Enhanced convective dissolution due to an \( A + B \rightarrow C \) reaction: control of the non-linear dynamics via solutal density contributions

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Chemical reactions can have a significant impact on convective dissolution in partially miscible stratifications in porous media and are able to enhance the asymptotic flux with respect to the non-reactive case. We numerically study such reactive convective dissolution when the dissolving species \( A \) increases the density of the host phase upon dissolution and reacts with a reactant \( B \) present in the host phase to produce \( C \) by an \( A + B \rightarrow C \) reaction. Upon varying the difference \( \Delta R_{CB} = R_C - R_B \) between the Rayleigh numbers of the product \( C \) and the reactant \( B \), we identify four regimes with distinct dynamics when the diffusion coefficients are the same. When \( \Delta R_{CB} < 0 \), the density profiles are non-monotonic and the non-linear dynamics are seen to depend on the relative values of the density at the interface and the initial density of the host phase. For \( \Delta R_{CB} > 0 \), the monotonic density profiles are destabilizing with respect to the non-reactive case above a certain critical value \( \Delta R_C \). We analyze quantitatively the influence of varying \( \Delta R_{CB} \) and the ratio \( \beta = B_0/A_0 \) of the initial concentration of \( B \) and the solubility of \( A \) on the asymptotic steady flux, the wavelength of the fingers and the position of the reaction front. In the context of \( CO_2 \) geological sequestration, understanding how such reactions can enhance the dissolution flux is crucial for improving the efficiency and safety of the process.

1 Introduction

\( CO_2 \) capture and sequestration (CCS) is one of the promising technologies for mitigating greenhouse gas emissions. 1 This technique involves capturing \( CO_2 \) at production sites, transporting it through pipelines and injecting it into geological storage sites such as saline aquifers. Upon injection under a cap rock, a layer of less dense \( CO_2 \) is formed over the brine. When \( CO_2 \) dissolves into this underlying brine, a buoyantly unstable stratification of denser \( CO_2 \)-rich brine lying on top of the less dense resident brine forms. A fingering instability can then develop, creating denser fingers sinking towards the bottom. 2–8 The convective motion facilitates further transfer of \( CO_2 \) to the host phase and increased mixing. This enhances the dissolution flux and leads to faster storage of \( CO_2 \), which is favourable to the sequestration process and instrumental in improving its efficiency and safety.

Recently, chemical reactions have been shown to be able to affect such convective dynamics. 9–13 In particular, it has been demonstrated theoretically 14–23 and experimentally 14,15,20,21,24–26 that \( A + B \rightarrow C \) type of chemical reactions can amplify or slow down convective fingering when all three species are in solution depending on their relative contribution to density. Reactions can therefore not only allow for the storage of larger amounts of \( CO_2 \) during convective dissolution because they consume \( CO_2 \) (reactive effect) but can also accelerate the development of convection (reaction-induced convective effects). 18 The two effects lead to larger dissolution fluxes of \( CO_2 \), which contributes to a faster and safer storage. Therefore understanding the impact of chemical reactions on flow dynamics and how the dissolving fluxes scale with the parameters of the problem, mainly the Rayleigh numbers measuring the contribution of each chemical species to the density, and the ratio of the initial concentration of the reactants, is of tantamount importance.

Following this motivation, we numerically study dissolution-driven convection in partially miscible phases when the dissolving species \( A \) reacts with a solute \( B \) to produce \( C \) via an \( A + B \rightarrow C \) reaction. If all three species contribute to the density of the host solution, it is possible to control the buoyancy-driven instability by selecting the properties of the reactant \( B \) for a given \( A \). In the present study, we focus on the case where the dissolving species \( A \) increases the density of the host solution. We consider equal diffusivities of the species to focus on the solutal effects. Our objective is to numerically quantify the relative contribution of the reactive effect and that of the reaction-induced convective effect on the dissolving flux by varying the difference

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in Rayleigh numbers between the product C and the reactant B i.e. \( \Delta R_{CB} = R_C - R_B \) and the ratio \( \beta = B_0/A_0 \) of the initial concentration of reactant B and solubility of A in the host phase.

It was previously shown that reactions can accelerate or decelerate the convective dynamics with respect to the non-reactive case\(^{14,16} \) and that the asymptotic dissolution flux of species A increases linearly with \( \Delta R_{CB} \) with a change of slope at \( \Delta R_{CB} = 0. \(^{18} \) More precisely, when the product C is denser than the reactant B (\( \Delta R_{CB} > 0 \)), the density profiles are monotonic with an increased density at the interface. If C is sufficiently denser (i.e. \( \Delta R_{CB} \) is larger than a critical value \( \Delta R_{C2} \)), convective dissolution is enhanced with a larger asymptotic flux than the non-reactive flux normalized by the reactive effect and the reaction is said to have a destabilizing effect on convection. Conversely, if reactions slow down convection such that the asymptotic flux is smaller than the normalized non-reactive flux, the reaction is said to be stabilizing. When C is less dense than B (\( \Delta R_{CB} < 0 \)), the density profiles are non-monotonic and the reaction is always stabilizing. However, a further classification of the non-monotonic density profiles based on their morphology is missing. Additionally, several questions still need to be answered: can the stabilizing reaction-induced-convective effect for \( \Delta R_{CB} < 0 \) overcome the reactive effect due to consumption alone? As a consequence, will this reduce the asymptotic flux value lower than that of the non-reactive equivalent or does the reactive asymptotic flux saturate when \( \Delta R_{CB} \approx 0 \)? How does the asymptotic flux scale with very large values of \( \Delta R_{CB} \)? What is the effect of changing \( \beta \) on the asymptotic fluxes? In this paper, we will address all the above questions.

