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Dissolution-driven convection in reactive systems

Abstract

Dissolution-driven convection develops when a buoyantly unstable density stratification builds in the gravity field upon dissolution of a species into a host fluid. This phenomenon has regained interest in the context of CO₂ sequestration in oil fields or saline aquifers because it accelerates the mixing between CO₂ and the host phase, thereby improving the safety of the storage process. Our objective is to understand to what extent the properties of such convective dissolution depend on the chemical composition of the storage site. Chemical reactions can indeed impact convection as they affect concentrations and thus the density stratification in the host phase, at the origin of convection. Using combined theoretical, numerical and experimental approaches, we show that a chemical reaction between the dissolving species and a reactant dissolved in the host phase can either accelerate or slow down the development of convection compared to the non-reactive case. We classify the various possible cases as a function of the contributions to density and diffusion coefficients of the chemical species involved. We also discuss the impact of chemistry on the interfacial flux of the dissolving species.

Keywords

Fluid dynamics, convection, physical chemistry, CO₂ sequestration

1. Introduction

The interplay between chemistry and fluid flows can produce a wide range of complex dynamics [1, 2]. Indeed, chemical species can sometimes be more than simple passive tracers entrained by fluid flows when variations in solute concentrations change the physical properties of the fluid such as density, viscosity, or surface tension. By modifying the local concentrations, reactions and diffusion can create dynamic spatial gradients of composition, which in turn alter physical properties of the flow and can induce convective flows. In particular, convection can develop due to gradients of density, when a denser fluid lies on top of a less dense one in the gravity field. This convection, resulting from a hydrodynamic instability, accelerates the transport of the solutes compared to the case of pure diffusive transport for which no flow motion is present. Such convective flows can thus be interesting in applications requiring mixing of chemicals, such as during CO₂ sequestration in geological formations for instance.

To mitigate climate change, Carbon Capture and Sequestration (CCS) is considered as one of the mandatory measures needed to reduce the increase in concentration of this greenhouse gas in the atmosphere. CO₂ is captured at the exhaust of plants and injected into soils in old mine or oil fields as well as in saline aquifers, widely distributed around the globe. When CO₂

is injected in an aquifer, it is less dense than brine (saline water) and hence first rises up to the impermeable cap rock constraining the fluid due to gravity currents before starting to dissolve into the brine located below, as shown in Fig. 1. As CO_2 increases the density of the aqueous solution upon dissolution, an unstable density stratification forms in the brine, where a boundary layer of denser brine rich in CO_2 grows over time. After an onset time depending on the physical parameters, the two-layer stratification becomes unstable and convection sets in, creating fingers of CO_2 -rich brine sinking in the host phase. This convective instability improves the safety of the sequestration as it transports the dissolved CO_2 downwards, further away from potential pathways to escape to the atmosphere [3-5]. Furthermore, geochemical reactions may occur between dissolved acidic CO_2 and minerals dissolved in the brine [5-7]. These reactions can modify the density profile in the aqueous phase, and thereby the unstable density gradient that triggers convective motions. As an example, it has been shown that a reaction between CO_2 and the solid porous matrix of the aquifer can slow down the onset of the convective instability, because it consumes the species at the very origin of convection [6, 7]. The impact of

reactive processes involving species in solution on the transport dynamics of CO_2 is, however, still poorly understood.

In this context, our goal is to understand and classify the effects of reactions involving species in solution on the properties of dissolution-driven convection, by means of combined theoretical, numerical and experimental approaches.

