Geophysical Research Letters

RESEARCH LETTER
10.1029/2019GL085175

Key Points:
- Capillary trapping, although known to be hydrodynamically stable, may be thermodynamically unstable due to gravity-induced Ostwald ripening.
- Gravity modifies Ostwald ripening of trapped CO₂ bubbles, potentially leading to the formation of a gas cap and subsequent leakage risk.
- A pore-scale model is upscaled to obtain a one-dimensional continuum model. Strategies for suppressing gravity-induced ripening are proposed.

Supporting Information:
- Supporting Information SI
- Movie S1

Correspondence to:
K. Xu and Y. Mehmani,
xukethu@mit.edu; ymehmani@stanford.edu

Citation:
Xu, K., Mehmani, Y., Shang, L., & Xiong, Q. (2019). Gravity-induced bubble ripening in porous media and its impact on capillary trapping stability. Geophysical Research Letters, 46, 13,804–13,813. https://doi.org/10.1029/2019GL085175

Received 28 AUG 2019
Accepted 16 NOV 2019
Accepted article online 19 NOV 2019
Published online 4 DEC 2019

Gravity-Induced Bubble Ripening in Porous Media and Its Impact on Capillary Trapping Stability

Ke Xu†, Yashar Mehmani‡, Luoran Shang§, and Qingrong Xiong¶

†Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA,
‡Department of Energy Resource Engineering, Stanford University, Stanford, CA, USA,
§John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA,
¶School of Mechanical, Aerospace & Civil Engineering, University of Manchester, Manchester, UK

Abstract: Capillary or residual trapping is considered one of the safest geologic CO₂ storage mechanisms due to its hydrodynamic stability. We present a first study of the impact of gravity on Ostwald ripening in porous media and show it may render capillary trapping thermodynamically unstable. Gravity induces a vertical chemical potential gradient that leads to the upwards diffusion of CO₂. Thus, bubbles at shallower depths grow at the expense of bubbles in deeper strata, leading to the formation of an overriding gas cap. We first develop a pore-scale model for two bubbles trapped within adjacent pores and then upscale it to obtain a one-dimensional continuum model. We use the latter to predict the macroscopic evolution of a trapped bubble population. Factors controlling the ripening process are isolated to assist in selecting CO₂ storage sites. Gravity-induced ripening may also play a role in geologic fluid emplacement and migration over millions of years.

Plain Language Summary: Capillary trapping is a mechanism that ensures that the CO₂ injected during geologic carbon sequestration remains stable and safe underground. However, the stability of sequestered CO₂ can be disrupted by another competing mechanism called Ostwald ripening. In Ostwald ripening, CO₂ is transported from smaller bubbles towards larger bubbles. This is undesirable since large bubbles may become remobilized and potentially leak towards the surface. In this study, we show that gravity plays a crucial role in modifying the behavior of Ostwald ripening. Specifically, gravity causes an upwards migration of CO₂ towards shallower depths, which over long periods of time can lead to the formation of a mobile gas cap at the risk of leakage. The models we develop herein reveal that it is possible to decelerate or even prevent CO₂ migration if we carefully select sequestration sites that have the right kind of geology and rock type.

1. Introduction

The long-term stability of trapped CO₂ is paramount in geological CO₂ sequestration. Within the first ~10⁴ years after injection, the dominant CO₂ trapping mechanisms include structural and stratigraphic trapping (as mobile gas caps), solubility trapping (dissolved into resident brine), and residual or capillary trapping (as bubbles in pores) (Benson et al., 2012; Benson & Cole, 2008; Benson & Orr, 2008). Solubility trapping is limited by the dissolution capacity of the in situ brine. Structural and stratigraphic trapping is less favorable over long times, as the mobile gas cap could leak through preexisting faults and fractures (Guo et al., 2014). By comparison, residual trapping offers higher storage capacity (bubbles need not dissolve) and is more stable due to strong capillary forces at the pore scale (Hagoort, 1988; Huppert & Neufeld, 2014; Pentland et al., 2011). If the above physical trapping mechanisms remain effective over very long timescales (>10⁴ years), mineral trapping would dominate and permanently transform CO₂ into carbonate minerals (Xu et al., 2004).

Maximizing capillary trapping has therefore been the subject of intensive study over the past decade (Gasda et al., 2011, Gasda et al., 2009, Hesse et al., 2008, Ide et al., 2007, Juanes et al., 2006). Some predictions have suggested that more than 95% of the undissolved CO₂ can be safely sequestered through capillary trapping over 10,000 years after injection (Gasda et al., 2009). By optimizing injection operations, residual trapping can be maximized while simultaneously preventing the formation of a gas cap (Ide et al., 2007). For these reasons Huppert et al. (Huppert & Neufeld, 2014) have claimed that “residual trapping of fluid within porous rock is one of the most effective methods for stably trapping CO₂ after injection.”

