Implications of Coupling Fractional Flow and Geochemistry for CO$_2$ Injection in Aquifers
M. Noh, L. W. Lake, S. L. Bryant, and A. Araque-Martinez / The University of Texas at Austin

Abstract
The geochemical changes caused by CO$_2$ injection into aquifers include acidification and carbonation of the native brine and potential mineral dissolution and precipitation reactions driven by the aqueous composition changes. The latter are important for evaluating the potential CO$_2$ storage capacity in the form of minerals and can also influence the performance of the injection well.

The theories of geochemical flows and of fractional flow provide useful insight into several aspects of CO$_2$ sequestration. This paper gives the mathematical formalism of combined geochemical and multi-phase flow. If local equilibrium applies, the theory leads to graphical solution, from which it is easy to see when and under what conditions mineralization will occur during the injection. The theory also illustrates the influence of post-injection flow on mode of CO$_2$ trapping (hydrodynamic, solubility, mineral, residual saturation). We also show that co-injection of water significantly alters the mode of trapping.

Introduction
Carbon dioxide sequestration was first discussed in the late 1970s. However, serious research and development in CO$_2$ sequestration only began in the early 1990s. The technical literature about CO$_2$ disposal in aquifers includes feasibility studies in The Netherlands and in the Alberta Basin, Canada. A field test is being performed in the North Sea in the Sleipner Vest project, which is the first CO$_2$ sequestration project in a brine-bearing formation.

Sequestering CO$_2$ in geologic formations offers numerous advantages, including:

1. The experience of the oil industry can directly provide the technology to enable the commercialization of this approach.

2. Several collateral economic benefits are possible, for example, enhancing oil and gas recovery while storing CO$_2$.

3. Suitable geologic formations, including oil, gas, brine, and coal formations are relatively easy to find.

4. The regulatory infrastructure associated with the injection into oil and gas formations and deep aquifers is well established.

5. Geologic analogs such as natural CO$_2$ reservoirs prove that geologic structures can sequester CO$_2$ for a very long time.

6. Public acceptance for geologic sequestration should grow as technological advances lead to innovative methods for creating permanent mineral sinks for CO$_2$.

Carbon dioxide can be sequestered in geologic formations by three principal mechanisms:

1. CO$_2$ can be trapped as a gaseous phase or supercritical fluid under a low-permeability caprock, similar to what occurs in natural gas reservoirs (hydrodynamic trapping).

2. Dissolution into an aqueous phase (solubility trapping).

3. CO$_2$ can react with the minerals and the organic matter in geologic formations to become a part of the solid (mineral trapping). Formation of carbonate minerals such as calcite or siderite and the adsorption onto coal are other examples of the mineral trapping. Mineral trapping will create stable repositories of CO$_2$ that decrease mobile hazards such as leakage to the surface.

An additional form of storage -- as a residual gas saturation -- is also studied in this and a companion paper. Here CO$_2$ remains as a gaseous phase, such as hydrodynamic trapping, but it is immobile because the gas is trapped by capillary forces. In this study, the immobile gas trapping is called the residual saturation trapping.

Siliciclastic aquifers should have greater potential for the mineral trapping of CO$_2$ compared to carbonate aquifers. Depending on whether the basic aluminosilicate minerals, such as feldspars, zeolites, illites, chlorites and smectites, contain an alkali or alkaline earth cation, two types of mineral trapping can be considered. Na/K-bearing minerals result in the development of bicarbonate brines. Fe/Ca/Mg-bearing minerals result in the precipitation of siderite, calcite or
of trapping and immobilization of CO₂. Gunter et al.⁵ performed an experimental and numerical study on CO₂-trapping reactions in a glauconitic sandstone aquifer, which is a typical sandstone aquifer from the Alberta Basin. Their study indicated that geochemical trapping of CO₂ is slow, but still fast enough to form effective CO₂ traps compared to the fluid flow in aquifers.

During CO₂ injection into geologic formations, geochemical processes are affected by multiphase fluid flow and solute transport. The dissolution of primary minerals and the precipitation of secondary minerals could change formation porosity and permeability and subsequently affect fluid flow patterns. These reactions also determine the mass of CO₂ that can be stored by mineral trapping. The theory of propagation of geochemical fronts (mineral precipitation / dissolution) provides insight into the time scales, spatial extents and composition changes associated with these reactions.¹⁴ The theory is well established for single-phase aqueous flows, but it requires extension when a second fluid, in this case CO₂, is also flowing, because the velocity and saturation of the aqueous phase is no longer constant. When mass transfer between the flowing phases is possible, the fractional flow fronts and geochemical fronts are still more tightly coupled. Both theories require extension in this case. In this study, we show an analytical approach to characterize the semi-miscible displacement of water by CO₂. The specific velocity of a concentration discontinuity is derived from the mass balance equation (see Appendix). For verification, analytical solutions are compared with simulation results.

### Mathematical model

**Introduction**

The simulation portion of this work uses the commercial program GEM⁶ from Computer Modeling Group Ltd. GEM is an implicit multi-phase flow simulator that assumes chemical equilibrium for each component within the fluid phases. A rate-dependent mineral precipitation / dissolution reaction model is employed. The governing equations are the material balances for each component and Darcy's law. Dispersion and diffusion also contribute to the transport of solutes in the aqueous phase.

