Will mercury impurities impact CO$_2$ injectivity in deep sedimentary formations?
II. Mineral dissolution and precipitation

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ABSTRACT

Numerical simulations of carbon dioxide (CO₂) injection in a sandstone reservoir (~2 km depth) were used to investigate the geochemical effects of trace amounts of mercury (Hg, 7 and 190 ppbV), with and without hydrogen sulfide (H₂S, 200 ppm). Geochemical reaction-path modeling shows that cinnabar precipitates as soon as the Hg-bearing CO₂ reacts with the formation. Mercury does not condense to liquid, and the net volume change from mineral dissolution and precipitation is found to be negligible. Two-dimensional radial reactive transport simulations of CO₂ injection at a rate of 14.5 kg/s (~0.5 Mt/y) into a 400 m-thick formation at 106°C and 215 bar, with varying amounts of Hg and H₂S, show that porosity changes only by about ±0.05% absolute (i.e., new porosity% = initial porosity% ±0.05), and that Hg readily precipitates as cinnabar in a zone mostly coinciding with the single-phase CO₂ plume. This essentially negligible porosity change is not expected to affect permeability and CO₂ injectivity. The precipitation of minerals other than cinnabar dominates the evolution of porosity. Although the predicted porosity change is small, the dissolution and precipitation predicted for individual minerals is not negligible. The main reactions include the replacement of primarily Fe-chlorite by siderite, of calcite by dolomite, and of K-feldspar by muscovite. Chalcedony is also predicted to precipitate from the dissolution of feldspars. Except for some replacement of pyrite by ankerite when H₂S is deficient, the cases with and without H₂S show similar results. Experimental measurements are needed to decrease uncertainty in simulation results.

1 Introduction

Carbon dioxide capture at point sources such as power plants and fuel processing facilities, followed by injection into deep geologic formations, is one approach that is being considered to allow continued use of fossil fuels with reduced CO₂ emissions, until such time as acceptable
alternative low-carbon energy sources can be found [1]. Trace amounts of mercury (Hg) are found naturally in fossil fuels (coal, oil, and natural gas), primarily as inorganic Hg (e.g., [2,3,4,5]), resulting in combustion products that contain small amounts of Hg. Because concurrent capture of CO₂ and Hg from flue gas and from high-CO₂ natural gas is being considered (e.g., [6]), the question arises whether Hg in CO₂ streams injected into deep geologic formations could negatively impact geologic carbon sequestration (GCS), specifically through reducing injectivity.

In a companion study [7], we applied simple volumetric calculations and phase-partitioning models to assess the potential for Hg condensation and/or precipitation as Hg sulfide (cinnabar) from a CO₂ stream containing ~190 ppbV Hg (1.6 mg/stdm³CO₂). These analyses showed that the total volumetric plugging that would occur from Hg deposition around a 300 m long injector (after 40 years of injection at a typical flow rate of ~0.5 Mt/y) is not expected to impact injection unless all Hg was deposited within centimeters of the injector. These investigations also showed that Hg concentrations much higher than the concentration considered here would be required for Hg condensation to occur, and that aqueous Hg would not concentrate by water evaporation into CO₂ because the volatility of Hg is higher than that of H₂O at reservoir conditions.

Although insightful, these previous initial analyses did not consider water-sediment chemical interactions, their effect on the speciation of Hg and its aqueous concentration, or the thermodynamic tendency for precipitation of cinnabar (HgSₙₙ) preferentially over the stability of liquid Hg (Hg(ℓ)) in the presence of sulfide, which occurs naturally in formation brines in addition to being an impurity in CO₂. For this reason, in the present study, we apply more sophisticated numerical models with the objective of evaluating the geochemical behavior of Hg as a contaminant in CO₂ upon injection into a deep reservoir, as well as the geochemical reactions
caused by the injected CO₂ and H₂S that could possibly either exacerbate or minimize potential
detrimental effects from Hg injection.

The present modeling study was carried out for expected compositions of CO₂ injectate,
groundwater chemistry, and formation mineralogy for the case of a typical marine sandstone
reservoir situated at a depth about 2 km and covering a lateral extent of over 2.5 km. Although our
results are strictly applicable to a limited range of injectate-groundwater-formation combinations,
this study presents a modeling approach that is applicable to a wider range of conditions and
injection scenarios.

2 Prior Work

Numerical models have been used for almost two decades to evaluate geochemical effects
accompanying the injection of CO₂ and co-contaminants into deep geologic formations. These
studies involved geochemical modeling without considering transport (e.g., [8,9,10]) as well as
more complex reactive transport simulations (e.g., [11,12,13,14,15,16]). Rochelle et al. [17]
presented a comprehensive review of earlier studies, including modeling work relating to chemical
reactions associated with CO₂ injection, and the impact of these reactions on CO₂ storage in
geologic formations. To our knowledge, none of these modeling studies have investigated the
effect of Hg co-injection with CO₂.

One of the earliest reactive transport modeling studies of CO₂ injection into a deep saline aquifer
was carried out by Johnson et al. [11] for the Sleipner gas field in the North Sea. Gauss et al. [15]
and Audigane et al. [16] further investigated hydrological and geochemical processes at this site,
using reactive transport simulations to assess the effect of injection on cap-rock integrity as well
as porosity and permeability in the reservoir. Knauss et al. [12] and Xu et al. [13,14] conducted
Similar modeling investigations for sandstone-shale systems typical of the Texas Gulf Coast, focusing on the CO$_2$ sequestration potential of minerals, as well as effects of co-injected H$_2$S and SO$_2$. These studies represent only a few important, earlier modeling investigations, among many others that are now almost routinely performed for GCS investigations.