©2019. American Geophysical Union. All Rights Reserved.
While it is known that capillary trapping is hydrodynamically stable, its thermodynamic stability has been the subject of investigation only recently (Xu et al., 2017, de Chalendar et al., 2018, Garing et al., 2017). In the absence of geometric confinement, Ostwald ripening (Fu et al., 2016, Voorhees, 1985, Voorhees, 1992) is the mechanism that causes the diffusion of CO2 from small bubbles towards large bubbles. The driving force is the capillary pressure difference between the bubbles (Figures 1a–1c). At equilibrium, Ostwald ripening leads to the formation of a single large bubble that may become hydrodynamically unstable (Fu et al., 2016). In the presence of confinement, however, the behavior of Ostwald ripening is modulated such that stable bubble configurations, with uniform capillary pressure, can exist. This observation has been confirmed by recent pore-scale (Xu et al., 2017) and core-scale (Garing et al., 2017) experiments and pore-scale modeling (de Chalendar et al., 2018). Confinement affects Ostwald ripening because it imposes a constraint between the volume of a bubble ($V_{\text{bubble}}$) and its capillary pressure ($P_c$). The specific relationship between $V_{\text{bubble}}$ and $P_c$ depends on pore geometry. Figure 1f shows such a relationship for the pore in Figures 1d–1e. Note that $P_c$ is a non-monotonic function of $V_{\text{bubble}}$, contrary to the case without confinement. $P_c$ incurs

**Figure 1.** Ostwald ripening in the presence and absence of confinement, without gravity. (a–c) In unconfined space, ripening leads to bubble coarsening. (d–e) In confined pores (here identically shaped), ripening results in stable bubbles with identical curvature. $R_0$ is the distance between the pore center to the throat center. (f) Dimensionless capillary pressure versus dimensionless bubble volume for a bubble in the presence (blue) and absence (red) of confinement. The dashed line represents $V_{\text{crit}}$ at $P_{c,\text{min}}$. 

10.1029/2019GL085175

Geophysical Research Letters
a minimum, $P_{c\min}$, at bubble volume $V_{crit}$. For $V_{bubble} < V_{crit}$ the bubble is sufficiently small and does not contact the pore walls. It is spherical in shape and behaves identical to an unconfined bubble. For $V_{bubble} > V_{crit}$, the bubble cannot form a stable sphere inside the pore and is therefore squeezed into the narrow crevices and throats adjacent to the pore. The result is that $P_c$ increases with $V_{bubble}$. Similar non-monotonic $P_c$ functions have been used to model fluid-fluid displacements (Thompson, 2002).

While recent studies (de Chalendar et al., 2018; Garing et al., 2017; Xu et al., 2017) have provided valuable insight into the effect of Ostwald ripening on capillary trapping, the influence of gravity has thus far been ignored. Neglecting gravity is indeed a reasonable assumption when studying hydrodynamic stability of trapped bubble because capillary forces at the pore scale are much stronger than buoyancy forces in the subsurface (Perkins & Johnston, 1963; Whitaker, 1967). However, during Ostwald ripening, bubbles interact with each other through molecular diffusion without the need to physically mobilize. Since gravity can alter the magnitude and direction of chemical potential gradients, its contribution can no longer be neglected over long time periods. In the following, we show that gravity can cause a vertical redistribution of trapped bubbles in the reservoir leading to the formation of an overlying gas cap, which may pose subsequent risks of CO$_2$ leakage towards the surface.

2. Gravity-Induced Ripening at the Pore Scale

2.1. Model Description

In this section, we consider gravity-induced Ostwald ripening at the pore scale and develop a simplified model that captures the salient aspects of the physics. Consider the idealized two-bubble system depicted in Figure 2a. Two identical non-wetting bubbles of initial volume $V_0$ are trapped within two identical pores separated by a vertical distance $L_c$. The throat connecting them has a cross-sectional area $A_t$ and is filled with brine, which is the wetting phase $w$. The CO$_2$ bubbles comprise the non-wetting phase $b$. The two phases are slightly miscible and can therefore form a binary mixture. We assume that such a mixture forms only in the brine phase and that the CO$_2$ bubbles remain pure. For simplicity, we also use $w$ and $b$ to denote the water and CO$_2$ components, respectively. We further assume that the binary mixture is ideal and that the fluids are incompressible and under isothermal conditions. We aim to develop a one-dimensional model for this two-bubble system.

The $P_c - V_{bubble}$ relation for a confined bubble is strongly dependent of the specific pore and throat shapes. For simplicity, but without loss of generality, we consider a linearized $P_c - V_{bubble}$ relation given by $P_c = \gamma \left( m_1 V_{bubble}^{-1/3} + m_2 V_{bubble} \right)$, where $\gamma$ is surface tension, $m_1 = 4(\pi/6)^{1/3}$, $m_2 \propto R_0^{-3}$, and $R_0$ is the pore half-length as marked in Figure 1d. The first term represents the contribution to $P_c$ when $V_{bubble} < V_{crit}$ and the bubble is spherical in shape. The second term captures the contribution when $V_{bubble} > V_{crit}$ and the bubble is deformed by the pore walls; $P_c \approx \gamma m_2 V_{bubble}$ in this regime. Figure If shows a graph of $P_c$ versus $V_{bubble}$ for $m_2 = 2R_0^{-4}$, which is the value used hereafter.

