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Publication Date
2014-04-21

Peer reviewed
The role of CO₂ in CH₄ exsolution from deep brine:  
Implications for geologic carbon sequestration

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May 31, 2013
Revised August 2, 2013

Abstract
The partial pressure exerted by dissolved CO₂ in water (aqueous phase) containing dissolved CH₄ at concentrations near-saturation can lead to the formation of a CH₄-rich gas phase. We have used numerical simulation with TOUGH2/EOS7C to investigate the process of CH₄ exsolution caused by CO₂ injection for geologic carbon sequestration. We validated the solubility model in TOUGH2/EOS7C against published measurements of solubility and corresponding Henry’s Law coefficients. We verified our simulation results against a previously published 1D test problem, and investigated the effects of numerical dispersion on the CH₄ exsolution and flow processes. In 2D radial simulations of a model system, we found that highly concentrated CH₄ gas regions form at the leading edge of the CO₂ injection front. Because the gas saturations are small in the CH₄-rich gas regions in the generic system studied here, (1) CH₄ exsolution does not appear to be a problem for seismic monitoring of CO₂ plumes, (2) reservoir pressurization due to dilution of supercritical CO₂ by CH₄ does not appear to be a concern, and (3) relative permeability to water is not strongly reduced.
Introduction

From the perspective of demonstrated reservoir integrity, some of the most promising targets for geologic carbon sequestration (GCS) are depleted oil and gas reservoirs that have accumulated buoyant hydrocarbons over millions of years. In these systems, methane (CH\textsubscript{4}) is ubiquitous as a major component in the gas phase, as a dissolved component in both the oil phase (if any) and the aqueous phase. Even in formations without economic hydrocarbon accumulations nearby, CH\textsubscript{4} is often present as a dissolved species in deep aquifers, some of which have been of interest as targets of natural gas extraction (1). These deep saline aquifers are also of great interest for GCS (2). One question that arises is what happens when CO\textsubscript{2} is injected into deep saline formations that contain dissolved CH\textsubscript{4} at or near (chemical) saturation (i.e., at or near the CH\textsubscript{4} concentration above which a CH\textsubscript{4}-rich gas would exsolve).

The first-order effect of the addition of CO\textsubscript{2} to water containing dissolved CH\textsubscript{4} at or very near saturation is the evolution of a CH\textsubscript{4}-rich gas phase (3). This process, explained here in Section 3, is expected to occur in CH\textsubscript{4}-saturated aquifers when CO\textsubscript{2} is injected for GCS. Some potential impacts of the exsolution of CH\textsubscript{4} are (i) decreased precision of seismic monitoring of the size of the CO\textsubscript{2} plume due to inability to distinguish between the injected CO\textsubscript{2} and exsolved CH\textsubscript{4} gas, (ii) increased pressurization (i.e., increase in compressibility factor, Z, where \( PV = ZnRT \)) of the stored supercritical CO\textsubscript{2} as it mixes with CH\textsubscript{4} (4, 5), and (iii) decreased relative permeability for water due to the evolution of CH\textsubscript{4} gas. Regarding point (i), the contrast in seismic properties in the reservoir between brine and CO\textsubscript{2} or between brine and CH\textsubscript{4} is much larger than the contrast between CO\textsubscript{2} and CH\textsubscript{4} (e.g., Figure 2 in (6)) making it impossible at present to distinguish between CO\textsubscript{2} and CH\textsubscript{4} by surface seismic methods.

In this paper, we first present background information on prior studies that considered CH\textsubscript{4} in deep saline formations, and solubility studies of CO\textsubscript{2} and CH\textsubscript{4} in water. Next, we validate TOUGH2/EOS7C (7) against measured solubility data and verify the model by comparing results of CH\textsubscript{4} exsolution observed in another modeling study in a simple 1D test problem (3). Finally, we present results of simulations of CO\textsubscript{2} injection into CH\textsubscript{4}-saturated water in a 2D radial model system to show the magnitude and locations of CH\textsubscript{4} exsolution and its evolution over time.
Background and Prior Work

There has been long interest in the potential for production of CH$_4$ from deep overpressured saline aquifers (8, 1, 9). While these reservoirs are potential energy sources by virtue of their high temperature and high CH$_4$ content, they are poor candidates for direct CO$_2$ injection for GCS because they are overpressured (aka geopressured). To address the challenges of sequestering CO$_2$ in geopressed systems, researchers have come up with novel concepts for coupled fluid production, energy extraction, and GCS (10). Dissolved CH$_4$ also occurs in many deep normally pressured reservoirs (8) that are candidates for GCS, and it is these saline formations that are the subject of this paper. In addition, the current study is relevant to deep reservoirs near or along the natural gas migration pathway to shallower natural gas reservoirs, and to aquifers near depleted natural gas reservoirs that will naturally contain large amounts of dissolved CH$_4$.

We previously investigated the effects of residual gas including CH$_4$ gas on CO$_2$ injection for GCS (11). The present study extends our work to consider the case of injection of CO$_2$ into single-phase water containing dissolved CH$_4$. In this case, CO$_2$ dissolution, and the associated increase in partial pressure exerted by the dissolved gases in particular, leads to the exsolution of CH$_4$ into the gas phase. While this phenomenon has been pointed out and simulated in a 1D domain (3), this prior study did not attempt to quantify or address the underlying implications of the effect for GCS. A more recent study examined both dissolved and residual-gas CH$_4$ effects on CO$_2$ injection by means of an analytical solution with emphasis on comparison of the analytical solution to numerical simulation results in terms of two-phase flow effects and relative permeability including hysteresis (12).