3 Technical Approach

3.1 Numerical Models

Geochemical speciation and reaction path simulations were performed using GeoT [18] and CHILLER [19,20], respectively. GeoT is a multicomponent homogeneous chemical equilibrium program specifically tailored toward geothermometry and the reconstruction of deep subsurface waters. This program automatically scans computed mineral saturation indices as a function of temperature and determines the temperatures at which a suite of specific minerals are in chemical equilibrium. It was used here to reconstruct the composition of the deep saline aquifer considered in this study. CHILLER is a multicomponent heterogeneous chemical equilibrium model suitable for assessing a wide range of geochemical processes affecting water-gas-rock systems, including the reaction of subsurface fluids with rocks or sediments, fluid-fluid and fluid-gas mixing, heating, cooling, boiling, and flash calculations. This computer program was applied to investigate the products of incremental reaction between an Hg-bearing CO$_2$ phase, formation water, and reservoir minerals, including porosity change from mineral precipitation and dissolution. The results of CHILLER were also used to further refine geochemical inputs for more complex reactive transport simulations under kinetic constraints.

TOUGHREACT V2 [21] and V3-OMP [22] coupled with the ECO2N module [23] was applied to simulate reactive transport of CO$_2$ injection with H$_2$S and Hg impurities. It is a reactive transport
simulator that incorporates full multicomponent aqueous-, gas-, and solid-phase reactive chemistry and transport into the multiphase flow simulator TOUGH2 [24]. Chemical reactions between aqueous, gas, and mineral species under either kinetic and/or equilibrium constraints were treated in a sequential non-iterative manner using an operator-splitting approach.

3.2 Modeling Procedure and Operational Data

The chemical reaction between formation water, sediments, and a CO$_2$+Hg mixture was initially simulated using CHILLER, without considering transport. These geochemical modeling analyses provided insights on the thermodynamic viability of key reactions and typical reaction products to be expected. In doing so, these simulations also served as a basis for the development of reactive transport simulations.

The injection of Hg- and H$_2$S-bearing CO$_2$ into a deep sandstone formation was then simulated using TOUGHREACT to investigate the coupled hydrological and geochemical processes taking place within the target formation around the injection well. Particular attention was given to the spatial distribution of Hg deposition and the porosity change around the injection well.

The same operational and reference data were used as in [7], including CO$_2$ injection rate, Hg concentration, and typical operating pressure and temperature conditions considered. These specifications are shown in Table 1.

Table 1. Operational data
Variable & Value & Units \\
--- & --- & --- \\
Operational Data: & & \\
Temperature & 106 & (C) \\
Pressure & 3125 & (psia) \\
Total CO$_2$ injection rate & 2.20E+08 & (std ft$^3$/d) \\
Number of injectors & 9 & \\
CO$_2$ injection rate per injector & 2.53E+08 & (std m$^3$/y) \\
Injection time period & 40 & (y) \\
Hg concentration in CO$_2$ & 1.58 & (mg/std m$^3$) \\
H$_2$S concentration in CO$_2$ & 0.19 & (ppmV) \\

3.3 Thermodynamic and Kinetic Data

Programs GeoT, CHILLER and TOUGHREACT all rely on input equilibrium constants for the dissociation of aqueous species, mineral dissolution/precipitation, and gas solubility under equilibrium constraints, as a function of temperature and pressure. The sources of these data are discussed in Appendix A. In addition, TOUGHREACT requires kinetic rate laws and parameters to simulate mineral precipitation and dissolution under kinetic constraints. These data are also discussed in Appendix A. It should be noted that the effect of pressure on equilibrium constants is neglected here (except for the solubility of CO$_2$) as it is considered second-order compared to the effect of temperature. Ideal-gas behavior is also assumed for trace Hg gas in CO$_2$. The impact of this assumption on the computed Hg partitioning between CO$_2$ and water is evaluated in Appendix B.
4 Geochemical Modeling

Geochemical modeling was conducted to reconstruct the deep reservoir brine chemistry and simulate the chemical interaction of a CO$_2$+Hg mixture with formation water and sediments. These computations consider the various possible reactions between gaseous, aqueous and solid phases, including the speciation of mercury and the thermodynamic tendency for precipitation of cinnabar preferentially over the stability of Hg$_{(l)}$ in the presence of sulfide, which occurs naturally in formation brines in addition to being an impurity in CO$_2$.

4.1 Mineralogy and Formation Brine Composition

Of most importance for numerical simulations is the reconciliation of measured water compositions and observed mineralogy into a consistent dataset that yields (essentially) chemically steady initial conditions for the geochemical system of interest. This was achieved using water chemistry and mineralogical data from the literature, appropriate for a site consisting of a typical marine sandstone/siltstone (Table 2). These data were used together with computations using GeoT to reconstruct the deep water composition and to correct for effects of degassing and mineral precipitation during sampling (e.g., [25]). The water obtained in this fashion is near equilibrium with calcite, dolomite, quartz, kaolinite, and pyrite at the formation temperature of 106°C (Table 3, middle column) and was used for CHILLER simulations. For the reactive transport simulations presented later, the reconstructed water was further reacted (using TOUGHREACT) under kinetic constraints with formation minerals (Table 2) for 1000 years, a point at which essentially steady conditions were achieved (Table 3, right-hand side column).
Table 2. Mineralogical composition of the deep marine sandstone formation assumed for the simulations. Other minerals were allowed to form in the simulations (see text).

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Estimated Wt %</th>
<th>Estimated Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>0.5</td>
<td>0.49</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.5</td>
<td>0.46</td>
</tr>
<tr>
<td>Ankerite</td>
<td>0.5</td>
<td>0.41</td>
</tr>
<tr>
<td>Glaucnite</td>
<td>7</td>
<td>6.95</td>
</tr>
<tr>
<td>Fe-chlorite</td>
<td>2</td>
<td>2.02</td>
</tr>
<tr>
<td>Quartz</td>
<td>75</td>
<td>75.36</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>K-spar</td>
<td>8</td>
<td>8.3</td>
</tr>
<tr>
<td>Plagioclase (An10)</td>
<td>1</td>
<td>1.01</td>
</tr>
<tr>
<td>Muscovite*</td>
<td>5</td>
<td>4.7</td>
</tr>
</tbody>
</table>

