Migration and Trapping of CO₂ in Saline Aquifers

by

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Abstract

Mitigation of climate change requires a reduction in atmospheric carbon dioxide (CO$_2$) emissions. One promising tool for achieving this is the large-scale injection of CO$_2$ into deep saline aquifers. After injection, upward leakage of the CO$_2$ is a primary concern because it will be buoyant relative to the ambient groundwater and, as a result, will rise toward the top of the aquifer and may migrate laterally away from the injection site. To assess leakage risks and estimate aquifer capacity requires an accurate understanding of the subsurface migration and trapping of the buoyant CO$_2$; however, many aspects of the fundamental physics of CO$_2$ migration and trapping are not fully understood, and traditional reservoir-simulation tools are currently unable to resolve the impact of small-scale trapping processes on these large-scale fluid flows.

In this Thesis, we develop a simple gravity-current model for the post-injection migration and trapping of a buoyant plume of CO$_2$ in a confined, sloping saline aquifer with a natural groundwater through-flow. We include both residual trapping, where small blobs of CO$_2$ are immobilized by capillarity along the trailing edge of the plume, and solubility trapping driven by convective dissolution, where CO$_2$ dissolves into the groundwater and sinks downward in dense, CO$_2$-rich fingers. Although idealized, this model offers physical insight into the processes controlling CO$_2$ migration and trapping, and is not limited by computational resources. We derive solutions to the model in several limiting cases, and we use these solutions to study the interplay between slope and groundwater flow, and the competition between residual and solubility trapping. We validate the model against laboratory analog experiments, finding good agreement between the experimental results and the predictions of the model. We then use the experiments to study the small-scale dynamics of the convective-dissolution instability: the formation, descent, and coarsening of the fingers. Finally, we use the model to study the migration and trapping of CO$_2$ in the Mt. Simon Sandstone, a large deep saline aquifer in the Midwestern United States that is considered to be a promising candidate for geological CO$_2$ storage.

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Contents

1 Introduction ........................................ 17
  1.1 Migration and trapping of CO$_2$ in saline aquifers .... 18
  1.2 Residual trapping under slope and groundwater flow ... 20
  1.3 Residual and solubility trapping ...................... 21
  1.4 Laboratory experiments .............................. 23
  1.5 Application, discussion & conclusions ................ 24

2 Residual trapping under slope and groundwater flow ....... 25
  2.1 Model for CO$_2$ injection and migration ............ 28
    2.1.1 Scaling ....................................... 34
    2.1.2 The injection period .......................... 36
    2.1.3 Post-injection migration .................... 36
  2.2 Injection and migration with residual trapping .......... 38
    2.2.1 The injection period .......................... 39
    2.2.2 Post-injection migration .................... 41
    2.2.3 Flow with weak slope ......................... 43
    2.2.4 Negative slope with weak flow ............... 53
    2.2.5 Positive slope with weak flow ............... 55
  2.3 Plume footprint and storage efficiency ................ 56

3 Residual and solubility trapping ........................ 61
  3.1 Model for CO$_2$ injection and migration ............ 63
  3.2 Model for solubility trapping due to convective dissolution .... 65
List of Figures

1-1 After injection into a saline aquifer, the buoyant CO₂ will migrate due to a combination of aquifer slope and groundwater flow. As the plume of CO₂ migrates, it will shrink due to residual trapping, where blobs of CO₂ are immobilized by capillarity at the trailing edge of the plume, and solubility trapping, where CO₂ dissolves into the groundwater and falls away from the plume in dense, CO₂-rich fingers.

1-2 The model for CO₂ migration and residual trapping is a nonlinear partial differential equation, and we solve it analytically in its hyperbolic limit (neglecting buoyant spreading) with the method of characteristics. Here, we illustrate a typical solution.

1-3 We incorporate solubility trapping into the model for CO₂ migration, and develop semi-analytical solutions to the new model in two limiting cases. Here, we illustrate a typical solution in the slow-saturation limit.

1-4 In order to conduct experiments with and without convective dissolution, we use two different pairs of analog fluids. We illustrate this here with snapshots of two gravity currents migrating up-slope in a sloping aquifer (a Hele-Shaw cell with no beads for illustration).

2-1 Residual trapping refers to the isolation and immobilization of small, residual blobs of CO₂ at the trailing edge of the migrating plume. It is an ideal mechanism for the geological storage of CO₂ because the residual gas is immobile and distributed over a large area.
Large-scale geological storage of CO$_2$ requires injection at the scale of a geologic basin. Here, we consider injection through a linear or “line-drive” array of wells. We assume line-symmetry along the well array and model the planar cross-section of the resulting plume of CO$_2$.

After injection stops, the injected CO$_2$ will migrate due to a combination of groundwater flow and aquifer slope, leaving residual CO$_2$ in its wake. To model this system, we employ a sharp-interface approximation, dividing the domain into three regions of uniform CO$_2$ and groundwater saturation separated by sharp interfaces.

CO$_2$ migration and trapping are dominated by advective effects, and are little affected by even large values of $N_g$ compared to $N_f$ or $N_s$. We illustrate this qualitatively here with the shape of the plume at a fixed time for several values of $N_g$ from numerical solutions to the model.

During injection, the plume spreads symmetrically outward from the injection well in a characteristic tongued shape. Here, we show the evolution of the plume in characteristic space and the shape of the plume at several times during injection.

The flux function for flow only is monotonic, whereas the flux function for slope only has a local extremum. The flux function for combined flow and slope may or may not have a local extremum, depending on the values of $M$, $N_f$ and $N_g$.

We identify three distinct intervals in CO$_2$ migration with flow and slope. We illustrate them here via the shape of the flux function and cartoons of the resulting plume motion.

A shock forms when a portion of a front is compressed into a discontinuity.

A peak forms when the left and right fronts touch, i.e., when all of the CO$_2$ between is trapped.

In order to determine when and where collisions occur, we examine the positions of four key points: the left-most and right-most points on each front.
2-11 We divide the flow-with-weak-slope interval into five cases based on the order in which collisions occur.

2-12 Here we illustrate post-injection migration for case 1 of the flow-with-weak-slope interval. We show the evolution of the plume in characteristic space and the shape of the plume at several times before all of the CO$_2$ is trapped.

2-13 Here we illustrate post-injection migration for case 2 of the flow-with-weak-slope interval. We show the evolution of the plume in characteristic space and the shape of the plume at several times before all of the CO$_2$ is trapped.

2-14 Here we illustrate post-injection migration for case 3 of the flow-with-weak-slope interval. We show the evolution of the plume in characteristic space and the shape of the plume at several times before all of the CO$_2$ is trapped.

2-15 Here we illustrate post-injection migration for case 4 of the flow-with-weak-slope interval. We show the evolution of the plume in characteristic space and the shape of the plume at several times before all of the CO$_2$ is trapped.

2-16 Here we illustrate one example of post-injection migration in the negative-slope-with-weak-flow interval. We show the evolution of the plume in characteristic space and the shape of the plume at several times before all of the CO$_2$ is trapped.

2-17 Here we illustrate one example of post-injection migration in the positive-slope-with-weak-flow interval. We show the evolution of the plume in characteristic space and the shape of the plume at several times before all of the CO$_2$ is trapped.

2-18 The storage efficiency, $\varepsilon$, increases with $\Gamma$, decreases with $\mathcal{M}$, and is a nonmonotonic function of $N_s/N_f$. 
3-1 After injection stops, the injected CO$_2$ will migrate due to a combination of groundwater flow and aquifer slope, leaving residual CO$_2$ in its wake while dense fingers of CO$_2$-rich groundwater fall downward. To model this system, we again employ a sharp-interface approximation, dividing the domain into three regions of uniform CO$_2$ and groundwater saturation separated by sharp interfaces.

3-2 We assume that total fluid volume is conserved as CO$_2$ dissolves into groundwater.

3-3 We assume that interface displacements due to solubility trapping do not contribute to residual trapping, effectively decoupling these two trapping processes locally.

3-4 The rate at which the water beneath the plume saturates with dissolved CO$_2$ depends on the speed of migration, the length of the plume, the rate of solubility trapping, and the amount of dissolved CO$_2$ the water can hold. We identify two limits: when the water saturates *slowly* relative to plume migration, solubility trapping is not limited by the amount of water beneath the plume, and when the water saturates very quickly (*instantaneously*) relative to plume migration, the water beneath the plume is completely saturated with dissolved CO$_2$ and only the leading edge of the plume dissolves as it migrates.

3-5 Here we illustrate post-injection migration in the slow-saturation limit for case 2 of the flow-with-weak-slope interval. We show the evolution of the plume in characteristic space and the shape of the plume at several times before all of the CO$_2$ is trapped.

3-6 In the instantaneous-saturation limit, the plume contracts at $\tau = 1^+$ as the water beneath the end-of-injection plume shape saturates instantaneously with dissolved CO$_2$. We therefore use a modified initial shape for post-injection migration in this limit.

64

66

70

80

87

90
3-7 Here we illustrate post-injection migration in the instantaneous-saturation limit for case 2 of the flow-with-weak-slope interval. We show the evolution of the plume in characteristic space and the shape of the plume at several times before all of the CO$_2$ is trapped.

3-8 Both the storage efficiency, $\varepsilon$, and the fraction of CO$_2$ trapped by solubility trapping, $\Phi_d$, increase monotonically with the dimensionless rate of solubility trapping, $N_d/N_f$, until both quantities plateau in the limit where the water beneath the plume is completely saturated with dissolved CO$_2$.

3-9 Solubility trapping can lead to a several-fold increase in storage efficiency even when the fraction of CO$_2$ trapped by solubility trapping is small.

3-10 Solubility trapping reduces the speed at which the nose of the plume advances, as shown here in the slow-saturation regime.

3-11 Solubility trapping is increasingly important as $N_d$ increases, but residual trapping plays an important role even for large $N_d$. We illustrate this here via the time-evolution of the volume fractions of mobile, residual, and dissolved CO$_2$.

4-1 Propylene glycol (PG) is denser and more viscous than water, but a mixture of the two is denser than either component for water mass fractions less than about 0.54, and this drives convective dissolution. Here we show the density and viscosity of PG as a function of water mass fraction, and a snapshot from an experiment where a layer of water dissolves into PG via convective dissolution in a Hele-Shaw cell.

4-2 In order to conduct experiments with and without convective dissolution, we use two different pairs of analog fluids. We illustrate this here with snapshots of two gravity currents migrating up-dip in a sloping aquifer (a Hele-Shaw cell with no beads for illustration).
4-3 Without trapping, a buoyant gravity current will migrate indefinitely. We illustrate this here with snapshots of an experiment where a buoyant plume of water migrates up-dip in a sloping aquifer (a quasi-two-dimensional flow cell packed with glass beads). The ambient fluid is a denser and more viscous mixture of glycerol and water.

4-4 The leading edge of the gravity current predicted by the model is extremely long and thin because of the high mobility ratio. In the experiments, this tongue is truncated as the plume thickness approaches the bead size.

4-5 The nose position predicted by the model for a gravity current without convective dissolution agrees well with that measured in the experiments across a wide range of slopes.

4-6 Convective dissolution will arrest the migration of a buoyant gravity current. The experimental system here is identical to that in Figure 4-3, except that the ambient fluid is now propylene glycol (light gray). The buoyant and ambient fluids are completely miscible, and mix via convective dissolution, which dissolves the buoyant fluid at a rate comparable to the rate of up-slope migration. Convective dissolution occurs here because, as with CO₂ and water, the mixture of the two fluids is denser than either individual component. We also include the solution to the model (red line).

4-7 The nose position predicted by the model for a gravity current with convective dissolution agrees well with that measured in the experiments across a wide range of slopes.

4-8 We propose a simple model for the growth of the fingering front beneath the plume, parametrized by a constant finger velocity and a constant onset time. We find that the model successfully captures the macroscopic evolution of the fingering front in the experiment, as illustrated here where we overlay the fingering front from the model (cyan line) onto several snapshots of the experiment.
4-9 The fingering pattern coarsens with the convective time because the fingers grow and merge as they fall. Here, we plot the spatial frequency of the fingering pattern along the fingering front as a function of the convective time from 25 snapshots over the duration of an experiment. Although the frequency data (grey circles) is noisy, the pattern clearly coarsens by about a factor of 3 over the course of the experiment, as highlighted by a five-point moving average of the data (black line)...

5-1 Solubility trapping is very effective for small slopes, whereas residual trapping is most effective for large slopes. The combination of the two traps all of the CO₂ very effectively over a large range of slopes. We illustrate this here in the context of CO₂ migration and trapping in the Mt. Simon Sandstone, a large saline aquifer in the Midwestern United States.
Chapter 1

Introduction

Mitigation of climate change requires a reduction in atmospheric carbon dioxide (CO₂) emissions; however, electric power generation is a primary source of CO₂ emissions, and demand for electric power is expected to rise steadily for the foreseeable future (e.g., Hoffert et al., 2002). One promising tool for reducing CO₂ emissions during the global transition to a low-carbon energy infrastructure is the large-scale injection of CO₂ underground into deep saline aquifers (e.g., Bachu et al., 1994; Lackner, 2003; Pacala and Socolow, 2004; Orr Jr., 2004; IPCC, 2005; Schrag, 2007; Orr Jr., 2009).

After injection, upward leakage of the CO₂ is a primary concern because it will be buoyant relative to the ambient groundwater and, as a result, will rise toward the top of the aquifer and may migrate laterally away from the injection site. To evaluate injection scenarios, estimate aquifer capacity, and assess leakage risks requires an accurate understanding of the physical mechanisms that drive the post-injection migration of the buoyant CO₂, as well as those that trap the CO₂ securely in the subsurface. At present, these mechanisms are not well understood.

In this Thesis, we present a theoretical model for the migration and trapping of a plume of buoyant CO₂ in a saline aquifer. We develop analytical and semi-analytical solutions to the model in several limiting cases, and we use these solutions to gain insight into the physics of CO₂ migration and trapping. We then validate the model against laboratory experiments in a simplified analog system. Finally, we use the model to study the migration and trapping of CO₂ in the Mt. Simon Sandstone, a
large deep saline aquifer in the Midwestern United States that is considered to be a promising candidate for geological CO$_2$ storage.

1.1 Migration and trapping of CO$_2$ in saline aquifers

Deep saline aquifers are thin layers of permeable rock such as limestone or cemented sand located roughly 1 to 3 km underground. They are saturated with salty groundwater and bounded above by a caprock, which is a layer of much less permeable rock such as clay or anhydrite. Saline aquifers are often weakly sloped and may have a natural groundwater through-flow.

At typical aquifer conditions, the injected CO$_2$ will be less dense and much less viscous than the ambient groundwater. Trapping of the buoyant CO$_2$ is essential in order to minimize the risk that it will leak upward into shallower layers through a fracture or an abandoned well, or via the activation of a fault. Physical mechanisms that trap the CO$_2$ include structural trapping, where the plume of free-phase CO$_2$ is contained beneath a domed caprock; residual trapping, where small blobs of free-phase CO$_2$ are immobilized by capillarity as the CO$_2$ plume migrates; and solubility trapping, where CO$_2$ dissolves into the groundwater. Dissolved CO$_2$ is considered trapped because it is no longer buoyant.

Structural trapping relies on injecting the CO$_2$ into an anticlinal fold where the buoyant spreading and lateral migration of the CO$_2$ are obstructed by the domed caprock. The CO$_2$ remains mobile and buoyant, so structural trapping is heavily dependent on the integrity of the caprock. In contrast, residual trapping rapidly immobilizes the CO$_2$ as it migrates (Kumar et al., 2005; Juanes et al., 2006), but is most effective when the plume of CO$_2$ is allowed to migrate over large lateral distances (Hesse et al., 2008; Juanes et al., 2010). Solubility trapping is driven by a fluid mechanical instability where dissolved CO$_2$ is carried away from the buoyant plume in dense fingers of CO$_2$-rich groundwater (Weir et al., 1996; Lindeberg and Wessel-Berg, 1997; Ennis-King et al., 2005; Riaz et al., 2006). This process of convective dissolution rapidly traps the CO$_2$, and will occur for both stationary and migrating
plumes of CO$_2$.

Here, we focus on CO$_2$ injection and migration into an aquifer that lacks a structural trap (i.e., into a synclinal fold). Once injected, the CO$_2$ will rise and spread against the caprock in a long, thin plume while migrating laterally up-slope, or with the natural groundwater flow, and leaving immobile blobs of residual CO$_2$ and dense groundwater with dissolved CO$_2$ in its wake (Figure 1-1).

![Figure 1-1: After injection into a saline aquifer, the buoyant plume of mobile CO$_2$ (dark gray) will migrate due to a combination of aquifer slope and groundwater flow. As the plume migrates, it will shrink due to residual trapping, where capillarity immobilizes blobs of CO$_2$ at the trailing edge of the plume (light gray), and solubility trapping, where CO$_2$ dissolves into the groundwater and falls away from the plume in dense, CO$_2$-rich fingers (blue). Saline aquifers are thin relative to their extent (typical length scales indicated), are often weakly sloped (typical angle $\sim 1^\circ$), and generally have a slow natural groundwater through-flow (black arrows; typical velocity $\sim 10$ cm/year).]

The traditional reservoir-engineering approach to such problems is numerical simulation (e.g., Pruess and García, 2002; Kumar et al., 2005; Juanes et al., 2006), which allows for the incorporation of coupled models for many aspects of the relevant
physics, including multiphase fluid flow, geomechanics, geochemistry, and detailed hydrogeology. However, such simulations are extremely computationally expensive, and it is currently intractable for a simulation at the scale of a geologic basin to simultaneously resolve the long, thin plume of CO$_2$ migrating along the caprock and the small-scale fingers of CO$_2$-saturated groundwater that fall away from it, driving convective dissolution (Ennis-King and Paterson, 2005; Lu and Lichtner, 2007; Pau et al., 2010).

More recently, various simple theoretical models based on the theory of gravity currents (Bear, 1972; Huppert and Woods, 1995) have been used to provide important insights into the injection (e.g., Nordbotten and Celia, 2006; Neufeld et al., 2009; Gunn and Woods, 2011), upward spreading (e.g. Bickle et al., 2007; Hesse et al., 2007; MacMinn and Juanes, 2009), and lateral migration (e.g., Hesse et al., 2008; Juanes et al., 2010; MacMinn et al., 2010, 2011) of CO$_2$ in saline aquifers. Although such models are necessarily idealized, relying on many simplifying assumptions, they offer insight into the physical processes controlling CO$_2$ migration and trapping, and are not limited by computational resources.

We develop such a model here, and use it to study the post-injection migration and trapping of a buoyant plume of CO$_2$ in a saline aquifer.

1.2 Residual trapping under slope and groundwater flow

In the first part of this Thesis (Chapter 2), we develop a theoretical gravity-current model for the post-injection migration and residual trapping of a buoyant plume of CO$_2$ in a confined, sloping aquifer with a natural groundwater through-flow. We include the tongued shape of the plume at the end of injection as the initial condition for post-injection migration, because the plume retains a "memory" of this shape indefinitely due to residual trapping (MacMinn and Juanes, 2009; Juanes et al., 2010).

We develop a complete analytical solution to the model in its hyperbolic limit
Figure 1-2: The model for CO₂ migration with residual trapping is a nonlinear partial differential equation, and we solve it in its hyperbolic limit (neglecting buoyant spreading) with the method of characteristics. Here, we illustrate a typical solution. The aquifer is in this case tilted slightly clockwise (not shown), and groundwater flow is down-slope, from left to right. We show (a) the evolution of the plume in characteristic space, with waves of the left and right fronts in red and green, respectively, and the peak and shock paths in blue, and (b)–(f) the shape of the plume at several times during migration, with mobile CO₂ in dark gray, the region containing residual CO₂ in light gray, and groundwater in white.

(Fig. 1-2), and we use this solution to study the interactions between aquifer slope, groundwater flow, and residual trapping. For example, the net direction of migration is not obvious in situations where the flow direction is down-slope, conditions which are known to occur in many continental sedimentary basins (Garven, 1995). We use this solution to identify the critical ratio between slope and flow, above which the plume always moves up-slope and below which the plume always moves downstream. We further show that the maximum storage efficiency (the minimum migration distance) is achieved precisely in aquifers where flow and slope compete. These results are published in the *Journal of Fluid Mechanics* (MacMinn et al., 2010).

1.3 Residual and solubility trapping

In the second part of this Thesis (Chapter 3), we consider the combination of residual and solubility trapping. We incorporate a simple model for solubility trapping into the migration model, and we develop semi-analytical solutions to the model in two limiting cases: when the water beneath the plume saturates with dissolved CO₂ very slowly or very quickly relative to plume motion (Fig. 1-3). We use these solutions to
Figure 1-3: We incorporate solubility trapping into the model for CO$_2$ migration, and develop some semi-analytical solutions to the model in its hyperbolic limit (neglecting buoyant spreading) with the method of characteristics. Here, we illustrate a typical solution in the limiting case where the water beneath the plume saturates very slowly with dissolved CO$_2$, so that solubility trapping is not limited by the supply of water beneath the plume. All parameters here are the same as in Fig. 1-2, but with the addition of solubility trapping. We show (a) the evolution of the plume in characteristic space, with waves of the left and right fronts in red and green, respectively, and paths of the peak, the shock, and the leading and trailing edges of the plume in blue, and (b)–(f) the shape of the plume at several times during migration, with mobile CO$_2$ in dark gray, the region containing trapped CO$_2$ in light gray, the curtain of groundwater with dissolved CO$_2$ in blue, and groundwater in white.

study the competition between residual and solubility trapping, and the impact of solubility trapping on CO$_2$ migration.

We show that solubility trapping can greatly slow the speed at which the plume advances, and we derive an explicit analytical expression for the position of the nose of the plume as a function of time. We further show that residual and solubility trapping are complementary in the sense that residual trapping acts at the short, trailing edge of the plume and is most effective when the mobility ratio is small, whereas solubility trapping acts primarily along the long, leading edge of the plume and is most effective when the mobility ratio is large. As a result, solubility trapping can increase the storage efficiency by several fold even when the fraction dissolved is small. These results are published in the *Journal of Fluid Mechanics* (MacMinn et al., 2011).
1.4 Laboratory experiments

In the third part of this Thesis (Chapter 4), we validate the model against laboratory experiments in a simplified analog system.

We first study the up-slope migration of a buoyant gravity current without solubility trapping (Fig. 1-4, left). The aquifer is a quasi-two-dimensional flow cell packed with spherical glass beads. Water plays the role of the buoyant CO$_2$, and a mixture of glycerol and water plays the role of the denser and more viscous ambient groundwater. We perform these experiments for several values of the aquifer slope to vary the importance of buoyant spreading relative to up-slope migration, and we show that the model agrees qualitatively and quantitatively with the experiments. Although this analog system is unable to capture residual trapping or other effects of capillarity because the two fluids are completely miscible, it is useful for validating the model in the limit where capillary effects are negligible.

We next study up-slope migration with solubility trapping (Fig. 1-4, right). Water

Figure 1-4: In order to conduct experiments with and without convective dissolution, we use two different pairs of analog fluids. We illustrate this here with snapshots of two gravity currents migrating up-slope in a sloping aquifer (a Hele-Shaw cell with no beads for illustration). Water (dark) plays the role of the buoyant CO$_2$ in both cases. When the denser and more viscous ambient fluid (light) is a mixture of glycerol and water (left), the fluids mix by diffusion-dispersion only and the gravity current migrates to the top of the cell and accumulates there. When the ambient fluid is propylene glycol (right), the dense mixture of the two fluids drives convective dissolution, which effectively withdraws fluid from the gravity current and arrests the plume after a finite distance.
again plays the role of the buoyant fluid, but propylene glycol now plays the role of the denser and more viscous ambient fluid. Water from the buoyant plume dissolves into propylene glycol via convective dissolution because, as with CO$_2$ and water, the mixture of these two fluids is denser than either individual component (Backhaus et al., 2011). This is not the case with glycerol and water. We again perform these experiments for several values of the aquifer slope, and we show that the model captures the macroscopic impact of solubility trapping on the migrating gravity current both qualitatively and quantitatively.

