation

Scaling occurs from the precipitation of low solubility dissolved solids onto the wetted surfaces in a dewatering process and will 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). In addition to precipitation of low solubility salts dewatering processes operating at high recovery may become sufficiently concentrated such that moderately soluble salts (i.e. sodium chloride, sodium sulfate, and calcium chloride) will precipitate and be similarly detrimental to a dewatering processes as scale that forms from less soluble salt.

Because evaporative processes are reliant upon large heat transfer surfaces, they will be affected by scaling via a reduction of the overall heat transfer coefficient, requiring a larger temperature gradient to obtain the same amount of heat transfer. An increase in the required temperature gradient leads to additional irreversible entropy generation and lowers the overall process efficiency. 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 (Budhiraja and Fares, 2008; El Din et al., 2002). Two bicarbonate salts of concern would be magnesium bicarbonate and calcium bicarbonate because decomposition of the bicarbonate anion forms a scale of magnesium hydroxide and calcium carbonate respectively (El Din et al., 2002).

Contrastingly, membrane processes typically operate at lower temperatures and would be less impacted by thermal decomposition of salts on membrane surfaces; however, external concentration polarization will play a role in the scaling of a membrane. External concentration polarization (ECP) is the accumulation of dissolved solutes and suspended particles at the selective barrier of a membrane. ECP is a mass transport boundary layer developed by the permeability of the membrane to water and its relative impermeability to dissolved salt and/or suspended particles. Water transported across a membrane causes a decrease in the local water concentration at a membrane's selective layer, generating an increase in the local concentration of dissolved solutes and suspended particles. For low solubility dissolved solutes, this increase in the local concentration will cause solids to precipitate in the external boundary layer close to or on the surface of a membrane (Shirazi et al., 2010). If present, suspended particles within a brine will also serve as nucleation sites for crystal growth (Sheikholeslami, 2000).

In addition to ECP, reverse draw solute permeation occurring in forward osmosis may also impact the formation of scale on a membranes surface. Reverse draw solute permeation refers to the diffusion of draw solutes in a forward osmosis process from the high osmotic pressure draw solution into the feed. Depending on the draw solute used, its permeation can affect the pH and/or ion concentrations at the selective layer interface within the external boundary layer and could facilitate the formation of scale on the selective layer. For example, if using an ammonia-carbon dioxide based draw solution, the reverse permeation of a scale forming anion, such as carbonate, can alter the concentration of ions in the external boundary layer of the feed solution. Ultimately, this can cause the precipitation of low solubility salts. Additionally, the diffusion of ammonia through a membrane's selective layer as an uncharged species, and upon speciation into ammonium, will increase the feed solution's pH and can cause an otherwise soluble concentration of a salt to precipitate on a membrane surface (Li et al., 2015).

3.3.1. Mitigation by adjusting water chemistry

As the occurrence of scaling from brine dewatering may be unavoidable, one route to mitigate scaling is by adjusting the water chemistry to promote the precipitation of low solubility salts. Lime and soda ash are common and long used additives to promote the softening of municipal and industrial water supplies by promoting the precipitation of calcium carbonate and magnesium hydroxide (Dow; Greeley and Bartow, 1916). These precipitates can be removed with other suspended solids via the processes discussed previously. Upon removal of the precipitated solids, the water chemistry can be readjusted to stabilize the residual concentration of the low solubility dissolved salts (Ayoub et al., 2014; Gabelich et al., 2007). In some instances, scaling can be mitigated by pH adjustment (i.e. calcium carbonate). Decreasing the pH of a brine by acid addition enhances calcium carbonate solubility (Dow; Fritzmann et al., 2007; Greenlee et al., 2009).

In addition to lime softening and pH adjustment, another chemical addition that may be relevant to GCS brines because of their high salinities is the addition of antiscalants. Antiscalants mitigate fouling by inhibiting crystallization and precipitation of dissolved salts by distorting the crystal formation by binding with cations on the crystal surface (Greenlee et al., 2010; Neofotistou and Demadis, 2004; Tang et al., 2008). Antiscalant can be used to control scale formation in the form of divalent cation salts having sulfate and/or carbonate, and typically these antiscalants are low molecular weight anionic polymers similar to polyacrylic acid,

organophosphonates, or polyphosphates that can complex with divalent cations (Amjad, 1996; Budhiraja and Fares, 2008; Greenlee et al., 2009; Greenlee et al., 2010; Hasson et al., 2011; Shih et al., 2006; Tang et al., 2008). Of the three listed, polyphosphates have become less prevalent because polyphosphate degradation can produce phosphates that can then cause scaling by the formation of divalent cation phosphate precipitates (Amjad, 1996; Greenlee et al., 2009). The use of an antiscalant needs to be balanced against the use of a coagulant because the cationic nature of a coagulant will compete with antiscalants via attraction between negatively charged antiscalants and positively charged coagulants reducing their effectiveness. The aggregation and sorption of an antiscalant and coagulant could also cause fouling (Kim et al., 2009; Shih et al., 2006). The need of antiscalants may preclude the use of coagulants; therefore, pretreatment technologies such as air flotation and media filtration may require coagulants for the removal of small particles may be unsuitable techniques for GCS brines.

In addition to scale formation by precipitation of low solubility salts, silica scale formation is another potential cause of inorganic fouling that may require mitigation. Silica fouling is not as easily mitigated compared to fouling by inorganic salts because the silica precipitates are amorphous (Demadis et al., 2005; Neofotistou and Demadis, 2004). Anionic antiscalants such as those used for mitigating carbonate and sulfate scaling are not applicable to silica control (Demadis et al., 2005; Hasson et al., 2011). Instead bench studies investigating suitable antiscalants for controlling silica fouling have used polyamines such as polyethyleneimine or polyaminoamide dendrimers blended with anionic polymer such as carboxymethylinulin or polyacrylate (Demadis et al., 2005; Demadis and Stathoulopoulou, 2006; Mavredaki et al., 2007; Neofotistou and Demadis, 2004).

3.3.2. Ion exchange resins

Ion exchange is the exchange of a cation or anion in solution with a cation or anion associated with a charged functional group on a cross-linked polymer (Clifford, 1999; Dow; Vermeulen et al., 1983). An ion exchange resin can be classified as one of four types: a strong acid cation exchange resin, a weak acid cation exchange resin, a weak base anion exchange resin, or a strong base anion exchange resin. The differences amongst the various resins originate from the main functional group which imparts the functionality to the ion exchange resin. Weak acid/weak base ion exchange resins have an inherent pH sensitivity, and only function as an ion exchanger above the pK_a of a weak acid cation exchange resin's functional group or below the pK_a of a weak base anion exchange resin's functional group. Strong acid cation exchange resins and strong base anion exchange resins have broader ranges of operation and have been used in tandem for the production of deionized water strictly by ion exchange (Clifford, 1999; Fritzmann et al., 2007; Weiss, 1966). Besides water deionization, ion exchange resins have been studied for the removal of divalent ions by the exchange of dissolved calcium and magnesium with sodium and dissolved sulfate by chloride (Klein et al., 1964; Smith and SenGupta, 2015, 2016; Vermeulen et al., 1983). The removal of calcium, magnesium, strontium or sulfate ions would be applicable to GCS brines if not for the high concentration of sodium and chloride in these GCS extracted brines. High concentrations of sodium and chloride ions are detrimental to selectivity because ion exchange occurs via chemical equilibrium between ions within a solution and ions associated with charged sites on the resin. As the concentration of exchanging ions increases in the feed solution, the selectivity of the ion exchange resin decreases (Smith and SenGupta, 2016);

409 therefore, the viability of softening via cation exchange depends on the concentrations of calcium
410 and sodium ions in the brine and the selectivity of the chosen cation exchange resin. In
411 considering anion exchange, given that the concentration of chloride can be 100–1000 times
412 greater than the concentration of sulfate (Figure 3), anion exchange resins will likely be of
413 limited usefulness for removal of sulfate ions prior to the dewatering stages for GCS brines. One
414 advantage of ion exchange, when applied to lower salinity brines where it has successfully been
415 employed for softening before dewatering, is the concentrate of the dewatering process could
416 then be used for regeneration of the resin (Klein et al., 1964; Smith and SenGupta, 2015, 2016;
417 Vermeulen et al., 1983).