With the critical importance of dissolution and exsolution in controlling the flow and transport processes of interest in the general area of hydrocarbon production, a large amount of research has been carried out focused on gas solubility in water (4, 13, 14, 15, 16, 17). Most relevant to the topic of CH$_4$ exsolution caused by CO$_2$ injection is the study of Qin et al. (17) in which laboratory measurements were made of coupled solubility effects in the system H$_2$O-CO$_2$-CH$_4$. The Qin et al. (17) study directly addressed the effects on solubility in water of one component due to the concentration in water of the other component. As we will discuss in more detail below, Qin et al. (17) showed that the effective Henry’s Law coefficient of CH$_4$ decreases with
dissolution of CO₂ (thus the solubility of CH₄, at a constant CH₄ partial pressure, actually increases with dissolution of CO₂). However, while the addition of CO₂ decreases the partial pressure of CH₄, it does not counter the tendency for the formation of a CH₄-rich gas phase that arises from the lower solubility of CH₄ relative to CO₂ and the sum of the partial pressures exerted by CH₄ and CO₂.

**Process Modeling**

In order to simulate the multiple processes involved in the injection of supercritical CO₂ into a porous medium containing water saturated with CH₄, we used TOUGH2/EOS7C (7) to model multiphase and multicomponent flow, along with multicomponent solubility including exsolution of a gas phase. TOUGH2/EOS7C uses an equilibrium constant approach to estimating Henry’s Law Coefficients for each volatile component and has been tested and demonstrated on a variety of problems. However, for the subtle questions of the effects of dissolution of one component, specifically CO₂, on the solubility of a second component (CH₄), we carried out additional testing to ensure the code was capable of simulating the processes of interest in GCS in CH₄-saturated systems.

**Validation of Solubility Model**

The most relevant papers for our purposes of validating the equilibrium constant-based solubility model implemented in our numerical code (TOUGH2/EOS7C) were determined to be Qin et al. (17), who carried out laboratory experiments of phase equilibria in the H₂O-CO₂-CH₄ ternary system, and Kiepe et al. (15) who determined the solubility of CH₄ in pure water and electrolyte solutions. We also compared EOS7C results against CO₂ solubility in pure water and brines calculated by the methods of (18) and references therein which was shown to reproduce a large number of solubility measurements mostly within experimental error.

**CO₂ and CH₄ aqueous solubility (as pure components)**

Qin et al. (17) reported on experimental measurements of CH₄ and CO₂ mutual solubility in the two-component systems H₂O-CO₂ and H₂O-CH₄. The CO₂ solubility values reported agree closely (2–8 %) with the solubility model of (18), which was based on previously published
experimental data. We present in Figures 1a–1c comparisons of EOS7C results (version 2, using the Peng-Robinson equation of state option) with CO₂ solubility values computed with the model of (18), and in Figure 1d comparisons with the experimental CH₄ solubility values of (17) and (15) (for pure H₂O, as a function of pressure). In general, the CO₂ solubility in water calculated by EOS7C agrees well with previously published solubility data, but EOS7C appears to slightly underestimate CH₄ solubility (Figure 1d).

Figure 1a. Comparisons of solubility of CO₂ as a function of pressure and temperature from the literature (18), and references therein) and EOS7C for (a) pure water, (b) 2m NaCl aqueous solution, and (c) 4m NaCl aqueous solution. (d) Comparison of CH₄ solubility in pure water as a function of pressure at various temperatures computed by EOS7C and from experimental data (17, 15).

Solubility in the three-component (H₂O-CO₂-CH₄) system

In a multicomponent system such as H₂O-CO₂-CH₄, it is essential to model correctly the effects of each component on the solubility of the other. Example results from (17) and EOS7C are shown in Figure 2. As shown in Figure 2, the decreasing partial pressure of Component 3 (CH₄) in the gas phase with increasing molar composition of Component 2 (CO₂) indicates increased...
solubility of CH$_4$ in the solution as the dissolved CO$_2$ concentration increases (for the same pressure). Such increased solubility is quantified by the effective Henry’s Law coefficient given by

$$H_{CH4} = P y_{CH4}/x_{CH4}$$  \hspace{2cm} (1)$$

where $y$ and $x$ denote mole fractions in the gas and aqueous phases, respectively, and $P$ stands for total pressure (with $P y_{CH4} = P CH4$, the partial pressure of CH$_4$). Therefore, the $y$-axis in Figure 2 represents an effective Henry’s Law coefficient. A smaller value of the Henry’s Law coefficient for a component implies lower partial pressure is exerted by that component (for the same aqueous concentrations), which is equivalent to a larger solubility in the aqueous phase for that component for the same partial pressure. Note that we assume the mole fraction in the gas is approximately equal to the total mole fraction in the cell plotted in (7) on the x-axis, a good approximation given the relatively low solubilities of these gases in water.