In addition to highlighting the fact that solubility trapping driven by convective dissolution is a crucial trapping mechanism for geological CO$_2$ storage, these experiments provide a window into the small-scale complexity of the convective-dissolution instability: the formation, descent, and coarsening of the fingers. We propose a simple model for the growth of the fingering front beneath the plume, parametrized by a constant finger velocity and a constant onset time, and we quantify the coarsening of the fingering pattern in terms of the evolution of the spatial frequency of the fingers.

1.5 Application, discussion & conclusions

In the last Chapter of this Thesis (Chapter 5), we consider the application of these models to the migration and trapping of CO$_2$ in the Mt. Simon Sandstone, a large deep saline aquifer in the Midwestern United States that is considered to be a promising candidate for large-scale geological CO$_2$ storage. We show that solubility trapping is very effective for small slopes, whereas residual trapping is most effective for large slopes, and the combination of the two traps all of the CO$_2$ very effectively over a wide range of slopes.

Finally, we conclude with a discussion of the broader applicability of the models presented here, as well as their physical limitations.
Chapter 2

Residual trapping under slope and groundwater flow

In this Chapter, we develop a model for the post-injection migration and residual trapping of a plume of CO$_2$ driven by groundwater flow in a confined, sloping aquifer. We develop a complete analytical solution to the model in its hyperbolic limit, and we use this solution to study the competition between slope and groundwater flow, and the interaction of these migration mechanisms with residual trapping (Figure 2-1). These results are published in the *Journal of Fluid Mechanics* (MacMinn et al., 2010).

This problem falls into the broad class of fluid flows known as gravity currents, where one fluid is released or injected into a second, ambient fluid of different density. The resulting flow is governed by the balance of buoyancy and viscous dissipation (*e.g.*, Huppert, 1982).\(^1\)

The fundamental models for gravity currents in porous media are well-known. For example, Bear (1972) presented a gravity-current model for the displacement of one fluid by another fluid of different density and viscosity in a confined, sloping porous layer with a background through-flow (Bear, 1972, pg. 535, Equation 9.5.64). Baren-

\(^1\)Inertia can also play an important role in the spreading of gravity currents (*e.g.*, Huppert and Simpson, 1980), but it is almost always negligible in natural fluid flows through porous rocks, where fluid velocities are on the order of centimeters per year and the characteristic size of the pore space ranges from microns to millimeters.
Residual trapping refers to the isolation and immobilization of small, residual blobs of CO$_2$ at the trailing edge of the migrating plume. Residual trapping is driven by capillarity, and occurs in flow through a porous medium when a non-wetting fluid (CO$_2$) is displaced by a wetting one (groundwater). We illustrate this here with a snapshot of residual trapping in an experimental analog system: residual blobs of gas immobilized in a porous medium saturated with a liquid that preferentially wets the solid. The gas, liquid, and solid here are air, a mixture of water and glycerol, and 0.8 mm glass beads, respectively. Residual trapping is an ideal mechanism for the geological storage of CO$_2$ because the residual gas is immobile and distributed over a large area, greatly decreasing the risk of leakage and promoting CO$_2$ dissolution into the groundwater (Kumar et al., 2005; Juanes et al., 2006).
blatt (1952) and Barenblatt et al. (1972) used such a model to study the slumping of an axisymmetric mound of dense, viscous fluid in a porous medium, showing that the shape of the slumping mound is asymptotically self-similar, and Kochina et al. (1983) introduced residual trapping to this problem and showed that the shape of mound then exhibits self-similarity of the second kind. Similarly, Dussan V. and Auzerais (1993) studied the injection of buoyant fluid into a confined, horizontal porous layer, whereas Huppert and Woods (1995) studied the spreading and migration of dense fluid in a confined, sloping porous layer.

More recently, Nordbotten et al. (2005) and Nordbotten and Celia (2006) studied the radially symmetric injection of CO$_2$ into a saline aquifer from a single well, deriving a similarity solution for the case where injection-driven flow dominates buoyancy. Hesse et al. (2006) studied the post-injection spreading and up-slope migration of CO$_2$, including residual trapping as in Kochina et al. (1983). Hesse et al. (2007) studied the planar post-injection spreading of a plume of CO$_2$ and gave early- and late-time similarity solutions for buoyant spreading in a horizontal aquifer without residual trapping, starting from a rectangular or “step” initial shape. Hesse et al. (2008) introduced residual trapping to this model, showing that the early-time spreading behavior remains self-similar when residual trapping is included, and gave scaling results for the late-time spreading behavior. Hesse et al. (2008) also considered the limit of up-slope migration with negligible spreading, starting from a “step” initial shape and including residual trapping; they derived a semi-analytical solution in this limit, and an analytical solution for the case of negligible viscosity contrast.

Juanes and MacMinn (2008) and Juanes et al. (2010) considered the migration and residual trapping of CO$_2$ in a confined, horizontal aquifer with a net groundwater through-flow, providing an explicit analytical solution for post-injection migration when buoyant spreading is negligible. Their solution included the reduced mobility of water in the region containing residual CO$_2$, and also accounted for the tongued shape of the plume at the end of injection. The latter is important because residual trapping causes the size of the plume at any time to depend strongly on the details of its evolution up to that time, and therefore the end-of-injection plume shape has
a strong effect on the plume evolution for all time despite the diffusive mathematical character of the model (MacMinn and Juanes, 2009).

Here, we study the post-injection migration and residual trapping of a buoyant plume CO$_2$ in a confined, sloping aquifer with a net groundwater through-flow. As in Juanes and MacMinn (2008) and Juanes et al. (2010), we include the tongued shape of the plume at the end of the injection period. After confirming that the buoyant spreading term has a negligible impact on the long-time evolution of the plume (Juanes and MacMinn, 2008; Hesse et al., 2008; Juanes et al., 2010), we derive a complete analytical solution to the model in the hyperbolic limit.

We use this solution to show that the migration behavior depends strongly on the mobility ratio, the amount of residual trapping, and the importance of aquifer slope relative to groundwater flow. We explore the effect of these parameters on the overall storage efficiency, a measure of the fraction of the aquifer pore space that can be used to store CO$_2$, and we show that the interplay between groundwater flow and aquifer slope can change the storage efficiency by a factor of two to five. In particular, we find that the maximum efficiency is achieved in sloping aquifers with a moderate down-dip groundwater flow, conditions which are known to occur in many continental sedimentary basins (Garven, 1995).

Although both residual and mobile CO$_2$ will dissolve gradually into the groundwater, we do not include this effect here. We incorporate solubility trapping into the model in Chapter 3, and we then study its interaction with residual trapping and its impact on CO$_2$ migration.

### 2.1 Model for CO$_2$ injection and migration

We are interested in large CO$_2$ storage projects, because large quantities of CO$_2$ would need to be stored in order to significantly reduce atmospheric emissions. We therefore study the evolution of the CO$_2$ plume at the scale of a geologic basin, as proposed by Nicot (2008) (Figure 2-2). We assume that the CO$_2$ is injected simultaneously through a linear or “line-drive” arrangement of a large number of wells. While the
Figure 2-2: Large-scale geological storage of CO$_2$ requires injection at the scale of geologic basins. (a) A bird’s-eye view of CO$_2$ injection into a saline aquifer via a linear or “line-drive” array of wells. The plumes from the individual wells merge together as the CO$_2$ spreads away from the well array (black dots), and we model the single resulting plume (dark gray) as two-dimensional in the $x$-$z$ plane, with some width $W$ in the $y$-direction equal to the length of the well array. (b) A section view of CO$_2$ injection into a saline aquifer. The mobile CO$_2$ (gray) is buoyant relative to the ambient groundwater (white). After injection, it will rise upward and spread against the caprock (thick line) while migrating laterally up-slope, or with the natural groundwater flow (black arrows). Typical horizontal and vertical scales are indicated. The vertical scale of the aquifer is greatly exaggerated.
injection from a single well is radially outward, the plumes from neighboring wells will merge as the radius of the plumes approaches the inter-well spacing. We assume line symmetry in the \( y \)-direction and model the single resulting plume as two-dimensional in the \( x-z \) plane, with some width \( W \) in the \( y \)-direction equal to the length of the well array. As a result, all volumes and fluxes discussed here are per-unit-length of the well array unless specifically noted otherwise. While a two-dimensional model cannot capture three-dimensional flow effects such as groundwater or counter-current flow around the plume, or buoyant spreading in the transverse (\( y \)-) direction, the assumption of line-symmetry is justified here when the well array is long relative to the typical extent of the \( \text{CO}_2 \) plume in the \( x \)-direction. Further, we are interested in scenarios where the volume of \( \text{CO}_2 \) injected is large, so that the typical extent of the plume in the \( x \)-direction is much larger than the thickness of the formation into which it is injected.

We take the aquifer to be homogeneous, with an arbitrary tilt relative to 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 denote the \( \text{CO}_2 \) density and viscosity by \( \rho_g \) and \( \mu_g \), respectively, and the water density and viscosity by \( \rho_w \) and \( \mu_w \).

We employ a sharp-interface approximation, neglecting the width of typical gradients in saturation (\textit{i.e.}, the capillary transition zone or “fringe”) compared to typical length scales in the horizontal and vertical directions, and we neglect the capillary pressure compared to typical hydrostatic and viscous pressure drops (\textit{e.g.}, Bear, 1972; Yortsos, 1995).

In accordance with the sharp-interface approximation, we divide the domain into three regions of uniform fluid saturation separated by sharp interfaces corresponding to saturation discontinuities (Figure 2-3). Region 1 is the plume of mobile \( \text{CO}_2 \), containing free-phase \( \text{CO}_2 \) and a saturation \( S_{wc} \) of connate or residual groundwater; Region 2 is the region from which the plume has receded, containing mobile groundwater and a saturation \( S_{gr} \) of residual, free-phase \( \text{CO}_2 \); and Region 3 contains only mobile groundwater. We then write the Darcy velocity of the mobile fluid in each
Figure 2-3: After injection stops, the plume of mobile CO₂ (dark gray) will migrate due to a combination of groundwater flow and aquifer slope, leaving residual CO₂ in its wake (light gray). 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 $S_{w, c}$ of connate (residual) groundwater; Region 2 (light gray) contains mobile groundwater and a saturation $S_{g, r}$ of residual CO₂; Region 3 (white) contains only mobile groundwater. 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 $x$ and $z$ coordinates are now tilted with the aquifer.

The Darcy velocities of the immobile fluids in each region are $\mathbf{u}_i^w = \mathbf{u}_2^g = \mathbf{u}_3^g = 0$. We denote by $\lambda_i^\alpha = k_i^{*\alpha} / \mu_\alpha$ the mobility of fluid $\alpha$, $\alpha = g, w$, in Region $i$, $i = 1, 2, 3$, where $k_i^{*\alpha}$ is the end-point relative permeability $k_i^*$ to fluid $\alpha$ in region $i$ and $\mu_\alpha$ is the viscosity of fluid $\alpha$. The relative permeabilities take their constant end-point values here because we assume constant and uniform fluid saturations in each region. We denote by $p_i^\alpha$ the pressure of fluid $\alpha$ in region $i$. Gravity appears in two pieces because the $x$ and $z$ coordinates are tilted with the aquifer; $\mathbf{e}_x$ and $\mathbf{e}_z$ are unit vectors in the tilted $x$- and $z$-directions.

We make the “vertical flow equilibrium” or Dupuit approximation, neglecting the
vertical component of the fluid velocity relative to the horizontal one (Coats et al., 1971; Bear, 1972; Yortsos, 1995). This is justified when the characteristic vertical flow length scale is much smaller than the characteristic horizontal one (i.e., $H/L \ll 1$). This is generally the case for aquifers, which are typically very thin compared to their horizontal dimensions, and is further justified here by the fact that we consider scenarios where the volume of CO$_2$ injected is large, so that the typical extent of the plume in the $x$-direction is much larger than the thickness of the formation into which it is injected. Neglecting the vertical fluid velocity, the pressure within the mobile fluid in each region is hydrostatic and can be derived by integrating the $z$-component of Equations 2.1. These pressures can be written

\begin{align}
 p_1^0 &= p'(x, t) - \rho_g g \cos \vartheta (H - z), \\
 p_2^w &= p'(x, t) - \rho_g g \cos \vartheta h_1 - \rho_w g \cos \vartheta (H - h_1 - z), \\
 p_3^w &= p'(x, t) - \rho_g g \cos \vartheta h_1 - \rho_w g \cos \vartheta h_2 - \rho_w g \cos \vartheta (H - h_1 - h_2 - z),
\end{align}

where $p'(x, t)$ is the unknown reference pressure along the underside of the caprock, and the pressure field is continuous across regions and fluid interfaces because we have neglected the capillary pressure relative to the hydrostatic pressure.

We eliminate the reference pressure $p'(x, t)$ via macroscopic conservation of mass, requiring that the total volume of fluid flowing through the aquifer must be equal at all cross sections if the fluids and the rock are incompressible:

\[ u_1^o h_1 + u_2^w h_2 + u_3 h_3 = Q, \]

where a net volume rate $Q$ of fluid flows through the aquifer from left to right and $u_i^o = u_i^o \cdot \hat{e}_x$ is the $x$-component of the fluid velocity.

Finally, we consider conservation of mass for Region 1 individually, accounting for the residual fluid that crosses the interface (Kochina et al., 1983; Hesse et al., 2006; Juanes and MacMinn, 2008). The resulting conservation law for the local thickness

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2That is, we neglect the component of the fluid velocity in the tilted $z$-direction, perpendicular to the caprock, relative to that in the tilted $x$-direction, parallel to the caprock.
of the buoyant plume of CO$_2$, $h_1(x,t)$, is

$$(1 - S_{wc})\phi \bar{R} \frac{\partial h_1}{\partial t} + \frac{\partial}{\partial x} \left[ Q f + (1 - S_{wc})\phi \kappa \sin \vartheta (1 - f) h_1 - (1 - S_{wc})\phi \kappa \cos \vartheta (1 - f) h_1 \frac{\partial h_1}{\partial x} \right] = 0. \quad (2.4)$$

The discontinuous accumulation coefficient $\bar{R}$ captures the volume loss due to residual trapping by taking different values for drainage ($h_1$ increasing) and imbibition ($h_1$ decreasing),

$$\bar{R} = \begin{cases} 1 & \text{if } \partial h_1/\partial t > 0 \text{ and } h_2 = 0, \\ 1 - \Gamma & \text{otherwise}. \end{cases} \quad (2.5)$$

The parameter $\Gamma = S_{gr}/(1 - S_{wc})$ is the residual trapping number, which measures the fraction of CO$_2$ that is left behind at the imbibition front and takes a constant value between zero (no trapping) and one. The nonlinear function $f(h_1,h_2,h_3)$ is given by

$$f(h_1,h_2,h_3) = \frac{\lambda_1^g h_1}{\lambda_1^g h_1 + \lambda_2^w h_2 + \lambda_3^w h_3}. \quad (2.6)$$

The thicknesses $h_i$ are related through the requirement that they sum to the total aquifer thickness, $h_1 + h_2 + h_3 = H$, and through the relationship

$$\frac{\partial h_1}{\partial t} = \begin{cases} \frac{\partial h_3}{\partial t} & \text{if } \partial h_1/\partial t > 0 \text{ and } h_2 = 0, \\ -\frac{\partial h_2}{\partial t} & \text{otherwise}, \end{cases} \quad (2.7)$$

which reflects the difference between imbibition, when residual CO$_2$ is left behind, and drainage, when it is not.

The characteristic buoyancy-driven velocity of the plume is

$$\kappa = \frac{\Delta \rho g k \lambda_1^g}{(1 - S_{wc})\phi}, \quad (2.8)$$

where $\Delta \rho = \rho_w - \rho_g$ is the density difference between the groundwater and the CO$_2$, $g$ is the force per unit mass due to gravity, and $k$ and $\phi$ are the intrinsic permeability
and porosity of the aquifer, respectively.

We expect the mobility of the groundwater in Region 2 to be less than that in Region 3 because of the presence of the residual gas there. Although this effect can be included (Juanes and MacMinn, 2008), we neglect it here for simplicity, taking $\lambda_2^w = \lambda_3^w$. As a result, the distinction between Regions 2 and 3 has no physical significance and the nonlinear function $f(h_1, h_2, h_3)$ can be rewritten as a function of $h_1$ only,

$$f(h_1) = \frac{\lambda_1^0 h_1}{\lambda_1^0 h_1 + \lambda_3^w (H - h_1)}.$$  \hspace{1cm} (2.9)

With Equation (2.9), Equation (2.4) is of the same form as that presented in Bear (1972, pg. 535, Equation 9.5.64) when $\Gamma = 0$ (no residual trapping), and agrees with that of Hesse et al. (2008) when $Q = 0$ (no flow) and with that of Juanes et al. (2010) when $\vartheta = 0$ (no slope).

### 2.1.1 Scaling

This model for CO$_2$ migration and residual trapping (Equations 2.4, 2.5 and 2.9) is a one-dimensional, nonlinear conservation law for the thickness of the buoyant plume of mobile CO$_2$ as a function of space and time. We write it in dimensionless form as

$$\tilde{R} \frac{\partial \eta}{\partial \tau} + N_f \frac{\partial f}{\partial \xi} + N_s \frac{\partial}{\partial \xi} \left[(1 - f) \eta\right] - N_g \frac{\partial}{\partial \xi} \left[(1 - f) \eta \frac{\partial \eta}{\partial \xi}\right] = 0. \hspace{1cm} (2.10)$$

The primary variable is $\eta = h_1/H$, which is the local thickness of the plume of CO$_2$ scaled by the thickness of the aquifer. The nonlinear function $f$ is given by

$$f(\eta) = \frac{M \eta}{M \eta + (1 - \eta)}$$  \hspace{1cm} (2.11)

where $M = \lambda_1^0 / \lambda_3^w$ is the mobility ratio. This function reflects the fact that the aquifer is confined, so that the plume of CO$_2$ must displace the ambient fluid (groundwater) in order to migrate.

The dimensionless time is $\tau = t/T$, where $T$ is an appropriate characteristic time. The dimensionless $x$-coordinate is $\xi = x/L$, where $L$ is an appropriate characteristic
length. We discuss the specific choice of these characteristic values for the injection period in §2.1.2, and for the post-injection period in §2.1.3.

The model includes residual trapping, migration due to groundwater flow and aquifer slope, and buoyant spreading against the caprock. The conditional accumulation coefficient \( \tilde{R} \) captures residual trapping, changing value depending on whether the interface is locally in drainage or imbibition,

\[
\tilde{R} = \begin{cases} 
1 & \text{if } \partial \eta / \partial \tau > 0, \\
1 - \Gamma & \text{otherwise},
\end{cases}
\]  

(2.12)

The residual trapping number \( \Gamma \) measures the amount of residual fluid that is left behind as the interface recedes during imbibition.

The conservation law has three nonlinear flux terms, with coefficients \( N_f, N_s, \) and \( N_g \). The first two have an advective mathematical character, capturing migration due to groundwater flow through the aquifer and migration due to aquifer slope. The third has a diffusive mathematical character, capturing buoyant spreading against the caprock due to gravity. The three coefficients are given by

\[
N_f = \frac{T}{T_i} \frac{Q}{Q_i/2} , \quad N_s = \frac{T}{L} \kappa \sin \vartheta , \quad N_g = \frac{T}{L} \kappa \cos \vartheta \frac{H}{L} ,
\]  

(2.13)

where \( L \) is the characteristic length (Equation 2.14), \( T \) is the characteristic time (§2.1.2 and §2.1.3), and \( Q \) is the net volume flow of fluid through the aquifer from left to right (§2.1.2 and §2.1.3). \( \kappa \) is the characteristic buoyancy-driven velocity of the plume (Equation 2.8).

Without loss of generality, we choose \( N_f \geq 0 \) so that groundwater flow is always to the right by convention. Aquifer slope can be either positive (\( N_s > 0 \)) for counterclockwise aquifer tilt or negative (\( N_s < 0 \)) for clockwise aquifer tilt.
2.1.2 The injection period

During injection, we assume that a constant volume flow rate $Q_i$ of CO$_2$ per unit length $W$ of the line-drive well array is pumped into the aquifer. We take the characteristic timescale to be the duration of injection, $T = T_i$, so that $\tau = 1$ is the end of the injection period.

We choose the characteristic length scale during injection to be the length of a rectangle of aquifer of height $H$ and containing a volume equal to one-half of the total volume of CO$_2$ to be injected, $Q_iT_i/2$:

$$L = Q_iT_i/2(1 - S_{wc})\phi H. \quad (2.14)$$

Injection typically dominates the flow, so we neglect natural groundwater flow and slope relative to injection and assume that the flow rate $Q_i$ is split evenly between the left and right sides of the injection well. On the right side of the well, we then have that $Q = U_nH + Q_i/2 \approx Q_i/2$, so that

$$N_j^i = 1 \quad , \quad N_s^i = \frac{\Delta \rho g k \lambda_0^i H}{Q_i/2} \sin \vartheta \quad , \quad N_g^i = \frac{\Delta \rho g k \lambda_0^i (1 - S_{wc})\phi H^3}{(Q_i/2)^2T_i} \cos \vartheta. \quad (2.15)$$

The superscript $i$ indicates that these are the values of these parameters during injection. Typically $N_s^i, N_g^i \ll 1$, so the plume shape will be symmetric across the injection well.

2.1.3 Post-injection migration

Once injection has stopped, the net flow of fluid through the aquifer, $Q$, is due only to natural groundwater flow. We therefore have that $Q = U_nH$ in the post-injection period.

The characteristic length scale from the injection period was based on the total amount of CO$_2$ injected (Equation 2.14). This is also an appropriate choice for the post-injection period because it is characteristic of the initial length of the now-migrating plume, so we retain it.
The characteristic time scale from the injection period was the injection time. This is not an appropriate choice for the post-injection period because CO₂ migration due to slope and/or groundwater flow is typically very slow relative to injection. In order to choose a new characteristic time while keeping \( \tau = 1 \) as the end of injection, we redefine the dimensionless time in post injection as

\[
\tau = 1 + \frac{t - T_i}{T}
\]

so that the end of injection, \( t = T_i \), corresponds to \( \tau = 1 \) for any choice of characteristic time \( T \). A characteristic time for post-injection can be derived from any one of the three rates associated with post-injection migration and trapping: the rate of migration due to groundwater flow, the rate of migration due to aquifer slope, or the rate of buoyant spreading against the caprock. For a specific aquifer, the choice should be guided by the dominant mechanism. When no one mechanism is dominant, which is often the case in continental sedimentary basins (Garven, 1995), the specific choice is arbitrary.

Here, we choose a characteristic time based on the rate of migration due to groundwater flow:

\[
T = \frac{Q_i T_i / 2}{U_n H}.
\]

For this choice, we have from Equations 2.13 with \( Q = U_n H \) and \( T = Q_i T_i / 2 U_n H \) that

\[
N_f = 1, \quad N_s = \frac{\Delta \rho g k \lambda_1^q}{U_n} \sin \vartheta, \quad N_g = \frac{\Delta \rho g k \lambda_1^q (1 - S_{we}) \phi H^2}{U_n (Q_i / 2) T_i} \cos \vartheta. \quad (2.18)
\]

Here, \( N_s \) gives the importance of advection due to slope relative to that due to groundwater flow and \( N_g \) gives the importance of diffusive spreading due to buoyancy relative to advection due to groundwater flow. \( N_g \) is mathematically analogous to the inverse of a Peclét number, although there is no physical mass transfer here.