To this end, we vary \( \Delta R_{CB} \in [-6,2] \) and identify four distinct regimes. When the product C is less dense than the reactant B (\( \Delta R_{CB} < 0 \)), the density profiles are non-monotonic and contain a local minimum. This creates a barrier to the development of the fingering instability and stabilizes the convective dynamics in comparison to the non-reactive one. We show here that these non-monotonic density profiles can be further differentiated in a regime IA and a regime IB depending on whether the density at the interface is smaller or larger than the initial density of the host solution. The stabilizing barrier of the non-monotonic profile is strongest in regime IA, which results in the formation of regular fingers that are locally stuck in space at intermediate times before merging and reaching a new steady regime. Nevertheless, the asymptotic flux of this regime IA never drops significantly below the non-reactive one, showing that the main contributor to the flux is the reactive effect occurring due to the consumption of A. Conversely, when the product C is denser than the reactant B (\( \Delta R_{CB} > 0 \)), the monotonic density profiles lead to rapid merging of fingers to reach a steady regime with a larger flux than in the non-reactive case. Beyond a critical \( \Delta R_{CB} \), in regime III, the reaction-induced convective effect is destabilizing in comparison to the non-reactive case. It is then possible to achieve an order of magnitude increase in the asymptotic fluxes compared to the non-reactive case and effectively increase the storage rate by increasing the difference \( \Delta R_{CB} \) between the density of the product C and the reactant B and by increasing the initial concentration of the reactant B.

The article is organized as follows. In Section 2 we define the model and the numerical methods used. We classify the various regimes in Section 3 based on the convective dynamics, the temporal evolution of the dissolution flux and the wavelength of the fingers. We further distinguish the regimes with non-monotonic density profiles based on the evolution of the flux, wavelength and position of the reaction front. Next, we analyze the dissolution flux, the relevant time scales including the onset time when the instability begins to grow, the fingering pattern and the storage capacity for the various parameters considered in Section 4. Finally, the main findings and highlights of our work are presented in Section 5.

2 Problem formulation

We consider a homogeneous, isotropic, isothermal porous medium in which two partially miscible aqueous phases are initially separated by a horizontal interface. The gravitational field \( g \) points downwards along the vertical \( z \) axis which is perpendicular to the horizontal \( x' \) axis. The upper phase A dissolves into the lower host phase containing a reactant B with an initial concentration \( B_0 \) to produce the reactant C by a second order A + B \( \rightarrow \) C reaction. All three species contribute to the density stratification. Assuming local chemical equilibrium, the concentration of A at the interface (\( z = 0 \)) remains constant over time, and equal to its finite solubility \( A_0 \) in the host phase. The concentrations of B and C are assumed to be small enough to not affect this solubility. The host phase extends from \( x' = 0 \) to \( x' = L' \) in the horizontal direction and from \( z = 0 \) to \( z = H' \) in the vertical direction.

To obtain the governing equations, the solute concentrations, time, spatial coordinates and velocity are normalized as:

\[
A = A'/A_0, \quad B = B'/B_0, \quad C = C'/A_0, \quad t = t'/t_c, \quad z = z'/l_c, \quad u = u'/u_c, \quad (1a)
\]

where the primes denote dimensional variables. The chemical time scale \( t_c = 1/(q A_0) \) with \( q \) the kinetic constant of the reaction A + B \( \rightarrow \) C, the reaction–diffusion (RD) length scale \( l_c = \sqrt{D_A A_0} = \sqrt{D_A/(q A_0)} \) with \( D_A \) the diffusion coefficient of A and the velocity scale \( u_c = \phi l_c/t_c = \phi \sqrt{D_A q A_0} \) with \( \phi \) the porosity of the medium.

Since all species diffuse at the same rate, the conservation relation

\[
B = \beta - C, \quad (2)
\]

where \( \beta = B_0/A_0 \) is the ratio of the initial concentration \( B_0 \) of the reactant B to the solubility \( A_0 \), allows the number of equations to be reduced. Thus, the reaction–diffusion–convection (RDC) equations for the temporal evolution of the dimensionless solute concentrations are given as

\[
\frac{\partial A}{\partial t} + (u \cdot \nabla) A = \nabla^2 A - A B, \quad (3a)
\]

\[
\frac{\partial C}{\partial t} + (u \cdot \nabla) C = \nabla^2 C + A B. \quad (3b)
\]
Periodic boundary conditions are used at $x = 0$ and $x = L$, no vertical flow and no flux conditions are used for $A$ and $C$ at $z = H$ (bottom boundary) while at $z = 0$ (interface), no vertical flow and no flux condition is used for $C$ along with $A = 1$. We solve the RDC eqn (3) with the initial conditions

$$A(x, z = 0, t = 0) = 1 + \varepsilon \cdot \text{rand}(x); \quad A(x, z > 0, t = 0) = 0,$$

$$C(x, z = 0, t = 0) = 0,$$  

(P4a)

