Typically, when a new subsurface flow and transport problem is first being considered, very simple models with a minimal number of parameters are used to get a rough idea of how the system will evolve. For a hydrogeologist considering the spreading of a contaminant plume in an aquifer, the aquifer thickness, porosity, and permeability might be enough to get started. If the plume is buoyant, aquifer dip comes into play. If regional groundwater flow is significant or there are nearby wells pumping, these features need to be included. Generally, the required parameters tend to be known from pre-existing studies, are parameters that people working in the field are familiar with, and represent features that are easy to explain to potential funding agencies, regulators, stakeholders, and the public.

The situation for geologic storage of carbon dioxide (CO2) in saline aquifers is quite different. It is certainly desirable to do preliminary modeling in advance of any field work since geologic storage of CO2 is a novel concept that few people have much experience with or intuition about. But the parameters that control CO2 plume behavior are a little more daunting to assemble and explain than those for a groundwater flow problem. Even the most basic question of how much volume a given mass of injected CO2 will occupy in the subsurface is non-trivial. However, with a number of simplifying assumptions, some preliminary estimates can be made, as described below.

To make efficient use of the subsurface storage volume available, CO2 density should be large, which means choosing a storage formation at depths below about 800 m, where pressure and temperature conditions are above the critical point of CO2 (P = 73.8 bars, T = 31°C). Then CO2 will exist primarily as a free-phase supercritical fluid, while some CO2 will dissolve into the aqueous phase.

A mass balance for CO2 may be written as

\[ M = \langle \phi S_g \rho_g \rangle V + \langle \phi S_l X_l \rho_l \rangle V \]  

where \( M \) is the total mass of CO2 injected, \( \phi \) is the porosity of the storage formation, \( S_g \) is the saturation of free-phase CO2 (that is, the fraction of pore space filled with free-phase CO2), \( S_l = 1 - S_g \) is the saturation of the aqueous phase (water plus dissolved salt plus dissolved CO2), \( \rho_g \) and \( \rho_l \) are densities of the CO2 and aqueous phases, respectively, \( X_l \) is the mass fraction of CO2 dissolved in the aqueous phase, and \( V \) is plume volume. Angle brackets represent a spatial average over the plume. The first term of Equation (1) represents the mass of free-phase CO2 and the second term the mass of dissolved CO2. Assuming that \( \phi, S, \rho, \) and \( X_l \) are not correlated enables the angle brackets to be dropped,
with the understanding that each variable represents the average value over the plume. Solving for $V$ yields

$$V = \frac{M}{\phi(S_g \rho_g + (1 - S_g)X_l \rho_l)}$$

(2)

To determine $V$, first we need a value for $\phi$, the average porosity of the storage formation, which is typically known, at least approximately, based on the geological setting.

Next, we need $\rho_g$, the density of the free-phase CO$_2$, at the pressure and temperature conditions of the storage formation. Often $(P, T)$ information is unknown for candidate sites, but assuming a hydrostatic pressure gradient and a geothermal temperature gradient provide a good first guess. In the absence of any site-specific information, $P = 1 + 0.1z$, with $P$ in bars and depth $z$ in meters, and $T = 15 + 0.025z$, which gives $T$ in degrees C, may be used. Armed with $(P,T)$ conditions, a standard CO$_2$ equation-of-state package (for example, http://lnx.lbl.gov/gaseos/gaseos.html) provides the density of free-phase CO$_2$, $\rho_g$, as illustrated in Figure 1. Values of $\rho_g$ for a range of conditions considered reasonable for geologic storage are shown in Table 1.

Next, we need $X_l$, the mass fraction of dissolved CO$_2$ in the aqueous-phase fluid. We approximate $X_l$ as the solubility of CO$_2$ in brine. That is, we assume that all dissolved CO$_2$ is in equilibrium with free-phase CO$_2$. With this assumption, $X_l$ depends only on pressure, temperature, and brine salinity, as illustrated in Table 1.

Next, we need $\rho_l$, the density of the aqueous phase, at the pressure, temperature, and salinity conditions of the storage formation. The aqueous-phase density $\rho_l$ depends weakly on $P$, $T$, and $X_l$ and varies more strongly with brine salinity, as illustrated in Table 1.

