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Fresh Water Generation from Aquifer-Pressured Carbon Storage: Interim Progress Report

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Interim Progress Report FEW0163
Project Title: Fresh Water Generation from Aquifer-Pressured Carbon Storage
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Project Objectives:

This project is establishing the potential for using brine pressurized by Carbon Capture and Storage (CCS) operations in saline formations as the feedstock for desalination and water treatment technologies including nanofiltration (NF) and reverse osmosis (RO). The aquifer pressure resulting from the energy required to inject the carbon dioxide provides all or part of the inlet pressure for the desalination system. Residual brine would be reinjected into the formation at net volume reduction. This process provides additional storage space (capacity) in the aquifer, reduces operational risks by relieving overpressure in the aquifer, and provides a source of low-cost fresh water to offset costs or operational water needs. Computer modeling and laboratory-scale experimentation are being used to examine mineral scaling and osmotic pressure limitations for brines typical of CCS sites. Computer modeling is being used to evaluate processes in the aquifer, including the evolution of the pressure field.

Overall Progress

This progress report deals mainly with our geochemical modeling of high-salinity brines and covers the first six months of project execution (September, 2008 to March, 2009). Costs and implementation results will be presented in the annual report. The brines typical of sequestration sites can be several times more concentrated than seawater, requiring specialized modeling codes typical of those developed for nuclear waste disposal calculations. The osmotic pressure developed as the brines are concentrated is of particular concern, as are precipitates that can cause fouling of reverse osmosis membranes and other types of membranes (e.g., NF). We have now completed the development associated with tasks (1) and (2) of the work plan. We now have a contract with Perlorica, Inc., to provide support to the cost analysis and nanofiltration evaluation. We have also conducted several preliminary analyses of the pressure effect in the reservoir in order to confirm that reservoir pressure can indeed be used to drive the reverse osmosis process.

Our initial conclusions from the work to date are encouraging.

1) The concept of aquifer-pressured RO to provide fresh water associated with carbon dioxide storage appears feasible.
2) Concentrated brines such as those found in Wyoming are amenable to RO treatment. We have looked at sodium chloride brines from the Nugget Formation in Sublette County. 20-25% removal with conventional methods is realistic; higher removal appears achievable with NF. The less concentrated sulfate-rich brines from the Tensleep Formation in Sublette County would support >80% removal with conventional RO.

3) Brines from other proposed sequestration sites can now be analyzed readily. An osmotic pressure curve appropriate to these brines can be used to evaluate cost and equipment specifications.
4) We have examined a range of subsurface brine compositions that is potentially pertinent to carbon sequestration and noted the principal compositional trends pertinent to evaluating the feasibility of freshwater extraction. We have proposed a general categorization for the feasibility of the process based on total dissolved solids (TDS).
5) Withdrawing pressurized brine can have a very beneficial effect on reservoir pressure and total available storage capacity. Brine must be extracted from a deeper location in the aquifer than the point of CO_2 injection to prevent CO_2 from migrating to the brine extraction well.

Geochemical Modeling Progress (Thomas J. Wolery):

The original intent of this project was to focus on brine compositions specific to sites (geographic locations plus injection formations) of primary interest to the carbon sequestration partnerships (CSPs). The expectation was that new samples of brine would be obtained from these sites, and that sampling and analysis would be state-of-the-art in order to overcome various well-known problems with historical chemistry data (e.g., volatile loss, mineral precipitation, incomplete analysis). It is anticipated that examples of new state-of-the-art data will become increasingly available. However, we have found it necessary to take a broader view at this time, using mostly historical data to generate a picture of the likely range of subsurface brine compositions that are potentially relevant to carbon sequestration efforts, both at sites of present interest and potential future interest.

Our focus is on subsurface brines with TDS > 10,000 mg/L (proposed EPA regulation excludes more dilute brines) found in sedimentary formations. We exclude surface brines (the subject of an extensive literature focusing on the role of chemical divides associated with evaporation and the evaporite mineral deposition) and brines found in hydrothermal systems associated with magmatism. Because of the geothermal gradient, ambient temperatures at production depths (some > 10,000 ft) for brines of interest could reach into the range 100-120°C. To assemble a picture of the compositional range, we used a database of "produced water" from the state of Wyoming (Geoffrey Thyne, 2009, personal communication to Roger Aines). We extracted representative examples of brines with TDS > 10,000 mg/L. We then added seawater as a reference, a reported Mt. Simon formation (Illinois Basin) brine, and a brine from the In Salah, Algeria carbon sequestration site. The resulting "catalog" of brine compositions extends from just over 10,000 mg/L TDS to over 300,000 mg/L.

Figure 1 shows the part of the catalog extending to 160,000 mg/L TDS. This would be expected to cover most if not all of the potentially treatable range. Seawater (35,928 mg/L TDS) is located near the middle. Most of the examples here, including seawater, are dominantly sodium chloride brines. They follow a "seawater" trend, in that they resemble in composition seawater that has been diluted or concentrated. For our purposes, their actual provenance is unimportant. Two other trends can be discerned. Some of the waters more concentrated than seawater are sodium chloride-calcium chloride brines. These are exemplified by "IL Mt. Simon Fm. #1" and "In

Salah KB502Z". Some of the waters more dilute than seawater are sodium sulfate-sodium chloride brines. These are exemplified by WY Sublette Co. #1 and WY Sublette Co. #2 (from the Tensleep formation). Figure 2 shows these brines in greater detail (it depicts only the part of the catalog extending to 40,000 mg/L TDS).