418 ### 3.3.3. Nanofiltration

419 Nanofiltration (NF) is a membrane separation process juxtaposed, in terms of selectivity,
420 between ultrafiltration and reverse osmosis. The most common use of NF is as an alternative to
421 lime softening for the treatment of groundwater to removed hardness and color (Bergman, 1995).
422 NF membranes are characterized by having high selectivity to a divalent salts such as
423 magnesium sulfate while being less selective to sodium chloride. Most NF membrane have a
424 strong negative surface charge with charge repulsion considered to be a large contributor to a NF
425 membrane's rejection properties. The repulsion of negative charges means that most NF
426 membranes are more selective to salts having divalent anions (such as sulfate and carbonate)
427 (Fane et al., 2011; Van der Bruggen and Vandecasteele, 2003). Monovalent salts that permeate a
428 NF membrane means that these monovalent salts do not exert potentials across it; therefore, NF
429 membranes can be used to remove water and monovalent ions from a brine while retaining
430 divalent ions. Despite this advantage, salts that an NF membrane is largely impermeable to will
431 be affected by concentration polarization. An increased concentration feed solutes in contact
432 with a NF membrane's selective layer can contribute to membrane scaling (Le Gouellec and
433 Elimelech, 2002; Van der Bruggen et al., 2008). In addition to scaling, NF can also be adversely
434 impacted by other types of fouling similar to reverse osmosis (Kim et al., 2011; Van der Bruggen
435 et al., 2008). In seawater desalination, NF has been evaluated to pretreat seawater for removal of
436 hardness prior to distillation (specifically multi-stage flash) (Al-Rawajfeh et al., 2012; Al-Sofi et
437 al., 1998). Because of the aforementioned inverse temperature-solubility relationship, removal of
438 hardness ions permits for high brine temperatures in a distillation system (Al-Rawajfeh et al.,
439 2012). NF has also been applied as pretreatment to reverse osmosis desalination systems;
440 however, since NF membranes typically have high rejection of both divalent cations and anions
441 along with typical operation at comparable temperatures to reverse osmosis there appears to little
442 advantage in applying NF as a preatrement to RO processes (Zhou et al., 2015). One advantage
443 of NF in the case of when one only needs to pretreat and reinject the extracted brine, is that NF
444 membranes can remove scale forming divalents keeping them from scaling within the receiving
445 formation (Kharaka et al., 1997; Su et al., 2012).

446 ## 4. Minimum work of dewatering/desalination

447 Brine pretreatment is important for sustained process productivity; however, the pretreatment
448 of the brine will likely consume significantly less energy than the steps required to separate
449 water from a brine. For example, the pretreatment steps discussed above typically have pressure
450 drops of 1-10 bar, whereas the osmotic pressure of the brines discussed in Section 2 is 100-300

bar. This excludes any increase in a brines osmotic pressure that may occur from the addition of pretreatment chemicals and/or the removal of water from the brine. A brine's osmotic pressure is related to the Gibbs free energy of mixing that is in turn linked to the theoretical minimum amount of useful work (kWh/m^3) required to dewater that saline brine in the limit of zero water removal at constant temperature in a reversible process. The theoretical minimum amount of useful work required to dewater a saline brine is independent of a process's operating principle (i.e. evaporative, membrane, electrochemical, etc.) (Elimelech and Phillip, 2011; Mistry and Lienhard, 2013; Mistry et al., 2011). This value is dependent on two primary attributes: 1] the concentration of solutes within the initial brine and 2] the water recovery (Elimelech and Phillip, 2011; Mazlan et al., 2016; Mistry and Lienhard, 2013; Semiat, 2008; Thiel et al., 2015).

The ELECNRTL method within AspenPlus V8.4 (Aspen Technology Inc., Bedford, MA, USA) was used to model an ideal reversible process and to calculate the Gibbs free energy of the three streams encountered in processes separating water from a brine (i.e. 1] the inlet or feed, 2] the reject, retentate or concentrate, and 3] the product or permeate). The difference in the Gibbs free energy of the products with respect to the feed was used to calculate the minimum useful work required to dewater a brine as a function of water recovery. Data for the selected GCS brines and representative saline water sources show the minimum useful work required per volume of pure water separated (minimum work of desalination) ($w\square_{min}/v\square_{p}$) (Figure 5a), the minimum useful work required per volume of original brine ($w\square_{min}/v\square_{b}$) (minimum work of dewatering) (Figure 5b), and the mass of precipitated sodium chloride normalized by the original mass of dissolved solids are shown as a function of water recovery fraction (Figure 5c). Here, the interconnectedness between salt concentration and the minimum useful work of separation can be seen in Figure 5a from the fact that the Frio formation brine (109 g/L) requires roughly three times more work than seawater (35 g/L).

The need for efficiency when dewatering a high salinity brine can be illustrated by comparing the minimum useful work to dewater these brines to the literature values for the actual energy consumption of pretreatment processes. For example, a conventional pretreatment process consisting of flocculation followed by a single stage media filter requires 0.015-0.10 kWh/m^3 of pretreated brine, where the relatively large variability in required energy is dependent on the flocculant mixing technique. A more energy intensive pretreatment consisting of dissolved air flotation followed by membrane filtration (i.e. ultrafiltration or microfiltration) requires 0.250 kWh/m^3 of pretreated brine. If a brine dewatering process was assumed to operate at 50% water recovery, then the required energy per m^3 of product water would be doubled in comparison to the required energy of brine pretreatment per m^3 of original brine (Lattemann et al., 2013). By changing the reference volume from the initial volume of brine needing pretreatment to amount of water generated, at 50% recovery the volume is halved; therefore, at 50% recovery a brine pretreatment using dissolved air flotation followed by membrane filtration requires 0.5 kWh/m^3 of **product water** (Lattemann et al., 2013). Comparing the energy demand of pretreatment against the data shown in Figure 5a, the work to pretreat the brine is only greater than the theoretical **minimum** work of desalination at 50% recovery for a brackish water feed of 2 g/L sodium chloride concentration, ~0.05 kWh/m^3 of product water. The 0.5 kWh/m^3 of product water at 50% recovery is slightly less than half the **minimum** work of desalination for seawater of 35 g/L sodium chloride concentration at 50% recovery, ~1.06 kWh/m^3. Compared to the GCS brines, the energy required for pretreatment is 13.3%, 13.1%, 9.3%, and 5.6% of the **minimum**

work of desalination at 50% recovery for the Frio, Mt. Simon, Lower Tuscaloosa, and Oriskany formations respectively.

In order to build intuition regarding the case of a pure sodium chloride brine at a salinity of 2 mol/L (117 g/L), Figure 6 shows the following parameters of interest as a function of water recovery fraction: the minimum useful work of separation per volume of pure water (w_{min}/v_p), the minimum useful work of dewatering per volume of inlet brine (w_{min}/v_b), the molarity of the concentrated brine, and the weight percentage of halite (i.e. the mass precipitated sodium chloride divided by the initial mass of total dissolved solids).

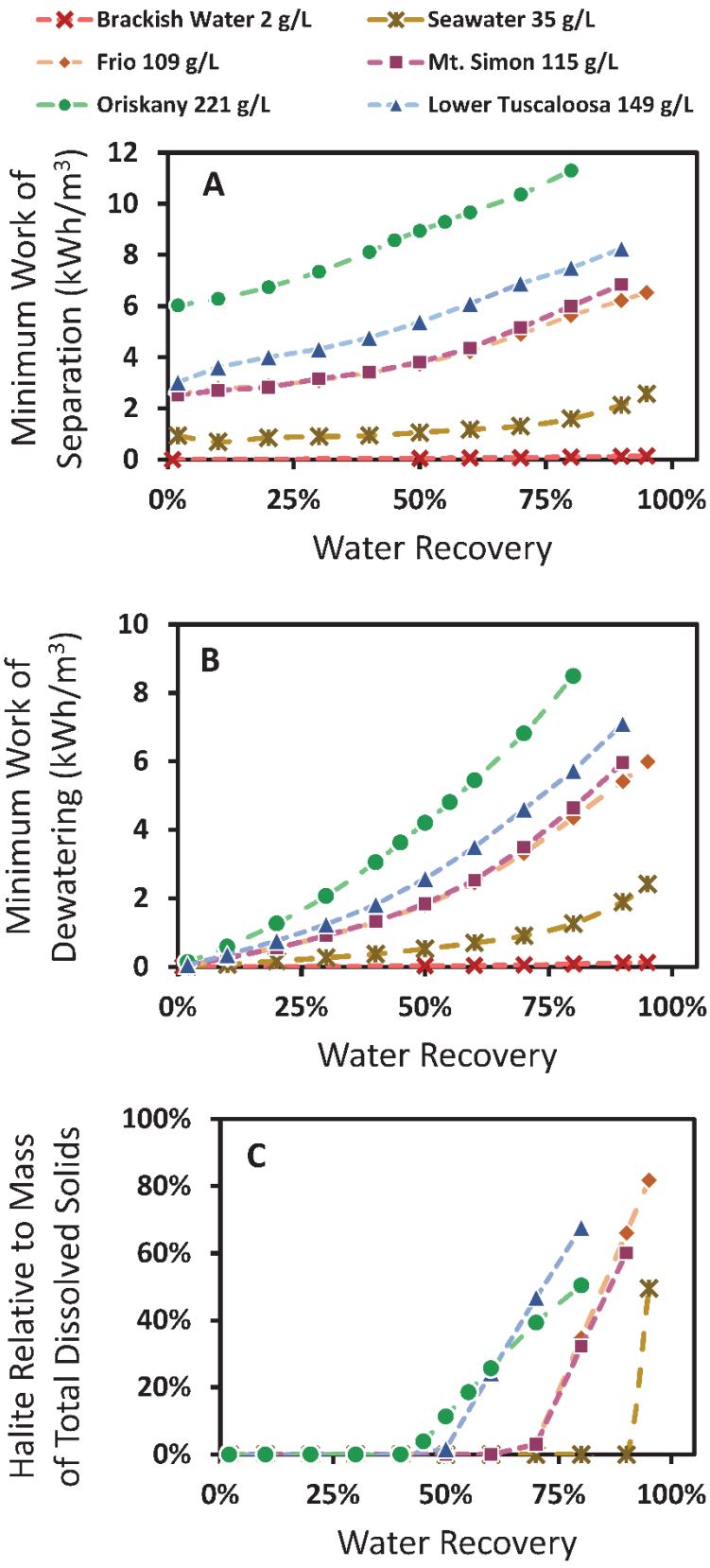


Figure 5. (a) Minimum work required to produce a m^3 of pure water (w_{min}/v_p), (b) minimum work required per m^3 of original brine (w_{min}/v_b), and (c) mass of precipitated halite ($NaCl_{(s)}$) normalized by original mass of total dissolved solids, as a function of the water recovery fraction for six different brines. Calculations were done at 20°C using the ELECNRTL method within AspenPlus V8.4.