2. Model

We consider an isothermal and isotropic two-dimensional system with the gravity field g pointing downwards along the vertical z axis, as shown in Fig.2. Two partially miscible phases are placed in contact along a horizontal interface in a porous medium. Phase A dissolves with a finite solubility A_0 into the fluid phase located below, called in this study "host" phase or solution. The concentration of A at the interface is considered to be equal to A_0 at all times (assumption of local chemical equilibrium). The interface is assumed to remain in time at the same position $z = 0$. In this situation, the model can focus on the dynamics in the host phase only. The host phase contains

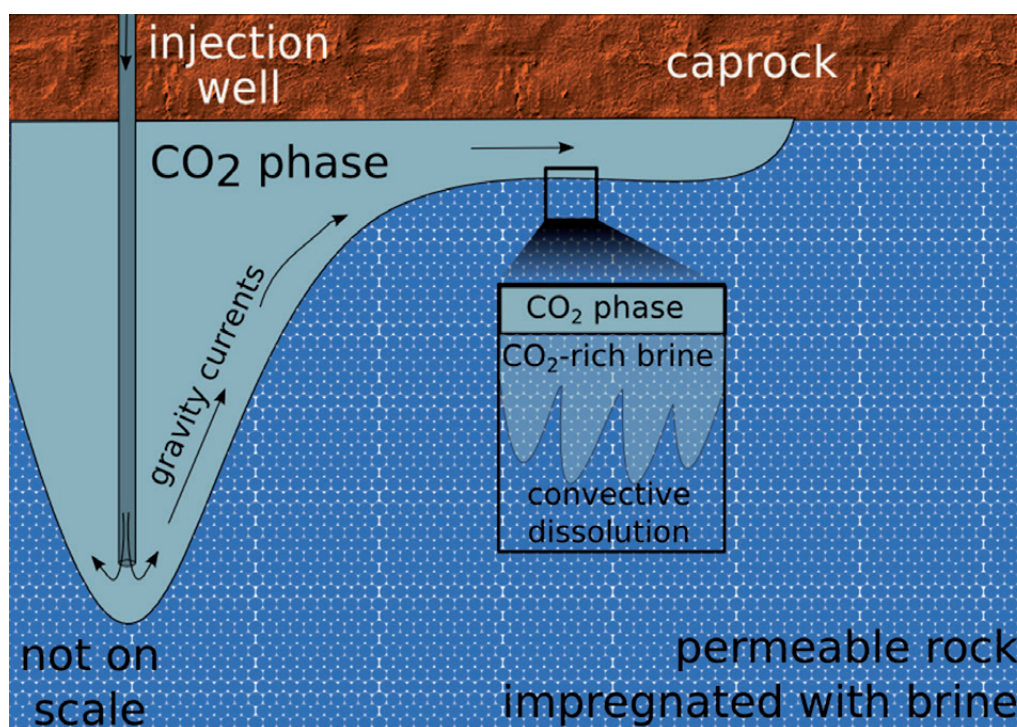


Figure 1: Convective dissolution taking place during CO_2 sequestration in a saline aquifer

a reactant B initially present in concentration B_0 . Species A and B react according to the simple kinetic scheme $A + B \rightarrow C$ to produce another solute C. The interface is assumed to be impermeable to the solvent and to solutes B and C. All three species A, B and C can contribute to changes in the density of the host phase.

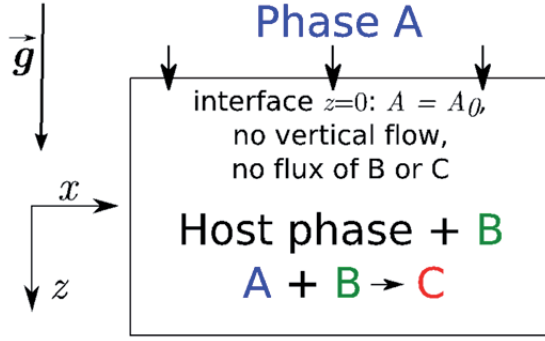


Figure 2: Model system

The equations describing the dynamics in the reactive host phase are nondimensionalized with the following scales: concentration A_0 , time $t_c = l/(qA_0)$, length $l_c = \sqrt{(D_A)/(qA_0)}$, velocity $u_c = \phi \sqrt{(D_A q A_0)}$, pressure $p_c = \phi D \mu / \kappa$, density $\rho_c = \phi D_A \mu / (g \kappa l_c)$, where q is the kinetic constant of the reaction, D_A the diffusion coefficient of A, ϕ the porosity of the medium, μ the viscosity of the host phase, κ the permeability of the porous matrix, g the norm of the gravity.