A consequence of this choice of characteristic time is that \( N_f \equiv 1 \). We retain \( N_f \) in the analysis (§2.2) and report our results (§2.3) in terms of the ratios \( N_s / N_f \) and
Figure 2-4: \( N_g \) migration and trapping are dominated by advective effects, and are little affected by even large values of \( N_g \) compared to \( N_f \) or \( N_s \). We illustrate this qualitatively here with the shape of the plume at \( \tau = 2.25 \) during post-injection migration for \( \mathcal{M} = 5, \Gamma = 0.3, N_f = 1, N_s = 0.5 \), and with \( N_g = 0, 0.1, 1, \) and \( 10 \) from numerical solutions to Equation (2.10). The prominent gravity tongue, the position of the leading edge, and the shape of the profile of trapped gas are little affected by non-negligible values of \( N_g \) compared to \( N_f \) or \( N_s \). In practice, the value of the mobility ratio \( \mathcal{M} \) is larger (usually between 10 and 20), and the impact of the spreading term is even smaller.

\[
\frac{N_g}{N_f} \text{ so that the results remain relevant for other choices of the characteristic time.}
\]

The choice of a characteristic time based on groundwater flow will not be appropriate when groundwater flow is “weak” compared to slope or buoyancy. In these cases, a different characteristic time should be used in Equations (2.13) to derive the appropriate expressions for \( N_f, N_s, \) and \( N_g \).

\[N = \frac{N_g}{N_s} \text{ so that the results remain relevant for other choices of the characteristic time.}
\]

2.2 Injection and migration with residual trapping

We now study injection and post-injection migration with residual trapping. In order to simplify the solution of Equation (2.10), we neglect the diffusive spreading term. This is justified because the macroscopic features of \( \text{CO}_2 \) migration and trapping—in particular, the prominent gravity tongue, the position of the leading edge, and the shape of the profile of residual gas—are dominated by advective effects and residual trapping, and are little affected by even large values of \( N_g \) compared to \( N_f \) or \( N_s \) (Juanes and MacMinn, 2008; Hesse et al., 2008) (Figure 2-4).

In this limit, Equation (2.10) is of hyperbolic character, and we write it

\[
\frac{\partial \eta}{\partial \tau} + \frac{1}{\mathcal{R}} \frac{\partial}{\partial \xi} F(\eta) = 0,
\]
where the flux function $F(\eta)$ is given by

$$F(\eta) = N_f f + N_s (1 - f) \eta.$$  \hspace{1cm} (2.20)

It will be useful to rewrite Equation (2.19) in terms of a scaled and shifted dimensionless plume thickness $g$,

$$\frac{\partial g}{\partial \tau} + \frac{1}{R} \frac{\partial}{\partial \xi} G(g) = 0,$$  \hspace{1cm} (2.21)

where $g = (\mathcal{M} - 1) \eta + 1$ remaps $0 \leq \eta \leq 1$ to $1 \leq g \leq \mathcal{M}$, and $G = (\mathcal{M} - 1) F$ is the corresponding flux function,

$$G(g) = \mathcal{M} N_f \left[ 1 - \frac{1}{g} \right] + \frac{N_s}{\mathcal{M} - 1} \left[ (\mathcal{M} + 1) - g \frac{\mathcal{M}}{g} \right].$$  \hspace{1cm} (2.22)

Equation (2.21) is a first-order, nonlinear, autonomous, hyperbolic conservation law. The solution to this equation depends on four dimensionless parameters: $\mathcal{M}$, $\Gamma$, $N_f$, and $N_s$. One of the latter two parameters can always be subsumed into the characteristic timescale, so the solution depends uniquely only on the ratio of one of them to the other. For generality, we retain both parameters in the analysis that follows; however, we present the results ($\S$2.3) in terms of the ratio $N_s/N_f$ because we choose a characteristic timescale based on groundwater flow ($\S$2.1.3).

Note that the values of $\mathcal{M}$ and $\Gamma$ used in the figures throughout this section (Figures 2-5 through 2-17) are chosen for illustration only, to make the noteworthy features of the plume shapes and characteristics clearly visible. In practice, these values of $\mathcal{M} = 2$ and $\Gamma = 0.5$ are too low and too high, respectively. We use realistic values of $\mathcal{M} = 5-15$ and $\Gamma = 0.3$ when presenting the key results in $\S$2.3 (Figure 2-18).

### 2.2.1 The injection period

We derive here the shape of the plume at the end of the injection period, because this serves as the initial condition for post-injection migration (Juanes and MacMinn, 2008; MacMinn and Juanes, 2009; Juanes et al., 2010).

We assume that a constant volume rate $Q_i$ of CO$_2$ per unit length of the line-drive
well-array is pumped into the aquifer. As discussed in §2.1.2, we assume that injection dominates the flow during the injection period, and we therefore take $N_f^{i} = 1$ and $N_s^{i}, N_g^{i} \ll 1$. As a result, the injected CO$_2$ is split evenly between the left and right sides of the injection well and the plume shape is symmetric across the injection well. Groundwater flow and aquifer slope would lead to some asymmetry in the plume shape, but we expect this to be negligible due to the dominance of injection. We therefore model the well as a line source located at $\xi = 0$ with strength $Q_i/2H$ per unit vertical length.

The solution of Equation (2.21) for the injection period has been discussed by Nordbotten et al. (2005) and Nordbotten and Celia (2006) for the radial geometry and, in a different context, by Verdon and Woods (2007) for the planar geometry. Here, we re-derive the latter in the context of CO$_2$ injection, as presented in Juanes and MacMinn (2008); Juanes et al. (2010).

The solution to a hyperbolic conservation law such as Equation (2.21) is a collection of waves traveling through space-time at constant speed. These waves behave independently of one-another unless they collide. The speed of each wave is determined by its thickness, $g$, and is given by $G'(g)/\tilde{R}$ where $G' = dG/dg$. The flux function $G(g)$ for the right front during injection is concave down and strictly increasing, so the right front evolves as a rarefaction: all waves travel to the right and the front is stretched horizontally. Because all waves correspond to CO$_2$ displacing groundwater to the right, all waves are in drainage with $\tilde{R} = 1$. The solution from the method of characteristics is then

$$
\xi_R^l(g, \tau) = -\left( \frac{M}{g^2} \right) \tau, \quad \xi_R^r(g, \tau) = \left( \frac{M}{g^2} \right) \tau,
$$

(2.23)

where the left front, $\xi_R^l$, is the reflection of the right front, $\xi_R^r$. Figure 2-5 shows the characteristics and the plume shape at several times during the injection period, which ends at $\tau = 1$. 40
Figure 2-5: During injection, the plume spreads symmetrically outward from the injection well in a characteristic tongued shape. Here, we show (a) the evolution of the plume in characteristic space and (b)-(d) the shape of the plume (gray) for $M = 2$ and at $\tau = 0.1, 0.5, \text{ and } 1$, respectively. In (a), we show several waves of the left and right fronts in red and green, respectively; the innermost and outermost waves on each front correspond to $g = M$ and $g = 1$ ($\eta = 1$ and $\eta = 0$), respectively.

2.2.2 Post-injection migration

Once injection has ended, the plume migrates due to slope and groundwater flow, and shrinks due to residual trapping. We solve Equation (2.21) for post-injection migration using the method of characteristics. The post-injection problem is more complex than the injection problem because the nonlinear interactions between slope, groundwater flow, and residual trapping cause waves to collide. We divide the analysis into parts based on the types of collisions that occur.

As during injection, the velocity of each wave of the left and right fronts is given by the corresponding derivative of the flux function, $G'(g)$, scaled by $\tilde{R}$. The direction in which each wave travels (i.e., to the left or to the right) is determined by the sign of $G'(g)$, and this in turn sets the appropriate value of $\tilde{R}$ for each wave. Waves of the left front moving to the left correspond to CO$_2$ displacing groundwater, and are then drainage waves; waves of the left front moving to the right correspond to groundwater displacing CO$_2$, and are imbibition waves. Waves of the right front moving to the left or to the right are similarly imbibition waves or drainage waves, respectively.

We plot the flux functions for flow only, for slope only, and for combined flow and slope in Figure 2-6. The flux function for flow only is concave down and strictly increasing. In other words, flow pushes all waves to the right. In contrast, the
Figure 2-6: The flux function for flow only is monotonic, whereas the flux function for slope only has a local extremum. The flux function for combined flow and slope may or may not have an extremum, depending on the values of $M$, $N_f$, and $N_s$. Here, we show the shape of the flux function for (a) flow only ($N_s = 0, N_f = 1$) for $M = 2, 5, 10, 20, \text{and } 50$; (b) positive slope only ($N_s = 1, N_f = 0$) for $M = 2, 5, 10, 20, \text{and } 50$; and (c) combined flow and slope for $M = 2, N_f = 1, \text{and } N_s$ varying from $-4$ to $4$.

The flux function for positive slope only is concave down with a local maximum at some $\eta = \eta_s$. This means that waves with $\eta < \eta_s$ move up-slope, the wave with $\eta = \eta_s$ is stationary, and waves with $\eta > \eta_s$ move down-slope (Hesse et al., 2008). The flux function for negative slope has the opposite behavior. We take the three limiting cases of negative slope only, flow only, and positive slope only to be three discrete points on the continuum of possible values of the ratio $N_s/N_f$: $N_s/N_f \rightarrow -\infty$, $N_s/N_f = 0$, and $N_s/N_f \rightarrow \infty$, respectively.

To understand qualitatively the effect of combined flow and slope, consider a flow-only system where all waves move to the right. Adding some amount of positive slope will speed the upper portion of the plume and slow the lower portion. If the amount of positive slope is large enough, a stationary point will be introduced at some $\eta = \eta_s$ and waves with $\eta > \eta_s$ will move to the left. Adding negative slope to a flow-only system will accomplish the opposite, slowing the upper portion of the plume and speeding the lower portion. If the amount of negative slope is large enough, a stationary point will be introduced at some $\eta = \eta_s$ and waves with $\eta < \eta_s$ will move to the left.

To understand this behavior quantitatively, consider the derivative of the flux
which changes sign once at stationary point \( g = g_s \) given by

\[
g_s = \sqrt{\mathcal{M}(\mathcal{M} - 1)N_f/N_s + \mathcal{M}}. \tag{2.25}
\]

From Equation (2.25), \( g_s \) exists on the interval \( 1 \leq g \leq \mathcal{M} \) only for \( N_s/N_f \leq -\mathcal{M} \) or \( 1 \leq N_s/N_f \). Accordingly, the continuum of possible values of the ratio \( N_s/N_f \) can be divided into three intervals based on the nature of the resulting plume migration.

For \( N_s/N_f \leq -\mathcal{M} \), the flux function is concave up and has a local minimum, so that \( G' \) vanishes at \( g = g_s \) and is negative for \( g < g_s \) and positive for \( g > g_s \). We refer to this interval as *negative slope with weak flow*. For \(-\mathcal{M} < N_s/N_f < 1\), the flux function is concave up for \( N_s/N_f < -(\mathcal{M} - 1) \), linear for \( N_s/N_f = -(\mathcal{M} - 1) \), and concave down for \( N_s/N_f > -(\mathcal{M} - 1) \), and in all cases strictly increasing so that \( G' \) is positive. We refer to this interval as *flow with weak slope*. For \( 1 < N_s/N_f \), the flux function is concave down and has a local maximum, so that \( G' \) vanishes at \( g = g_s \) and is positive for \( g < g_s \) and negative for \( g > g_s \). We refer to this interval as *positive slope with weak flow*. The flux functions and the resulting plume motion for these three intervals are illustrated in Figure 2-7.

### 2.2.3 Flow with weak slope

We consider \(-\mathcal{M} < N_s/N_f < 1\), for which \( G' \) is strictly positive. Starting from the end-of-injection shape, all waves propagate to the right at speed \( G'(g)/\tilde{R} \) until two or more waves collide. The right front is a drainage front with \( \tilde{R} = 1 \), and the left front is an imbibition front with \( \tilde{R} = (1 - \Gamma) \). Because of this, a given wave on the left front travels faster than the corresponding wave on the right front.

As the plume migrates, one of the two fronts will be compacted and the other will be stretched. If the flux function is concave up \(( N_s/N_f < -(\mathcal{M} - 1) \)), waves for
larger values of \( g \) will travel faster than waves for smaller values and the left front will be stretched as the right front is compacted; if the flux function is concave down \( (N_s/N_f > -(M - 1)) \), waves for larger values of \( g \) will travel more slowly than waves for smaller values and the left front will be compacted as the right front is stretched. In the particular case when the flux function is a straight line \( (N_s/N_f = -(M - 1)) \), all waves on each front move at the same speed and the fronts will not change shape as they travel.

It is possible that the compacting front will eventually become a discontinuity or shock. Shocks are a common feature of nonlinear hyperbolic conservation laws. The formation of a shock corresponds to multiple waves meeting at a single point and thereafter traveling together through space-time. The formation of a shock is illustrated in Figure 2-8. It is also possible that a wave from the left front will catch the corresponding wave from the right front, meaning that all of the CO\(_2\) in between has been trapped. When this occurs, we refer to the point of intersection of the
Figure 2-8: A shock forms when a portion of a front is compressed into a discontinuity. Here ($\mathcal{M} = 2$, $\Gamma = 0.5$, $N_f = 1$, $N_s = 0.5$), the entire left front becomes a shock as (a) the characteristics collide at a single point. The shapes of the plume at (b) the end of injection, (c) an intermediate time, and (d) the time of shock formation are also shown. Here and in all characteristics diagrams that follow, we include the injection period but denote that portion of the time axis ($\tau < 1$) with dashed lines. This is to emphasize that the characteristic timescale may change dramatically from injection to post injection, across $\tau = 1$ (§2.1.2 and 2.1.3).

left and right fronts as a peak. The formation of a peak is illustrated in Figure 2-9. Peak formation is unusual in that the collision of two waves at a peak corresponds to the end of those characteristics in space-time: those two waves cease to exist. Peak formation is possible here because residual trapping causes imbibition waves to travel faster than drainage waves.

The formation of a shock or peak leads to a fundamental change in the migration behavior, so we must determine when and where these collisions occur. To do so, we examine the positions of four key points: the left-most and right-most points on each front, as shown in Figure 2-10. A shock or peak will form when any two key points collide. The positions of these key points are

$$\xi_{LL}(\tau) = -\mathcal{M} + \frac{1}{1 - \Gamma} (\mathcal{M} N_f + N_s) (\tau - 1), \quad (2.26a)$$

$$\xi_{LR}(\tau) = -\frac{1}{\mathcal{M}} + \frac{1}{1 - \Gamma} \left( \frac{N_f - N_s}{\mathcal{M}} \right) (\tau - 1), \quad (2.26b)$$

$$\xi_{RL}(\tau) = \frac{1}{\mathcal{M}} \left( \frac{N_f - N_s}{\mathcal{M}} \right) (\tau - 1), \quad (2.26c)$$

$$\xi_{RR}(\tau) = \mathcal{M} + (\mathcal{M} N_f + N_s) (\tau - 1), \quad (2.26d)$$
Figure 2-9: A peak forms when the left and right fronts touch, i.e., when all of the CO$_2$ between is trapped. Here ($M = 2, \Gamma = 0.5, N_f = 1, N_s = -0.8$), a peak forms at the bottom of the plume as (a) the two innermost characteristics collide. The shapes of the plume at (b) the end of injection, (c) an intermediate time, and (d) the time of peak formation are also shown. Here and in all characteristics diagrams that follow, we include the injection period but denote that portion of the time axis ($\tau < 1$) with dashed lines. This is to emphasize that the characteristic timescale may change dramatically from injection to post injection, across $\tau = 1$ ($\S$2.1.2 and 2.1.3).

Figure 2-10: In order to determine when and where collisions occur, we examine (a) the positions of four key points: $\xi_{LL}$ and $\xi_{LR}$ are the left-most and right-most points, respectively, on the left front, and $\xi_{RL}$ and $\xi_{RR}$ are the left-most and right-most points on the right front. The mobile CO$_2$ is shown in dark gray, the region with trapped gas in light gray. We can see that (b) a shock forms on the left when point $\xi_{LL}$ collides with point $\xi_{RR}$, or that a peak forms (c) when point $\xi_{LR}$ collides with point $\xi_{RL}$. It is also possible for a shock to form on the right when point $\xi_{RL}$ collides with point $\xi_{RR}$ (see the discussion of cases 4 and 5, below).
Figure 2-11: We divide the flow-with-weak-slope interval into five cases by comparing the collision times from Equations (2.27) with one-another. Note that case 5 exists only if $M < \sqrt{2/\Gamma - 1}$, which is typically not the case; otherwise, case 4 extends to $-M$. The case of flow only studied by Juanes and MacMinn (2008) and Juanes et al. (2010) is within case 1.

where $\xi_{LL}$ and $\xi_{LR}$ are the left-most and right-most points, respectively, on the left front, and $\xi_{RL}$ and $\xi_{RR}$ are the left-most and right-most points on the right front. These expressions remain valid until the first collision occurs.

We use the notation $\xi_{\alpha\beta} \rightarrow \xi_{\gamma\delta}$ to indicate the collision of the former key point with the latter. Because all points move to the right in this interval, it is clear that the first collision must be one of $\xi_{LL} \rightarrow \xi_{LR}$, $\xi_{LR} \rightarrow \xi_{RL}$, or $\xi_{RL} \rightarrow \xi_{RR}$. The times at which these three collisions would occur are readily derived from Equations (2.26):

$$
\tau_{LL}^{LR} = 1 + \frac{(1 - \Gamma)(M - 1)}{(M - 1)N_f + N_s}, \\
\tau_{LR}^{RL} = 1 + \frac{2(1 - \Gamma)}{\Gamma(N_f - N_s)}, \\
\tau_{RL}^{RR} = 1 - \frac{(M - 1)}{(M - 1)N_f + N_s},
$$

where $\tau_{\alpha\beta}^{\gamma\delta}$ is the time corresponding to $\xi_{\alpha\beta} \rightarrow \xi_{\gamma\delta}$. By comparing these collision times with one-another, we can divide the flow-with-weak-slope interval, $-M < N_s/N_f < 1$, into five cases based on the order in which collisions occur, as illustrated in Figure 2-11.
Case 1

The development of case 1 is a simple generalization of the flow-only case. The flux function is concave down, so the left front is compacted while the right front is stretched. The first collision is $\xi_{\text{LL}} \rightarrow \xi_{\text{LR}}$, which occurs at position

$$\xi_{\text{LL}}^{\text{LR}} = \frac{-N_s/N_f}{(M - 1) + N_s/N_f}$$

(2.28)

and at time $\tau_{\text{LL}}^{\text{LR}}$ from Equations (2.27). When this occurs, the entire left front becomes a shock that propagates to the right at a constant speed until it collides with $\xi_{\text{RL}}$. The speed of the shock, $\sigma$, during this period is evaluated from the Rankine–Hugoniot condition (e.g., Lax, 1972),

$$\sigma = \frac{1}{1 - \Gamma} \left[ G \right] = \frac{N_f}{1 - \Gamma},$$

(2.29)

where the notation $[\phi]$ indicates the difference or “jump” in the indicated quantity across the shock. The shock collides with $\xi_{\text{RL}}$ at position

$$\xi_{\text{RL}}^{\text{RL}} = \frac{(2 - \Gamma) - (1 - \Gamma)N_s/N_f}{(M - (1 - \Gamma)) + (1 - \Gamma)N_s/N_f}$$

(2.30)

and time

$$\tau_{\text{RL}}^{\text{RL}} = 1 + \frac{(1 - \Gamma)(M + 1)}{(M - (1 - \Gamma))N_f + (1 - \Gamma)N_s}.$$  

(2.31)

Thereafter, the shock collides continuously with the right front. We develop a differential equation for the shock height by posing the collision of the shock with an arbitrary wave $g^*$ on the right front at some time $\tau^*$. The position of the shock at time $\tau^*$ can be written

$$\xi_{\sigma}(\tau^*) = \xi_{\sigma}^{\text{RL}} + \int_{\tau_{\text{RL}}^{\text{RL}}}^{\tau^*} \sigma(\tau) \, d\tau,$$

(2.32)

where the shock speed at any time is evaluated from the Rankine–Hugoniot condition for the instantaneous shock height. The position of the wave $g^*$ on the right front
prior to collision with the shock can be written

\[ \xi_{g^*}(\tau^*) = \frac{\mathcal{M}}{g^{*2}} + G'(g^*)(\tau^*-1). \]  

(2.33)

Equating \( \xi_\sigma(\tau^*) \) with \( \xi_{g^*}(\tau^*) \), since these must be equal by the definition of \( \tau^* \) and \( g^* \), we differentiate the resulting expression with respect to \( \tau^* \) and rearrange to find an ordinary differential equation (ODE) for the shock height as a function of time,

\[ \frac{dg^*}{d\tau^*} = \frac{\sigma(g^*) - G'(g^*)}{-2\mathcal{M}/g^{*3} + G''(g^*)(\tau^*-1)}. \]  

(2.34)

Equation (2.34) is separable,

\[ \int_{\mathcal{M}}^{\sigma} \frac{-2\mathcal{M}}{\sigma(g^*) + G'(g^*) g^{*3}} \frac{dg^*}{g^{*3}} = \int_{\tau_{RL}}^{\tau} \frac{d\tau^*}{(N_f + N_s/(\mathcal{M} - 1))(\tau^* - 1) + 1}, \]  

(2.35)

where \( g_\sigma \) is the height of the shock at time \( \tau \), and has implicit solution

\[ \mathcal{I}(g_\sigma) - \mathcal{I}(\mathcal{M}) = \ln \left[ \frac{(N_f + N_s/(\mathcal{M} - 1))(\tau - 1) + 1}{(N_f + N_s/(\mathcal{M} - 1))(\tau_{RL} - 1) + 1} \right] \]  

(2.36)

where the integral \( \mathcal{I}(g) \) is given by

\[ \mathcal{I}(g) = \ln \left[ \frac{(1 - \Gamma)g^2}{(1 - \Gamma) - g + B\Gamma g^2} \right] + 2A \arctan \left[ A(2B\Gamma g - 1) \right], \]  

(2.37)

with constants \( A \) and \( B \),

\[ A = \frac{1}{\sqrt{4B\Gamma(1-\Gamma)-1}}, \quad B = \frac{N_s/N_f}{\mathcal{M}(\mathcal{M}-1)+\mathcal{M}N_s/N_f}. \]  

(2.38)

We now have an implicit analytical relationship for the shock height as a function of time, and the plume evolves accordingly until \( g_\sigma \to 1 \) when the shock catches \( \xi_{RR} \), at which point the plume vanishes. The complete evolution of the plume for case 1 is shown in Figure 2-12.
Case 2

In case 2, the flux function remains concave down so that the left front is again compacted as the right front is stretched, but $\xi_{LR} \rightarrow \xi_{RL}$ now occurs before $\xi_{LL} \rightarrow \xi_{LR}$ and a peak forms. This occurs at position

$$
\xi_{RL}^{LR} = \frac{1}{\mathcal{M}} \left( \frac{2}{\Gamma} - 1 \right)
$$

(2.39)

and time

$$
\tau_{LR}^{RL} = 1 + \frac{2(1 - \Gamma)}{\Gamma (N_f - N_s)}.
$$

(2.40)

The height of the peak $g_p$ as a function of time is simply the height at which the left and right fronts intersect,

$$
g_p = \sqrt{\mathcal{M} \left[ (\mathcal{M} - 1)N_f/N_s + 1 \right] - \frac{2\mathcal{M}(\mathcal{M} - 1)(1 - \Gamma)}{\Gamma N_s(\tau - 1)}}.
$$

(2.41)

The left and right fronts, meeting at the peak, then continue to compact and stretch, respectively, until the left front compacts into a shock, which occurs at position $\xi_{p}^{LR} = \xi_{LL}^{LR}$ from Equations (2.26) and time $\tau_{p}^{LR} = \tau_{LL}^{LR}$ from Equations (2.27).
Figure 2-13: Post-injection migration for case 2 with $\mathcal{M} = 2$, $\Gamma = 0.5$, $N_f = 1$, and $N_s = -0.75$: (a) the evolution of the plume in characteristic space with waves of the left and right fronts in red and green, respectively, and the peak and shock paths in blue; (b)–(f) the shape of the plume at several times during migration, with mobile $\text{CO}_2$ in dark gray, the region containing trapped $\text{CO}_2$ in light gray, and groundwater in white.

The height of the peak when this occurs is

$$g_p^{LR} = \sqrt{\mathcal{M} \left[ (\mathcal{M} - 1)N_f/N_s + 1 \right] \left( 1 - \frac{2}{\Gamma} \right)}.$$  \hspace{1cm} (2.42)

This shock then travels to the right, colliding continuously with the right front until the plume vanishes. The evolution of the shock during this final period is analogous to the final period of evolution from case 1, but beginning at a different position and time, and with a different initial shock height. The complete evolution of the plume for case 2 is shown in Figure 2-13.

