Abstract

We incorporate CO\textsubscript{2} dissolution due to convective mixing into a sharp-interface mathematical model for the post-injection migration of a plume of CO\textsubscript{2} in a saline aquifer. The model captures CO\textsubscript{2} migration due to groundwater flow and aquifer slope, as well as residual trapping and dissolution. We also account for the tongue shape of the plume at the end of the injection period. We solve the model numerically and identify three regimes in CO\textsubscript{2} migration with dissolution, based on how quickly the brine beneath the plume saturates with dissolved CO\textsubscript{2}. When the brine saturates slowly relative to plume migration, dissolution is controlled by the dimensionless dissolution rate. When the brine saturates “instantaneously” relative to plume migration, dissolution is instead controlled by the solubility of CO\textsubscript{2} in brine. We show that dissolution can lead to a several-fold increase in storage efficiency. In a companion paper, we study migration and pressure limitations on storage capacity [Szulczewski et al., GHGT-10, Paper 917 (2010)].

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Carbon capture and storage in geological formations is widely regarded as a promising tool for reducing atmospheric CO\textsubscript{2} emissions, and deep saline aquifers are an attractive target for long-term CO\textsubscript{2} storage [1]. Deep saline aquifers are permeable layers of, for example, limestone or cemented sand that are saturated with brine and bounded above and below by layers of much less permeable rock such as clay or anhydrite. They are located roughly 1 to 3 km underground, are horizontal or weakly sloped, and many have a slow natural groundwater through-flow. While the properties of CO\textsubscript{2} at aquifer conditions vary with temperature and pressure, the CO\textsubscript{2} will always be less dense and less viscous than the groundwater, making it buoyant and mobile in the aquifer. After injection, the CO\textsubscript{2} plume will spread upward against the top boundary of the aquifer while migrating due to a combination of groundwater flow and aquifer slope. Several trapping mechanisms act to prevent the migration of buoyant CO\textsubscript{2} back to the surface—these include (1) structural or stratigraphic trapping: the mobile CO\textsubscript{2} is kept underground by a relatively impermeable caprock [2]; (2) capillary trapping: disconnection of the bulk CO\textsubscript{2} plume into immobile (trapped) blobs [3;4]; (3) solubility trapping: dissolution of the CO\textsubscript{2} into the ambient brine [5;6]; and (4) mineral trapping: geochemical binding of CO\textsubscript{2} to the aquifer rock due to mineral precipitation [2].
In a previous study [7], we developed a complete solution to a hyperbolic gravity-current model for CO₂ migration in a deep saline aquifer due to groundwater flow and aquifer slope, subject to residual trapping, and including the tongued end-of-injection plume shape. We showed that the migration behavior depends strongly on three parameters: the importance of aquifer slope relative to groundwater flow, the mobility ratio, and the capillary trapping number. We also explored the impact of these parameters on the overall storage efficiency, a measure of the fraction of the aquifer pore space that can be used to store CO₂, and we showed that the competition between groundwater flow and aquifer slope leads to nontrivial results in terms of the storage efficiency. Here, we incorporate CO₂ dissolution into this model and study the interaction of dissolution with migration and residual trapping. We do not include mineral trapping because it occurs over very long timescales, and is unlikely to influence plume migration.

It is well-known that CO₂ is weakly soluble in groundwater, and therefore that both residual CO₂ and CO₂ from the mobile plume will dissolve slowly into the nearby groundwater as the plume migrates. Because the density of groundwater increases with dissolved CO₂ content, the boundary layer of CO₂-saturated groundwater near the mobile plume is unstable. This unstable density stratification eventually results in a Rayleigh–Bénard-type flow referred to as convective mixing, where fingers of “heavy”, CO₂-saturated brine sink away from the plume as fingers of “fresh” groundwater rise upward. This process has been studied in various contexts [8–10]. The implications of convective mixing for the geological storage of CO₂ were first pointed out by [11] and discussed by [12]. Several studies have since been made of the onset of the instability for a stationary layer of CO₂ overlying a layer of water [5,6;13;14]. In all cases, the onset time for convective mixing has been shown to be relatively short compared to timescales of interest in geological CO₂ storage. It has also been shown that convective mixing dramatically increases the rate of CO₂ dissolution compared to diffusive transport alone [5;15;16], and that the time-averaged rate of CO₂ dissolution due to convective mixing is approximately constant. We take advantage of these results here.