**Gas solubility in an aqueous phase**

The gaseous phase CO₂ dissolution in the aqueous phase is viewed as the following chemical reaction.

\[
\text{CO}_2 \text{(gas)} \leftrightarrow \text{CO}_2 \text{(aqueous)}
\]

The CO₂ concentration in the gas and aqueous phases is assumed to be in local equilibrium for which the following discussion applies.

The solubility of CO₂ in an aqueous phase depends on the partial pressure of CO₂ in the gaseous phase. It also depends on temperature and water salinity. At low pressure, the equilibrium of a gas phase dissolved into water can be modeled by Henry's law, which states that the concentration \( C_i \) of dissolved gas phase \( i \) linearly depends on the partial pressure \( p_i \) of that component in the gaseous phase.

\[
p_i = C_i / H_i
\]

where \( H_i \) is the reciprocal of Henry's law constant for component \( i \) in units of pressure per units of concentration. However, CO₂ solubility at large pressure does not follow Henry's law. In GEM, the fugacity is used instead of partial pressure.

At equilibrium the fugacities of CO₂ in the gas and aqueous phases are equal. The fugacity of CO₂ in the gaseous phase, \( f_{ig} \), is calculated from an equation of state and \( f_{ia} \) is calculated by¹³

\[
f_{ia} = y_{ia} k_i
\]

where the subscript \( i \) is a component, e.g. CO₂ and \( k_i \) is the Henry's law constant of component \( i \) in units of pressure. \( y_{ia} \) is a mole fraction of \( i \) in the aqueous phase. At equilibrium \( f_{ia} = f_{ig} \).

**Mineral precipitation/dissolution rates**

The reaction rates of minerals in contact with an aqueous phase are controlled by reactions at the surface of the minerals. The rates are expressed as

\[
r_\beta = \hat{A}_\beta k_\beta \left[ 1 - \frac{Q_\beta}{K_{sp,\beta}} \right]
\]

where the subscript \( \beta \) refers to the reaction of mineral \( \beta \). \( \hat{A}_\beta \) is the reactive surface area of mineral reaction \( \beta \) per unit bulk volume of porous medium \([m^2/m^3]\) and \( k_\beta \) is a rate constant of the mineral reaction \( \beta \), \([mol/(m^2-s)]\). \( Q_\beta \) is the activity product of mineral reaction \( \beta \) and \( K_{sp,\beta} \) is the solubility product of mineral reaction \( \beta \). The units of \( r_\beta \) in Equation (1) are moles per unit bulk volume of porous medium per time, \([mol/(m^3-s)]\).

If \( Q_\beta \) is greater than \( K_{sp,\beta} \), the aqueous phase is supersaturated and mineral precipitation occurs. Otherwise, the mineral dissolves into the aqueous phase. The reaction rate constant is a function of temperature, \( T \),

\[
k_\beta = k_{0,\beta} \exp \left[ \frac{-E_{a,\beta}}{R T} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]
\]

where \( E_{a,\beta} [J/mol] \) is the activation energy for a reaction \( \beta \), and \( k_{0,\beta} \) is the reaction rate constant (frequency factor) for a reaction \( \beta \) at \( T_0 \). \( R \) is the universal gas constant, \([8.314 J/mol-K]\).

**Results and discussion for CO₂ sequestration model**

**Analytical considerations**

We will refer to CO₂ displacing water and vice versa as a semi-miscible displacement because of the substantial solubility of CO₂ in water. We assume that the injected CO₂ is dry (contains no water vapor).
Specific shock velocity when gas displaces water

For a semi-miscible displacement, the specific velocity of the saturation discontinuity can be derived using fractional flow theory. The derivation is discussed in the Appendix.

Fractional flow theory provides analytical solutions to one-dimensional incompressible two-phase flows. When the phases do not change composition, the gas saturation profile is calculated by Equation (2).

\[
x_D = \frac{x}{L} = \frac{Q}{\phi AL} \frac{df_g}{dS_g} = t_d \frac{df_g}{dS_g}
\]

where \(x\) is the distance from the inlet and \(L\) is a characteristic length scale so that \(x_0\) represents a dimensionless distance. \(Q\) is the cumulative volume of injected fluid, \(\phi\) is the porosity and \(A\) is the cross-sectional area. Therefore, \(t_0\) is a dimensionless time, the pore volume injected. \(f_g\) and \(S_g\) are the fractional flow and the saturation of the gaseous phase, respectively. Figure 1 shows a schematic fractional flow curve of a gaseous phase when the gas displaces water in an aquifer. \(I\) and \(J\) represent the initial and the injection conditions, respectively. Retardation factors \(D\) are defined in Table A-1. Initially, the aquifer has 100\% water and the CO₂ injection displaces water. The relationship is a first drainage curve because of the absence of the non-wetting CO₂-rich gaseous phase in the aquifer initially.

A tangent line (1) is drawn from the point \(I\) to the gaseous phase fractional flow curve as shown in Figure 1. Here \(i\) is CO₂ component and the concentrations are evaluated at equilibrium between gas and aqueous phases. The slope of the tangent line, \(\frac{df_g}{dS_g}|_{S_g}\), represents the specific velocity of a fast shock as shown in Equation (A-11). This segment represents a saturating front of the miscible displacement of CO₂-free water by CO₂-saturated gas.