Note that 1 kWh/m^3 = 36 bar

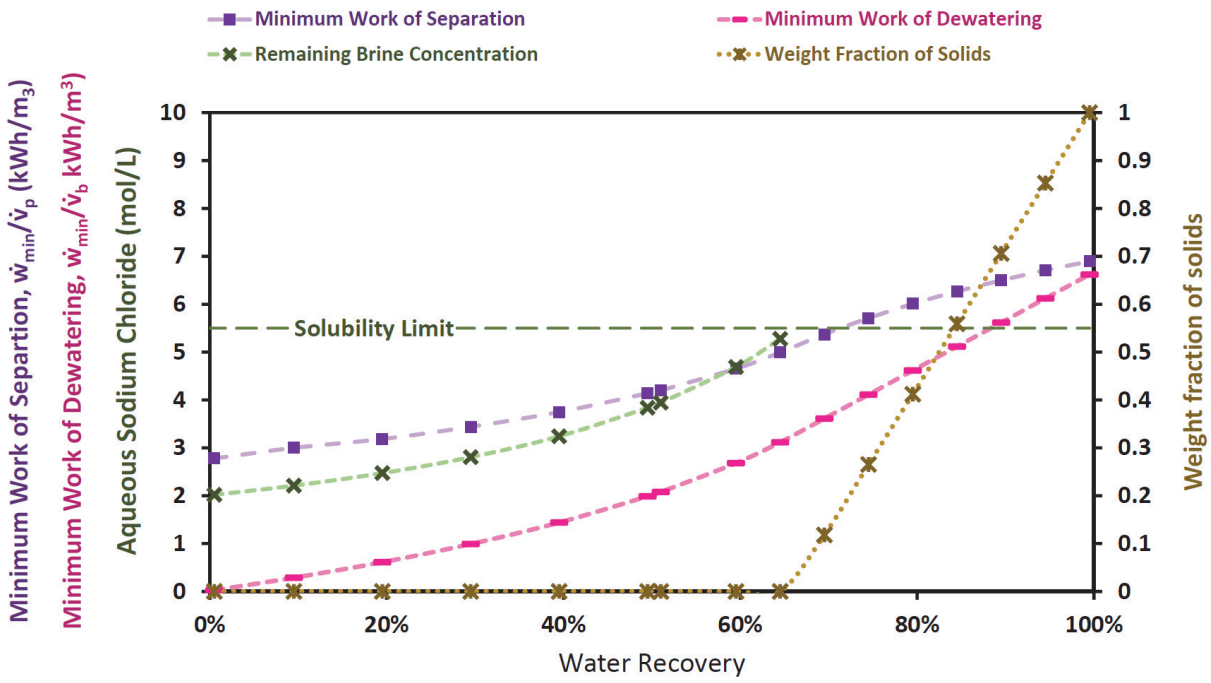


Figure 6. Minimum work required to produce a m^3 of pure water ($w\square_{min}/v\square_p$), minimum work of dewatering per m^3 of inlet brine ($w\square_{min}/v\square_b$), remaining brine concentration, and solid weight fraction for a 2 mol/L (117 g/L) sodium chloride solution as a function of the water recovery fraction. Calculations were done at 20°C using the ELECNRTL method within AspenPlus V8.4. ***Note that 1 kWh/m^3 = 36 bar***

For brine extraction to reduce formation pressure, it would generally be desirable that the produced brine be as concentrated as possible before final disposition; however, as shown in Figure 5 and Figure 6, there are unavoidable useful work requirements associated with dewatering a brine for volume reduction. As shown in Figure 6, the amount of useful work increases significantly if all the water in the brine is removed and solids are all that remain. For example, a 117 g/L brine will at minimum require 2.0 kWh/m^3 to reduce the volume of the original brine by 50%. This equates to a power consumption of approximately 0.75 MW, assuming that the volume of produced brine is equal to 50% of the volume of the 600,000 kg/h of sequestered supercritical CO_2 captured from a 550 MW power plant (Black, 2013); however, when completely dewatering the brine (i.e. 100% water recovery), the minimum work required per m^3 of original brine increases by over threefold, from 2.0 kWh/m^3 to 6.6 kWh/m^3 of original brine produced. This will increase the minimum power consumption from 0.75 MW to 2.5 MW for a 550 MW power plant. This is the case for a hypothetical process with no irreversible generation of entropy, but due to irreversible entropy generation, the actual amount of power consumption in commercially-available desalination processes is often an order of magnitude larger than the theoretical minimum.

5. Dewatering/desalination technology

5.1. 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 water vapor, 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 (Fane et al., 2011; Greenlee et al., 2009; Lonsdale, 1982).

Characteristically, an evaporative process requires 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. Several 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_{H_2O} at 100°C (Semiat, 2008; Smith et al., 2005). 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 $kWh/m^3_{liqH_2O}$) 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 9 kWh/m^3 above the minimum useful work needed to separate pure water from a brine. The 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 (Mistry et al., 2011; Nafey et al., 2008). 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 increases from 2.0 kWh/m^3 or 6.6 kWh/m^3 of original brine produced to 20 kWh/m^3 or 66 kWh/m^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 power plant using carbon capture and GCS. One further issue associated with evaporative technologies is corrosion. Corrosion may be increasingly problematic for highly saline brines because the 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., 2001; Sommariva et al., 1999).

5.1.1. Multi-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 with 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 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 7 (Darwish et al., 2006).

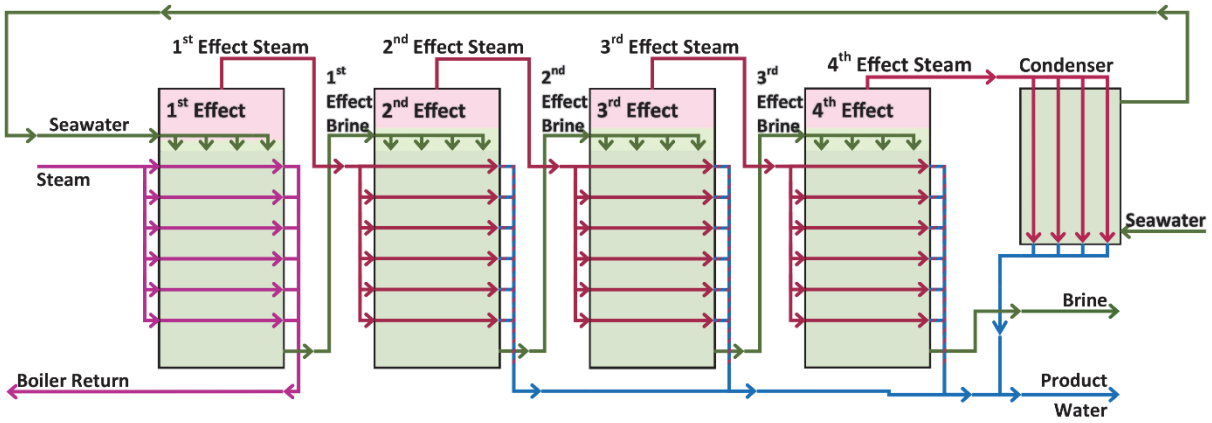


Figure 7. Principle of the MED process. Redrawn from Darwish et al. (2006).

5.1.2. 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 a dominant technology for the desalination of seawater because many MSF plants have outlived their design lifetime; however, MSF's market share has decreased due to competition from more energy efficient membrane technologies and improvements in the MED process (Greenlee et al., 2009; Lattemann et al., 2013; Sommariva et al., 1999). A diagram of the MSF process is shown in Figure 8 (El-Dessouky et al., 1998; El-Dessouky et al., 1995).

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 hence 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; however, the CO_2 emissions from the combustion of these fossil fuels would ultimately be assigned to the power plant at which CO_2 capture occurred. As such, there is

likely limited applicability of MED and MED processes to the dewatering/desalination of produced GCS brines.