Finally, we need an estimate for CO$_2$ saturation, $S_g$. Recall that when CO$_2$ is injected into a saline aquifer, the brine is not simply pushed away from the well and replaced with CO$_2$. A two-phase flow region develops, with CO$_2$ bypassing some of the brine. The pore-scale details of interaction between the CO$_2$ phase and the aqueous phase are generally represented at the macro-scale by what are known as characteristic curves: capillary pressure and relative permeability as functions of phase saturation. The parameters and functional forms of the characteristic curves, along with the viscosity ratio of the CO$_2$ and brine, determine $S_g$ within the CO$_2$ plume. Basic arguments about molecular structure indicate that for saline aquifers, supercritical CO$_2$ is the non-wetting phase and brine is the wetting phase. Thus CO$_2$ is analogous to oil in oil/water two-phase systems, enabling us to tap into the extensive petroleum literature for information on characteristic curves. Two key parameters of the characteristic curves are the residual phase saturations: the saturations below which a phase is immobile. In practical terms, residual liquid saturation $S_{lr}$ determines how much water is bypassed as CO$_2$ invades the pore space, and residual gas saturation $S_{gr}$ determines how much CO$_2$ is trapped when water imbibes back into the pore space (Doughty et al., 2007). The value of $S_g$ to use in Equation (2) can best be determined by numerical simulation, but theoretically it should fall between $S_{gr}$ and (1
However, it is unlikely that these parameters will be known at the early stage of an investigation. To make matters worse, there is no single value of \( S_{gr} \) that can be specified for the CO\(_2\) plume as a whole – \( S_{gr} \) depends on the saturation history of each location within the plume. For moderate to high permeability saline aquifers that are typical CO\(_2\) storage targets, literature values of \( S_{lr} \) are generally less than 0.3 and \( S_{gr} \) is generally less than 0.4. Thus, it is reasonable to expect \( S_g \) to be in the range 0.4–0.7. A good first guess is \( S_g = 0.5 \).

Substituting estimated values of \( \phi, S_g, \rho_g, \rho_l, \) and \( X_l \) into Equation (2) provides an estimate of \( V \), the volume that a mass \( M \) of injected CO\(_2\) occupies in the subsurface. Moreover, because \( S_g \) and \( S_l \) are comparable, \( \rho_g \) and \( \rho_l \) differ by less than a factor of two, and \( X_l \) is just a few percent, we find that the fraction of CO\(_2\) in the supercritical phase is much larger than the fraction that is dissolved.

The next natural question is when are these estimates of \( V \) and phase partitioning applicable? For early-stage investigations, we are likely most interested in the time period during and shortly after CO\(_2\) injection. For this time frame, we can safely neglect slow processes such as mineral reactions (Xu et al., 2004) and aqueous-phase convection (Ennis-King and Paterson, 2005). Then the only parameter in Equation (2) likely to change significantly as the CO\(_2\) plume evolves is \( S_{gr} \).

The variation of \( S_{gr} \) is intimately connected with the functional form of the characteristic curves (Doughty, 2007). In the petroleum industry, it is well accepted that characteristic curves are hysteretic. That is, the drainage process (non-wetting-phase CO\(_2\) replacing wetting-phase brine) is not simply reversed in the imbibition process (wetting-phase brine replacing non-wetting-phase CO\(_2\)). The key parameter of the characteristic curves for trapping CO\(_2\), the residual gas saturation \( S_{gr} \), is considered to be zero during drainage, and to be non-zero and history-dependent during imbibition (Land, 1968).

As shown in the top frame of Figure 2, while CO\(_2\) injection is occurring, the CO\(_2\) plume is growing everywhere, so drainage is the dominant process and \( S_{gr} = 0 \). To calculate \( V \) at the end of the CO\(_2\) injection period, the Buckley-Leverett (1942) analytical solution for a radial-geometry plume may be used to approximate \( S_g \). For viscosity ratios in the range shown in Table 1, the simple relation \( S_g = 0.5(1 - S_{li}) \) provides a reasonable fit to the Buckley-Leverett solution employing the commonly-used Corey (1954) relative permeability functions.

