

Reactive precipitation during overlaying CO₂ dissolution into brine: The role of porous structure

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ABSTRACT

After sequestration of CO₂ into subsurface saline aquifer, CO₂ cap forms at the top of a stratum. As overlaying CO₂ dissolves into brine, precipitation reactions between CO₂ and in-situ ions emerge. The role of reactive precipitation during this process has long been under debate due to the lack of direct observation. Here we conduct visualized experiments on high-pressure CO₂ convective dissolution into Ca(OH)₂ solution, where CaCO₃ precipitation forms. We show that the presence of a porous structure largely shapes the dissolution pattern. In absence of porous structure, sharp and flat reactive front is observed, with cloudy particle suspension chaotically flowing; however, in presence of a porous structure, symmetric fingers are observed above the reactive front, and precipitates locally deposit at the pore-scale without participating in convection. We theoretically rationalize these observations and discuss their impacts on CO₂ dissolution kinetics. Inspired by these experimental observations, we propose several major simplifications for numerical modeling. This work also provides a benchmark for future experimental and numerical studies of CO₂ convective dissolution with reactive precipitation during CO₂ sequestration.

1. Introduction

Geological carbon dioxide sequestration (GCS) into deep saline aquifers is a promising strategy to mitigate global climate change. The injected CO₂ is less dense and thus rises above the connate brine, presenting leakage risks (Little and Jackson, 2010). The overlaying CO₂ further dissolves into brine, which increases local brine density near the overlaying gas cap. Higher density at the top results in Rayleigh-Darcy instability, which induces density-driven convection in brine. Resolving the kinetics of this convective dissolution is critical for evaluating the safety, capacity, and efficiency of sequestration (Huppert and Neufeld, 2014).

Chemical reactions between dissolved CO₂ and metal ions in connate brine highly complicate the process of CO₂ convective dissolution (De Silva et al., 2015; Gunter et al., 1997; Yang et al., 2017). Homogeneous reactions can modify the density profile and reshape the convective patterns, that have been extensively investigated (Jotkar et al., 2019; Lei and Luo, 2019; Thomas et al., 2016). Through numerical simulation, researchers such as Loodts et al. (2016), Jotkar et al. (2019) and Lei and Luo (2019) have demonstrated that the density changes can either

enhance or suppress the convection, depending on the aqueous phase density change after reaction. These predictions align well with the experimental findings by Thomas et al. (2016). More recently, Tanaka et al. (2024) experimentally measured convective flow in a cylinder filled with sodium hydroxide (NaOH) solution, revealing a tremendous effect on plume progression, for which a theoretical model has also been developed.

However, in practical scenarios, many in-situ reactions are not homogeneous. For example, carbonate precipitation may emerge when a CO₂ solution meets ions like Ca²⁺, in a neutral or base environment (pH > 7.3 for Ca²⁺ ~ 1000 mg/L), which is very common for subsurface saline aquifers (De Silva et al., 2015; Ghesmat et al., 2011; Matter et al., 2016). In case of high CO₂ concentration, Ca²⁺ can undergo carbonation and bicarbonation reactions sequentially, resulting in precipitation and subsequent redissolution (Thomas et al., 2020).

Precipitation reactions in porous media do not only change the concentration field and thus density field (Jotkar et al., 2019; Lei and Luo, 2019; V. Loodts et al., 2016), but also are suspected to modify the porous structure and fluid rheology (Thomas et al., 2020; Zhang et al., 2010). These strongly coupled multi-phase, multi-component, and multi-physics processes cover across vastly different spatial scales

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Nomenclature		ρ_s	Density of CaCO_3 precipitates, kg/m^3
Acronyms		$\Delta\rho$	Density difference of CO_2 -saturated brine with host brine, kg/m^3
CO_2	Carbon dioxide	$\Delta\rho_s$	Density difference of precipitates with host brine, kg/m^3
GCS	Geological carbon dioxide sequestration	Latin Symbols	
SEM	scanning electron microscope	b	Nucleation coefficient, $\text{m}^5/(\text{mol}\cdot\text{s})$
Ra	Rayleigh number	C_{Ca}	Calcium concentration, mol/L
Da	Damkohler number	d	Bead sizes/characteristic length of porous media, m
Stk	Stokes number	D	Diffusion coefficient, m^2/s
Greek Symbols		g	Gravitational acceleration, m/s^2
β	Solute expansion coefficient, m^3/mol	H	Height of convective dissolution, m
ϕ	Porosity	k	Permeability, m^2
ϕ'	Porosity after precipitation	k_c	Critical permeability, m^2
Φ	Diameter of cylindrical bottle, m	r_s	Precipitation particle size, m
τ_c	Characteristic time of convection, s	t_r	Resident time, s
τ_s	Characteristic time of sedimentation, s	v_c	Characteristic velocity of convection, m/s
μ	Viscosity, $\text{Pa}\cdot\text{s}$	v_s	Characteristic velocity of particles' sedimentation, m/s
ρ	Density of fluid, kg/m^3	V_{CaCO_3}	Molar volume of CaCO_3 particle, m^3/mol

(precipitation particle scale, pore-scale, Darcy-scale, etc.), that brings considerable challenges in numerical simulation (De Silva et al., 2015; Yoon et al., 2019, 2012). Therefore, the role of precipitation reactions on CO_2 convective dissolution is still an open question. Direct experimental observation is required to inspire physically-reasonable simplifications and benchmarks to enable affordable and accurate numerical simulation of CO_2 convective dissolution integrated with reactive precipitation.

As a compromise for limited direct imaging techniques, some observations are conducted after *in-situ* operations, such as hydrothermal or flooding experiments, utilizing scanning electron microscopy (SEM) (Rosenbauer et al., 2005; Xu et al., 2017; Yu et al., 2012). For example, Xu et al. (2017) conducted SEM imaging after CO_2 -brine flooding, that reported a negligible amount of CaCO_3 precipitation. However, these visual observations are limited to the post-reaction state and conducted under normal pressure, without the information on the time-dependent process that occurs under *in-situ* conditions.

To characterize the dynamics of reactive precipitation in porous media, some innovative experimental and characterization methods have been adopted. To avoid high-pressure experiments while providing adequate CO_3^{2-} , Zhang et al. (2010) employ an analog fluid pair, Na_2CO_3 and CaCl_2 solutions, to imitate precipitation reaction of CaCO_3 in microfluidic chips. Similar analog aqueous-aqueous fluid pairs for generating CaCO_3 or BaCO_3 sediments can also be combined with high resolution dynamic characterization methods such as μCT , NMR, or microfluidics (Bere et al., 2021; Bray et al., 2017; Moosavi et al., 2019; Schuszter et al., 2016). In all experiments these analog fluid pairs are applied, generation of dense precipitates are observed. These precipitates impede further mixing by blocking the pore throat and impairing the permeability, which conflict with previous observations after CO_2 -brine flooding experiments by Xu et al. (2017). However, in actual reservoirs, CO_2 is far more abundant the Ca^{2+} , thus the absence of subsequent bi-carbonization reactions in these systems limits their geological implications.