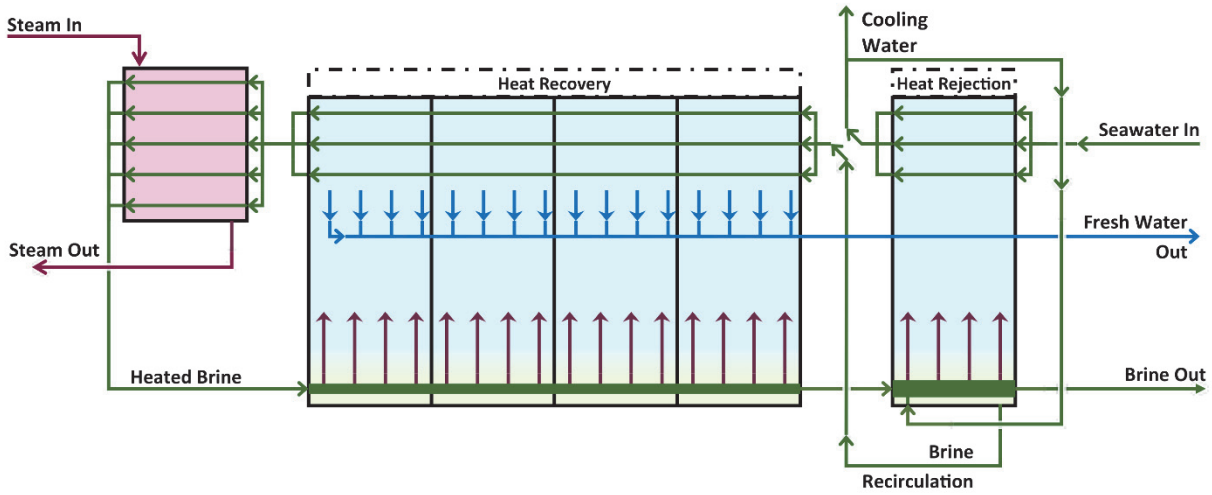


Figure 8. Principle of the MSF process. Redrawn from El-Dessouky et al. (1995) and El-Dessouky et al. (1998).

5.1.3. 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 (Hayes and Severin, 2012; Koren and Nadav, 1994; 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 this effect, water vapor from a preheated brine is 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 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 principle 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 the 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 driven by electricity only (Igunnu and Chen, 2012; Shaffer et al., 2013). The electricity to drive the MVC process can come either from local solar power and/or from the power plant at which the CO_2 was originally captured. For this reason, MVC is likely to be of greater interest than TVC, MED, or MSF in GCS applications.

The MVC process has been implemented for the desalination of seawater and the dewatering of oil/gas produced waters and so some data for the energy demands of this process are available. By calculating the minimum work of separation for these brines, it becomes possible to determine the 2nd law efficiency for these processes. As such in **Table 1**, the values for 2nd Law efficiency for actual operating MVC systems varies between 5% and 10%: Koren and Nadav (1994) and Veza (1995) (Hayes and Severin, 2012). If considering a MVC having an efficiency of roughly 10%, which is consistent with the data reported by Koren and Nadav (1994) and Veza (1995), then approximately 33 kWh per m^3 of permeate water would be required to dewater a 117 g/L brine at 65% water recovery (**Figure 6**).

Table 1. Comparison of reported values on energy consumption for MVC systems to theoretical minimum calculated at 20°C using the ELECNRTL method within AspenPlus V8.4. Data from Koren and Nadav (1994) presents averaged values from two reported trials.

Inlet Brine Salinity (g/L)	Outlet Brine Salinity (g/L)	Recovery	Energy Consumption (kWh/m^3)	Theoretical Minimum (kWh/m^3)	2nd Law Efficiency	Reference
38.7	65.9	42 %	11.5	1.12	9.7%	Veza (1995)
56±1	83.1±0.8	32.5±0.5 %	13.6	1.54	11.3%	Koren and Nadav (1994)
49±10	187±29	72.5%	40.3	2.1± 0.5	5.2±1.2%	Hayes and Severin (2012)

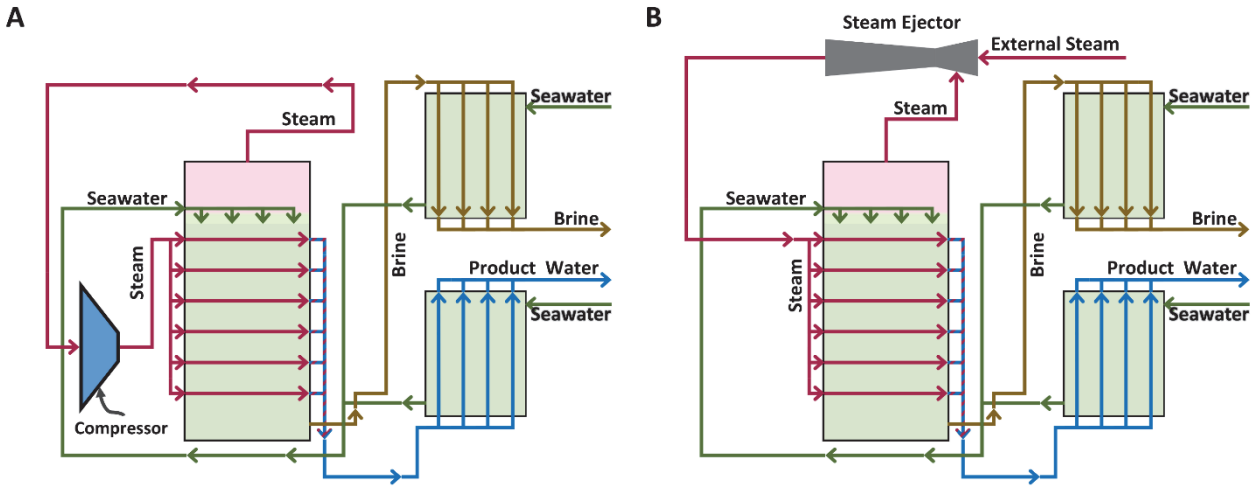


Figure 9. Principle of a) mechanical vapor compression and b) thermal vapor compression distillation processes. Redrawn from Miller (2003).

5.2. Membrane processes and technology

Membrane technology can be applied to achieve the goal of brine management where specific membranes 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 process; 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 that comprises only the material that crosses the membrane; however, in some membrane processes, such as forward osmosis or direct contact membrane distillation, the permeate that crosses the membrane is mixed with a solution that flows along the permeate side of a membrane (Alkhudhiri et al., 2012; Lonsdale, 1982; Van der Bruggen and Luis, 2015).

The 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). The flux of water vapor is typically driven by the transmembrane vapor pressure (Alkhudhiri et al., 2012; Mistry et al., 2011; Shao and Huang, 2007). 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 the 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 (Chen et al., 2011; McCutcheon et al., 2006). 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 (Fane et al., 2011; Paul, 2004; Wijmans and Baker, 1995). 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.

5.2.1. Reverse osmosis

Reverse osmosis (RO) is the most selective of the four established hydraulic pressure driven membrane separation techniques, which include the aforementioned microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF). RO refers to both the phenomena of driving water from a solution across a semi-permeable membrane by applying a hydrostatic pressure to it that exceeding the osmotic pressure of a solution from which water is being removed and the process of desalination technology capable of removing all dissolved salts within a solution by a reverse osmosis behavior (Chen et al., 2011; Dow; Fane et al., 2011; Lonsdale, 1982). RO has more recently received attention for its expanded application to the concentration of some of the lower

salinity, GCS 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 an osmotic pressure difference across the semi-permeable membrane. The osmotic pressure of a solution is its potential to draw pure solvent into it if the solution were separated from pure solvent by perfectly selective semi-permeable membrane (Wilson and Stewart, 2013). An osmotic pressure is only exerted across a membrane by solutes to which the membrane is impermeable (Lee et al., 1981). The most accurate calculation of 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. (1) (Hamer and Wu, 1972; Wilson and Stewart, 2013). As shown in Figure 10, as the concentration of solutes increases in solution, so does the osmotic pressure of that solution. Figure 11 shows the streams common to a hydraulic pressure driven membrane process.

$$\pi = -\frac{RT}{v_w}\ln(a_w) = \varphi\sum_{i\neq w} m_i \rho_w RT \qquad (1)$$

