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Volumetrics of CO_2 Storage in Deep Saline Formations

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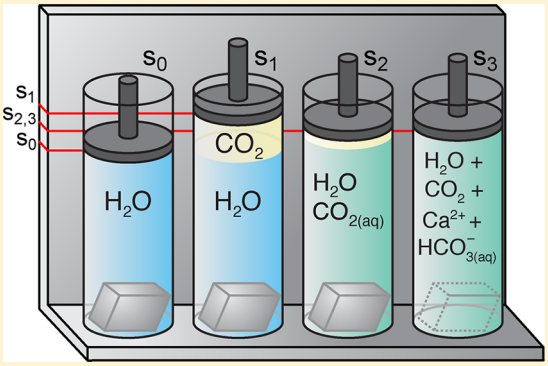
ABSTRACT: Concern about the role of greenhouse gases in global climate change has generated interest in sequestering CO_2 from fossil-fuel combustion in deep saline formations. Pore space in these formations is initially filled with brine, and space to accommodate injected CO_2 must be generated by displacing brine, and to a lesser extent by compression of brine and rock. The formation volume required to store a given mass of CO_2 depends on the storage mechanism. We compare the equilibrium volumetric requirements of three end-member processes: CO_2 stored as a supercritical fluid (structural or stratigraphic trapping); CO_2 dissolved in pre-existing brine (solubility trapping); and CO_2 solubility enhanced by dissolution of calcite. For typical storage conditions, storing CO_2 by solubility trapping reduces the volume required to store the same amount of CO_2 by structural or stratigraphic trapping by about 50%. Accessibility of CO_2 to brine determines which storage mechanism (structural/stratigraphic versus solubility) dominates at a given time, which is a critical factor in evaluating CO_2 volumetric requirements and long-term storage security.



INTRODUCTION

Managing climate-altering CO_2 emissions by carbon capture and storage (CCS) presents significant economic, political, and technological challenges.[1−4] One option for mitigating CO_2 emissions is to capture and inject CO_2 into confined saline formations.

Pore space in deep saline formations is initially filled with brine, and no "free" volume is available to accommodate injected CO_2. Injection of CO_2 must, therefore, be accompanied by increase in formation pressure,[5] compression of fluid and rock, and/or displacement of brine[5] (Figure 1). Whereas natural subsurface accumulations of CO_2[6] in environments similar to those proposed for CCS formed slowly and equilibrated with their surroundings over long periods, captured CO_2 will be injected at high volumetric rates over short time spans (tens of years). Numerical modeling has assessed the rate and magnitude of pressure build-up, brine migration, and the potential for CO_2 injection-induced seismicity[8] associated with rapid injection of large volumes of CO_2 into the subsurface.[7] Here, we assess equilibrium fluid volume changes in a confined formation after CO_2 injection, based on volumetric properties of the system CO_2-H_2O-NaCl-$CaCO_3$. The results are relevant to estimates of end-point storage capacity and potential long-term security of CO_2 sequestration in saline formations.

Estimates of reservoir CO_2 storage capacity depend on the storage mechanism(s) being considered.[2,12] Previous studies estimated CO_2 storage capacity based on structural or stratigraphic trapping of CO_2, without including the effects of CO_2 or calcite dissolution.[11,12] However, multiple CO_2 trapping mechanisms define the *ultimate* long-term storage capacity.[2,13,14] Analyses of fluids from natural CO_2 accumulations indicate that, in at least some cases, the total CO_2 capacity is largely determined by solubility trapping,[15] and thermodynamic modeling has quantified the capacity for CO_2 dissolution into formation waters.[16,17] Recent studies have emphasized potential benefits of CO_2 injection protocols designed to promote CO_2-brine dissolution, in order to enhance storage security.[5,18] The effect of CO_2 dissolution and mineral reaction on storage capacity estimates is not yet fully characterized.[12]

The objectives of this study were to compare the subsurface volume required to store an amount of CO_2 as a supercritical fluid with that required to store the same amount of CO_2 as a dissolved component in brine. We applied thermodynamic modeling of the system CO_2-H_2O-NaCl-$CaCO_3$ to assess the volumetric properties of supercritical CO_2 coexisting with formation brine, CO_2-saturated brine, and CO_2+calcite-saturated brine. Thus, we characterized the volumetric effects