Denote the density and molar volume of the $w$ and $b$ phases by $\rho_w, V_{mw}, \rho_b$ and $V_{mb}$. Since CO$_2$ is buoyant in brine in most common cases, we only consider $\Delta \rho = \rho_w - \rho_b > 0$. We initialize the bubble volumes such that $V_0 > V_{crit}$. Specifically, we set $V_0 = 1.2R^3$. We do not consider bubbles with $V_b < V_{crit}$ because they are thermodynamically unstable (similar to unconfined bubble ripening) and thus uncommon after long timescales. We denote the pressure of the brine phase $w$ with $P$ and assume that it follows a steady state hydrostatic profile.

We take the positive $z$-axis to coincide with the upward direction and place $z = 0$ at the throat entrance connected to the bottom bubble. We choose a reference pressure $P_0$ as the wetting phase pressure at $z = 0$. We denote the molar fraction of $b$ dissolved in $w$ by $x_b$. Taking the contribution of gravity into account, we can write the chemical potential of $b$ dissolved in $w$ at position $z$ as $\mu_b^w = \mu_b^w + RT \ln \frac{\rho_b}{\rho_w} - V_{mb} \Delta \rho g z$ (Muskat, 1930; Sage & Lacey, 1939), where $\mu_b^w$ is the reference chemical potential of pure $b$ at $P_0$ and $x_{b0}$ is the reference molar fraction of $b$ dissolved in $w$ at $P_0$. Similarly, the chemical potential of pure $b$ within each bubble can be expressed as $\mu_b = \mu_b^b + V_{mb} (P_c - \Delta \rho g z)$, where $P_c$ is the capillary pressure at the bubble interface. For simplicity, we assume that $x_b$ at $z = 0$ and $z = L_i$ is equal to the equilibrium concentration at the
bubble surface at all times. We can therefore calculate it by equating $\mu_w^b$ and $\mu_b$ to obtain $\frac{x_{bl}}{x_0} = \exp\left(\frac{V_m P_c}{RT C_0 C_1}\right)$. Finally, we initialize the dissolved CO$_2$ concentration in the throat by uniformly setting it to $\frac{x_{bl}|_{t=0}}{x_0} = x_0 \exp\left(\frac{V_m P_c}{RT C_0 C_1}\right)$, where $P_c$ is the initial bubble capillary pressure.

Having described the problem setup, we can now write the governing equations for the two-bubble system. The first equation is a species balance for the dissolved component $b$ along the throat described by equation (1). Note that equation (1) is obtained by combining mass conservation with Fick’s law for molecular diffusion. We have used the generalized Fick’s law, which describes the dependence of molar mass flux $J_b$ on chemical potential gradient, that is, $J_b = -D \frac{\partial \mu_b}{\partial z}$. $D$ is the diffusion coefficient and $\mu_b = x_b/V_m$. We can simplify the nonlinear equation (1) by linearizing it around the reference pressure $P_0$. Specifically, we take $P_0$ to be orders of magnitude larger than both $P_c$ and $\Delta \rho g L_t$. Under these conditions, quite typical in geologic CO$_2$ storage, $\frac{x_{bl}|_{t=0}}{x_0}$ becomes orders of magnitude larger than any variations in $x_b$. We can therefore make the approximation outlined on the right-hand side (RHS) of equation (1).

**Figure 2.** Simplified pore-scale model of gravity-induced ripening for a two-bubble system. (a) Schematic of the system setup at $t = 0$. $L_t$ and $R_0$ are not to scale. Evolution of the (normalized) bubble volumes over time at (b) fixed $R_0 = 50$ $\mu$m with varying $L_t$, and at (c) fixed $L_t = 5$ mm with varying $R_0$. Note that there are two equilibrium regimes. Regime I at small $L_t$ and $R_0$, and Regime II at large $L_t$ and $R_0$. (d) Plot of dimensionless equilibrium time ($t_d$) versus dimensionless throat length ($L_{td}$). Note that we do not show the results for $L_t < 1$ cm in (b) as they all fall into Regime I, although those data have been incorporated in (d).
\[
\frac{\partial x_b}{\partial t} = \frac{D x_b \partial \mu^w_{mb}}{RT \partial z^2} \approx D \frac{\partial^2 x_b}{\partial z^2}.
\] (1)

The boundary conditions of equation (1) consist of setting \(x_b\) to the equilibrium \(x_b|_z = 0, L_t\) concentration derived above. To close the system, we need equations describing the evolution of the bubble volumes over time. This is achieved by simply imposing mass conservation at the interface between the bubble surface and the throat entrances. The result is equations (2) and (3).

\[
\frac{dV_{\text{bubble}}}{dt}|_{\text{bottom}} = \frac{A_t}{} DV_{mb} \frac{\partial \mu^w_{mb}}{RT_{mw}} \bigg|_{z=0}.
\] (2)

\[
\frac{dV_{\text{bubble}}}{dt}|_{\text{top}} = \frac{A_t}{} DV_{mb} \frac{\partial \mu^w_{mb}}{RT_{mw}} \bigg|_{z=L_t}.
\] (3)