We are interested in large CO₂ storage projects, and therefore in the evolution of the CO₂ plume at the geologic-basin scale as proposed by [17]—a schematic of the basin scale geologic setting is shown in Figure 1.

![Figure 1](image_url)

**Figure 1.** Geological storage of CO₂ in a saline aquifer at the basin scale: (a) From a bird’s eye view, the plumes from individual wells merge together as CO₂ (dark gray) is injected via a “line-drive” array of wells (black dots) [17], and we model the single resulting plume as symmetric in the y direction; (b) in cross-section, the buoyant plume of CO₂ (dark gray) migrates after the end of injection due to a combination of aquifer slope and groundwater flow (arrows), dissolving due to convective mixing and leaving behind residual CO₂ (light gray). Typical horizontal and vertical scales are indicated—note that the vertical scale of the aquifer is greatly exaggerated.
We take the aquifer to be homogeneous, with an arbitrary tilt relative to the horizontal and a net groundwater through-flow to the right. We take the fluids to be incompressible and Newtonian, with constant and uniform properties within the aquifer. We employ a sharp-interface approximation, neglecting saturation gradients as well as the capillary pressure. We further assume vertical equilibrium, neglecting the vertical component of the fluid velocity relative to the horizontal one. We divide the domain into three regions of uniform fluid saturation with sharp interfaces corresponding to saturation discontinuities, as illustrated in Figure 2. Region 1 is the plume of mobile CO2, containing free-phase CO2 and a saturation $S_{wc}$ of connate brine; Region 2 is the region from which the plume has receded, containing mobile brine and a saturation $S_{gr}$ of trapped, free-phase CO2; and Region 3 contains mobile brine with some dissolved CO2, and no free-phase CO2.

![Figure 2](image.png)

Figure 2. A schematic of the plume during post-injection migration, as the mobile CO2 (dark gray) is pushed to the right by a combination of groundwater flow and aquifer slope, leaving trapped CO2 (light gray) in its wake. CO2 dissolves from the plume due to convective mixing, as indicated by the fingers of “heavy” brine (blue) falling away from the plume. We divide the domain into three regions of uniform CO2 and groundwater saturation, separated by sharp interfaces corresponding to saturation discontinuities. Region 1 (dark gray) contains mobile CO2 and a saturation $S_{wc}$ of connate brine; Region 2 (light gray) contains mobile brine and a saturation $S_{gr}$ of residual CO2; Region 3 (white, blue) contains mobile brine with some dissolved CO2. The aquifer has a total thickness $H$, and the thickness of Region $i$, $i = 1, 2, 3$, is denoted $h_i(x, t)$. Groundwater flows naturally through the aquifer from left to right with velocity $U_n$; the aquifer has permeability $k$ and porosity $\phi$, as well as an arbitrary angle of tilt $\theta$ measured counterclockwise from the direction of gravity.

The complete derivation of the model and the details of the underlying assumptions are given elsewhere [18–21]—the resulting equations in dimensionless form are

$$\tilde{R} \frac{\partial \eta}{\partial \tau} + N_f \frac{\partial f}{\partial \xi} + N_s \frac{\partial}{\partial \xi} [(1 - f) \eta] - N_s \frac{\partial}{\partial \xi} [(1 - f) \eta \frac{\partial \eta}{\partial \xi}] = -\tilde{R} N_d, \quad (1)$$

and

$$\tilde{R} \frac{\partial \eta_d}{\partial \tau} + N_f \frac{\partial f_d}{\partial \xi} - N_s \frac{\partial}{\partial \xi} [(1 - f_d) \eta] + N_s \frac{\partial}{\partial \xi} [(1 - f_d) \eta \frac{\partial \eta}{\partial \xi}] = \tilde{R} N_d / \Gamma_d, \quad (2)$$