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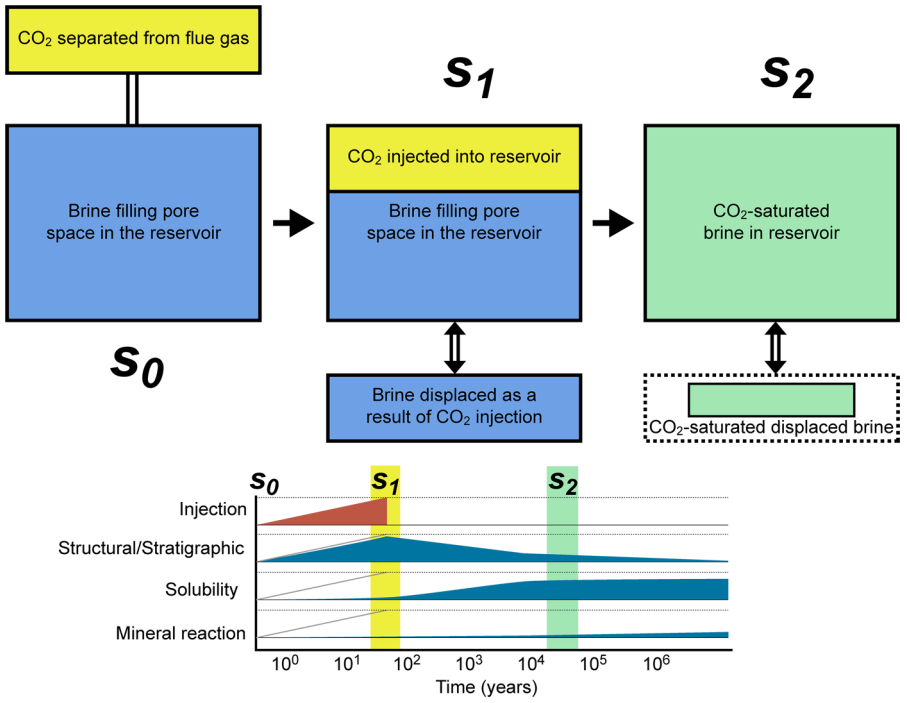

Figure 1. Conceptual model of volume changes associated with various CO_2 storage mechanisms following injection of CO_2 into a saline formation. At s_0 the system is represented by a volume of CO_2 captured from flue gases (yellow box) and a subsurface saline formation in which all of the pore volume is filled with brine (blue box). As a result of injection of supercritical CO_2 into the formation (s_1), an equal volume of brine is displaced from the formation. Some of the CO_2 dissolves into the brine. The volume of the CO_2-saturated brine (green box at s_2) is less than that of the supercritical CO_2 plus brine (s_1) but greater than the original brine volume before CO_2 injection (s_0). Bottom: Approximate time scales over which various trapping mechanisms become significant (modified from the IPCC 2005 report).[2]

of CO_2 dissolution and reaction with calcite, so that these results can be used to refine storage capacity estimates and to design effective protocols to maximize storage capacity and long-term storage security.

METHODS

Various mechanisms are recognized for geological storage of CO_2, including structural or stratigraphic trapping, trapping as a dissolved component in brine, and trapping by reaction with carbonate minerals.[2] Our conceptual model for volumetrics of CO_2 storage in saline formations considers the equilibrium end points of these three processes in a stepwise fashion. The total system is represented by an initial mass of CO_2 and a known mass of brine filling the formation pore space (Figure 1). In the first step, the pore space contains only brine. Supercritical CO_2 is injected into the reservoir and a volume of brine equal to the volume of injected CO_2 is displaced from the reservoir (Figure 1; s_1). In this scenario, we do not consider possible changes in reservoir volume owing to compressibility or deformation. In the second step, CO_2 dissolves into the brine to produce a CO_2-saturated solution (Figure 1; s_2). The volume occupied by the CO_2-saturated solution is less than the volume of the injected CO_2 plus brine at step s_1 because the apparent molar volume of dissolved CO_2 is less than the molar volume of supercritical CO_2 at the storage pressure−temperature (PT) conditions.[9] Thus, fluid volume decreases as the system evolves from s_1 to s_2, enhancing the storage capacity of the reservoir. In step three, some CO_2 and water react with calcite to form Ca^{2+} and HCO_3^-. Because of the fast dissolution rates of carbonate minerals compared to silicates, dissolution of calcite will be the most important mineral reaction initially, but additional mineral solution reactions are expected as the system evolves.[10]

Fluid volumetric properties were estimated using published equations of state (EOS).[19−22] The density of supercritical CO_2 is represented by a virial-type EOS.[20] The solubility of CO_2 in water and brine is modeled based on Pitzer's formalism.[21,23] The density of the aqueous fluid is calculated from the apparent molar volumes of CO_2[19] and NaCl[24] and the molar volume of H_2O.[22] The CO_2 solubility model[21] has been tested by modeling CO_2 storage in natural brines and yielded good results.[25] To compare the volume required to store CO_2 as a supercritical fluid (structural or stratigraphic trapping) with the volume required to store the same amount of CO_2 as a dissolved component in brine (solubility trapping), we selected initial amounts of brine and CO_2 such that all injected CO_2 could be dissolved to produce CO_2-saturated brine. Next, we added increments of calcite and as much additional CO_2 as can be dissolved by reaction with calcite. This approach allows comparison of volumetric changes for three trapping processes − s_1 in which all CO_2 is stored as a supercritical fluid, s_2 in which all CO_2 is stored as a dissolved component in brine, and s_3 in which additional CO_2 is dissolved via the calcite dissolution reaction. All calculations assume constant pressure, although in real-world scenarios, pressure and fluid volume will both increase somewhat upon injection.