In addition, Hele-Shaw cell or microfluidic experiments are conducted to mimic subsurface porous media, that are able to use $\text{Ca}(\text{OH})_2$ solution and CO_2 gas for real-time experimental observation (Thomas et al., 2020; White and Ward, 2012). Thomas et al. (2020) observed intense solid precipitates and downwelling plumes by placing a $\text{Ca}(\text{OH})_2$ -saturated Hele-Shaw cell within a CO_2 atmosphere. This experimental setup allows reactions that are much closer to realistic conditions and capturing the dynamics of reaction – convection coupling. Nevertheless, the normal pressure (thus low CO_2 solubility) and lack of porous structure (the role of which is still largely unexplored) make this study

still not adequate to finally reveal the mechanism of precipitation reaction during convective dissolution in porous media.

In summary, our understanding of CO_2 convective dissolution with reactive precipitation is limited. Direct experimental observations are required to reveal its multi-physics and multi-scale mechanisms and provide benchmarks, to inspire physically-reasonable simplifications for numerical modeling. However, current experiments on density-driven convective dissolution of CO_2 can hardly realize realistic-ratio chemical reactions, representative porous structure and high spatial & temporal resolution at the same time.

Here we establish an experimental platform to directly visualize convective dissolution of overlaying CO_2 into brine that simultaneously allows 1) flexible spatial resolution, 2) high temporal resolution, 3) high pressure to match realistic species ratio, and 4) adjustable porous structure. We employ $\text{Ca}(\text{OH})_2$ solution and artificial porous media as the saline aquifer, high-pressure CO_2 as the gas cap over the brine, to restore realistic scenario of solubility sequestration. Both macroscopic images on the whole medium and microscopic images at sub-pore scale are recorded to demonstrate the reactive precipitation and convective dissolution dynamics at different scales. The behavior of precipitates in different media is recorded to identify the role of porous structure, followed by theoretical analysis to rationalize the observations. We aim to demonstrate the physics during CO_2 convective dissolution with reactive precipitation in porous media, and also hope to provide benchmarks that benefit future studies.

2. Material and methods

2.1. Fluid preparation

Calcium (Ca^{2+}) is a typical metal ion contributes to precipitation in subsurface aquifers. We use saturated calcium hydroxide ($\text{Ca}(\text{OH})_2$) aqueous solutions as host brine. The $\text{Ca}(\text{OH})_2$ solution is saturated, with a pH of 12.6 and a concentration of 0.01 mol/L. All experiments are conducted under 1 MPa, 30 °C. CO_2 solubility at this condition is 0.33 mol/L (pH = 3.3) (Diamond and Akinfiev, 2003; Peng et al., 2013). In addition, deionized (DI) water is chosen as a precipitation-free system for comparison, which has been extensively investigated before (Emami-Meybodi et al., 2015; Huppert and Neufeld, 2014; Slim, 2014).

The reaction between Ca^{2+} and CO_2 involves two steps, i.e., carbonation and bicarbonation, depending on local concentration ratio. In our experiments, we note that the available $\text{CO}_2/\text{Ca}^{2+}$ ratio is greater than 33 in this work, which is consistent with practical conditions (De

Silva et al., 2015; Diamond and Akinfiev, 2003).

2.2. Model preparation

For model without porous structure, both cylindrical bottle ($\Phi = 25$ mm, $H = 95$ mm) and Hele-Shaw cell (space between two parallel plates) are applied, as the pictures shown in Fig. 1a. We note that flow in Hele-Shaw cell follows a similar formula to Darcy's law (pressure gradient proportional to velocity), but it lacks of porous structure so exhibits differences in solute and suspension dispersion from that in porous media.

For models with porous media, glass beads are employed to construct porous structure in cylindrical bottle and Hele-Shaw cell (Fig. 1a). We vary the bead diameter (d) from 0.1 mm to 3 mm, corresponding to changing the permeability (k) from 10^{-11} to 10^{-8} m² (Carman, 1939) while keeping the porosity (ϕ) almost constant at 0.42. All glass beads are washed with DI water and then dried before experiments to remove soluble ions attached to the glass surface.

By posing higher permeability than that in field applications, similar Rayleigh numbers (Ra) to field applications are reproduced in lab. Here Ra is defined by the ratio of mass transfer rate between convection to diffusion as $Ra = k\Delta\rho gH/(\mu\phi D)$. The Ra in our experiments is ranges from $70 \sim 7 \times 10^5$, align well with field observed (Hassanzadeh et al., 2007).

2.3. Experimental setup and visualization

Fig. 1b shows the schematic of experimental setup. The experiments are conducted in a high-pressure chamber with circular visualization windows. The chamber is connected to a high-pressure CO₂ pump. After positioning the brine-saturated media into the chamber, the pressure is quickly leveled-up to a desired value by injecting CO₂ into the chamber and then maintained constantly, to imitate the dissolution of overlaying CO₂ cap into host brine beneath it. The pressurization time (~ 5 s) is negligible compared to the dissolution time.

We recorded the experiments with camera (Basler, ac2440-75 u), which can be used for both macroscopic (entire cell) imaging and microscopic imaging under *in-situ* conditions, by adjusting the lens. To enhance visualization of dissolution and reaction, two pH indicators with different effective ranges, namely alizarin yellow R and methyl red, are used at a concentration of 0.004 %w/w. Alizarin Yellow R responds to alkaline range of pH = 10.2 (yellow) $\sim$ 12.0 (red), while methyl red indicates the transition in acidic range of pH = 4.4 (red) $\sim$ 6.2 (yellow). We note that optical effects of glass bead pack turns fluid color lighter than that in empty bottle/cell, as shown Fig. 1. As a consequence, the

solution with Alizarin Yellow R turns white, instead of red, in beadpack under acidic environment. Details of this color change in bead pack are illustrated in supplementary. To further improve the visualization, some images are converted into HSV (Hue, Saturation, Value) color space, and the Hue channel is selected for enhancement and re-colorization, with details presented in S4 (Liang et al., 2018).

To systematically study the dissolution and reaction front in Ca(OH)₂ system, we design a parallel experiment, which contains two 'identical' bead packs parallelly positioned in the chamber with different pH indicators (the last picture in Fig. 1a), to allow simultaneous capture both CO₂ dissolution and Ca²⁺ consumption in a single experiment.

3. Results and discussion

3.1. Convective dissolution in absence of porous structure

We first conduct convective CO₂ dissolution in bulk fluid without porous structure. Experimental images at different times for DI water in Hele-Shaw cell, Ca(OH)₂ solution in Hele-Shaw cell and Ca(OH)₂ solution in cylinder bottle are shown in Fig. 2.

When pure water is the overlaid liquid in Hele-Shaw cell, a classic Rayleigh-Taylor instability pattern is observed, in which a diffusion boundary layer (Fig. 2a) gradually develops into descending fingers towards the bottom of the cell (Fig. 2b,c).