2.2. Results and Discussion

We solve equations (1)–(3) numerically with input parameters corresponding to typical CO₂-water systems at ~1-km depth (see Table S1) (Chiquet et al., 2007; Duan & Sun, 2003; Lu et al., 2013). Figures 2b–c show the evolution of the two bubble volumes for different \(L_t\) and \(R_0\) (see Text S1). In all cases, CO₂ is transferred from the bottom bubble to the top bubble. However, two different regimes can be identified. In Regime I, the bottom bubble shrinks, and the top bubble grows, but they both stop at some finite equilibrium size. In Regime II, the bottom bubble disappears completely, and its mass is entirely transported into the top bubble. The occurrence of either regime is governed by the relative importance of capillary versus gravitational forces in this two-bubble system. Specifically, Regimes I and II correspond to dominating capillary and gravitational forces, respectively. Increasing \(L_t\) (proportional to gravitational potential difference) and \(R_0\) (inversely proportional to capillary forces) can drive the system from Regime I to II.

In order to better understand the regimes, we proceed to derive scaling relationships for each regime and verify them against numerical solutions of equations (1)–(3). We first simplify equations (1)–(3) by assuming that the rate of molecular diffusion along the throat is much faster than the rate of change in bubble volumes. Diffusion is therefore regarded as a quasi-static process limited by changes in bubble volumes. Under these conditions, the time derivative term in equation (1) can be neglected, and integration of equation (1) over \(z\) thus yields equation (4). Note that equation (4) is simplified by approximating \(\frac{V_{mb}P_c}{RT} << \frac{V_{mb}P_c}{RT} - O(1)\). Note that \(P_c\) is the capillary pressure difference between the two bubbles, which in turn depends on the bubble volumes. The latter is governed by equation (5), which we obtain by subtracting equation (2) from equation (3). Equation (5) is further simplified on the RHS by linearizing the chemical potential gradient (similar to section 2.1) and combining the result with equation (4). Note that equation (5) suggests that, aside from \(L_t\), the ripening process directly depends on \(A_t, D,\) and \(x_{b0} - \text{ref.}\)

\[
\frac{\partial x_b}{\partial z} = x_{b0} \left( \exp \left( \frac{V_{mb}P_c}{RT} \right) \bigg|_{\text{top}} - \exp \left( \frac{V_{mb}P_c}{RT} \right) \bigg|_{\text{bottom}} \right) \approx x_{b0} \frac{V_{mb}P_c}{RT} \Delta P_c.
\] (4)

\[
\frac{d(\Delta V_{\text{bubble}})}{dt} = \left( \frac{A_tDV_{mb}}{RT_{mw}} \frac{\partial \mu^w_{mb}}{RT_{mw}} \bigg|_{\text{bottom}} \right) \bigg|_{\text{top}} \approx \left( 2A_tDV_{mb} x_{b0} V_{mb} \frac{\Delta P_c - \Delta \rho g L_t}{L_t} \right).
\] (5)

We now use equations (4) and (5) to derive scaling relations between the time required to reach equilibrium, \(t_e\), and throat length, \(L_t\). We define \(t_e\) as the time at which 99% of the cumulative mass transfer between the two bubbles is complete. In Regime I, capillarity dominates and we can approximate \(P_c \approx \gamma m_2 V_{\text{bubble}}\). Subsequent integration of equation (5) yields equation (6). Invoking our definition for \(t_e\) we obtain \(\Delta P_c / \Delta \rho g L_t = 0.99\), which upon substituting it into equation (6) yields ln0.01 = \(-2A_tDV_{mb} x_{b0} V_{mb} \gamma m_2 L_t^2\). We thus obtain a linear \(t_e \sim L_t^2\) scaling for Regime I, which is different from \(t_e \sim L_t\) in classical Fickian diffusion (Whitaker, 1967). In Regime II, since gravity dominates, we can neglect the capillary term in equation (5)
and integrate to yield equation (7). We thus see that \( t_e \) is independent of \( L_t \) in Regime II. As an aside, notice that \( t_e \) depends on \( \gamma \) only in Regime I and on \( \Delta \rho \) only in Regime II.

\[
\ln \left( 1 - \frac{\Delta P_c}{\Delta \rho g L_t} \right) = -2A_i D \frac{V_{mb} x_0 V_{mw} \gamma m_2}{RT L_t t_e}. 
\]

(6)

\[
t_e = V_0/\left( A_i D \frac{V_{mb} x_0 V_{mw} m_2}{RT \Delta \rho g} \right).
\]

(7)

We test the validity of the above scaling relations between \( t_e \) and \( L_t \) by plotting numerical simulation data in an alternative dimensionless form. Namely, we plot the dimensionless equilibrium time \( t_d = m_2 A_i L_t t_e \) against the dimensionless throat length \( L_d = V_{mb} x_0 V_{mw} m_2/\Delta \rho g L_t \) in Figure 2d. As expected, all data points in Regime I collapse onto a single straight line and all the data points in Regime II plateau into constant values. The peaks in Figure 2d correspond to a regime, in which capillary and gravity forces are comparable in magnitude. In this case, \( P_c \approx \gamma m_2 V_{bubble} \) is not a good approximation, and accurate predictions require computation.