*This mineral can be regarded as representing illitic phases as well

The computed concentrations of most components in the reconstructed and reacted waters do not depart significantly from their original values (Table 3). This, along with the fact that these computed compositions yield a typical equilibrium mineral assemblage for a deep marine sedimentary formation, provides reasonable confidence in the reconstruction approach, the selected mineral assemblage, and the thermodynamic data used in the simulations. It should be noted, however, that the recomputed total dissolved concentrations of Fe and sulfate (as SO₄) are significantly lower than typical measured values (Table 3). It is likely that measured Fe concentrations often do not reflect true dissolved Fe, which is common with Fe analyses, and/or possibly that it reflects contamination from engineered components. For SO₄, calculated concentrations that are below typical measured values reflect a chemical reduction to sulfide during the computations, which is most pronounced in the reacted water after 1000 years (Table 3). This suggests that typical measured SO₄ concentrations could represent sulfide that was oxidized upon sampling, and/or that redox equilibrium is not fully achieved in this system. The decrease in K and Fe concentrations compared to the initially reconstructed water when it is reacted
for 1000 years occurs due to some minor precipitation primarily of muscovite and Fe-chlorite (note that muscovite in these simulations can also be regarded as a proxy for illite).

Table 3. Composition of the formation water considered in this study (in ppm). The “Reconstructed” and “Reacted” columns show, respectively, computed initial compositions used for geochemical modeling with CHILLER, and reactive transport modeling with TOUGHREACT.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Measured</th>
<th>Reconstructed</th>
<th>Reacted 1000 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (25°C)</td>
<td>8.47</td>
<td>6.9</td>
<td>7.1</td>
</tr>
<tr>
<td>pH (106°C)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cl</td>
<td>2185</td>
<td>2208</td>
<td>2209</td>
</tr>
<tr>
<td>SO₄</td>
<td>31</td>
<td>3.6</td>
<td>0.033</td>
</tr>
<tr>
<td>HCO₃*</td>
<td>2167</td>
<td>2331</td>
<td>3114</td>
</tr>
<tr>
<td>H₂S**</td>
<td>--</td>
<td>0.15</td>
<td>0.52</td>
</tr>
<tr>
<td>Si</td>
<td>--</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td>Al</td>
<td>--</td>
<td>1.4E-03</td>
<td>2.1E-03</td>
</tr>
<tr>
<td>Ca</td>
<td>13.1</td>
<td>6.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Mg</td>
<td>3.1</td>
<td>1.6</td>
<td>0.71</td>
</tr>
<tr>
<td>Fe</td>
<td>6.86</td>
<td>1.70E-03</td>
<td>7.1E-04</td>
</tr>
<tr>
<td>K</td>
<td>449</td>
<td>549</td>
<td>59</td>
</tr>
<tr>
<td>Na</td>
<td>2250</td>
<td>2266</td>
<td>2874</td>
</tr>
<tr>
<td>Acetate</td>
<td>--</td>
<td>1181</td>
<td>1181</td>
</tr>
<tr>
<td>log(fO₂)</td>
<td>--</td>
<td>-53</td>
<td>-54</td>
</tr>
</tbody>
</table>

*Total dissolved inorganic carbon as HCO₃; **total dissolved sulfide as H₂S.
Figure 1. Computed saturation indices (log(Q/K)) of various minerals using the reconstructed formation water composition shown in Table 3. Most of the formation minerals considered in this study (Table 2) cluster near zero (the equilibrium point) at the formation temperature of 106°C (clchl-30 stands for Fe-chlorite).

4.2 Incremental Reaction of Hg-Bearing CO₂ with Formation Water and Sediments

The following set of simulations was run using CHILLER as a prelude to full reactive transport simulations, and do not consider transport. The modeling consisted of first reacting (numerically “titrating”) CO₂ into the formation water (Table 3) until the development of a separate CO₂ phase (~40% by volume) at a system pressure of about 200 bar. Mercury was included into the titrated CO₂ at a concentration of 190 ppbV. In a second stage, the sediment mineralogy (Table 2) was reacted (in small, finite increments) with the brine-CO₂+Hg assemblage until the water/sediment ratio became ~1, a point at which little further reaction took place (Figure 2). Minerals reaching (or already at) equilibrium with the solution were not further titrated at each reaction step (as long as the solution remained saturated with respect to these minerals), thus approximating dissolution of the formation minerals until thermodynamic equilibrium. At each reaction step, new minerals
produced by reaction were selected automatically from a large list (>200) of minerals on the basis of their thermodynamic viability. Minerals that were not deemed to belong to the geochemical system (on grounds of slow precipitation kinetics inferred by their known formation only in high-temperature and/or high-pressure systems, such as metamorphic Al, Ca, Mg silicates) were not allowed to precipitate. Such simulations were useful to examine Hg speciation, and also reaction products (i.e., secondary minerals) that were then considered for reactive transport simulations under full kinetic constraints using TOUGHREACT.

Results of these simulations show that the pH (in-situ) initially drops down from 7 to about 4.7 (without sediments added in the system) from the carbonic acid released by the dissolution of CO₂. The pH then becomes buffered near 5.2 when sediments are titrated in the system (Figures 2b,c). The main reaction products are chalcedony forming from feldspar dissolution, and siderite from primarily Fe-chlorite dissolution. Kaolinite initially forms at the expense of plagioclase dissolution but is replaced by muscovite as the pH increases. The dissolution of calcite and chlorite yields enough Mg and Ca in solution for the precipitation of magnesite and ankerite to take place after a certain amount of sediment has been reacted (about 40 g per initial kilogram of water, Figure 2c). These alteration products are typical for reactions expected to occur in GCS systems (e.g., [17]). In the present case, the volume balance between dissolving (Table 2) and precipitating (Figure 2c) minerals yields an unnoticeable porosity change (Figure 2b).

Cinnabar is found to be thermodynamically stable as soon as the Hg-bearing CO₂ reacts with the formation water, which contains small amounts of dissolved sulfide. This is expected given that cinnabar is known to readily form in the presence of sulfide (e.g., [26]). The precipitation of cinnabar is predicted to continue upon reaction with the sediments (Figure 2c). Liquid Hg is not found to be thermodynamically stable at any point during the simulation, with a saturation index
remaining near -2.5, and consistent with our initial analyses [7]. As shown by the reaction and equilibrium constants below, the formation of cinnabar is strongly favored, thermodynamically, relative to Hg(l) when sulfide is present, even in small concentrations:

\[
\text{HgS(s) + H}_2\text{O} = \text{Hg(l) + 0.25 SO}_4^{2-} + 0.75 \text{H}_2\text{S(aq) + 0.5 H}^+}
\]

\[
\log(K) = -13.30 \text{ (25°C) and -10.42 (100°C)} \quad (2)
\]

This reaction also shows that low pH (high H\(^+\)) further favors the precipitation of cinnabar relative to liquid mercury.