When Ca(OH)₂ solution is the overlaid brine, CO₂ dissolution pattern is largely reshaped. In Hele-Shaw cell, as depicted in Fig. 2d-f, massive precipitation particles are produced. In addition, although convection is extremely strong in the upper layer, a clear reaction front is observed that moves gradually downward. Below the front, convection is relatively weak, with particles falling down. Fig. 2 g-i shows parallel experiments using Ca(OH)₂ solution in cylindrical bottles. Similar reaction front is observed, and different pH indicators clearly show that this front is the reaction front: pH is below 4.4 above the front and exceeds 12 below it, with very quick transition between them. Here we observe cloudy convection of particle suspension above the front, while only some falling particles below the front. Since CaCO₃ should be bi-carbonized and re-dissolved at pH below 4.4 and cannot form at pH beyond 12, the precipitation should predominantly form near the reactive front and then disperse with the convection.

The reaction front divides the whole domain into an upper convective particle suspension and lower static fluid with falling particles. It indicates that CaCO₃ precipitation reaction modifies the fluid density profile which is different from that in pure water system (Fig. 3a). In Ca(OH)₂ system, the CaCO₃ particles are formed at the reaction front, and some of them downwelling to the bottom and others are circulating

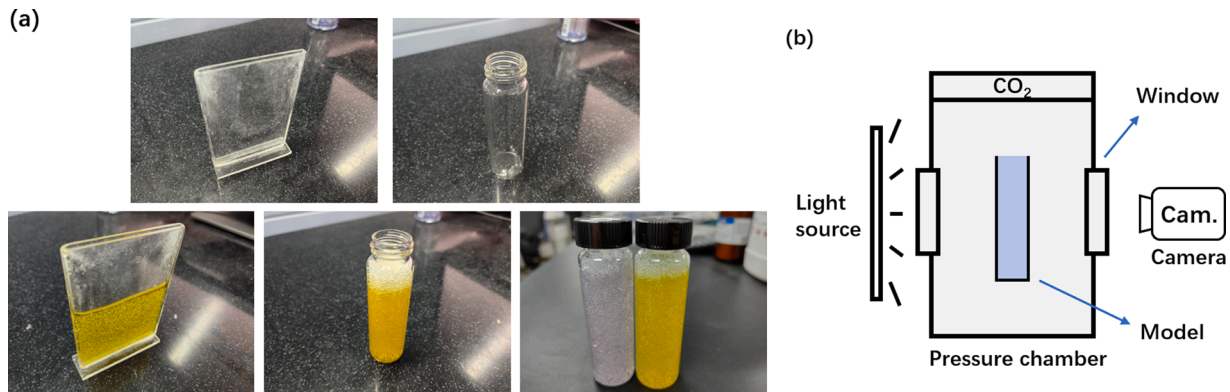


Fig. 1. (a) Models adopted in experiments. Hele-Shaw cell and cylindrical bottle are used to be the models without porous structure; after filled with glass beads of different sizes, porous media with various permeability are constructed (dyed with methyl red). The last picture shows the designed parallel system, consisting of two cylindrical bottles with pH indicators of distinct ranges (alizarin yellow R in left, and methyl red in right). (b) The schematic of experimental setup, including a pressure chamber with windows, light source, camera, and models. Once the models are in place, the chamber is sealed and the CO₂ will be pumped in under constant pressure.

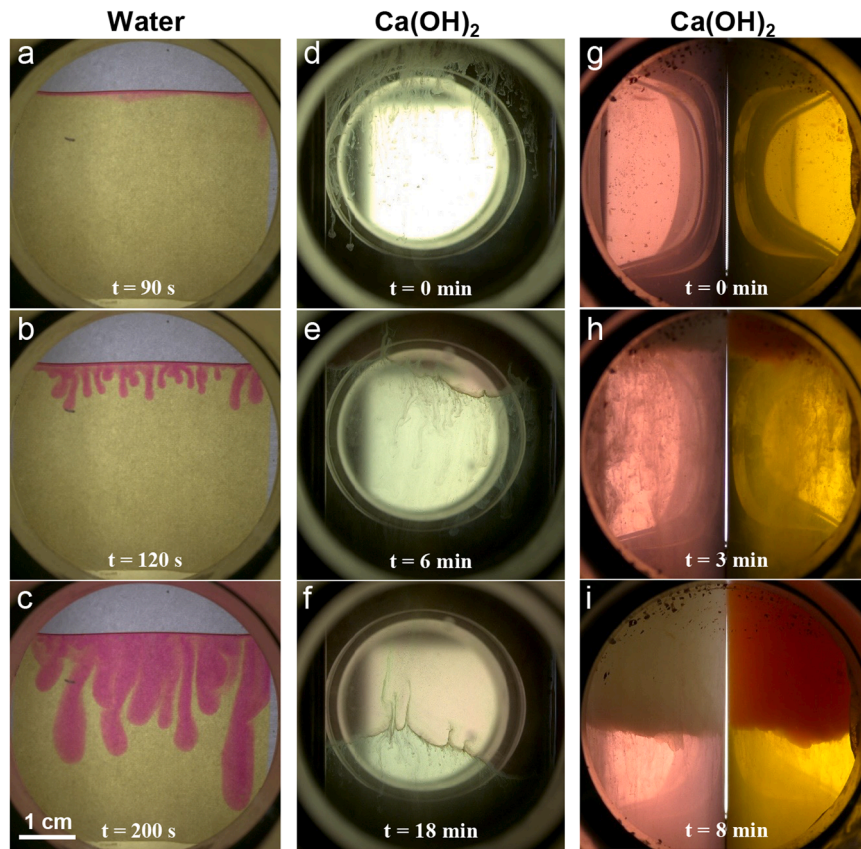


Fig. 2. Dynamic dissolution results of Hele-Shaw cell experiments of CO_2 dissolution in (a-c) water and in (d-f) Ca(OH)_2 solution. For (a-c), a paper is positioned behind the Hele-Shaw cell to enhance the visualization. (g-i) Parallel experiments in bead packs for Ca(OH)_2 solution. The two experiments in Hele-Shaw cell (first two columns) employ acidic and alkaline range pH indicator, respectively. The parallel experiments (third column) use two indicators to separately dye the two packs. All experiments presented here are conducted under 1 MPa, 30 °C. The corresponding movies for these three experiments (Movie S1-S3) are provided in Supplementary.

