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Dissolution Potential of SO₂ Co-Injected with CO₂ in Geologic Sequestration

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Sulfur dioxide is a possible co-injectant with carbon dioxide in the context of geologic sequestration. Because of the potential of SO₂ to acidify formation brines, the extent of SO₂ dissolution from the CO₂ phase will determine the viability of co-injection. Pressure-, temperature-, and salinity-adjusted values of the SO₂ Henry's Law constant and fugacity coefficient were determined. They are predicted to decrease with depth, such that the solubility of SO₂ is a factor of 0.04 smaller than would be predicted without these adjustments. To explore the potential effects of transport limitations, a nonsteady-state model of SO₂ diffusion through a stationary cone-shaped plume of supercritical CO₂ was developed. This model represents an end-member scenario of diffusion-controlled dissolution of SO₂, to contrast with models of complete phase equilibrium. Simulations for conditions corresponding to storage depths of 0.8–2.4 km revealed that after 1000 years, 65–75% of the SO₂ remains in the CO₂ phase. This slow release of SO₂ would largely mitigate its impact on brine pH. Furthermore, small amounts of SO₂ are predicted to have a negligible effect on the critical point of CO₂ but will increase phase density by as much as 12% for mixtures containing 5% SO₂.

Introduction

Geologic sequestration of carbon dioxide is emerging as a promising carbon mitigation strategy (1–3). Electric power plants, which are the largest point sources from which CO₂ will be captured, emit other important pollutants such as sulfur dioxide, and there is the possibility that such pollutants could be disposed of by co-injection with CO₂ into deep geologic formations. Every year, the electric power industry collectively spends more than \$5 billion on permits for the right to emit SO₂ (4). Given the environmental and human health benefits of controlling SO₂ emissions (5), it may be economically advantageous to dispose of SO₂ with CO₂. However, the effects that impurities in the CO₂ stream will have on injection and long-term storage are largely unknown. Regulations governing the injection of CO₂ have been proposed by the U.S. EPA; however, there has been no specification of the required purity of the injected stream except that it must not meet the definition of a hazardous waste (6). John Gale, of the IEA, recently commented on the need to understand the effects of impurities on capture, transport, and storage before setting purity regulations (7).

In aqueous solution, SO₂ may form sulfurous acid, sulfuric acid, and even H₂S (8). With the exception of H₂S, these are acids stronger than carbonic acid, formed from aqueous CO₂. Acidity in the context of geologic CO₂ sequestration will accelerate mineral dissolution and precipitation, which may affect formation porosity and permeability, integrity of well-bore cements, and caprock integrity (9–13). Gunter et al. (11) examined water-rock reactions for injection streams of CO₂, H₂SO₄, and H₂S and predicted that these acids could be effectively buffered by the formation mineralogy, thus reducing the potential for long-term brine acidification. However, other geochemical modeling studies (14–16) predict that storage of sulfur co-injectants with CO₂ would create persistent, highly acidic conditions. Knauss et al. (15) used a reactive transport simulation and predicted that even small amounts of SO₂, such as 10^{−6} bar partial pressure, would create pH conditions near unity. Under these acidic conditions, porosity will be increased because of mineral dissolution and carbonate mineral precipitation will be inhibited. Similarly, Xu et al. (16) predicted that co-injection of SO₂ would create a larger and more acidic zone than injection of CO₂ alone and would increase porosity in the acidic zone due to mineral dissolution and decrease porosity at the acid front due to sulfate precipitation.

The magnitude of brine acidification will depend on the extent and rate of dissolution of SO₂ out of the injected CO₂. One of the objectives of this work was to determine a means of predicting the solubility of SO₂ in formation brines under geologic sequestration conditions. Solubility of CO₂ under these conditions has been fairly well examined (17–19); however, little is known of SO₂ solubility at high temperature, pressure, and salinity conditions. At injection depths below 800 m, where CO₂ would exist as a supercritical fluid (20), temperatures are greater than 30 °C, and pressures are greater than 74 bar. The solubility of SO₂ in pure water has been determined at temperatures up to 130 °C, but at pressures up to only 25 bar (21–23). Furthermore, at depths relevant for geologic sequestration, brine salinity in sedimentary basins is as high as 225 g/L (approximately 3.8 M) (20). SO₂ solubility has been measured in 0.1–6 M NaCl solutions (24–26), and in mixed electrolyte solutions (27–29) but not at the pressures relevant for geologic sequestration.

In this work, we present a means of determining the phase partitioning of SO₂ from supercritical CO₂ (scCO₂) by using pressure-, temperature-, and salinity-adjusted parameters including the Henry's Law constant and the CO₂-phase fugacity coefficient. We examine how these parameters and the resulting SO₂ brine concentrations would vary with depth, in comparison to CO₂ concentrations. Additionally, densities of CO₂–SO₂ mixtures under relevant pressure and temperature (*PT*) conditions, along with mixture critical points, are calculated. These properties are important to demonstrate the effects of SO₂ additives on CO₂ injection depth and migration potential. Finally, the diffusivity of SO₂ in scCO₂ is estimated, and its variation with depth and *PT* conditions is examined.