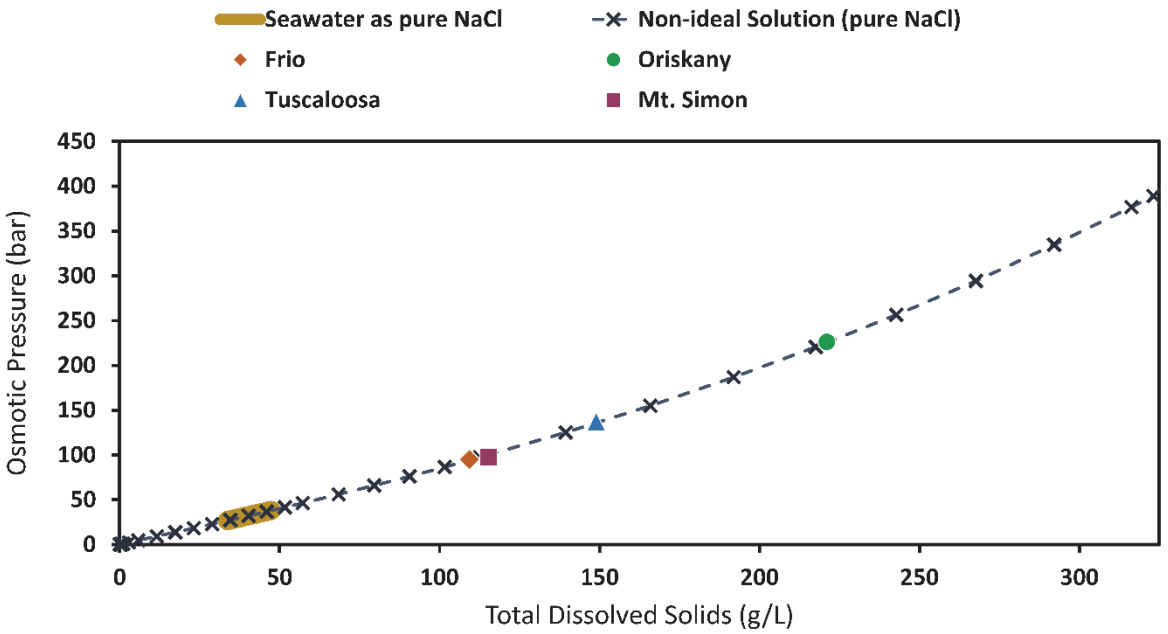
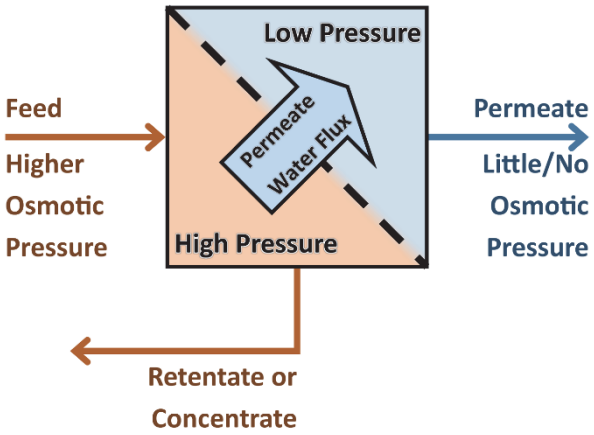


Figure 10. Osmotic pressure of a sodium chloride solutions calculated using osmotic coefficients compiled by Hamer and Wu (1972) at 25°C. Also shown are the osmotic pressures of four GCS-relevant, extracted brines, using the activity of water calculated by Geochemist's Workbench v9 with the thermo_phrqpitz database. Gold line represents the range of global seawater concentrations (Dow).

Figure 11. Streams common to membrane separation. Dashed line represents the semi-permeable membrane.



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 (Elimelech and Phillip, 2011; Greenlee et al., 2009). RO membranes typically operate at pressures less than 82.8 bar (1200 psi) (Bourcier et al., 2011; Dow). 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 10, have significantly 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 a brine can only be reduced in volume to the point at which its osmotic pressure is equal to the applied hydraulic pressure (Aines et al., 2011; Greenlee et al., 2009). At this point, the net driving force across reverse osmosis membrane is zero; therefore, water will cease to permeate across the membrane (Lonsdale, 1982). If further reduction in volume is desired and/or if the initial osmotic pressure of the brine is greater than the allowed applied hydraulic pressure, then RO membranes must be coupled with another process that reduces the concentration of the feed solution entering the RO stage of a multi-stage process.

5.2.2. Membrane distillation and pervaporation

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

719 (Alkhudhiri et al., 2012); while, pervaporation membranes are dense and can be tailored to have
720 a selective affinity for components of feed stream (Shao and Huang, 2007). Pervaporation
721 membranes designed for desalination are hydrophilic and have an affinity for water (Liang et al.,
722 2014; Zwijnenberg et al., 2005).

723 Despite differences in membrane properties, there is significant commonality between the
724 configurations of MD and pervaporation processes. In most embodiments, the side of the
725 membrane that does not contact the feed solution is in contact with an air stream or a gap that
726 serves as the carrier or medium for diffusion to a condenser. If the air gap is stagnant, water
727 vapor needs to diffuse through the air gap to a condenser within the membrane module
728 (Alkhudhiri et al., 2012; Zwijnenberg et al., 2005). Alternatively, the air stream can be flowing,
729 carrying with it the water vapor that permeated the membrane and ultimately sending the water
730 vapor to a condenser outside of the membrane module (Alkhudhiri et al., 2012; Liang et al.,
731 2014; Quiñones-Bolaños et al., 2005).

732 Another configuration not usually employed for pervaporation but commonly used for MD is
733 direct contact, where both the feed and permeate streams contact the membrane. In a direct
734 contact process, the membrane mediates vapor transport directly from a warmer feed solution to
735 the cooler permeate solution. This application gives the shortest distance of water diffusion since
736 water vapor from the feed solution will condense into the distillate. Though, the higher mass
737 transfer associated with direct contact must be balanced against the higher heat transfer
738 (Alkhudhiri et al., 2012).

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

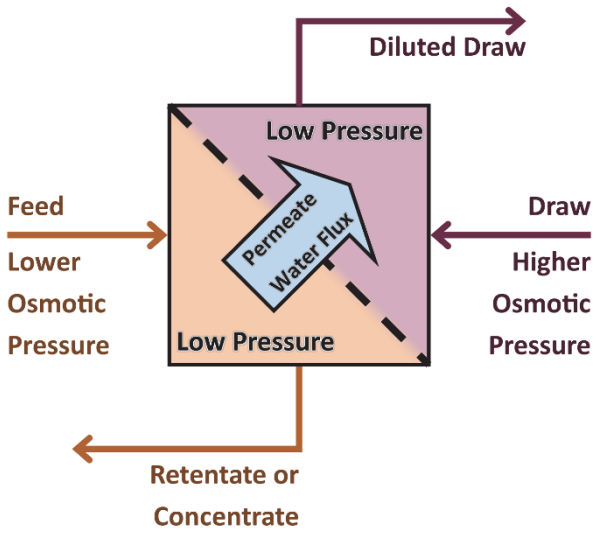
748 One advantage of the MD process is that the elevated temperature of these brines can be used
749 as a driving force for brine-water separation. Depending on the depth, the temperatures of these
750 brines are typically between 30°C and 75°C (Dilmore et al., 2008; Knauss et al., 2005; Lu et al.,
751 2012; Sass et al., 1998). This elevated temperature can be used as a driving force for brine-water
752 separation provided that the thermal energy that passes through the membrane can be effectively
753 dissipated to the environment. For example, the amount of useful work inherent to a 50°C brine
754 with respect to a 20°C environment is approximately 1.7 kWh/m^3 of hot brine. As shown in
755 Figure 5b, this value is on the same order of magnitude as the minimum work of dewatering, and
756 this means that the elevated temperature of these brines can help to decrease overall electricity
757 consumption.

758 **5.2.3. Forward osmosis**

759 Forward osmosis (FO) is a membrane technology where water flux is driven by an osmotic
760 pressure differences between two solutions separated by a semi-permeable membrane. In FO, a

draw solution with a high osmotic pressure flows on the permeate side of a membrane in a direction counter-current to the feed solution being dewatered. 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 (Achilli et al., 2010; Cath et al., 2006; 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 (Lee et al., 2010; Mazlan et al., 2016; McGinnis and Elimelech, 2007; Mi and Elimelech, 2010a, 2013).

Figure 12. Streams common to a FO process when a lower osmotic pressure feed solution is dewatered by a counter-current flowing draw solution with a higher osmotic pressure at each point along the length of the membrane. Permeate that crosses the membrane is mixed with and dilutes the draw solution. Dashed line represents the semi-permeable membrane



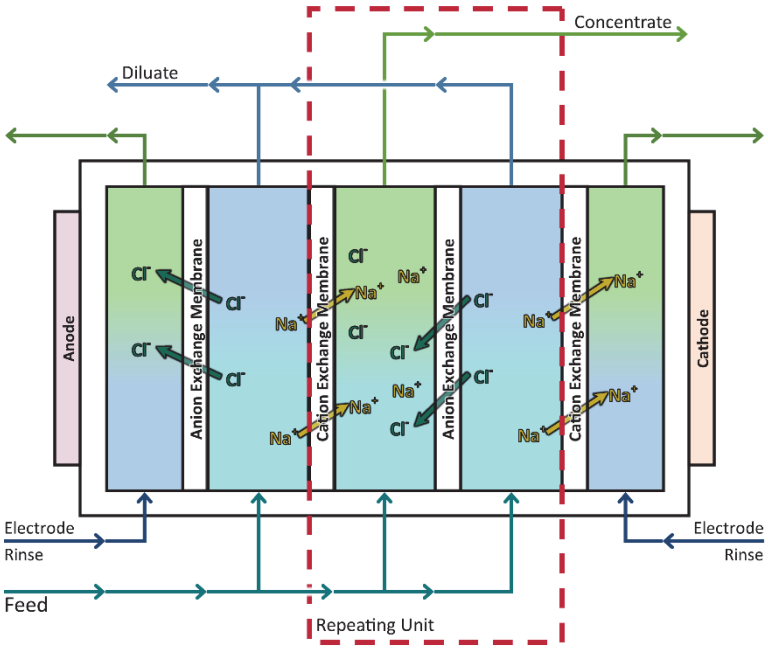
One important consideration unique to FO processes is that, unlike other membrane separations, water that crosses a membrane in FO is mixed with and dilutes the draw solution (Van der Bruggen and Luis, 2015). It is not directly converted to a low salinity water, meaning that a single standalone FO stage 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, at most GCS sites, 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).