Case 3

In case 3, the first collision is $\xi_{LR} \rightarrow \xi_{RL}$, forming a peak, and the second is $\xi_{LL}^{RR}$, at which point the plume is completely trapped. This occurs before either front is compressed into a shock; as a result, the expressions for the position and time at which the plume vanishes are particularly simple, and are given by

$$\xi_{LL}^{RR} = \mathcal{M} \left( \frac{2}{\Gamma} - 1 \right).$$  \hspace{1cm} (2.43)
Figure 2-14: Post-injection migration for case 3 with $\mathcal{M} = 2$, $\Gamma = 0.5$, $N_f = 1$, and $N_s = -1.2$: (a) the evolution of the plume in characteristic space with waves of the left and right fronts in red and green, respectively, and the path of the peak in blue; (b)–(e) the shape of the plume at several times during migration, with mobile CO$_2$ in dark gray, the region containing trapped CO$_2$ in light gray, and groundwater in white.

and

$$\tau_{LL}^{RR} = 1 + \frac{2\mathcal{M}(1 - \Gamma)}{\Gamma(\mathcal{M}N_f + N_s)},$$  \hspace{1cm} (2.44)

respectively. The complete evolution of the plume for case 3 is shown in Figure 2-14. Note that the curvature of the flux function changes sign at $N_s/N_f = -(\mathcal{M} - 1)$, for which value the flux function is a straight line. This is always within case 3.

Case 4

In case 4, the flux function is now concave up and the left front is stretched while the right front is compacted. In other words, we now expect shocks to form on the right. The first collision is again $\xi_{LR} \rightarrow \xi_{RL}$, forming a peak. The second collision is $\xi_p \rightarrow \xi_{RR}$, at which point the right front has been compacted into a shock. The shock then propagates slowly to the right, colliding continuously with the left front as the latter overtakes it. The ODE for the shock height as a function of time differs only slightly from that of case 1; the construction is analogous, and the result can again be integrated analytically. The complete evolution of the plume for case 4 is shown in Figure 2-15.
Figure 2-15: Post-injection migration for case 4 with $M = 2$, $\Gamma = 0.5$, $N_f = 1$, and $N_s = -1.5$: (a) the evolution of the plume in characteristic space with waves of the left and right fronts in red and green, respectively, and the peak and shock paths in blue; (b)–(f) the shape of the plume at several times during migration, with mobile CO$_2$ in dark gray, the region containing trapped CO$_2$ in light gray, and groundwater in white.

**Case 5**

In case 5, the flux function remains concave up and the first collision is $\xi_{RL} \rightarrow \xi_{RR}$ as the right front is compacted into a shock. The shock then evolves in the same manner as in case 4 until the plume is completely trapped. This case exists only if $M < \sqrt{2/\Gamma - 1}$, which is generally not the case for typical values of $M$ and $\Gamma$ for the CO$_2$ problem, and otherwise case 4 extends to $N_s/N_f = -M$. Note that for the particular case of $N_s/N_f = -M$ the speed of the points $\xi_{LL}$ and $\xi_{RR}$ is exactly 0; the plume thins as the shock travels slowly to the right, but the shock height approaches zero asymptotically and the plume never becomes fully trapped, although in reality it would be arrested by capillarity as it becomes very thin.

### 2.2.4 Negative slope with weak flow

When $N_s/N_f \leq -M$, the flux function is concave up and has a local minimum at some $g = g_s$. The wave on each front corresponding to $g = g_s$ is stationary and does not move from its end-of-injection position. We must introduce these as two
additional key points,

\[ \xi_{LS}(\tau) = \frac{-1}{(\mathcal{M} - 1)N_f/N_s + 1}, \]  
\[ \xi_{RS}(\tau) = \frac{1}{(\mathcal{M} - 1)N_f/N_s + 1}, \]

where \( \xi_{LS} \) and \( \xi_{RS} \) are the stationary points on the left and right fronts, respectively. Waves corresponding to \( g < g_s \) travel to the left, and those corresponding to \( g > g_s \) travel to the right; \textit{i.e.}, the “upper” portion of the plume travels up-slope, against the flow, and the “lower” portion of the plume travels down-slope, with the flow. As in cases 4 and 5, the left front will be stretched while the right front is compacted. Note that unlike all of the previous cases, the net motion of the plume in this interval is now to the left, or up-slope.

The positions of the other four key points are

\[ \xi_{LL}(\tau) = -\mathcal{M} + (\mathcal{M}N_f + N_s)(\tau - 1), \]  
\[ \xi_{LR}(\tau) = -\frac{1}{\mathcal{M}} + \frac{1}{1 - \Gamma} \left( \frac{N_f - N_s}{\mathcal{M}} \right) (\tau - 1), \]  
\[ \xi_{RL}(\tau) = \frac{1}{\mathcal{M}} + \left( \frac{N_f - N_s}{\mathcal{M}} \right) (\tau - 1), \]  
\[ \xi_{RR}(\tau) = \mathcal{M} + \frac{1}{1 - \Gamma} (\mathcal{M}N_f + N_s)(\tau - 1). \]

The first collision in this interval must be one of three possibilities: \( \xi_{RR} \rightarrow \xi_{RS}, \xi_{RL} \rightarrow \xi_{RS}, \) or \( \xi_{LR} \rightarrow \xi_{RL}. \) Ultimately, a shock must form at \( \xi_{RS} \) because it is stationary. This can either happen as the first collision (\( \xi_{RR} \rightarrow \xi_{RS} \) or \( \xi_{RL} \rightarrow \xi_{RS} \)) or, if \( \xi_{LR} \rightarrow \xi_{RL} \) occurs first, as the second. Once the shock forms, it must eventually collide with the peak if one has formed, or with \( \xi_{RL} \) and then with \( \xi_{LR} \) if one has not. It must then collide with \( \xi_{LS} \) and ultimately with \( \xi_{LL}. \) The shock may change direction during its evolution, switching from drainage to imbibition or vice versa, but this is at all times consistent with the Rankine–Hugoniot condition.

In the flow-with-weak-slope interval, the formation of the shock (if a shock forms) is always the last collision. This allowed us to examine the behavior preceding the
shock formation in great detail, and to divide the interval into cases accordingly. In the negative-slope-with-weak-flow interval, the formation of the shock is always one of the first two collisions and it is no longer tractable to determine the order of collisions in an explicit fashion. Instead, we implement a decision-tree algorithm to handle each stage of the plume evolution in sequence. The algorithm evaluates and compares the times at which possible collisions would occur, and evolves the plume accordingly. This process is entirely algebraic, consisting only of the evaluation of complex and sometimes implicit expressions.

We illustrate one example of the evolution of the plume in this interval in Figure 2-16; the order of collisions in this example is $\xi_{RR} \rightarrow \xi_{RS}$ forming a shock, $\xi_{RL} \rightarrow \xi_{\sigma}$, $\xi_{LR} \rightarrow \xi_{\sigma}$, $\xi_{\sigma} \rightarrow \xi_{LS}$, and $\xi_{\sigma} \rightarrow \xi_{LL}$.

### 2.2.5 Positive slope with weak flow

When $1 \leq N_s/N_f$, the flux function is concave down and has a local maximum at some $g = g_s$. The waves corresponding to $g = g_s$ are again stationary, and we again
have three key points on each front. Waves corresponding to $g < g_s$ now travel to the right, and those corresponding to $g > g_s$ travel to the left; i.e., the “upper” portion of the plume travels up-slope, with the flow, and the “lower” portion of the plume travels down-slope, against the flow. As in cases 1 and 2 of the flow-with-weak-slope interval, the left front will be compacted while the right front is stretched. Additionally, the net motion of the plume is again to the right.

The evolution of the plume is analogous to that in the negative-slope-with-weak flow interval. The first collision must be one of three possibilities: $\xi_{LL} \rightarrow \xi_{LS}$, $\xi_{LR} \rightarrow \xi_{LS}$, or $\xi_{RL} \rightarrow \xi_{LR}$. Ultimately, a shock must form at $\xi_{LS}$ because it is stationary. This can either happen as the first collision ($\xi_{LL} \rightarrow \xi_{LS}$ or $\xi_{LR} \rightarrow \xi_{LS}$) or, if $\xi_{RL} \rightarrow \xi_{LR}$ occurs first, as the second. Once the shock forms, it must eventually collide with the peak if one has formed, or with $\xi_{LR}$ and then with $\xi_{RL}$ if one has not. It must then collide with $\xi_{RS}$ and ultimately with $\xi_{RR}$. As before, it is not tractable to perform further analysis explicitly and we instead use a decision-tree algorithm; however, as before, the process is entirely algebraic.

We illustrate an example of the evolution of the plume in this interval in Figure 2-17; the order of collisions in this example is $\xi_{LL} \rightarrow \xi_{LS}$ forming a shock, $\xi_{LR} \rightarrow \xi_{\sigma}$, $\xi_{\sigma} \rightarrow \xi_{RL}$, $\xi_{\sigma} \rightarrow \xi_{RS}$, and $\xi_{\sigma} \rightarrow \xi_{RR}$.

### 2.3 Plume footprint and storage efficiency

We are primarily interested here in macroscopic measures of the plume evolution. One such measure is the volume of CO$_2$ stored per unit volume of aquifer “used.” This is the storage efficiency, an important metric in capacity estimation (Bachu et al., 2007). We define the storage efficiency $\varepsilon$ as

$$\varepsilon = \frac{V_{CO_2}}{V_T} \rightarrow \frac{Q_i T_i}{H L_T (1 - S_{wc}) \phi}, \quad (2.47)$$

where $V_{CO_2}$ is the volume of CO$_2$ injected and $V_T$ is the total volume of aquifer used; we define $V_T$ to be the total pore volume available for CO$_2$ storage in a rectangle of
Figure 2-17: Post-injection migration in the positive-slope-with-weak-flow interval with $\mathcal{M} = 2$, $\Gamma = 0.5$, $N_f = 1$, and $N_s = 4$: (a) the evolution of the plume in characteristic space with waves of the left and right fronts in red and green, respectively, and the peak and shock paths in blue; (b)–(f) the shape of the plume at several times during migration, with mobile CO$_2$ in dark gray, the region containing trapped CO$_2$ in light gray, and groundwater in white.

thickness $H$ and length $L_T$, where $L_T$ is the total extent in the $x$-direction of the fully trapped CO$_2$ plume (Juanes and MacMinn, 2008; Juanes et al., 2010). Taking $\xi_T = L_T/L$ and using $L$ as defined in §2.1, we have that

$$\varepsilon = \frac{2}{\xi_T}.$$  \hspace{1cm} (2.48)

The storage efficiency takes a value between 0 and $\Gamma$, and is inversely proportional to the dimensionless plume footprint, i.e., for a given volume of CO$_2$ injected, a larger footprint corresponds to less efficient storage.

The storage efficiency can be readily evaluated from the solution to the migration equation as a function of $N_s/N_f$, $\mathcal{M}$, and $\Gamma$, and this can be done quickly and comprehensively over a large range of parameters owing to the analytical nature of the solution (Figure 2-18).

The shape of the storage efficiency curve has several noteworthy features. The storage efficiency drops to exactly zero at $N_s/N_f = -\mathcal{M}$, although in reality plume motion would be arrested by capillarity as the plume becomes very thin. The plateau of highest efficiency is achieved in case 3, where the plume becomes fully trapped...
Figure 2-18: The storage efficiency, $\varepsilon$, increases with $\Gamma$, decreases with $\mathcal{M}$, and is a nonmonotonic function of $N_s/N_f$. Here, we plot $\varepsilon$ against $N_s/N_f$ for several values of $\Gamma$, as indicated, at $\mathcal{M} = 15$. The black points correspond to the black points on the $N_s/N_f$ line in Figure 2-11. Note that case 5 does not exist for these values of $\mathcal{M}$ and $\Gamma$. Case 5 does not introduce any noteworthy features.

before a shock forms. This case is sufficiently simple that the storage efficiency can be evaluated explicitly, and is given by $\varepsilon_{\text{max}} = \Gamma/\mathcal{M}$ for all of case 3. The flow-only efficiency ($N_s/N_f = 0$) is also known explicitly, and is given by $\varepsilon_f = 2\Gamma^2/[\mathcal{M}\Gamma^2 + (2 - \Gamma)(\mathcal{M} - (1 - \Gamma))]$ (Juanes and MacMinn, 2008; Juanes et al., 2010). The storage efficiency approaches its slope-only value asymptotically from above or below as $N_s/N_f$ becomes large or small, respectively. This quantity does not have a simple analytical expression, but is given to very good approximation by $\varepsilon_s = \Gamma^2/[0.9\mathcal{M} + 0.49]$. This collection of expressions, used together with knowledge of the qualitative shape of the storage efficiency curves shown in Figure 2-18, is sufficient to quickly and easily estimate the storage efficiency for any particular values of $N_s/N_f$, $\mathcal{M}$, and $\Gamma$.

It is clear that storage efficiency always decreases with $\mathcal{M}$. This is because increasing $\mathcal{M}$ strengthens the "tonguing" of the plume during both injection and post-injection migration. These long, thin layers of CO$_2$ slow residual trapping and therefore reduce storage efficiency. Similarly, the storage efficiency always increases with $\Gamma$.  

58
This is because more CO$_2$ is left behind upon imbibition, and so the plume becomes fully trapped over a shorter migration distance.

In this Chapter, we have presented a gravity-current model for CO$_2$ migration and residual trapping in a sloping saline aquifer with a natural groundwater through-flow, accounting for the tongued end-of-injection plume shape. We have developed a complete analytical solution to the model in its hyperbolic limit, and we that the migration behavior depends strongly on the mobility ratio, the amount of residual trapping, and the importance of aquifer slope relative to groundwater flow. In particular, we have explored how groundwater flow, aquifer slope, and residual trapping interact to determine the overall storage efficiency, a measure of the fraction of the aquifer pore space that can be used to store CO$_2$, and we showed that the interplay between groundwater flow and aquifer slope can change the storage efficiency by a factor of two to five. In particular, we found that the maximum efficiency is achieved in sloping aquifers with a moderate down-dip groundwater flow, conditions which are known to occur in many continental sedimentary basins (Carven, 1995).

In the next Chapter, we incorporate solubility trapping due to convective dissolution into the migration model, and we study the interactions between residual and solubility trapping and the impact of solubility trapping on the storage efficiency.
Chapter 3

Residual and solubility trapping

In Chapter 2, we presented a gravity-current model for the migration and residual trapping of a buoyant plume of CO$_2$ in a confined, sloping aquifer with a natural groundwater through-flow. We did not consider solubility trapping in Chapter 2, but CO$_2$ is weakly soluble in groundwater and both residual and mobile CO$_2$ will dissolve slowly into the nearby groundwater as the plume migrates. Dissolved CO$_2$ is considered trapped because it is no longer buoyant: water with dissolved CO$_2$ is denser than either water or free-phase CO$_2$. As a result, the boundary layer of CO$_2$-saturated groundwater near the buoyant plume of mobile CO$_2$ is unstable, and this unstable density stratification eventually results in so-called convective dissolution, where fingers of dense, CO$_2$-rich groundwater sink away from the interface as fingers of fresh groundwater rise upward.

The convective-dissolution instability has been studied in various contexts. For example, Elder (1968) considered heat transfer in a porous medium heated from below, and Wooding et al. (1997a,b) considered salt transport in a porous medium with a salt source at the top. The implications of this process for geological CO$_2$ storage were first pointed out by Weir et al. (1996) and discussed by Lindeberg and Wessel-Berg (1997). Several studies have since investigated the onset of the instability for a stationary layer of CO$_2$ overlying water. Riaz et al. (2006) performed a linear stability analysis, and used high-resolution numerical simulations to study the early-time nonlinear development of the fingers. Ennis-King and Paterson (2005) and
Ennis-King et al. (2005) showed that permeability anisotropy slows the onset of the instability, and Hidalgo and Carrera (2009) showed that hydrodynamic dispersion can speed the onset of the instability. Rapaka et al. (2008, 2009) studied the onset of the instability using non-modal stability theory, and used these techniques to investigate onset in the context of anisotropic and layered porous media. Slim and Ramakrishnan (2010) studied the onset of convective dissolution in an aquifer of finite thickness, and explored two different types of boundary condition at the CO₂-water interface. In all cases, the onset time for convective dissolution was found to be short relative to timescales of interest in geological CO₂ storage.

Ennis-King and Paterson (2005) predicted by a simple scaling analysis that convective dissolution dramatically increases the rate of solubility trapping compared to diffusive transport, and noted that the small-scale features of convective dissolution would likely necessitate an upscaled model for solubility trapping at the basin scale. Pau et al. (2010) and Neufeld et al. (2010) used high-resolution numerical simulations to study macroscopic features of the convective-dissolution process, showing that the time-averaged rate of CO₂ solubility trapping due to convective dissolution is approximately constant. Kneafsey and Pruess (2010), Neufeld et al. (2010), and Backhaus et al. (2011) have confirmed this experimentally. By taking advantage of these results, an upscaled model for solubility trapping due to convective dissolution can be incorporated into models for CO₂ migration at large scales (Gasda et al., 2011).

Here, we incorporate a simple upscaled model for solubility trapping due to convective dissolution into the theoretical model presented in Chapter 2. We develop semi-analytical solutions to the new model in two limiting cases—when the water beneath the plume saturates with dissolved CO₂ very slowly or very quickly (“instantaneously”) relative to plume motion—and we solve it numerically in general. We use these solutions to study the importance of solubility trapping relative to residual trapping during post-injection migration, and the impact of solubility trapping on the migration behavior and the storage efficiency. We show that solubility trapping can greatly slow the speed at which the plume advances, and we derive an explicit analytical expression for the position of the nose of the plume as a function of time. We
then study the competition between residual and solubility trapping, and the impact of solubility trapping on the storage efficiency. We show that solubility trapping plays a major role in CO$_2$ migration, and can increase the storage efficiency by several fold even when the fraction of CO$_2$ trapped by solubility trapping is small. These results are published in the *Journal of Fluid Mechanics* (MacMinn et al., 2011).

In §3.1, we review the model for CO$_2$ migration without solubility trapping. In §3.2, we develop the model for solubility trapping due to convective dissolution. In §3.3, we present the model for CO$_2$ migration with solubility trapping. In §3.4, we develop semi-analytical solutions to the model in some limiting cases. In §3.5, we use the model and solutions to study the competition between residual and solubility trapping, and their impact on migration.

### 3.1 Model for CO$_2$ injection and migration

As in Chapter 2, we are interested in CO$_2$ injection and migration at the scale of a geologic basin because large quantities of CO$_2$ would need to be stored in order to significantly reduce atmospheric emissions (Nicot, 2008) (Figure 2-2).

Again assuming line symmetry in the $y$ direction, we model the cross section of the plume in the $x$-$z$ plane. We again adopt a sharp-interface approximation and divide the domain into three regions of uniform fluid saturation with sharp interfaces corresponding to saturation discontinuities (Figure 3-1): Region 1 is the plume of mobile CO$_2$, containing free-phase CO$_2$ and a saturation $S_{wc}$ of connate or residual groundwater; Region 2 is the region from which the plume has receded, containing mobile groundwater and a saturation $S_{gr}$ of residual, free-phase CO$_2$; and Region 3 contains mobile groundwater and now also some dissolved CO$_2$ (Figure 3-1).

With the assumptions above, and neglecting solubility trapping, we derived a conservation law for the local thickness of the plume, $h_1(x, t)$. This can be written

$$
(1 - S_{wc})\phi R \frac{\partial h_1}{\partial t} + \frac{\partial F_g}{\partial x} = 0,
$$

(3.1)
Figure 3-1: After injection stops, the plume of mobile CO$_2$ (dark gray) will migrate due to a combination of groundwater flow and aquifer slope, leaving residual CO$_2$ in its wake (light gray). CO$_2$ will dissolve from the plume by convective dissolution, as indicated by the fingers of dense, CO$_2$-rich groundwater (blue) falling away from the plume. We divide the domain into three regions of uniform CO$_2$ and groundwater saturation, separated by sharp interfaces corresponding to saturation discontinuities: Region 1 (dark gray) contains mobile CO$_2$ and a saturation $S_{mc}$ of connate (residual) groundwater; Region 2 (light gray) contains mobile groundwater and a saturation $S_{gr}$ of residual CO$_2$; Region 3 (white, blue) contains mobile groundwater with some dissolved CO$_2$. 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. As in Chapter 2, the $x$ and $z$ coordinates are tilted with the aquifer.
where

\[ F_g(h_1(x, t)) = Q_f + (1 - S_{wc})\phi\kappa \sin \theta (1 - f) h_1 \]

\[- (1 - S_{wc})\phi\kappa \cos \theta (1 - f) h_1 \frac{\partial h_1}{\partial x} \]  

(3.2)

is the total horizontal flow of CO\textsubscript{2} through the plume at some position \(x\) and time \(t\). All quantities are as defined in §2.1.

We did not derive the conservation law for the layer of water beneath the plume in Chapter 2 because without solubility trapping it is redundant: since the layer of water has thickness \(h_w = h_2 + h_3 = H - h_1\), we need only solve Equation (3.2). However, this second conservation law will be useful when we include solubility trapping (§3.2.4). It is readily derived from conservation of mass, or by rewriting Equation (3.1) in terms of \(h_w\):

\[ (1 - S_{wc})\phi R \frac{\partial h_w}{\partial t} + \frac{\partial F_w}{\partial x} = 0, \]

(3.3)

where

\[ F_w(h_1(x, t)) = Q (1 - f) - (1 - S_{wc})\phi\kappa \sin \theta (1 - f) h_1 \]

\[ + (1 - S_{wc})\phi\kappa \cos \theta (1 - f) h_1 \frac{\partial h_1}{\partial x} \]

(3.4)

is the total horizontal flow of groundwater at position \(x\) and time \(t\), and \(Q = F_g + F_w\) is the total horizontal flow of fluid through the aquifer.

### 3.2 Model for solubility trapping due to convective dissolution

We now consider solubility trapping of CO\textsubscript{2} from the mobile plume due to convective dissolution. We denote by \(\chi_m\) the maximum or saturated mass fraction of dissolved CO\textsubscript{2} in groundwater. We denote by \(\rho_d\) the density of groundwater containing mass fraction \(\chi_m\) of dissolved CO\textsubscript{2}. It is convenient here to work in terms of a volume
(a) and (b)

Figure 3-2: We assume that total fluid volume is conserved as CO₂ dissolves into groundwater. Consider (a) a closed box containing a volume \( V_g \) of free-phase CO₂ (dark gray) and a volume \( V_w \) of groundwater (white). We assume that a volume \( \delta V_g \) of the CO₂ then dissolves into the groundwater to form (b) a volume \( V_d = V_w + \delta V_g \) of groundwater with dissolved CO₂ (blue), and the total fluid volume within the box is unchanged. This assumption violates conservation of mass, introducing a relative error of size \( \chi_v \) into the mass balance, but we adopt it for simplicity. To eliminate this error would require a complete treatment of the kinetics and thermodynamics of the CO₂-water system. The saturated volume fraction \( \chi_v \) (Equation 3.5) is here

\[
\chi_v = \frac{\delta V_g}{V_d},
\]

which measures the equivalent free-phase volume of CO₂ dissolved per unit volume of groundwater saturated with dissolved CO₂. The values of \( \chi_m \) and \( \chi_v \) depend strongly on the aquifer temperature and pressure, and on the salinity of the groundwater. Typical values of \( \chi_v \) range from 0.03 to 0.1 (García, 2001; Bachu, 2003; Duan and Sun, 2003; Kharaka and Hanor, 2003; Carbon Capture and Sequestration Technologies @ MIT, 2010). We take \( \chi_v \) to be constant within a given aquifer.

We assume that total fluid volume is conserved as free-phase CO₂ dissolves into groundwater (Figure 3-2). This assumption introduces a relative error in the mass balance of size \( \chi_v \), but we adopt it for simplicity. To eliminate this error would require a complete treatment of the kinetics and thermodynamics of the CO₂-water system.