A slow shock exists where the dry (water-free) injected gaseous phase evaporates the aqueous phase. A tangent line (2) is drawn from the point \(J\) to the fractional flow curve as shown in Figure 1. The slope of line (2) corresponds to the specific velocity of the slow shock in Equation (A-12). The point of tangency defines \(S_g\), the gaseous phase saturation at the shock. The slope of tangent line (2) depends on the solubility of the water component in the gaseous phase. If the water solubility to the gaseous phase is zero (\(C_w = 0\)), the slope is zero so that the slow shock has zero velocity. Note that two open circles (points \(I\) and \(J\)) in Figure 1 are located on the line with a slope of one through the origin.

A schematic of a gas saturation profile for displacing water with CO₂ is shown in Figure 2. Between \(x_D|_{S_g=1}\) and \(x_D|_{S_g=2}\), the water component is dissolved into the gaseous phase and vice versa. Downstream of the fast shock at \(x_D = x_D|_{S_g=S_g'}\), the aqueous phase contains only water at the initial condition. Upstream of the slow shock at \(x_D = x_D|_{S_g'=S_g}\), the gaseous phase is 100\% CO₂ at the injection condition. If H₂O-saturated gas were to be injected, the slow shock in Figure 2 would have zero velocity. The CO₂-saturated aqueous phase represents the solubility trapping. The H₂O-saturated gas is subject to hydrodynamic trapping, though this effect cannot be directly accounted for in this one-dimensional model.

It is instructive to compare this semi-miscible displacement to the immiscible displacement that would occur were there no mutual solubility between the CO₂ and the H₂O. The points \(I\) and \(J\) would coincide with the origin and (1,1), respectively, on the fractional flow diagram. Thus the tangent line (1) in Figure 1 will be drawn from the origin so that the downstream shock velocity would be larger than that of the semi-miscible displacement. Therefore, the saturating front would be ahead of that shown for the semi-miscible displacement in Figure 3. If the water solubility in the gaseous phase is zero, the gaseous phase saturation upstream of the fast shock is \((1 - S_{ar})\), where \(S_{ar}\) is the irreducible aqueous phase saturation. The amount of CO₂ contained in the aqueous phase in Figure 2 is equal to region (B) in Figure 3. Similarly, the amount of the water component vaporized into the gaseous phase in Figure 2 is equivalent to region (A) in Figure 3.

Specific shock velocity when water displaces gas

After CO₂ is injected, the slug can be pushed further into the aquifer by subsequent water injection or by natural flow. Figure 4 shows a schematic of a gas fractional flow curve when water displaces the gaseous phase after the gas injection. The initial condition now is \(J\) and the inlet condition \(K\).

When water displaces the gaseous phase, the gas fractional flow is different from that in Figure 1 because of relative permeability hysteresis. Figure 1 is a drainage fractional flow curve with the initial condition of \(S_0 = 1\) and Figure 4 is an imbibition fractional flow curve with \(S_0 = 0\).

The displacement again creates two shocks whose specific velocities are shown by the slopes of the tangent lines in Figure 4. The velocity \(v_{(j)}\) is determined by the slope of a tangent line (3) drawn from the point \(J\) to the gas fractional flow curve. \(v_{(4)}\) is the slope between \((S_{gr},0)\) and the point \(K\) so that it is calculated as

\[
v_{(4)} = \frac{-(C_{i_{gr}})(C_{i_{wa}} - C_{i_{ga}})}{S_{gr} - C_{i_{wa}}/C_{i_{ga}}}
\]

A schematic of a gas saturation profile in this semi-miscible displacement is in Figure 5. It shows two shocks corresponding to the shock velocities (3) and (4) in Figure 4. As discussed in Figure 2, the shock at \(x_{p(4)}\) will not arise (its velocity vanishes) if CO₂-saturated aqueous phase were injected. In Figure 5, the H₂O-saturated gaseous phase is the
residual saturation trapping and the CO2-saturated water is the solubility trapping.

**Comparison of analytical solutions with simulation results**

The graphical solutions are instructive but they are based on several assumptions (Appendix) that are not needed in GEM, foremost of which is the assumption of incompressible flow. We also included the effects of the geochemical reactions with GEM.

**Test case description**

To confirm the analytical solutions, we perform a one-dimensional displacement simulation in a homogeneous and horizontal domain with two minerals, anorthite and calcite using GEM. These represent a path of mineral trapping:

Anorthite + 2H2O + CO2 → Calcite + Kaolinite

suggested by Gunter et al. The one-dimensional example is a simplified case from the test run by Nghiêm.12

There are 100×1×1 cells in the x–y–z directions; fluid and formation properties are in Figure 6. There is a production well at the outlet (on the right) maintained at a constant pressure. The injection well (on the left) is set at a constant rate of 4 m³/day at the reservoir condition.

Henry's law constant is set to 2.74×10⁴ kPa. The relative permeability curves shown in Figure 7 were generated analytically from the exponential form of Corey type curve. Capillary pressure is ignored. We account for hysteresis of relative permeabilities as shown in Figure 7. Dotted lines represent drainage relative permeabilities and solid lines are imbibition curves. The aqueous reactions and the mineral dissolution reactions are shown in Table 1 and Table 2, respectively. Here, the equilibrium constants, solubility products and reaction rate constants are expressed in logarithmic functions with base 10. The rate constants kβ, reactive surface area $\hat{A}_β$, and activation energies $E_{aβ}$ are also listed.