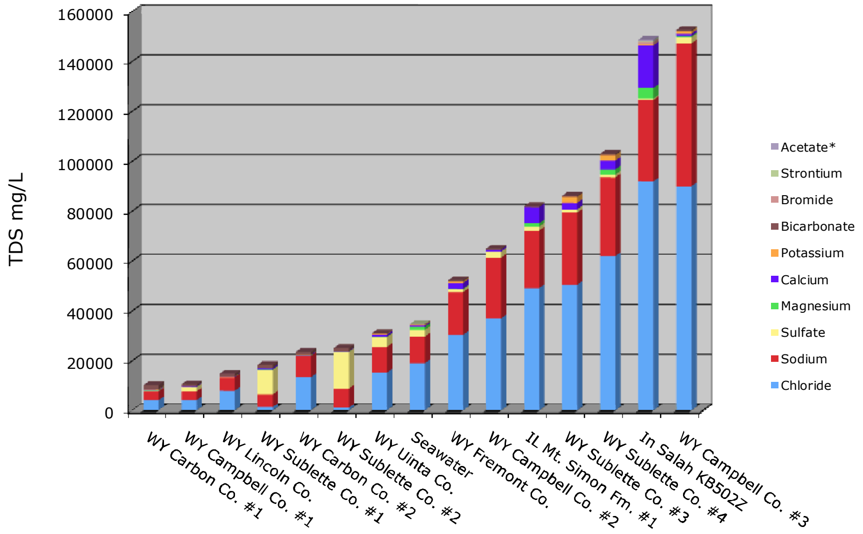


Figure 1. Catalog of subsurface brine compositions (brines with TDS > 160,000 mg/L are not shown). *Acetate includes related organic acid anions such as propionate).

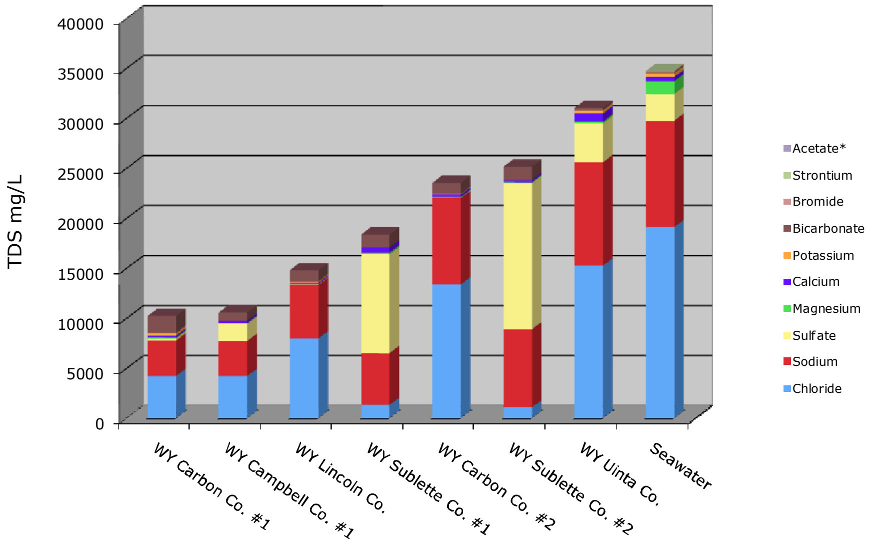


Figure 2. Catalog of subsurface brine compositions (lower range only, brines with TDS > 40,000 mg/L are not shown). *Acetate includes related organic acid anions such as propionate).

One would expect the more dilute brines to be more easily treatable. It is therefore natural to inquire about the distribution of brine concentrations. Our catalog of representative brines is not designed to represent frequency. We examined the frequency issue using the Wyoming "produced waters" database, which includes 9722 water compositions. We excluded a subset of waters lacking data for TDS and/or depth (as "UPPERDEPTH"). Then we computed a cumulative frequency curve and a histogram for all waters produced from > 3000 ft. depth and repeated in 2000 ft. depth increments for depths to 11,000 ft. The histograms for >3000 ft. and > 11,000 ft. depths are shown in Figures 3 and 4, respectively. This analysis indicates that brines with TDS in the range 10,000-40,000 mg/L are common at basically all depths of interest.

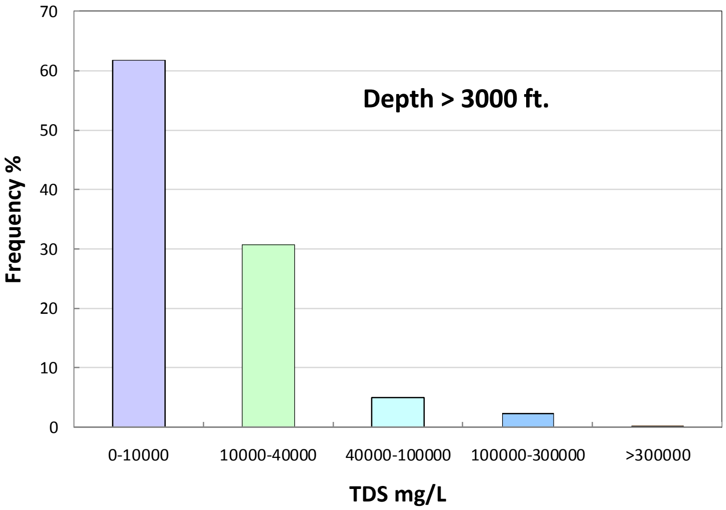


Figure 3. TDS distribution for Wyoming brines produced from below 3000 ft.