The dissolved Hg concentration is very small (on the order of 10\(^{-8}\) molal, or ~2 ppb) (Figure 2a). Aqueous Hg is computed to consist entirely of the dissolved Hg\(^0\) species. It will be shown later that at higher sulfide concentrations, when H\(_2\)S is included as an impurity in the CO\(_2\), Hg-S aqueous species can become dominant and approximately double the Hg solubility under the present conditions, which yields still quite low dissolved Hg concentrations.

It should be noted that the simulated total dissolved sulfide (expressed as HS\(^-\)) and Hg concentrations in Figure 2a, as well as pyrite amounts in Figure 2c, display a dense saw-tooth pattern. This is an artifact from stopping the titration (reaction) of a mineral (in this case pyrite) once this mineral reaches equilibrium with the solution. Under the conditions of low pH and low sulfide concentration here, cinnabar forms preferentially to pyrite, consistent with the reaction:

\[
\text{HgS(s) + Fe}^{+2} + \text{H}_2\text{S(aq)} = \text{FeS}_2(s) + \text{Hg(aq) + 2H}^+
\]

\[
\log(K) = -7.40 \text{ (25°C) and -6.19 (100°C)} \quad (3)
\]
The precipitation of cinnabar thus competes with pyrite (FeS$_2$) which is not replenished by the reacting sediment until it becomes fully depleted (below saturation). This behavior yields alternating cycles of complete pyrite dissolution followed by reprecipitation, which cannot be avoided in this type of simulation (except at extremely small prescribed reaction increments which create very long and impractical simulation times).

Figure 2. Simulated reaction of sediments (“rock”), formation water, and Hg-bearing CO$_2$ at 106°C and 213 bar. (a) Total dissolved concentrations of major aqueous species, sulfide, and Hg. (b) CO$_2$ phase amount and fugacity, pH, and porosity. (c) Precipitating minerals (shown only for the first 100 grams of reaction increment, for detail; these trends remain steady with further reaction). See text for discussion.

The results of these simulations are consistent with the calculations presented by Oldenburg and Spycher [7], in that the condensation of liquid mercury from the CO$_2$ phase is not expected in this system (even if sulfide-free). However, the presence of even a very small amount of dissolved sulfide in the formation water causes cinnabar precipitation. This mineral has a very low solubility,
and therefore the predicted dissolved Hg concentrations in the formation water are very low (ppb range). Essentially all the Hg initially in the CO₂ is expected to precipitate in the formation as cinnabar. As discussed by Oldenburg and Spycher [7], the effect of cinnabar precipitation on porosity (and thus permeability) depends on the scale over which such precipitation takes place.

5 Reactive Transport Modeling

To address the spatial aspect of Hg precipitation, a full reactive transport model was developed using TOUGHREACT. The injection of Hg- and H₂S-bearing CO₂ into a deep sandstone formation was simulated, with particular interest given to the distribution of Hg and the porosity change around the injection well.

5.1 Model Setup and Input Parameters

The model was setup as a two-dimensional (2D) vertical X-Z radial numerical mesh, as shown in Figures 3 and 4. CO₂ injection is taking place at 14.5 kg/s (~0.5 Mt/y) within a 300 m-long open borehole (radius 0.08 m) centered on a storage formation with a total thickness of 400 m. The numerical mesh comprises 9700 grid blocks, including 100 horizontal layers, each of a constant 4 m thickness, with increasing grid spacing in the horizontal direction, starting at a well radius of 0.08 m, then increasing progressively away from the well (with \( \Delta x = 0.1–2 \) m for the first 100 m away from the well, the area of principal interest here; Figure 4).

Simulations were run using a maximum time step of 6 hours. This time step value was found to remain below the Courant limit computed for aqueous-phase flow in all model gridblocks and at all times. However, because of the high CO₂ injection rate and fine space discretization near the
well, this value was found to exceed the Courant limit for the CO2-phase flow for up to a distance of about 2 to 3 m from the injection well. Nevertheless, test simulations at time steps below the Courant limit for the CO2 (“gas”) phase, over limited simulated time periods, indicated that a maximum time step of 6 hours should provide a reasonable compromise between computing efficiency and numerical accuracy.

For simplicity, hydrological properties were assumed homogeneous throughout (Table 4), and model boundaries were closed, with the lateral boundary located far away from the injection well (10 km). Tests using a fixed-pressure lateral boundary showed somewhat more lateral spreading of the CO2 plume than with a closed boundary (~ 2100 m versus ~ 2500 m after 40 years of injection), but otherwise similar results.

It should be noted that hydrodynamic dispersion is not explicitly modeled in these simulations. Results are subject to numerical dispersion, however, which can be viewed as some “proxy” for hydrodynamic dispersion. Numerical dispersivity values are approximately given by the model gridblock sizes ($\Delta x/2$ in the $X$ direction and $\Delta z/2$ in the $Z$ direction).

Figure 3. Schematic representation of the reactive transport model setup (not to scale). The injection interval (300 m) is shown in red (not to scale).
Figure 4. Spatial discretization of the radial X-Z numerical mesh shown in Figure 4-1. The center of the injection well is located at X = 0.

Table 4. Hydrological properties of the reactive transport model.
The temperature was assumed to remain constant throughout the simulations, thus thermal effects from CO₂ injection were neglected because these are considered second-order effects. Initial hydrostatic pressure conditions were established throughout the model domain prior to running injection simulations, with a pressure of ~213 bar (21.3 MPa) at the middle of the injection interval. Initially near-steady chemical conditions for injection simulations were obtained by running the reactive transport model without injection for about 1000 years, starting with the reconstructed formation water composition discussed earlier.