With these scales, the reaction-diffusion-convection equations describing the spatio-temporal evolution of the solute concentrations c_A, c_B, c_C in the host phase become:

$$\frac{\partial c_i}{\partial t} + (\mathbf{u} \cdot \nabla) c_i = \delta_i \nabla^2 c_i + f(c_i), \quad (i = A, B, C) \quad (1)$$

with $\delta_i = D_i/D_A$ the ratio of the diffusion coefficients and $f(c_i)$ the reaction rate equal to $-c_A c_B$ for reactants A and B and $+c_A c_B$ for product C. The flow velocity \mathbf{u} is computed using Darcy's equation for an incompressible fluid flow:

$$\mathbf{u} = -\nabla p + \rho \mathbf{e}_z, \quad \nabla \cdot \mathbf{u} = 0, \quad (2)$$

where \mathbf{e}_z is a unit vector pointing along the vertical z axis, p is the pressure and ρ the density

of the host fluid. The equations for the solute concentrations (1) and for the fluid flow (2) are coupled via an equation of state for the density ρ of the host fluid:

$$\rho = \sum_{i=A,B,C} R_i c_i, \quad (3)$$

expressing the fact that the density profile in the solution depends on the concentration profiles. Here $R_i = \rho_0 \alpha_i g \kappa l_c / (\phi \mu D_A)$ are the Rayleigh numbers quantifying the contributions of the different species to the density of the solution, ρ_0 is the density of the solvent and $\alpha_i = \frac{1}{\rho_0} \frac{\partial \tilde{\rho}}{\partial \tilde{c}_i}$ is the solutal expansion coefficient of species i with tildes denoting dimensional variables. The dimensionless parameters of the model are $\delta_B, \delta_C, R_A, R_B$ and R_C , depending on the nature of the chemicals involved, as well as the ratio $\beta = B_0/A_0$ between the initial concentration B_0 of reactant B dissolved in the host fluid and the solubility A_0 of A in the host phase.

3. Classification of the reaction-diffusion density profiles

The type of density stratification in the host fluid existing in the reaction-diffusion (RD) regime, i.e. before convection sets in, helps us predict different scenarios for the onset of convection. We thus theoretically compute RD density profiles along the vertical axis z and classify them in a parameter space spanned by the diffusivity and Rayleigh number ratios. While only two different types of density profiles can develop in the non-reactive case (monotonically decreasing or increasing along z), eight different types of profiles can be observed in the reactive case [8], as shown in Fig. 3. The coupling between dissolution and diffusion on the one hand, and chemistry on the other hand, thus multiplies the number of possible scenarios for the development of buoyancy-driven instabilities. This enlarged complexity can be explained by the increased number of parameters as three species A, B and C are involved in the dynamics instead of only one in the non-reactive case.