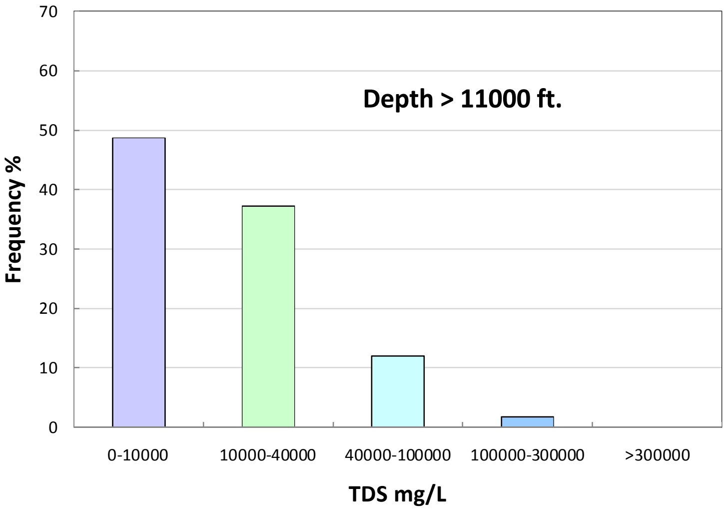


Figure 4. TDS distribution for Wyoming brines produced from below 11,000 ft.

The brine catalog is a work in progress. We are continuing to add to and refine it using data from other sites and regions.

A thermodynamic model has been used to evaluate the effects of reverse osmosis (RO) treatment of subsurface brines representative of potential CO_2 injection sites. Calculations were made using the Livermore EQ3/6 code and a database consistent with Pitzer's equations for thermodynamic activity coefficients, assuming temperatures of 25, 50, 70, and 90°C. Many potential injection sites involve subsurface brines in the 50-110°C range. The thermodynamic model itself is applicable to temperatures of about 150°C for the typical major components of subsurface brines. An alternative thermodynamic model based on the Extended UNIQUAC theory is also available in EQ3/6.

We first discuss calculations for two cases, a "seawater" brine and a representative brine from the Big Sky CSP site in Sublette County, Wyoming ("WY Sublette Co. #3). 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 reverse osmosis today, and much of today's RO technology and practical knowledge base pertinent to treatment of brines is centered on it. Some subsurface brines are similar in composition to seawater (as shown in Figures 1 and 2), and many subsurface brines are thought to have been derived from it. Thus, seawater is a useful reference. A subsurface "seawater" brine would have some differences from surface seawater. For example, it would not likely be supersaturated with respect to calcium and magnesium carbonate phases, as is surface seawater, and it would not contain the same biological or organic components. The representative brine from the Big Sky CSP 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.

Results of the calculations simulating the evolution of the residual fluids were obtained. Most of the calculations were made for batch systems, though some were also made for flow-through systems (in which cases precipitated minerals become separated from the residual fluid and cannot later back-react). Only the results for 50°C batch simulations will be shown here. For materials reasons, we consider this to be the most likely treatment temperature.

Figure 5 shows the calculated mineral precipitation for the seawater brine and the Big Sky CSP site brine (WY Sublette Co. #3) as a function of % H_2O removed. Only the upper ranges in which major mineral precipitation occurs are shown. Minor calcite ($CaCO_3$) appears near the start of the water removal process and persists, but this is not very significant quantitatively. Anhydrite ($CaSO_4$) is the first major precipitate, appearing at 79% H_2O removed in the case of the seawater brine, and at 62% H_2O removed in the case of the Big Sky CSP brine. In the seawater case, anhydrite is replaced at higher extent of water removal by glauberite ($Na_2Ca(SO_4)_2$). Glauberite does not appear in the Big Sky CSP brine case. The calculations are stopped shortly after halite (NaCl) begins to precipitate. At higher extents of H_2O removed, the amount of halite would be very substantially higher than the range shown in Figure 5. Once halite starts to precipitate, brine treatment is essentially infeasible. At other temperatures, calcite and halite behave similarly. However, at lower temperature the precipitation of anhydrite (the principal sulfate) shifts right to higher extent of water removed, while at higher temperature it shifts left (to only 8% water removed for the Big Sky brine at 90°C, to 45% water removed for the seawater brine at the same temperature.

The precipitation of sulfates (e.g., anhydrite, glauberite) is generally sufficient to be problematic in a treatment process. Calculations such as those represented in Figure 5 are therefore useful in planning a treatment process. If it were desired to push the treatment process into the range in which sulfate minerals precipitate, mitigation measures (e.g., to inhibit precipitation, or to inhibit sticking of precipitates to the treatment apparatus) or alternative treatment (e.g., nanofiltration) would be necessary.

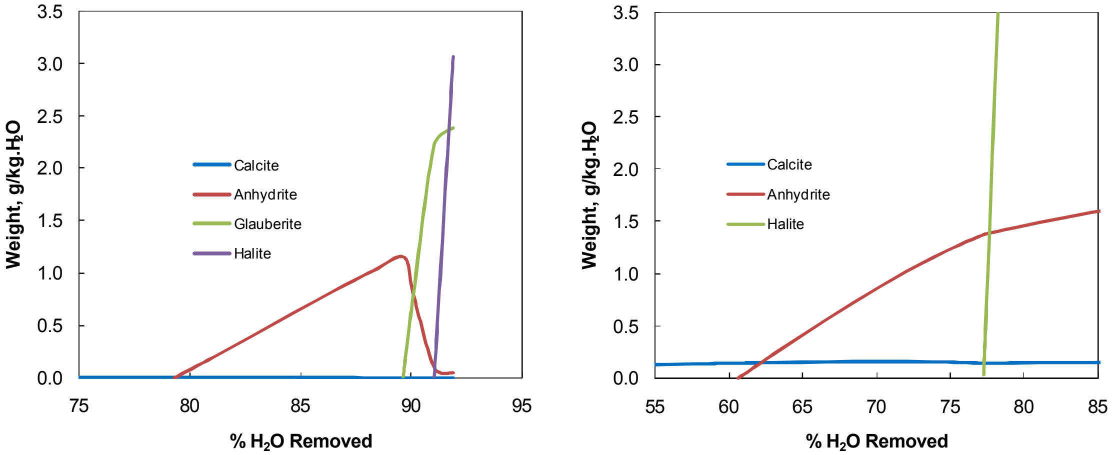


Figure 5. Predicted mineral precipitation as a function of water removal due to reverse osmosis at 50°C in a batch system. Left: seawater brine. Right: representative brine (WY Sublette Co. #3) near the Big Sky CSP site. Minor calcite ($CaCO_3$) precipitates at the start (not shown) and persists. The calculations are stopped shortly after halite (NaCl) begins to precipitate. Water treatment at this point becomes infeasible.