As a sidelight, we note that ripening happens majorly among neighboring pores. Therefore \( L_t \) is much smaller than 1 mm thus evolution of two neighboring identical bubbles always fall in Regime I in most cases. However, much larger \( L_t \) (up to centimeters) may be realistic when describing ripening between gas ganglia trapped in neighboring micro-fractures or vugs (i.e., with large \( R_0 \) thus smaller \( m_2 \)), in which case the evolution dynamics may fall into Regime II.

3. Upscaling From Pore Scale to Continuum Scale

The above pore-scale analysis demonstrated that gravity-induced ripening causes bubbles at the shallower depths to grow at the expense of bubbles at deeper strata. To understand the implications of this observation over geologic scales (meters in thickness and thousands of years), we develop a simplified one-dimensional continuum model based on the pore-scale results of section 2. We recognize that geologic CO\(_2\) storage is a multiscale multiphysics problem that does not easily lend itself to simplifications. However, reduced-order models are very valuable in that they allow the effects of a subset of the physics to be rapidly analyzed and extrapolated over engineering scales for the purposes of project design and operations. Our aim here is to achieve exactly such an understanding of the long-term effects of gravity-induced Ostwald ripening.

For realistic geological systems, \( L_t \) is always sufficiently small for the quasi-static assumption leading to equation (5) to be valid. Equation (5) is also consistent with a previously validated model for bubble ripening (excluding gravity) at the scale of multiple interconnected pores (Xu et al., 2017). We proceed by defining a modified Henry’s constant as \( K_{px} = 8P_v/\Delta \rho g \); similar to Xu et al. (2017). We also define the average number of bubbles residing in adjacent pores of a trapped bubble as \( n \). Adjacency means that there is a throat connecting the two bubbles. We can now impose mass conservation on each bubble via equation (8).

\[
dV_{bubble}/dt = kn \Delta P_b/L_t , \quad \text{where} \quad k \approx \frac{V_{mb} A_i D}{V_{mw} K_{px}}.
\]

(8)

In equation (8), \( \Delta P_b \) is the average potential difference between a bubble and its neighboring bubbles. The total potential of each bubble is \( P_b = P_c - \Delta \rho g z + P_0 \). Equation (8) is a generalization of a previously reported model (Xu et al., 2017) that accounts for gravity. Notice that equation (8) has a discrete form as it applies between individual bubbles. In order to transforming equation (8) into a differential or continuum form, we can first take its limit as \( L_t \to 0 \), and assume that all pores are identical, to obtain equation (9) (details in supporting information).

\[
\frac{\partial (V_{bubble}/V_{pore})}{\partial t} = \left( \frac{kn_0 I_{pore}^2}{V_{pore}^2 2L_t} \right) \frac{\partial}{\partial z} \left( \frac{n}{n_0} \frac{\partial P_b}{\partial z} \right).
\]

(9)

In equation (9), \( I_{pore} \) is the center-to-center distance between two neighboring pores, and \( V_{pore} \) is the volume of each pore. \( n_0 \) is the number of neighboring pores (not bubbles) adjacent to each pore. Here we introduce...
an assumption of local capillary equilibrium, that is, bubbles in an REV (representative elementary volume) are in equilibrium, sharing identical capillary pressure as well as gravitational potential. That said, although there could be complex interactions among multiple neighboring bubbles, the time required to get equilibrium inside an REV (<cm) is negligible compared to that of gravity-driven ripening process. Therefore, we ignore the complex dynamics in an REV and always assume local thermodynamic equilibrium, similar to most of other large-scale simulations.

Further, if we denote $V_{\text{bubble}}/V_{\text{pore}}$ as the non-wetting phase saturation $S$ and $n/n_0$ as the “pore occupancy” parameter $C$ (i.e., fraction of neighboring pores occupied by bubbles), equation (9) is rewritten into the one-dimensional continuum model given by equation (10). Note that we have implicitly assumed uniformity of all dependent and independent variables across any given depth $z$.

$$\frac{dS}{dt} = K \frac{d}{dz} \left( C \frac{dP_b}{dz} \right),$$

where $P_b = P_c - \Delta \rho g z + P_0$. (10)

Both $P_c$ and $C$ are functions of $S$ (detailed in supporting information). The rate constant is given by $K = n_0 B_0 F_0$, where $B_0 = \frac{A}{V_{\text{pore}}^2} \frac{d^2}{dz^2}$ depends only on pore shape (not size) and $F_0 = \frac{V_{\text{max}}}{V_{\text{max}} \rho} D$ depends only of fluid properties. Without loss of generality, we assume $B_0 = 1$. $P_c$ is the local capillary pressure of trapped bubbles, which is different from the conventional definition of capillary pressure in typical continuum (or Darcy) models. The latter corresponds to a continuous non-wetting phase relevant in fluid-fluid displacement process (Andrew et al., 2014).

4. Continuum Scale Simulation Results and Discussion

4.1. A Demonstration Case

We solve equation (10) numerically to predict the long-term evolution of gravity-induced Ostwald ripening after supercritical CO$_2$ injection into a 1-m thick stratum. We set $C = 1$ at the beginning of the simulation. The profile of CO$_2$ saturation versus depth is randomly initialized from a uniform distribution with mean residual saturation $S_r = 0.3$. We use CO$_2$ and water properties corresponding to 10 MPa and 60 °C typical of ∼1-km depths (see Table S1) (Chiquet et al., 2007; Duan & Sun, 2003; Lu et al., 2013).

