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Fresh water generation from aquifer-pressured carbon storage: feasibility of treating saline formation waters

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Abstract

Brines up to 85,000 ppm total dissolved solids produced during Carbon Capture and Storage (CCS) operations in saline formations may be used as the feedstock for desalination and water treatment technologies via reverse osmosis (RO). The aquifer pressure resulting from the injection of carbon dioxide can provide all or part of the inlet pressure for the desalination system. Residual brine from such a process could be reinjected into the formation at net volume reduction, such that the volume of fresh water extracted is comparable to the volume of CO₂ injected into the formation. Such a process could provide additional CO₂ storage capacity in the aquifer, reduce operational risks (e.g., fracturing, seismicity, leaking) by relieving overpressure in the formation, and provide a source of low-cost fresh water to offset costs or operational water needs equal to about half the water usage of a typical coal ICGG power plant. We call the combined processes of brine removal, treatment, and pressure management active reservoir management.

We have examined a range of saline formation water compositions propose a general categorization for the feasibility of the process based total dissolved solids (TDS):

- 10,000–40,000 mg/L TDS: Standard RO with $\geq 50\%$ recovery
- 40,000–85,000 mg/L TDS: Standard RO with $\geq 10\%$ recovery; higher recovery possible using 1500 psi RO membranes and/or multi-stage incremental desalination likely including NF (nanofiltration)
- 85,000–300,000 mg/L TDS: Multi-stage process using process design that may differ significantly from seawater systems
- > 300,000 mg/L TDS brines: Not likely to be treatable

Brines in the 10,000–85,000 mg/L TDS range appear to be abundant (geographically and with depth) and could be targeted in planning CCS operations. Costs for desalination of fluids from saline aquifers are in the range of \$400–1000/ acre foot of permeate when storage aquifer pressures exceed 1200 psi. This is about half of conventional seawater desalination costs of \$1000–1400/acre foot. Costs increase by 30 to 50% when pressure must be added at the surface. The primary reason for the cost reduction in pressurized aquifers relative to seawater is the lack of need for energy to drive the high-pressure pumps. An additional cost savings has to do with less pre-treatment than is customary for ocean waters full of biological activity and their degradation products. An innovative parallel low-recovery approach is proposed that would be particularly effective for saline formation waters in the 40,000–85,000 mg/L TDS range.

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Carbon sequestration; water; reverse osmosis

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1. Introduction

Storage of carbon dioxide in deep saline aquifers may be limited by the buildup of pressure in the aquifer, particularly in cases where the shape of the aquifer is such as to provide closure. This is advantageous for limiting the movement of the CO₂, but the pressure buildup can reduce the total amount of CO₂ storable in the site. The case of reservoirs without closure is also of interest because the mobility of CO₂ can cause it to move further from the injection site than desired. In both cases it is readily imaginable that withdrawal of brine from the aquifer at propitious locations could mitigate these issues. However, the brines in storage aquifers have been regarded as of low utility, and difficult to dispose of at the surface. This study examines the feasibility and cost of treating extracted saline formation waters (brines) using reverse osmosis (RO). Our concept is to remove brine (under pressure when appropriate) and treat it to produce a portion of fresh water usable at the surface. The residual brine, now somewhat more concentrated than the original, is returned to the aquifer with a net reduction in subsurface volume. Questions about this concept include whether mineral precipitates pose a significant limitation, and what range of salinities would be treatable by RO. A companion study (Buscheck et al., this volume) examines strategies for hydrologic management of the reservoir. Additional details of this study’s methods and results may be found in Wolery et al. 2009. Our cost evaluation concentrated on aquifers where significant pressure builds up during storage, sufficient to provide the drive force for the RO process. While not true in all cases, such pressure buildup is observed today at the In Salah and Cranfield sites (Havorka 2009 pers. comm., Anderson 2009 pers. comm.). Such systems present possibilities for energy efficient designs that conserve pressure. Cost calculations for aquifers that would not build up significant pressure, such as the Illinois basin (Birkholzer and Zhou, 2009), can be estimated from conventional RO designs. In both cases there will be limits to operation, and perhaps economics, arising from the much higher salinities possible in storage aquifers.