### 3.2.1 Onset time for convective dissolution

It has been shown from linear stability analysis (Ennis-King and Paterson, 2005; Riaz et al., 2006; Pau et al., 2010) that the onset time for convective dissolution can be
written
\[ t_{\text{onset}} = \alpha_0 D_{\text{eff}} \left( \frac{\phi}{\Delta \rho_d g k \lambda_w^3} \right)^2, \]  
(3.6)

where \( \Delta \rho_d = \rho_d - \rho_w \) is the density difference that drives convective dissolution and \( \alpha_0 \sim 10^3 \) is a dimensionless constant (Pau et al., 2010). \( D_{\text{eff}} \) is the effective diffusion/dispersion coefficient for CO\(_2\) in brine in the aquifer rock; velocity-dependent dispersion can speed the onset of the instability (Hidalgo and Carrera, 2009), but is not included here. We compare this time to the time it would take the leading edge of the CO\(_2\) plume to travel one characteristic length in the horizontal direction during migration due to groundwater flow or aquifer slope (Juanes and MacMinn, 2008; Hesse et al., 2008; MacMinn et al., 2010),

\[ t_{\text{flow}} = \frac{Q_i T_i / 2}{M U_n H}, \quad t_{\text{slope}} = \frac{Q_i T_i / 2}{\Delta \rho g k \lambda_1^g H \sin \vartheta}. \]  
(3.7)

When \( t_{\text{onset}}/t_{\text{flow}} \ll 1 \) and \( t_{\text{onset}}/t_{\text{slope}} \ll 1 \), the onset time for convective dissolution is negligible compared to typical migration timescales, meaning that convective dissolution begins instantaneously along the entire plume in post-injection migration. We assume here that this is always the case.

### 3.2.2 Rate of solubility trapping due to convective dissolution

We denote the upscaled mass flux of solubility trapping due to convective dissolution by \( q_d^m \). In principle, this flux is a function of the details of the complex convective flow beneath the plume. It is natural to expect that this flux should scale with the characteristic speed \( \kappa_d \) at which fingers of heavy water sink away from the plume,

\[ \kappa_d = \frac{\Delta \rho_d g k \lambda_w^w}{\phi}, \]  
(3.8)

and with the concentration of CO\(_2\) carried by those fingers, \( \rho_d \chi_m \) (e.g., Ennis-King and Paterson, 2005). The results of Pau et al. (2010) confirm this scaling, showing that the time-average of the mass flux is essentially constant after some relatively
short onset time, and can be estimated as

\[ q_d^m = \alpha \rho_d \chi_m \phi \kappa_d, \quad (3.9) \]

where \( \alpha \approx 10^{-2} \) is a dimensionless constant. The volume flux \( q_d \) of CO\(_2\) leaving the mobile plume due to convective dissolution can then be written

\[ q_d = q_d^m / \rho_g = \alpha \chi_v \phi \kappa_d. \quad (3.10) \]

We expect this expression to be valid until the water beneath the plume begins to saturate with dissolved CO\(_2\), at which time the rate of solubility trapping should decrease. For simplicity, we account for this saturating effect by setting the rate of solubility trapping to zero at each position \( x \) when the water at that position becomes completely saturated with dissolved CO\(_2\). For this purpose, we track the thickness \( h_d(x, t) \) of the ‘curtain’ of water with dissolved CO\(_2\) that builds beneath the plume (i.e., the blue region in Figure 3-1). We set the rate of solubility trapping to zero when the water beneath the plume is completely saturated, i.e., when \( h_1 + h_d = H \). We discuss the curtain in §3.2.4.

### 3.2.3 Solubility trapping and residual trapping

Solubility trapping enters the mass balance as a loss term \( \mathcal{L} < 0 \) on the right-hand side of Equation (3.1),

\[ (1 - S_{wc}) \phi \tilde{R} \frac{\partial h_1}{\partial t} + \frac{\partial F_g}{\partial x} = \mathcal{L} \quad (3.11) \]

where \( F_g \) is as defined in Equation (3.2). When \( \partial F_g / \partial x = 0 \), Equation (3.11) implies that the interface retreats at characteristic speed \( \mathcal{L} / (1 - S_{wc}) \phi \tilde{R} \). Equation (2.5) gives \( \tilde{R} = 1 - \Gamma \) in this scenario since \( \partial h_1 / \partial t < 0 \), but we argue that residual trapping should not contribute to the speed of the interface here because residual CO\(_2\) should also dissolve as the interface is displaced upward. We further argue that when \( \partial F_g / \partial x > 0 \) such that the interface retreats faster than by solubility trapping alone, it is only this flow-driven component of imbibition that contributes to residual
trapping (Figure 3-3). This motivates the definition,

\[
\mathcal{L} = \begin{cases} 
-\tilde{R} (1 - S_{wc}) q_d & \text{if } h_d < H - h_1, \\
0 & \text{otherwise},
\end{cases}
\]

where the rate of solubility trapping is reduced by \((1 - S_{wc})\) because the presence of the connate water reduces the CO\(_2\)-water interfacial area by this amount, and \(\mathcal{L} \to 0\) where the water beneath the plume is saturated (§3.2.4). We include \(\tilde{R}\) in \(\mathcal{L}\) so that interface displacements due to solubility trapping do not contribute to residual trapping. We also modify the definition of \(\tilde{R}\),

\[
\tilde{R} = \begin{cases} 
1 & \text{if } \partial h_1 / \partial t > -q_d / \phi \text{ and } h_2 = 0, \\
1 - \Gamma & \text{otherwise.}
\end{cases}
\]

Again, this is physically motivated by the expectation that residual CO\(_2\) must also dissolve as the interface is displaced unless the interface moves faster than by solubility trapping alone (Figure 3-3). These definitions effectively decouple the processes of residual and solubility trapping.

### 3.2.4 The curtain of water with dissolved CO\(_2\)

We assume that a layer of fully-saturated water builds beneath the plume as CO\(_2\) dissolves. We denote the thickness of this ‘curtain’ of water with dissolved CO\(_2\) by \(h_d(x, t)\). We write the conservation law for the thickness of the curtain as

\[
\chi_v \phi \frac{\partial h_d}{\partial t} + \chi_v \frac{\partial F_d}{\partial x} = -\frac{\mathcal{L}}{\tilde{R}} - \chi_v S_{wc} \phi \frac{\partial h_1}{\partial t} - \frac{1 - \tilde{R}}{\tilde{R}} \frac{\partial F_g}{\partial x},
\]

where \(F_d\) is the total horizontal flow of groundwater with dissolved CO\(_2\) through the curtain. The curtain gains volume due to convective dissolution via the term \(-\mathcal{L}/\tilde{R}\), where we divide by the conditional coefficient \(\tilde{R}\) because dissolution of residual CO\(_2\) at the imbibition front also contributes to the curtain (c.f., §3.2.3). The curtain either gains or loses volume as connate water is left behind by the plume or swept into
Figure 3-3: We assume that interface displacements due to solubility trapping do not contribute to residual trapping (§3.2.3). Here, we consider this modeling choice in the context of three possible scenarios for local interface displacement. The local position of the CO₂-water interface is shown before (solid black line) and after (shaded dark gray) displacement due to solubility trapping and flux of mobile CO₂ through the plume. Although these processes occur simultaneously, we suppose for illustration that they occur sequentially. We suppose that solubility trapping occurs first, displacing the interface from its original position (solid black line) to a hypothetical intermediate position (solid blue line), as indicated (vertical blue arrow). We then consider the net flux of mobile CO₂ through this portion of the plume. (a) When the flux of mobile CO₂ into this portion of the plume (small, horizontal black arrow) is less than the flux of mobile CO₂ out of this portion of the plume (large, horizontal black arrow), the net flux is negative and the interface retreats (vertical black arrow) to its final position (shaded light gray). Solubility trapping enhances imbibition in this scenario, but we assume that the component of interface motion due to solubility trapping (vertical blue arrow) does not cause additional residual trapping. (b) When the net flux is positive and large, the interface experiences net drainage as the interface advances to its final position and no residual trapping occurs. (c) When the net flux is positive and small, the interface may experience net imbibition. However, we assume that no residual trapping occurs because any residual CO₂ would dissolve as the water imbibes. As a result of this modeling choice, residual and solubility trapping are effectively decoupled locally.
the plume during imbibition or drainage, respectively, via the term proportional to $S_{wc}$. We assume that all connate water is supplied from the curtain, and is therefore fully saturated with dissolved CO$_2$ before entering the plume. This is a very good assumption in most cases, but will lead to an underestimate of the rate of solubility trapping when the amount of connate water swept into the plume at the drainage front exceeds the volume of saturated water available in the curtain. Lastly, residual CO$_2$ in the wake of the plume takes up a fraction of the available pore space, and the curtain gains macroscopic volume as a result via the term proportional to $\partial F_g/\partial x$. This term vanishes on portions of the interface that are in drainage.

The curtain is a subset of the groundwater region, so the total horizontal flow of water through the curtain is simply a fraction of the total horizontal flow of groundwater, $F_d = (h_d/h_w)F_w$. We neglect the migration of the dense curtain relative to the ambient groundwater because this occurs with characteristic velocity $\kappa_d \ll \kappa$, much slower than the characteristic velocity of CO$_2$ migration.

Equations (3.1) and (3.14) are coupled through the loss term $\mathcal{L}$, so we must solve them simultaneously. We discuss this in §3.4.

We emphasize that this model for solubility trapping features several key simplifications. First, we have assumed that convective dissolution ends abruptly when the water becomes saturated, rather than decreasing gradually. This assumption is reasonable if the rate of solubility trapping decreases quickly to zero as the water saturates; we adopt it here for simplicity, and because we believe it captures the essential dissolution-limiting feature of the finite amount of water beneath the plume. Second, we have assumed that the curtain of water with dissolved CO$_2$ builds beneath the plume as a layer fully saturated water. Third, we have not accounted for dissolution of the residual CO$_2$ except immediately at the imbibition front. This is motivated by the fact that residual CO$_2$ is located primarily in the wake of the plume, so we do not expect it to impact the migration or solubility trapping of the mobile plume. Fourth, we have neglected lateral spreading of the dense, CO$_2$-rich groundwater relative to the ambient groundwater. This is motivated by the fact that the CO$_2$ plume spreads and migrates much faster than this water. The importance of these effects has not
yet been studied, but our emphasis here is on deriving insight from a simple but physically reasonable model and we do not expect these effects to have an order-one impact on our results.

3.3 Model for CO$_2$ migration with residual and solubility trapping

We now incorporate the model for solubility trapping (Equations 3.12 and 3.13) into the model for CO$_2$ migration (Equations 3.1 and 3.14). The complete model for CO$_2$ migration with residual and solubility trapping consists of two coupled conservation laws, one for the buoyant plume of mobile CO$_2$ and the other for the curtain of water saturated with dissolved CO$_2$. We write them in dimensionless form,

\[ \tilde{R} \frac{\partial \eta}{\partial \tau} + N_f \frac{\partial f}{\partial \xi} + N_s \frac{\partial}{\partial \xi} \left[ (1-f) \eta \right] - N_g \frac{\partial}{\partial \xi} \left[ (1-f) \eta \frac{\partial \eta}{\partial \xi} \right] = -\tilde{R} N_d, \tag{3.15} \]

and

\[ \frac{\partial \eta_d}{\partial \tau} + (1-S_{wc})N_f \frac{\partial f_d}{\partial \xi} - (1-S_{wc})N_g \frac{\partial}{\partial \xi} \left[ f_d \eta \right] + (1-S_{wc})N_g \frac{\partial}{\partial \xi} \left[ f_d \eta \frac{\partial \eta}{\partial \xi} \right] \]
\[ = \frac{N_d}{\Gamma_d} - S_{wc} \frac{\partial \eta}{\partial \tau} - (1-\tilde{R}) \left( \frac{\partial \eta}{\partial \tau} + N_d \right). \tag{3.16} \]

The primary variables are $\eta = h_1/H$, which is the local thickness of the plume of CO$_2$ scaled by the thickness of the aquifer, and $\eta_d = h_d/H$, which is the local thickness of the curtain of water saturated with dissolved CO$_2$, again scaled by the thickness of the aquifer. The nonlinear functions $f$ and $f_d$ are given by

\[ f(\eta) = \frac{\mathcal{M} \eta}{\mathcal{M} \eta + (1-\eta)}, \quad f_d(\eta, \eta_d) = \frac{\eta_d}{\mathcal{M} \eta + (1-\eta)}, \tag{3.17} \]

where $\mathcal{M} = \lambda^s_\eta / \lambda^w_\eta$ is the mobility ratio. These functions reflect the fact that the aquifer is confined, so that the plume of CO$_2$ must displace the ambient fluid (groundwater) in order to migrate.
The dimensionless time is \( \tau = t/T \), where \( T \) is an appropriate characteristic time. The dimensionless \( x \)-coordinate is \( \xi = x/L \), where \( L \) is an appropriate characteristic length. We discuss the specific choice of these characteristic values for the injection period in §3.3.1, and for the post-injection period in §3.3.2.

The model includes residual and solubility trapping, migration due to groundwater flow and aquifer slope, and buoyant spreading against the caprock. The conditional coefficient \( \tilde{\mathcal{R}} \) captures residual trapping, changing value depending on whether the interface is locally in drainage or imbibition,

\[
\tilde{\mathcal{R}} = \begin{cases} 
1 & \text{if } \partial \eta/\partial \tau > -N_d, \\
1 - \Gamma & \text{otherwise.}
\end{cases}
\]  

The residual trapping number \( \Gamma \) measures the amount of residual fluid that is left behind as the interface recedes during imbibition.

Both conservation laws have three flux terms, with coefficients \( N_f, N_s, \) and \( N_g \). These terms capture migration due to groundwater flow, migration due to aquifer slope, and buoyant spreading due to gravity, respectively. The coefficients are given by

\[
N_f = \frac{T}{T_i} \frac{Q}{Q_i/2}, \quad N_s = \frac{T}{L} \kappa \sin \vartheta, \quad N_g = \frac{T}{L} \kappa \cos \vartheta \frac{H}{L},
\]  

where \( L \) is the characteristic length (Equation 3.21), \( T \) is the characteristic time (§3.3.1 and §3.3.2), and \( Q \) is the net volume flow of fluid through the aquifer from left to right (§3.3.1 and §3.3.2). \( \kappa \) is the characteristic buoyancy-driven velocity of the plume (Equation 2.8).

The sink term with coefficient \( N_d \) on the right-hand side of Equation (3.15) captures the loss of CO\(_2\) from the plume due to solubility trapping via convective dissolution. \( N_d \) is given by

\[
N_d = \begin{cases} 
\alpha \chi_v \kappa_d \frac{T}{H} & \text{if } \eta(\xi, \tau) > 0 \text{ and } \eta_d(\xi, \tau) < (1 - \eta(\xi, \tau)), \\
0 & \text{otherwise,}
\end{cases}
\]  

[73]
taking a constant value until the water beneath the plume becomes saturated with
dissolved CO$_2$, and changing to zero locally as the water saturates. We assume that
the water beneath the plume is locally saturated with dissolved CO$_2$ when the curtain
of water saturated with dissolved CO$_2$ reaches the bottom of the aquifer ($\eta + \eta_d = 1$).

The curtain grows as CO$_2$ dissolves from the plume. Each unit volume of CO$_2$
that dissolves from the plume becomes $1/\Gamma_d$ units of volume in the curtain, where
the constant $\Gamma_d = \chi_v/(1 - S_{we})$. The curtain also gains and loses volume due to the
transfer of residual CO$_2$ and connate (residual) water across the CO$_2$-water inter-
face as the plume migrates (§3.2.4); the source/sink terms on the right-hand side of
Equation (3.16) account for these effects.

Without loss of generality, we choose $N_f \geq 0$ so that groundwater flow is al-
ways to the right by convention. Aquifer slope can be either positive ($N_s > 0$) for
clockwise aquifer tilt or negative ($N_s < 0$) for clockwise aquifer tilt.

3.3.1 The injection period

During injection, we assume that a constant volume flow rate $Q_i$ of CO$_2$ per unit
length of the line-drive well array is pumped into the aquifer. We take the character-
istic timescale to be the duration of injection, $T = T_i$, so that $\tau = 1$ is the end of the
injection period.

As in Chapter 2, we choose the characteristic length scale during injection to be
the length of a rectangle of aquifer of height $H$ and containing a volume equal to
one-half of the total volume of CO$_2$ to be injected, $Q_i T_i / 2$:

$$L = Q_i T_i / 2 (1 - S_{we}) \phi H.$$ (3.21)

Injection typically dominates the flow, so we neglect natural groundwater flow and
slope relative to injection and assume that the flow rate $Q_i$ is split evenly between the
left and right sides of the injection well. We then have that $Q = U_n H + Q_i / 2 \approx Q_i / 2$,
so that

\[ N_i^{i} = 1, \quad N_s^{i} = \frac{\Delta \rho g k \lambda_1^2 H}{Q_i/2} \sin \theta, \quad N_g^{i} = \frac{\Delta \rho g k \lambda_1^2 (1 - S_{wc}) \phi H^3}{(Q_i/2)^2 T_i} \cos \theta, \quad (3.22) \]

and

\[ N_d^{i} = \begin{cases} \alpha \chi \kappa_d \frac{T_i}{H} & \text{if } \eta(\xi, \tau) > 0 \quad \text{and} \quad \eta_d(\xi, \tau) < (1 - \eta(\xi, \tau)), \\ 0 & \text{otherwise.} \end{cases} \quad (3.23) \]

The superscript \( i \) indicates that these are the values of these parameters during injection. Typically \( N_s^{i}, N_g^{i} \ll 1 \), so the plume shape will be symmetric across the injection well. We discuss the impact of solubility trapping during injection in §3.4.1.

### 3.3.2 Post-injection migration

Once injection has stopped, the net flow of fluid through the aquifer, \( Q \), is due only to natural groundwater flow. We therefore have that \( Q = U_n H \) in the post-injection period.

The characteristic length scale from the injection period was based on the total amount of \( CO_2 \) injected (Equation 3.21). This is also an appropriate choice for the post-injection period because it is characteristic of the initial length of the now-migrating plume, so we retain it.

The characteristic time scale from the injection period was the injection time. This is not an appropriate choice for the post-injection period because \( CO_2 \) migration due to slope and/or groundwater flow is typically very slow relative to injection. In order to choose a new characteristic time while keeping \( \tau = 1 \) as the end of injection, we redefine the dimensionless time in post injection as

\[ \tau = 1 + \frac{t - T_i}{T} \quad (3.24) \]

so that the end of injection, \( t = T_i \), corresponds to \( \tau = 1 \) for any choice of characteristic time \( T \). A characteristic time for post-injection can be derived from any
one of the four rates associated with post-injection migration and trapping: the rate of migration due groundwater flow, the rate of migration due to aquifer slope, the rate of buoyant spreading against the caprock, or the rate of solubility trapping due to convective dissolution. For a specific aquifer, the choice should be guided by the dominant mechanism. When no one mechanism is dominant, which is often the case in continental sedimentary basins (Garven, 1995), the specific choice is arbitrary.

Here, we choose a characteristic time based on the rate of migration due to groundwater flow:

\[ T = \frac{Q_i T_i / 2}{U_n H}. \]  

(3.25)

For this choice, we have that (Equations 3.19 and 3.20 with \( Q = U_n H \) and \( T = Q_i T_i / 2 U_n H \))

\[ N_f = 1, \quad N_s = \frac{\Delta \rho g k \lambda^3}{U_n} \sin \vartheta, \quad N_g = \frac{\Delta \rho g k \lambda^3 (1 - S_{vc}) \phi H^2}{U_n (Q_i / 2) T_i} \cos \vartheta \]  

(3.26)

and

\[ N_d = \begin{cases} 
\alpha X_v \kappa_d \frac{Q_i T_i / 2}{U_n H^2} & \text{if } \eta(\xi, \tau) > 0 \text{ and } \eta_d(\xi, \tau) < (1 - \eta(\xi, \tau)), \\
0 & \text{otherwise.} 
\end{cases} \]  

(3.27)

Here, \( N_s \) gives the importance of advection due to slope relative to that due to groundwater flow; \( N_g \) gives the importance of diffusive spreading due to buoyancy relative to advection due to groundwater flow, mathematically analogous to the inverse of a Peclet number; and \( N_d \) gives the importance of loss due to solubility trapping relative to advection due to groundwater flow, analogous to a Damköhler number in reactive transport.

A consequence of this choice of characteristic time is that \( N_f \equiv 1 \). We retain \( N_f \) in the analysis (§3.4) and report our results (§3.5) in terms of the ratios \( N_s / N_f, N_g / N_f, \) and \( N_d / N_f \) so that the results remain relevant for other choices of the characteristic time.

The choice of a characteristic time based on groundwater flow will not be appro-
appropriate when groundwater flow is "weak" compared to slope, buoyancy, or solubility trapping. In these cases, a different characteristic time should be used in Equations (3.19) and (3.20) to derive the appropriate expressions for $N_f$, $N_s$, $N_g$, and $N_d$.

### 3.4 Injection and migration with residual and solubility trapping

We now study injection and post-injection migration with residual and solubility trapping. We note that the macroscopic features of CO$_2$ migration and trapping—in particular, the prominent gravity tongue, the position of the leading edge, and the shape of the profile of residual gas—are little affected by even large values of $N_g$ compared to $N_f$ or $N_s$ (Juanes and MacMinn, 2008; Hesse et al., 2008). We therefore neglect the buoyant spreading term to simplify the analysis, as in Chapter 2 (Figure 2-4). In this limit, Equations (3.15) and (3.16) are of hyperbolic character.

After neglecting the spreading term, it will be useful to rewrite Equation (3.15) in terms of a scaled and shifted dimensionless plume thickness $g$, as in Chapter 2,

$$\frac{\partial g}{\partial \tau} + \frac{1}{R} \frac{\partial}{\partial \xi} G(g) = -(M - 1)N_d,$$  \hspace{1cm} (3.28)

where $g = (M - 1)\eta + 1$ remaps $0 \leq \eta \leq 1$ to $1 \leq g \leq M$, and $G$ is the corresponding flux function,

$$G(g) = MN_f \left[1 - \frac{1}{g}\right] + \frac{N_s}{M - 1} \left[(M + 1) - g - \frac{M}{g}\right].$$  \hspace{1cm} (3.29)

Equation (3.28) is a first-order, nonlinear, autonomous, hyperbolic conservation law with a loss term. The solution to this equation depends on seven dimensionless parameters: $M$, $\Gamma$, $\Gamma_d$, $S_{wc}$, $N_f$, $N_s$, and $N_d$. One of the latter three parameters can always be subsumed into the characteristic timescale, so the solution depends uniquely only on the ratios of any two of them to the third. For generality, we retain all three parameters in the analysis that follows; however, we present the results (§3.5)
in terms of the ratios $N_e/N_f$ and $N_d/N_f$ because we choose a characteristic timescale based on groundwater flow ($§3.3.2$).

Note that the values of $\mathcal{M}$ and $\Gamma$ used in the figures throughout this section (Figures 2-5–3-7) are chosen for illustration only, to make the noteworthy features of the plume shapes and characteristics clearly visible. In practice, these values of $\mathcal{M} = 2$ and $\Gamma = 0.5$ are too low and too high, respectively. We use realistic values of $\mathcal{M} = 5–15$ and $\Gamma = 0.3$ when presenting the key results in $§3.5$ (Figures 3-8–3-11).

3.4.1 The injection period

We derive here the shape of the plume at the end of the injection period, because this serves as the initial condition for post-injection migration (Juanes and MacMinn, 2008; MacMinn and Juanes, 2009; Juanes et al., 2010).

As discussed in $§3.3.1$, we assume that injection dominates the flow during the injection period, and we therefore take $N^i_j = 1$ and $N^i_g, N^i_g \ll 1$. As a result, the injected $\text{CO}_2$ is split evenly between the left and right sides of the injection well and the plume shape is symmetric across the injection well.