Figures 3a–3d show that within a geologically short time after injection (∼1 year), the saturation profile becomes locally uniform. This observation agrees with previous experimental studies in the absence of gravity (Garing et al., 2017; Xu et al., 2017). Several decades (∼60 years) later, the onset of vertical redistribution of CO$_2$ emerges. During this time, CO$_2$ is transferred from deeper strata towards shallower depths leaving a bubble-free zone at the bottom. When the CO$_2$ saturation at the top of the reservoir reaches a critical value ($S_{\text{max}} = 0.7$ in this case study), bubbles coalesce into a continuous mobile gas cap. Finally, 2,000 years after injection, the CO$_2$ saturation profile reaches an equilibrium configuration, in which capillary trapping dominates only in an interval between the gas cap and the bubble-free zone. We refer this interval as the “stable capillary trapping belt” (SCTB). This case study shows that even though 100% of the initially trapped CO$_2$ is in the form of isolated bubbles, a mobile gas cap is eventually formed at the top of the formation (i.e., $S > S_{\text{max}}$).

It is noteworthy that the gas cap forms far earlier than mineral trapping can have any significant impact on either the injected CO$_2$ or the rock matrix (Gasda et al., 2011; Krevor et al., 2015; Xu et al., 2004) in this case study. While ∼1-m thick strata are quite typical as hydrocarbon reservoirs or shallow water aquifers, they are likely too thin to be considered ideal storage sites. In the next section, we develop dimensional analysis on ripening dynamics based on equation (10) and study the scaling of gas cap growth as well as equilibrium time with more simulation results. Therefore, we extend our discussion to thicker stratum over longer timescales.

4.2. Scaling of Ripening Dynamics and Equilibrium

Assuming that capillarity is only locally significant, dimensional analysis of equation (10) yields the scaling between time $\Delta t$ and the corresponding change in gas cap thickness $\Delta L$:
Denoting the gas cap thickness by $h_c$, and assuming $h >> h_c$, equation (11) can be transformed into equations (12) for estimating the growth of a gas cap:

$$S_r \frac{\Delta P_h}{\Delta L^2} = K \frac{\Delta \rho g}{\Delta L}.$$  \hspace{1cm} (11)

Note that $h_c$ is proportional to $t$, instead of $t^{1/2}$ and does not depend on $h$. Equation (12) agrees with the numerical simulations in Figure 3e during the growth stage of the gas cap. If the formation is sufficiently thick, a ~3-m thick gas cap may form after 10,000 years. Equation (11) can also be transformed to estimate the time needed to reach equilibrium $t_{eq}$:

$$t_{eq} \sim \frac{S_r}{\Delta \rho g K} h.$$  \hspace{1cm} (13)
With a factor 0.6 multiplying the RHS, equation (13) agrees well with numerically simulated \( t_{eq} \) for \( h \) between 1 and 100 m as shown in Figure 3f. We see that it takes \( \sim 8,000 \) years for a 5-m thick stratum and \( \sim 80,000 \) years for a 50-m thick stratum to reach equilibrium. For such thick strata, the timescale of gravity-driven ripening is comparable to that of mineral trapping, which complicates the accurate prediction of the fate of stored CO2.

The final shape of the macroscopic saturation profile depends on the competition between gravity and capillary forces in the reservoir. In the section S2.5, we show that the SCTB thickness, \( h_{SCTB} \), can be calculated by solving max\{\( P_1(S) \) \} − min\{\( P_1(S) \)\} = \( \Delta\rho g h_{SCTB} \). If capillarity dominates, \( h_{SCTB}/h > > 1 \) and capillary trapping is globally stable (similar to Regime I at the pore scale). If gravity dominates, \( h_{SCTB}/h < < 1 \) and almost all of the trapped CO2 evolves into an overlying gas cap (similar to Regime II at the pore scale). This is confirmed by Figures 3g–3i.

Equations (12) and (13) may be applied to devise strategies to decelerate gravity-induced ripening for reducing the risk of gas-cap formation and leakage. In practice, they involve either decreasing \( K \) or \( \Delta\rho \); recall \( K = n_0 B_0 F_0 \) where \( B_0 = \frac{\Delta \rho g h_{SCTB}^2}{n_0 \mu_0} \) and \( F_0 = \frac{\mu_0 d_{max}^2}{n_0^2} \), which are very sensitive to the thermodynamic properties of CO2. Therefore, storage sites with low temperature, high pressure, and high salinity are preferred scenarios, which seem representative of strata underneath deep sea floors. On the other hand, drilling and injection into deep offshore strata is both economically expensive and ecologically risky (Eccles et al., 2009), which must be taken into assessment.