RO treatment of seawater in current industrial practice generally does not exceed 60% H_2O removed, although at lower temperature the precipitation of sulfates is displaced toward even higher extent of H_2O removed than is shown in Figure 5 (left). Something other than the precipitation of sulfates is the limiting factor in conventional RO treatment of seawater. This is likely due a combination of membrane limitations (discussed below), energy requirements, the ready availability of "fresh" seawater at seawater RO facilities, and potential environmental concerns regarding disposal of the residual brine. The limit of water extraction is nonetheless being pushed upward. In the case of an equivalent subsurface brine produced at a CO_2 sequestration site, the overall analysis supporting a feasible or optimal extraction of freshwater would be subject to a somewhat different set of constraints. A higher degree of freshwater extraction, or equivalently a more concentrated residual brine, could well be supportable. This especially true if the subsurface pressure due to CO_2 injection can be used to provide part or all of the pressure needed to run the reverse osmosis (or nanofiltration) process, and an appropriate value is place on limiting the pressure in the subsurface injection formation (e.g., maintaining a safety margin for caprock integrity).

A key factor in evaluating the energetic is the minimum pressure that must be applied to drive the process. The thermodynamic limit is the osmotic pressure. For high ionic strength brines, an accurate value can only be obtained using a thermodynamic model, such as ours based on Pitzer's equations. In this approach, the osmotic pressure is obtained from the thermodynamic activity of water using first principles. In the literature, the osmotic pressure is often calculated from the van't Hoff equation, which is a limiting approximation valid only in relatively dilute solutions. The Dow model used in industrial practice is essentially equivalent to the van't Hoff equation (it uses molality for the total solute concentration instead of molarity). Figure 6 shows the osmotic pressure results obtained from our calculations using the Pitzer model, compared with results from the Dow model. The Dow model underpredicts the osmotic pressure starting above 60% water removed for the seawater brine, and above only 20% water removed for the Big Sky CSP brine (WY Sublette Co. #3). At high extent of water removal, the underprediction becomes severe, and only results based on an accurate thermodynamic model should be used. At higher temperature, the osmotic pressure increases nearly linearly with the absolute temperature (exactly linearly for the Dow model). This dependency is not strong in the range of absolute temperature of interest here.

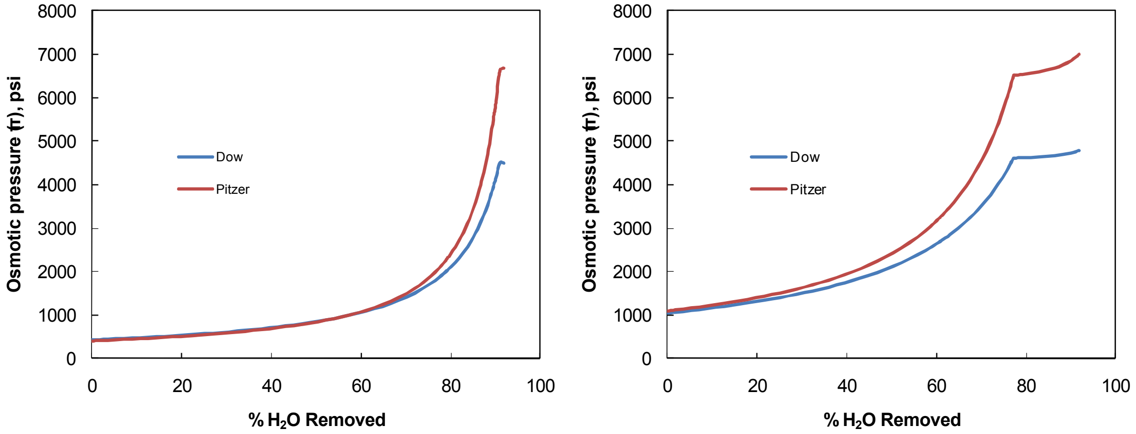


Figure 6. Predicted osmotic pressure in residual brine as a function of water removal due to reverse osmosis at 50°C in a batch system. Left: seawater brine. Right: representative brine (WY Sublette Co. #3) near the Big Sky CSP site . The "Pitzer" curves show the osmotic pressure as obtained from the activity of water calculated from a thermodynamic model using Pitzer's equations. The Dow model is a minor variation on the classic van't Hoff equation, neither of which is generally valid in high ionic strength brines.

RO works by applying a pressure difference across the membrane. Thermodynamically, the pressure difference (Δp) between feed or residual brine and the permeate solution must overcome the osmotic pressure difference ($\Delta\pi$) between the two solutions. The ideal permeate would be pure water, which would have an osmotic pressure of zero. In practice this is not quite achievable, but nearly so. Thus, the osmotic pressure of the feed or residual brine approximately equates to the minimum pressure difference to make the process work. To obtain a good flux, a somewhat greater pressure difference is normally applied. In theory, greater water extraction can be obtained by applying enough pressure on the feed or residual brine side to overcome whatever resistance is applied by the brine's osmotic pressure. Real membranes, however, can only withstand so much pressure. Until recently, RO membranes were limited to a pressure difference of 1000 psi. New membranes are rated to withstand 1500 psi.

