

Supporting Information for "Flow-driven Control of Calcium Carbonate Precipitation Patterns in a Confined Geometry"

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S1: Properties of Reactant Solutions

Table 1: Molar concentration c , density ρ , and dynamic viscosity μ of reactant solutions.

Chemicals	c (mol/L)	ρ (g/mL)	μ (mPa s)
CaCl ₂	0.5	1.043	1.18
	1.5	1.128	1.61
	4.5	1.360	5.99
Na ₂ CO ₃	0.25	1.023	1.19
	0.75	1.072	1.48
	1.5	1.141	2.13

S2: Reproducibility of the Patterns

Each experiment with given initial conditions, *i.e.* reactant concentration and flow rate, are performed three times. The error bars in Figs. 4-10 of the main text are generally small and show that the reproducibility of the patterns is quite robust. In Fig. 1, we show images of the patterns obtained in three different experiments for some given initial conditions.

S3: Ion Activity Product and Solubility Product

Considering the precipitation of CaCO₃, its solubility product $K_{SP} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 3.3 \times 10^{-9}$ where the square brackets mean equilibrium concentrations. However, when the reactants are put into contact, the system is far from equilibrium and highly non-ideal, thus concentrations have to be replaced by activities. The ion activity product at the initial step of reaction can be written as $\text{IAP}_0 = \{\text{Ca}^{2+}\}\{\text{CO}_3^{2-}\}$, where the curly brackets

mean the actual activity (activity coefficients taken from Ref.^{2,3}).

S4: Image Analysis

As a first step, a background image containing no precipitate is recorded before the experiment starts. This background image is characterized by a gray scale intensity distribution, $I_{\text{back}}(x, y)$, and its minimum, I_{min} , and maximum, I_{max} , values where x and y are the spatial coordinates. Next, we measure the gray scale value, $I(x, y, t)$, of the images of dynamics and compute a normalized intensity $I_n \in [0, 1]$ as $I_n(x, y) = [I(x, y) - I_{\text{back}}(x, y)] / [I_{\text{max}} - I_{\text{min}}]$. Finally, $I_n(x, y)$ is set to 0 if it is smaller than some threshold, I_{th} . This threshold fixes the smallest intensity below which we cannot determine with certainty the presence of a precipitate. An example of the spatial distribution of $I_n(x, y, t)$ is shown in Fig.2(a). The radius R_{max} is computed as the largest radial distance between the injection point and the pattern perimeter (Fig.2(a)). For each image, we also compute: (i) The area A covered by the pattern (Fig.2(b)) *i.e.* the area of the zone in which pixels have $I_n > I_{\text{th}}$; (ii) The area A_p of the zone inside the perimeter of the pattern (Fig.2(c)). On the basis of the normalized intensity I_n , the radius R_{max} and the two given areas, we then define five quantities to classify the patterns and measure their properties in the sense of precipitation efficiency.

1. The first, extensive quantity we measure is the total gray scale intensity I_{tot} of the white CaCO₃ in a given image, defined as $I_{\text{tot}}(t) = \int I_n(x, y, t) dx dy \in [0, A]$ where $0 < A < N$ ($N = 1280 \times 1024$ pixels image