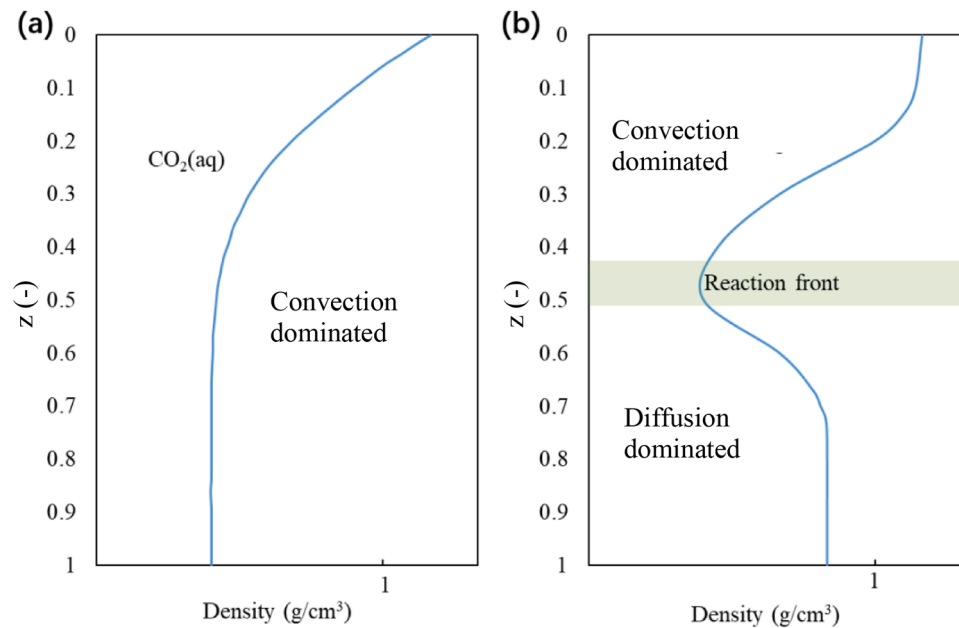


Fig. 3. Sketch of density profile for CO_2 dissolution in (a) DI water and (b) Ca(OH)_2 solution. The solute transport in water is dominated by convection, with density monotone decreasing. However, the presence of precipitation reaction result in a minimum front in density, which suppress the downwelling convection and leads to distinct flow dynamics on two sides of the front.

above the front, which reduce the density at the upper layer and also may change the rheology above the front. As discussed by Jotkar et al. (2019), such a convective-static two-layer pattern corresponds to a non-monotonic vertical fluid density profile, where the density at the front is of global minimum, as shown by the sketch in Fig. 3b (Almarcha et al., 2010; Lei and Luo, 2019; V. Loodts et al., 2016). Moving velocity of the front can be used to characterize CO₂ dissolution kinetics.

To declare the density distribution in Ca(OH)₂ system, we investigate the solute expansion coefficients, $\beta = (1/\rho_0)(\partial\rho/\partial c)$ (by Mettler Toledo density meter D4). The values of β for components above the front, namely CO₂ and CaCO₃ suspension, are 4.4×10^{-6} and 6.34×10^{-5} m³/mol, respectively; the value of β for component below front, Ca(OH)₂, is 1.5×10^{-4} m³/mol (Thomas et al., 2020). At the reaction front the density-contributing components (CO₂ and Ca²⁺) are consumed, so the density at the front is the global minimum, that highly suppress the downwelling convection. It aligns well with the distinct patterns observed across the front, where convection dominating above it and diffusion dominating beneath it.

In summary, in absence of porous structure, precipitation forms cloudy suspension, that chaotically flow above the reaction front and fall down below the reaction front. These observation matches with literature. A question then comes: if porous structure exists, would particles clog the media and suppress the convective dissolution?.

3.2. Convective dissolution with porous structure

We then conduct convective dissolution of overlaying CO₂ in porous media. Experimental images at different times for experiments using DI water in Hele-Shaw cell filled with glass beads, Ca(OH)₂ solution in

Hele-Shaw cell filled with glass beads, and Ca(OH)₂ solution in cylinder bottle filled with glass beads are shown in Fig. 4. All experiments are under 1 MPa, 30 °C.

When pure water is filled in the porous Hele-Shaw cell, a Rayleigh-Darcy convective dissolution pattern emerge (Huppert and Neufeld, 2014). As shown in Fig. 4a, multiple dissolution fingers form initially from the gas-brine interface. Asymmetric fingers grow, compete and merge, with fewer dominant fingers finally touch the bottom (Fig. 4b,c). Such behavior is qualitatively similar to that without porous structure.

However, when Ca(OH)₂ solution is filled in the porous Hele-Shaw cell, as shown in Fig. 4d-f, the dissolution pattern is qualitatively different from that without porous structure:

- 1) **Symmetric fingers above reaction front.** Fingers emerge and move down at the same speed, which is distinct from the competing and asymmetric fingers in pure water system. We can still define the a reaction front as the shared tip of fingers; however, different from the intensive mixing in absence of porous structure, the transversal mixing in porous media is suppressed so that Rayleigh-Darcy convective finger pattern is preserved. This observation can be supported by the parallel two-bottle experiments as shown in Fig. 4 g-i, where blurred front can be identified. This pattern can support earlier numerical prediction on convective dissolution patterns integrated with homogeneous chemical reaction as classified by Jotkar et al. (2019).
- 2) **Precipitation not observed.** The transparency of the fluid during convective dissolution & reaction experiments in porous media does not change as shown in Fig. 4 g-i, unlike the emergence of cloudy precipitates in absence of porous structure. In the next two