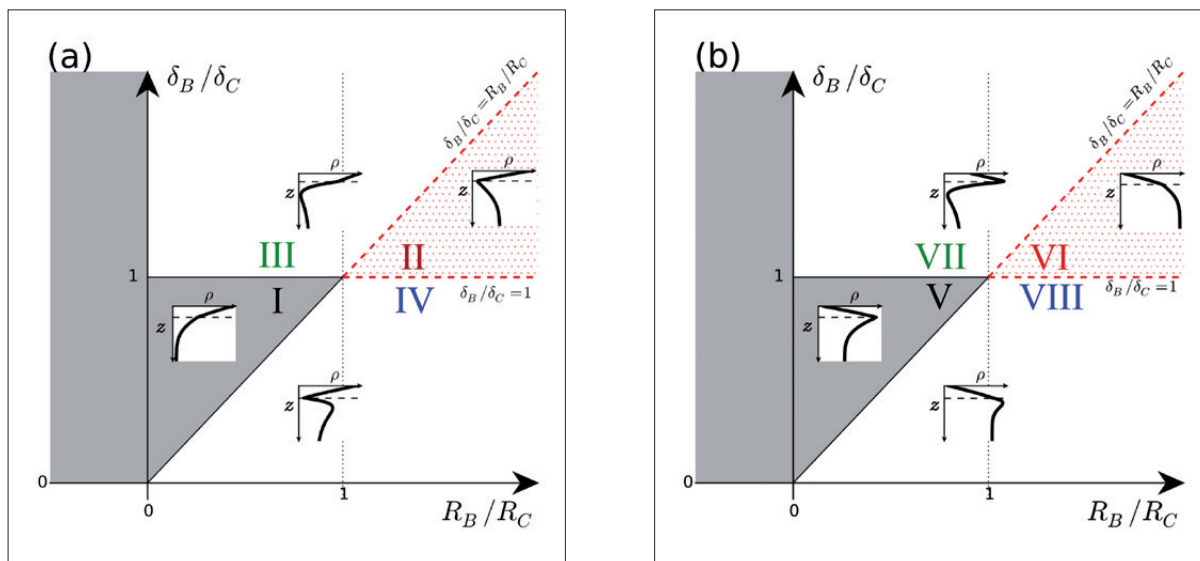


Figure 3: Classification of RD density profiles in the parameter space ($\delta_B/\delta_C, R_B/R_C$) adapted from Loodts *et al.* [8].

(a) For $R_A > 0$ (species A increases the density of the solution), four types of density profiles are possible: I: monotonically decreasing along z ; II: minimum at the reaction front, indicated as a dashed line; III: minimum below the reaction front; IV: minimum at the reaction front followed by a maximum below.

(b) For $R_A < 0$ (species A decreases the density of the solution), four other types of density profiles are possible: V: maximum at the reaction front; VI: monotonically increasing along z ; VII: maximum at the reaction front followed by a minimum below; VIII: maximum below the reaction front.

4. Effects of reactions on the convective dynamics

On the basis of this classification, we now analyze how reactions affect the convective dynamics by using a linear stability analysis and numerical simulations. We here consider more specifically $R_A = 1 > 0$, i.e. species A increases the density of the solution, and all diffusion coefficients equal (line $\delta_B/\delta_C = 1$ in Fig. 3a). In this situation, it can be shown that the dynamics only depend on the initial dimensionless concentration β of reactant and on the difference $\Delta R_{CB} = R_C - R_B$ between the contributions to density of reactant B and product C [9, 10].

The fingering dynamics are illustrated in Fig. 4 in the non-reactive case and two specific reactive cases with $\beta=1$ and different ΔR_{CB} . Without reaction (Fig. 4a), fluid motion occurs because less dense fluid pour in dissolving species A tends to float up towards the surface while denser fluid rich in A sinks downwards in the form of fingers. In the presence of a reaction $A+B \rightarrow C$, the other solutes B and C also contribute to the density of the host solution, thereby affecting the density stratification and thus the fluid flow [9, 10].

If $\Delta R_{CB} = 1$ (C is denser than B), the density profile is monotonically decreasing (zone I in Fig. 3a) and convection develops faster than in the non-reactive case (Fig. 4b). If $\Delta R_{CB} = -1$ (C is less dense than B), the density profile developing in the host phase has a minimum where locally, less dense fluid lies on top of denser one in the gravity field (zone II in Fig. 3a). Due to this local buoyantly stable zone, the instability develops more slowly than in the non-reactive case (Fig. 4c).

In order to generalize these observations to other values of parameters, we measure the growth rate σ of the instability as a function of the parameters ΔR_{CB} and β . Taking into account these results and the classification of the RD density profiles (Fig. 3), we divide the ΔR_{CB} axis in three zones Ia, Ib and II as illustrated in Fig. 5.