The same initial mineralogical composition was assumed as for the geochemical simulations presented earlier (Table 2). In addition, the following secondary phases were allowed to form (as potential products of water-CO₂-sediment chemical interactions): kaolinite, illite, magnesite, siderite, and dawsonite. This list of potentially forming phases was established on the basis of the geochemical modeling results as well as typical alteration products of CO₂-sediment interactions.
reported in published experimental and modeling studies. It should be noted that dawsonite has rarely been observed in natural systems under conditions typical of those expected during CCS operations [27,28], one exception being in volcaniclastic, tuffaceous sandstones of the Hailar Basin, China [29, 30]. Cinnabar and liquid Hg were also added to this list as potential Hg-precipitating phases. The composition of the formation water was discussed earlier and shown in the last column of Table 3.

The same thermodynamic data were used as for the geochemical modeling simulations. Thermodynamic and kinetic constraints applied in the simulations, and relevant input data, are discussed in Appendix A. The effect of mineral precipitation and dissolution was coupled to porosity using volumetric data (molar volume) for minerals from the literature to compute volume changes upon dissolution or precipitation. Porosity was coupled to permeability using a cubic Kozeny-Carman relationship [21], and to capillary pressure through the Leverett scaling relationship [31]. As discussed later in the paper, the computed change in porosity was found to be very small (about ±0.05% absolute) with negligible effect on permeability. Other porosity-permeability relationships accounting for non-uniform mineral precipitation/dissolution (e.g. [32]) were not implemented as these were deemed to also yield essentially negligible permeability changes, largely within the uncertainty of model input parameters.

5.2 Reactive Transport Model Results

The model was run for a total injection period of 40 years. Three simulations were run, considering the injection of CO₂ with: (1) 200 ppmV H₂S and 190 ppbV Hg (~1.6 mg/std.m³CO₂) (the base case), (2) 200 ppmV H₂S and 7 ppbV Hg (~0.058 mg/std.m³CO₂) (low Hg case), and (3) no H₂S
but 190 ppbV Hg (no-H$_2$S case). These simulations yield results qualitatively similar to the geochemical simulation presented earlier, in that Hg is predicted to readily precipitate from the CO$_2$ as cinnabar, and that porosity is not affected significantly by mineral precipitation and dissolution. The results of these simulations are discussed in more detail below.

After 40 years, supercritical CO$_2$ is predicted to migrate to about 2100 m from the injection well, spreading away from the well mostly by buoyancy, and accumulating below the top impermeable model boundary (Figure 5, top). The single-phase CO$_2$ zone remains within about 60 m of the injection well (Figure 5, and expanded-scale Figure 6). Note that for the same total injection rate, a thinner formation would result in farther migration, however it is unlikely that a thinner formation could sustain the high injection rate considered here (~0.5 Mt/y).
Figure 5. Simulated CO₂ phase (physical) saturation, aqueous phase pH (with the zone of single-phase CO₂ shown as white), and mineral volume fraction change after 40 years of injection. “Total volume fraction change” corresponds to the opposite of the absolute change in porosity.
Figure 6. Simulated evolution of the CO₂ plume during 40 years of injection, within 300 m from the injection well. The dashed boundary at 40 years shows a zone where the CO₂ residual saturation has dissolved away.

Carbonic acid from the dissolution of CO₂ into the formation water causes a zone of low pH (~4.5–5) that follows the shape of the two-phase CO₂ plume (Figure 5, top and middle). A zone of intermediate pH (~5–6) develops at the fringe of this plume. This zone is very thin along the upper edge of the two-phase CO₂ plume, but wide and most noticeable within about 300 m around the lower two thirds of the injection well (Figure 5, middle). This wider zone of intermediate pH corresponds to a region that was initially invaded by supercritical CO₂ but where this CO₂ phase was later displaced by buoyancy flow and residually saturated CO₂ fully dissolved, as shown on Figure 6 (bottom right-hand side). This region coincides with a zone of maximum mineral
dissolution (Figure 5, bottom), however, because the dissolution of minerals is accompanied by the precipitation of other minerals, the computed overall porosity change in this zone is much less than the volume change of individual minerals. In the present case, the absolute porosity increases from 0.15 to a maximum of ~0.1505 (an absolute change of 0.05%; Figure 5, bottom), which is insignificant.

Although the maximum predicted porosity change is quite small, the amount of dissolution and precipitation predicted for individual minerals is not negligible. After 40 years of CO₂ injection, Fe-chlorite shows the most volume decrease (~ –1.6 %), and muscovite the most volume increase (~ +0.9%) (Figure 7). The main reactions include the replacement of primarily Fe-chlorite by siderite, of calcite by dolomite, and of K-feldspar by muscovite (which can also be viewed as a proxy for illite) (Figure 7). Chalcedony is also predicted to precipitate from the dissolution of feldspars (volume change up to ~ +0.5%), as well as dawsonite, although in volumetric amounts about an order of magnitude smaller (not shown). Other minerals considered in the simulations, including cinnabar (discussed further below), play an insignificant role in the overall predicted porosity change. Note that these results should be considered more qualitative than quantitative given the fact that reaction rates are constrained by estimated, uncertain surface areas and a generalized rate law (Appendix A) that may not be most accurate close to equilibrium and for precipitation. Nevertheless, these results are qualitatively mostly consistent with the geochemical modeling results presented earlier, one difference being the precipitation of dolomite in the present case instead of magnesite in the earlier thermodynamic model.
Figure 7. Modeled volume fraction changes for the main reacting minerals after 40 years (case with H$_2$S in the injected CO$_2$; the case without H$_2$S shows similar results for these minerals). The contours show volume fraction changes (for each individual mineral) with positive values corresponding proportionally to decreases in porosity, and vice versa.