While the principal benefit of this approach may be to control aquifer pressures to within safe limits, it could also provide fresh water at a significant rate. A typical 1 GW coal plant emits more than 7 million tons of carbon dioxide per year. A well-designed capture system might provide 6 million tons for sequestration. Sequestered at a depth of 10,000 ft, this CO₂ would displace about 7.5 million cubic meters of water, or a little less than a billion gallons per day. Reverse osmosis treatment of that brine would produce about 6000 acre-feet of fresh water, which could serve the needs of 10,000 homes, irrigate 2000 acres of cropland, or provide half of the total fresh water usage of a typical 1 GW IGCC power plant.

2. Treatability of Storage Brine

The total dissolved solids (TDS) is a key parameter in determining whether a brine can be desalinated by reverse osmosis. Higher TDS of feed water is associated with higher osmotic pressure (approximated by the van’t Hoff

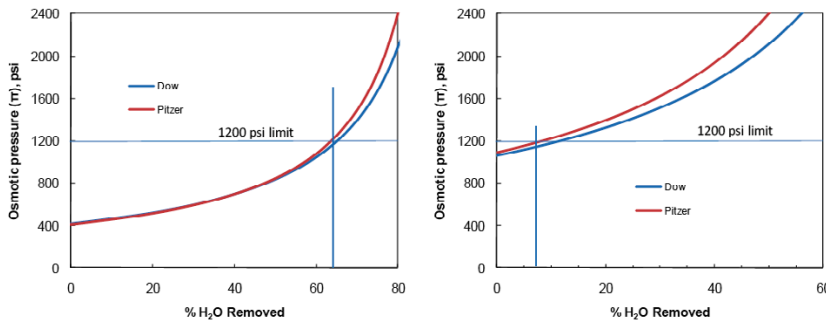


Figure 1. Comparison of the osmotic pressure limitation to treatment of seawater (left) and Sublette #3 (right). The “Pitzer” curves show the osmotic pressure as obtained from the activity of water calculated from our thermodynamic model using Pitzer’s equations. The Dow model is commonly used in the water treatment industry and is a minor variation on the classic van’t Hoff equation, neither of which is generally valid in high ionic strength brines.

equation, Dow, 2009), which requires more energy (pressurization) to drive water through an RO membrane. It is also associated with increased difficulties with mineral deposition (scaling), although specific chemistry (e.g., hardness) is also an important factor. The TDS of residual brine increases during processing as fresh

water is produced, increasing these problems, resulting in a practical limit to how much fresh water can be extracted from the original briny feed water. In general, the higher the TDS of the feed water, the smaller the fraction of fresh water that can be obtained.

To determine the range of applicable brine chemistries we used existing databases for produced waters and compositions from proposed or actual CCS injection sites. Saline formation waters range in total dissolved salts (TDS) up to about 400,000 mg/L. We have analyzed data from the USGS Produced Water Database (Breit, 2002) for the State of Wyoming and the United States as a whole and found that saline formation waters in the TDS ranges 10,000-85,000 mg/L (discussed below as reasonable targets for conventional desalination) are abundant, more so in Wyoming than in the United States as a whole. About half of sampled brines fall into this concentration range. The coverage of this database is skewed toward certain states and regions. For example, there is an abundance of data for the states of Texas, Wyoming, Oklahoma, and Kansas, while there are relatively few data for Ohio, Pennsylvania, New York, and West Virginia. A notable observation is that there is little shift toward more highly concentrated brines with increasing depth. Most saline formation waters in the United States belong to one of three compositional families based on major ion chemistry: Na-Cl, Na-Ca-Cl, and Na-Cl-SO₄. Na-Cl brines are much like diluted or concentrated seawater. Actual seawater (a focus of industrial RO treatment) has a TDS about 36,000 mg/L. Na-Cl brines range in concentration up to about 350,000 mg/L. Na-Ca-Cl brines are typically have TDS greater than seawater, ranging up to 400,000 mg/L. Na-Cl-SO₄ brines are common in Rocky Mountain basin regions, and have TDS mainly in the range 1,000-110,000 mg/L. In the United States, CCS operations are anticipated to be restricted to formations containing saline waters with TDS > 10,000 mg/L.