Table 3 gives the initial aqueous component concentrations. The aqueous concentrations of each component correspond to chemical equilibrium conditions for the three aqueous reactions in Table 1. At the initial condition, the activity equilibrium product of the components making up the minerals is equal to the solubility product. GEM requires that the mineral precipitation/dissolution rate be set to zero if the mole fraction of CO₂ in the aqueous phase is less than 10⁻³.

Table 4 shows the mineral properties and initial volume fractions of minerals, i.e. the initial volume of minerals per bulk volume.

**Comparison of shock velocities for gas displacing water**

Figure 8 shows the gaseous phase fractional flow curve for the test case. In this example, $\frac{C_{CO2,a}}{C_{CO2,a} - C_{CO2,g}} = -0.45$ and the shock front is located at $S_g = 0.212$. The derivative $df/dS_g$ in Equation (2) is determined to be 2.02, so that the dimensionless distance $x/L$ is 0.488 for 30 years of CO₂ injection.

Figure 9 compares the fractional flow solution (solid lines) with simulation results (dotted line). The two results are in good agreement. As discussed above, if there were no CO₂ solubility in the aqueous phase, i.e. assume an immiscible displacement, the shock velocity would be larger than for the miscible displacement as described in Figure 3. Therefore, the gas saturation front moves faster than that of miscible displacement. For example, a saturation shock for immiscible displacement at 30 years will be at the 1115 m of distance rather than 488 m. After 3000 years the water saturation around the injector increases to 0.25, the irreducible water saturation. If we allow the water dissolution in the gaseous phase, the gas saturation at the inlet should increase to 1.

The principal conclusion from Figure 9 is that the fractional flow solutions are reasonable approximations to the actual flow.

**Specific velocity of a concentration discontinuity for a base component**

When fluid moves sufficiently slowly, the chemical reactions satisfy the local equilibrium assumption (LEA). Equivalently, local equilibrium is a reasonable approximation when chemical reactions are fast enough to instantaneously restore equilibrium. The Damköhler number, the ratio of the chemical reaction rate to the fluid convection rate, is a convenient criterion for invoking LEA.17

The Damköhler number in one-dimensional reactive transport can be defined as

$$N_{Da} = \frac{r \cdot qL}{C_1 \cdot u}$$

where $r$ is a reaction rate and $L$ is the total length. The subscript I represents the initial condition. With 4 m³/day of injection, the Damköhler number is on the order of 10² for the calcite mineral reaction. Therefore, the injection rate is slow enough to assume local equilibrium. This provides a limiting case for understanding behavior at the larger injection rates (smaller Damköhler numbers) that will be typical of field sequestration projects.

Figure 10 shows the concentration profiles at 30 years ($t_p = 0.244$) of the CO₂ injection. The mineral concentration is expressed in units of volume fraction of the bulk volume. For reactive transport, multiple concentration waves are possible, and all waves involving mineral concentrations move more slowly than the saturation wave. At 30 years of CO₂ injection, the gaseous phase saturation front in Figure 9 is around 480 m at which position the aqueous concentrations also show shocks in Figure 10. The concentration shocks are caused by the CO₂ reacting with other aqueous components to form bicarbonate and carbonate anions.

The change in concentrations also causes a small change (dissolution) of the calcite whose concentration is also shown in Figure 10. In single-phase flow under LEA minerals dissolve or precipitate completely, never partially. The partial dissolution of calcite shown in Figure 10 is a consequence of the interactions of two-phase flow and the geochemistry. The capacity of the aqueous phase to dissolve calcite is limited by the capacity of the aqueous phase to solubilize the calcite and the velocity of the aqueous phase.
To illustrate the last point further, we made a run in which equal volume of CO$_2$ and calcium-free water is injected simultaneously. Concentration profiles, illustrated in Figure 11, show a clear calcite dissolution wave located at about 170 m, immediately downstream of the injection condition. This wave moves very slowly and calcite dissolves complete across it. Without dispersion, the velocity of a dissolution wave is calculated by

$$v_{\Delta C_{Ca}} = \frac{1}{9} \frac{\Delta N_{Ca}}{u} \frac{\Delta C_{Ca}^T}{\Delta C_{Ca}^T + \Delta C_{CaCO_3}^T} \quad (3)$$

For this case $\Delta C_{Ca}^T$ and $\Delta C_{CaCO_3}^T$ are 0.018 mol/l and 1.42 mol/l, respectively. Therefore, the dimensionless velocity of the shock is 0.006 by Equation (3). As shown in Figure 11, the dissolution wave is located at 170 m after $t_D = 24.2$; this corresponds to a specific velocity of 0.007. The difference between the simulation result and the analytical solution is a result of the water compressibility of $4.35 \times 10^{-7}$ kPa$^{-1}$. The analytical solution and the GEM simulation results are in good agreement.

Equation (3) says that the dissolution wave velocity will be zero if either the aqueous fractional flow is zero or if the calcium concentration change is zero. Both effects contribute to the absence of a complete dissolution of calcite in Fig. 10.

The concentration of Ca$^{2+}$ decreases abruptly and then gradually to zero because the reaction rate constant of the anorthite dissolution ($10^{-12}$) is much smaller than the calcite dissolution ($10^{-8.8}$). The flow is not in local equilibrium with respect to the anorthite dissolution.