Perturbations shown in eqn (4a) are introduced in the initial concentration of $A$ at the interface in order to trigger the instability. The Rayleigh numbers are linearly dependent on the concentrations of the species $A$, $B$ and $C$. The Rayleigh numbers $R_i$ ($i = A, B, C$) are given as

$$R_i = \frac{\xi_i A_0 g k l_c}{\nu D_A},$$  

where $\xi_i$ is the solutal expansion coefficient of species $i$ and $r = \mu / \nu$ is the kinematic viscosity of the solvent.

The dimensionless equation of state for the density reads

$$\rho = \rho^' - \rho_0 \rho^* - R_0 \beta = R_A + \Delta R_{CB} C,$$  

where $\rho^'$ is the dimensional density of the solution, $\rho_0$ is the density of the solvent, and $\rho^* = \phi_i \mu D_A (g k l_c)$ is the density scale with $k$ the permeability of the porous medium and $\mu$ the viscosity of the fluid. Eqn (5) expresses that density is assumed to be linearly dependent on the concentrations of the species $A$, $B$ and $C$. The Rayleigh numbers $R_i$ ($i = A, B, C$) are given as

$$R_i = \frac{\xi_i A_0 g k l_c}{\nu D_A} = \frac{\xi_i A_0 g k l_c}{\nu D_A} A_0 (6)$$  

where $\xi = \frac{1}{\rho_0} \frac{\partial \rho^'}{\partial C_0}$ is the solutal expansion coefficient of species $i$ and $A_0$, $\nu = \mu / \rho_0$ is the kinematic viscosity of the solvent.

The difference in the contributions to the density of $C$ and $B$ defined as

$$\Delta R_{CB} = R_C - R_B$$  

is the key parameter of the problem.

Eqn (3) and (5) are closed using the Darcy equation for the velocity of an incompressible flow in porous media, given as

$$\nabla p = -u + \rho e_z,$$  

with $\rho$ the dimensionless pressure and $e_z$ the unit vector along the gravity field.

Thus, for equal diffusivities, the problem is completely determined by three parameters only: $R_A$, $\Delta R_{CB}$ and $\beta$. We focus on the unstable density stratification problem with $R_A = 1$ and study the effect of varying $\Delta R_{CB}$ and $\beta$.

To this end, we solve the RDC eqn (3) numerically along with eqn (5) and (8) with the given boundary and initial conditions using the YALES software with the Darcy_SOLVER module. The width of the computational domain is $L = 3072$ and a height $H = 2048$ is used for most of the work unless specified otherwise for some particular destabilizing cases. The dynamics depends on the specific realization of the random noise added to the initial condition in eqn (4a). We therefore average the results over 15 different realizations for a given set of parameters $(R_A, \Delta R_{CB}, \beta)$ to obtain robust results. Further details on the numerics can be found in ref. 18 and 31.

### 3 Classification of regimes

We identify four distinct regimes as shown in Fig. 1 when varying the difference $\Delta R_{CB}$ between the contribution to the density of the product $C$ and the reactant $B$. The characteristic reaction–diffusion (RD) density profiles are plotted for each regime. The regime at the interface is denoted by $\rho_I$ while the initial density of the host phase is denoted by $\rho_b$.

When $\Delta R_{CB} \geq 0$, the density profiles are monotonic with $\rho_I > \rho_b$, similar to the non-reactive equivalent. Above a critical value of $\Delta R_{CB}$ referred to as $\Delta R_{cr}$, which is close to 0.1 for $R_A = 1$, the contribution of $C$ to density is sufficiently large to compensate for the consumption of both $A$ and $B$. The monotonic density stratifications for $\Delta R_{CB} > \Delta R_{cr}$ (classified as regime III) are then destabilizing with respect to the non-reactive case (explained later in this section) while regime II for $0 < \Delta R_{CB} < \Delta R_{cr}$ is stabilizing.

When the product $C$ is less dense than the reactant $B$ ($\Delta R_{CB} < 0$), there exists a local minimum in the density profile due to the formation of $C$ at the reaction front and the density profile is non-monotonic. Although the stabilizing non-monotonic profiles were studied previously, we further differentiate here regimes IA and IB based on the amplitude of the end point values ($\rho_I$, $\rho_b$). In regime IA, the density at the interface $\rho_I$ is smaller than or equal to the initial density of the host solution $\rho_b$ ($\rho_I \leq \rho_b$) while in regime IB, the density at the interface is larger than or equal to the initial density of the host solution ($\rho_I > \rho_b$). At $z = 0$, we have $A = 1$ and $C = \beta$ for equal diffusivities, and hence

$$\rho_I = R_A + \beta \Delta R_{CB},$$  

while far in the bulk, where $A = C = 0$, the initial density of the host solution is

$$\rho_b = 0.$$  

We find that the curve for which $\rho_I = \rho_b$ is given by $\Delta R' = -R_A / \beta$. We will show that depending on whether the density at the