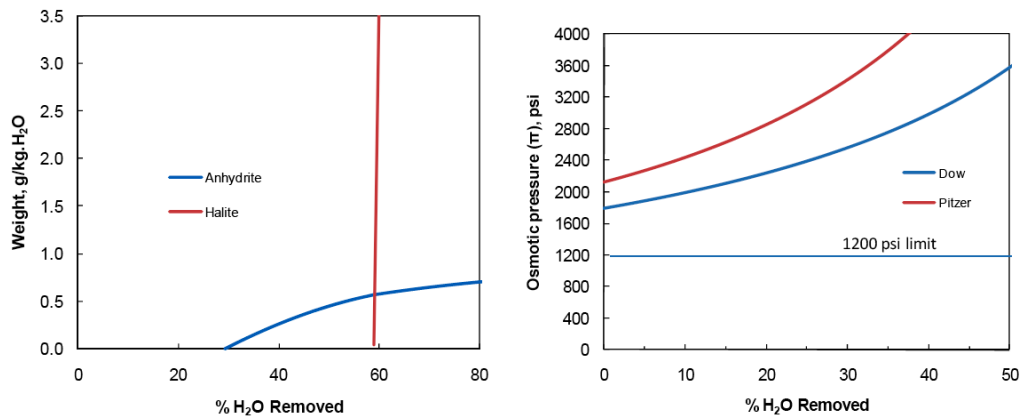


Figure 2. Calculated results for reverse osmosis at 50°C of WY Sublette Co. #2 brine in a batch system. Left: mineral precipitation. Right: osmotic pressure. WY Sublette Co. #2, 13004-13092 ft. depth) is Na-Cl-SO₄ brine with TDS of only 24,501 mg/L. For this brine, the 1200 psi membrane would permit 86% water extraction. The left hand diagram shows the effects of mineral precipitation in the same system. Anhydrite precipitation is readily suppressed by conventional additives, but glauberite would represent a firm upper limit to concentration. In all cases we studies, we found that osmotic pressure became limiting before mineral precipitation.

We used thermodynamic modeling (EQ3/6 software) (cf. Wolery and Jarek, 2003) using Pitzer's equations (cf. Pitzer, 1991) to evaluate mineral deposition and osmotic pressure limitations for representative compositions. We have also performed more generic calculations for brines in the Na-Cl ("seawater") family. The brine thermodynamic model (Bechtel/SAIC Company, 2007) was originally developed for use on the Yucca Mountain Project. It is based on the work of Pabalan and Pitzer (1987), Greenberg and Møller (1989), and many other sources, and supports to evaluate mineral scaling and osmotic pressures resulting from RO. An alternative thermodynamic model based on Extended UNIQUAC theory (cf. Thomsen 1997, 2005) is also available in EQ3/6. Other usage suggests that it would have given essentially the same results for the systems modeled here. We made these calculations for a suite of representative brine compositions over a range of temperatures (25–50°C), with 40–50°C being the likely range for RO owing to materials issues. The actual subsurface brines are expected to be this warm or warmer owing to the natural geothermal gradient and expected formation depths (800–1000 m). The pressure that can be applied to overcome that osmotic pressure is limited by the RO membrane strength, which is typically 1200

psi (8274 kPa), although 1500 psi (10342 kPa) membranes are now available. Higher initial TDS also increase the effects of mineral scaling.