Figure 2. Results from Qin et al. (17) at $T = 102$ °C with EOS7C results for pure water (0 m NaCl) at 20 MPa superimposed showing reasonably good agreement. These results show that CH$_4$ (Component 3) solubility increases with higher CO$_2$ (Component 2) concentration in the water. EOS7C results assume the total mole fraction in the reaction cell ($n_2/(n_2+n_3)$) is
approximately equal to the mole fraction in the gas \( y_{n_2} = y_{CO_2} \) a good approximation because the solubilities of CO\(_2\) and CH\(_4\) in water are relatively low.

We tested EOS7C at other pressure, temperature, and salinity conditions to further examine solubility trends in the multicomponent system H\(_2\)O-NaCl-CO\(_2\)-CH\(_4\), with the expectation that the \( H_{CH4} \) trends shown in Figure 2 would not change, except for lower \( H_{CH4} \) values at lower pressures and higher \( H_{CH4} \) values at higher salinity (salting out). The results shown in Figures 3 and 4 confirm this expectation. As shown, \( H_{CH4} \) is much larger (lower solubility in the aqueous phase) for the 4 m brine (Figure 4) than for pure water at the same temperatures and pressures (Figure 3), and the trend remains toward lower \( H_{CH4} \) values at higher CO\(_2\) concentration in the aqueous phase. From this testing, we conclude that the solubility model implemented into TOUGH2/EOS7C is appropriate for use in studying CH\(_4\) exsolution in H\(_2\)O-NaCl-CO\(_2\)-CH\(_4\) systems.

![Figure 3](image_url)

Figure 3. Effective Henry’s Law coefficients computed with EOS7C for CO\(_2\)-CH\(_4\) mixtures in pure water at 102 and 51 °C at 10 MPa.
Discussion of the CH₄ exsolution mechanism

One well-known example of the dissolution of one component affecting the solubility of a second component is the case of NaCl and CO₂ in water. When the salt concentration increases in the aqueous solution, the solubility of components such as CO₂ decreases. The process of gases coming out of solution (exsolving) as the salinity goes up is called the “salting out” effect, and is caused by the increase in ionic strength of the solution (from the dissociation of NaCl), which increases the effective concentration (activity) of dissolved gases, thus driving exsolution. One might expect a similar effect with the dissolution of other compounds in water. Specifically, one might expect dissolved CO₂ to diminish CH₄ solubility. However, exactly the opposite occurs. The measurements in (17) and the solubility model built into EOS7C both show the CH₄ solubility in the aqueous phase increases with the dissolution of CO₂ into the aqueous phase for a range of pressures and temperatures relevant for GCS (Figures 2-4).
Nevertheless, the result of adding dissolved CO$_2$ to a nearly saturated CH$_4$-water solution is the exsolution of a gas phase. The reason for this is that each gas species in the aqueous phase exerts partial pressure. When the sum of the partial pressures of all of the gas species exceeds the liquid pressure, a gas bubble forms. Technically, the formation of a gas bubble would require a pressure somewhat above the static liquid pressure to overcome surface tension effects (19), however, we ignore this effect here. Thus the appearance of gas bubbles in the aqueous phase is not an indication that CH$_4$ solubility goes down as CO$_2$ dissolves in water. It is simply that the sum of the partial pressures (i.e., the new total vapor pressure of the solution, see Dalton’s Law) exceeds the liquid pressure.

The composition of a gas bubble exsolving from the aqueous phase is controlled by the Henry’s Law coefficients of the various gas species and the concentrations of the gas components dissolved in the aqueous phase. Similarly, the composition of an aqueous phase at the boundary of a gaseous plume front is also controlled by the (effective) Henry’s Law coefficients of the various gas species and the concentrations of the gas components in the gas phase.

Advection, diffusion, and dispersion are the mechanisms of transport in the fluid phases. These mechanisms control the length scales over which mixing in the aqueous and gas phases will occur during flow through porous media. In the simulations presented below, there is numerical dispersion which, depending on the grid discretization and numerical solution approach, can in some cases approximately mimic hydrodynamic dispersion. When free-phase CO$_2$ first invades a water-filled grid block containing CH$_4$ at near-saturation concentrations, a local equilibrium within the grid block is established that places a small amount of CO$_2$ into the CH$_4$-saturated water of the grid block as controlled by the total mass of CO$_2$ invading the grid block and by the Henry’s Law coefficients. This results in an increase in the (total) gas pressure in the solution, which leads to exsolution of CH$_4$ into the gas phase. Because the solution is nearly at saturation with respect to CH$_4$, the gas phase becomes highly enriched in CH$_4$.

*Verification of TOUGH2/EOS7C*

The prior theory and modeling results of the injection of CO$_2$ into a one-dimensional horizontal column containing CH$_4$-saturated water have been presented (3). The main conclusion of that prior work was that CO$_2$ causes CH$_4$ exsolution, resulting in the generation of a gaseous CH$_4$.
bank ahead of the CO\(_2\) plume. The CH\(_4\) bank was predicted to have very high CH\(_4\) concentrations, but was of small volume, such that the predicted total flowing CH\(_4\) amount was small.

Later, modeling results of injection of CO\(_2\) into reservoirs with and without residual CH\(_4\) gas were presented (11). These simulations also showed that CO\(_2\) causes CH\(_4\) exsolution resulting in the generation of a narrow CH\(_4\) bank at the front of the CO\(_2\) plume, but the focus was on relative permeability effects rather than gas exsolution. Here, we apply TOUGH2/EOS7C to the problem presented in (3) for code verification.