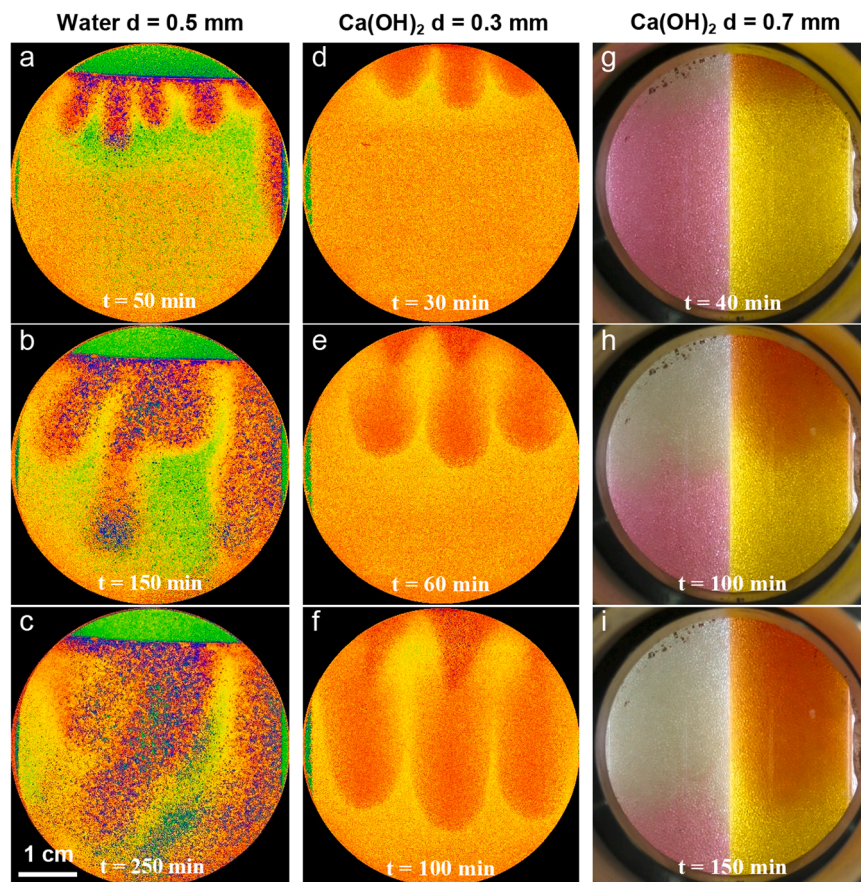


Fig. 4. Dynamic dissolution results of CO₂ dissolution in (a-c) water and (d-f) Ca(OH)₂ solution within porous media. (g-i) Experiments in parallel bead packs for Ca(OH)₂ solution. The results displayed in first two columns have been enhanced and re-colored for better visualization, while the results in last column is in their original state. The corresponding movies for these three experiments (Movie S4-S6) are provided in Supplementary.

subSections (3.3&3.4), we are to rationalize this “disappearance” of precipitation in porous media.

3.3. Microscopic observation of precipitates local retention in porous media

To identify the fate of these “missing” precipitates, we conduct micro-scale observations in a reproduced CO₂ convective & reactive dissolution experiment in Ca(OH)₂ solution, in the same porous Hele-Shaw cell. Details about experiment setup are available in supplementary material S5.

We set the water level higher than the beadpack, so cloudy precipitate suspension can be generated above the porous layer at the beginning, as shown in Fig. 5a. Therefore, we can focus at the top region of porous layer to observe the fate of generated particles after entering porous structure. Fig. 5b presents the dynamics of precipitates in a single pore of $d = 0.7$ mm which is near the top of porous structure. The corresponding video can be found in supplementary movie S8.

Initially, the fluid in the pore is with no evident sediments present. At $t = 386$ s, fluid flow carrying CaCO₃ particles enters the pore, forming an arc-shaped band of solid precipitate population. The precipitates are with an average size of about 5 μ m. However, these precipitates do not flow deeper into the downstream pores. Instead, the particles quickly settle down and attach on the grain surface. In subsequent observation, the particles remain in the local pore until they redissolve, without being remobilized by the convection. The dissolution timescale is much longer than both precipitation and convection timescale in our experiments. In deeper places in the porous media, flowing particles are hardly observed.

Emergence of precipitation local retention indicates that CaCO₃ particles neither contribute to fluid density in presence of porous structure, nor modify fluid rheology. In addition, as precipitates cannot migrate into a second pore after generation, there would be little chance for large amounts of precipitates to aggregate and block a pore.

3.4. Theoretical analysis of precipitate local retention in porous media

This quick local retention of precipitates in porous media is driven by gravitational effect and allowed by the pore confinement, that has not been reported before under pressurized condition. To identify whether this local retention of precipitates can also occur in other media, we theoretically evaluate the fate of precipitate particles in a pore under gravity-driven convection.

We define a Stokes number (Stk) as the ratio of characteristic time of convection (τ_c) to sedimentation (τ_s) in a pore body. When $Stk < 1$, the

particles tend to follow the fluid flow; in contrast, if $Stk \gg 1$, particles deviate from the fluid flow and settle down locally. Assuming a precipitate particle is spherical, we can calculate its terminal falling velocity as $v_s = 2\Delta\rho_s g r_s^2 / (9\mu)$ based on the Stokes' law (Brennen, 2005) where $\Delta\rho_s$ is the density difference between precipitate and host brine; and r_s is the typical radius of precipitate particles. We assume that a particle is initially produced at the center of a pore body so the settling distance is characterized of $d/2$. The characteristic time for particle sedimentation can thus be expressed as:

$$\tau_s = \frac{d/2}{v_s} = \frac{9}{4} \frac{\mu}{\Delta\rho_s g} \frac{d}{r_s^2} \quad (1)$$

The scaling $\tau_s \propto d$ indicates that smaller pore size leads to shorter sedimentation time.

The characteristic time for fluid flow through the pore can be easily derived from Darcy's law, and integrated the relation between permeability and grain size, $k \sim d^2$, the τ_c is given by:

$$\tau_c = \frac{d}{v_c} = \frac{d\phi\mu}{k\Delta\rho g} = 108 \frac{(1-\phi)^2}{\phi^2} \frac{\mu}{\Delta\rho g d} \quad (2)$$

where v_c is the characteristic velocity in pore scale, $v_c = k\Delta\rho g / (\phi\mu)$; $\Delta\rho$ is the density difference between CO₂ saturated brine and host brine. The scaling $\tau_c \propto 1/d$ indicates that smaller pore size results in longer flow time.

Furthermore, we estimate the precipitates' size, r_s . Given that the CO₂ concentration is significantly larger than Ca²⁺, which holds true under both practical and experimental condition, the growth of CaCO₃ precipitate can be considered as limited by Ca²⁺ concentration. Thus, based on nucleation theory, the particle size, r_s , can be estimated as (Lacmann et al., 1999; Myerson and Ginde, 2002):

$$r_s^2 = b C_{Ca} t_r \quad (3)$$

where the C_{Ca} is the calcium concentration contribute to participate in reaction; t_r is the resident time, representing the time scale of particle growth; and b is the nucleation coefficient. Combine the Eq. (1-3) and replace resident time with convective timescale τ_c , the relation between Stk number with fluid properties ($\Delta\rho$, $\Delta\rho_s$, μ , C_{Ca}) and porous media properties (ϕ , k) is established as:

$$Stk = 4.6b C_{Ca} \frac{\mu}{g} \frac{\Delta\rho_s}{\Delta\rho^2} (1-\phi)\phi^{0.5} k^{-1.5} \propto d^{-3} \quad (4)$$

Therefore, Stk sensitively reduces with pore size increase, indicating the particles are likely to sediment in local pores with lower permeability. A critical permeability (k_c) exists at $Stk = 1$, which can be