Because the behavior of Hg is closely tied to sulfide, we first examine the general effect of injecting trace H$_2$S concentrations (200 ppmV) with CO$_2$. The cases of injection without and with H$_2$S show essentially no differences in the distribution of pH (Figure 8). A very narrow band of lower porosity (i.e., higher mineral volume fraction, by about 0.05% absolute change) is predicted in the case without H$_2$S at the bottom edge of the single-phase zone (Figure 8, top right-hand side). It is attributed to the replacement of pyrite (FeS$_2$) by ankerite (CaFe(CO$_3$)$_2$) when H$_2$S is deficient. Except for this difference, both cases show essentially the same trends and amounts of porosity change: a slight porosity increase (~ 0.05%, absolute) ahead of the single-phase CO$_2$ plume arising from mineral dissolution driven by the pH decrease, and a slight decrease (also ~ ± 0.05 %,
absolute) within the single-phase CO$_2$ plume arising from mineral precipitation driven in part by water evaporation into the supercritical CO$_2$ (Figure 8, top).

Figure 8. Simulated volume fraction change (for all minerals, top, and pyrite, middle) and pH after 40 years of CO$_2$ injection within 100 m of the injection well, showing simulations with H$_2$S (left-hand side) and without H$_2$S (right-hand side) included as an impurity (200 ppm) into the injected CO$_2$. The area blanked out (white color) on the pH plots corresponds to the zone of single-phase CO$_2$ (no water present). “Total volume fraction change” corresponds directly to the opposite of the absolute change in porosity. Thus, positive volume fraction values correspond proportionally to decreasing porosity.

The effect of H$_2$S as an impurity in the injected CO$_2$ is most visible on the aqueous sulfide concentration plots (Figure 9), which show a clear band of elevated total aqueous sulfide concentrations directly adjacent to the single-phase CO$_2$ zone (Figure 9, top left-hand side). H$_2$S
is quite soluble in water (much more than CO₂), and essentially fully dissolves into the formation water at first contact with it (e.g., [33]). As a result, the predicted distribution of aqueous sulfide farther away from the edge of the single-phase CO₂ plume remains similar for the cases with and without H₂S co-injection with CO₂. As shown experimentally by Palandri and Kharaka [34], Fe(III) minerals could act as a sink for sulfide in GCS systems. In our simulated case, the reductive dissolution of Fe(III) in glauconite by sulfide results in a zone of depleted aqueous sulfide, relative to background concentrations (~15 micromolal), directly in front of the single-phase CO₂ plume (Figure 9).

Figure 9. Simulated total aqueous sulfide concentrations (left-hand side) after 40 years of CO₂ injection, for cases with and without H₂S included as an impurity (200 ppmV) in the CO₂. The zone of single-phase CO₂ is blanked out (no water present). Aqueous sulfide is oxidized by the dissolution of glauconite (right-hand side) resulting in concentrations below background where this mineral dissolves. Negative values for the volume fraction contours (right-hand side) correspond proportionally to increasing porosity.

Looking more closely at the Hg behavior, a zone of cinnabar precipitation is predicted to develop in the vicinity of the injection well (Figure 10), with a shape mostly matching the single-phase CO₂ plume. The case with low Hg concentration (7 ppbV) in the CO₂ shows about two orders of
magnitude less cinnabar precipitation. In the higher-Hg case, the total amount of Hg input into the system is large (~16 metric tons after 40 years). However, even though essentially this entire amount precipitates as cinnabar, the resulting volume increase as a fraction of formation volume (solid+water) is quite small, and corresponds to an absolute porosity decrease of only 0.005% (i.e., an insignificant drop from 0.15 to 0.14995) (Figure 10, top right-hand side). This is because of the high density of this mineral. The reactions leading to cinnabar precipitation can be written as:

\[
\text{Hg}(g) \rightarrow \text{Hg}(aq)
\]

\[
\log(K) = -0.95 \text{ (25°C) and } -2.02 \text{ (100°C) } (4)
\]

\[
\text{Hg}(aq) + 0.25 \text{SO}_4^{2-} + 0.75 \text{H}_2\text{S}(aq) + 0.5 \text{H}^+ \rightarrow \text{HgS(s)} + \text{H}_2\text{O}
\]

\[
\log(K) = 19.83 \text{ (25°C) and } 16.07 \text{ (100°C) } (5)
\]

The dissolved Hg concentrations are quite small (mostly < 8 ppb; Figure 10, bottom). In the higher-Hg case, a thin band of increased dissolved Hg concentrations (in the 20 ppb range) develops at the fringe of the single-phase CO\textsubscript{2} plume (12, bottom right-hand side), from the formation of Hg-S aqueous complexes that result from the dissolution of H\textsubscript{2}S from the CO\textsubscript{2} into the aqueous phase at this location:

\[
\text{HgS(s)} + 2\text{H}_2\text{S}(aq) \leftrightarrow \text{HgS(H}_2\text{S}_2)(aq)
\]

\[
\log(K) = -4.41 \text{ (25°C) and } -2.80 \text{ (100°C) } (6)
\]

Except for this difference, away from the single-phase CO\textsubscript{2} plume, the distribution of aqueous Hg concentrations in the low- and higher-Hg cases are essentially the same, and are controlled primarily by the cinnabar solubility as a function of aqueous sulfide concentrations and pH, as well as Hg transport in the aqueous phase.
Aqueous sulfide becomes depressed ahead of the single-phase CO$_2$ plume (from glauconite dissolution; Figure 9), and as pH increases away from the CO$_2$ plume, aqueous H$_2$S(aq) dissociates to HS$^-$ (around pH ~ 6.5). This causes a somewhat complex distribution of aqueous Hg concentrations, including a thin band of higher concentrations at the bottom of the Hg plume, predicted for both the low- and higher Hg cases (Figure 10, bottom). In both cases the aqueous Hg concentrations remain small at all locations.

The presence of H$_2$S in the CO$_2$ phase affects the distribution of cinnabar precipitation, but only slightly. When H$_2$S is absent from the injected CO$_2$, cinnabar is not predicted to precipitate much beyond the extent the single-phase CO$_2$ plume. When H$_2$S is present as an impurity in the CO$_2$, the zone of cinnabar precipitation extends by up to about 10 m in front of the single-phase CO$_2$
plume (Figure 10, top right-hand side). Both cases, however, display about the same maximum amount of cinnabar precipitation (~0.005% of total volume). Note that the presence of cinnabar within the single-phase CO₂ zone (Figure 10, top right-hand side) is not caused by evaporative concentration but by continuous and cumulative precipitation at the (moving) plume front.