5.2.4. Electrodialysis

In addition to the various pressure driven membrane separations be it hydrostatic pressure, vapor pressure, osmotic pressure, a saline brine can be deionized electrochemically using membranes. 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 processes, 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, which 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 GCS produced brines typically have high salinities, conventional ED is likely not viable without significant reduction in the amount of electricity consumed.

Figure 13. Principle of an electrodialysis process redrawn from Strathmann (2010).



5.3. 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. Combined separation processes seek to synergize multiple separation processes to improve overall thermal efficiency or to take advantage of different types of useful work in different stages.

5.3.1. 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 potentially 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).

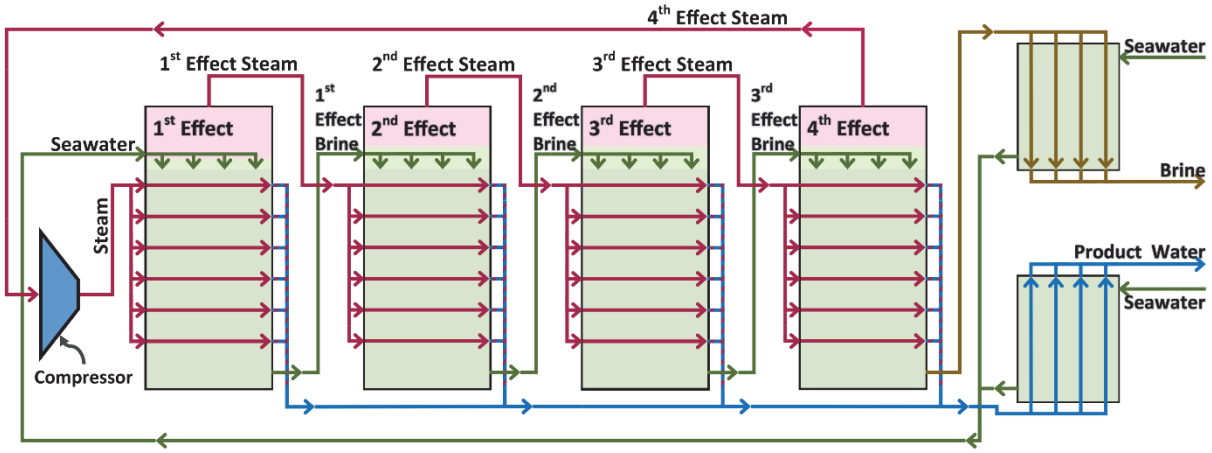


Figure 14. Multi-effect distillation– mechanical vapor compression hybrid operating principle. Redrawn from El-Dessouky et al. (2000).

5.3.2. 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 used for draw solution concentration is/are dependent on the draw solute selected. As stated by Achilli et al. (2010) 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 be capable of having 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.

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 (Luo et al., 2014; McCutcheon et al., 2005; Qasim et al., 2015; Yen et al., 2010). Sugars, inorganic salts, and polyelectrolytes can be recovered by various pressure driven membrane separations, membrane distillation, or evaporative processes. 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 can form a

water soluble tertiary ammonium salt and can be separated by removal of dissolved carbon dioxide that causes the tertiary amine to revert to its non-polar state (Orme and Wilson, 2015; Reimund et al., 2016; Stone et al., 2013). Thermolytic salts are made from anions and cations formed from water soluble gases, such as ammonia or trimethylamine and carbon dioxide, that when heated cause dissolved solutes to come out of solution as gases (Boo et al., 2015; McCutcheon et al., 2005).

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 (Mazlan et al., 2016; McGinnis and Elimelech, 2007). 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. As originally envisioned, the ammonia-carbon dioxide FO process is not currently viable as the continuous 2-step process due to the incompatibility between the draw solution and available membrane chemistries. For example, the ammonia-carbon dioxide draw solution is highly alkaline, which causes accelerated hydrolysis in cellulose acetate membrane and facilitates cation exchange across thin film composite membranes (Arena et al., 2015a; Arena et al., 2015b; Arena et al., 2014; Vos et al., 1966).

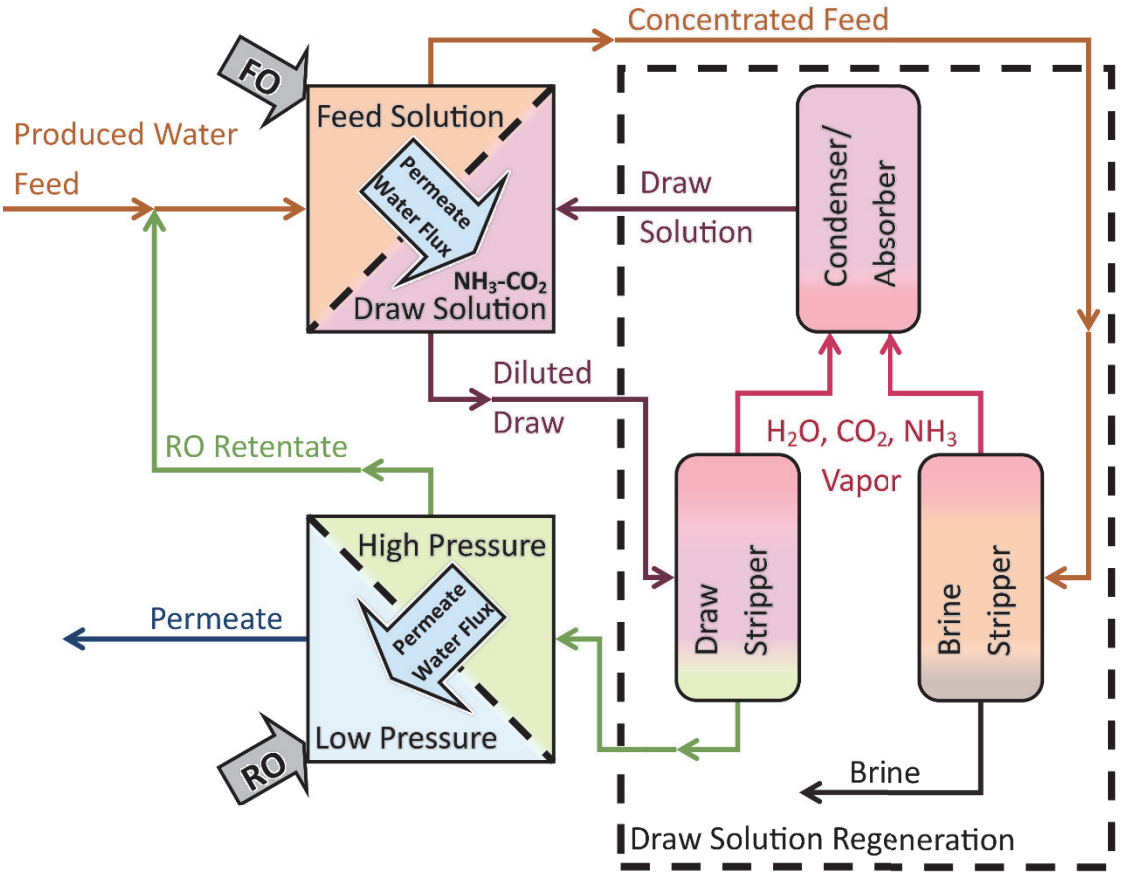


Figure 15. Flow diagram of a thermolytic FO brine concentrator using a draw solution of ammonia and carbon dioxide. Redraw from McGinnis et al. (2013). Flow diagram of a thermolytic FO brine concentrator using a draw solution of ammonia and carbon dioxide. Redraw from McGinnis et al. (2013).

FO using a thermolytic draw solute is capable of dewatering high salinity brines 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.

5.3.3. Combined hydrostatic/osmotic pressure processes

There have been some recent developments in using processes that leverage two driving forces to either increase productivity or drive a separation that would otherwise be impossible. One such process is called pressure assisted forward osmosis or simply assisted forward osmosis (AFO). AFO 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). 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 in the same direction as 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, hydraulic pressure rather than osmotic pressure could be the primary driving force for water flux (Figure 16). Such apparatus go by different names, such as osmotic dehydration coupled to RO concentration, membrane assisted crystallization using RO, or cascading RO (Karode et al., 2000; Lakerveld et al., 2010; Wohlert, 2012). In spite of the differing nomenclature, each of these processes all describe a similar concept, which also shares elements with a single stage AFO process. All of these processes have two solutions separated by a semi-permeable membrane, and one of the solutions has a not insignificant hydraulic pressure applied to it. The difference lies in the solution to which the hydraulic pressure is applied. In AFO, the hydraulic pressure is applied in addition the osmotic pressure difference, whereas in these other processes, the hydraulic pressure is applied in opposition to the osmotic pressure difference. These concepts each describe a new sort of hybrid, which could be described as osmotically assisted reverse osmosis (OARO). An OARO process differs from a typical RO process because the osmotic pressure difference across the membrane is being adjusted by circulating a lower osmotic pressure sweep solution on the permeate side of a membrane. An OARO process remains similar to RO in that water is being driven through the membrane by an applied hydraulic pressure gradient. These OARO applications take advantage of a lowered bulk osmotic pressure difference across a semi-permeable membrane leveraged by this lower osmotic pressure sweep solution to concentrate a stream in excess of what would be physically and mechanically feasible using only an applied hydraulic pressure (Karode et al., 2000; Lakerveld et al., 2010; Lucas and Sawyer, 2012; Wohlert, 2012). A drawback to OARO is that, like FO, it not

a process of direct desalination but one of dilution by stages arranged in series. The OARO process would allow for a gradual stepping down of the osmotic pressure using a hydraulic pressure comparable to those typically employed within a conventional RO process (Lucas and Sawyer, 2012; Wohlert, 2012). A multi-stage OARO process, having a sequential dilution of saline solutions, could be relevant to dewatering of GCS produced brines because it appears applicable to dewatering high salinity brines with only electrical energy as a source of useful work.