![Fig. 1](image-url)

Classification of the RD density profiles $\rho(x)$ in the $(\beta, \Delta R_{CB})$ space: regimes IA (non-monotonic with $\rho_I \leq \rho_b$), IB (non-monotonic with $\rho_I > \rho_b$), and II (monotonic with $\rho_I > \rho_b$) are stabilizing and regime III (monotonic with $\rho_I > \rho_b$) is destabilizing. $\rho_I$ is the density at the interface and $\rho_b$ is the initial density of the host solution.
interface is larger or not than the initial density of the host solution i.e. whether the system is in regime IA ($\Delta R_{\text{CB}} < -R_A/\beta$) or IB ($0 > \Delta R_{\text{CB}} > -R_A/\beta$), a different nonlinear dynamics can be observed. We now analyze the various regimes successively.

### 3.1 Monotonic regimes ($\Delta R_{\text{CB}} > 0$)

Fig. 2 shows the density fields at different times for the destabilizing regime III ($\Delta R_{\text{CB}} > \Delta R_{\text{cr}}$). After a diffusive transient, the convective instability begins to grow with fingers of a given initial wavelength (Fig. 2a). Thereafter, the fingers merge rapidly reducing in number. At larger times, new fingers known as protoplumes are formed at the interface and join the older ones. Eventually, the fingers reach the bottom of the system. Species A is consumed by the reaction to produce the denser C. The rapid merging and birth of fingers enhances the mixing between the two phases and leads to strong convective mixing in the host phase. The process is very rapid and the system goes to shut-down as soon as the fingers reach the bottom of the solution. In order to compute the asymptotic properties, we carry out the simulations with a larger domain height i.e. $H = 4096$. We note that the evolution of the dynamics is similar to that of the non-reactive case\(^3\) although on a faster time scale.

To quantify the storage rate of species A in the host solution, we compute the dissolution flux $J$ as

$$J = -\frac{1}{L} \int_0^L \frac{\partial A}{\partial z} \, dz,$$

while the power-averaged mean wavelength $\bar{\lambda}$ is computed as

$$\bar{\lambda} = \left( \frac{\int_{-L/2}^{L/2} N |\mathcal{F}(\tilde{\rho})|^2 dN}{\int_{-L/2}^{L/2} |\mathcal{F}(\tilde{\rho})|^2 dN} \right)^{-1},$$

where $N = 1/\bar{\lambda}$ is the inverse of the wavelength and $\mathcal{F}(\tilde{\rho})$ is the Fourier transform of the vertically-averaged density profile $\rho(x,z) = \frac{1}{2H} \int_0^H \rho(x,z,t) \, dz$.

The spatio-temporal dynamics for this case can be visualized in Fig. 3 in terms of the space–time plot of the density computed at location $z = 64$ below the interface along with the temporal evolution of the corresponding flux $J$ and the mean wavelength $\bar{\lambda}$. The rapid growth of the fingering instability and merging or birth of fingers can be seen in the space–time plot. The evolution of $J$ suggests that the flux deviates rapidly away from the diffusive curve as the instability grows and features two peaks before reaching an asymptotic value $J_{\text{RDC}*}$. The asymptotic fluxes $J_{\text{RDC}*}$ are larger than the non-reactive one $J_{\text{NR}*}$. The two main contributions to the dissolution fluxes are the reactive effect due to consumption of A and the reaction-induced convective effect when convection is enhanced by the reaction. The reactive effect can be measured by the quantity $(1 + \beta)$ corresponding to $J_{\text{RDC}}/J_{\text{RD}}$, the ratio between the reactive-diffusive flux and the diffusive one. We wish to quantify the contribution of the reaction-induced convective effect by comparing $J_{\text{RDC}*}$ to the non-reactive case coupled with the reactive effect $(1 + \beta)J_{\text{NR}*}$, referred to as the scaled non-reactive case for the sake of simplicity. We find that above a certain critical $\Delta R_{\text{CB}}$, which is independent of $\beta$ and close to 0.1 for $R_A = 1$, the convective effect is destabilizing in regime III with respect to the scaled non-reactive case i.e. leads to a larger asymptotic flux ($J_{\text{RDC}*} > (1 + \beta)J_{\text{NR}*}$). This confirms the findings of previous linear stability analyses\(^4,6\) and numerical studies.\(^8\) In regime II, the convective effect is relatively weak and the dissolution flux increase is mainly due to the reactive effect. For example, we compare the evolution of $J$ for regimes II ($\Delta R_{\text{CB}} = 0.1$) and III ($\Delta R_{\text{CB}} = 1.5$) in Fig. 3. Regimes II and III are qualitatively similar to all other aspects. Lastly, we see that the mean wavelength grows with time up to the shut-down limit. Large fluctuations in the values of $\bar{\lambda}$ may be attributed to the strong convective mixing and formation of protoplumes.