To assess the impact of solubility trapping on the plume shape during injection, we compare the rate of $\text{CO}_2$ injection, $Q_i$, to an estimate of the rate of solubility trapping, $Q_d$. The upscaled rate of solubility trapping per unit length of $\text{CO}_2$-water interface is $(1 - S_{wc})q_d$ ($§3.2.2$). Without solubility trapping, the extent of the plume at the end of injection is $2\mathcal{M}Q_iT_i/(1 - S_{wc})\phi H$ ($§2.2.1$). We then estimate

$$
\frac{Q_d}{Q_i} \sim \frac{q_d \mathcal{M}Q_iT_i}{\phi H Q_i} = \mathcal{M} N^i_d.
$$

Taking typical but conservative values, $\mu_w = 5.5 \times 10^{-4}$ Pa·s, $\mu_g = 6 \times 10^{-5}$ Pa·s, $\chi_v = 0.1$, $S_{wc} = 0.4$, $\phi = 0.15$, $\Delta \rho_d = 10 \text{ kg/m}^3$, $k = 100 \text{ md} = 10^{-13} \text{ m}^2$, $T = T_i = 30$ years, $H = 100$ m, we find that $Q_d/Q_i \sim 10^{-2}$, implying that the fraction of the $\text{CO}_2$ that dissolves during injection is negligible. Note that we have neglected the onset time for convective dissolution as well as the finite supply of water, both of which would decrease the amount of $\text{CO}_2$ that would dissolve during injection. We have also used
the extent of the plume at the end of injection, again giving an overestimate of the amount of CO$_2$ that would dissolve during injection. We therefore conclude that solubility trapping is negligible during injection and we use the injection solution of Nordbotten and Celia (2006) and Verdon and Woods (2007), as in Chapter 2. Modeling the well as a line source located at $\xi = 0$ with strength $Q_i/2H$ per unit length, the solution from the method of characteristics is

$$
\xi^i_L(g, \tau) = -\left( \frac{M}{g^2} \right) \tau, \quad \xi^i_R(g, \tau) = \left( \frac{M}{g^2} \right) \tau, \quad (3.31)
$$

where the left front, $\xi^i_L$, is the reflection of the right front, $\xi^i_R$ (Figure 2-5).

### 3.4.2 Post-injection migration

Once injection has ended, the plume migrates due to slope and groundwater flow, and shrinks due to residual and solubility trapping. The migration behavior is given by the solution to Equations (3.15) and (3.16), which are nonlinear conservation laws coupled by mass transfer due to convective dissolution. These must be solved numerically in general, but we are able to derive semi-analytical solutions in two limiting cases: when the water beneath the plume saturates with dissolved CO$_2$ very slowly or very quickly relative to plume migration (Figure 3-4). When the water beneath the plume saturates with dissolved CO$_2$ slowly relative to plume migration, the curtain does not interact with the bottom of the aquifer. In this slow-saturation limit, Equation (3.28) can be solved independently of Equation (3.16). When the water beneath the plume saturates with dissolved CO$_2$ very quickly relative to plume migration, the water beneath the plume will be completely saturated except at the leading edge. In this instantaneous-saturation limit, the majority of the plume will not experience solubility trapping as it migrates and Equation (3.28) can again be solved independently of Equation (3.16). Below, we develop semi-analytical solutions to Equation (3.28) in these two limits.
Figure 3-4: The rate at which the water beneath the plume saturates with dissolved CO₂ depends on the speed of migration, the length of the plume, the rate of solubility trapping, and the amount of dissolved CO₂ the water can hold. Here we show the shape of the plume (dark gray) and the curtain (blue) at \( t = 2.5 \) from numerical solutions to (3.15) and (3.16) for fixed \( M = 2, \Gamma = 0.5, \Gamma_d = 0.1, N_f = 1, N_s = -0.75, N_g = 0 \), and for \( N_d \) increasing from 0 to 4, as indicated. Where the curtain reaches the bottom of the aquifer, convective dissolution has stopped because the water is saturated. We identify two limits: (b) when the water saturates slowly relative to plume migration, solubility trapping is not limited by the amount of water beneath the plume, and (d) when the water saturates very quickly (instantaneously) relative to plume migration, the water beneath the plume is completely saturated with dissolved CO₂ and only the leading edge of the plume dissolves as it migrates.

3.4.3 The slow-saturation limit

When the water beneath the plume saturates with dissolved CO₂ slowly compared to plume motion, solubility trapping from the plume is not limited by the supply of water and Equation (3.28) can be solved independently of Equation (3.16). In this limit, we develop semi-analytical solutions to Equation (3.28) via the method of characteristics. Note that CO₂ migration becomes independent of \( \Gamma_d \) in this limit because the water does not saturate. All of the expressions and results for this limit simplify to those from Chapter 2 when \( N_d = 0 \).

Post-injection migration in the slow-saturation limit

We begin with Equation (3.28), moving the loss term inside the time derivative,

\[
\frac{\partial}{\partial \tau} \left[ g + (M - 1)N_d(\tau - 1) \right] + \frac{1}{\mathcal{K}} \frac{\partial}{\partial \xi} G(g) = 0. 
\]
We then introduce a new variable $g_0$ such that $g = g_0 - (\mathcal{M} - 1)N_d(\tau - 1)$, and we write

$$\frac{\partial g_0}{\partial \tau} + \frac{1}{\mathcal{R}} \frac{\partial}{\partial \xi} \left[ G(g_0 - (\mathcal{M} - 1)N_d(\tau - 1)) \right] = 0. \quad (3.33)$$

Equation (3.33) is a nonlinear hyperbolic conservation law in $g_0$; note that it is not autonomous because $\tau$ appears explicitly in the flux function $G$. The solution is a collection of waves traveling through space-time. Physically, $g_0$ is the thickness of each wave at the end of injection ($g = g_0$ at $\tau = 1$) and this initial thickness is constant in time for each wave. The current thickness of each wave is $g = g_0 - (\mathcal{M} - 1)N_d(\tau - 1)$, which shrinks in time at a constant rate due to solubility trapping. Waves travel with speed $G'/\mathcal{R}$, where

$$G' = \frac{\partial G}{\partial g_0} = -\left[ \frac{1}{\mathcal{M} - 1} N_s \right] + \left[ \mathcal{M} N_f + \frac{\mathcal{M}}{\mathcal{M} - 1} N_s \right] \frac{1}{g_0^2}. \quad (3.34)$$

Note that the velocity at which each wave propagates is a function of its current thickness, and that this function $G'(g)$ is the same as in Chapter 2. Unlike in Chapter 2, waves no longer travel at constant velocity because all waves now shrink in time due to solubility trapping.

As in Chapter 2, the post-injection problem is more difficult than the injection problem because of the complex interactions between slope, groundwater flow, residual trapping, and now solubility trapping—waves collide, and we divide the analysis into parts based on the types of collisions that occur. The derivative of the flux function again changes sign once at the stationary point $g = g_s$ given by

$$g_s = \sqrt{\mathcal{M}(\mathcal{M} - 1)N_f/N_s + \mathcal{M}}, \quad (3.35)$$

and we can again divide the range of possible values of the ratio $N_s/N_f$ into three intervals based on the nature of the resulting plume migration, and these intervals are the same as in Chapter 2 since $G'$ is unchanged. For $N_s/N_f \leq -\mathcal{M}$, the negative-slope-with-weak-flow interval, the flux function is concave up and has a local minimum, so that $G'$ vanishes at $g = g_s$ and is negative for $g < g_s$ and positive for
$g > g_s$. For $-\mathcal{M} < N_s/N_f < 1$, the *flow-with-weak-slope* interval, the flux function is concave up for $N_s/N_f < -(\mathcal{M} - 1)$, linear for $N_s/N_f = -(\mathcal{M} - 1)$, and concave down for $N_s/N_f > -(\mathcal{M} - 1)$, and in all cases strictly increasing so that $G'$ is positive. For $1 \leq N_s/N_f$, the *positive-slope-with-weak-flow* interval, the flux function is concave down and has a local maximum, so that $G'$ vanishes at $g = g_s$ and is positive for $g < g_s$ and negative for $g > g_s$. Note that, unlike in Chapter 2, any single wave is only instantaneously stationary as its current thickness passes through the value $g_s$, which occurs at time

$$\tau_s = 1 + \frac{g_0 - g_s}{(\mathcal{M} - 1)N_d}. \quad (3.36)$$

For simplicity, we restrict our analysis here to the flow-with-weak-slope interval, $-\mathcal{M} < N_s/N_f < 1$, for which $G'$ is strictly positive. Outside of that interval, a stationary point exists on the plume and both fronts have a portion that is in drainage and a portion that is in imbibition. This complicates the solution because waves may change direction as they shrink. That is, drainage waves may at some point become imbibition waves and vice-versa. While the procedure presented below is general and could be used to develop semi-analytical solutions outside of the flow-with-weak-slope interval, the complexity of doing so is prohibitive in practice.

It is straightforward to rewrite the definition of the conditional accumulation coefficient $\tilde{R}$ in terms of $g_0$,

$$\tilde{R} = \begin{cases} 1 & \text{if } \partial g_0/\partial \tau > 0, \\ 1 - \Gamma & \text{otherwise}. \end{cases} \quad (3.37)$$

The direction in which each wave travels (i.e., to the left, or to the right) is again determined by the sign of $G'(g)$, and this in turn sets the appropriate value of $\tilde{R}$ for each wave. Waves of the left front moving to the left correspond to CO$_2$ displacing groundwater, and are then drainage waves; waves of the left front moving to the right correspond to groundwater displacing CO$_2$, and are imbibition waves. Waves of the right front moving to the left or to the right are similarly imbibition waves or drainage waves, respectively. Note that all waves shrink vertically in time due to
solubility trapping, but this component of imbibition does not contribute to residual trapping by construction of the model (§3.2.3).

Now starting from the end-of-injection shape, all waves propagate to the right at speed $G'(g)/\tilde{R}$ until two or more waves collide. The right front is a drainage front with $\tilde{R} = 1$, and the left front is an imbibition front with $\tilde{R} = (1 - \Gamma)$. Because of this, a given wave on the left front travels faster than the corresponding wave on the right front.

Given the position of each wave at $\tau = 1$ and its instantaneous velocity in post-injection, we can write the position of each wave on the left and right fronts by integrating the velocity in time,

$$\xi_L = -\frac{\mathcal{M}}{g_0^2} + \frac{1}{1 - \Gamma} \left( -\left\lfloor \frac{N_s}{\mathcal{M} - 1} \right\rfloor + \left[ \frac{\mathcal{M} \mathcal{N}_f + \frac{\mathcal{M}}{\mathcal{M} - 1} N_s}{g g_0} \right] (\tau - 1),
\right.$$  

$$\xi_R = \frac{\mathcal{M}}{g_0^2} + \left( -\left\lfloor \frac{N_s}{\mathcal{M} - 1} \right\rfloor + \left[ \frac{\mathcal{M} \mathcal{N}_f + \frac{\mathcal{M}}{\mathcal{M} - 1} N_s}{g g_0} \right] (\tau - 1),
\right.$$  

where, again, $g_0$ is the initial thickness of each wave and $g = g_0 - (\mathcal{M} - 1)N_d(\tau - 1)$ is the current thickness of each wave. These expressions are valid for all waves with current thickness $g > 1 (\eta > 0)$, and that have not yet collided with other waves.

When the current thickness of a wave decreases below $g = 1$, that wave has dissolved completely and ceases to exist. The left and right edges of the plume are then formed by the leftmost and rightmost waves that still exist at time $\tau$. As in Chapter 2, we refer to the position of the leftmost wave on left front and of the rightmost wave on the right front as $\xi_{LL}$ and $\xi_{RR}$, respectively. These positions correspond to the waves with current thickness $g = 1$ and therefore with original thickness $g_0 = 1 + (\mathcal{M} - 1)N_d(\tau - 1)$. These waves do not correspond to characteristics because the characteristics here are waves with constant original thickness and shrinking current thickness. The expressions for $\xi_{LL}$ and $\xi_{RR}$ are readily evaluated from Equations (3.38) for these values of $g$ and $g_0$.

Depending on the shape of the flux function, waves will either accelerate or decelerate as they shrink. When the flux function is concave down ($N_s/N_f > -(\mathcal{M} - 1)$), wave velocity increases monotonically with wave thickness and waves accelerate as
they shrink. Because of this acceleration, the entire left front does not compact into a shock simultaneously. Rather, an incipient shock forms at the leftmost point on the left front, $\xi_{LL}$, and builds from left to right as waves accelerate, until the entire left front is part of the shock. We find the time $\tau_{LL}^\sigma$ at which this incipient shock would form by solving for the time at which $\partial \xi_L / \partial g$ vanishes at the leftmost point. This gives the time of shock formation implicitly,

$$\begin{align*}
(M - 1)^2 N_d^2 (\tau_{LL}^\sigma - 1)^3 + 3(M - 1) N_d (\tau_{LL}^\sigma - 1)^2 \\
+ 2 (\tau_{LL}^\sigma - 1) &= 2 \frac{(1 - \Gamma)(M - 1)}{(M - 1) N_f + N_s}.
\end{align*}$$

(3.39)

With $N_d = 0$, this expression simplifies readily to the time at which the entire left front would compact into a shock in the absence of solubility trapping ($\tau_{LL}^R$ from Equation 2.27a).

Similarly, wave velocity decreases monotonically with wave thickness when the flux function is concave up ($N_s / N_f < - (M - 1)$), and waves decelerate as they shrink. Here, shock formation begins with an incipient shock at the rightmost point on the right front, $\xi_{RR}$, and builds from right to left as waves decelerate, until the entire right front is part of the shock. We find the time $\tau_{RR}^{\sigma}$ at which this incipient shock would form by solving for the time at which $\partial \xi_R / \partial g$ vanishes at the rightmost point. This gives the time of shock formation implicitly,

$$\begin{align*}
(M - 1)^2 N_d^2 (\tau_{RR}^\sigma - 1)^3 + 3(M - 1) N_d (\tau_{RR}^\sigma - 1)^2 \\
+ 2 (\tau_{RR}^\sigma - 1) &= -2 \frac{(M - 1)}{(M - 1) N_f + N_s}.
\end{align*}$$

(3.40)

With $N_d = 0$, this expression simplifies readily to the time at which the entire right front would compact into a shock in the absence of solubility trapping ($\tau_{RR}^R$ from Equation 2.27c).

In the particular case when the flux function is a straight line ($N_s / N_f = -(M - 1)$), wave speed is independent of wave thickness. The fronts will not change shape as they migrate and dissolve, and no shock will form. Accordingly, Equations (3.39) and
(3.40) degenerate for this value of $N_s/N_f$, and have no solution.

The migration behavior may also change if the rightmost point on the left front, $\xi_{LR}$, collides with the leftmost point on the right front, $\xi_{RL}$, forming a peak. Unlike $\xi_{LL}$ and $\xi_{RR}$, these positions correspond to characteristics: they are the waves with original thickness $g_0 = \mathcal{M}$ and current thickness $g = \mathcal{M} - (\mathcal{M} - 1)N_d(\tau - 1)$. Expressions for $\xi_{LR}$ and $\xi_{RL}$ can be evaluated from Equations (3.38). The time $\tau_{LR}^{RL}$ at which these two waves would collide to form a peak is given implicitly by the expression

$$N_s N_d (\tau_{LR}^{RL} - 1)^2 + \left[ \frac{2(1 - \Gamma)(\mathcal{M} - 1)N_d}{\mathcal{M}\Gamma} + (N_f - N_s) \right] (\tau_{LR}^{RL} - 1) = \frac{2(1 - \Gamma)}{\Gamma}. \quad (3.41)$$

With $N_d = 0$, this expression simplifies to the time at which this collision would occur in the absence of solubility trapping (Equation 2.27b).

What remains is to divide the flow-with-weak-slope interval into cases based on the order in which these collisions occur. We did so explicitly in Chapter 2, finding five cases within this interval. The five possible cases here are the same as in Chapter 2, and are as follows: in case 1, an incipient shock forms on the left and consumes the entire left front before a peak forms; in case 2, an incipient shock forms on the left and a peak forms at the bottom of the plume, and then shock collides with the peak; in case 3, a peak forms at the bottom of the plume and no shock forms; in case 4, an incipient shock forms on the right and a peak forms at the bottom of the plume, and then the peak collides with the shock; and in case 5, an incipient shock forms on the right and consumes the entire right front before a peak forms. The delineation between these cases now depends on $N_d$ in addition to $\mathcal{M}$, $\Gamma$, and $N_s/N_f$, and we are no longer able to delineate them explicitly because the collision times (in particular, $\tau_{LL}^2$ and $\tau_{RR}^2$) are defined implicitly. Instead, we implement a decision-tree algorithm to evaluate and compare these times, and evolve the plume accordingly. We describe in detail the remainder of the development for case 2.
Flow with weak slope, case 2, in the slow-saturation limit

In case 2, the first two collisions are the development of an incipient shock at the left, which occurs at time $\tau_{L_L}^*$, and the formation of a peak at the bottom, which occurs at time $\tau_{RL}^*$. The ordering of these two collisions is unimportant. The peak is formed by the intersection of the left and right fronts, and the initial thickness $g_{0,p}$ of the waves forming the peak at time $\tau$ is given implicitly by

$$
\left[ \frac{N_s}{M-1} (\tau - 1) \right] g_{0,p}^3 + \left[ \frac{2M(1-\Gamma)}{\Gamma} - \left( MN_f + \frac{M}{M-1} N_s \right) (\tau - 1) \right] g_{0,p} \\
+ \left[ N_s N_d (\tau - 1)^2 \right] g_{0,p}^2 - \left[ \frac{2M(1-\Gamma)}{\Gamma} (M-1) N_d (\tau - 1) \right] = 0.
$$

(3.42)

The shock, once it has formed, collides continuously with waves of the left front as it grows. To construct the differential equation describing the growth of the shock, we begin by posing the collision of the shock at time $\tau^*$ with an arbitrary wave of the left front of initial thickness $g^*$ and current thickness $g^*$. The position of the shock at time $\tau^*$ can be written

$$
\xi_* = \xi_*(\tau^*) = \xi_{LL}^* + \int_{\tau_{LL}^*}^{\tau^*} \sigma \, d\tau.
$$

(3.43)

The shock speed $\sigma$ is evaluated from the Rankine–Hugoniot condition (e.g., Lax, 1972),

$$
\sigma(g^*) = \frac{1}{1-\Gamma} \left[ G \right] = \frac{1}{1-\Gamma} \frac{G(g^*)}{g^* - 1},
$$

(3.44)

where the notation $\left[ \phi \right]$ indicates the difference or “jump” in the indicated quantity across the shock. Note that only the current thicknesses of the waves on either side of the shock influence the instantaneous shock speed. The position at time $\tau^*$ of the wave with initial thickness $g_0^*$ is

$$
\xi^* = \xi(g^*, \tau^*) = -\frac{M}{g_0^{*2}} + \frac{1}{1-\Gamma} \int_1^{\tau^*} G'(g^*) \, d\tau.
$$

(3.45)
Figure 3-5: Post-injection migration in the slow-saturation limit for case 2 of the flow-with-weak-slope interval, with $\mathcal{M} = 2$, $\Gamma = 0.5$, $N_f = 1$, $N_s = -0.75$, and $N_d = 0.04$: (a) the evolution of the plume in characteristic space with waves of the left and right fronts in red and green, respectively, and the paths of the peak, the shock, and the leading and trailing edges of the plume in blue; (b)–(f) the shape of the plume at several times during migration, with mobile CO$_2$ in dark gray, the region containing residual CO$_2$ in light gray, the curtain of groundwater with dissolved CO$_2$ in blue, and groundwater in white. The curtain is approximate (drawn for $\Gamma_d = 0.1$) because we do not solve Equation (3.16) in this limit. The characteristics are not straight lines here because the waves shrink and therefore change speed as they migrate, and also that the leading and trailing edges of the plume are not characteristics, but rather cut across characteristics. For comparison, the characteristics and the plume shapes here are drawn on the same scale in space and time as those in Figure 2-13 above and Figure 3-7 below. We include the injection period here, but denote that portion of the time axis ($\tau < 1$) with dashed lines to emphasize that the characteristic timescale may change dramatically from injection to post injection, across $\tau = 1$ ($\S 3.3.1$ and 3.3.2).

Equating $\xi^*$ with $\xi^*$ since these must be equal by the definition of $g^*$ and $\tau^*$, we differentiate the resulting expression with respect to $\tau^*$ and rearrange to find an ordinary differential equation for the shock height as a function of time,

$$ \frac{dg^*}{d\tau^*} = \frac{\sigma(g^*) - \partial \xi^*/\partial \tau^*}{\partial \xi^*/\partial g^*}. $$

This ODE is not separable unless $N_d = 0$, so we integrate it numerically from time $\tau^* = \tau_{LL}^*$ until it collides with the peak, at which time $g^*(\tau^*) = g_p(\tau^*)$. The shock then collides continuously with the right front until the plume vanishes. The development of the ODE for the shock height as a function of time during this period is analogous to that above. We plot the characteristics and plume shapes for case 2 in the slow-saturation limit in Figure 3-5.
3.4.4 The instantaneous-saturation limit

When the water beneath the plume saturates with dissolved CO$_2$ very quickly relative to plume migration, the majority of the plume migrates over saturated water and is therefore not influenced by solubility trapping. Only the leading edge of the plume encounters unsaturated water as it migrates, and all of this water must saturate instantaneously as the leading edge travels over it. In this limit, we can again develop semi-analytical solutions to Equation (3.28) via the method of characteristics. Note that CO$_2$ migration becomes independent of $N_d$ in this limit because the water is assumed to saturate instantaneously. All of the expressions and results for this limit simplify to those from Chapter 2 when $\Gamma_d = 0$. Although the procedure we use here is general, we again restrict our analysis to the flow-with-weak-slope interval, $-\mathcal{M} < N_s/N_f < 1$, for simplicity.

Initial condition in the instantaneous-saturation limit

Because the water beneath the plume saturates instantaneously relative to plume migration, the initial condition for post-injection migration changes instantly from the end-of-injection plume shape to a modified shape as CO$_2$ from the plume dissolves to saturate the water beneath. Recall from §3.4.1 that the end-of-injection shape is assumed to be symmetric across $\xi = 0$. Rearranging Equation (3.31), the right half of the end-of-injection shape is given by

$$
\eta_i = \begin{cases} 
1 & 0 < \xi < 1/\mathcal{M}, \\
(\sqrt{\mathcal{M}/\xi - 1})/(\mathcal{M} - 1) & 1/\mathcal{M} < \xi < \mathcal{M}, \\
0 & \mathcal{M} < \xi.
\end{cases}
$$

(3.47)

The dimensionless volume of the end-of-injection shape is 2. The volume of free-phase CO$_2$ within an infinitesimal section of the end-of-injection plume at some position $\xi$ is $(1 - S_{wc})\phi\eta_i(\xi)\,d\xi$. The volume of CO$_2$ that can be dissolved in the water at the same position $\xi$ is $\phi\chi_v (1 - \eta_0(\xi))\,d\xi$, where $\eta_0$ is the shape of the plume after saturating the water. Conserving the total mass of CO$_2$ at position $\xi$ before and after the water
saturates with dissolved CO$_2$, we have that

$$(1 - S_{wc})\phi_i = (1 - S_{wc})\phi_0 + \phi_{X_V}(1 - \eta_0),$$  \hspace{1cm} (3.48)$$

which can be rearranged to give

$$\eta_0 = \frac{\eta_i - \Gamma_d}{1 - \Gamma_d}. \hspace{1cm} (3.49)$$

The new initial thickness $\eta_0$ goes to 0 at $\eta_i = \Gamma_d$, which occurs at position

$$\xi^* = \frac{M}{((M - 1)\Gamma_d + 1)^2}. \hspace{1cm} (3.50)$$

This is the position where the water column can dissolve exactly as much free-phase CO$_2$ as was present. For $\xi < \xi^*$, the water saturates completely before dissolving all of the free-phase CO$_2$; for $\xi > \xi^*$, the free-phase CO$_2$ dissolves completely but is not sufficient to saturate the water. We then have

$$\eta_0 = \begin{cases} 
1 & 0 < \xi < 1/M, \\
(\eta_i - \Gamma_d)/(1 - \Gamma_d) & 1/M < \xi < \xi^*, \\
0 & \xi^* < \xi.
\end{cases} \hspace{1cm} (3.51)$$

We plot Equation (3.51) in Figure 3-6 for several values of $\Gamma_d$. The dimensionless volume of this new initial shape is $2/((M - 1)\Gamma_d + 1)$, where a dimensionless volume $2(M - 1)\Gamma_d/((M - 1)\Gamma_d + 1)$ of free-phase CO$_2$ has dissolved. Rewriting Equation (3.51) in terms of characteristics, we have

$$\xi_L^0(g) = -\frac{M}{((1 - \Gamma_d)g + M\Gamma_d)^2}, \hspace{1cm} \xi_R^0(g) = \frac{M}{((1 - \Gamma_d)g + M\Gamma_d)^2}. \hspace{1cm} (3.52)$$

This will be the initial condition for post-injection migration in the instantaneous-saturation limit.
Figure 3-6: In the instantaneous-saturation limit, the plume contracts at $\tau = 1^+$ as the water beneath the end-of-injection plume shape saturates instantaneously with dissolved CO$_2$. We therefore use a modified initial shape for post-injection migration in this limit, as illustrated here for $M = 2$ (a) at the end of injection (Equation 3.47) and (b)–(c) after saturating the water for $\Gamma_d = 0.1–0.3$, as indicated (Equation 3.51). Free-phase CO$_2$ is shown in dark gray, water is shown in white, the curtain of water saturated with dissolved CO$_2$ is shown in blue, and the end-of-injection shape from (a) is indicated in (b)–(c) as a dashed black line.