6 Conclusion

Numerical investigations were carried out to assess the potential for Hg to impact injectivity through precipitation (or condensation) from injection of supercritical CO₂, including Hg and H₂S, impurities into a deep sandstone formation at 106°C and near 200 bar. The results of this purely computational study are consistent with previous simple analyses [7] suggesting that the co-injection of Hg (at 190 ppbV) with CO₂ is not expected to significantly impact injectivity through either condensation or precipitation as cinnabar. The present study further suggests that any impacts on injectivity would be more likely to result from the reaction of CO₂ with formation minerals than from the Hg itself, at the concentrations considered here (7 and 190 ppbV Hg). Because H₂S is another impurity typically difficult to entirely remove from natural gas and from the captured CO₂, and because Hg exhibits a strong affinity for sulfide, the effect of trace H₂S concentrations (200 ppmV) into the CO₂ was also investigated. We found that cinnabar would precipitate in the formation through the reaction of Hg and aqueous sulfide, whether or not H₂S is co-injected with CO₂, because sulfide occurs naturally in the targeted reservoir. Because liquid Hg is much less thermodynamically favored than cinnabar when sulfide is present, even in very small concentrations, Hg is not expected to condense from the CO₂. This is the case even with sulfide-free waters, because at the pressure and temperature of interest here, the considered gaseous Hg
concentrations remain well below liquid Hg saturation limits. When aqueous sulfide is present in
the formation and/or in the injected CO₂ in excess of co-injected Hg amounts, it is expected that
cinnabar will precipitate and inhibit the condensation of liquid Hg, even at Hg gas concentrations
exceeding the saturation limit for a pure CO₂+Hg gas stream, because of the strong thermodynamic
favorability of cinnabar relative to liquid mercury.

The reactive transport simulations, using homogeneous geochemical and hydrologic properties,
predicts that the cinnabar deposition is disseminated over scales of tens of meters in a zone
extending up to 70 m from the injection well, and not affecting porosity enough to affect injection
rates. The exact spatial distribution of deposition in the storage formation (especially if
heterogeneities are considered) remains uncertain, as localized cinnabar precipitation in some
areas cannot be ruled out. However, given the need for large injection rates inherent in GCS, which
require long perforated intervals in injection wells, we speculate that such long injectors will
reduce the potential for localized concentration of cinnabar to plug up the pore space around
injection wells enough to negatively impact injectivity.

Our simulations suggest that reactions involving formation minerals are more likely to affect
injectivity than the Hg itself. In the present case, the effect of noticeable dissolution of chlorite,
calcite, and K-feldspar on porosity is essentially balanced by the precipitation of primarily
chalcedony, dolomite, siderite and muscovite (which can be considered a proxy for illite). As a
result, the computed porosity and permeability changes are negligible. The addition of H₂S (at 200
ppmV) into the injected CO₂ essentially does not affect the simulations results and conclusions.

We conclude by noting that the models applied in this study rely on various assumptions and data
that have an inherent uncertainty. The phase partitioning of Hg between CO₂ and water predicted
here relies on scarce thermodynamic data with significant uncertainty, as well as assumption of
ideal gas behavior for Hg. Mineral reaction rates are also quite uncertain, relying on rate constants
from the literature but also on mostly unknown and/or poorly constrained reactive surface areas.
Mechanisms and rate laws for the precipitation of secondary phases are particularly uncertain,
especially far from equilibrium where precipitation rates are poorly predicted using rate laws and
parameters that apply primarily to dissolution. The coupling of permeability to porosity, especially
when secondary minerals form in various textures and at various locations within pores, is also
difficult to predict. Therefore, laboratory experiments making use of site-specific core samples and
fluids tailored to better understand 1) the phase partitioning of Hg between supercritical CO₂ and
pore fluids and 2) the precipitation mechanisms and rates of secondary phases (including Hg
phases) as well as their texture and impact on permeability, would significantly constrain further
efforts toward predicting permeability and injectivity for CCS operations.

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Appendix A – Thermodynamic and Kinetic Constraints

The geochemical modeling and reactive transport simulations were run using thermodynamic data primarily from the database soltherm.h06 [35], which relies on Gibbs free energy data primarily from Holland and Powell [36] for minerals, and primarily from SUPCRT92 [37,38] for aqueous species. This database includes data derived by Spycher and Reed [39] for Hg aqueous, solid and gas species, in part from studies by Barnes et al. [41] and Varekamp and Buseck [42]. Some of these Hg data were later updated with data from Shock et al. [38] before inclusion in the soltherm.h06 database. The equilibrium constants (as a function of temperature) for the reaction Hg(v) ↔ Hg(l) were originally derived by Spycher and Reed [39] using published Gibbs free energy data, and compare reasonably well at low temperatures with more recent data from Huber et al. [43] (see Appendix A in [7]). These equilibrium constants were not corrected for pressure, which tends to overestimate somewhat the solubility of Hg (by about 10% at 106°C and 215 bar [7]). The effect of pressure above the saturation pressure of pure water on the equilibrium constants of minerals, aqueous species, and H²S was also neglected, as it is considered a second-order effect compared to the effect of temperature. The solubility of CO₂ as a function of temperature and pressure follows the model of Spycher and Reed [40] in CHILLER, and the model of Spycher and Pruess [44] in TOUGHREACT. The partitioning of trace Hg and H₂S in the gas phase was computed assuming ideal-gas behavior, thus assuming equality of partial pressure and fugacity. This assumption is likely to result in an overestimated amount of Hg deposition from the gas phase (see Appendix B), and thus is deemed conservative as far as computing the porosity change from Hg deposition.