Once injection ceases, and the plume moves upward and updip due to buoyancy forces, different locations experience drainage and imbibition at different times, as illustrated in the bottom frame of Figure 2. At the leading edge of the plume, drainage continues with \( S_{gr} = 0 \). At the trailing edge, imbibition occurs with \( S_{gr} > 0 \). Thus the plume is more mobile at the leading edge than at the trailing edge, so it stretches out as it moves, which lowers \( S_g \). When saturation everywhere drops to \( S_{gr} \), the entire plume becomes immobilized, a phenomenon known as capillary trapping. To estimate \( V \) at this time, the maximum value of \( S_{gr} \), a material property denoted \( S_{grmax} \), provides an upper limit for \( S_g \). The petroleum literature (Holtz, 2005) suggests that \( S_{grmax} \) decreases as porosity increases,
and typically ranges between 0.2 and 0.4 for moderate to high permeability saline aquifers.

Note from Equation (1) that as $S_g$ decreases, the fraction of injected CO$_2$ that is dissolved increases. This leads to an interesting trade-off between capillary trapping and dissolution. For smaller values of $S_{gr_{max}}$, capillary trapping is less effective in that the plume moves farther and spreads more before becoming immobilized, but this exposes the CO$_2$ plume to more native brine, enabling more dissolution (Doughty and Myer, 2008).

The simple methodology described here for estimating plume volume can provide a useful starting point for subsequent numerical modeling, which is necessary to capture the complex interplay between phase interactions, buoyancy flow, and geologic heterogeneity that occurs as CO$_2$ is injected into a saline aquifer.

Acknowledgments

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References


Table 1. Properties of free-phase CO₂ and CO₂-saturated brine for a range of conditions considered reasonable for geologic storage of CO₂ in saline aquifers. Pressure *P* (bars) and temperature *T* (℃) determined using hydrostatic and geothermal gradients, respectively. Density *ρ* (kg/m³), viscosity *μ* (Pa·sec), and dissolved CO₂ mass fraction *Xₗ* calculated with the TOUGH2 numerical simulator (Pruess et al., 1999) using the ECO2N equation of state package (Pruess, 2005; Spycher and Pruess, 2005).

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>CO₂ 0 mg/L Brine</th>
<th>50 mg/L Brine</th>
<th>100 mg/L Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ρₗ µₗ Xₗ</td>
<td>ρₗ µₗ Xₗ</td>
<td>ρₗ µₗ Xₗ</td>
</tr>
<tr>
<td>z=1000</td>
<td>P=101 T=40</td>
<td>635 0.49E-4 0.052</td>
<td>1037 0.72E-3 0.042</td>
</tr>
<tr>
<td>z=1500</td>
<td>P=151 T=52.5</td>
<td>681 0.55E-4 0.052</td>
<td>1034 0.58E-3 0.041</td>
</tr>
<tr>
<td>z=2000</td>
<td>P=201 T=65</td>
<td>694 0.57E-4 0.052</td>
<td>1030 0.48E-3 0.041</td>
</tr>
<tr>
<td>z=2500</td>
<td>P=251 T=77.5</td>
<td>701 0.58E-4 0.053</td>
<td>1025 0.41E-3 0.042</td>
</tr>
</tbody>
</table>
Figure 1. Density of CO$_2$ as a function of pressure $P$ and temperature $T$. The black line shows the saturation line, which separates liquid and gaseous phases. Beyond the critical point, CO$_2$ exists as a supercritical phase. Assuming functional forms for the dependence of $P$ and $T$ on depth enables CO$_2$ density at various depths to be estimated, as shown by the dashed line.
Figure 2. Schematic of CO₂ injection period (top), in which drainage occurs at all plume boundaries (orange), and post-injection period (bottom), in which drainage occurs at the leading edge of the plume on the right (orange) and imbibition occurs at the trailing edge of the plume on the left (green) as the plume migrates, e.g. by buoyancy forces.