Based on various economic and geological constraints, the storage horizon in saline formations will likely be between 1.0 and 4.5 km depth, with temperature of 50−140 °C, and pressure before injection of 10−75 MPa.[2,14,26] The minimum pressure represents hydrostatic pressure, and the maximum pressure represents 0.6 × lithostatic pressure at the depth of interest. At pressure above this value, vertically oriented hydrofractures may develop.[27,28] This PT range is highlighted in gray on the PT plots displaying the results. Previous studies

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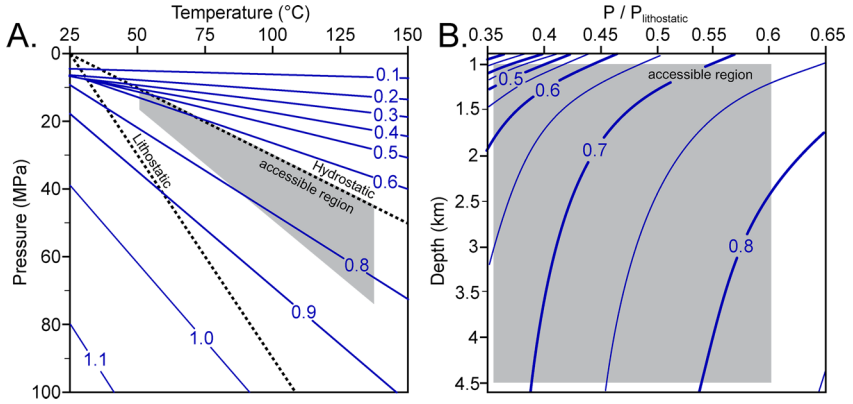

Figure 2. Density of CO_2 (in g/cm^3) as a function of pressure and temperature, shown in pressure−temperature space (A) and in depth-fraction of lithostatic pressure space (B). Hydrostatic and lithostatic pressure gradients shown in (A) assume a geothermal gradient of 25 °C/km. The shaded area represents the *PT* conditions technologically and economically accessible for CO_2 storage in saline formations. Notice that A and B contain the same data presented on different axes.

considered the feasibility of injecting large volumes of CO_2 into deep saline formations,[7,29,30] including various economic and engineering constraints not considered here. Briefly, these studies suggest that pressure build-up during injection may be a limiting factor in determining storage capacity of a formation but that both passive (diffuse leakage) and active (brine extraction) methods can attenuate pressure and allow large-scale injection to proceed.[7]

In the following sections, volumetric changes accompanying s_1) CO_2 injection (physical trapping), s_2) dissolution in brine, and s_3) reaction with calcite are described at discrete times following injection. The motivation for presenting results at discrete stages is to differentiate the volumetric contributions of each mechanism. We emphasize that during and after injection, several trapping mechanisms will likely contribute to the overall storage capacity simultaneously.[2] However, as a first approximation it is reasonable to separate the various processes based on the different time scales at which each is dominant. Field and laboratory experiments and numerical simulations have semiquantitatively constrained the times required for CO_2 dissolution and mineral reactions in saline aquifers. Although time estimates show wide variability (owing mainly to differences in local reservoir conditions and hydrology), a compilation of those results[2] suggests overall agreement that physical trapping dominates in the first years to decades, while dissolution of CO_2 and calcite becomes significant over decades to centuries. Other mineral reactions contribute centuries to millennia *after* injection (Figure 1).[2]

Immediately following CO_2 injection, the system consists of brine and supercritical CO_2, and the system volume equals the initial volume of brine plus the volume of injected supercritical CO_2 (Figure 1, s_1). The increase in fluid volume when CO_2 is injected into an H_2O- or H_2O-NaCl-filled formation is

$$\%\text{volume increase} = \frac{\overline{V}_{CO_2} m_{CO_2}}{\overline{V}_{H_2O-NaCl}\left(m_{NaCl} + \frac{1000\ g/kg}{M_{H_2O}}\right)} \times 100\% \quad (1)$$

where $\overline{V}_{CO_2}$ and $\overline{V}_{H_2O-NaCl}$ are the molar volumes of the CO_2 phase and aqueous phase, respectively (cm^3/mol), m_{CO_2} and m_{NaCl} are the CO_2 solubility and brine salinity, respectively (mol/kg H_2O), and M_{H_2O} is the molar mass of H_2O (g/mol).