A sketch of Taggart’s problem (3) is presented in Figure 5, and parameters of the problem are given in Table 1. In the problem, dry CO\(_2\) is injected into a horizontal column that is initially fully liquid saturated and at (chemical) saturation with CH\(_4\). The compositional outflow from the domain is quantified by the flowing mole fraction (\(q^i\)), defined, for example, for \(i = \text{CO}_2\), as

\[
q^{\text{CO}_2} = \frac{q^{\text{CO}_2}}{q^{\text{CO}_2} + q^{\text{CH}_4} + q^{\text{H}_2\text{O}}}
\]

(2)

where the molar flows (\(q^i\)) are summed over both gas and aqueous phases. Results from TOUGH2/EOS7C and from (3) for this problem are shown in Figure 6. Figure 6a shows pressure, gas saturation, and mass fractions of CO\(_2\) and CH\(_4\) as a function of distance along the horizontal column at \(t = 3\) days as simulated by TOUGH2/EOS7C. As shown in Figure 6a, the CO\(_2\) displaces the CH\(_4\)-saturated water and produces a bank of gas with elevated CH\(_4\) concentration at the gas-phase front at \(d = 42\) m. The entry of two-phase mixture into previously single-phase aqueous grid blocks at the injection front is predicted to cause the gas phase to become predominately CH\(_4\) as that small amount of CO\(_2\) partitions between the aqueous and gas phases. Note that the maximum total mass fraction of CH\(_4\) occurs just as the gas-phase saturation reaches zero. This is a critical aspect of this process relevant to questions about recovering CH\(_4\) and about the CH\(_4\) bank potentially interfering with efforts to image the injected CO\(_2\) plume. In simulations not shown here, we determined that increasing the residual gas (physical) saturation
$S_{gr}$ (aka $S_{crit}$) causes a delay in the arrival of the CH$_4$ bank due to the additional time it takes for the gas (physical) saturation to become high enough to allow gas-phase mobility, but does not otherwise affect the results. Figures 6b and 6c display the flowing mole fractions of CO$_2$, CH$_4$, and H$_2$O at the outlet of the model computed with TOUGH2/EOS7C and as shown in (3), and demonstrate good agreement between the two. The main processes displayed in this 1D problem are water displacement, CO$_2$ invasion, and partitioning of CO$_2$ and CH$_4$ between gas and aqueous phases.

Table 1. Properties of the 1D displacement problem after Taggart (2009).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity ($\phi$)</td>
<td>0.25</td>
</tr>
<tr>
<td>Permeability ($k$)</td>
<td>$1.0 \times 10^{-12}$ m$^2$</td>
</tr>
<tr>
<td>Capillary Pressure ($P_{cap}$)</td>
<td>0.0</td>
</tr>
<tr>
<td>Relative Permeability ($k_r$)</td>
<td>power-law $k_i$ and $k_{rg}$ with power = 2, $S_{rg} = 0.15$, $S_{gr} = 0$</td>
</tr>
<tr>
<td>Pressure (initial and right-hand side boundary condition)</td>
<td>$2.04 \times 10^7$ Pa (3000 psi)</td>
</tr>
<tr>
<td>Temperature (isothermal)</td>
<td>$91.8$ °C ($197.2$ °F)</td>
</tr>
<tr>
<td>CO$_2$ injection rate</td>
<td>$9.4 \times 10^{-4}$ kg/s (1 res. Bbl/day)</td>
</tr>
<tr>
<td>Initial aqueous phase saturation</td>
<td>$S_l = 1.0$</td>
</tr>
<tr>
<td>Grid spacing</td>
<td>0.5 m</td>
</tr>
</tbody>
</table>

Figure 5. Sketch of 1D model flow domain after (3).
Figure 6. (a) TOUGH2/EOS7C simulation results at $t = 3$ days as a function of distance from the inlet. (b) TOUGH2/EOS7C simulation results of flowing mole fractions ($q_x^{H_2O}$, $q_x^{CO_2}$, $q_x^{CH_4}$) at the outlet for power-law $k_{rl}$ and $k_{rg}$ with power = 2. Note the sharp peak in the CH$_4$ profile, consistent with (c) prior results (3).

**Numerical dispersion**

Because CH$_4$ exsolution due to CO$_2$ injection relies on CO$_2$ invasion into the CH$_4$-rich waters at the phase front, and such advection is enhanced by numerical dispersion in discretized numerical models, we undertook an investigation of the effects of numerical dispersion. Numerical dispersivity in this 1D problem with upstream weighting in TOUGH2 is equal to one-half the grid spacing multiplied by the Darcy velocity ($\Delta Y/2 * v$) (e.g., (20) p. 238). To investigate the effects of numerical dispersion, we carried out simulations of the 1D test problem with three
different grids, coarse (15 grid blocks in the Y-direction), medium (60 grid blocks in the Y-direction), and fine (240 grid blocks in the Y-direction). As shown in Figure 7, numerical dispersion does influence the results. Specifically, the coarser gridding causes greater width of the CH$_4$ front, and the faster propagation of the injected CO$_2$. Numerical dispersion also affects the peak CH$_4$ concentration in the CH$_4$ bank, but these changes are not completely systematic with grid refinement as seen in Figure 7. By $t = 3$ days, it seems that the trend is apparent that coarser gridding causes a wider CH$_4$ bank with lower peak concentration and finer gridding causes a narrower CH$_4$ bank with higher peak concentration. In addition, the peak concentration of the CH$_4$ bank tends to grow with time over the three days and 60 m length of the system.