Post-injection migration in the instantaneous-saturation limit

The instantaneous velocity of each wave in this limit is again $G'/\bar{R}$, with $G'$ as given in Equation (3.34). Because only the leading edge of the plume experiences solubility trapping in this limit, all other waves have constant thickness and therefore travel at constant speed. The value of $\bar{R}$ is again determined by the sign of $G'$. Given the position of each wave at $\tau = 1$ and its instantaneous velocity in post-injection, we can write the position of each wave on the left and right fronts by integrating the velocity in time,

\[
\xi_L = \xi_L^0(g) + \frac{1}{1 - \Gamma} \left( - \left[ \frac{N_s}{M - 1} \right] + \left[ MN_f + \frac{M}{M - 1} N_s \right] \frac{1}{g^2} \right) (\tau - 1),
\]

\[
\xi_R = \xi_R^0(g) + \left( - \left[ \frac{N_s}{M - 1} \right] + \left[ MN_f + \frac{M}{M - 1} N_s \right] \frac{1}{g^2} \right) (\tau - 1),
\]

The analysis then proceeds exactly as in Chapter 2—waves collide, forming shocks or peaks, and we divide the analysis into parts based on the types of collisions that occur. For $-(M - 1) N_s / N_f$, the left front compacts as it migrates. A shock will begin to build from the leftmost point on the left front at time

\[
\tau_{\sigma}^{LL} = 1 + \frac{(1 - \Gamma)(M - 1)(1 - \Gamma_d)}{((M - 1) N_f + N_s)((M - 1) \Gamma_d + 1)^3}.
\]
For \( N_s/N_f < -(\mathcal{M} - 1) \), the right front compacts as it migrates. A shock will begin to build from the rightmost point on the right front at time

\[
\tau_{RR}^a = 1 - \frac{(\mathcal{M} - 1)(1 - \Gamma_d)}{((\mathcal{M} - 1)N_f + N_s)((\mathcal{M} - 1)\Gamma_d + 1)^3}.
\]

(3.55)

For any value of \( N_s/N_f \), the rightmost point on the left front and the leftmost point on the right front will collide at time

\[
\tau_{LR}^{RL} = 1 + \frac{2(1 - \Gamma)}{\Gamma(N_f - N_s)}.
\]

(3.56)

We must then divide the flow-with-weak-slope interval into cases based on the order in which these collisions occur. The possible cases here are again the same as in Chapter 2, but the delineation between them now depends on \( \Gamma_d \) in addition to \( \mathcal{M} \), \( \Gamma \), and \( N_s/N_f \). Unlike in the slow-saturation limit, the comparison of collision times can be carried out explicitly for the first collision. For the collisions thereafter, however, the expressions are implicit and we therefore again implement a decision-tree algorithm to evaluate and compare these collision times, and evolve the plume accordingly. We describe in detail below the remainder of the development for case 2.

First, we handle the propagation of the leading edge of the plume.

Nose position in the instantaneous-saturation limit

The leading edge of the plume dissolves rapidly in this limit, so we must handle its propagation separately. As the leading edge propagates to the right, it must lose enough mobile CO\(_2\) to saturate the water that passes beneath. As a result, the plume is truncated at some moving position \( x^* \) where all of the CO\(_2\) to the right of \( x^* \) has dissolved and all of the water to the left of \( x^* \) is saturated. By definition, then, \( x^* \) is the position across which there is no flux of CO\(_2\). The volume flow rate of mobile CO\(_2\) to the right at \( x^* \) can be written

\[
F^*_g(x^*, t) = F_g(x^*, t) - (1 - S_{wc})\phi h_1(x^*, t)s_d,
\]

(3.57)

91
where \( F_g \) is the total horizontal flow of CO\(_2\) from Equation (3.2) and \( s_d = dx*/dt \). Similarly, the volume flow rate of water to the left at \( x^* \) can be written

\[
F_w^*(x^*, t) = \phi h_w(x^*, t) s_d - F_w(x^*, t),
\]

(3.58)

where \( F_w \) is the total horizontal flow of water from Equation (3.4). The water flowing to the left must dissolve and carry away the entire amount \( F_g^* \) of CO\(_2\) so that no mobile CO\(_2\) crosses \( \xi^* \), and we therefore have that \( F_g^* = \chi_v F_w^* \). Rearranging this expression gives

\[
s_d = \frac{F_g + \chi_v F_w}{(1 - S_w)\phi h_1 + \chi_v \phi h_w},
\]

(3.59)

where the right-hand side is evaluated at \( x^* \). This is the speed of the instantaneous-saturation shock at the leading edge of the plume, given by difference in the total flux of CO\(_2\) across the shock divided by the difference in the total thickness of the CO\(_2\) layer across the shock. Making \( s_d \) dimensionless and writing it in terms of \( g \) in the hyperbolic limit, we have

\[
\sigma_d = \frac{\chi_v(M - 1)N_f g + (1 - \chi_v)(MN_f(g - 1) + N_s(M - g)(g - 1)/(M - 1))}{(1 - \Gamma_d)(g - 1)g + (M - 1)\Gamma_d g},
\]

(3.60)

where \( \sigma_d \) is the dimensionless shock speed and the right-hand side is evaluated at \( \xi^* \). We can then formulate an ODE for the height of the shock as a function of time via the same construction used in Equation (3.46), but where the shock speed is given by Equation (3.60). This ODE is not separable for \( \Gamma_d \neq 0 \), so we integrate it numerically.

**Flow with weak slope, case 2, in the instantaneous-saturation limit**

In case 2, the first two collisions are the development of an incipient shock at the left, which occurs at time \( \tau_{LL}^* \) from Equation (3.54), and the formation of a peak at the bottom, which occurs at time \( \tau_{LR}^* \) from Equation (3.56). The ordering of these two collisions is unimportant. The initial height of the peak is \( M \), and the height of the peak as a function of time is given by the value of \( g \) at which \( \xi_L \) and \( \xi_R \) intersect, which yields a fourth-order polynomial in \( g \). The height of the peak is
Figure 3-7: Post-injection migration in the instantaneous-saturation limit for case 2 of the flow-with-weak-slope interval, with $\mathcal{M} = 2$, $\Gamma = 0.5$, $N_f = 1$, $N_s = -0.75$, $S_{wc} = 0.4$, and $\Gamma_d = 0.1$: (a) the evolution of the plume in characteristic space with waves of the left and right fronts in red and green, respectively, and the paths of the peak, the shock, and the leading and trailing edges of the plume in blue; (b)-(f) the shape of the plume at several times during migration, with mobile CO$_2$ in dark grey, the region containing residual CO$_2$ in light gray, the curtain of groundwater with dissolved CO$_2$ in blue, and groundwater in white. The curtain is approximate because we do not solve Equation (3.16) in this limit. Note that the characteristics contract instantaneously across $\tau = 1$, where the characteristic timescale changes from the injection timescale to the post-injection timescale. This corresponds to the instantaneous saturation of the water beneath the end-of-injection plume shape (§3.4.4). Unlike in the slow-saturation limit, the characteristics here are straight lines. The leading edge of the plume is the instantaneous-saturation shock, which truncates the plume by cutting across characteristics. For comparison, both the characteristics and the plume shapes are drawn here on the same scale in space and time as those in Figures 2-13 and 3-5 above. We include the injection period here, but denote that portion of the time axis ($\tau < 1$) with dashed lines to emphasize that the characteristic timescale may change dramatically from injection to post injection, across $\tau = 1$ (§3.3.1 and 3.3.2).

the smallest root of this polynomial on the interval $g \in [1, \mathcal{M}]$. Meanwhile, the right front is truncated as the instantaneous-saturation shock evolves. The shock on the left evolves according to an ODE constructed as in Equation (3.46), but where $\partial \xi / \partial g$ and $\partial \xi / \partial \tau$ are calculated using the expression for the shape of the left front from Equation (3.53). The shock evolves until it collides with the peak, at which time the entire left front has become a shock. Thereafter, the shock collides continuously with the right front until it collides with the instantaneous-saturation shock at the leading edge of the plume. We plot the characteristics and plume shapes for case 2 in the instantaneous-saturation limit in Figure 3-7.
3.5 Storage efficiency and migration speed

We now use the analysis of §3.4 to study the competition between residual and solubility trapping, and the impact of solubility trapping on CO₂ migration.

Recall that we have chosen a characteristic time in post-injection migration based on groundwater flow so that $N_f = 1$. We retain this choice here, but we report the results in this section in terms of the ratios $N_s/N_f$ and $N_d/N_f$ so that they remain valid for other choices of the characteristic time (§3.3.2 and §3.4).

Further, recall that we have neglected the buoyant spreading term (the term proportional to $N_g$) in the analysis for simplicity (§3.4), because the macroscopic features of CO₂ migration and trapping are little affected by even large values of $N_g$ compared to $N_f$ or $N_s$ (Juanes and MacMinn, 2008; Hesse et al., 2008). All of the results reported here are therefore strictly valid for $N_g/N_f \to 0$.

As in Chapter 2, we interpret these results in the context of the storage efficiency, a macroscopic measure of CO₂ migration. The storage efficiency is the volume of CO₂ stored per unit pore volume of aquifer “used,” and is an important metric in capacity estimation (Bachu et al., 2007). As defined in Equations (2.47) and (2.48), the storage efficiency $\varepsilon$ is inversely proportional to the dimensionless footprint of residual CO₂, i.e., for a given volume of CO₂ injected, a larger footprint corresponds to less-efficient storage.

We also consider an additional parameter here, which is the fraction $\Phi_d$ of CO₂ that has been trapped by solubility trapping once all of the CO₂ has been trapped. This is a measure of the importance of solubility trapping relative to residual trapping since the remaining fraction $1 - \Phi_d$ must be trapped by capillarity.

Our focus in Chapter 2 was the competition between flow and slope, as measured by the ratio $N_s/N_f$. Here, we focus on the interactions between migration, residual trapping, and solubility trapping. For this purpose, we fix $N_s/N_f$, $\Gamma$, $\Gamma_d$, and $S_{wc}$, and evaluate the storage efficiency and the fraction trapped by solubility trapping as a function of the ratio $N_d/N_f$ for several values of $\mathcal{M}$.

Both the storage efficiency and the fraction trapped by solubility trapping increase
monotonically with $N_d/N_f$ (Figure 3-8). However, storage efficiency decreases with $\mathcal{M}$ whereas fraction trapped by solubility trapping increases with $\mathcal{M}$. This is because the plume becomes longer and thinner as $\mathcal{M}$ increases, which slows residual trapping but increases the amount of solubility trapping. In this sense, residual and solubility trapping are complementary trapping mechanisms.

Comparing storage efficiency to the fraction trapped by solubility trapping at the same value of $N_d/N_f$, we find that the combination of residual and solubility trapping can greatly increase storage efficiency even when the fraction trapped by solubility trapping is small (Figure 3-9). This is a consequence of the complementary nature of residual and solubility trapping: capillarity traps CO$_2$ at the short, trailing edge of the plume, while convective dissolution acts most strongly along the long, leading edge.

In particular, solubility trapping slows the speed at which the leading edge advances, decreasing total migration distance and increasing the storage efficiency (Equation 2.48). Without solubility trapping, the dimensionless speed of the nose of the plume is constant (taking $\partial/\partial \tau$ of Equation 2.26d),

$$v_{\text{nose}} = \frac{d \xi_{RR}}{d \tau} = \mathcal{M} N_f + N_s. \quad (3.61)$$

With solubility trapping, the speed of the nose in the slow-saturation limit can be evaluated from Equation (3.38), and is given by

$$v_{\text{nose}}(\tau) = \frac{\mathcal{M} N_f + \mathcal{M} N_s/(\mathcal{M} - 1)}{(1 + (\mathcal{M} - 1) N_d(\tau - 1))^2} - \frac{N_s}{\mathcal{M} - 1} - \frac{2 \mathcal{M} (\mathcal{M} - 1) N_d}{(1 + (\mathcal{M} - 1) N_d(\tau - 1))^3}. \quad (3.62)$$

The speed of the nose is no longer constant in time, so the nose now traverses a curved path in space-time (Figure 3-10a). In addition, the time-averaged speed of the nose decreases monotonically with $N_d$ (Figure 3-10b). Slowing the leading edge of the plume has a twofold impact on migration distance and therefore on storage efficiency: it decreases both migration speed and total migration time. Slowing the leading edge of the plume decreases total migration time because the plume of mobile
Figure 3-8: Both (a) the storage efficiency, $\varepsilon$, and (b) the fraction of CO$_2$ trapped by solubility trapping, $\Phi_d$, increase monotonically with dimensionless rate of solubility trapping, $N_d/N_f$. Here, we fix the values of $\Gamma = 0.3$, $N_f = 1$, $N_s = -0.75$, $S_{uc} = 0.4$, and $\Gamma_d = 0.06$, and show curves for three typical values of $\mathcal{M}$, as indicated. Storage efficiency decreases monotonically with $\mathcal{M}$, as in Chapter 2, because the plume becomes longer and thinner as $\mathcal{M}$ increases; $\Phi_d$ increases monotonically with $\mathcal{M}$ because the amount of solubility trapping is proportional to the length of the plume. The water beneath the plume saturates more quickly as $N_d$ increases, and both $\varepsilon$ and $\Phi_d$ approach a plateau in the instantaneous-saturation limit where the water is completely saturated. The height of this plateau depends on $\Gamma_d$, but not on $N_d$. The semi-analytical solutions in the slow-saturation limit (solid black line) and the instantaneous-saturation limit (dashed black line) agree with numerical solutions to Equations (3.15) and (3.16) (black dots) to within a few percent.
Figure 3-9: Solubility trapping can lead to a several-fold increase in storage efficiency even when the fraction trapped by solubility trapping is small. For $\mathcal{M} = 8.5$, we plot here the storage efficiency $\varepsilon$ from Figure 3-8(a), scaled by the storage efficiency without solubility trapping, $\varepsilon_0$, against the corresponding fraction trapped by solubility trapping $\Phi_d$ from Figure 3-8(b). Both quantities increase monotonically with $N_d/N_f$ (Figure 3-8). Several values of $N_d/N_f$ are indicated for reference (black dots). Results shown here are from the semi-analytical solutions for the limiting cases of slow-saturation (solid black line) and instantaneous-saturation (black star). The transition from slow to instantaneous saturation is not shown. The storage efficiency is twice the no-solubility-trapping value with only 20% of the CO$_2$ trapped by solubility trapping, increasing in the instantaneous-saturation limit to about 6.6 times the no-solubility-trapping value with 52% of the CO$_2$ trapped by solubility trapping.
Figure 3-10: Solubility trapping reduces the speed at which the nose of the plume advances, as shown here in the slow-saturation regime for $\mathcal{M} = 8.5$, $\Gamma = 0.3$, $N_f = 1$, and $N_s = -0.75$. (a) In space-time, we superpose the path of the nose for several values of $N_d$ (solid blue lines) onto the characteristics without solubility trapping (faded red, green, blue lines). Without solubility trapping ($N_d = 0$), the path of the nose is a straight line in space-time because the speed of the nose is constant (Equation 3.61). With solubility trapping, the nose travels more slowly and its path in space-time is curved because its speed is no longer constant (Equation 3.62). (b) The mean velocity of the nose (solid black line) decreases by more than a factor of 2 from its no-solubility-trapping value (dashed black line) as $N_d$ increases from 0 to 0.02. For $N_d > 0.02$, plume migration is no longer in the slow-saturation limit for these parameters.

CO$_2$ shrinks from the rear due to residual trapping, becoming fully trapped when the trailing edge catches the leading edge. This occurs more quickly when solubility trapping slows the leading edge (Figure 3-10a). Note that Equation (3.62) is valid for all $N_s/N_f > -\mathcal{M}$, except for the narrow interval near $N_s/N_f = -\mathcal{M}$ where the leading edge of the plume is a shock ($\S 2.2.3$); for $N_s/N_f < -\mathcal{M}$, the expression is identical except that the last term changes sign. The advancement of the nose in the instantaneous-saturation regime is more complicated because the leading edge is a shock, but the behavior is qualitatively similar.

Because solubility trapping acts most strongly along the long, leading edge of the plume, residual trapping remains important even for large values of $N_d$. We illustrate the complementary nature of residual and solubility trapping via the time-evolution of the volume fractions of mobile, residual, and dissolved CO$_2$ (Figure 3-11). This provides a quantitative, physical understanding of the time-evolution of the role of trapping mechanisms in immobilizing the buoyant CO$_2$, as recognized qualitatively in terms of perceived storage security in IPCC (2005, pg. 208, Figure 5.9).
Figure 3-11: Solubility trapping is increasingly important as $N_d$ increases, but residual trapping plays an important role even for large $N_d$. Here, we show the time-evolution of the volume fractions of mobile, residual, and dissolved CO$_2$ for $N_d = 0, 0.01,$ and 1 from bottom to top, respectively, and for $M = 5$ (left) and 15 (right). The three volume fractions must add to 100% at all times. Residual CO$_2$ does not dissolve in this model, so the fraction trapped by solubility trapping is constant once all of the CO$_2$ is trapped. We fix $\Gamma = 0.3$, $N_f = 1$, $N_s = -0.75$, $S_{wc} = 0.4$, $\Gamma_d = 0.06$. As $N_d$ increases, the combination of residual and solubility trapping traps the plume more quickly (total migration time decreases, as indicated here by the vertical, dashed, white lines), and over a shorter distance (storage efficiency increases). Note that in the instantaneous-saturation limit (top row), the amount of dissolved CO$_2$ increases sharply at $\tau = 1$ as the water beneath the end-of-injection plume saturates with dissolved CO$_2$; thereafter, solubility trapping occurs only at the leading edge (§3.4.4).
Chapter 4

Laboratory experiments

In Chapter 3, we developed a simple model for solubility trapping by convective dissolution and incorporated it into the model for CO₂ migration presented in Chapter 2. In developing the model for solubility trapping, we assumed that the onset time for the convective-dissolution instability is short and that the rate of solubility trapping due to convective dissolution is approximately constant on average (Pau et al., 2010; Kneafsey and Pruess, 2010; Neufeld et al., 2010). In this Chapter, we use laboratory analog experiments to validate these assumptions and our model in the context of a migrating gravity current in a sloping aquifer, and to study the small-scale dynamics of the convective-dissolution instability: the formation, descent, and coarsening of the fingers.

4.1 Laboratory analog system

We work with analog fluids rather than CO₂ and water to allow experiments at room temperature and pressure, where the solubility of CO₂ in water is extremely low (≈ 0.15% by mass) and the density and viscosity of CO₂ are much lower than at reservoir conditions. In order to conduct experiments with and without convective dissolution, we use two different pairs of analog fluids.

In the analog system with convective dissolution, water plays the role of the buoyant CO₂ and propylene glycol (PG) plays the role of the denser and more viscous
ambient groundwater (Backhaus et al., 2011). Although pure PG is denser than water \((\Delta \rho \approx 36 \text{ kg/m}^3)\), the density of water-PG mixtures is non-monotonic with water concentration and mixtures of the two with up to about 54\% water are denser than pure PG (Figure 4-1b). As a result, a layer of water will float above a layer of PG while simultaneously dissolving into the PG by convective dissolution, as fingers of the dense mixture that forms at the interface between the two sink downward into the PG (Figure 4-1a). Additionally, the large viscosity contrast between the water and

\[
\begin{align*}
\text{(b)} \\
\Delta \rho &= \rho - \rho_{\text{PG}} \\
\chi_w &= \text{water mass fraction} \\
\Delta \rho &= \text{density increase on dissolving a mass fraction } \chi_w \text{ of water into PG. Lastly, we show (c) the viscosity of a water-PG mixture as a function } \chi_w, \text{ plotted as the ratio of the viscosity of the mixture to the viscosity of pure water. The viscosity of pure PG is about 53 times that of pure water. We include in (b) and (c) experimental measurements at } 25 \degree \text{C (Dow Chemical, 2011; Dow Chemical) and polynomial fits to the experimental data (solid lines).}
\end{align*}
\]

\[
\begin{align*}
\text{(c)} \\
\frac{\mu}{\mu_{\text{PG}}} &= \text{viscosity increase on dissolving a mass fraction } \chi_w \text{ of water into PG. Lastly, we show (c) the viscosity of a water-PG mixture as a function } \chi_w, \text{ plotted as the ratio of the viscosity of the mixture to the viscosity of pure water. The viscosity of pure PG is about 53 times that of pure water. We include in (b) and (c) experimental measurements at } 25 \degree \text{C (Dow Chemical, 2011; Dow Chemical) and polynomial fits to the experimental data (solid lines).}
\end{align*}
\]

Figure 4-1: Propylene glycol (PG) is denser and more viscous than water, but a mixture of the two is denser than either component for water mass fractions less than about 0.54, and this drives convective dissolution (Backhaus et al., 2011). Here we show (a) a snapshot from an experiment in a Hele-Shaw cell where a layer of buoyant water floats above denser PG while dissolving into PG via convective dissolution. The water is dyed blue for visualization, and we show here the red component of the image. We also show (b) the density of a water-PG mixture as a function of water mass fraction \(\chi_w\), plotted as the density increase on dissolving a mass fraction \(\chi_w\) of water into PG. Lastly, we show (c) the viscosity of a water-PG mixture as a function \(\chi_w\), plotted as the ratio of the viscosity of the mixture to the viscosity of pure water. The viscosity of pure PG is about 53 times that of pure water. We include in (b) and (c) experimental measurements at 25 \degree \text{C (Dow Chemical, 2011; Dow Chemical) and polynomial fits to the experimental data (solid lines).}

the pure PG \((\mathcal{M} \approx 53; \text{ Figure 4-1c})\) is appropriate for studying CO\textsubscript{2} gravity currents,
Figure 4-2: In order to conduct experiments with and without convective dissolution, we use two different pairs of analog fluids. We illustrate this here with snapshots of two gravity currents migrating up-dip in a sloping aquifer (a Hele-Shaw cell with no beads for illustration). The CO$_2$ analog is water (dark) in both cases. When the denser and more viscous ambient fluid (light) is a mixture of glycerol and water (left), the fluids mix by diffusion-dispersion only and the gravity current migrates to the top of the cell and accumulates there. When the ambient fluid is propylene glycol (right), the dense mixture of the two fluids drives convective dissolution, which dissolves the buoyant current as it migrates.

which are much less viscous than the ambient groundwater.

To study gravity currents without convective dissolution, we replace the PG with a mixture of glycerol and water. All such mixtures are denser and more viscous than water, so we choose one for which the viscosity contrast is similar to the water-PG system (77.5% glycerol by mass, for which $\Delta \rho \approx 200$ kg/m$^3$ and $\mathcal{M} \approx 40$). As in the water-PG system, the buoyant water will mix with the dense glycerol-water mixture along their shared interface. Unlike in the water-PG system, this will never trigger convective dissolution because the density of water-glycerol mixtures is monotonic in water concentration.

With these two fluid pairs, we are able to study gravity currents with and without convective dissolution while keeping other parameters approximately constant. To perform such an experiment, we release a fixed quantity of the buoyant fluid in the lower corner of a sloping aquifer (a quasi-two-dimensional flow cell packed with glass beads). This fluid rises toward the top of the cell and migrates up-slope as a buoyant gravity current. Without convective dissolution, the gravity current migrates to the
upper corner of the cell and accumulates there. With convective dissolution, the
upward migration of the gravity current slows and is ultimately arrested as the current
dissolves completely (Figure 4-2).