Comparison of shock velocities for water displacing gas

As discussed in Figure 5, there are two shocks when water displaces the gaseous phase. We use the gas saturation profile at 3000 years in Figure 9 for an initial condition into which 4 m$^3$/day of the water is injected. The gas fractional flow curve is redrawn in Figure 12 to account for hysteresis. There are two specific shock velocities, $V_{f(3)}$ and $V_{f(4)}$ corresponding to Figure 4. Since the gas saturation at 3000 years is not 1, the average gas saturation is used to estimate $V_{f(3)}$; $V_{f(4)}$ is the slope between $\left( \frac{C_{la}}{C_{la} - C_{lg}^T}, \frac{C_{la}}{C_{la} - C_{lg}^T} \right)$ and $(S_{po}, 0)$.

Gaseous phase saturation profiles are shown in Figure 13. The dotted lines represent the analytical solutions of the gas saturation fronts from the fractional flow curve at 3030 years. The analytical solutions are in good agreement with the simulation result. The amount of CO$_2$ between $x_D(3)$ and $x_D(4)$ represents the residual saturation trapping.

Conclusions

In this paper, we derive an analytical solution for one-dimensional two-phase semi-miscible displacement. Coupling of fractional flow and geochemical theories yields wide range of retardation factors. From fractional flow theory and entropy condition, specific velocities of shocks are calculated and compared with numerical results. Analytical solutions are in good agreement with numerical results.

After CO$_2$ injection, an undersaturated aqueous phase can remobilize the CO$_2$ slug and push it further into the aquifer. When the aqueous phase displaces the gaseous phase, a residual gas saturation remains between fast and slow shock. The calculations of the fast shock and the slow shock indicate the amount of residual saturation trapping. Because of the large solubility of carbon dioxide in water, the fast and slow shocks have similar velocities.

Carbon dioxide dissolved in an aqueous phase and flowing under local equilibrium conditions can cause dissolution of resident minerals. These effects tend to be suppressed by two-phase flow. This occurs in two ways: the two phase flow reduces the velocity of the aqueous phase and equilibrium with the gaseous phase tends to limit the solubility of the metal cations. Unlike single-phase flow, geochemical reactions in two phase flow can result partial dissolution of minerals.

Nomenclature

- $A$ = area, $m^2$
- $\hat{A}$ = reactive surface area per unit bulk volume, $m^2/m^3$
- $C$ = concentration, mol/l
- $D$ = retardation factor
- $E_a$ = activation energy, J/mol
- $F$ = fractional flux, mol/(m$^2$.s)
- $f$ = fractional flow
- $H_i$ = reciprocal of Henry’s law constant for component i, atm-l/mol
- $K$ = equilibrium constant
- $k$ = reaction rate constant, mol/(m$^2$.s)
- $k_i$ = Henry’s law constant for component i, kPa
- $K_{sp}$ = solubility product
- $N_{Da}$ = Damköhler number
- $p_i$ = partial pressure of component i
- $Q$ = activity product
- $r$ = reaction rate, mol/(m$^2$.s)
- $R$ = universal gas constant, 8.314 J/(mol.K)
- $S$ = saturation
- $T$ = temperature, K
- $t$ = time, s
- $v$ = specific velocity
- $x$ = distance, m
- $y$ = mole fraction
- $\phi$ = porosity
- $\nu$ = stoichiometric coefficient
- $\xi_i$ = dimensionless variable for retardation factor, $H_i/zRT$

Superscript

$+$ = downstream

$-$ = upstream

Subscript

- $\beta$ = mineral reaction
- $0$ = standard condition
- $i$ = component
- $a$ = aqueous phase
- $g$ = gaseous phase
- $w$ = water component
- $D$ = dimensionless variable
References


Appendix
This Appendix develops the equations upon whose solutions rest the conclusions of this work.

Geochemical Mass Balances
The mass balances solved in the analytical portion of this paper are

$$\frac{\partial C_i^T}{\partial t_D} + \frac{\partial F_i}{\partial X_D} = 0 \quad \text{A - 1}$$

for each component $i$. The independent variables are

Dimensionless time:

$$t_D = \frac{\int q d\xi}{\int A \phi d\xi} = \frac{\text{Cumulative volume of fluid injected up to time } t}{\text{Pore volume of the medium}}$$

Dimensionless position:

$$x_D = \frac{\int A \phi d\xi}{\int A \phi d\xi} = \frac{\text{Pore volume upstream of position } x}{\text{Pore volume of the medium}}$$

where $q (= A t/D)$ is the time-varying volumetric flow rate of the sum of the aqueous and gaseous phases, $A$ is the spatially-varying cross sectional area of the medium and $\phi$ is the spatially varying porosity of the medium. The $L$ in these definitions is arbitrarily chosen to be the lateral (x-direction) length of the medium. Other definitions are possible; for slugs we will choose $L$ such that $t_D = 1$ at the time slug injection ceases.

Equation (A - 1) presumes one-dimensional flow and incompressible fluid and rock. Base components are elements such as carbon C, and calcium Ca. We also assume that local equilibrium holds between and within all phases.