where $\eta = h_1/H$ is the scaled thickness of the CO2 plume, $\eta_d = h_d/H$ is the scaled thickness of the “curtain” of brine with dissolved CO2, $\tau = t/T_c$, and $\xi = x/L_c$. We choose the characteristic length $L_c$ to be the length of a rectangle of aquifer containing a volume $Q_T/2$ of CO2, $L_c = Q_T/2(1 - S_{wc})\phi H$, where $Q_T$ is the volume rate of CO2 injection during the injection period, per unit length of the well array, and $T_c$ is the duration of the injection period such that $Q_T$ is the total volume of CO2 injected. The characteristic time $T_c$ is arbitrary. The discontinuous coefficient $\tilde{R}$ captures capillary trapping by changing value depending on whether the CO2-brine interface is locally in drainage or imbibition.
\[ \tilde{R} = \begin{cases} 
1 & \text{if } \frac{\partial \eta}{\partial \tau} > -N_d, \\
1 - \Gamma & \text{otherwise}, 
\end{cases} \]

where \( \Gamma = \frac{S_{dc}}{1 - S_{wc}} \) is the capillary trapping number, which measures the fraction of mobile CO\(_2\) that is left behind due to capillary trapping as the plume migrates. The fractional flow functions \( f \) and \( f_d \) are given by

\[ f(\eta) = \frac{M \eta}{(M-1)\eta + 1}, \quad f_d(\eta_d, \eta) = \frac{\eta_d}{(M-1)\eta + 1} \]

where \( M = \lambda_i / \lambda_3 \) is the mobility ratio and \( \lambda_i \) is the mobility of the fluid in Region \( i \). The constants \( N_f, N_s, \) and \( N_g \) measure the relative importance of groundwater flow, up-slope migration, and buoyant spreading, respectively, and are given by

\[ N_f = \frac{T_i Q}{T_i Q_s / 2}, \quad N_s = \frac{T_c \kappa \sin \theta}{L_c}, \quad N_g = \frac{T_c \kappa \sin \theta H}{L_c} \]

where \( \kappa = \Delta \rho g \kappa_3 / (1 - S_{wc}) \phi \) is the characteristic buoyancy velocity of CO\(_2\) in this system, \( \Delta \rho \) is the density difference between mobile CO\(_2\) and brine, and \( Q \) is the total volume rate of fluid flow through the formation from left to right, per unit length of the well array. The parameter \( N_d \) measures the rate of dissolution, and is given by

\[ N_d = \begin{cases} 
CT_d \kappa_d \frac{T_c}{H} & \text{if } \eta > 0 \text{ and } \eta_d < 1 - \eta, \\
0 & \text{otherwise}, 
\end{cases} \]

where \( \Gamma_d = c_s / \left(1 - S_{wc}\right) \), \( c_s \) is the volume fraction of CO\(_2\) dissolved in brine at saturation, and \( C \approx 0.017 \) is a dimensionless constant [16]. \( \kappa_d = \Delta \rho_d g \kappa_3 / \phi \) is the characteristic buoyancy velocity of brine saturated with dissolved CO\(_2\) in this system and \( \Delta \rho_d \) is the density difference between brine and brine saturated with dissolved CO\(_2\). Note that we assume that CO\(_2\) dissolves at a constant rate until the “curtain” of brine containing dissolved CO\(_2\) reaches the bottom of the aquifer (i.e., until the brine underneath the plume saturates with dissolved CO\(_2\)), at which point we assume that dissolution stops abruptly.

Equations 1 and 2 are coupled, nonlinear conservation laws for migration of the mobile CO\(_2\) and migration of the “curtain” of brine containing dissolved CO\(_2\), respectively. They are coupled by the fluid flow, and also by dissolution. We need not solve Equation 2 when there is no dissolution, or when the brine underneath the plume saturates with dissolved CO\(_2\) slowly compared to the migration of the plume. Otherwise, we must solve both equations simultaneously. Here we do so numerically for several values of the dissolution rate \( N_d \) for fixed values of \( M, \Gamma, N_f, N_s, N_g, \) and \( \Gamma_d \)—the results are illustrated in Figure 3.