In addition to the need to quantify the potential for equilibrium phase partitioning of SO₂, there is a need to estimate the flux of SO₂ from the injected CO₂ to the bulk brine phase. Previous modeling studies (15, 16) of co-injection of SO₂ with CO₂ assume sustained phase equilibrium between all the scCO₂ and brine. This is an extreme case scenario in which there is no limitation on contact of SO₂ with the brine. The opposite extreme case is a scenario in which SO₂ is limited by diffusion through a stationary scCO₂ phase. These two extremes bound reality in which the actual rate of SO₂ contact

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with brine is controlled by process complexities and system heterogeneities.

To address the need to understand the diffusion-limited bounding scenario, the second major objective of this work was to describe diffusion-limited dissolution behavior of SO₂ into brines in the context of co-injection with CO₂ in geologic sequestration. A nonsteady-state model of SO₂ diffusion through a stationary cone-shaped plume of scCO₂ was developed and used to simulate fluxes of SO₂ into the brine outside the scCO₂ plume. Pressure- and temperature-adjusted binary diffusion coefficients of SO₂ in scCO₂ were estimated. A variety of depths were considered to determine how changes in temperature and pressure affect the properties. Two different mixture compositions, 1 and 5% SO₂, were considered, corresponding to moderate-to-high ratios of SO₂ to CO₂ in emissions from electric power plants.

Methods

CO₂–SO₂ Mixture Properties. Critical points for mixtures of CO₂ and SO₂ were estimated by using the corresponding states method as given by Lee and Kesler (30). Yang et al. (31) examined the accuracy of this method in describing CO₂ mixtures and concluded that Lee–Kesler type equations of state are as accurate, sometimes more so, than more complex cubic equations of state. This estimation used values of the pure component critical molar volumes, critical temperatures, and acentric factors from reported data (31–34) (Supporting Information, Table S1).

The densities of mixtures of CO₂ and SO₂ were estimated by using the method given in Lee and Kesler (30). For consistency, this method was also used to estimate the densities of pure CO₂ despite the availability of CO₂ equations of state (35). Densities were calculated at *PT* conditions corresponding to a variety of depths, based on gradients from reported data (36, 37) as described in the Supporting Information (Section S-1).

Partitioning into Brine. For the case of phase equilibrium partitioning of SO₂ between scCO₂ and brine, the convention of the infinite-dilution reference state for the aqueous phase is adopted. This results in an expression relating the SO₂ concentration in the brine phase, *C* [M], to the partial pressure in the scCO₂ phase, *P*_{SO₂} [atm]:

$$C = \phi_{\text{SO}_2} P_{\text{SO}_2} K_H \quad (1)$$

where ϕ_{SO_2} is the fugacity coefficient of SO₂ in the scCO₂ phase and *K_H* is the Henry's Law constant in [M/atm].

The adjustment of the Henry's Law constant for high pressures was done by using the Krichevsky–Ilinskaya equation, which also adjusts for variation in activity coefficient, important for highly soluble gases (38). This equation relates the Henry's law constant, *K_{H,P}*, at system pressure, *P*, to the Henry's law constant at a lower reference pressure, *K_{H,P*}*, through

$$\ln K_{H,P} = \ln K_{H,P^*} - \frac{A}{RT} (x_j^2 - 1) - \frac{\bar{v}_{\text{SO}_2} (P - P^*)}{RT} + \ln \left(\frac{\bar{V}_{P^*}}{\bar{V}_P} \right) \quad (2)$$

where *A* is the Margules constant, *x_j* is the mole fraction of water in the brine phase, \bar{v}_{SO_2} is the partial molar volume of SO₂ at infinite dilution, *P** is the reference pressure, *R* is the universal gas constant, *T* is the temperature, and \bar{V}_P is the molar volume of water. In this work, the last term is ignored because changes in the molar volume of water with pressure are assumed negligible. Henry's Law constants for SO₂ at *P** of 1 bar were taken from Rabe and Harris (21) for several temperatures representative of geologic sequestration conditions (given in Table S2 in the Supporting Information).

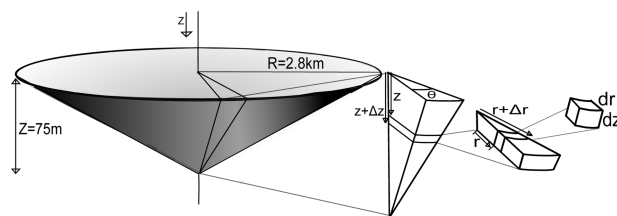


FIGURE 1. Diagram of model injection plume showing an example differential volume element.