Equation 1 is based on constant mass of H_2O in the system during and after CO_2 injection, representing the pre-existing brine in the pore volume, and the total fluid volume implicitly includes any brine displaced or extracted during injection. Thus, eq 1 (and all subsequent equations) computes volumes in units of *cm^3 per kg H_2O*. Whereas the total amount (number of moles) of fluid in the system is not constant (it increases, as CO_2 is injected), the total mass of H_2O in the system *is* constant. Therefore, volume changes per kg H_2O represent changes in total fluid volume.

The injected CO_2 phase and aqueous brine are not in chemical equilibrium. Over time CO_2 dissolves into the aqueous phase. The volume change as the system evolves from CO_2-free brine to CO_2-saturated brine is

$$\%\text{volume increase} = \frac{\left(\frac{\overline{V}_{H_2O-NaCl-CO_2}}{X_{H_2O} M_{H_2O}} \times 1000\ g/kg\right)}{\overline{V}_{H_2O-NaCl}\left(m_{NaCl} + \frac{1000\ g/kg}{M_{H_2O}}\right)} \times 100\% \quad (2)$$

where $\overline{V}_{H_2O-NaCl-CO_2}$ is the molar volume of the CO_2-saturated aqueous phase (cm^3/mol), and X_{H_2O} is the mole fraction of H_2O in the aqueous phase.

Reaction with calcite allows dissolution of additional CO_2, according to the reaction

$$CO_2(v) + H_2O(l) + CaCO_3(cal) = Ca^{2+} + 2HCO_3^-(aq) \quad (3)$$

The equilibrium constant for eq 3 was calculated based on the Henry's Law constant for CO_2 dissolution, the calcite solubility product, and the first and second $H_2CO_3(aq)$ dissociation constants. The solubility of calcite (and resulting enhanced CO_2 solubility) was calculated by extrapolating the temperature functions for the relevant equilibrium constants[32] over the *PT* range of the model. The volume change of the aqueous phase resulting from calcite dissolution is estimated by approximating the volume occupied by dissolved Ca^{2+} and HCO_3^- ions based on the apparent molar volume of dissolved $CaCl_2$.[31] The volume change is expressed as

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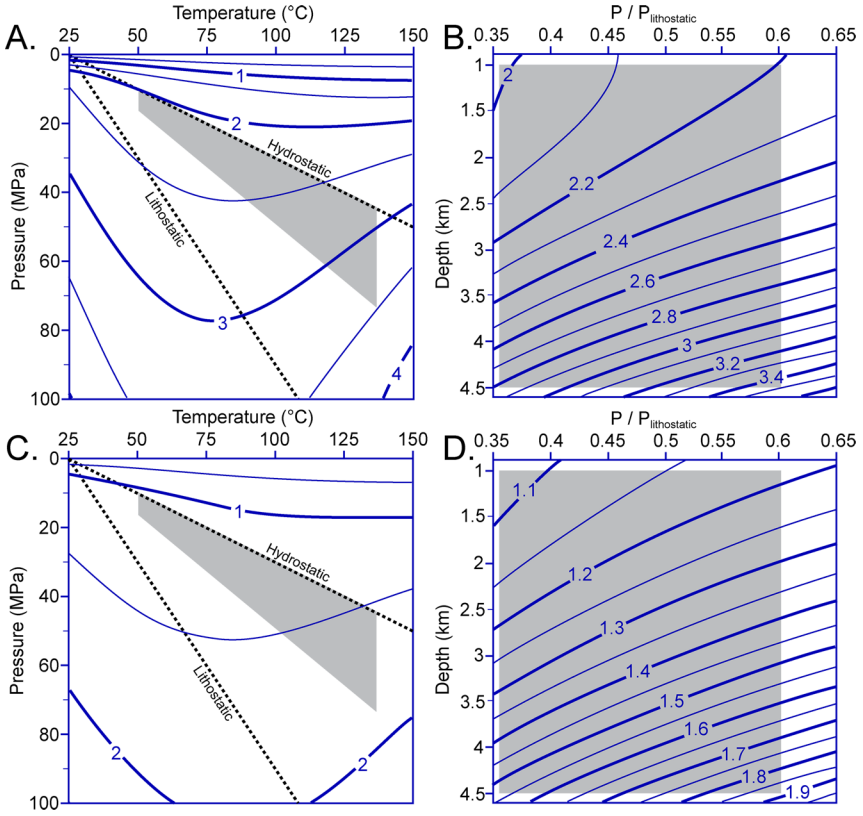

Figure 3. Solubility of CO_2 (mol %) as a function of pressure and temperature in H_2O (A and B) and in 15 wt % NaCl brine (C and D). The data are plotted in pressure−temperature space (A and C) and in depth-fraction of lithostatic pressure space (B and D). The shaded area represents the *PT* conditions accessible for CO_2 storage in saline formations.

$$\%\text{volume change} = \frac{S_{cal} V_{Ca(HCO_3)_2(aq)}}{V_{CO_2\text{-saturated solution}} + S_{cal} V_{Ca(HCO_3)_2(aq)}} \times 100\% \quad (4)$$

where $V_{Ca(HCO_3)_2(aq)}$ is the apparent molar volume of dissolved calcium and bicarbonate ions, and S_{cal} is the solubility of calcite (mol/kg H_2O).