For this study, equilibrium constants for a few minerals were either updated, or added from recent sources. These include data from Bénézeth et al. [45] for dawsonite, Arnorsson and Stefansson [46] for feldspars (adjusted for consistency with the aqueous silica data in the database), and Yang and Steefel [47] for kaolinite. Equilibrium constants for Fe-rich chlorite were computed by assuming an ideal solution of 70 mol% clinochlore and 30 mol% daphnite, using the equilibrium constants derived from the data of Holland and Powell [36] for these endmembers. Glaucconite data were taken from Tardy and Fritz [48] and extrapolated to higher temperature following the trend of the muscovite equilibrium constants.
Most minerals were assumed to react under kinetic constraints, using the rate law and data discussed below. Potentially forming Hg phases (cinnabar and liquid Hg) were assumed to precipitate under (local) equilibrium constraints, which represent the equivalent of very fast rates of reaction. In doing so, the amount of Hg deposition was rather overestimated than underestimated. Kinetic data for these Hg phases were not readily available, and thus equilibrium was deemed to be a conservative case for looking at potential porosity changes from Hg precipitation.

Reactions between aqueous species, including redox reactions, and between the formation water and gaseous species (CO₂, Hg, and H₂S) were assumed to proceed under (local) thermodynamic equilibrium. Because the precipitation of cinnabar (Hg(²⁺)S(²⁻)) from zero-valent Hg in the gas phase represents the oxidation of Hg with concomitant sulfate (S(⁶⁺)O(⁴⁻)) reduction to sulfide (H(⁺)S(⁻²)) (reactions 4 and 5), assuming redox equilibrium can be deemed conservative in terms of maximizing the amount of cinnabar precipitation. In terms of maximizing the condensation of Hg(l), the assumption of cinnabar equilibrium is not conservative, however, because slow cinnabar precipitation would increase the potential for Hg(l) deposition. However, the concentration of Hg in the CO₂ phase is much smaller than the concentration required for Hg(l) to condense [7], thus slowing down the precipitation of cinnabar would have no effect on the condensation of Hg(l) for the conditions simulated here.

A general rate law derived from transition state theory [49] was used for the dissolution and precipitation of minerals other than cinnabar and liquid Hg:

\[ R_m = \pm A_m k_m (\Omega_m^n - 1)^p \]  

(B-1)

where \( k \) is the rate constant (moles per unit mineral surface area and unit time), \( A_m \) is the specific reactive surface area per kg H₂O, \( \Omega_m \) is the mineral saturation ratio (\( Q/K \)), and exponents \( n \) and \( p \) are either determined from experiments or taken equal to one. The value of the kinetic rate constant \( k \) can vary with the activity of other species, such as with pH [49, 50], as follows:

\[ k = k_{25}^{nu} \exp \left[ - \frac{E_{nu}^a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25}^{H} \exp \left[ - \frac{E_{H}^a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] a^{n_H}_{H}^{+} + k_{25}^{OH} \exp \left[ - \frac{E_{OH}^a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] a^{n_{OH}}_{H^{+}} \]  

(B-2)

where superscripts or subscripts \( nu, H, \) and \( OH \) indicate neutral, acid and base mechanisms, respectively; \( a \) is the activity of the species (in this case \( H^+ \)); \( n_H \) and \( n_{OH} \) are power terms (constant); and \( E_a \) is the activation energy for each mechanism.

These kinetic rate parameters were taken primarily from the compilation of Palandri and Kharaka [50] and updated with data from Yang and Steefel [47] for kaolinite, Hellevang et al. [51] for dawsonite, Golubev et al. [52] and Duckworth and Martin [53] for siderite (and applying the same data to ankerite), and Alekseyef [54] and Brandt et al. [55] for chlorite (Table B1). Glauconite was given the same kinetic parameters as muscovite. Rates were assumed reversible, except for quartz which was only allowed to dissolve. The rate law and data of Carrol et al. [56] for the precipitation of amorphous silica was used for chalcedony.

Input-specific surface areas used in the computation of \( A_m \) in Eq. A1 were calculated assuming spherical grain sizes of about 0.2 mm, yielding input surface areas of \( 3 \times 10^4 \text{ m}^2/\text{m}^3 \) (on the order of \(-10 \text{ cm}^2/\text{g}, \) depending on density). It should be noted that the uncertainty in \( A_m \) is typically quite large, and can be up to several orders of magnitude.
Table 4-2. Kinetic parameters for equation 4-2, with \( k \) values in mol m\(^{-2}\) s\(^{-1}\) and \( E_a \) values in kJ mol\(^{-1}\).

See text for data sources.

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<th>( E_a_H ) (acid)</th>
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* Re-fitted data; use with \( n = 0.333 \) in Eq. B-1.

Appendix B – Non-ideal mixing of CO\(_2\), Hg, and H\(_2\)O

For all simulations presented in this report, the assumption was made that Hg behaves as an ideal gas (fugacity=pressure). To quantify the effect of this assumption, the fugacity coefficient of Hg in a Hg-CO\(_2\) mixture was estimated using the Redlich-Kwong equation of state, with parameters for CO\(_2\) from Spycher and Pruess [44], and parameters for Hg estimated from critical properties \((T_c = 1764K, P_c = 1670\) bar [43]). Following the same approach as Spycher and Pruess [44] for water in CO\(_2\), the fugacity coefficient of Hg in CO\(_2\) was computed by assuming infinite dilution of Hg in the CO\(_2\), which is a good assumption at small Hg concentrations. In doing so, the density of the Hg-CO\(_2\) mixture at elevated temperatures and pressures is assumed to be the same as that of pure CO\(_2\), but the mixing effect of CO\(_2\) on Hg is taken into account in the calculation of the Hg fugacity coefficient. Standard mixing rules were applied, without consideration of specific interaction parameters between Hg and CO\(_2\). Using these approximations, the calculated fugacity coefficient of Hg in compressed CO\(_2\) was found to be small, around 0.07 at 106°C and 213 bar. It
is likely, however, that the actual fugacity coefficient values are higher than the values estimated here (but still significantly lower than 1), because the density of pure liquid Hg was somewhat overestimated using this approach. Fugacity coefficient values significantly less than 1 suggest that Hg precipitation could be significantly overestimated when assuming ideal behavior. Therefore, the assumption of ideal-mixing is likely conservative in terms of predicting a porosity decrease from Hg precipitation.