Many saline formation waters prove to amenable to conventional treatment by this method. We have examined Na-Cl brine (86,000 mg/L TDS) from the Nugget Formation in Sublette County, Wyoming (Figure 1). Here 7.5–24% fresh water removal is possible. The less concentrated 24,500 mg/L TDS Na₂SO₄ brine from the underlying Tensleep Formation would support >80% removal with conventional RO (Figure 2). On the other hand, brine water from the In Salah, Algeria CCS site (sample KB502Z, Na-Cl brine, 150,000 mg/L TDS) has an osmotic pressure > 1500 psi and thus cannot be treated by single stage conventional RO and would require nanofiltration as well. A nanofiltration membrane passes a substantial fraction of dissolved ions, while discriminating against divalent ions such as calcium. The produced water is less saline than the feed water, with a finite osmotic pressure, such that the osmotic pressure difference (and the applied pressure difference) is small compared with that often occurring for RO.

Figure 2 compares a seawater brine to a representative brine from Sublette County, Wyoming (“WY Sublette Co. #3) (Breit, 2002). The latter is significantly higher in TDS (total dissolved solutes) than the former: 85,926 g/L, versus 35,928 g/L. Seawater is the brine most commonly treated by RO today, and much of the present technology and practical knowledge base pertinent to treatment of brines is focused on it. Some subsurface brines are similar in composition to seawater and many subsurface brines are thought to have been derived from it. Thus, seawater is a useful reference. The representative brine from the Wyoming site is based on historical data for brines produced from the Nugget Formation at depths of about 10,000–11,000 ft. Matching direct measurements of subsurface temperatures were not available, but estimates of the local geothermal gradient suggest in situ temperatures in the range 72–104°C.

Figure 1 shows the effect of a membrane strength of 1200 psi on conventional RO at 50°C of the seawater brine and the representative brine (WY Sublette Co. #3). For the seawater brine, the osmotic pressure reaches the conventional membrane strength of 1200 psi at about 64% water extraction. For the more concentrated Wyoming brine, this condition occurs at about 7.5% water extraction. Using a higher membrane strength of 1500 psi would help, increasing these results to 71% and 24%, respectively.

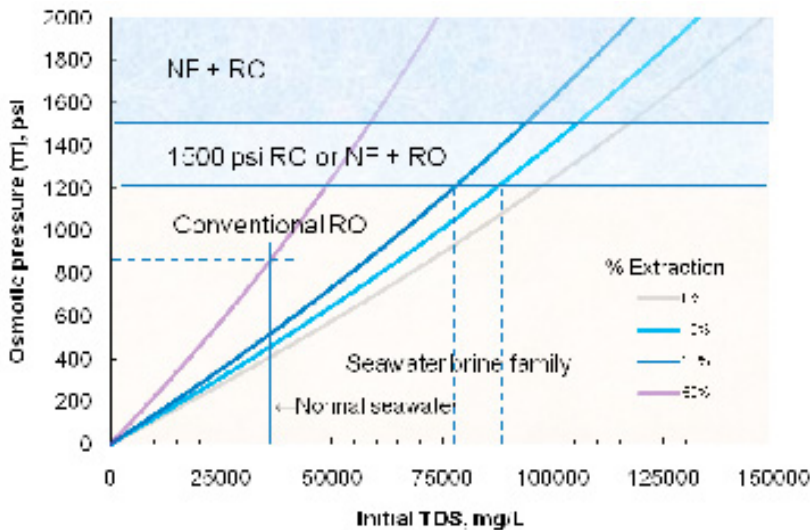


Figure 3. Limits of processability as a function of initial total dissolved solids in the brine and the amount of fresh water removed during reverse osmosis. At 10% extraction (light blue line), brines of around 85,000 mg/l TDS can be treated by conventional RO processes with 1200 psi membranes. Stronger 1500 psi membranes would allow 10% extraction at about 105,000 mg/l TDS.

Brines from other proposed sequestration sites can now be analyzed readily. An accurate osmotic pressure curve appropriate to these brines can be used to evaluate cost and equipment specifications. Figure 3 shows representative curves based on consistent removal fraction as a function of TDS. The current 1200 psi standard membrane limits treatment to around 85,000 ppm TDS for brines that are chemically similar to seawater – that limit varies by a few thousand ppm as a

function of the individual details of brine chemistry (Wolery et al., 2009).