These values of *K_{H,P*}* refer to aqueous SO₂ in the unreacted form, as opposed to the total SO₂ in solution. Partial molar volumes of SO₂ at infinite dilution (Table S1 in the Supporting Information) were taken from Brelvi and O'Connell (39). The Margules constants were estimated via regression of measurements of SO₂ solubility in pure water at pressures up to 11 bar (22).

The Henry's Law constants were adjusted for saline conditions by using the Schumpe model (27) for mixed electrolyte solutions with an adjusted gas-specific parameter given by Rodriguez-Sevilla et al. (24). A 1 M NaCl solution was selected to represent the brine.

The fugacity coefficient for SO₂ in the scCO₂ was determined from the second virial coefficients, determined from the reduced-virial-coefficient method in Tarakad and Danner (40).

SO₂ Diffusivity in scCO₂. The diffusion coefficient for SO₂ in scCO₂, *D*_{SO₂,CO₂} at high pressures was estimated by using the Takahashi correlation (41) as described in the Supporting Information (Section S-4). Values of *D*_{SO₂,CO₂} at relevant conditions are also given in the Supporting Information (Section S-4).

Model System and Simplifications. A model system was conceptualized to represent an extreme-end-member scenario in which SO₂ contact with the bulk brine is entirely diffusion-limited within the scCO₂ phase. By "bulk brine", we refer to the brine phase outside the scCO₂ plume. The system is a scCO₂ phase within a geologic formation after the injection period (Figure 1). We selected a cone as simplified geometry to mimic the shape of a CO₂ plume trapped underneath a caprock seal. For simplicity, the scCO₂ is assumed to be stationary. During the injection process, pressure will force the CO₂ to flow into the formation (see e.g. refs 42–44). Post-injection, however, these pressures will dissipate, and CO₂ flow will be slower, driven only by buoyancy override and hydrodynamic flow. Furthermore, in deep aquifers, the flow of water is slow, 1–10 cm/yr (45), which means that hydrodynamic forces are minimal.

The other type of CO₂ flow, which is not considered here, is the flow driven by the new density gradients that will be created because of spatial differences in SO₂ concentrations within the scCO₂ phase. A circulation pattern may emerge in which SO₂-rich CO₂ near the top, center of the cone will exchange with the less dense CO₂ that is depleted of SO₂. (Note that this does not affect mixing between the brine phase and the scCO₂ phase because the density of the SO₂-rich scCO₂ phase is still significantly less than the density of the brine phase.) This advective transport is one of the processes that will enhance SO₂ flux relative to the extreme case of diffusion in a stagnant fluid, modeled here.

Another process not considered is partitioning of SO₂ into residual brine trapped within the volume of the cone. Partitioning to residual brine may be significant. The effect, relative to what is modeled here, is that the diffusive flux to the bulk brine would be diminished because of the reduced SO₂ concentrations in the scCO₂ phase.

A cone volume of $6.1 \times 10^8 \text{ m}^3$ was calculated on the basis of a CO₂ density of 750 kg/m³, an aquifer porosity of 20%, and a 50 year injection period at a rate of 1.83 Mton/year

(46). By assuming a formation thickness of 75 m and by assuming that the height of the cone equals this thickness, a cone with the selected injection volume would extend to a radius of 2.8 km.

SO₂ Diffusion Modeling. The cone radius was discretized in radial coordinates by first dividing it into wedges with angle θ . The wedges with total height Z were divided into slices with thickness Δz . Slices were then divided into segments with width Δr , as shown in Figure 1. The derivation of the equation for diffusive mass transport of SO₂ in scCO₂ in a differential volume element is presented in detail in the Supporting Information (Section S-5). The resulting model equation is

$$\frac{\partial C}{\partial t} = D_{\text{eff}} \left(\frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (3)$$

where C is the concentration of SO₂ and D_{eff} is the effective diffusion coefficient. The effective diffusion coefficient is calculated from $D_{\text{SO}_2, \text{CO}_2}$, formation porosity, n , and tortuosity, σ (47).

$$D_{\text{eff}} = D_{\text{SO}_2, \text{CO}_2} \frac{n}{\sigma} \quad (4)$$

For this work, tortuosity was selected as $\sigma = 2$ to represent high diffusive flux.