Figure 7 shows the effect of membrane strength on conventional RO at 50°C of the seawater brine and the representative brine (WY Sublette Co. #3) near the Big Sky CSP site. The information is essentially that given in Figure 6, although the scale has been changed and the membrane strength is marked. For the seawater brine, the osmotic pressure reaches the membrane strength at about 71% water extraction. For the more concentrated Wyoming brine, this condition occurs at about 24% water extraction. What this means is that if higher extraction is required, it is necessary to apply a somewhat less conventional treatment methodology.

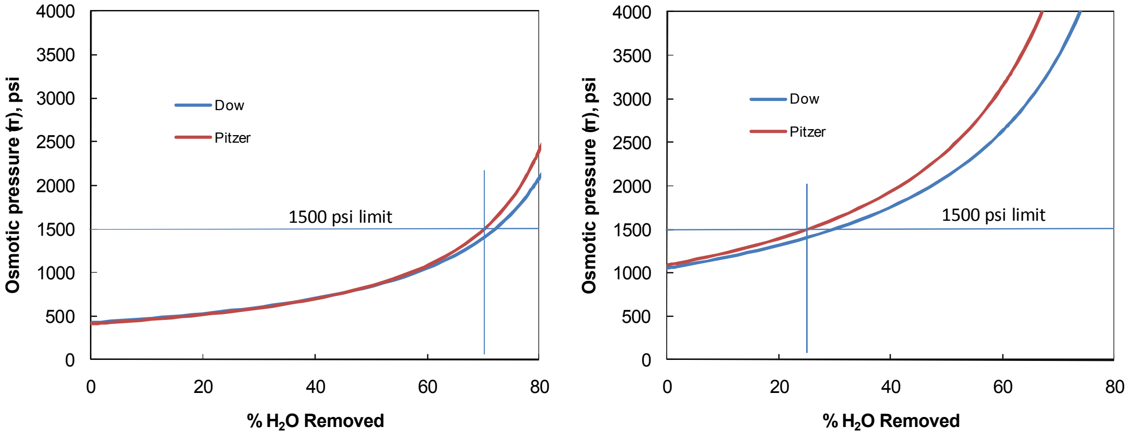


Figure 7. Predicted osmotic pressure in residual brine as a function of water removal due to reverse osmosis at 50°C in a batch system, showing the effective of a maximum membrane strength of 1500 psi. Left: seawater brine. Right: representative brine (WY Sublette Co. #3) near the Big Sky CSP site .

Achieving a higher level of extraction (beyond the limit for direct production of high-quality permeate) is possible if desalination takes place incrementally. The idea here is to raise the osmotic pressure on the permeate side so that the osmotic pressure difference is kept within the membrane strength. The salty permeate (less salty than the feed or residual brine) then becomes the feed to a subsequent RO step. A final RO step produces high-quality permeate. There are several ways to accomplish this staged RO process. Perhaps the least unconventional is to use a nanofiltration (NF) membrane, which preferentially rejects highly charged anions, notably sulfate. NF membranes produce a relatively salty permeate, but do so under pressure differences of only a few hundred psi. Permeate from an NF step can be fed into a subsequent NF step to produce a less concentrated permeate. A “high flux” RO membrane can be run at “low flux,” which will also produce a salty but less concentrated permeate. Finally, there is also the possibility of borrowing from forward osmosis methods and using a carrier electrolyte such as ammonium carbonate on the permeate side. The resulting permeate would be treated in a subsequent step to regenerate the carrier electrolyte. We note that the term “staged RO” is also used to refer to a process in which residual brine from an RO step is taken to a higher pressure and then treated in subsequent step. Both forms of “staging” could be used in a brine treatment process.

The In Salah KB502Z brine is a good example of a substantially more concentrated brine (149,958 mg/L TDS). Results are shown in Figure 8. The mineral precipitation suggests that water extraction of 58% might be achievable. However, the osmotic pressure is a more limiting factor. The starting brine (feed composition) has an osmotic pressure that already exceeds the 1500 psi membrane strength. Therefore, a staged treatment process would be required to extract any freshwater, and the fraction of extracted water would likely not be high, perhaps 25% at most.

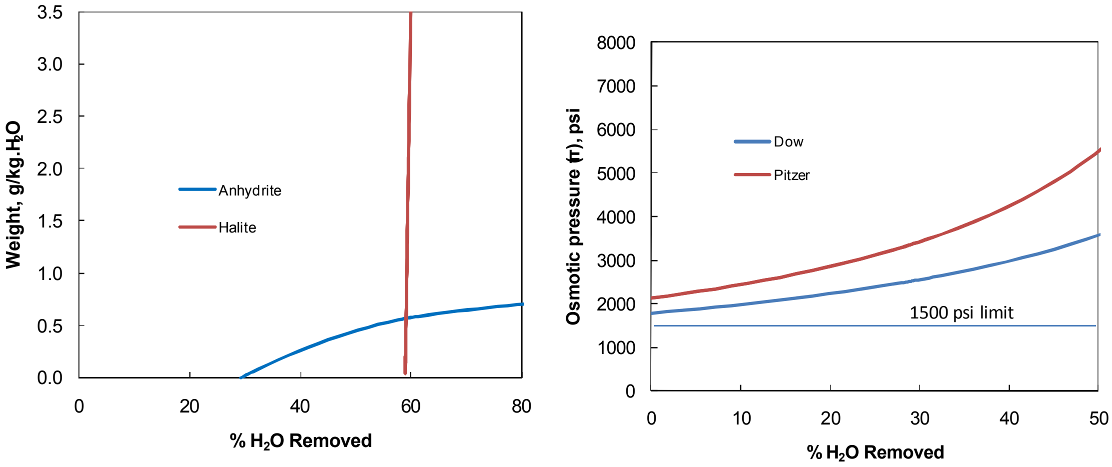


Figure 8. Calculated results for reverse osmosis at 50°C of In Salah KB502Z brine in a batch system. Left: mineral precipitation. Right: osmotic pressure (only shown to 50% water removal). Note that the feed brine composition has an osmotic pressure greater than 1500 psi.