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Fig. 2  Destabilizing regime III: density field at different dimensionless times $t$ for $\Delta R_{\text{CB}} = 1.5$, $\beta = 1$ and $R_A = 1$ for height $H = 4096$. The scale varies between 0 (blue) and 2.5 (red).
Characteristics of the regime III shown in Fig. 2. Top: Space–time plot of density for $\Delta R_{CB} = 1.5$ at $z = 64$ below the interface showing the onset of the instability at early times and rapid merging and birth of new fingers thereafter. Middle: Temporal evolution of the flux $J$ showing the diffusive flux $J_0 = 1/\sqrt{\pi t}$, the reactive–diffusive flux $J_{RD} = (1 + \beta)/\sqrt{\pi t}$, the non-reactive flux $J_{ur}$, the scaled non-reactive flux $(1 + \beta)J_{ur}$ and the reaction–diffusion–convection flux $J_{RDC}$ for $\Delta R_{CB} = 0.1$ (green, regime II) and 1.5 (blue, regime III). In regime III, $J_{RDC}$ is significantly larger than $(1 + \beta)J_{ur}$ and increases with $\Delta R_{CB}$. Bottom: Temporal evolution of the power-averaged mean wavelength $\lambda$ for $\Delta R_{CB} = 1.5$.

3.2 Non-monotonic regimes ($\Delta R_{CB} < 0$)

Fig. 4 shows the density field at different times for regime IA for which the density profile is non-monotonic with $\rho_I < \rho_B$. The fingers formed at the interface experience therefore a strong stabilizing barrier extending from the minimum in the density downwards. The convective dynamics in this regime is typically very slow. Once the instability begins to grow the regular fingers move away from the interface and are locally ‘stuck’ due to the barrier created by the larger density in the lower bulk (Fig. 4a–c). The initial number of fingers is 24 which corresponds to a wavelength $\sim 128$. Beyond a certain time, referred to as the merging time $t_{merg}$, the fingers merge to give rise to a new increased wavelength stabilized by the density barrier (Fig. 4e and f). For this particular case with $\Delta R_{CB} = -2$, $t_{merg}$ is equal to 38 600. The number of fingers after merging is equal to 8, which corresponds to a wavelength of $\sim 384$. This merging with different constant wavelengths before and after merging is characteristic of regime IA. To illustrate this behaviour we show the spatio-temporal dynamics in Fig. 5. The space–time plot of density shows the formation of regular fingers that remain undisturbed until $t_{merg}$ after which they merge to reach a new steady regime. Initially, the flux $J$ follows the diffusive one $J_{RD}$. Following the onset of the instability where the regular fingers are formed, a peak in the value of $J$ is observed. Thereafter, the flux scales as $J \sim t^{-1/2}$ at intermediate times where the locally ‘stuck’ fingers are observed. After $t_{merg}$, a second step increase in $J$ is seen, followed by the steady flux $J_{RDC}$. Meanwhile, after the onset of the instability, a constant value of the power-averaged mean wavelength $\lambda$ is observed until $t_{merg}$ where a step increase occurs leading to a new larger value.

In regime IA with $\rho_I \leq \rho_B$, the regular fingers formed are locally ‘stuck’ due to the stabilizing barrier created by the local minimum in the density profiles. This constrains the wavelength of the fingers formed and decreasing $\Delta R_{CB}$ further increases the amplitude of the local minimum and hence the strength of the barrier. This implies that the regular locally ‘stuck’ fingers exist for longer transients before merging.

Fig. 6 shows the density fields at different times for regime IB, for which the density profile is still monotonic but $\rho_I > \rho_B$. Characteristics of regime IA including merging of fingers at $t_{merg}$ and a constant number of fingers before and after merging are seen here too. However, because here $\rho_I > \rho_B$, the stabilizing barrier is not strong enough to block the convective dissolution strength at the interface. The dynamics are then typically faster than in regime IA and transitions between regimes are smoother. For $\Delta R_{CB} = -0.5$, the number of fingers before merging is equal to 30 (Fig. 6a and b) which is larger than in regime IA. The equivalent wavelength is $\sim 102$. The merging occurs at much shorter times compared to regime IA and is much less abrupt. The uniform number of fingers after merging is equal to 12 for this case (Fig. 6f) with equivalent wavelength $\sim 256$. The number of fingers formed...
1. After merging increases with $\Delta R_{CB}$, whereas, in regime IA, it is similar for all values of $\Delta R_{CB}$ as will be detailed below. Fig. 7 shows the space–time plot of density, $\lambda$ and $J$ for regime IB. The first peak in $\lambda$ close to the onset of the instability and the second step increase close to merging of fingers are seen here at shorter time scales compared to regime IA. Merging occurs less abruptly than in regime IA as can also be seen in the temporal evolution of $\lambda$.

2. Comparison between regimes IA and IB

To further quantify the difference between the dynamics in regimes IA and IB, we compare the temporal evolution of the position of the reaction zone $z_f$, $\lambda$ and $J$ in Fig. 8 for various $\Delta R_{CB} < 0$.