In zone II ($\Delta R_{CB} < 0$), the growth rate σ is smaller than its non-reactive counterpart because the minimum in the RD density profile acts as a stabilizing barrier and slows down the development of convection. Zone I ($\Delta R_{CB} \geq 0$), corresponding to monotonic RD density

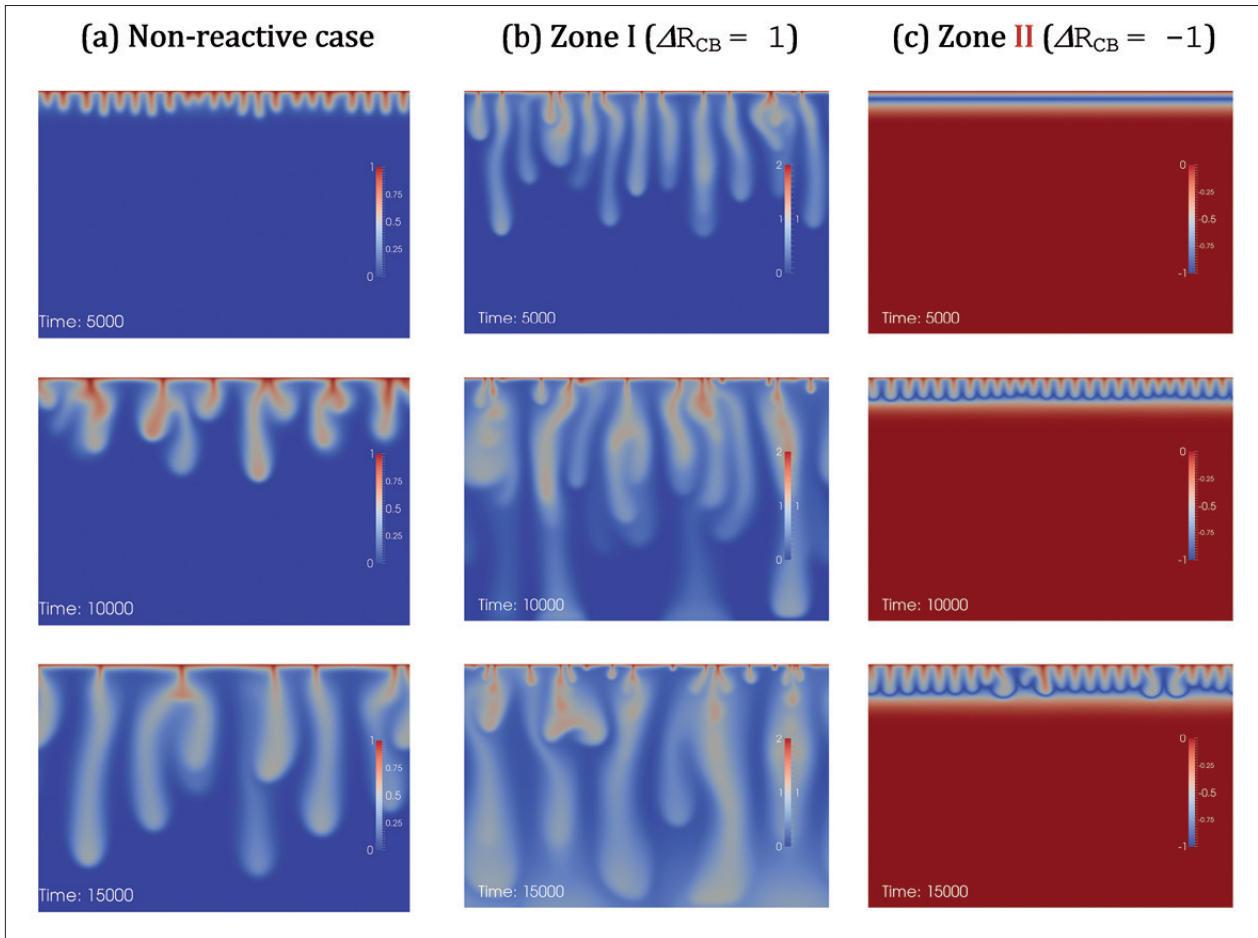


Figure 4: Density field at three successive times (from top to bottom) computed from numerical simulations ($R_A = 1$, $\delta_B = \delta_C = 1$).