An element can exist as part of a compound in the aqueous, gas, or mineral phase. The total concentration for carbon in Equation (A - 1) is therefore

$$C_c^T = S_g^{\text{gaseous}} C_{CO_2}^g + S_a \left( C_{CO_2}^a + \sum_{j=1}^{j=1} v_{ij} C_j^a \right) + \sum_{k=1}^{k=K} v_{ik} C_k^m$$

A - 3
where the i in the sums on the right of this equation refers to carbon. Other terms in Equation (A - 3) are:

\[ S_g, S_a = \text{saturation (pore space volume fraction) of gas and aqueous phases} \]

\[ C_{CO_2,g}, C_{CO_2,a} = \text{concentration of CO}_2 \text{ in the gas and aqueous phases} \]

\[ C_j = \text{concentration of component j (j=1...J) in the aqueous phase} \]

\[ \bar{C}_k = \text{concentration of mineral k (k =1…K) moles of k/pore volume} \]

\[ v_{ij}, v_{ik} = \text{stoichiometric coefficient}; the number of moles of i in component j or mineral k] \]

\[ C_{CO_2,a}, \text{the concentration of dissolved CO}_2 \text{ in the aqueous phase, accounts for the solubility of CO}_2 \text{ in the aqueous phase.} \]

\[ C_{CO_2,g}, \text{accounts for the water solubility in the gaseous phase; if the gaseous phase contains no water vapor, } C_{CO_2,g} \text{ would be the molar density.} \]

\[ C^{T}_{C} = S_g C_{CO_2,g} + S_a \left( C_{CO_2,a} + C_{HCO_3} + C_{CO_2} \right) \]

\[ \bar{C}_{CaCO_3} + \bar{C}_{FeCO_3} \]

\[ \text{The fractional flux of carbon in Equation (A - 1) is} \]

\[ F_C = f_g C_{CO_2,g} + f_a \left( C_{CO_2,a} + \sum_{j=1}^{J} v_{ij} C_j \right) \]

\[ \text{where } f_g \text{ is the fractional flow of the gaseous phase.} \]

\[ F_C = f_g C_{CO_2,g} + f_a \left( C_{CO_2,a} + C_{HCO_3} + C_{CO_2} \right) \]

Waves and wave velocities

The solution to Equation (A - 1) occurs in the form of waves or propagating changes in either flux or concentration. Three types of waves are relevant here. Spreading waves, whose specific velocity is given by

\[ \text{Spreading: } v_{C_i} = \frac{dF_{C_i}}{dC^{T}_{C_i}} \]

Where the derivative is evaluated at the concentration C_i which is propagating and sharpening waves with specific velocity

\[ \text{Sharpening: } v_{\Delta C_i} = \frac{\Delta F_{C_i}}{\Delta C_{C_i}} \]

where the \( \Delta \) means a change across a shock

\[ \Delta ( \cdot )_{\text{upstream}} - ( \cdot )_{\text{downstream}} = ( \cdot )^+ - ( \cdot )^- \]

Sharpening waves become less diffuse on propagation; in this work they are synonymous with shocks as they will therefore be designated. The velocities in Equations (A - 5) and (A - 6) are specific velocities because they are normalized by the average velocity of the fluid phases \( u = q/A \); this could be measured by observing the transport of a non-reactive tracer in each phase.

A mixed wave, the third type, is a combination of spreading and shock. The continuity of the solution of a mixed wave is the entropy or Lax condition that sets the two velocities in Equations (A - 5) and (A - 6) equal at a specific concentration.

Semi-miscible wave

In terms of multiphase flow, CO_2 displacing water forms a mixed wave, across which the mineral concentration does not change, except perhaps at a point. Both the phase saturation and the component concentrations may change across and within this wave. This possibility is one manifestation of the coupling of fractional flow and geochemical flows, for such changes do not occur when single-phase flow induces precipitation/dissolution. The generalization of the above velocities is straightforward, and we obtain the specific velocity of the shock from Equations (A - 3) ~ (A - 6).

\[ v_{\Delta C} = \frac{\Delta \left( f_g C_{CO_2,g} + f_a \left( C_{CO_2,a} + \sum_{j=1}^{J} v_{ij} C_j \right) \right)}{\Delta \left( S_g C_{CO_2,g} + S_a \left( C_{CO_2,a} + \sum_{j=1}^{J} v_{ij} C_j \right) \right)} \]

\[ = \frac{\Delta (f_g C_{CO_2,g} + f_a C_{Ca})}{\Delta (S_g C_{CO_2,g} + S_a C_{Ca})} \]

where we introduce the shorthand \( C_{Ca} \) for the total aqueous carbon.

Carbon dioxide displacing water

Figure 2 shows a gas saturation profile for the injection of a single-phase, single-component CO_2 gas into an aquifer. The profile consists of one mixed wave that contains two shocks (between regions II and I, and between regions J and II). The spreading portion of the mixed wave is region II. Region II contains wet CO_2; the gaseous phase is saturated with respect to water. Similarly, the aqueous phase is saturated with CO_2. The following discussion regards all the concentrations as known. In this section we neglect the concentration of all carbon-containing components in the aqueous phase except dissolved CO_2.