The initial condition assumes a spatially uniform concentration of 1 or 5% SO₂, within the scCO₂. A no-flux boundary was assumed at the top of the cone, representing an aquifer bounded by an impermeable caprock. Diffusion within the cone is driven by a concentration gradient created by preferential dissolution of SO₂ into the bulk brine at the cone boundary. SO₂ dissolution was predicted by using eq 1 and the estimated Henry's Law constant and fugacity coefficient. The model does not account for dissolution of CO₂. In Ellis et al. (8), we describe this process and examine the change in the scCO₂ plume size by considering different scenarios for brine-phase transport. To create a maximum driving force for dissolution, at each time step, the brine at the cone boundary was reset to have a zero concentration of SO₂. This is a realistic condition because dissolved SO₂ will quickly convert to acid reaction products (see Ellis et al. (8)). The diffusion equation was numerically solved by using a time-split explicit difference method as described in the Supporting Information (Section S-5).

Results and Discussion

CO₂–SO₂ Mixtures. The critical points estimated for mixtures of CO₂ and SO₂ are shown in the phase diagram in Figure 2. For reference, gas–liquid phase boundaries for pure CO₂ and SO₂ are also shown. (Published correlations were used for the phase boundaries for CO₂ (48) and SO₂ (34).) Whereas the critical temperature of SO₂ is much higher than that of CO₂, pure SO₂ and pure CO₂ have similar critical pressures. Also, critical points for mixtures of SO₂ and CO₂ are predicted to be fairly constant in pressure. This implies that, in the context of injection, to ensure a supercritical mixture, less than an additional 1 m depth is required for 1% SO₂ mixtures and an additional 3.5 m for 5% SO₂ mixtures.

Estimated densities are shown in Figure 3, along a trajectory corresponding to a surface temperature of 10 °C. Uncertainties are 5.3% (see Supporting Information). The density of pure CO₂ ranges from 754 to 759 kg/m³ from depths of 0.8 to 2.4 km (Figure 3a). This variation is small because, coincidentally, the PT depth trajectory is closely aligned with an iso-density (isopycnic) line in the supercritical regime. Densities of mixtures of CO₂ and SO₂ (Figure 3b,c) are larger than those of pure CO₂. For the conditions of interest, densities are up to 3% larger for 1% SO₂ mixtures and up to 12% larger for 5% SO₂ mixtures. This increase is expected

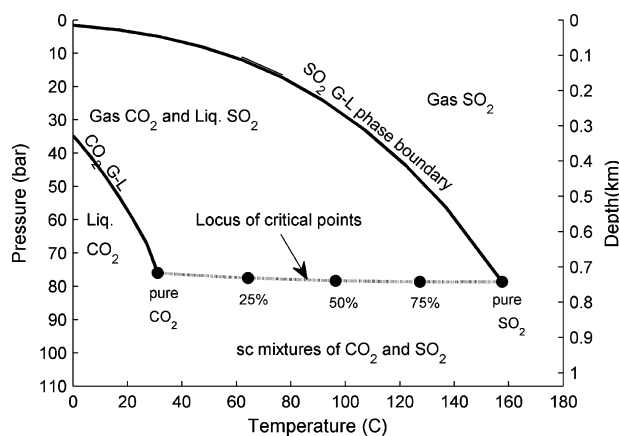


FIGURE 2. Pressure–temperature phase diagram for CO₂, SO₂, and their mixtures. Gas–liquid (G-L) phase boundaries are shown for the pure substances, along with the locations of critical points for mixtures of CO₂ and SO₂. The diagram is inverted, showing pressure decreasing on the left ordinate axis to correspond to variation with depth, depicted on the right ordinate axis.

given the larger density of pure SO₂. For pressures and temperatures that correspond to depths between 0.8 and 2.4 km, the density of SO₂, as measured by Ihmels (49), ranges from 1373 to 1300 kg/m³. Thus, small amounts of SO₂ have a large effect on the mixture density. In the context of geologic sequestration, this may be beneficial. The densities of brines vary from 950 to 1200 kg/m³ (50). A decrease in the density difference between the two phases would decrease the buoyancy of scCO₂ and may decrease leakage potential.

Equilibrium Partitioning of SO₂ into Brine. Salinity-adjusted values of the Henry's Law constant for SO₂ were determined at 20, 40, 60, and 70 °C, for pressures from 1 to 260 bar, corresponding to depths up to 2.4 km. These values have estimated errors of 14% (see Supporting Information). For example, at 1.2 km depth, the Henry's Law constant is predicted to be 0.58 ± 0.08 M/atm. Interpolations of the computed values are shown as contours in a PT plot in the Supporting Information (Section S-6). Values of $K_{H,P}$ decrease with temperature and pressure. Therefore, the Henry's Law constant decreases with increasing injection depth such that SO₂ solubility at geologic sequestration conditions is less than that under conditions at the land surface (value given in Table S1 in the Supporting Information).