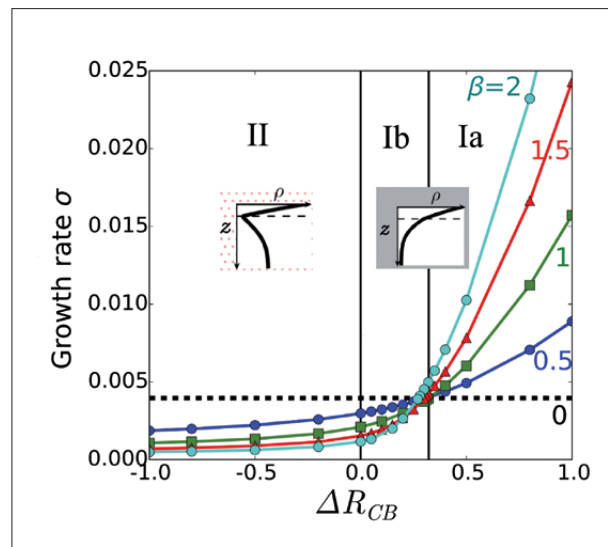


Figure 5: Growth rate σ of the instability as a function of ΔR_{CB} and β with typical RD density profiles as insets. The dashed line corresponds to the non-reactive case. Figure adapted from Loodts *et al.* [10].

profiles, is further subdivided in zones Ib and Ia depending on whether σ is smaller or larger than its non-reactive counterpart. In zone Ib corresponding to small positive values of ΔR_{CB} , reactions slow down the development of convection. We can better understand this stabilizing effect of reactions in zone Ib when $\Delta R_{CB} = 0$: the consumption of B is exactly compensated by the production of C in terms of density, but the species A, which increases the density, is consumed by the chemical reaction. In zone Ia, C is dense enough to more than compensate for the consumption of A, so that convection develops faster than in the non-reactive case. Furthermore, for all values of ΔR_{CB} , increasing the initial concentration β of reactant amplifies the stabilizing or destabilizing effect of reaction. We can thus tune the properties of the dissolution-driven convection either by modifying the nature of the reactant (impacting ΔR_{CB}) or the initial quantity of the reactant (impacting β) [10-12].

5. Experiments on the convective dissolution of CO₂ into aqueous alkaline solutions

To validate those theoretical predictions, we perform experiments in quasi-two-dimensional systems, more specifically vertical Hele-Shaw cells made of two transparent glass plates separated by a small gap. Pure gaseous CO₂ is injected through the top of the cell at atmospheric pressure and flows above aqueous solutions containing various chemicals. Dynamics occurring within the transparent fluids are visualized with the help of a schlieren technique, which tracks dynamical changes in refractive index related to density gradients in the solutions.

We experimentally study the convection developing upon dissolution of gaseous CO₂ into reactive aqueous solutions of CsOH, KOH, NaOH and LiOH of increasing concentration. As shown in Fig.6, we observe that convection arises sooner and develops faster when (1) the concentration of the base is increased in the