We define the horizontally-averaged reaction rate profile $\tilde{r}(z)$ as

$$\tilde{r}(z, t) = \frac{1}{L} \int_0^L A(x, z, t)B(x, z, t)dx,$$

and next compute the position of the reaction front as the first moment of $\tilde{r}(z, t)$ i.e.

$$z_f(t) = \frac{\int_0^H z\tilde{r}(z, t)dz}{\int_0^H \tilde{r}(z, t)dz}. \quad (14)$$

Initially, in the diffusive regime, the reaction front moves away from the interface as $z_f \sim \sqrt{t}$. After the onset of convection, at the intermediate times where regular fingers are observed, there exists a slight jump in the values of $z_f$ and thereafter it scales once again as $z_f \sim \sqrt{t}$ up to the merging time $t_{merg}$. In Fig. 8(a), $t_{merg}$ computed as the time at which $\lambda$ experiences an inflection point, is denoted by the vertical dashed lines in the respective colours for the different $\Delta R_{CB}$. After the regular fingers merge to increase the wavelength to another larger steady value, the reaction zone scales as $z_f \sim t$.

However, in regime IB for $\Delta R_{CB} > -0.8$, such an intermediate scaling of $z_f \sim \sqrt{t}$ is not observed and beyond the initial diffusive behaviour, the $z_f \sim \sqrt{t}$ scaling is seen, as illustrated for $\Delta R_{CB} = -0.2$ and $-0.5$. It is to be noted that regime IB acts as a transition between regimes IA and II. More precisely, close to $\Delta R'$ in regime IB, characteristics similar to regime IA with intermediate fingers locally ‘stuck’ in space and merging to reach a new steady regime are observed. However, closer to $\Delta R_{CB} = 0$, for example for $\Delta R_{CB} = -0.2$ and $-0.5$ the fingers overcome the barrier created by the minimum in the density profile and in the steady regime the fingers are very irregular, similar to that seen for the monotonic density profiles in regimes II and III.

After the departure from the diffusive regime, when the instability grows, a peak in the values of $\lambda$ is observed (see Fig. 8(b)); thereafter $\lambda$ remains steady for intermediate times up to $t_{merg}$. After $t_{merg}$ a step change in the wavelength to a higher constant value is observed for regimes IA. The values of $\lambda$ reached

![Fig. 5](image1.png) Characteristics of regime IA shown in Fig. 4. Top: Space–time plot of density showing the formation of regular fingers after the onset of the instability that remain locally stuck up to $t_{merg} \sim 40,000$ and merge afterwards to reach a new steady regime. Middle: Temporal evolution of the reactive flux $J_{RD}$ (in blue) showing that initially the flux follows $J_{RD} = (1 + \beta)/\sqrt{\alpha}$, followed by an increase close to the onset of the instability, a scaling $J \sim 1/\sqrt{t}$ at intermediate times up to a second step at $t_{merg}$ to reach a steady value. Bottom: Power-averaged mean wavelength $\lambda$ showing the intermediate uniform wavelength that increases after $t_{merg}.$

![Fig. 6](image2.png) Stabilizing regime IB: density field at different dimensionless times $t$ for $\Delta R_{CB} = -0.5, \beta = 1$ and $R_A = 1$. The scale varies between $-0.5$ (blue) and 0.5 (red).
at asymptotic times is the same for all $\Delta R_{CB} < -R_A/\beta$ in regime IA. In contrast, in regime IB, a gradual increase from the initial wavelength to an asymptotic one is seen occurring at shorter times and the asymptotic value of $\lambda$ is different for the different $\Delta R_{CB}$.

Simultaneously, the transient flux scales as $t^{-1/2}$ initially in the diffusive regime before it experiences a first peak when the instability begins to grow (see Fig. 8(c)). Thereafter in regime IA, the second step increase corresponds to the merging of the fingers at $t_{\text{merg}}$ after which a steady regime is reached. This time increases with a decrease in $\Delta R_{CB}$. In regime IB, the occurrence of the second step increase is almost immediate after the first one and followed by a steady regime at relatively short times. Thus, the dynamics of the two regimes are distinct and dictated by the morphology of the density profiles.

To summarize this section, we have characterized the distinct convective dynamics of regimes IA, IB, II and III. Non-monotonic density profiles in regime IA with $\rho_I \leq \rho_b$ are the most stabilizing ones with typically slow dynamics, merging of fingers with uniform wavelength before and after merging, and characteristically ‘stuck’ fingers. Non-monotonic density profiles with $\rho_I > \rho_b$ in regime IB are less stabilizing compared to IA and reach a steady regime sooner with a wavelength after merging that depends on $\Delta R_{CB}$. Regime II is faster than IA and IB but the asymptotic flux values are lower than $(1 + \beta)J_{NR}^*$ as the product $C$ and reactant $B$ are almost equally dense. Beyond $\Delta R_{C_b} \approx 0.1$ for $R_A = 1$ in regime III, the convective dynamics is very fast and destabilizing with an asymptotic flux larger than $(1 + \beta)J_{NR}^*$.

### 4 Parametric study

In this section we first recall the effect of increasing $\Delta R_{CB}$ on the dissolution flux for $\beta = 1$ and next, we analyze the effect of varying $\beta$.