We identify three regimes in CO\(_2\) migration with dissolution, as illustrated qualitatively in Figure 3: (1) slow saturation: the brine beneath the plume saturates with dissolved CO\(_2\) slowly relative to plume migration; (2) fast saturation: at least some of the brine beneath the plume becomes saturated with dissolved CO\(_2\) as the plume migrates; and (3) instantaneous saturation: all of the brine beneath the plume saturates very quickly (“instantaneously”) relative to plume migration. To illustrate qualitatively the transition from the slow saturation regime to the instantaneous saturation regime, we fix \( M, \Gamma, N_f, N_s, N_g, \) and \( \Gamma_d \), and solve Equations (1) and (2) numerically for \( N_d \) ranging from \( 10^{-5} \) to 100. The results are presented in Figure 4. We are also able to solve Equations (1) and (2) semi-analytically in some cases in the slow- and instantaneous-saturation regimes. We include a semi-analytical solution to Equation (1) in the slow-saturation regime in Figure 4—these rest of these semi-analytical results are presented elsewhere [20].
Figure 3. Numerical solutions to Equations 1 and 2 for the shape of the plume during post-injection migration at $\tau = 2.25$ for $M = 5$, $\Gamma = 0.3$, $N_f = 1$, $N_s = 0.5$, $N_g = 0$, $\Gamma_d = 0.1$, and $N_d = 0, 0.02, 0.08$, and 2. As in Figure 2, mobile CO$_2$ is shown in dark gray, residual CO$_2$ is shown in light gray, and the “curtain” of brine with dissolved CO$_2$ is shown in blue. Qualitatively, we identify three regimes: (b) slow saturation, where the dissolution front does not interact with the bottom of the formation and the entire plume dissolves as it migrates; (c) fast saturation, where the brine below the plume becomes saturated at some point in space so that the leading portion of the plume dissolves but the trailing portion does not; and (d) “instantaneous” saturation, where all of the brine below the plume is saturated with dissolved CO$_2$ and the plume subsequently dissolves only at the leading edge.

Figure 4. The storage efficiency as a function of the dimensionless rate of dissolution, $N_d$ for $M = 5$, $\Gamma = 0.3$, $N_f = 1$, $N_s = 0.5$, $N_g = 0$, and $\Gamma_d = 0.1$ from numerical solutions to Equations (1) and (2) (black dots) and a semi-analytical solution to Equation (1) in the slow-saturation limit (solid black line). The numerical solutions depart from the semi-analytical curve when $N_d$ is large enough that some of the brine beneath the plume saturates with dissolved CO$_2$ as the plume migrates. The three saturation regimes are indicated, separated by dotted gray lines. The storage efficiency increases monotonically from the no-dissolution value as the rate of dissolution increases, reaching a plateau when $N_d$ is sufficiently large that the brine underneath the plume saturates “instantaneously”. In this limit, dissolution leads to a six-fold increase in storage efficiency for this particular case.
We have presented a model for CO₂ migration due to groundwater flow and aquifer slope, and subject to capillary trapping and dissolution due to convective mixing. We have identified three regimes in migration with dissolution, depending on how quickly the brine beneath the plume saturates with dissolved CO₂ relative to plume migration. Note that while the model characterizes dissolution with two parameters, dissolution in the slow- and instantaneous-saturation regimes depends only on one of the two parameters. In the slow-saturation regime, dissolution behavior depends only on \( N_d - \Gamma_d \) is unimportant because the brine beneath the plume does not saturate. In the instantaneous-saturation limit, dissolution depends only on \( \Gamma_d - N_d \) is unimportant because the brine beneath the plume is completely saturated. Finally, we have shown that dissolution can lead to a several-fold increase in storage efficiency over the value for capillary trapping alone. In a companion paper, we study migration and pressure limitations on storage capacity [Szulczewski et al., GHGT-10, Paper 917 (2010)].

References