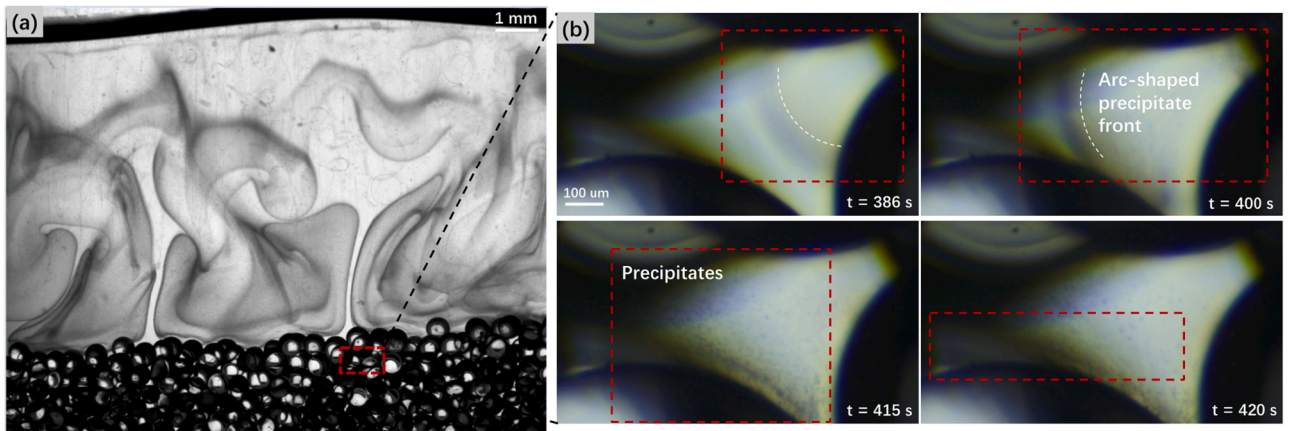


Fig. 5. (a) bulk fluid overlaying the beadpack and cloudy particles are formed, and (b) overall process of convection, precipitation reaction, and subsequently precipitate particles' flow dynamics in pore space under microscope. The pore space part is extracted with image matting, and stitch it back after enhanced. The corresponding movies for this experiment (Movie S7&8) are provided in Supplementary.

calculated with Eq. (4) under experimental condition where $\Delta\rho = 2 \text{ kg/m}^3$, $C_{Ca} = 10^{-2} \text{ mol/L}$, $\rho_s = 2700 \text{ kg/m}^3$. Value of b can be obtained from micromodel experiments (see Supplemental Information S6) as $b \sim 2.5 \times 10^{-14} \text{ m}^5/(\text{mol}\cdot\text{s})$. This theoretical boundary agrees well with experimental observation using different pore sizes, as shown in Fig. 6a.

3.5. Discussion: local precipitation retention under field conditions and in literature

We further investigate how key variables affect the local precipitate retention, under practical CO_2 sequestration scenarios. Fig. 6b shows the critical permeability under different porosity and depth assuming vertical pressure gradient 15 MPa/km and vertical temperature gradient 30°C/km . Integrated the influence of pressure and temperature, the density contrast between CO_2 -saturated water and host brine narrows down as it goes deeper ($\Delta\rho$ from 13.752 to 10.876 kg/m^3 , other parameters remain as described previously). The k_c we obtained is around 10^{-13} m^2 (100 mD). It is significantly larger than most field situations for carbon sequestration. It implies that for most saline aquifer, the precipitates generated from aqueous reactions will sediment locally within the pore that they are produced.

As the precipitates tend to sediment at local pores, it's important to calculate the proportion of the precipitates' volume in a pore space to assess the impact of precipitates on porous structure. The porosity reduction can be calculated according to the local pH value as Ca^{2+} concentration is excessive in most stratum, which denoted as:

$$\left| \frac{\phi' - \phi}{\phi} \right| = C_{Ca} V_{\text{CaCO}_3} = \frac{1}{2} 10^{\text{pH}-14} V_{\text{CaCO}_3} \quad (5)$$

where ϕ' is the porosity after precipitation, V_{CaCO_3} is the molar volume of

CaCO_3 particle. Fig. 6c illustrates the porosity reduction caused by precipitation under different pH. It demonstrates that even under maximum reactive Ca^{2+} concentration (pH=12.6), the reduction on porosity is only 0.369% , which has a trifling impact on porosity and is consistent with our experimental observation.

In practical subsurface scenarios, pH in most aquifers ranges from 6 $\sim$ 10. The amounts of precipitates reduce with the decrease in pH. If under typical pH of subsurface saline aquifer (pH = 9), the reduction is only $1.85 \times 10^{-5}\%$. It declares the negligible impact on porous structure. These theoretical inference and observation are aligned with the experiment in core sample after hydrothermal reaction by Xu et al. (2017). In addition, Ca^{2+} concentration in some recent analog studies ($\sim 1 \text{ M}$) is far higher than field, and under our estimation the resulting porosity reduction is approximately 4% , which may interpret the pore-blocking observed in these studies (Bere et al., 2021; Schuszter et al., 2016).

3.6. Experiment-inspired simplifications for numerical simulation

As discussed above, direct numerical modeling of multi-phase, multi-scale heterogeneous reactive transport in complex medium is extremely challenging. Fortunately, our experimental observation and theoretical rationalization of the local CaCO_3 precipitation retention may allow major simplifications on numerical modeling:

- The precipitation does not affect fluid rheology. This simplification holds as 1) the precipitate generalized in single pore is insufficient to affect rheology, and 2) local retention prevents the accumulation and enrichment of particles from different pores.