A very contrasting picture appears from calculations for WY Sublette Co. #2 brine, which is a sodium sulfate-sodium chloride brine (from the Tensleep Formation) with 24,501 mg/L TDS (less than the TDS of seawater). Results are shown in Figure 9. They suggest that mineral precipitation is manageable to at least 89% water extraction. At 94% water extraction, thenardite (Na_2SO_4) precipitation is a definite limiting factor. Here thenardite plays the role played by halite in the brine examples discussed previously. The osmotic pressure does not achieve the 1500 psi lmit until about 89% extraction. It appears that very conventional RO treatment of this brine could easily achieve >80% extraction. Note that for this brine, the thermodynamic ("Pitzer") estimation of the osmotic pressure is generally less than what is predicted by the Dow model. That is the reverse of what was seen for the sodium chloride and sodium chloride-calcium chloride brines.

The calculations presented above do not account for potential transfer of components other than water through the treatment process. CO_2 pressures would build up in the residual brine, and $CO_{2(aq)}$ (or carbonic acid) would readily pass through a treatment membrane. This could alter the chemistry of the residual brine. A likely result of this would be calcite precipitation (more substantial than shown in Figure 4, for example) at or near the membrane surface. Such a process can be addressed by our modeling technology, but results are not included here. Figure 10 shows the buildup of CO_2 partial pressure (pCO_2) ignoring CO_2 passage through the membrane. The primary thing to note is that the scales are quite different between the seawater brine and the WY Sublette Co. #3 (Big Sky CSP site) brine. There is a small buildup of pCO2 in the seawater case,

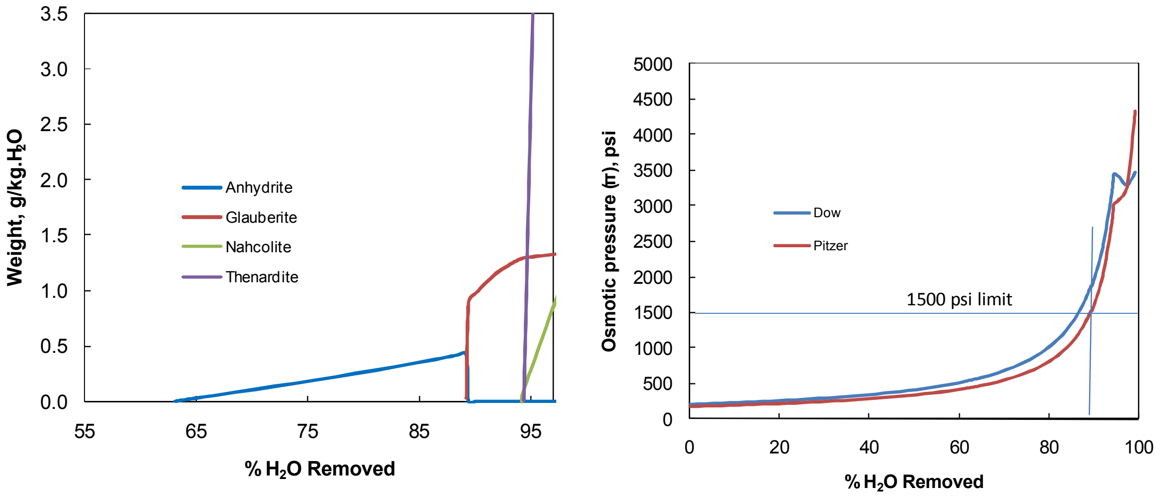


Figure 9. Calculated results for reverse osmosis at 50°C of WY Sublette Co. #2 brine in a batch system. Left: mineral precipitation. Right: osmotic pressure.

followed by a decline once anhydrite starts to precipitate. The consequences of CO_2 passage through a membrane would be relatively small. There is a much larger buildup in the case of the WY Sublette Co. #3 brine, and there is no decline in pCO_2, despite the precipitation of anhydrite. The behavior in these systems is not simple, and is in part a function of the complex behavior of activity coefficients at high ionic strength. A thermodynamic model such as ours is required to be able to evaluate such effects. This is also true in regard to potential effects such changes in pH, which may be significant for some brines.

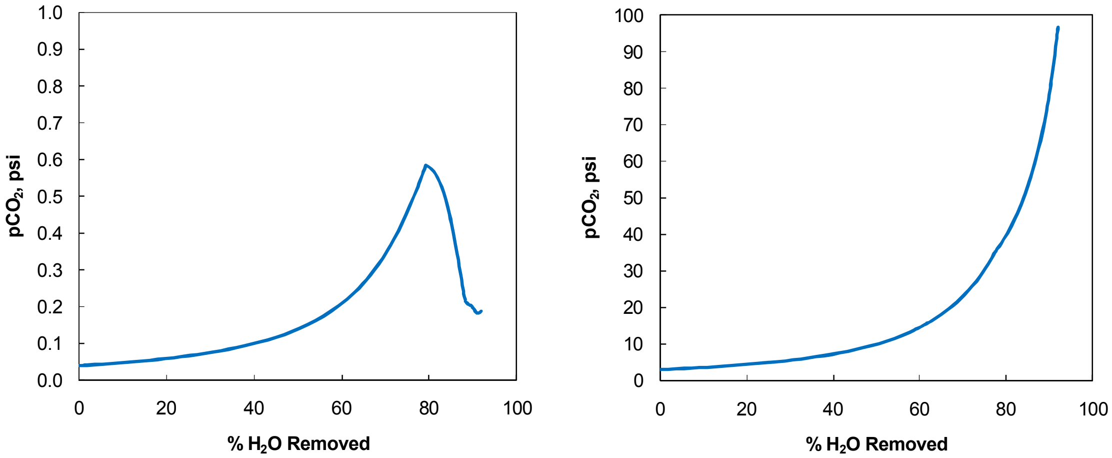


Figure 10. Predicted CO_2 pressure in residual brine as a function of water removal due to reverse osmosis at 50°C in a batch system. Left: seawater brine. Right: representative brine (WY Sublette Co. #3) near the Big Sky CSP site. Note the approximately two order-of-magnitude difference in the scale of the pCO_2 for the two cases.