Our model considers the system H_2O-NaCl-CO_2-$CaCO_3$, whereas natural saline brines contain other salts, and injected CO_2 may contain other gaseous species. Lack of experimental data over the complete *PT* range of interest limits our ability to quantitatively model these effects. However, we expect that overall trends in solubility and volumetric properties are reasonably approximated by the H_2O-NaCl-CO_2-$CaCO_3$ system. For example, CO_2 solubility experiments in natural connate brines from the Oriskany formation (eastern USA) showed good agreement with the CO_2 solubility model used here.[21,25]

RESULTS AND DISCUSSION

At *PT* conditions of CO_2 storage in saline formations, CO_2 density ranges from about 0.4 to 0.8 g/cm^3 (Figure 2). At the same conditions, the solubility of CO_2 in H_2O ranges from about 2 to 3.4 mol % (Figure 3A and B), and CO_2 solubility in 15 wt % NaCl brine (throughout this section, the term "brine" refers to an aqueous fluid of 15 wt % NaCl) ranges from about 1.1 to 1.8 mol % (Figure 3C and D).[16,17,21,33]

When an amount of CO_2 equal to the amount required to saturate the aqueous phase (i.e., the amount of CO_2 that could be stored as a dissolved component in the brine) is injected, its volume is between 75 and 140 cm^3 per kg water or 50−70 cm^3 per kg brine. During injection, the total fluid volume (*before* dissolution) increases by approximately 7.3 to 10% for pure H_2O (Figure 4A and B) or by about 3.9 to 5.4% for brine (Figure 4C and D). The larger volume increase for H_2O compared to brine reflects higher solubility of CO_2 in pure H_2O compared to brine at the same *PT* conditions (requiring injection of a greater amount of CO_2 to saturate pure H_2O, Figure 3).

The maximum amount of CO_2 that can be dissolved in brine is limited by the CO_2 solubility at the formation *PT* conditions (Figure 3). The apparent volume of dissolved CO_2 at saturation is between 40 and 80 cm^3 per kg water or 25−55 cm^3 per kg brine. Therefore, the volume occupied by the CO_2-saturated aqueous phase is greater than the brine (H_2O) volume before injection (Figure 1). Within the *PT* range considered here, the volume increases by about 3.5 to 8% if the pore fluid is pure H_2O (Figure 5A) and by about 2.2 to 4% if the pore fluid is brine (Figure 5B).

Owing to the low solubility of calcite, dissolution of calcite increases the volume of the aqueous phase by only 0.01−0.04% (Figure 6). Thus, the contribution of calcite dissolution to the net volume change is insignificant compared to the contributions of supercritical CO_2 or dissolved CO_2.

The volume changes described above (Figures 4−6) are compared to the initial fluid volume before CO_2 injection (Figure 1). We also compared volume change as the CO_2 phase (s_1; Figure 1) dissolves into the brine (s_2; Figure 1). As shown by the reduced area of the displaced brine box between s_1 and s_2 (Figure 1), dissolution of CO_2 into brine reduces the net fluid volume (compared to the sum of the volumes of brine and CO_2

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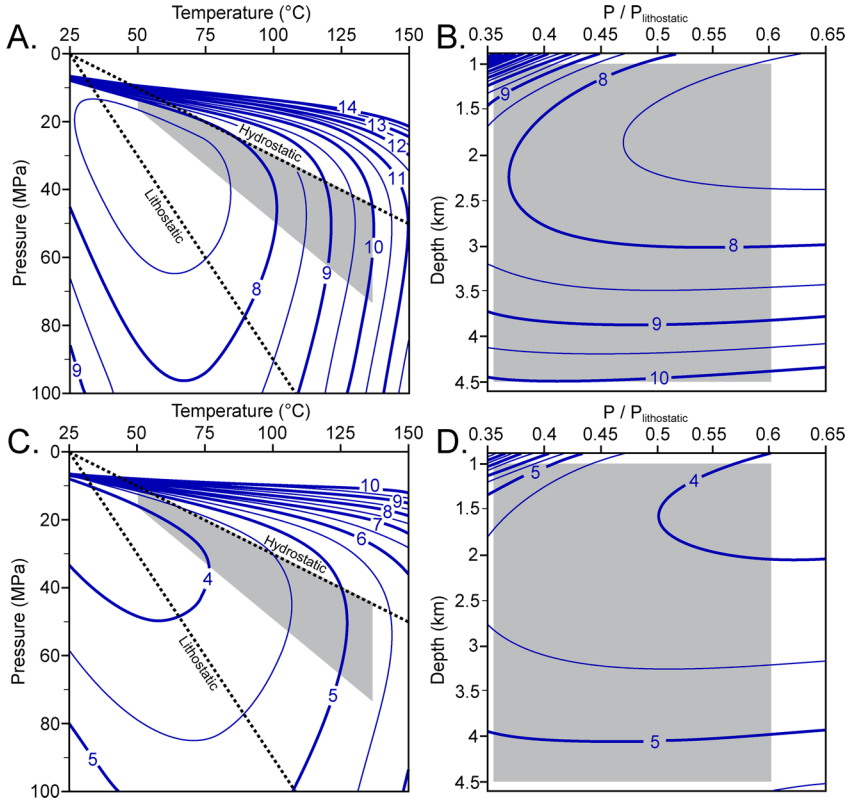