Fig. 9 shows the temporal evolution of the dissolution flux $J$ in the different regimes for $\Delta R_{CB} \in [-2,1.5]$ with $\beta = 1$. As mentioned in Section 3, the dissolution flux $J$ asymptotically fluctuates around an asymptotic value, referred to as $J^*$. The flux for the non-reactive case is denoted $J_{NR}$ here along with the scaled non-reactive $(1 + \beta)J_{NR}$ fluxes are denoted by black solid and dotted lines, respectively.
non-reactive case. The asymptotic flux $J^*$ can be increased by increasing $\Delta R_{CB}$ from regime IA to III. More precisely, the storage can be faster when the product C is denser than the reactant B. We note however that below $\Delta R_{CB} \approx 0.1$, in regimes IA, IB and II the $J^*$ values are lower than the non-reactive case scaled by the reactive effect alone $(1 + \beta) J_0^*$.

In these regimes, the increase of the dissolution flux is mainly due to the reactive effect occurring due to the consumption of A by $/C_0$ with $\text{erf}$ its minimum before it begins to grow as in the non-reactive case on the basis of the magnitude of velocity computed as $J$. We define $t$ averaged mean wavelength $\lambda_m$ experiences an inflection point. However, after some time, non-linearities become significantly large and the dynamics differ from a diffusive one. We define $t_{NL}$ as the time when the relative difference between the averaged mixing length $z_m$ (defined as the most advanced position along z where $A + C > s$, with s being a small arbitrary threshold chosen here to be 0.01) and its diffusive prediction $z_m^{RD}$ is greater than 5%. Here $z_m^{RD}(t) = 2\sqrt{t} \text{erf}^{-1}(1 - s/(1 + \beta))$ with $\text{erf}^{-1}$ being the inverse error function. We recall that the merging time $t_{merg}$ for regimes IA and IB, defined as the time when the regular locally ‘stuck’ fingers merge to reach a new steady regime, is computed as the time at which the power-averaged mean wavelength $\lambda$ experiences an inflection point.

Fig. 10 shows the different relevant times $t_0$, $t_{NL}$ and $t_{merg}$ (for regimes IA and IB) for different $\beta$ and $\Delta R_{CB}$. For $\Delta R_{CB} \leq 0$, all characteristic times increase with a decrease in $\Delta R_{CB}$ for a given $\beta$ and this effect increases with $\beta$. To explain this behaviour, we recall that in these regimes the non-monotonic density profiles contain a local minimum which acts like a stabilizing barrier to the convective dynamics. For $\Delta R_{CB} < 0$, as $|\Delta R_{CB}|$ increases, the amplitude of the local minimum increases in magnitude and the stabilizing barrier becomes stronger. Thus, decreasing $\Delta R_{CB}$ below 0 implies a longer transient before the onset of convection, its non-linear breakdown and merging to reach a steady regime. Increasing $\beta$ leads to an even larger stabilizing barrier created by the increased magnitude of the local minimum in the density profiles. Additionally, this barrier fixes the wavelength of the fingers formed as observed in the formation of regular intermediate locally ‘stuck’ fingers. In contrast, if $\Delta R_{CB} > 0$, the various times become substantially smaller with an increase in $\Delta R_{CB}$ for a given $\beta$ and this effect increases with $\beta$. A cross-over in the values of $t_{NL}$ and $t_0$ is observed close to $\Delta R_{cr} \approx 0.1$. This confirms the stabilizing effect of regimes IA, IB and II and the destabilizing effect of regime III.

To understand the fingering pattern, we also analyze the number of fingers soon after the onset of the instability $t \geq t_0$ and after merging $t \geq t_{merg}$ for regimes IA and IB. This is shown in Fig. 11 for different $\beta$ and $\Delta R_{CB}$ (for one realization). In regime IA, the number of fingers is more or less constant irrespective of the value of $\beta$ and $\Delta R_{CB} < \Delta R^*$. This is due to the fact that the density barrier created by the local minimum blocks the development of the convective instability. Any decrease in the value of $\Delta R_{CB}$ only increases the strength of the stabilizing barrier but does not change the difference between the density at the interface $\rho_I$ and the density in the minimum equal to $\beta \Delta R_{CB}$ (eqn (5) with $A = 0$ and $C = \beta$). There exists a slight difference in the formation of fingers in regime IB where an increase in $\Delta R_{CB}$ leads to an increase in the number of fingers formed after $t_0$ and after $t_{merg}$. When $\Delta R_{CB} > 0$, the number of fingers formed at the onset of the convective instability $t_0$ increases with $\Delta R_{CB}$ in regimes II and III. Thus, an increase in $\Delta R_{CB}$ has a destabilizing effect.
Finally, we quantify in Fig. 12 the long-time fate of A or the asymptotic dissolution flux $J^\ast$ as a function of $\Delta R_{CB}$ for different $\beta$ indicated with different colours for $R_A = 1$. The corresponding asymptotic flux for the NR case $J_{NR}^\ast$ is denoted by the horizontal black dashed-dotted line and that for the scaled NR $(1 + \beta)J_{NR}^\ast$ is denoted by horizontal dotted lines for each $\beta$ in the respective colours. Transition from regime IA to regime IB at $\Delta R_{CB} = -R_A/\beta$ is indicated by the solid black rectangles for the different $\beta$ in the inset. The vertical black dashed line $\Delta R_{CB} \sim 0.1$ corresponds to the transition from II to III.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig12.png}
\caption{Asymptotic dissolution flux $J^\ast$ as a function of $\Delta R_{CB}$ for different $\beta$ indicated with different colours for $R_A = 1$. The "corresponding" asymptotic flux for the NR case $J_{NR}^\ast$ is denoted by the horizontal black dashed-dotted line and that for the scaled NR $(1 + \beta)J_{NR}^\ast$ is denoted by horizontal dotted lines for each $\beta$ in the respective colours. Transition from regime IA to regime IB at $\Delta R_{CB} = -R_A/\beta$ is indicated by the solid black rectangles for the different $\beta$ in the inset. The vertical black dashed line $\Delta R_{CB} \sim 0.1$ corresponds to the transition from II to III.}
\end{figure}