4.2 Simplified model for up-slope migration
with solubility trapping

Both pairs of analog fluids are perfectly miscible, so residual trapping plays no role
in these analog experiments. Additionally, there is no net fluid flow through the
flow cell and we work with a rectangular initial condition of height $H$ and width $L$.
Simplifying Equation 3.15 appropriately, we have

$$
\frac{\partial \eta}{\partial \tau} + \frac{\partial}{\partial \xi} \left[ \sin \vartheta (1 - f) \eta - \cos \vartheta \frac{H}{L} (1 - f) \eta \frac{\partial \eta}{\partial \xi} \right] = -N_d,
$$

(4.1)

where $\xi = x/L$ is the dimensionless horizontal coordinate, $\tau = t/T$ is the dimension-
less time, $\eta(\xi, \tau) = h(x,t)/H$ is the local dimensionless plume thickness, $\vartheta$ is the
aquifer slope measured from horizontal, and the nonlinear function $f$ is unchanged
from Equation (2.11).

We have chosen characteristic time $T = L/\kappa$, where $\kappa = \Delta \rho \gamma k/\phi \mu_g$ is the character-
istic velocity of the buoyant current (Equation 2.8). This choice allows us to write
the model directly in terms of the experimental parameters for this simpler system:
instead of $N_s$ and $N_g$, we have simple expressions involving the slope, $\vartheta$, and the as-
pect ratio, $H/L$. We retain the dimensionless dissolution rate $N_d = (q_d/H)/(\phi \kappa/L)$,
which here measures the rate of convective dissolution relative to the characteristic
rate of lateral spreading and migration.

Only two of the three coefficients $\sin \vartheta$, $\cos \vartheta H/L$, and $N_d$ are independent because
one can always be subsumed into the characteristic timescale, but we retain all three
for physical clarity. We will consider horizontal aquifers ($\sin \vartheta = 0$) in addition to
sloping aquifers, and gravity currents without convective dissolution ($N_d = 0$) in
addition to those with convective dissolution. In addition, solutions to Equation 4.1

104
approach hyperbolic behavior as the gravity current becomes long and thin \((H/L \to 0)\).

By performing experiments at different values of \(\vartheta\), we vary the relative importance of up-slope migration (the term proportional to \(\sin \vartheta\), which represents flow due to the component of gravity tangential to the aquifer); buoyant spreading against the top of the aquifer (the term proportional to \(\cos \vartheta\), which represents flow due to the component of gravity normal to the aquifer); and convective dissolution (the sink term on the right-hand side) while keeping the values of \(\mathcal{M}\), \(H/L\), and \(N_d\) fixed.

4.3 Gravity currents without convective dissolution

In order to compare the model with a gravity current experiment in the flow cell packed with glass beads, we must measure the properties of the packed cell. For simplicity, we work with only one bead size: spherical beads with a nominal mean diameter of 1.25 mm.\(^1\)

We measure the porosity of the packed cell directly as the ratio of the volume of fluid required to fill cell to the bulk internal volume of the cell. From four measurements, we find that the mean porosity of the packed flow cell is \(\phi = 0.388\) with a standard deviation of 0.002. This is consistent with the expected porosity of a poured random packing of monodisperse spheres. Because we disassemble, clean, reassemble, and repack the flow cell after each measurement, the small standard deviation indicates that the properties of the packed cell are sufficiently consistent across experiments.

Rather than measuring the permeability of the packed cell directly, we measure it indirectly by treating it as a fitting parameter: when comparing the model to an experiment for a gravity current without convective dissolution, this is the only unknown quantity. Since we expect the properties of the packed cell to be consistent across experiments.

---

\(^1\)We use soda-lime glass spheres from Mo-Sci Specialty Products, LLC, with a nominal size range of 1.0–1.5 mm (Mo-Sci GL0191SB/1000-1500).
experiments, we fit the permeability for one experiment and use this same value for all other experiments, with and without convective dissolution. We find the permeability of the packed cell to be $k = 9.5 \times 10^{-10} \text{m}^2$. For comparison, the Kozeny-Carman relation for the permeability of a packed bed of monodisperse spheres predicts, for the same nominal diameter and porosity, a permeability of $13.5 \times 10^{-10} \text{m}^2$, or about 50% larger. That our measured value is somewhat lower than the prediction is consistent with the fact that we use polydisperse beads.

To perform an experiment, we orient the packed flow cell “vertically” (long direction aligned with gravity) and inject the dense fluid from the bottom. We then add the buoyant fluid via an injection port at the top, close all ports, and quickly rotate the cell to the desired orientation (an angle $\theta$ from horizontal) to initiate the fluid flow. The buoyant fluid spreads against the top of the cell and migrates up-slope as a buoyant gravity current, and we record the experiment with a digital still camera.

We find that the model agrees very well with the experiments, capturing the shape and evolution of the gravity current (Figure 4-3). We carry out several experiments for several different slopes, and from each we measure the position of the leading edge or nose of the gravity current as a function of time. Although there is some subtlety associated with appropriately defining the nose in the model (Figure 4-4), we find that the nose position from the model agrees well with the experiment across a wide range of slopes (Fig. 4-5).

4.4 Gravity currents with convective dissolution

We introduce convective dissolution to this system by replacing the ambient glycerol-water mixture with PG. This introduces one additional parameter, which is the rate of convective dissolution $q_d$. We measure the rate of convective dissolution in the packed flow cell directly via an experiment where we leave the flow cell in the vertical orientation (long direction aligned with gravity) after adding the buoyant fluid, instead of rotating it. We then have a stationary layer of water at the top of the cell that dissolves into the underlying PG. The rate at which the water-PG interface
Figure 4-3: Without trapping, a buoyant gravity current will migrate indefinitely. Here, a buoyant plume of water (dark gray) migrates up-dip in a sloping aquifer. The ambient fluid is a denser and more viscous mixture of glycerol and water (light gray). The aquifer—a quasi-two-dimensional flow cell packed with glass beads (1.25 mm diameter)—is tilted 2.5° counterclockwise from horizontal, as indicated. We also include the solution to the model (red line). The buoyant and ambient fluids are completely miscible, but mix here only by diffusion/dispersion along their shared interface, which occurs very slowly relative to the migration of the plume.
Figure 4-4: The leading edge of the gravity current predicted by the model (red line) is extremely long and thin because of the high mobility ratio. In the experiments, this tongue is truncated as the plume thickness approaches the bead size (indicated with a black circle). We identify the "nose" of the gravity current in the experiment as the rightmost point of the gravity current, whereas we identify the "nose" from the model as the point where the thickness of the gravity current reaches the bead size (horizontal position indicated with a red triangle). In principle, the continuum approximation for fluid flow in a porous medium is no longer valid at this scale. As a result, we expect some qualitative and quantitative discrepancies when comparing these nose positions.

Figure 4-5: Position of the nose of the gravity current as a function of time in the water-glycerol analog system for several different inclination angles. All of the gravity current here hit the end of the cell, located at a dimensionless distance of about 10. We truncate the data about one characteristic length before this to avoid the influence of the boundary on the flow. We show experimental measurements (circles) as well as the predictions of the model (solid lines). The two agree well across the full range of slopes. The results for $\theta = 2.5^\circ$ (green) are from the experiment shown in Figure 4-3.
retreats is a direct measurement of the rate of convective dissolution (Neufeld et al., 2010). We measure this rate to be $q_d = 7.0 \times 10^{-8}$ m/s.$^2$

We follow the same experimental procedure with this system as with the water-glycerol system. Comparing the model to the experiments using the measured rate of convective dissolution, as well as the porosity and permeability measured previously, we again find that the model agrees very well with the experiments. The model captures the shape and evolution of the gravity current (Figure 4-6) as well as the evolution of the nose position across a wide range of slopes (Figure 4-7).

Figure 4-6: Convective dissolution will arrest the migration of a buoyant gravity current. The experimental system here is identical to that in Figure 4-3, except that the ambient fluid is now propylene glycol (light gray). The buoyant and ambient fluids are completely miscible, and mix via convective dissolution, which dissolves the buoyant fluid at a rate comparable to the rate of up-slope migration. Convective dissolution occurs here because, as with CO$_2$ and water, the mixture of the two fluids is denser than either individual component. We also include the solution to the model (red line).

By comparing the predictions of the model from Chapter 3 with laboratory experiments in a simplified analog system, we have shown that the model successfully

\footnote{The rate of convective dissolution has dimensions of length per time because it is the volume of buoyant fluid dissolved per unit interfacial area per unit time. The dissolving interface retreats at velocity $q_d/\phi$.}
Figure 4-7: Position of the nose of the gravity current as a function of time in the water-PG analog system for several different inclination angles. In contrast with the results from the water-glycerol system (Figure 4-5), all of the gravity currents here except for $\vartheta = 16.0^\circ$ reach a maximum run-out distance and then retreat before completely dissolving by convective dissolution. We truncate this data when the buoyant fluid begins to break up into patches, no longer behaving as a gravity current. This always occurs here shortly after the maximum nose position is reached. We show experimental measurements (circles) as well as the predictions of the sharp-interface model (solid lines). The results for $\vartheta = 2.5^\circ$ (green) are from the experiment shown in Figure 4-6.

captures the up-slope migration of a buoyant gravity current relative to a denser and much more viscous ambient fluid in a confined aquifer, both with and without solubility trapping. These results validate the assumption that the onset time for the convective-dissolution instability is unimportant when it is small relative to the characteristic time for up-slope migration, as in the analog system studied here. Further, these results show that the finding that convective dissolution traps the buoyant fluid at a constant rate remains valid in the context of a migrating gravity current.

### 4.5 Coarsening dynamics of the convective-dissolution instability

Although we have thus far focused on the macroscopic impact of solubility trapping on the migrating gravity current, our experiments in the Hele-Shaw cell also reveal the small-scale complexity of the convective-dissolution instability (Fig. 4-2). This
experimental system provides a convenient setting for studying the nonlinear growth of the instability: the formation, descent, and coarsening of the fingers.

We focus here on two quantities that have direct practical relevance: the speed at which the fingers fall and evolution of the finger spacing. The finger velocity plays a direct role in the rate of solubility trapping since the dynamics of convective-dissolution will change once fingers begin to interact with the bottom of the aquifer, and faster fingers will hit the bottom of the aquifer sooner. The finger spacing informs the minimum spatial resolution at which a detailed reservoir simulation can operate, since the simulation must resolve the fingers in order to accurately capture the physics of convective dissolution. The size and spacing of the fingers also play a strong role in how they interact with heterogeneity, which may have a correlation length much smaller than, comparable to, or much larger than the scale of fingers.

Instead of studying the speed of individual fingers, we propose a simple model for the thickness, $h_f$, of the entire fingering front that grows beneath the plume:

$$h_f(x, t) = \begin{cases} 
0 & \text{if } t_{\text{conv}}(x, t) < 0, \\
v_f t_{\text{conv}}(x, t) & \text{if } t_{\text{conv}}(x, t) \geq 0, 
\end{cases}$$

where $v_f$ is the speed at which the fingers fall and $t_{\text{conv}}(x, t)$ is the convective time, which measures the amount of time that has passed since fingers first formed at location $x$. The convective time is given by $t_{\text{conv}} = t - t_N(x) - t_{\text{onset}}$, where $t_N(x)$ is the time at which the nose of the migrating plume arrives at position $x$ and $t_{\text{onset}}$ is the onset time for the instability. We assume that the finger velocity and the onset time are both constant for the duration of the experiment.

We measure the function $t_N(x)$ from the experiment directly by measuring the position of the nose as a function of time. We estimate the finger velocity and the onset time from the experiment, finding $v_f \approx 0.9 \times 10^{-4}$ m/s and $t_{\text{onset}} \approx 25$ s. This value of the finger velocity is consistent with our assumption in Chapter 3 that the fingers fall with characteristic speed $v_d = \Delta \rho_d g k / \mu_w \phi$ (Equation 3.8),\(^3\) where for this\(^3\)Since $\mu_w$ in this expression refers to the viscosity of the ambient fluid, this is the viscosity of PG rather than that of water in the context of these analog experiments.
experiment we find $\kappa_d \approx 1.5 \times 10^{-4}$ m/s.$^4$

For these values of finger velocity and onset time, we find that this model successfully captures the macroscopic evolution of the fingering front (Fig. 4-8). This

![Figure 4-8: We propose a simple model for the growth of the fingering front beneath the plume, parametrized by a constant finger velocity and a constant onset time. We find that the model successfully captures the macroscopic evolution of the fingering front in the experiment, as illustrated here where we overlay the fingering front from the model (cyan line) onto several snapshots of the experiment.](image)

validates our assumptions of constant finger velocity and constant onset time.

We next study the finger spacing and, in particular, the coarsening of the fingering pattern. Since the pattern coarsens as the fingers fall, we quantify coarsening by measuring the spatial frequency of the fingering pattern as a function of the convective time. We measure the spatial frequency of the pattern by counting the number of fingers contained in a sampling window that travels from left to right, traversing the entire fingering front in each snapshot of the experiment. The spatial frequency is the number of fingers contained in the window per unit window width, and the mean

$^4$We measure the permeability of the Hele-Shaw cell to be $0.95 \times 10^{-7}$ m$^2$, which compares well with the estimated value of $b^2/12 = 1.6 \times 10^{-7}$ m$^2$ for the permeability of a Hele-Shaw cell with gap thickness $b = 1.4$ mm.
convective time captured by the window is uniquely related to the position of the window along the front. The results show that the spatial frequency of the fingering pattern decreases by about a factor of 3 over the course of the experiment, meaning that the finger spacing increases by the same amount (Figure 4-9).

![Graph showing fingering pattern coarsening with convective time](image)

**Figure 4-9**: The fingering pattern coarsens with the convective time because the fingers grow and merge as they fall. Here, we plot the spatial frequency of the fingering pattern along the fingering front as a function of the convective time from 25 snapshots over the duration of an experiment. Although the frequency data (grey circles) is noisy, the pattern clearly coarsens by about a factor of 3 over the course of the experiment, as highlighted by a five-point moving average of the data (black line).

Our experiments highlight the fact that solubility trapping driven by convective dissolution is a crucial trapping mechanism for geological CO₂ storage. In addition to slowing and ultimately arresting the migrating plume, convective dissolution mitigates the risk of leakage by rapidly converting the buoyant, free-phase CO₂ into dense, aqueous CO₂. Further, the experiments provide a window into the small-scale complexity of the convective-dissolution instability, allowing us to explore two quantities of immediate practical interest: the velocity and spacing of the fingers.
Chapter 5

Application, discussion & conclusions

We have developed a gravity-current model for the migration and trapping of a buoyant plume of CO$_2$ in a confined, sloping saline aquifer with a net groundwater throughflow. The model includes both residual and solubility trapping, and accounts for the tongued shape of the plume at the end of the injection period because this serves as the initial condition for post-injection migration.

In Chapter 2, we developed a complete analytical solution to the model without solubility trapping in its hyperbolic limit. We showed that the migration behavior depends strongly on the mobility ratio, the amount of residual trapping, and the importance of aquifer slope relative to groundwater flow. We explored how groundwater flow, aquifer slope, and residual trapping interact to determine the overall storage efficiency, and we found that the maximum storage efficiency is achieved in sloping aquifers with a gentle down-slope groundwater flow.

In Chapter 3, we incorporated solubility trapping into the model, including the dissolution-limiting effect of the finite amount of water beneath the plume. We identified two limiting cases in CO$_2$ migration with solubility trapping: when the water beneath the plume saturates very slowly or very quickly ("instantaneously") relative to the motion of the plume. We developed semi-analytical solutions to the model in these limits. We showed that residual and solubility trapping are complementary
trapping mechanisms because residual trapping acts primarily at the short, trailing edge of the plume, whereas solubility trapping acts primarily along the long, leading edge. Solubility trapping is most effective at large values of $M$, when the plume is long and thin, and this is precisely when residual trapping is least effective. We further showed that solubility trapping can lead to a several-fold increase in storage efficiency even when the fraction of CO$_2$ dissolved is small, because solubility trapping slows the speed at which the plume advances. However, residual trapping plays an important role even when the rate of solubility trapping is large. As the rate of solubility trapping increases, the combination of the two mechanisms traps the plume more quickly (total migration time decreases) and over a shorter distance (storage efficiency increases).

In Chapter 4, we validated the model against laboratory experiments in a simplified analog system and we showed that the model successfully captures the macroscopic impact of solubility trapping on the migration of a buoyant gravity current. We then used the experiments to study the small-scale dynamics of the convective-dissolution instability.

In this Chapter, we use the model to study the post-injection migration and trapping of a plume of CO$_2$ in the Mt. Simon Sandstone, a large deep saline aquifer in the Midwestern United States. We discuss the impact of slope, residual trapping, and solubility trapping on the amount of time it takes until all of the CO$_2$ is trapped, and on the total migration distance. Finally, we conclude with a discussion of the physical limitations of the model.
5.1 Migration and trapping of \( \text{CO}_2 \) in the Mt. Simon Sandstone

We consider the injection of 10 Gt of \( \text{CO}_2 \) into a portion of the Mt. Simon Sandstone.\(^1\) We assume that the \( \text{CO}_2 \) is distributed uniformly along a 200 km array of wells, and we model the evolution of the planar cross-section of the single resulting plume (Figure 2-2). From the geological and hydrogeological properties of the aquifer (Szulczewski et al., 2011a), we estimate \( \mathcal{M} \approx 13, \ H/L \approx 0.448, \) and \( N_d \sim 1.7 \times 10^{-6} \). For simplicity, we neglect connate water \((S_{wc} \to 0)\) and also the tongued initial plume shape, although these can be readily included. We also neglect natural groundwater flow because it is very weak in this aquifer, although this too can be included.

Although this is a real aquifer with an actual slope of about 0.5° (Szulczewski et al., 2011a), we use it here as a test case for studying the impact of slope on \( \text{CO}_2 \) migration and trapping at the basin scale. To do so, we consider the total time until all of the \( \text{CO}_2 \) is trapped, \( t^F \), and the maximum migration distance \((i.e., \text{the maximum nose position}), x_{N}^{max} \), for different slopes \( \vartheta \) ranging from horizontal \( (\vartheta = 0°) \) to aggressive \( (\vartheta = 2°) \) (Fig. 5-1). With residual trapping only, both the total time and the maximum migration distance are very large when the slope is small, and both decrease as the slope increases. This is because the rate of residual trapping is proportional to both the migration speed of the plume and its areal sweep through the aquifer: more residual \( \text{CO}_2 \) is left behind when the sweep is large, and this occurs more quickly when the plume migrates quickly. Total migration time and maximum migration distance both decrease as the slope increases because migration speed is roughly proportional to the slope, and because the sweep of the plume increases as upslope migration dominates buoyant spreading and the migration behavior approaches its hyperbolic limit, where the trailing edge is a steep shock (Chapter 2).

Unlike the rate of residual trapping, the rate of solubility trapping is directly proportional to the length of the plume. Solubility trapping therefore traps \( \text{CO}_2 \) very

\(^{1}\)For reference, a single 500 MW coal-fired power plant produces about 3 Mt of \( \text{CO}_2 \) per year (mit, 2007). 10 Gt corresponds, for example, to about 100 years' worth of emissions from 30 such coal plants.
Figure 5-1: Solubility trapping is very effective for small slopes, whereas residual trapping is most effective for large slopes. The combination of the two traps all of the CO$_2$ very effectively over a large range of slopes. Here, we use the model to examine the impact of slope on the migration and convective dissolution of CO$_2$ in the Mt. Simon Sandstone, a large saline aquifer in the Midwestern United States. For 10 Gt of CO$_2$ injected uniformly along a 200 km array of wells, we show (a) the time $t^F$ when all of the CO$_2$ is trapped and (b) the maximum migration distance (maximum nose position) $x_N^{\text{max}}$, both as a function of the slope $\vartheta$ for solubility trapping alone (blue), for residual trapping alone (gray), and for both residual and solubility trapping (black). The CO$_2$ is trapped more quickly ($t^F$ decreases) as $\vartheta$ increases, but this effect must be balanced against the increase in migration distance with $\vartheta$. 
effectively when the plume is long and thin, but needs time to operate. As a result, solubility trapping alone does not arrest the plume quickly enough when the slope is large and the plume migrates quickly.

The combination of residual and solubility trapping traps the CO$_2$ quickly and efficiently over the entire range of slopes: solubility trapping arrests the plume when the slope is small and the CO$_2$ migrates slowly, whereas residual trapping arrests the plume when the slope is large and the plume migrates quickly. Although the quantitative migration times and distances will change when, for example, we include connate water in this analysis, this physical insight into CO$_2$ migration and trapping will still apply.

5.2 Broader applicability and physical limitations of the model

We have derived and studied a simple but physics-based model for CO$_2$ migration and trapping. Although the main contribution of this model is the insight it provides into the physics of CO$_2$ migration and trapping, its simplicity allows it to capture the macroscopic impact of pore-scale trapping processes on CO$_2$ migration over very large length and time scales, while still being much less computationally expensive than a detailed reservoir simulation. As a result, it can be very useful in practice for benchmarking or interpreting the predictions of more complicated numerical models, or for analyses that would be prohibitively expensive with more complicated models. For example, the model can be used to perform extensive sensitivity and uncertainty analysis, or to quickly estimate the storage capacity of a large number of aquifers based on aquifer-specific properties (Szulczewski and Juanes, 2009; Szulczewski et al., 2011b,a).

In developing the model, we have made many simplifying assumptions. For example, our analysis is planar, assuming line-symmetry and neglecting lateral flow. This assumption is justified by the injection scenario we consider, injection at the scale
of a geologic basin via a line-drive array of wells. However, three-dimensional flow may become important at later times as the plume migrates sufficiently far from the injection wells, or if the direction of groundwater flow is not completely aligned with the slope. We have also assumed that the thickness of the aquifer is uniform and that the caprock is flat—in practice, this is rarely the case. These effects are not included here, but can be accounted for in a computational framework (Gasda et al., 2009, 2011).

We have not included leakage here; however, the CO₂ plume will likely encounter faults or fractures in the caprock as it migrates because its areal footprint will be very large. Pritchard (2007), Farcas and Woods (2009), Woods and Farcas (2009), Neufeld et al. (2009), Neufeld et al. (2011), and Vella et al. (2011) have recently studied leakage in some detail, and have shown that the impact of leakage depends strongly on the distribution, permeability, and capillary entry pressure of the leakage pathways. These considerations are beyond the scope of this Thesis, but the model presented here provides an attractive framework for studying the coupling of leakage with CO₂ migration and trapping.

Although we have assumed that the aquifer is homogeneous, all natural rocks are heterogeneous at some scale. The impact of heterogeneity is an interesting and important aspect of CO₂ migration and trapping that remains poorly understood. One reason for this is that the answers to even fundamental questions, such as whether heterogeneity will increase or decrease the storage efficiency, will depend strongly on the nature, scale, and distribution of the heterogeneity. A variety of stochastic techniques for tackling such questions have been developed in the context of groundwater hydrology (e.g., Gelhar, 1986), and many of these techniques, such as computational Monte Carlo studies or the development of moment equations, use models like the one presented here as a starting point.

Additionally, although CO₂ and water are immiscible, we have neglected the capillary pressure. This is a valid assumption when the capillary pressure is negligible relative, for example, to the hydrostatic pressure. When this is not the case, capillarity may play an important role in CO₂ migration. One effect of capillarity is to smear
the interface between the CO$_2$ and the water so that it is not sharp. Nordbotten and Dahle (2011) and Golding et al. (2011) have incorporated this capillary fringe into simple models for CO$_2$ injection and migration, showing that it may have an important impact on residual trapping by increasing the effective thickness of the CO$_2$ plume. Another important effect of capillarity is capillary pressure hysteresis. Zhao et al. (2011) showed that capillary pressure hysteresis can have a striking impact on the shape of the CO$_2$ plume and may ultimately arrest its migration, even when the capillary fringe is negligible. This effect can be included in the model (Zhao et al., 2011).

These considerations are beyond the scope of this study, but they will have some quantitative bearing on the results presented here. However, it is unlikely that they will have a strong qualitative impact on the fundamental nature of the interaction between slope and groundwater flow, or the competition between residual and solubility trapping.