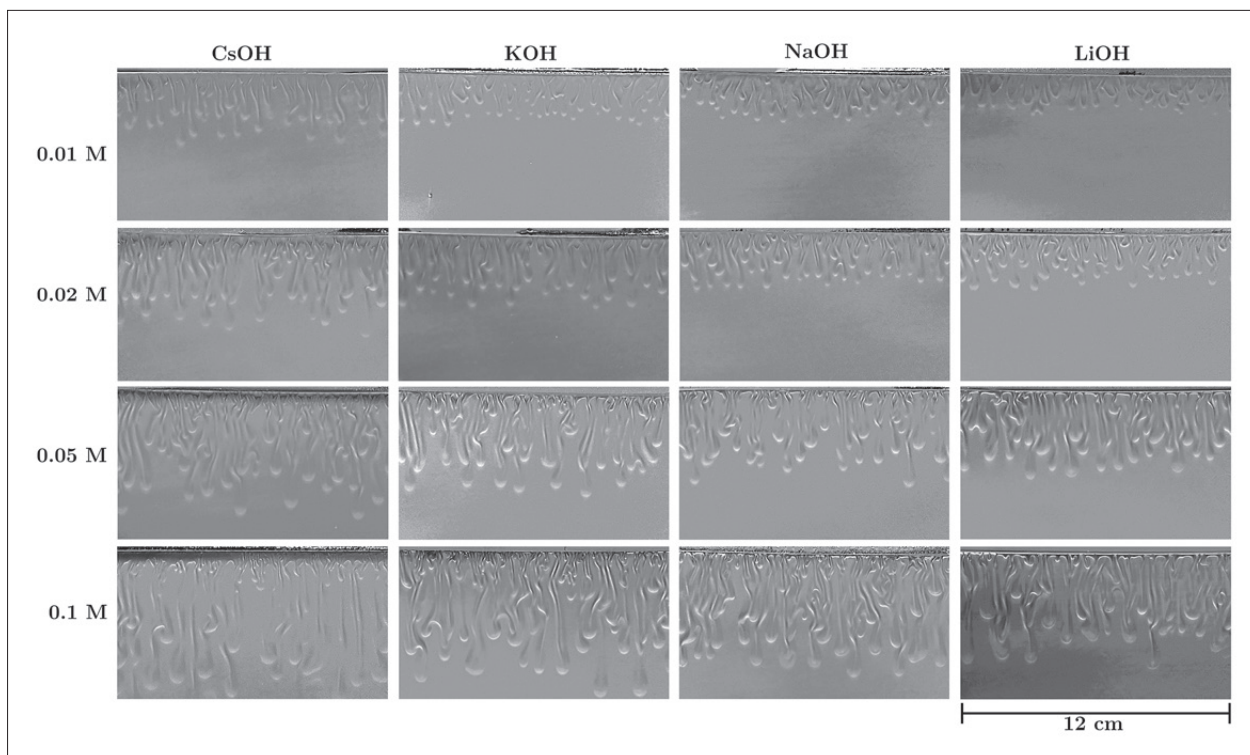


Figure 6: Convective fingering patterns recorded at a time $t = 13$ min when CO₂ dissolves into solutions of CsOH, KOH, NaOH and LiOH in increasing concentrations [13]. The dimensions of the pictures are 12 cm x 7 cm.

aqueous solution; (2) the counter ion of the hydroxide is replaced with an element located further down in the alkali metal column ($\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$). Indeed, the reaction between dissolved CO_2 and the base MOH (with M^+ an alkali metal) modifies the density stratification in the solution and thus the development rate of the dissolution-driven convection [13]. Additionally, changing the counter-ion M^+ of the base also modifies the density profile, through a combination of solutal and differential diffusivity effects. These experimental findings highlight that chemical reactions between CO_2 and a reactant dissolved into the host aqueous phase can accelerate the development of dissolution-driven convection and thus the mixing between both CO_2 and aqueous phases.

7. Conclusion

In conclusion, our work has contributed to a better understanding of the influence of chemical reactions on the development of dissolution-driven convection. Our theoretical classification has shown that reactions can accelerate or slow down the development of convection, depending on the parameters of the problem, in particular the relative contributions to density of the reactants and the product. We have illustrated the case where reactions increase the growth rate of the instability with laboratory experiments on the convective dissolution of gaseous CO_2 into aqueous alkaline solutions of MOH. Our results thus help understand the fundamental physicochemical processes impacting transport in fluids, which are important for various industrial applications, in particular CO_2 sequestration in geological formations. Dissolution-driven convection can improve the safety of the sequestration by transporting dissolved CO_2 faster downwards, further away from faults, fracks and other pathways for a potential escape to the atmosphere. As reactions affect the time scales for the development of convection, it would be possible to control convective dissolution with chemistry, by selecting the most appropriate storage site from a geochemical point of view.

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