4.3. Limits of the Proposed Models

The analysis in this paper focused on a single geological stratum. For intervals consisting of multiple strata, equation (10) remains valid in each storage layer except in the cap rock. One reason for this is that cap rocks consist of very small pores and thus very high capillary entrance pressures that injection pressures cannot overcome. This violates assumptions (5) and (7) listed in section S3. Classical single-phase Fickian diffusion may be more appropriate for describing CO2 migration within cap rocks, although the exact physics are debated (Neuzil, 2013; Neuzil & Person, 2017). A detailed study is deferred to the future.

Throughout this work, we also neglected the impact of CO2 dissolution on brine density. It is known that CO2 dissolution increases brine density, which in turn induces Rayleigh-Taylor instabilities and convective dissolution (Loodts et al., 2014; Neufeld et al., 2010; Thomas et al., 2018). While not captured by our model, we argue that convective dissolution and gravity-induced ripening occur at different stages of the CO2 sequestration process. Convective dissolution typically occurs at the underside edges of an overriding CO2 plume and is driven by density differences within the brine phase. By contrast, gravity-induced ripening is driven by density differences between two undissolved phases. Our models assume that the surrounding brine is already saturated with dissolved CO2, which is representative of the region adjacent to the wellbore in the wake of an injected CO2 plume. Incidentally, the same region will have undergone an initial drainage (by CO2) followed by a subsequent imbibition (by brine) leading to trapped CO2 bubbles and ganglia. The brine in this region is likely to have had sufficient time to be saturated by CO2, rendering density differences within the brine of secondary importance. Nevertheless, future work must confirm this hypothesis by including convection in the modeling framework.

We note that gravity-induced ripening may also play a crucial role in geologic fluid emplacement and migration (e.g., hydrocarbons). The millions of years in timescale match our model predictions for thick strata. That said, the model must be generalized to include multicomponent geochemistry and mixed wettability, if it is to correctly capture hydrocarbon migration.

5. Conclusions

We develop pore-scale and continuum models of gravity-induced Ostwald ripening. The models demonstrate that capillary trapping may not be as stable a trapping mechanism as previously assumed. We show that gravity can induce the redistribution of otherwise hydrodynamically stable bubbles and transport significant quantities of CO2 from deeper strata towards shallower depths over geologic timescales. The result may be the formation of a gas cap at the top of the reservoir. The timescale of this process is predicted to be less than or comparable to that of mineral trapping. We outline potential strategies for decelerating the ripening
rate by a careful selection of CO₂ storage sites. The above findings, while subject to several assumptions, may provide new insights for assessing CO₂ storage security. The findings herein might also be of relevance to gravity-induced ripening in the context geologic fluid emplacement and migration over millions of years (e.g., hydrocarbons).

Acknowledgments

Authors declare no competing interests. All parameters used are available in the main text or in the supporting information texts with necessary references. We aim at establishing a zero-order conceptual model thus no field data is applied. We gratefully thank Prof. Bo Guo from University of Arizoman for his helpful suggestions.

References

Andrew, M., Bijeljic, B., & Blunt, M. J. (2014). Pore-by-pore capillary pressure measurements using X-ray microtomography at reservoir conditions: Curvature, snap-off, and remobilization of residual CO₂. *Water Resources Research*, 50, 8760–8774. https://doi.org/10.1002/2014WR015970

Benson, S. M., Bennaceur, K., Cook, P., Davison, J., de Coninck, H., Farhat, K., et al. (2012). Chapter 13 - Carbon capture and storage. In *Global energy assessment-Toward a sustainable future* (Vol. 993, pp. 993–1068). Cambridge, UK and New York, NY and Laxenburg, Austria: Cambridge University Press/International Institute for Applied Systems Analysis.

Benson, S. M., & Cole, D. R. (2008). CO₂ sequestration in deep sedimentary formations. *Elements*, 4, 325–331.

Benson, S. M., & Orr, F. M. (2008). Carbon dioxide capture and storage. *MRS Bulletin*, 33, 303–305.

Chiquet, P., Daridon, J.-L., Brosset, D., & Thibau, S. (2007). CO₂/water interfacial tensions under pressure and temperature conditions of CO₂ geological storage. *Energy Conversion and Management*, 48, 736–744.

de Chalendar, J. A., Garing, C., & Benson, S. M. (2018). Pore-scale modelling of Ostwald ripening. *Journal of Fluid Mechanics*, 835, 363–392.

Duan, Z., & Sun, R. (2003). An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical Geology*, 193, 257–271.

Eccles, J. K., Pratson, L., Newell, R. G., & Jackson, R. B. (2009). Physical and economic potential of geological CO₂ storage in saline aquifers. *Environmental Science & Technology*, 43(6), 1962–1969. https://doi.org/10.1021/es803572e

Fu, X., Cueto-Felgueroso, L., & Juanes, R. (2016). Thermodynamic coarsening arrested by viscous fingering in partially miscible binary mixtures. *Physical Review E*, 94, 033111.

Garing, C., de Chalendar, J. A., Voltolini, M., Ajo-Franklin, J. B., & Benson, S. M. (2017). Pore-scale capillary pressure analysis using multi-scale X-ray microtomography. *Advances in Water Resources*, 104, 223–241.