The depth variations of all the factors that govern SO₂ equilibrium phase partitioning into brine (eq 1) are shown in Figure 4. Partial pressure increases linearly with depth, but ϕ_{SO_2} and K_H decrease nonlinearly. At shallow depths, SO₂ would behave ideally in the CO₂ phase, with ϕ_{SO_2} approximately equal to unity, and at greater depths, substantial negative deviations from ideality are predicted. Also shown in Figure 4 is the resulting molar concentration of SO₂ in brine and its variation with depth. This was computed with the simplifying assumptions that, over the entire depth, the aqueous phase is a 1 M NaCl brine, and the brine is in equilibrium with scCO₂ containing 1 or 5% of SO₂. Also, this calculation does not account for the fact that phase partitioning of a finite mass of SO₂ would deplete it from the scCO₂ phase, and the resulting concentration of SO₂ in the brine would be much smaller than what is computed here. (This more realistic case is considered in Ellis et al. 2009 (8).) However, this simplified case is examined for the sake of illustration. At land-surface conditions of 1 bar and 10 °C, the solubility of SO₂ would be 0.02 M for 1% SO₂ and 0.09 M for 5% SO₂. As depth increases, the increase in partial pressure causes phase partitioning to increase by one-to-two orders of magnitude to a maximum of 0.45 M at 0.8 km

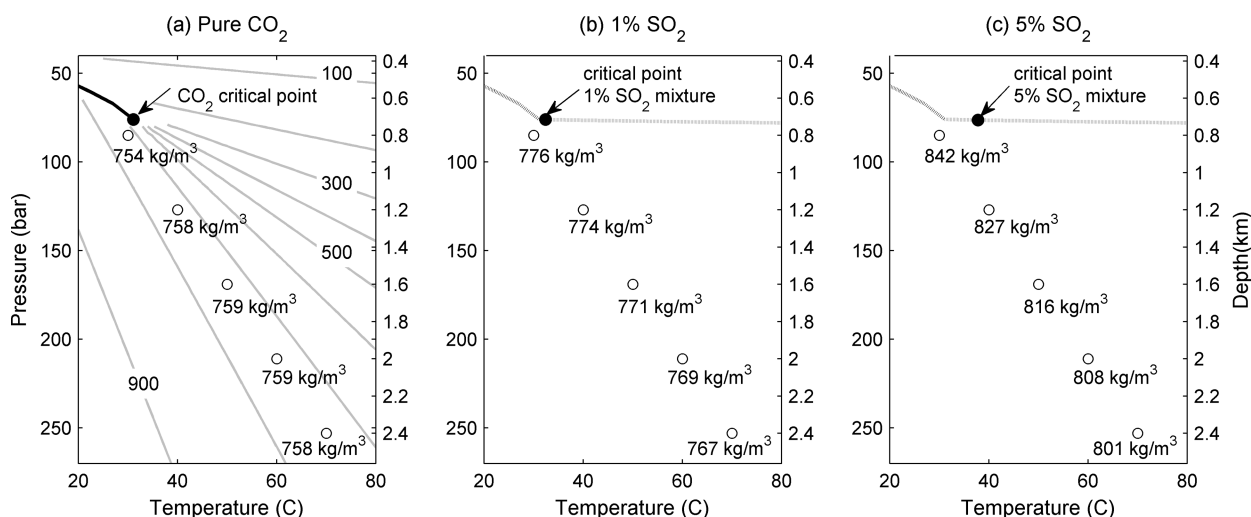


FIGURE 3. Densities of pure CO₂ (a) and mixtures of 1% (b) and 5% (c) SO₂ with CO₂ along a *PT* trajectory corresponding to a pressure gradient of 105 bar/km and a temperature gradient of 25 °C/km, with a surface temperature of 10 °C. Contours in (a) correspond to constant densities of pure CO₂ in kg/m³.