Figure 4. Percent increase in fluid volume when CO_2 is stored in a subsurface reservoir as a separate supercritical fluid. The volume increase represents the percent difference between the volume of the brine *plus* the volume supercritical CO_2 injected (Figure 1, s_1), compared to the volume of brine before injection (Figure 1, s_0). The data are plotted in pressure−temperature space (A and C) and depth-fraction of lithostatic pressure space (B and D). The shaded area represents the *PT* conditions accessible for CO_2 storage in saline formations. Parts A and B are for H_2O and C and D are for 15 wt % NaCl brine.

immediately following injection). Throughout most of the *PT* region of CO_2 storage, the apparent volume of dissolved CO_2 is about half of the volume of the same mass of supercritical CO_2. Therefore, the volume decrease from s_1 to s_2 is between 45 and 65%, independent of whether the pore fluid is H_2O (Figure 7A and B) or brine (Figure 7C and D). In other words, although the volume required to store injected CO_2 is greater than the initial brine volume regardless of whether CO_2 is dissolved or is present as a separate supercritical fluid, solubility trapping requires only 50% of the volume required for structural or stratigraphic trapping of the same amount of CO_2.

Previous studies[34] have emphasized that dissolution of CO_2 increases the density of the brine, making CO_2-saturated brine negatively buoyant compared to CO_2-free brine. Thus, CO_2-saturated brine will sink in the reservoir,[34] enhancing storage security. Based on volumetric modeling, we show that this mechanism has the additional advantage of enhancing storage capacity (Figure 7). The rate of CO_2 dissolution depends on the contact area between the CO_2 and brine phases and how quickly aqueous CO_2 diffuses into the brine. Unassisted, the contribution of solubility trapping becomes significant only after centuries (Figure 1).[2,9] Some studies have suggested reservoir engineering approaches to accelerate the dissolution of CO_2 into brine, with the aim of enhancing storage security.[5,18] Our results suggest such procedures will also enhance storage capacity.

As a simple example, consider a target formation at a depth of 2 km, with an injection interval of 50 m. If 28 million tonnes of CO_2 were injected over 30 years, based on simplifying assumptions for formation properties, injection rate, and fluid characteristics, then the maximum estimated plume radius is 7.4 km.[26] A reasonable estimate of microscopic brine displacement efficiency (the proportion of brine that is swept out of the CO_2 plume during injection) for a clastic reservoir is ~50%.[11] Therefore, about 50% of the brine initially present in the pore volume within the plume remains available to dissolve CO_2. The residual brine volume accessible for CO_2 dissolution within the plume is 4×10^7 m^3. The volume of brine outside the plume but within the cylindrical volume of the maximum plume radius is 8×10^8 m^3. The proportion of brine outside the plume that is accessible for CO_2 dissolution is unconstrained, although we can reasonably expect that this proportion will increase with time (as CO_2 diffuses outward from the plume). We consider two endmember scenarios, assuming either 10% or 100% of available brine outside the plume is accessible for CO_2 dissolution.