3. System Design and Costs

We used standard RO industry design methods to estimate that the cost of RO treatment of 10,000,000 mg/L TDS brines assuming use of aquifer pressure in place of surface pressurization. A detailed evaluation of formation pressure management aspects, which are equally important, is addressed by Buscheck et al. 2010.

Reverse osmosis is a membrane-based desalination process. It uses a microporous polyamide membrane that is permeable to water, but does not allow passage of salt (ions). The solution to be desalinated is placed on one side of the membrane and then pressurized. The pressure drives water across the membrane but leaves most of the dissolved salt behind. The pressure used to drive the process is equal to the osmotic pressure plus an additional “driving” pressure to cause water to flow in a direction opposite to that of the osmotic pressure gradient, thus the term reverse osmosis. The process is generally carried out in a spiral-wound tubular geometry in order to achieve a large membrane surface area in a small volume.

Desalination of seawater using reverse osmosis is a fairly mature technology. Figure 4 shows a schematic of the process, which consists of three main steps: 1. Pretreatment of the feed using one or more of physical filtration, coagulation, chemical sterilization, and contact with granular activated carbon (GAC) 2. Reverse osmosis 3. Permeate storage and distribution. The reverse osmosis step is often carried out in two or three stages at successively

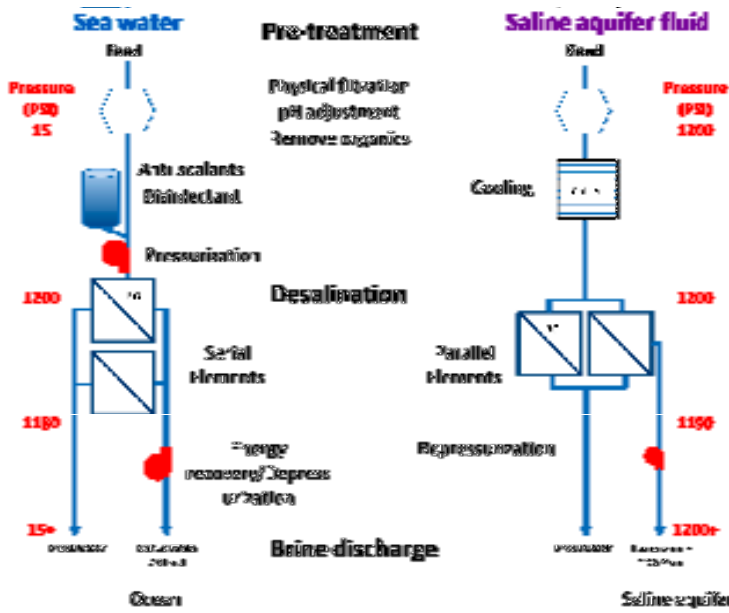


Figure 4. Schematic representation of conventional ocean water desalination (left) and proposed brine aquifer desalination (right). Pressure at each process step is shown in red.

higher pressures, the goal of which is to maximize water recovery. Each stage extracts additional fresh water from the residual brine provided from the previous stage. The operating pressure and membrane types of each stage are optimized for the salinity of the water being processed. Seawater is similar in composition worldwide, varying only about ± 10 to 15% in total dissolved solids (TDS), with the relative concentrations of components remaining essentially the same. The major exceptions to this generalization are the biologically-affected components

such as calcium, silica, and phosphate. These species are incorporated into living organisms in sea water and so are affected on a local scale by the extent of biological activity.

Because of the uniformity of sea water composition, design of reverse osmosis (RO) seawater systems are similar for most applications, with the major influencing factors being feed temperature and feed water quality with respect to organic and suspended solids concentrations, which are a function of the feed source. If possible, open ocean intakes are avoided due to entrainment of organic matter and microorganisms. Instead, intake systems that take water from wells drilled into beach sand are used to filter out much of these materials that would otherwise necessitate extensive pretreatment in order to avoid membrane fouling. Biofilm fouling is especially problematic for RO membrane desalination because the chemicals commonly used to kill microorganisms, such as chlorine and ozone, will damage the polyamide layer on RO membranes.