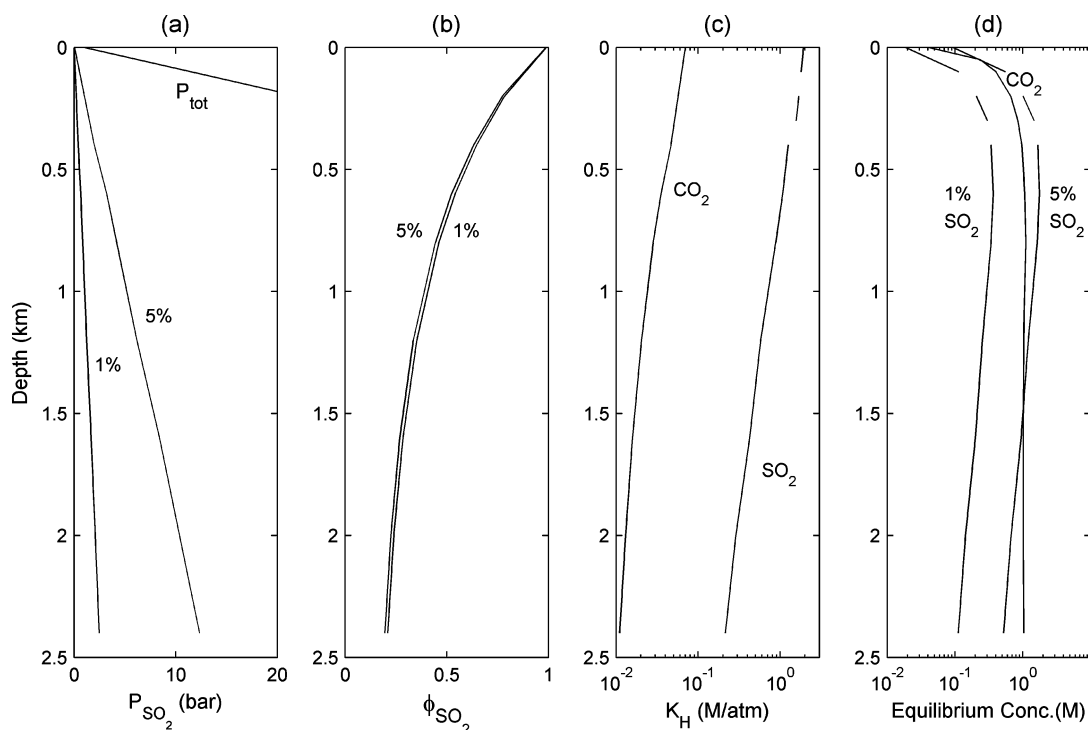


FIGURE 4. (a–c) Variation with depth of the factors that determine phase partitioning between scCO₂ and 1 M NaCl brine and (d) resulting brine-phase concentrations.

for 1% SO₂ and 2.2 M at 0.6 km for 5% SO₂. At greater depths, the effects of increasing nonideality in the scCO₂ phase and decreasing Henry's Law constant reverse the trend, causing the phase partitioning of SO₂ to decrease with depth.

SO₂-phase partitioning can be compared with the solubility of CO₂ by using the values calculated by Duan and Sun (18). A major difference between the two cases is that SO₂ is a minor mixture component with significant nonideal solution behavior and CO₂ is a nearly pure component with less extreme deviations from ideality. Consequently, the value of ϕ is not as important for CO₂ as it is for SO₂. At *PT* conditions representative of the land surface, the solubility of CO₂ in 1 M NaCl is 0.04 M, and it increases by two orders of magnitude to a value of 1.06 M at a depth of 1.2 km (Figure 4d). This similarity to our findings for SO₂ at shallow depths is expected

because the determining factor is the change in pressure. Beyond a depth of 1.2 km, the solubility of CO₂ levels off (Figure 4d), which is explained mostly by the increasing importance of the Henry's Law constant. By using the K_H correlations presented by Bachu and Adams (17) and correcting them for salinity by using the Schumpe model (27), the pressure-adjusted Henry's Law constants for CO₂ were calculated. These values were found to decrease from 0.053 M/atm at the surface to 0.009 M/atm at a depth of 2.4 km (Figure 4c). In comparison with SO₂, values of $K_{H,p}$ for CO₂ are always smaller, reflecting the higher aqueous solubility of SO₂. In fact, the solubility of SO₂ is so much higher that its concentration in the brine phase is comparable to that of CO₂ despite the fact the mole fraction of SO₂ is so small. At 1.2 km, the equilibrium concentration in the brine