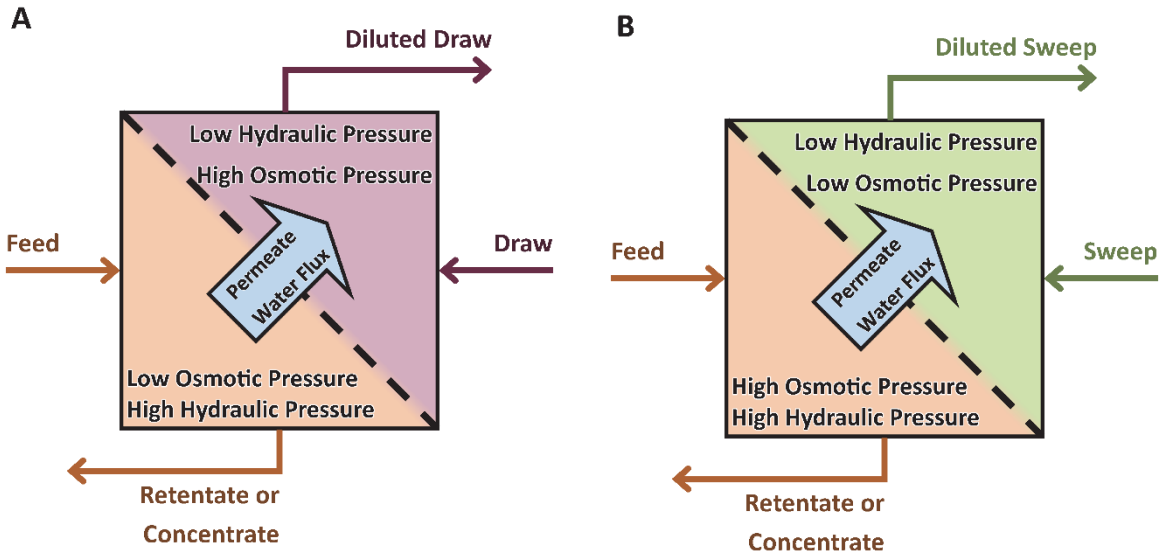


Figure 16. Streams of an a) AFO and b) OARO process. Dashed line represents the semi-permeable membrane.

Figure 17 shows one possible configuration of a multi-stage OARO process that could dewater a high salinity brine (*Note: that the value of inlet and outlet brine composition were chosen somewhat arbitrarily, and the number of stages was chosen to convey the process as simply as possible*). Multi-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 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 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 would be concentrated to 120 g/L while the 90 g/L solution would be diluted to 30 g/L. The 30 g/L solution would now be 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 would be circulated back to the prior OARO stage

as a 90 g/L solution for dilution. This three stage OARO-RO process shown in Figure 17 could operate continuously, concentrating the 90 g/L brine into a 150 g/L brine using only electricity and without requiring evaporation. Additional components not shown in Figure 17 that would be included in an assembled OARO process are the pumps and the pressure exchangers, which would be necessary for energy recovery of the high-pressure streams in the OARO process.

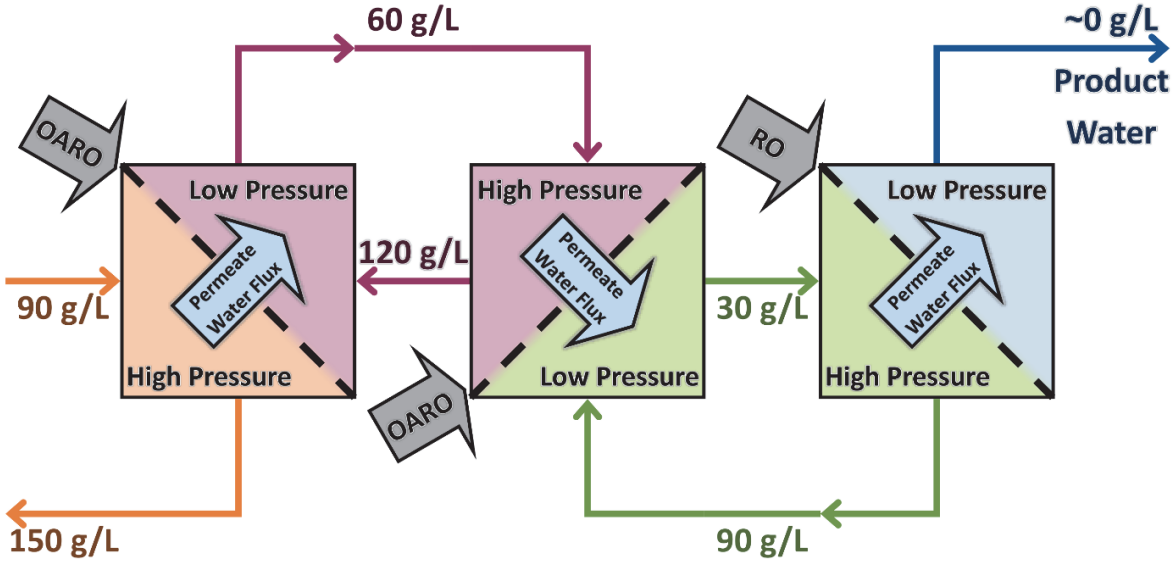


Figure 17. Principle of an osmotically assisted reverse osmosis process.

6. Concentrate management

Processes that dewater a GCS brine will most likely not concentrate these brines past saturation of dissolved NaCl. 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.

6.1. 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., 2016; Buscheck et al., 2011; IEAGHG, 2012); however, reinjection may be limited in some locations due to subsurface pressure limitations. Besides entrainment of suspended solids within formation porosity, there is the obvious need for compatibility between the injected brine and formation brine to ensure that mineral precipitation will not occur from their mixing within the formation. With respect to mixing between the injected brine and formation, one also needs to consider the influence of added pretreatment chemicals such as inorganic coagulants and antiscalant. Ultimately, each case will need to be evaluated on an individual basis using reactive transport simulations and possibly experiments (Castillo et al., 2015; Kharaka et al., 1997).

6.2. 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; Sethi et al., 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 further 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). Should available land requirements be insufficient for natural evaporation there exists a few different approaches to enhance the natural evaporation rate. Firstly is the use of sprayer that circulate and spray the brine into the air over the surface of an evaporation pond for better heat and mass transfer (Gault, 1986). Another approach for evaporation enhancement is the use of wind aided intensified evaporation or WAIV which sprays brine onto vertically mounted hydrophilic surfaces that coupled with wind currents enhance evaporation (Gilron et al., 2003; Sethi et al., 2006). In considering an enhanced evaporation ponds the additional energy demands for brine recirculation needs to be balanced against the fact that added energy inputs to enhance evaporation do not facilitate the generation of low salinity water and water lost by evaporation is difficult to recover.

6.3. Crystallizers

Crystallizers are the main option if a solid product is desired for disposal or sale. Although the forms of crystallizers can vary be they a spray evaporator or a fluidized bed crystallizer, such as those used in the production sea salt, they are used for production of a solid from extracted brines (Hofmann and Melches, 2013; Noyes, 1994). 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 (Morillo et al., 2014; Xu et al., 2013). As shown in Figure 6, the minimum useful work consumed per m^3 of original brine is over threefold larger for the 100% water recovery case compared to the 50% recovery case. This large increase in useful work consumed should only be considered if there is considerable local demand for solid salt. When making crystals, the composition of the brine being dewatered is important 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 and damage the economics of crystallizing GCS brines (Xu et al., 2013). For example, if all of the 1360 billion kg of CO_2 per year were captured at U.S. coal-fired power plants, if all of this CO_2 were sequestrated in saline formations, if one needed to extract a ~120 g/L brine from the formation with a volume equal to 50% of the volume of all of the sequestered supercritical CO_2, and finally if all of this 120 g/L brine were converted into crystal and fresh water, then this would entail the production of roughly 100 million metric tonnes of crystal salt per year due to GCS operations. This is significantly greater than the current consumption rate of salt in the U.S., which is roughly 44 million metric tonnes of salt per year (Bolen, 2015). Using the assumptions listed above, the power consumption to generate all of this salt would be on the order of 6 GW, if the electrical efficiency of the process was around 10%. Hence, for GCS

applications, crystallizers are likely to be pursued in only a select few cases where there is local demand.