Figure 7. Simulation results for the 1D model problem showing evolution of the peak concentration and width of the CH$_4$ bank as a function of grid resolution where fine corresponds to $\Delta Y = 0.25$ m (240 grid blocks), medium to $\Delta Y = 1$ m (60 grid blocks), and coarse to $\Delta Y = 4$ m (15 grid blocks).
To investigate the growth in intensity of the CH$_4$ bank over time, we lengthened the 1D problem from 60 m to 240 m while keeping the same grid size as the fine grid ($\Delta Y = 0.25$ m). As shown in Figure 8, the peak concentration of the CH$_4$ bank grows until about 12 days and then stabilizes with nearly pure CH$_4$ in the bank. The width of the CH$_4$ bank continues to grow, as more CH$_4$ is continually exsolved as the bank moves along. Note that this CH$_4$ bank occurs mostly within a region where the aqueous phase saturation is increasing rapidly to one. The overall conclusion here is that simulation results are affected by numerical dispersion, but the effects are generally predictable in this 1D problem, with higher resolution models producing sharper CH$_4$ banks with higher CH$_4$ concentration within the bank.

Figure 8. Simulation results for an extended 1D model problem (240 m in length) for a fine grid ($\Delta Y = 0.25$ m) showing the peak $X_g^{CH4}$ increases with time as does the width of the CH$_4$ bank.
Because our 2D simulations (next section) are in a radial system, we also investigated the width and intensity of the CH$_4$ bank for the 1D system but with a radial geometry. In the radial system, the width of the CH$_4$ bank seems to stabilize after about 4 days (bank volume continues to grow because of the radial geometry), while the peak concentration is still changing at 14 days as shown in Figure 9.

Figure 9. Simulation results for a 1D radial grid showing small changes in peak concentration and width of the CH$_4$ bank due to the geometric effect of the radial grid.
Simulation of 2D radial model system

Model Properties

In order to understand and evaluate the extent and implications of CH₄ exsolution induced by CO₂ injection for large-scale CO₂ injection projects, we carried out TOUGH2/EOS7C (22, 7) simulations of CO₂ injection into an idealized 2D radial system. The properties of the model system were chosen to include features of interest such as multiple layers with different permeability, including a low-permeability layer (baffle) with potential for structurally trapping exsolved CH₄. The main features of the system include zero dip, fresh water, isothermal conditions, constant isotropic permeability within each layer, uniform porosity, capillary pressure strength proportional to the inverse square root of permeability (i.e., Leverett scaling), a multilayer CO₂ injection rate set to be proportional to the permeability-thickness product of each layer at a rate of 14 kg/s (0.44 Mt CO₂/yr). Injection lasts for 40 years. Details of the system properties are presented in Table 2.

The domain discretization and layering are shown in Figure 10. The gradually changing grid-block size in the radial direction was chosen to resolve flow features near the well (where grid block width is 1 m), and economize on simulation time at greater distances. Note the domain is 10 km in radius to avoid strong influence of the outer boundary. The model is 400 m thick and contains 40 layers, each 10 m thick. Given the properties of the formations and the assumed injection interval, most of the injected CO₂ is expected to flow into Layers 2 and 3 (the most permeable units). With the assumed properties and configuration, including a continuous shale layer (Layer 4), it is expected that buoyant CO₂ and/or exsolved CH₄ will accumulate for some period under the shale in the model system.

The initial conditions for all simulations have hydrostatic pressure (thus no horizontal pressure gradient) and constant temperature (104 °C). The top and bottom boundaries are closed to flow, while the outer (right-hand side) boundary is held at a constant hydrostatic pressure. In the first set of simulations, we assumed fully saturated initial conditions in the model with water containing dissolved CH₄ just below the concentration at which CH₄ bubbles would form (i.e., just below chemical saturation). In the second set of simulations, initial conditions with residual
CH$_4$ were produced by running a preliminary simulation with a small amount of gaseous CH$_4$ to a gravity equilibrium, to examine the effect of initial residual gas.