$\Delta R_{CB} < \Delta R^\prime$, any further decrease in $\Delta R_{CB}$ has a negligible effect on the convective dynamics and $J^\ast$ gets saturated with $\Delta R_{CB} \ll 0$. This can be explained as follows. For equal diffusivities of all three species assumed here, we recall that the density at the interface is $\rho_I = \rho_A + \Delta R_{CB} \rho_B$, the density at the reaction front is $\Delta R_{CB}$ while the initial density of the host solution is 0. For $\Delta R_{CB} < 0$ in regimes IA and IB, the RD density profiles contain a local minimum in the host solution. The difference of density at the origin of the instability is given by the difference in density between the interface and at the minimum i.e. at the reaction front; and is equal to $R_A$. Changing the values of $\Delta R_{CB}$ or $\beta$ does not alter this difference but increases the amplitude of the stabilizing barrier, i.e. the difference of density $-\Delta R_{CB} \beta$ between the minimum and the bulk of the solution. This explains that any decrease in the values of $\Delta R_{CB}$ or $\beta$ has a very mild effect on $J^\ast$ in regimes IA and IB.

To summarize, the dissolution fluxes and their asymptotic values show that the convective effects in regimes IA, IB and II are stabilizing with respect to the non-reactive case whereas this effect is destabilizing in regime III. When C is denser than B, the asymptotic flux increases with $\beta$ and conversely, when C is less dense than B, $J^\ast$ decreases slightly with an increase in $\beta$. However, when $\Delta R_{CB} \ll 0$ the asymptotic flux saturates to a constant value which never significantly drops below the non-reactive one $J_{NR}^\ast$.

\section{5 Conclusions}

We have numerically studied the non-linear convective dynamics developing when a solute A dissolves with a finite solubility $A_0$ into a host solution containing B to produce C by an A + B $\rightarrow$ C type of reaction. In particular, we have studied the influence of varying (i) $\Delta R_{CB}$, the difference in the contribution to density of the product C and reactant B, up to relatively extreme values and (ii) the ratio $\beta = B_0/A_0$ on the properties of convective dissolution. We have focused here on the case where the dissolving species A increases the density of the host solution ($R_A > 0$), i.e. when the non-reactive density stratification is buoyantly unstable and all species diffuse equally. While in the non-reactive case only one type of density profile can develop, two types of density profiles are possible in the reactive case: a monotonic one similar to the non-reactive case for $\Delta R_{CB} > 0$ and a non-monotonic one for $\Delta R_{CB} < 0$. We have shown here that the non-monotonic profiles can be further classified into two different regimes depending on the difference between the density at the interface and the initial density of the host solution.

We identify four regimes with distinct dynamics upon increasing $\Delta R_{CB}$. Regime IA obtained for $\Delta R_{CB} \leq \Delta R^\prime = -R_A/\beta$ features non-monotonic density profiles where the density at the interface is smaller than or equal to the initial density in the host solution, $\rho_I \leq \rho_B$. Dynamics in regime IA are characterized by regular fingers formed after the onset of instability that remain ‘stuck’ locally in space due to the large stabilizing barrier created by the local minimum in the density...
profile. Beyond a certain time, referred to as merging time or $t_{\text{merg}}$, the fingers merge to reach a new steady regime in which the wavelength of fingers is larger than at short times but constant as well. In this frozen regime, the steady flux is of the order of the one in the non-reactive case. Regime IB ($\Delta R' < \Delta R_{\text{CB}} < 0$) corresponds to non-monotonic density profiles where the density at the interface is larger than the initial density in the host solution, $\rho_I > \rho_0$. Similar to regime IA, the formation of regular fingers and their merging to reach a steady regime is also observed in regime IB, with a few distinct features. The density barrier created by the local minimum in the profiles is relatively weaker than in regime IA. As a consequence, the regular fingers formed after the onset of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$). As a consequence, the regular fingers formed after the onset of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster of the instability merge ($t_{\text{merg}}$) at earlier times. Moreover, the number of fingers after merging is larger than in regime IA and this number increases with $\Delta R_{\text{CB}}$. Regimes II and III with monotonic density profiles and dynamics similar but faster.