Gasad, S., Nordbotten, J., & Celia, M. (2011). Vertically averaged approaches for CO₂ migration with solubility trapping. *Water Resources Research*, 47, W05528. https://doi.org/10.1029/2010WR009075

Gasad, S. E., Nordbotten, J. M., & Celia, M. A. (2009). Vertical equilibrium with sub-scale analytical methods for geological CO₂ sequestration. *Computational Geosciences*, 13, 469.

Guo, B., Bandilla, K. W., Doster, F., Keilegavlen, E., & Celia, M. A. (2014). A vertically integrated model with vertical dynamics for CO₂ storage. *Water Resources Research*, 50, 6269–6284. https://doi.org/10.1002/2013WR015215

Hagoort, J. (1988). *Fundamentals of gas reservoir engineering*. New York: Elsevier.

Hesse, M. A., Orr, F. M., & Tchelepi, H. (2008). Gravity currents with residual trapping. *Water Resources Research*, 44, 4254. https://doi.org/10.1029/2007WR006007

Huppert, H. E., & Neufeld, J. A. (2014). A vertically integrated model with vertical dynamics for CO₂ storage. *Advances in Water Resources*, 73, 744–758.

Huppert, H. E., & Neufeld, J. A. (2014). The fluid mechanics of carbon dioxide sequestration. *Annual Review of Fluid Mechanics*, 46, 255–272.

Ide, S. T., Jessen, K., & Orr, F. M. Jr. (2007). Storage of CO₂ in saline aquifers: Effects of gravity, viscous, and capillary forces on amount and timing of trapping. *International Journal of Greenhouse Gas Control*, 1, 481–491.

Juanes, R., Sipieri, E., Orr, F., & Blunt, M. (2006). Impact of relative permeability hysteresis on geological CO₂ storage. *Water Resources Research*, 42, W12418. https://doi.org/10.1029/2005WR004806

Krevor, S., Blunt, M. J., Benson, S. M., Pentland, C. H., Reynolds, C., Al-Menhali, A., & Niu, B. (2015). Capillary trapping for geologic carbon dioxide storage—From pore scale physics to field scale implications. *International Journal of Greenhouse Gas Control*, 40, 221–237.

Loodts, V., Thomas, C., Rongy, L., & De Wit, A. (2014). Control of convective dissolution by chemical reactions: General classification and application to CO₂ dissolution in reactive aqueous solutions. *Physical Review Letters*, 113, 114501.

Lu, W., Guo, H., Chou, I.-M., Burrrus, R., & Li, L. (2013). Determination of diffusion coefficients of carbon dioxide in water between 268 and 473 K in a high-pressure capillary optical cell with in situ Raman spectroscopic measurements. *Geochemistry Geophysics Geosystems*, 14, 2013–204.

Muskat, M. (1930). Distribution of non-reacting fluids in the gravitational field. *Physical Review*, 55, 3384.

Neufeld, J. A., Hesse, M. A., Riuze, A., Hallworth, M. A., Tchelepi, H. A., & Huppert, H. E. (2010). Convective dissolution of carbon dioxide in saline aquifers. *Geophysical Research Letters*, 37, L22404. https://doi.org/10.1029/2010GL044728

Neuzil, C. (2013). Can shale safely host US nuclear waste? *Eos, Transactions American Geophysical Union*, 94, 261–262.

Neuzil, C. E., & Person, M. (2017). Reexamining ultrafiltration and solute transport in groundwater. *Water Resources Research*, 53, 4922–4941. https://doi.org/10.1002/2017WR020492

Pentland, C. H., El-Maghraby, R., Iglauser, S., & Blunt, M. J. (2011). Measurements of the capillary trapping of super-critical carbon dioxide in Berea sandstone. *Geophysical Research Letters*, 38, L06640. https://doi.org/10.1029/2011GL046683

Perkins, T., & Johnston, O. (1963). A review of diffusion and dispersion in porous media. *Society of Petroleum Engineers Journal*, 3, 70–84.

Sage, B. H., & Lacey, W. N. (1939). Gravitational concentration gradients in static columns of hydrocarbon fluids. *Transactions of AIIME*, 132, 120–131.

Thomson, C., Dehaeck, S., & De Wit, A. (2018). Convective dissolution of CO₂ in water and salt solutions. *International Journal of Greenhouse Gas Control*, 72, 105–116.

Thompson, K. E. (2002). Pore-scale modeling of fluid transport in disordered fibrous materials. *AICHE Journal*, 48, 1369–1389.

Voorhees, P. W. (1985). The theory of Ostwald ripening. *Journal of Statistical Physics*, 38, 231–252.

Voorhees, P. W. (1992). Ostwald ripening of two-phase mixtures. *Annual Review of Materials Science*, 22, 197–215.

Whitaker, S. (1967). Diffusion and dispersion in porous media. *AICHE Journal*, 13, 420–427.

Xu, K., Bonnecaze, R., & Balhoff, M. (2017). Egalitarianism among bubbles in porous media: An Ostwald ripening derived anticoarsening phenomenon. *Physical Review Letters*, 119, 264502.

Xu, T., Apps, J. A., & Prues, K. (2004). Numerical simulation of CO₂ disposal by mineral trapping in deep aquifers. *Applied Geochemistry*, 19, 917–936.