If CO_2 is injected to a maximum pressure of 90% of the fracture pressure (~54% of lithostatic pressure) and after injection the pressure is allowed to relax back to hydrostatic (~20 MPa in this example), and 10% of the brine outside the plume is accessible for CO_2 dissolution, then about 10% of the injected CO_2 can be dissolved in the available brine (~3% dissolved in residually trapped brine and ~7% dissolved in brine outside the plume). This reduces the total CO_2 volume by ~5%. If 100% of the brine outside of the plume (but within the plume maximum radial extent) were available for CO_2 dissolution, then the proportion of CO_2 that can dissolve increases to about 70%. This results in a reduction in the

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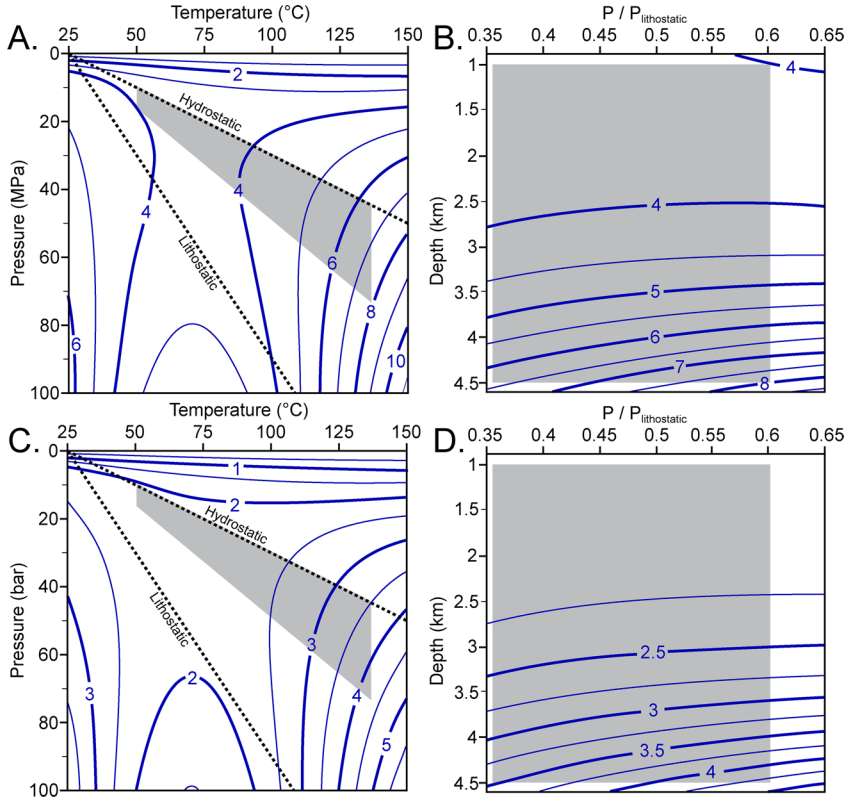

Figure 5. Percent increase in fluid volume after injected CO_2 has dissolved to produce a single-phase, CO_2-saturated brine, shown as percent difference between the volume of CO_2-bearing brine at s_2 compared to the volume of brine before injection (Figure 1, s_0). The data are plotted in pressure−temperature space (A and C) and depth-fraction of lithostatic pressure space (B and D). The shaded area represents the *PT* conditions accessible for CO_2 storage in saline formations. Parts A and B are for H_2O and C and D are for a 15 wt % NaCl brine.

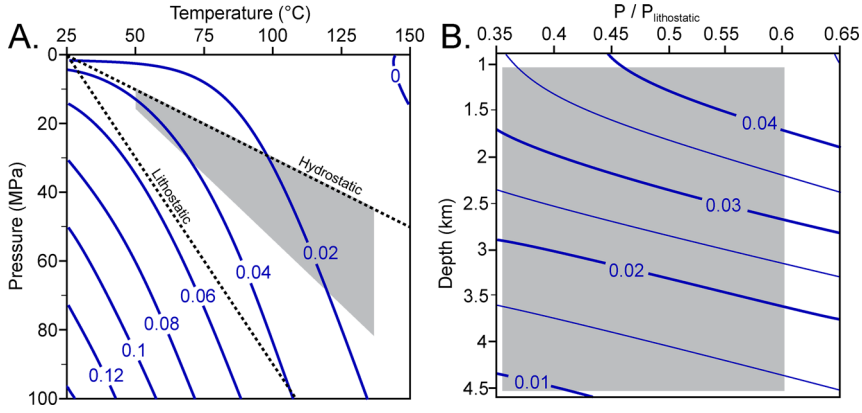

Figure 6. Percent fluid volume change as a result of CO_2-promoted calcite dissolution, relative to the initial volume of pore water. The data are plotted in pressure−temperature space (A) and depth-fraction of lithostatic pressure space (B). The shaded area represents the *PT* conditions accessible for CO_2 storage in saline formations.

apparent volume of CO_2 of ~45%. Thus, the *accessibility* of brine for CO_2 dissolution is a critical parameter in reducing volumetric requirements associated with solubility trapping. Ultimately, reservoir simulations incorporating lithological and hydrological parameters are required to predict the capacity of solubility trapping in saline formations.[12]

Our results indicate that the CO_2 storage capacity of a formation is influenced by the volumetric changes associated with CO_2 dissolution into brine. We have not attempted comparisons with previous storage capacity estimates from literature because previous comparisons have shown large variations and sometimes contradictory results, making such comparisons uninformative.[12]