Table 1. Major cost elements.

Assumed Discount Rate	7.00%	
Plant Lifetime / Evaluation Period, yrs (20-25)	25.00	
Operating Cost escalation, %/yr	0.00%	
Base Operating Pressure at reference conditions	1,200	psi
Base recovery	40%	
Cleaning, times/year	0.5	
Chemicals	\$3	
Consumables		
Activated Carbon	\$ 30	\$/ft ³
Filter cartridges	\$ 4	\$/each
Power, Repressurization	\$0.07	\$/kWh, \$/yr
Power, Misc uses	200.00	kWh/day, \$/yr
Labor		
Fringe & Overhead Multiplier	2.00	factor
Supervisor	\$ 150,000	Salary
Operators	\$ 60,000	Salary
Technicians	\$ 75,000	Salary
Mechanical Maintenance, % of Capital	3%	
Length of high pressure piping	125	ft

In contrast, reservoir fluids are diverse in composition due to the variety of subsurface interactions they have experienced and rock types they have contacted. Although most pore fluids in sedimentary rocks started as seawater, their compositions have been altered by reactions with rocks, biological activity, and mixing with other fluids. As a result, reservoir waters vary in TDS, pH, amounts of dissolved species such as reduced iron and manganese (not commonly present in surficial oxidized waters), relative amounts of hardness (Ca +Mg) to alkalis (Na +K), alkalinity, and dissolved gases. The design of systems to desalinate such waters has to adapt to this variability, making some reservoir waters acceptable for standard or modified

sea water RO treatment, while other fluids are unsuitable for such processing.

Figure 4 shows how the saline aquifer process differs from the standard sea water process. The major differences are: 1. The need for a heat exchanger (chiller) prior to membrane treatment to cool the fluids to the working range of standard water treatment components (<60oC or 140oF) 2. Less need for filtration and pretreatment due to the better quality of fluid in terms of total suspended solids (TSS) and less biological organic matter 3. Reduced need for a high-pressure pump to pressurize the feed water when it leaves the well head under relatively high pressure, which can be equal to or higher than that required for seawater membrane processing. Pressurization of seawater feed is a major and very costly component of seawater desalination. With the reservoir water already at high pressure, this costly capital and operating component is thus eliminated for a reservoir RO treatment process. Wolery et al. 2009 lists the detailed elements in each design.

Depending on the reservoir characteristics, iron and manganese in their reduced states maybe present. Since, under normal seawater or RO applications, the feed water is aerated, such metals are typically dealt with by oxidation and removal prior to RO treatment. Since oxidation and subsequent metal removal in a closed, high pressure system is undesirable and unnecessary, the metals will be maintained in their reduced state by isolating them from oxidizing conditions as they pass through the RO membranes. As divalent ions, iron and manganese will be highly rejected by the membranes so that they will be retained in the reject stream and will subsequently be deep well injected for ultimate disposal. Care will have to be taken to maintain reducing conditions within the entire feed, reject and deep well systems. Some chemical addition in the form of bisulfite may be warranted if there is a danger of oxidation due to atmospheric contact during the repumping operation. With greater than 99.7% membrane rejection of divalent ions, the permeate will be essentially free of these metals so that oxidizing conditions will not be a factor for the permeate water.