In general, we conclude that the potential for freshwater extraction can be approximately categorized as follows:

- 10,000–40,000 mg/L TDS brines
  - Standard RO; good recovery (50% at least)

- 40,000-100,000 mg/L TDS brines
  - Standard RO with lower recovery
  - Higher recovery possible with less conventional multi-stage (incremental desalination) process likely including NF
- 100,000-300,000 mg/L TDS brines
  - Multi-stage process required (NF + RO), on the leading edge
  - Low recovery anyway

- >300,000 mg/L TDS brines: Not likely to be treatable.

This analysis is subject to further refinement. Many oil field brines contain minor petroleum components that would require pre-treatment to remove these components prior to desalination. This factor could significantly tip the cost issue for a given well. It may be possible to manage brine production wells to minimize this factor, either by choice of sequestration site, exact production well site, or choice of production depth.

Preliminary Reservoir Modeling (Yue Hao):

There are two main pressure benefits associated with reservoir-pressured brine treatment: (1) reduced-cost treatment of water providing fresh water, and (2) reduced aquifer pressure and increased storage volume. These two benefits are in some degree in opposition to each other; extracting too much water to reduce pressure can drop the inlet pressure below the beneficial point for RO.

In order to understand how to balance these two benefits we conducted preliminary analyses using NUFT (the standard LLNL code used to study sequestration flow, transport, and geochemical reaction). A two-dimensional simulation domain, as seen in Figure 11, is selected to represent a 200m-thick reservoir at a depth of about 2000 m. While the top and bottom boundaries are kept impermeable the hydrostatic pressure conditions are assigned along the lateral boundary. The permeability and porosity of the reservoir are assumed as 100 mD and 20%, respectively. The injection well with an area of 1x1 m^2 is located at the top of the formation, and the supercritical CO_2 is injected at a constant rate of 1000 ton/yr-m for 5 years. The injection rated used for this 2-D simulations corresponds roughly to an injection rate of 10^6 ton/yr through a 1000 m-long horizontal injection well. The water pumping well is placed at the bottom of the reservoir and 2 km laterally apart from the injection well. The water extraction rate is chosen as the same as the injection rate. Figure 12 and 13 show the comparison of pressure and liquid saturation profiles at 5 years after the injection starts for the cases with and without water pumping/extraction. It can be seen that water extraction readily helps to reduce the peak overpressure from ~65 bars to ~34 bars. It should also be noted that due to the pumping/extraction effects there is a tendency for the CO_2 plume to migrate towards the pumping well especially when the injection and production wells are placed closer to each other. Therefore further parametric and sensitivity studies are needed in order to address this concern and also help achieve maximum benefits from implementing this technology.

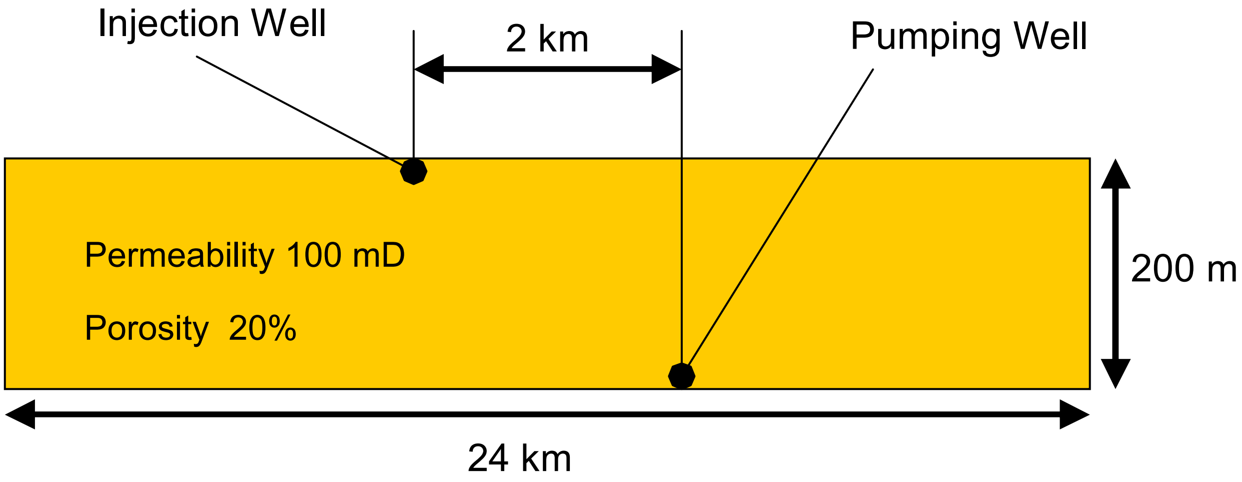
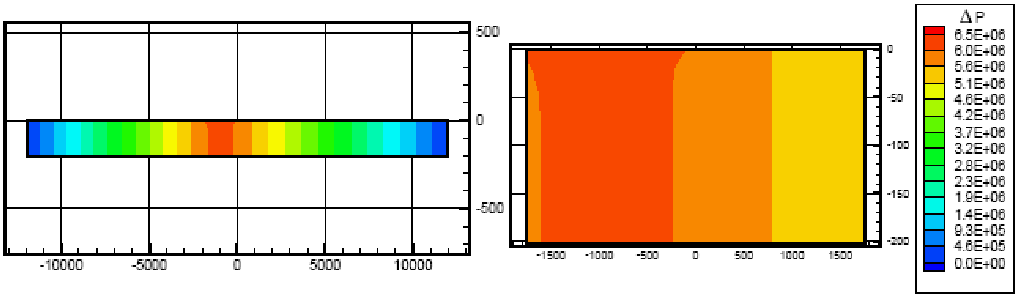