The present study considers final equilibrium states and does not consider effects of fluid flow, pressure gradients, or other factors associated with injection. Figure 1 shows the approximate time intervals over which various trapping mechanisms are expected to become significant, based on reservoir studies and simulations,[2] but the actual time scales depend on the formation geometry and rock properties.[12] For example, dissolution of CO_2 into brine in a low permeability unit will take significantly longer compared to a high permeability unit.[12] Elucidating the time scales of CO_2-brine-

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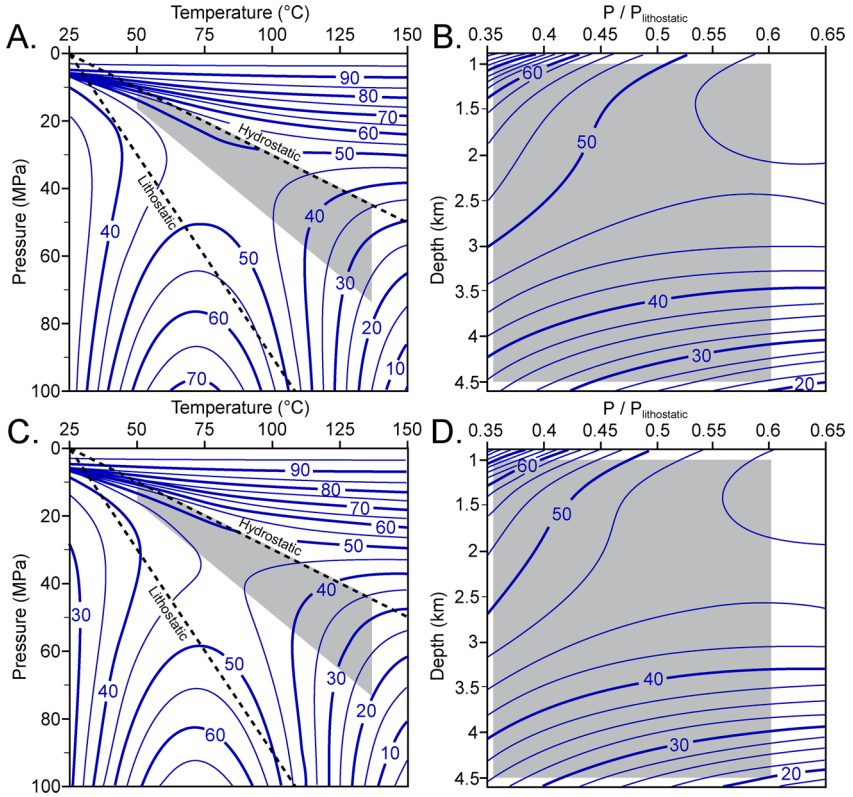

Figure 7. Percent difference in CO_2 apparent volume for CO_2 storage as a supercritical fluid, compared to storage as a dissolved component in brine. The values represent the difference in volume increase between s_2 (Figure 5) and s_1 (Figure 4). The data are plotted in pressure−temperature space (A and C) and depth-fraction of lithostatic pressure space (B and D). The shaded area represents the *PT* conditions accessible for CO_2 storage in saline formations. Parts A and B are for H_2O and represent the percent difference between values shown in Figure 5A and B for CO_2 storage as a supercritical fluid, compared to volume required for CO_2 storage as a dissolved component in the brine shown in Figure 4A and B). Parts C and D show the same comparison for 15 wt % NaCl brine (Figure 5C and D compared to Figure 4C and D).

mineral interactions during and after injection requires site-specific reservoir simulations on a case-by-case basis.[12] Regardless of the time needed to reach equilibrium, these results document that storing CO_2 as a dissolved component in brine reduces the volume required to store a given amount of CO_2.

IMPLICATIONS

There appear to be significant advantages to solubility trapping for CO_2 storage in brine-filled formations. Our results document that storage volume requirements are reduced by about 50% if CO_2 is dissolved in the brine (solubility trapping), rather than a separate supercritical fluid (structural or stratigraphic trapping). In addition, CO_2-bearing brine is denser than CO_2-free brine, so that CO_2-saturated brine will migrate downward within the formation, thus enhancing long-term storage security. Although the present study does not permit rigorous evaluation of the time scales required to achieve these advantages, the results suggest that storage volume requirements may be reduced by sequestration protocols involving extraction of brine, dissolution of CO_2 into the extracted brine at the surface, followed by reinjection of the CO_2-saturated brine into the formation.[5,18] To fully evaluate this alternative operational paradigm for geologic CO_2 storage requires comprehensive reservoir simulations that consider pressure evolution, fluid flow, and temporal changes in CO_2 trapping mechanisms. In addition, associated process requirements including characterization of life cycle energy, emissions, and economic implications must be considered.

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Notes

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