Table 2. Properties of the simplified single-well radial case study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity ($\phi$)</td>
<td>0.15</td>
</tr>
<tr>
<td>Dip</td>
<td>0 degrees</td>
</tr>
<tr>
<td>Pressure at top of domain (initial)</td>
<td>$2.24 \times 10^7$ Pa</td>
</tr>
<tr>
<td>Temperature (isothermal)</td>
<td>104 °C</td>
</tr>
<tr>
<td>Permeability ($k$)</td>
<td></td>
</tr>
<tr>
<td>Reservoir Layer 1</td>
<td>$1.0 \times 10^{-14}$ m$^2$</td>
</tr>
<tr>
<td>Reservoir Layer 2</td>
<td>$5.0 \times 10^{-14}$ m$^2$</td>
</tr>
<tr>
<td>Reservoir Layer 3</td>
<td>$2.5 \times 10^{-14}$ m$^2$</td>
</tr>
<tr>
<td>Shale Layer 4</td>
<td>$1.0 \times 10^{-15}$ or $1.0 \times 10^{-16}$ m$^2$</td>
</tr>
<tr>
<td>Reservoir Layer 5</td>
<td>$2.5 \times 10^{-14}$ m$^2$</td>
</tr>
<tr>
<td>Capillary Pressure ($P_{cap}$) and Relative Permeability ($k_r$)</td>
<td>van Genuchten (22) capillary pressure and relative permeability for liquid, Corey (23) relative permeability for gas</td>
</tr>
<tr>
<td>Terminology:</td>
<td></td>
</tr>
<tr>
<td>$\lambda = m = 1 - 1/n =$ power in expressions for $P_{cap}$</td>
<td></td>
</tr>
<tr>
<td>$S_{lr} =$ aqueous-phase residual saturation</td>
<td></td>
</tr>
<tr>
<td>$S_{gr} =$ gas-phase residual saturation</td>
<td></td>
</tr>
<tr>
<td>$P_{c0} = \alpha^{-1} =$ capillary pressure strength between aqueous and gas phase</td>
<td></td>
</tr>
<tr>
<td>$P_{cmax} =$ maximum possible value of $P_{cap}$</td>
<td></td>
</tr>
<tr>
<td>$\lambda = 0.40$</td>
<td></td>
</tr>
<tr>
<td>$S_{lr} = 0.27$</td>
<td></td>
</tr>
<tr>
<td>$S_{gr} = 0.01$</td>
<td></td>
</tr>
<tr>
<td>$P_{c0} =$ 1190 Pa (for Layer 2)</td>
<td></td>
</tr>
<tr>
<td>$P_{cmax} = 1 \times 10^8$ Pa</td>
<td></td>
</tr>
<tr>
<td>Single-well injection rate of 0.44 Mt/yr for 40 years$^1$</td>
<td>14 kg/s</td>
</tr>
</tbody>
</table>

$^1$M = million
Figure 10. Refined discretization showing gradual increase of grid block width throughout the radial extent of the domain, and uniform spacing in the vertical direction. Top two plots are successive blow-ups of the bottom plot near the injection well (left side).

Results

Case 1: Dissolved CH₄

Figures 11-13 show results for the case of CH₄ dissolved initially in the water (no residual gas). As expected, injection of CO₂ into CH₄-saturated water results in the exsolution of CH₄ at the leading edge of the CO₂ plume. While the concentration of CH₄ in the gas at the leading edge is very high (nearly 100%), the amount of gas there is very small ($S_g < 0.1$). Buoyancy forces on the lighter CH₄ gas result in strong upward movement of the bank of CH₄, which is barely apparent at 100 days (Figure 11), and dominant at later times (Figures 12-13). The blob-like nature of the CH₄ bank seen in Figures 12-13 is a numerical artifact, caused by the rectangular grid’s poor representation of the sloping bank. Exsolved CH₄ accumulates under the shale layer for a time (Figures 11-12), but eventually moves through it to accumulate at the top of the model.
domain (Figure 13). The sweep of CO₂ effectively strips all of the CH₄ from the aqueous phase within the region of the CO₂ plume. The gas concentrations in the CO₂-swept region are dominated by the CO₂ that is injected.

As shown in Figure 11 the shale limits the flow of injected buoyant CO₂ upward, creating a strong pressure gradient across this formation. Gas saturations reach about 30%, and the vast majority of the gas-phase plume is filled with nearly pure CO₂. By a time of five years (Figure 12), there is enhanced spreading under the shale where gas saturation is higher due to accumulation of CO₂. Also, by five years the gas saturation becomes very high near the well, due to dry-out of the formation as residual-phase water evaporates into the gas phase. The 40-year results (Figure 13) indicate that enhanced spreading under the shale persists, even as near the well some gas flows upward through the shale. The gas saturation distribution in Figure 13 shows that \( S_g \) remains notably lower in the shale than in the underlying sand, due to a combination of the shale’s lower permeability and higher capillary pressure strength.
Figure 11. Results at $t = 100$ days of mass fraction CH$_4$ in the aqueous phase ($X_l^{CH_4}$), mass fraction CO$_2$ in the aqueous phase ($X_l^{CO_2}$), mass fraction CH$_4$ in the gas phase ($X_g^{CH_4}$), mass fraction CO$_2$ in the gas phase ($X_g^{CO_2}$), gas saturation (Sg) and pressure change ($DP$). The dashed lines identify the model layering. The CH$_4$ exsolution bank is clearly visible as the maximum
$X_g^{CH4}$ just inside of the boundary of the gas-phase plume. The single solid black contour line most easily seen in the last frame is the $S_g = 1 \times 10^{-5}$ isopleth, showing the extent of the gas-phase in the domain.
Figure 12. Results at $t = 5$ years of mass fraction CH$_4$ in the aqueous phase ($X_{t}^{CH_4}$), mass fraction CO$_2$ in the aqueous phase ($X_{t}^{CO_2}$), mass fraction CH$_4$ in the gas phase ($X_{g}^{CH_4}$), mass fraction CO$_2$ in the gas phase ($X_{g}^{CO_2}$), gas saturation ($S_g$) and pressure change ($DP$). The dashed lines identify the model layering. Note the CH$_4$ exsolution bank extends through the shale. The single solid
black contour line most easily seen in the last frame is the $S_g = 1 \times 10^{-5}$ isopleth, showing the extent of the gas-phase in the domain.
Figure 13. Results at $t = 40$ years of mass fraction CH$_4$ in the aqueous phase ($X_{i}^{CH4}$), mass fraction CO$_2$ in the aqueous phase ($X_{i}^{CO2}$), mass fraction CH$_4$ in the gas phase ($X_{g}^{CH4}$), mass fraction CO$_2$ in the gas phase ($X_{g}^{CO2}$), gas saturation ($S_g$) and pressure change ($DP$). The dashed lines identify the model layering. Exsolved CH$_4$ is spread out in the shale and Layer 5, but only
in regions with very small gas saturation. The single solid black contour line most easily seen in
the last frame is the $S_g = 1 \times 10^{-5}$ isopleth showing the extent of the gas-phase in the domain.
Case 2: Initial residual CH$_4$ gas