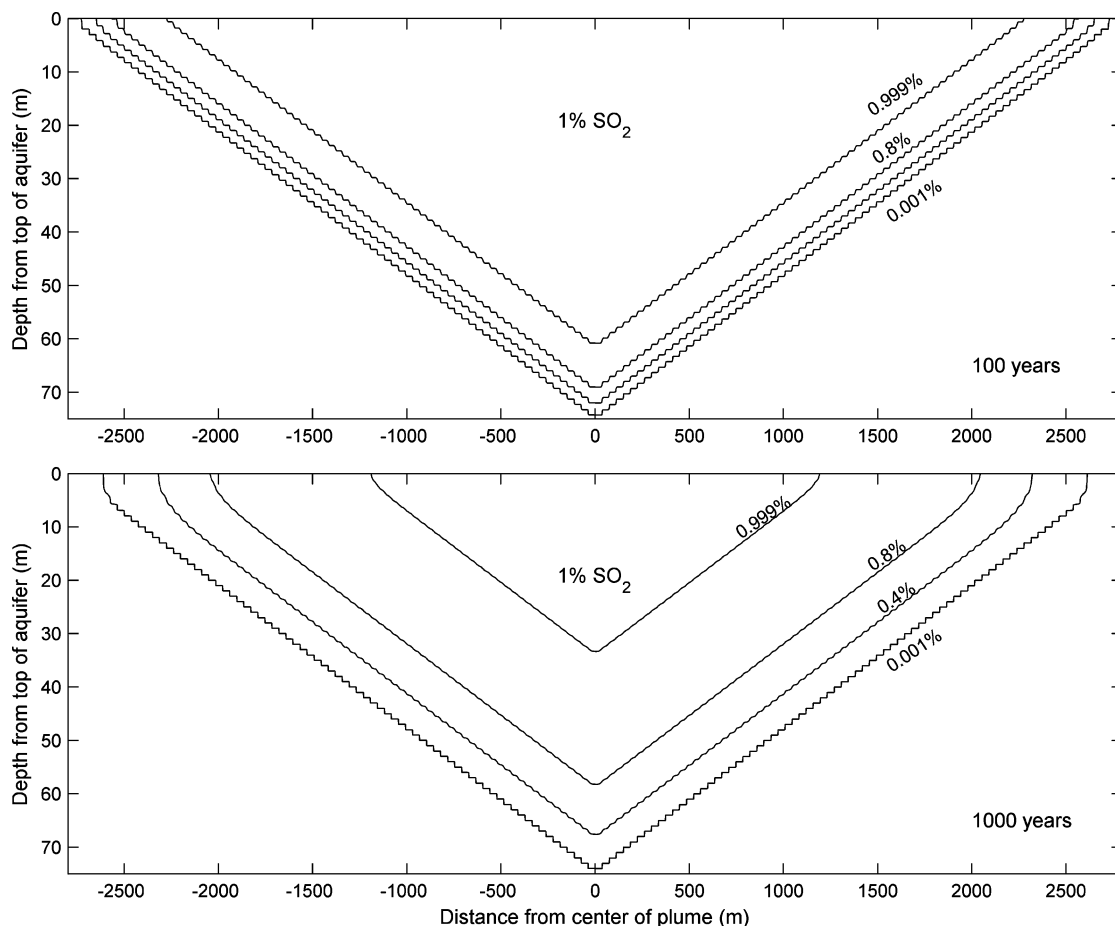


FIGURE 5. Concentration contours for SO_2 within the model scCO_2 cone after 100 and 1000 years for the case of an initial condition of 1% SO_2 , temperature of 40 °C, and pressure of 127 bar corresponding to a depth of 1.2 km. The phase boundary between scCO_2 and brine is coincident with the 0.001% line.

is 0.38 and 1.8 M for 1 and 5% SO_2 , respectively and 1.03 M for CO_2 at 1.2 km (Figure 4d).

SO_2 Diffusion through scCO_2 . The predicted diffusion of SO_2 through the model scCO_2 cone is shown in Figure 5, for the case of 1% SO_2 , as concentration profiles through a vertical section of the cone. The concentration of SO_2 near the cone boundary decreases early on because of the relatively high solubility of SO_2 in the bulk brine. The resulting depletion of SO_2 at this boundary creates a concentration gradient within the scCO_2 that causes diffusive flux of SO_2 from the center of the plume. The simulations predict that the concentration contours are roughly parallel with the cone boundary. The parallel contours establish a “zone of depletion” of fairly uniform thickness at the boundary of the cone. If we arbitrarily define the zone of depletion to be bounded by where the SO_2 concentration equals 0.999%, after 100 years, it is 15 m thick, and after 1000 years, it is approximately 41 m thick. Even after 1000 years, the concentration of SO_2 in a large portion of the center of the cone remains unchanged.

The effective flux of SO_2 from the entire cone over time is shown in Figure 6a for depths of 0.8 and 2.4 km. Initially, the flux of SO_2 into the bulk brine is limited mostly by solubility, and later, the thick zone of depletion acts as a barrier for diffusion. For both PT conditions, after the first 200 years, the flux is two orders of magnitude less than the flux during the initial years. If the model allowed for SO_2 to accumulate in the bulk brine, the flux of SO_2 from the cone would be even slower (see Ellis et al. (8)). Slower flux would also be predicted in the case of a model that described SO_2 partitioning to a residual brine phase within the scCO_2 cone.

Figure 6b shows the total amount of SO_2 that remains in the cone over time. Even though the effective flux in the case of 5% SO_2 is consistently five times larger than the effective flux for the 1% case (Figure 6a), this difference has a negligible effect on the percent of SO_2 remaining. In the first few years, nearly 5% of the SO_2 leaves the cone. After this, there is a more gradual change in the percent of SO_2 removed because of a slower flux of SO_2 from the cone during these years. After 1000 years, 64–75% of SO_2 still remains in the cone for all of the PT conditions simulated.