Using the cost items in Table 1 and in order to effectively compare different systems, a Levelized Cost of Water was computed over the 25 year time frame using methodology analogous to Levelized Cost of Energy computations as published by NREL (Short et al., 1995) or California Energy Commission, 2007. Essentially this method computes a NPV for the capital and operating costs over the period at the assumed discount rate. On the production side, the NPV of the production rate per year over the period is also computed. The

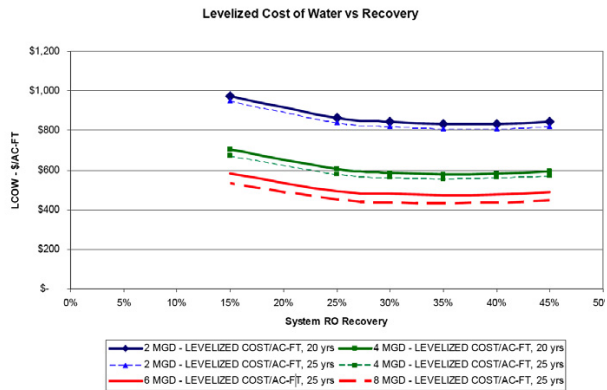


Figure 5. Levelized cost of water per acre-foot (326,000 gallons) of permeate produced as a function of the water recovery, or fraction of fresh water obtained from the feed.

cost divided by the NPV of production gives the Levelized Cost of Water (LCOW).

$$LCOW = \frac{\text{Initial Investment} + \sum_{t=1}^n \frac{\text{Investment}_t + O\&M_t}{(1 + Disc)^t}}{\sum_{t=1}^n \frac{\text{Water}_{t-1} \text{ year}}{(1 - Disc)^t}} \quad t = \text{year of operation, Disc} = \text{Discount Rate}$$

Results for cases in which the initial pressure is supplied by extracting pressurized aquifer water are displayed in Figure 5, which shows that levelized water costs per acre-foot of permeate vary from about \$450 to \$1000, and that the costs decrease as the size of the operation increases. In addition, there is a most cost effective recovery point (minimum) in plots of recovery vs. cost. This assumes that the water chemistry supports the range of recoveries i.e. the higher recoveries are possible using pressures of less than 1500 psi. Most importantly, however, the lower recovery options are economically close to the higher recovery options – that is the curve is fairly flat. With conventional pumped systems the curve is much more pronounced, greatly favoring higher recovery. (One acre foot equals 325,851 gallons or 1,233 cubic meters.)

For a conventional pumped system the costs are shown in Figure 6. Details for both calculations are available in Wolery, 2009. The advantage for aquifer-pressured systems is substantial, but treatment using supplied pressure is also feasible at a higher cost.

4. Conclusions

Many saline formation waters are amenable to conventional or largely conventional RO treatment. We propose a general categorization for the feasibility of the process based total dissolved solids (TDS):

- 10,000–40,000 mg/L TDS: Standard RO with ≥ 50% recovery
- 40,000–85,000 mg/L TDS: Standard RO with ≥ 10% recovery; higher recovery possible using 1500 psi RO membranes and/or multistage incremental desalination likely including NF (nanofiltration)
- 85,000–300,000 mg/L TDS: Multistage process (NF + RO) using process design that may differ significantly from seawater systems
- > 300,000 mg/L TDS brines: Not likely to be treatable

Brines in the 10,000–85,000 mg/L TDS range appear to be abundant (geographically and with depth) and could be targeted in planning CCS operations. Costs for desalination of fluids from saline aquifers are in the range of \$400–1000/ acre foot of permeate. This is about half of conventional seawater desalination costs of \$1000/acre foot.

5. Acknowledgements

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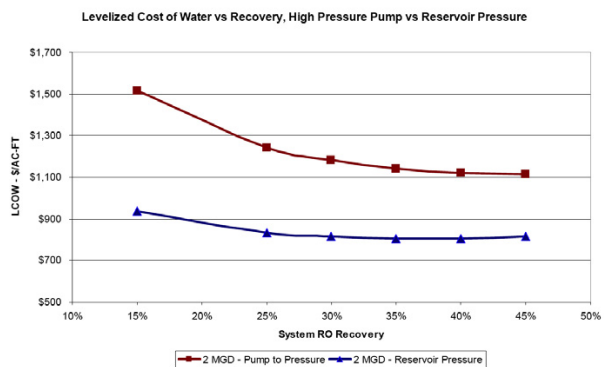


Figure 6. Comparison of aquifer-pressured RO costs (blue, bottom) to conventional pressurized seawater system costs (red, top).

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