The downstream state (superscript II) of the fast shock between regions II and I has negligible carbon so that the specific velocity of the shock becomes
where \( f^g_\text{tr} \) is the fractional flow of the gaseous phase just upstream of the shock so that \( f^g_\text{tr} \) is evaluated at at \( S^g_\text{II} \) in Figure 1. Equation (A - 8) can be cast in a chromatographic form

\[
V_{\Delta C} = \frac{f^g_\text{in} C^\text{II}_{\text{CO}_2,\text{g}} + f^g_\text{tr} C^\text{II}_{\text{CO}_2,a}}{S^g_\text{II} C^\text{II}_{\text{CO}_2,\text{g}} + S^a_\text{II} C^\text{II}_{\text{CO}_2,a}} = f^g_\text{tr} - \frac{C^\text{II}_{\text{CO}_2,a}}{\left( S^g_\text{II} C^\text{II}_{\text{CO}_2,\text{g}} - S^a_\text{II} C^\text{II}_{\text{CO}_2,a} \right)}
\]

where the superscript \( J \) represents the inlet (upstream condition). \( f^g_\text{in} \) is the gaseous phase fractional flow just downstream of the trailing shock; thus it is evaluated at \( S^g_\text{II} \) in Figure 1. If the inlet condition is only the gaseous phase \( f^g_\text{in} = 1 \) we have

\[
V_{\Delta C} = \frac{C^J_{\text{CO}_2,\text{g}} - \left( f^g_\text{in} C^\text{II}_{\text{CO}_2,\text{g}} + f^g_\text{tr} C^\text{II}_{\text{CO}_2,a} \right)}{C^J_{\text{CO}_2,\text{g}} - \left( S^g_\text{II} C^\text{II}_{\text{CO}_2,\text{g}} + S^a_\text{II} C^\text{II}_{\text{CO}_2,a} \right)}
\]

\[
f^g_\text{in} - \frac{C^J_{\text{CO}_2,\text{g}} - C^\text{II}_{\text{CO}_2,a}}{C^\text{II}_{\text{CO}_2,\text{g}} - C^\text{II}_{\text{CO}_2,a}}
\]

\[
S^g_\text{II} - \frac{C^J_{\text{CO}_2,\text{g}} - C^\text{II}_{\text{CO}_2,a}}{C^\text{II}_{\text{CO}_2,\text{g}} - C^\text{II}_{\text{CO}_2,a}}
\]

In the region between the two shocks (Figure 2), the concentrations are constant meaning that the specific velocity of a carbon concentration in this region is

\[
V_C = \frac{d f^g_\text{in}}{d S^g_\text{II}} = \frac{d f^g_\text{tr}}{d S^a_\text{II}}
\]

where \( D_{\text{I} \rightarrow \text{II}} \) is the retardation factor for the shock between regions I and II. Similarly, we have for the trailing shock

**Upstream:**

\[
V_{\Delta C} = \frac{f^g_\text{in} - D_{\text{II} \rightarrow \text{I}}}{S^g_\text{II} - D_{\text{II} \rightarrow \text{I}}} = \left( \frac{d f^g_\text{in}}{d S^g_\text{II}} \right)
\]

\[
A - 12
\]

where \( D_{\text{II} \rightarrow \text{I}} \) the retardation factor is given in Table A - 1. If we neglect vaporization of water into the gaseous phase, the upstream saturation \( S^g_2 \) is \((1 - S^a_2)\), where \( S^a_2 \) is the aqueous phase residual saturation as shown in Figure 2. The downstream wave is saturating and the upstream wave drying.

**Water displacing carbon dioxide**

After a volume of \( \text{CO}_2 \) has been injected natural aquifer flow can push the \( \text{CO}_2 \) slug further into the aquifer. Now the most downstream condition is \( J \) and the most upstream is \( K \). See Figure 5.

There is again a mixed wave consisting of two shocks (between regions III and \( J \), and regions \( K \) and III) and a spreading portion (region III). The spreading wave portion is smaller here than for Figure 2 because of the more favorable mobility ratio in the \( K \) displacing \( J \) case compared to \( J \) displacing I. The most important detail in Figure 5 is the presence of a residual gas saturation that was absent in Figure 2. The residual gas saturation exists because of hysteresis in the relative permeability.

The shock saturations are given by

**Downstream:**

\[
V_{\Delta C} = \frac{f^g_\text{in} - D_{\text{III} \rightarrow \text{II}}}{S^g_\text{III} - D_{\text{III} \rightarrow \text{II}}} = \left( \frac{d f^g_\text{in}}{d S^g_\text{III}} \right)
\]

\[
A - 13
\]

\[
The gas saturation \( S^*_g \) is often the residual gas saturation \( S^g_\text{III} \).

Between these saturations a concentration moves with a specific velocity given by Equation (A - 10).

The table also shows the value of the retardation factors under ideal conditions when the real gas law \( C^\text{CO}_2,\text{g} = \frac{p y^\text{CO}_2,\text{g}}{z RT} \) and Henry's law \( C^\text{CO}_2,\text{a} = \frac{p y^\text{CO}_2,\text{a}}{H^\text{CO}_2} \) relate the phase concentrations of \( \text{CO}_2 \) to the gaseous phase mole fraction \( y^\text{CO}_2 \). \( H^\text{CO}_2 \) is the reciprocal of the Henry's law constant. These values are presented for illustration only; Henry's law is inaccurate for pressures in excess of 1000 psia. These ideal forms point out the symmetry in the retardation factors where, if there is no difference in \( y^\text{CO}_2 \) between region II in Figure 2 and region III in Figure 5. Furthermore, \( D_{\text{I} \rightarrow \text{II}} = D_{\text{III} \rightarrow \text{K}} \) if the injected water is free of \( \text{CO}_2 \).
The forms of Equations (A - 10) through (A - 14) are similar but the actual solutions are quite distinct owing to (a) the inherent irreversibility of fractional flow solutions and (b) hysteresis in the relative permeability curves. The importance of these effects is a major finding of this work and discussed more fully in the body of the text.