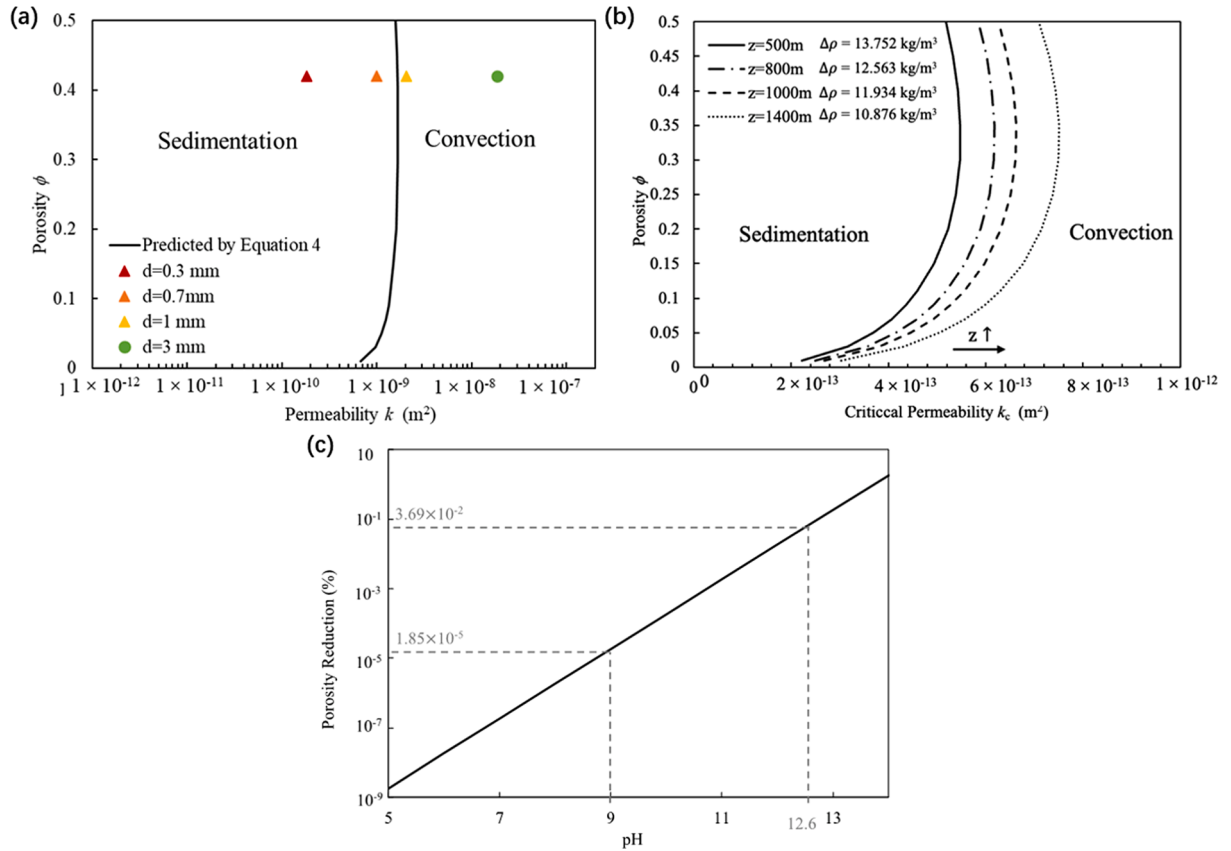


Fig. 6. (a) A comparison of particles' flow behaviors between experimental observation and prediction based on Eq. (4), triangular markers indicate sedimentation and circular indicates convection; (b) prediction of precipitates flow dynamics at various depth, z , under reservoir condition ($dP/dz = 15 \text{ MPa/km}$, $dT/dz = 30^\circ\text{C/km}$); and (c) the calculation of porosity reduction with different pH values corresponding to different reactive Ca^{2+} concentrations.

- Precipitation mass does not need to be counted into fluid density. This simplification holds as these particles attach on grain surface and does not involve in advection.
- Porosity and permeability are not affected by carbonized precipitation. This simplification is supported by the local-retention observations and porosity reduction predictions. We note that porosity and permeability may still change due to other mechanisms such as mineral dissolution and brine evaporation (Assayag et al., 2009; Fu et al., 2015; Ling et al., 2022; Miri and Hellevang, 2016).
- Re-dissolution of precipitates due to bi-carbonization does not affect fluid flow. That is because precipitates dissolve relatively slow, that local CO_2 concentration has already been much higher than maximum Ca^{2+} concentration when its redissolution is significant (discussed in supplementary information). Therefore, impact of re-dissolution on fluid density, CO_2 concentration and pH is insignificant in the cases of interest.

We then implement a simplified numerical implementation after counting these above simplifications using COMSOL 5.6 with Forchheimer module (Huang and Ayoub, 2006; Macdonald et al., 1979).

The setup of model geometry and parameters are consistent with the experiments, and the detailed setup is shown in Supplementary information. We observe similar symmetric fingering patterns in simulation (Fig. 7a), and compare it with those observed in experiment of Fig. 4a-c. Regular fingers are formed after the onset of instability and remain statically-developed due to the stabilizing barrier created by the local minimum in density profile, where the phenomenon aligns well with experiments. In addition, the same clear reaction front and convective-static flow patterns across the front are observed in simulation results (Fig. 7b), as we observed in experiments of Fig. 2g-i. Then, we characterize the CO_2 dissolution rate in porous media with $\text{Ca}(\text{OH})_2$ solution by measuring downward movement velocity of reaction front (U), and compare the experimental results with simplified modeling in media of different permeabilities, as shown in Fig. 7c. The good agreement between experiments and numerical simulation indicates the effectiveness of the simplifications inspired by experimental observations of local particle retention.