In Case 2, we investigated the effect of injection of CO$_2$ into a system with residual gas, similar to our previous work (11), but with emphasis on CH$_4$ exsolution rather than relative permeability and injectivity. We establish initial conditions with residual CH$_4$ gas by specifying a constant saturation of $S_g = 0.26$, then letting the system evolve for 1000 years. This results in a slight stratification, with the saturation distribution shown in Figure 14. Gas with $S_g > S_{gr}$ is slightly mobile. The value of residual gas saturation is $S_{gr} = 0.27$.

Results for Case 2 are shown in Figures 15-17. Because residual CH$_4$ gas was present everywhere initially, the composition of the gas-phase near the leading edge of the CO$_2$ plume is nearly pure CH$_4$, which means the generation of a CH$_4$ front does not show up as a distinct bank because all of the existing gas away from the CO$_2$ plume is pure CH$_4$. Nevertheless, the tendency for exsolution to occur is still present as CO$_2$ dissolves into the aqueous phase. As was observed in (11), the main effect of the presence of residual gas is to restrict the flow of water (aqueous phase) through relative permeability effects such that the pressure rise ($DP$) for a given CO$_2$ injection rate is much higher than when residual gas is not present. This can be seen by comparing $DP$ in Figures 11 and 15. As for the growth and evolution of the CO$_2$ plume, at early time (100 days), the systems with zero residual gas and with residual gas are similar (Figures 11 and 15), but by $t = 5$ years, significant differences arise as relative permeability effects play out (Figures 12 and 16). The larger pressure gradients required to drive flow when residual gas is present make buoyancy flow relatively less important, resulting in much less upward flow of the CO$_2$ plume. Figure 16 shows that the extent of the CO$_2$ plume in each layer is roughly proportional to layer permeability, with just a small accumulation under the shale layer. By 40 years, however, buoyancy flow again dominates (Figures 13 and 17), with strong upward gas-phase flow and extensive spreading under the shale layer. In fact, the radial extent of the CO$_2$ plume is greater for the case with residual CH$_4$ present. Near the well, Figure 17 shows that while mobile gas phase has moved through the shale all the way to the top of the formation, the composition of the gas above the shale is mainly CH$_4$, and saturation remains significantly lower than below the shale.
Figure 14. Initial distribution of residual CH$_4$ gas along with the $S_g = S_{gr} = 0.27$ isopleth (black line).
Figure 15. Results at $t = 100$ days of mass fraction CH$_4$ in the aqueous phase ($X_i^{CH_4}$), mass fraction CO$_2$ in the aqueous phase ($X_i^{CO_2}$), mass fraction CH$_4$ in the gas phase ($X_g^{CH_4}$), mass fraction CO$_2$ in the gas phase ($X_g^{CO_2}$), gas saturation ($S_g$) and pressure change ($DP$). The single
solid black contour line is the $S_g = 0.27$ isopleth, showing the extent of the residual gas-phase that is present throughout the domain. The dashed lines identify the model layering.

Figure 16. Results at $t = 5$ years of mass fraction CH$_4$ in the aqueous phase ($X_l^{CH_4}$), mass fraction CO$_2$ in the aqueous phase ($X_l^{CO_2}$), mass fraction CH$_4$ in the gas phase ($X_g^{CH_4}$), mass fraction CO$_2$
in the gas phase ($X_g^{CO2}$), gas saturation ($S_g$) and pressure change ($DP$). The single solid black contour line is the $S_g = 0.27$ isopleth, showing the extent of the residual gas-phase that is present throughout the domain. The dashed lines identify the model layering.
Figure 17. Results at $t = 40$ years of mass fraction CH$_4$ in the aqueous phase ($X_l^{CH_4}$), mass fraction CO$_2$ in the aqueous phase ($X_l^{CO_2}$), mass fraction CH$_4$ in the gas phase ($X_g^{CH_4}$), mass fraction CO$_2$ in the gas phase ($X_g^{CO_2}$), gas saturation ($S_g$) and pressure change ($DP$). The single
solid black contour line is the $S_g = 0.27$ isopleth, showing the extent of the residual gas-phase that is present throughout the domain. The dashed lines identify the model layering.