Tables

Table 1: Equilibrium constants for aqueous reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant [log_{10} K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$\rightarrow$H$^+$+OH$^-$</td>
<td>-13.2631</td>
</tr>
<tr>
<td>CO$_2$(aq)+H$_2$O$\rightarrow$H$^+$+HCO$_3^-$</td>
<td>-16.5563</td>
</tr>
<tr>
<td>CO$_2$(aq)+H$_2$O$\rightarrow$2H$^+$+CO$_3^{2-}$</td>
<td>-6.3221</td>
</tr>
</tbody>
</table>

Table 2: Properties for mineral reactions

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Calcite+H$^+$ ↔Ca$^{2+}$+HCO$_3^-$</th>
<th>Anorthite+8H$^+$ ↔4H$_2$O +Ca$^{2+}$+2Al$^{3+}$+2SiO$_2$(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $K_{sp}$</td>
<td>1.36</td>
<td>-8</td>
</tr>
<tr>
<td>log $k_g [mol^{-1}m^2/s]$</td>
<td>-8.8</td>
<td>-12.0</td>
</tr>
<tr>
<td>$\Delta\beta [m^2/mol]$</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>$E_{ad} /[J/mol]$</td>
<td>41870</td>
<td>67830</td>
</tr>
</tbody>
</table>

Table 3: Initial concentrations for aqueous components

<table>
<thead>
<tr>
<th>Aqueous species</th>
<th>Initial moleality</th>
<th>Aqueous species</th>
<th>Initial moleality</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>1.0E-07</td>
<td>Ca$^{2+}$</td>
<td>9.12E-05</td>
</tr>
<tr>
<td>SiO$_2$(aq)</td>
<td>2.35E-08</td>
<td>Al$^{3+}$</td>
<td>2.32E-11</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>5.46E-07</td>
<td>CO$_3^{2-}$</td>
<td>2.49E-02</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>1.17E-05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Mineral properties

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>Density [kg/m$^3$]</th>
<th>Initial volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>100.1</td>
<td>2710</td>
<td>0.0088</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl$_2$Si$_2$O$_8$</td>
<td>278.2</td>
<td>2740</td>
<td>0.0088</td>
</tr>
</tbody>
</table>

Table A - 1: Retardation factors

<table>
<thead>
<tr>
<th>Case</th>
<th>Downstream</th>
<th>Upstream</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ displacing water (non-ideal)</td>
<td>$D_{I-II} = C^I_{CO_2,g} - C^I_{CO_2,a}$</td>
<td>$D_{II-I} = C^I_{CO_2,a} - C^I_{CO_2,g}$</td>
</tr>
<tr>
<td>CO$_2$ displacing water (ideal)</td>
<td>$D_{I-II} = (1 - \xi^I)^{-1}$</td>
<td>$D_{II-I} = (\frac{C^I_{CO_2,g}}{C^I_{CO_2,a}})^{-1} - (\frac{C^I_{CO_2,a}}{C^I_{CO_2,g}})^{-1}$</td>
</tr>
</tbody>
</table>

Water displacing CO$_2$ (non-ideal) 

$$D_{I-II} = C^I_{CO_2,g} - C^I_{CO_2,a}$$

Water displacing CO$_2$ (ideal) 

$$D_{I-II} = (1 - \xi^I)^{-1}$$

where $\xi$ is $\frac{H_{CO_2}}{zRT}$ and superscripts represent regions in Figure 2 and Figure 5.

Figures

Figure 1: Schematic of graphical construction for a gaseous phase displacing an aqueous phase. The figure shows a drainage fractional flow curve for a gaseous phase with zero gas saturation initially in the medium. Tangents (1) and (2) define velocities at which saturation fronts propagate. Superscripts refer to regions in the saturations profiles of Figure 2. I and J represent initial and injection conditions, respectively.

Figure 2: Schematic of a gaseous phase saturation profile in a semi-miscible displacement when a gaseous phase displaces water. The cross-hatched regions represent mutual solubility.
Figure 3: Schematic of a gas saturation profile in an immiscible displacement when gas displaces water. The shaded regions A and B represent amount lost to the other phase if there were mutual solubility.

Figure 4: Schematic of an aqueous phase displacing a gaseous phase. The fractional flow curve differs from that in Figure 1 because the displacement is an imbibition process.

Figure 5: Schematic of a gas saturation profile for semi-miscible displacement when water displaces gas.

Figure 6: Schematic of simulated one dimensional flow field.

Figure 7: Relative permeability curves for aqueous and gaseous phases. The solid lines are imbibition curves and the ditted lines drainage.

Figure 8: Drainage fractional flow curve for the gaseous phase. The point I is off the scale in this plot (compare Figure 1).

Figure 9: Comparison of gaseous phase saturation profiles between fractional flow approach (solid lines) and simulation result (dotted lines).
Figure 10: Concentration profiles after 30 years of CO₂ injection.

Figure 11: Concentration profiles after 3000 years with 2 m³/day of CO₂ and 2 m³/day of water injection show a calcite dissolution wave.

Figure 12: Imbibition fractional flow construction for aqueous phase displacing gaseous phase.

Figure 13: Gaseous phase saturation profiles for water displacing gaseous phase.