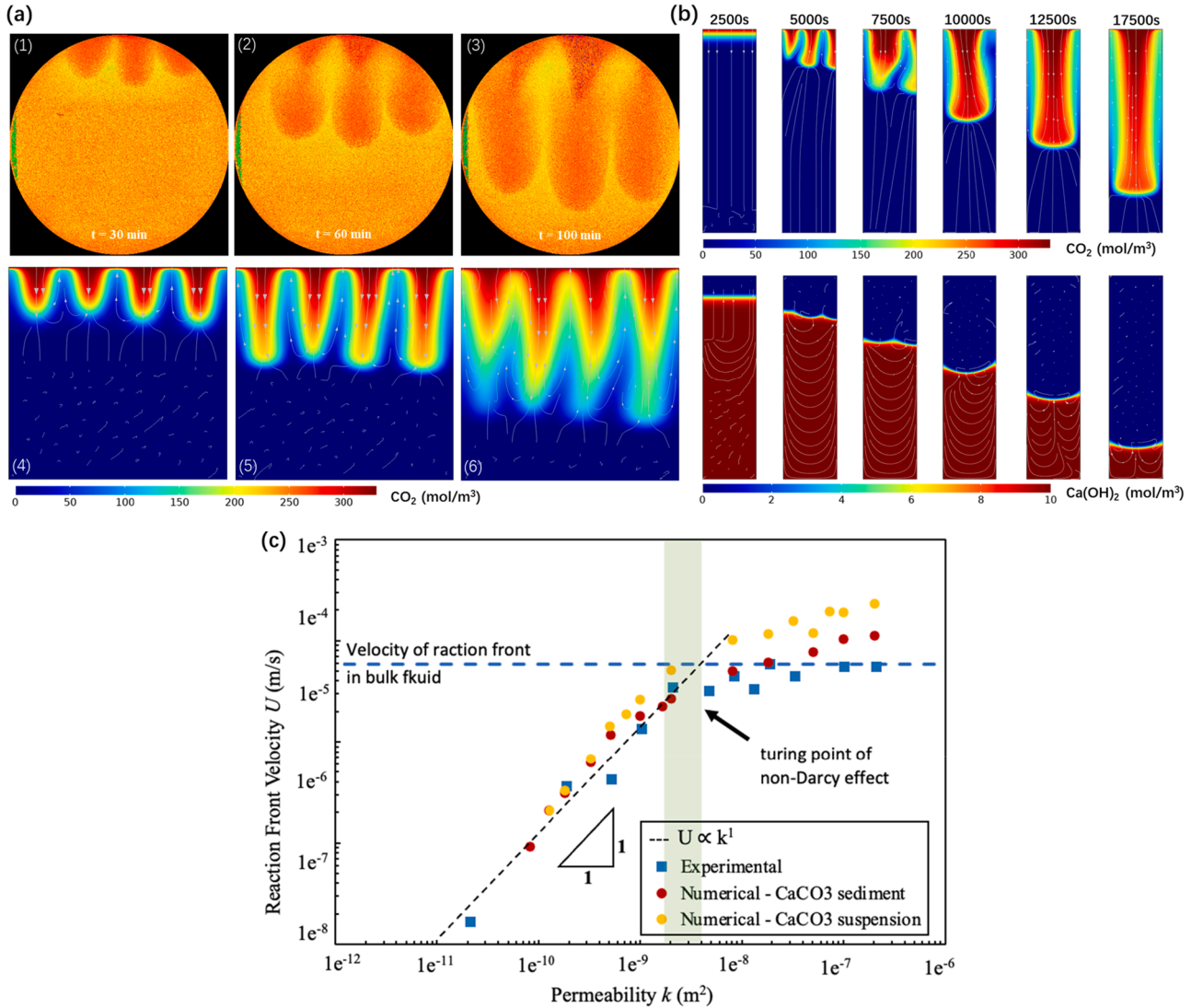


Fig. 7. (a) Experimental and numerical results of fingering patterns in $\text{Ca}(\text{OH})_2$ solution system, (b) the CO_2 and $\text{Ca}(\text{OH})_2$ concentration field in numerical simulation of CaCO_3 sediment, and (c) experimental and numerical results of reaction front velocity in $\text{Ca}(\text{OH})_2$ solution system under different permeability. Similar regular, and convective-static patterns, as well as the reaction front as experiment observed are also obvious in numerical simulation. The horizontal dotted line donates the front velocity in bulk fluid obtained from experiments. The migration of reaction front is controlled by the convection above front, and there is a turning point which induced by non-Darcy effect in high permeability regime. The numerical results agree well with the experimental results, in both tendency and turning point.

4. Implications and limitations

4.1. From lab to field parameters

While our experimental setup differs from real reservoir conditions in terms of pressure, temperature, permeability, and porosity, we bridge these gaps by employing dimensionless numbers to ensure a meaningful comparison. For convective dissolution, a reaction-diffusion-convection problem, two dimensionless numbers matters: Rayleigh number (Ra) and Damkohler number (Da) (Huppert and Neufeld, 2014; Lei and Luo, 2019).

Ra has been defined in earlier sections as the ratio of convective to diffusive rates: $Ra = k\Delta\rho gH/(\mu\phi D)$. Ra in our experiments ranges from 70 to 7×10^5 by varying permeability, which closely align with real data (Hassanzadeh et al., 2007). This suggests that our experiments effectively reproduce the convection-diffusion scenario present in reservoirs.

Da is to characterize reaction rate and diffusion rate, defined as $Da = k_r C_{CO_2} H/(\phi D)$, where k_r is the reaction rate and C_{CO_2} is the concentration of CO_2 . If $Da \gg 1$, the reaction is controlled by mass transfer, i.e., Ra, instead of reaction kinetics. In terms of the precipitation reaction, the Da is certainly larger than 1 and reactant ratio CO_2/Ca^{2+} is sufficiently large, ensuring the $CaCO_3$ is produced instantaneously and completely, which mirrors the reservoir scenarios (Erfani et al., 2022).

4.2. Limitations

Nevertheless, some field conditions are not fully reproduced in the experiments, that we need to keep cautious in directly adopting our conclusions to field applications:

- CO_2 exists in a supercritical state rather than in gas phase in many field cases (Parisio and Vilarrasa, 2020). While dissolution and reactions occur in the water phase, the CO_2 phase state primarily influences the process by determining its solubility (Versteeg et al., 2024), which plays key role in convective dissolution as the upper boundary.
- Higher temperature could accelerate the $CaCO_3$ dissolution process, potentially altering fluid density and convection dynamics. This issue could have a more significant impact on CO_2 storage at field scale (Erfani et al., 2022; Fu et al., 2015).
- Fingering patterns can be highly affected by heterogeneity of porous media (Lei and Luo, 2019; Soltanian et al., 2017; Zhang et al., 2024), while our setup is highly homogenous. The effect of heterogeneity on this reactive and convective dissolution in porous media would be a focus of future investigation.
- Higher pressure in field application increases CO_2 solubility, thus results in higher density contrast. This may lead to a distinct fingering pattern than the stable front in our experiment, as that numerically discussed by Jotkar et al. (2019).
- Other factors, such as rock dissolution and reprecipitation, as well as salt precipitation, may further affect the efficiency and dynamics of CO_2 dissolution, potentially altering the overall trapping mechanisms within the reservoir (Ho and Tsai, 2020; Liang et al., 2018; Zhang et al., 2017).

These limitations highlight the need for further experimental investigation to better understand the full scope of CO_2 convective dissolution in real-world conditions.

5. Conclusion

We conduct visual experiments to investigate the dynamics of CO_2 convective dissolution in porous media cooperated with aqueous reactive precipitation, which is a critical process of carbon subsurface sequestration. We investigate the effect of precipitation on dissolution

kinetics, and reveal the critical interaction between precipitates migration and porous structure.

Different from overlaying CO_2 dissolution into pure water, when dissolution into $Ca(OH)_2$ solution, precipitation reaction occurs and a clear dissolution front is observed. Above the front, Rayleigh-Taylor or Rayleigh-Darcy instability emerge; below the front, the fluid is relatively static. The emergence of this phenomenon is rationalized by the fact that the precipitation reaction results in a minimum density at the reaction front.

When porous structure exists, two major differences in dissolution patterns are identified compared to that without porous structure, when overlaying CO_2 dissolves into $Ca(OH)_2$ solution:

- 1) Distinct fingering pattern. Symmetric fingers are observed above front in porous media, while the fluid is well mixed above the front without porous structure. This difference is attribute to the suppressed transversal dispersion in presence of porous structure, which may have major geological consequence if the porous structure can also react with carbonized aqueous solution.
- 2) Absence of flowing particles. Little precipitation particles flow in porous media, while cloud of precipitates are observed without porous structure. Microscopic images show that precipitation particles, once formed, almost immediately sediment on the surface of local pore surface that hardly mobilize again. We rationalize the local retention of precipitation particles by Stocks number (Stk) analysis. Theoretical derivation implies that this local precipitation retention can emerge in most field applications, that results in negligible impact of fluid density and rheology by the involvement of precipitation particles. In addition, we show that local retention of precipitates is insufficient to modify the porosity and permeability or even to block any pore that many studies concerned.

We accordingly propose some major simplifications to allow efficient numerical simulation on this complicated reactive and convective dissolution with precipitations in porous media. Primary numerical implementations based on above simplifications agree well with experimental results.

This study provides direct experimental evidences on the role of aqueous precipitation reactions in overlaying CO_2 convective dissolution during its subsurface sequestration. We note that minerals in subsurface containing ions like Mg^{2+} , Fe^{2+} , may go through similar process to Ca^{2+} as we discussed in this work. It thus provides a benchmark for further modeling approaches to compare.

CRediT authorship contribution statement

Shuai Zheng: Writing – original draft, Visualization, Software, Methodology, Investigation. **Ke Xu:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Dongxiao Zhang:** Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Ke Xu reports financial support was provided by National Key Research and Development Program of China. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.advwatres.2024.104880](https://doi.org/10.1016/j.advwatres.2024.104880).

Data availability

The supplementary material and associated videos for this manuscript can be downloaded from a public repository of research data, Zenodo, through the following link: <https://doi.org/10.5281/zenodo.14028848>.

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