Figure 11. Two-dimensional model domain and geometry


5 year after injection (without water pumping)

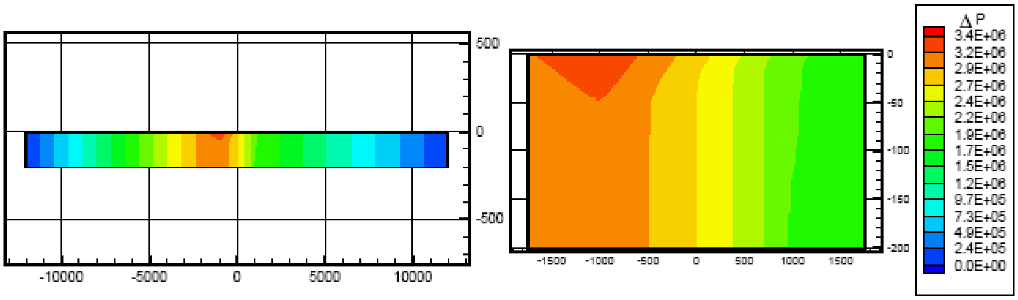
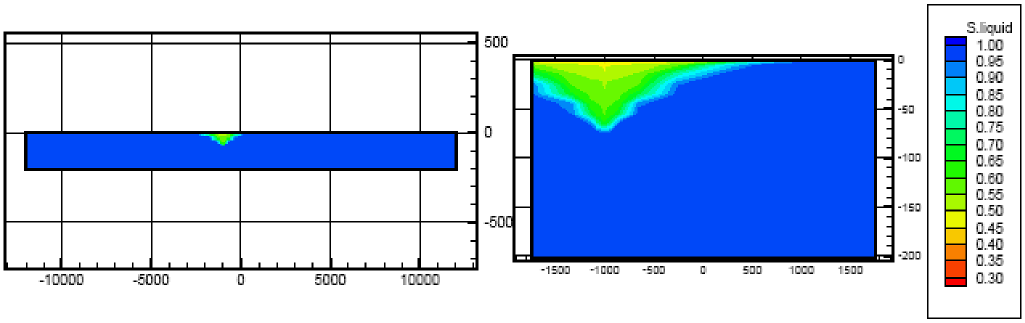
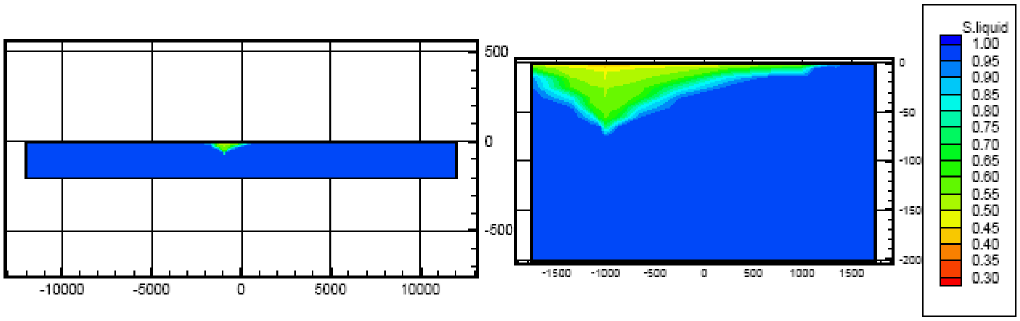

5 year after injection (with water pumping)

Figure 12. Pressure profile at 5 years after injection for the cases with and without water pumping/extraction



5 year after injection (without water pumping)



5 year after injection (with water pumping)

Figure 13. Liquid saturation profile at 5 years after injection for the cases with and without water pumping/extraction

Conclusions

1) The concept of aquifer-pressured RO to provide fresh water associated with carbon dioxide storage appears feasible.
2) Concentrated brines such as those found in Wyoming are amenable to RO treatment. We have looked at sodium chloride brines from the Nugget Formation in Sublette County. 20-25% removal with conventional methods is realistic; higher removal appears achievable with NF. The less concentrated sulfate-rich brines from the Tensleep Formation in Sublette County would support >80% removal with conventional RO.
3) Brines from other proposed sequestration sites can now be analyzed readily. An osmotic pressure curve appropriate to these brines can be used to evaluate cost and equipment specifications.
4) We have examined a range of subsurface brine compositions that is potentially pertinent to carbon sequestration and noted the principal compositional trends pertinent to evaluating the feasibility of freshwater extraction. We have proposed a general categorization for the feasibility of the process based on total dissolved solids (TDS).
5) Withdrawing pressurized brine can have a very beneficial effect on reservoir pressure and total available storage capacity. Brine must be extracted from a deeper location in the aquifer than the point of CO_2 injection to prevent CO_2 from migrating to the brine extraction well.

Costing of the RO and NF/RO cycles is now being conducted. Initial results indicate that the costs will be low due to the aquifer pressure which enables the RO system to be sized differently than must be done for seawater systems where any water treated must be initially raised to high pressure.