7. Integrating brine treatment processes into sustainable cost effective CO_2 management systems

While brine dewatering processes will be critical for the pressure management of saline formations for high volume GCS, they are but a single facet to a complex network of processes for capturing, transporting, and storing CO_2. As such, the criteria for brine dewater process selection and design will necessarily extend beyond first order metrics, such as levelized cost or energy efficiency, to include higher-order considerations, such as a) scalability or modularity of the process, b) robustness to variability in flow rate, c) operation and maintenance requirements, and d) the process recovery, which in turn dictates concentrate disposal volume. Finally, the human health and environmental externalities of brine management activities, including both the direct emissions associated with the energy inputs to the separation processes and the indirect emissions associated with chemical manufacturing, should factor into selection criteria. Multi-criteria decision models will be essential to weighing the relative advantages of specific technologies during the system planning phase.

In addition to questions around the selection of brine dewatering technology, there are also optimization questions relevant to reservoir design and management that will impact the operation of that technology (Cihan et al., 2015). For example, there are tradeoffs between added brine withdrawals to increase reservoir storage capacity and incurred costs for brine management. There will also be tradeoffs in the siting of brine processing facilities either as several distributed and possibly model systems adjacent to the point of brine withdrawal or as a centralized facility. Herein lies the tradeoff between the savings in capital cost for dewatering equipment at the centralized facility and the added capital and operational costs of transporting the brine to the centralized site.

The complexity of tradeoffs in brine management technology selection and system integration draw parallels to similar tradeoffs observed with brine management activities in unconventional oil and gas operations. Previous work has developed mixed integer linear and nonlinear programming models to assess the financial and environmental tradeoffs of shale gas brine management (Bartholomew and Mauter, 2016; Gao and You, 2015; Yang et al., 2015). A critical aspect of optimization models for GCS brine management will be the incorporation of uncertainty in the variable CO_2 storage rates, which would be dictated by policy and climate uncertainty. The field of stochastic and robust optimization can address this uncertainty and provide some insight into cost effective and sustainable brine management systems.

8. Conclusions

Because of their large available volumes, deep saline formations will be key to long-term reduction in CO_2 emissions from fossil fueled power plants. To mitigate the risk of induced seismic activity in closed or low porosity formations, pressure management will require the extraction of brine from the formation. While also increasing formation capacity for CO_2 storage, the extracted brines can be dewatered to generate a 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, presented herein is a quantitative evaluation of four GCS-relevant brines in the eastern United States, 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, strontium, and/or sulfate ions. The TDS of these GCS brines is significantly higher than seawater (35 g/L) for which most desalination processes have been optimized.

Due to the factors discussed herein, many commercially-available dewatering processes are not applicable to GCS brines. For example, conventional RO and ED processes are best suited to salinities less than seawater. Also, MSF, MED, MD, 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 likely be the only reliable source of useful work to dewater the brine, and the electricity consumed should ultimately be subtracted from the electricity generated at the power plant when calculating key environmental parameters, such as kg_{CO_2} emitted per kWh of net electricity generated. In regards to process performance, broadly speaking there is limited information of the applicability of the majority of these processes to dewatering brines that are significantly more saline than seawater with at minimum reporting of feed inlet salinity, recovery, energy requirement, and distillate concentration.

The current standard in high salinity brine dewatering is MVC, which can dewater a high salinity brine using an electrically-driven compressor to generate and extract steam from an evaporator. There is an irreversible generation of entropy when the extracted steam is condensed to pure water via heat exchange with the incoming brine results in low electrical efficiency for MVC (~10%). Because of there exists a need for more efficiently technologies to dewater high salinity brines, there is significant driving force for research and development of more efficient membrane processes such as thermolytic FO, MD, and multi-stage OARO.

9. Acronyms, abbreviations, and symbols

Term	Description
ED	Electrodialysis
GCS	Geologic carbon dioxide storage
FO	Forward osmosis
MED	Multi-effect distillation
MED-MVC	Multi-effect distillation with mechanical vapor compression
MD	Membrane distillation
MF	Microfiltration

MSF	Multi-stage flash distillation
MVC	Mechanical vapor compression
NF	Nanofiltration
RO	Reverse osmosis
TDS	Total dissolved solids, g/L
TVC	Thermal vapor compression
UF	Ultrafiltration
a_w	Activity of water
$c_{f,b}$	Feed molar concentration in the bulk, mol/L
$c_{f,m}$	Feed molar concentration at the membrane, mol/L
c_i	Molar concentration of component i, mol/L
$c_{s,b}$	Sweep molar concentration in the bulk, mol/L
$c_{s,m}$	Seep molar concentration at the membrane, mol/L
c_p	Permeate molar concentration, mol/L
m_i	Molal concentration of component i, mol/kg
p_w	Vapor pressure of water, bar
$p_{solution}$	Vapor pressure of solution, bar
v_w	Molar volume of water, 0.01797 L/mol @ 25°C
A	Water permeance of a membrane, $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$
B	Solute permeability of a membrane, $L \cdot m^{-2} \cdot h^{-1}$
D	Diffusion coefficient of solute in water, m^2/s
M_w	Molecular weight of water, 18.02 g/mol
P_f	Feed hydraulic pressure, bar
P_s	Sweep hydraulic pressure, bar
R	Ideal gas constant, 0.08314 $L \cdot bar \cdot mol^{-1} \cdot K^{-1}$
S	Structural Parameter, m
T	Absolute Temperature, K

w_{min}/v_p	Minimum work of separation per volume of produced water, kWh/m^3
w_{min}/v_b	Minimum work of dewatering per volume of original brine, kWh/m^3
δ_f	Feed external boundary layer thickness, m
κ	Conversion factor, $3.6 \cdot 10^6 \frac{L \cdot s}{m^3 \cdot h}$ $3.6 \cdot 10$
φ	Osmotic coefficient
π	Osmotic pressure, bar
ρ	Density of Water, $0.9970 \frac{kg}{L}$ @ 25°C

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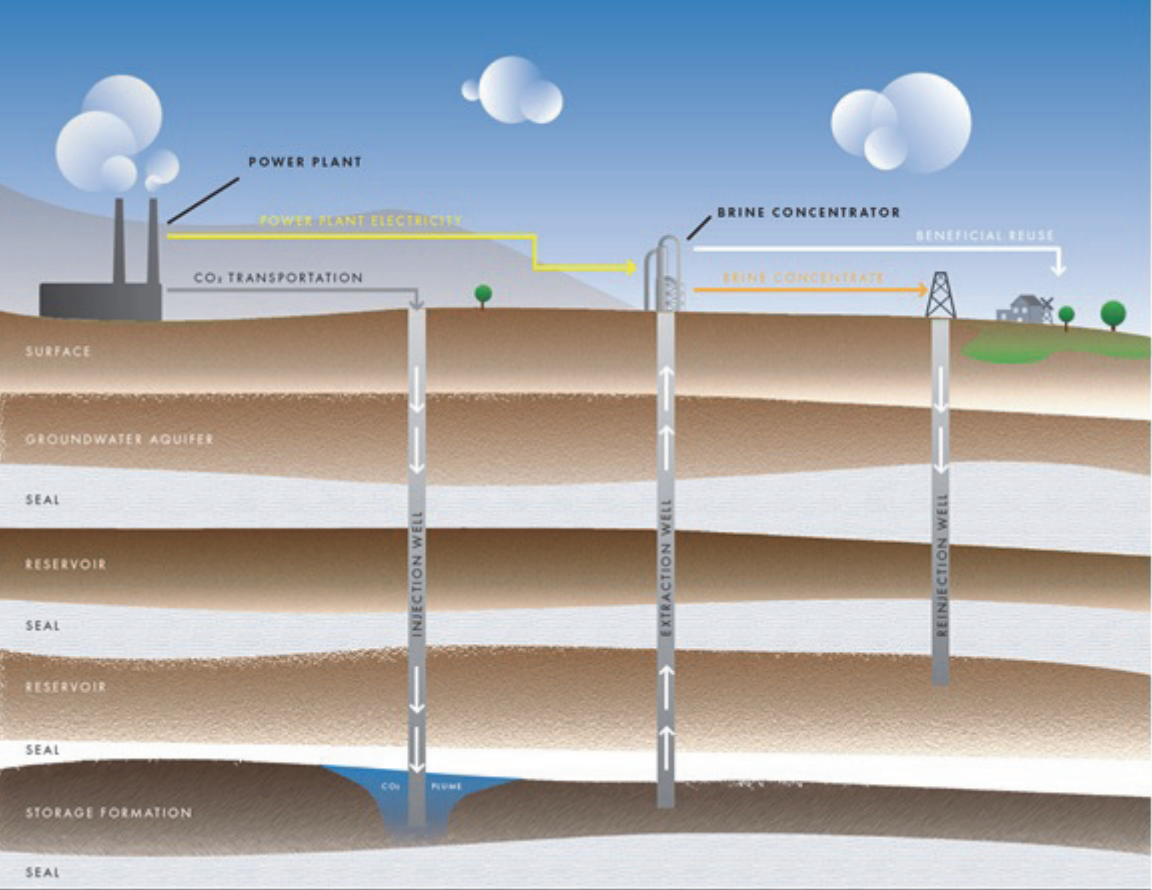
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STORAGE FORMATION
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EXTRACTION WELL
REINJECTION WELL
CO_2
PLUME