Long-term post-injection results are shown in Figures 18 and 19. Figure 18 shows that gas saturation steadily decreases towards $S_{gr}$, and that the shale layer continues to provide a barrier to buoyancy flow. The dry-out region around the well shrinks until it has disappeared by 500 years. Figure 19 shows that the mass fraction of CO$_2$ within the gas-phase plume is not changing much. In a system with a dipping formation or regional flow, there would be an opportunity for the CO$_2$ plume to come into contact with brine not already saturated with dissolved CO$_2$, so the plume would gradually disappear as CO$_2$ dissolved. Similarly, if brine not already saturated with dissolved CH$_4$ entered the system, the residual CH$_4$ could dissolve as well.
Figure 18. Long-term post-injection results of gas saturation (color contours) and $S_g = 0.27$ isopleth. The dashed lines identify the model layering. The baffle effect of the shale remains as higher gas saturations are observed under it.
Figure 19. Long-term post-injection results of mass fraction CO₂ in the gas phase ($X_g^{CO_2}$) showing very small changes after 100 years.
Summary of 2D radial simulations

A CH₄ bank forms at the leading edge of CO₂ injected into water containing dissolved CH₄. The CH₄ bank occurs in a region of very small gas saturation. The CH₄ bank tends to rise upward by the buoyancy effect. For the case of residual CH₄ gas present initially, the pressure rise due to injection is larger, all other things being equal, due to decreased relative permeability of the formation to the water (aqueous phase) as observed in previous 1D simulations (11). In the 2D case study shown here, we also observe that buoyancy flow is less when there is residual gas present, presumably because the density contrast between injected CO₂ and the water-CH₄ gas mixture is smaller, and because the buoyancy force is smaller compared with the advective pressure increase. With less buoyancy flow, there is diminished flow upward through the shale, and greater radial extent of the CO₂ plume. For the post-injection period out to hundreds of years, there is very little movement of the CO₂ plume. Over time, the gas saturation gradually decreases to nearly the residual gas saturation as CO₂ continues to dissolve and diffuse into the aqueous phase.

Summary

The solubility model of TOUGH2/EOS7C agrees with laboratory measurements (17) which show that CH₄ solubility actually increases with dissolved CO₂ content. But the partial pressure exerted by dissolved CO₂ in water with CH₄ dissolved at near-saturation values causes the formation of a CH₄-rich gas phase despite the increase in CH₄ solubility.

TOUGH2/EOS7C has been verified against another numerical solution (3) on a 1D horizontal CO₂ injection problem. Numerical dispersion causes a wider and lower concentration CH₄ bank, but the CH₄ bank strength levels off when the grid resolution is fine enough.

Numerical experiments in a 2D model system show the formation of the CH₄ bank and its tendency to migrate upwards. But as in the 1D problem, the nearly pure CH₄ bank occurs in a region with very small gas saturation, meaning the amount of CH₄ is modest and what is present is not very mobile.
Implications for geologic carbon sequestration

The interference of CH₄ exsolution on seismic monitoring of CO₂ injection does not appear to be a concern. First, the gas saturation in the CH₄-rich leading-edge region is very small, and second, the CH₄ bank is adjacent to the CO₂ phase front. Granted the p-wave velocity is very sensitive to gas saturation at small values of gas saturation, but the detection of gas (e.g., CH₄ or supercritical CO₂) at this location would indicate the region of the CO₂ plume anyway because the CH₄ bank is located at the leading edge of the CO₂ plume. While we are not aware of ways to distinguish between CO₂ and CH₄ by surface seismic methods, modeling of the details of the geophysical response of CH₄ adjacent to CO₂ could be carried out as a way to investigate whether CO₂ and CH₄ gas regions could be resolved by seismic monitoring.

Regarding the possibility of substantial increase in pressure that could occur due to CH₄ diluting supercritical CO₂, this does not appear to be likely. The reason is that the exsolution occurs at the edge of the CO₂ plume, and the main CO₂ plume tends to push CH₄ out to the periphery of the plume. The main plume remains nearly pure CO₂ through its overwhelming ability to dilute trailing edge CH₄.

As for the effect on injection arising from relative permeability effects of an exsolving CH₄-rich gas phase, the saturations are very small and this does not seem to be a big factor in the simulations. This result is also relevant to the question of whether CH₄ could be produced for beneficial use from an artificially created CH₄ bank. In short, the feasibility appears low because the gas-phase saturations are too small. The simulations show that any region of high gas saturation is dominated by CO₂. We note that our simulations assumed a fresh water (zero salinity) which allowed even more dissolved CH₄ to exist than would exist in an actual saline brine, and still we found the amounts of CH₄ exsolved to be too small in the general case to create obvious accumulations that could strongly impact GCS or be available for commercial exploitation. Although not investigated here, we can speculate that engineered heterogeneity through hydraulic fracturing and/or less regular and more creative injection and fluid manipulation schemes could conceivably be developed to optimize CH₄ exsolution and accumulation for potential beneficial extraction.

In summary, our simulations suggest that dissolved CH₄ in formation waters produces some interesting exsolution effects, but dissolved CH₄ and its exsolution do not appear to have serious
implications for geologic carbon sequestration. This conclusion is based on our experiences with the simulations presented here that make use of relatively homogeneous systems and a simple injection process as envisioned for geologic carbon sequestration.

Acknowledgment

We thank two anonymous reviewers for helpful comments that allowed us to refine the presentation. Support for this work was provided by Chevron with project management and guidance from Scott Imbus (Chevron). Additional support was provided by the Assistant Secretary for Fossil Energy (DOE), Office of Coal and Power Systems, through the National Energy Technology Laboratory (NETL), and by Lawrence Berkeley National Laboratory under Department of Energy Contract No. DE-AC02-05CH11231.

References


   http://www.springerlink.com/content/e0pt67n28j264374/  


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