The variation in flux with depth seen in Figure 6 is due to the variation in the diffusion coefficient of SO_2 in scCO_2 . For 1% SO_2 , at 0.8 km, the diffusion coefficient is $4.76 \times 10^{-8} \text{ m}^2/\text{sec}$, compared with $1.9 \times 10^{-8} \text{ m}^2/\text{sec}$ for the 2.4 km depth, both with error of $\pm 7\%$ (see Supporting Information). As shown in Figure S-1 in the Supporting Information, at shallower depths, there is little change in $D_{\text{SO}_2, \text{CO}_2}$ with temperature, and values are quite sensitive to changes in pressure. A pressure increase from 80 bar to only 100 bar produces a decrease in $D_{\text{SO}_2, \text{CO}_2}$ from 6×10^{-8} to $3 \times 10^{-8} \text{ m}^2/\text{sec}$. At greater depths, $D_{\text{SO}_2, \text{CO}_2}$ values decrease slightly with pressure, and the increase with temperature is more substantial than at shallower depths. The balance of these two effects means that, for depths of 1.2–2.4 km, the $D_{\text{SO}_2, \text{CO}_2}$ contours align with the PT gradient such that there is little change in $D_{\text{SO}_2, \text{CO}_2}$ values.

Implications for Geologic CO_2 Sequestration. As mentioned in the Introduction, prior co-injection modeling studies predicted low pH conditions because of the formation of sulfur-containing acids and that these conditions would be sustained for decades. It is certainly the case that SO_2 is

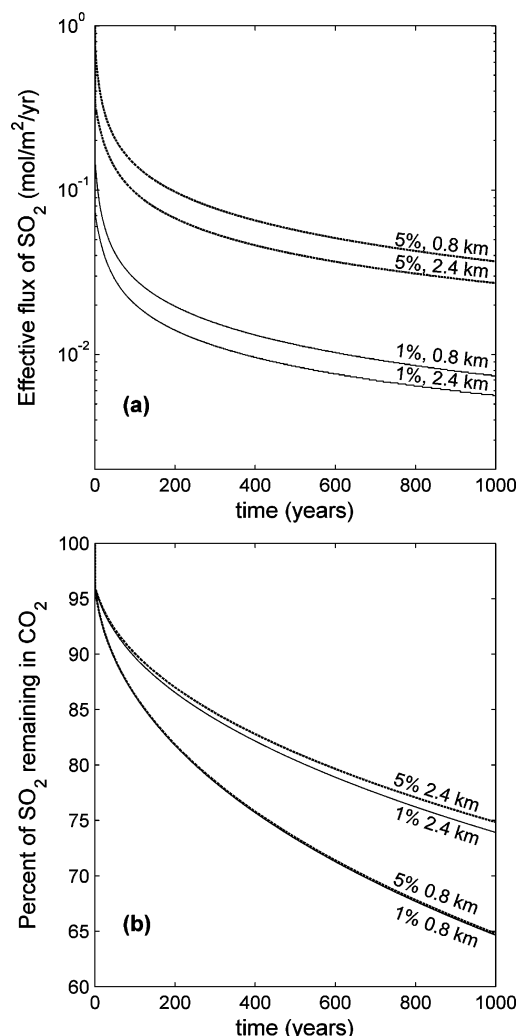


FIGURE 6. (a) Effective flux of SO_2 from scCO_2 cone and (b) percent of SO_2 remaining in the cone for 1 and 5% SO_2 at depths of 0.8 and 2.4 km.

very soluble and much more soluble than CO_2 . However, our results show that SO_2 solubility decreases substantially with depth. By not accounting for changes in K_H and ϕ with depth, the partitioning of SO_2 would be overestimated by more than an order of magnitude at depths of 2.4 km. Furthermore, if the fluids are fairly stationary for long time periods, conditions that would not favor mixing of the brine and scCO_2 , diffusion limitations may significantly limit the extent of SO_2 mass transfer to the bulk brine. This would limit the formation of sulfur-containing acids and their impact on brine pH. This finding is very different from the conclusions presented in other studies. Of course, reality is represented neither by the perfectly mixed phase-equilibrium scenario of previous studies nor by the perfectly stagnant diffusion-limited scenario modeled here. Reality lies somewhere between these two extremes, in which some degree of mixing will occur and some degree of transport limitations will exist. This work has demonstrated the important role of such transport limitations in governing the fate of co-injected SO_2 . Future reactive transport studies should account for the possibility of diffusion-limited release of SO_2 from the scCO_2 phase. Some of these effects are discussed in Ellis et al. 2009 (8) who considered a variety of reaction and transport scenarios to estimate the potential for brine acidification from SO_2 fluxes.

Acknowledgments

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Supporting Information Available

Supporting Information includes sedimentary basin PT gradients, data used to estimate Henry's Law constants and mixture properties, PT contour plot of adjusted Henry's Law constants for SO_2 , derivation of the diffusion model equations, diffusion coefficients for SO_2 in scCO_2 and error propagation for calculations of Henry's law constant, mixture density, and the diffusion coefficient. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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