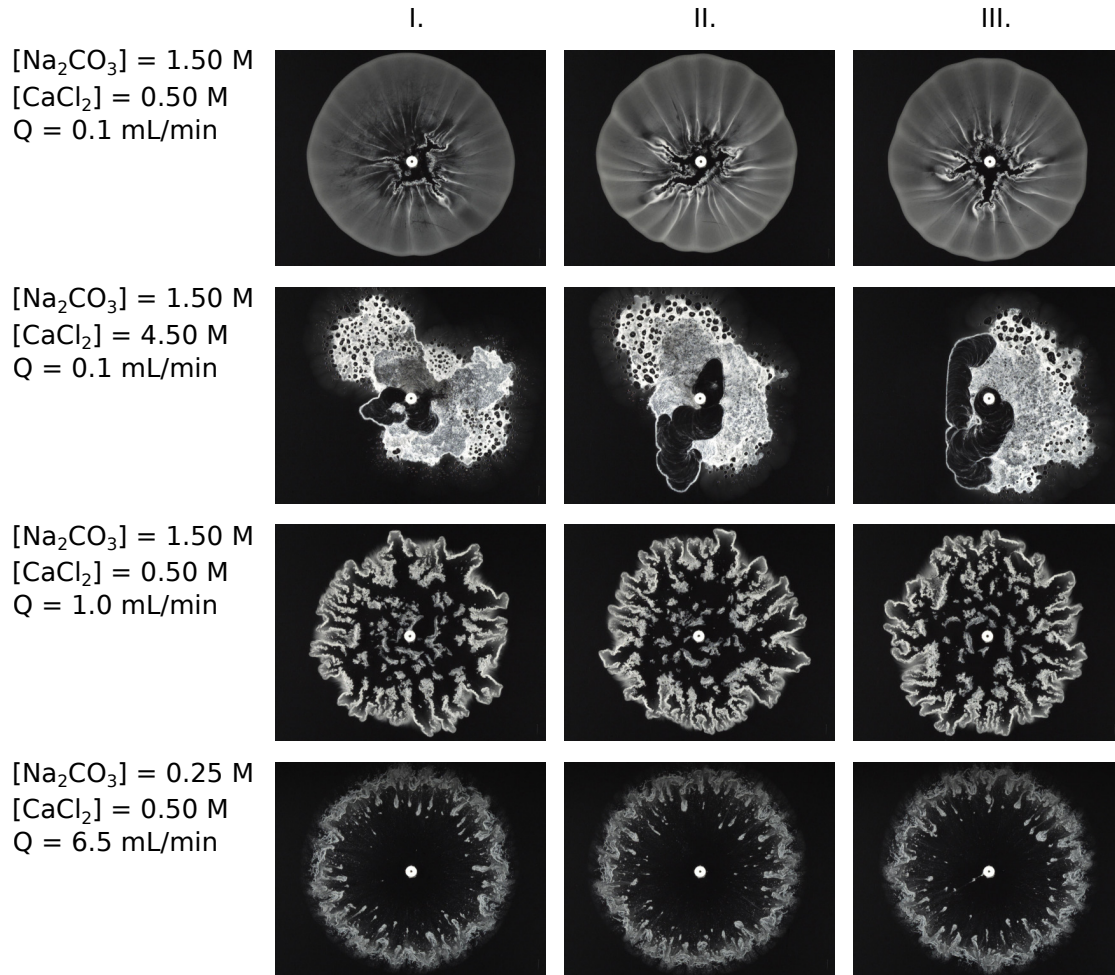


Figure 1: Precipitation patterns obtained after the injection of 2.5 mL of sodium carbonate solution in three different experiments (I, II and III) performed at some given initial conditions. Field of view: $123 \text{ mm} \times 98 \text{ mm}$.

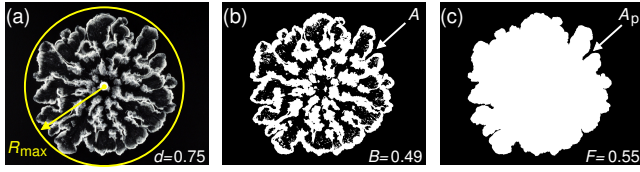


Figure 2: Quantities used to characterize the patterns. (a) gray scale intensity $I(x, y)$ used to compute I_{tot} and d . The yellow circle centered on the inlet and passing by the tip of the longest finger defines the radius R_{max} . (b) The area A of the region covered by the solid phase is used to compute $B = I_{\text{tot}}/A$. (c) The area A_p inside the pattern perimeter is used to compute $F = A/A_p$.

resolution). Even though a given I_{tot} might correspond to various precipitate thickness within the cell gap, I_{tot} is nevertheless a qualitative indicator of the amount of precipitate in the cell thanks to its white color.

2. Not only the total amount of precipitate but also its spatial distribution are important. In this context, the brightness B of a precipitate layer, is the second intensive quantity used to characterize the patterns. The brightness is defined as $B = I_{\text{tot}}/A$, normalizing the total gray scale intensity I_{tot} of precipitate by the area A it is covering (Fig.2(b)). B varies between 0 and 1 with values close to 1 indicating a more compact, brighter precipitate.
3. Precipitation fingering can lead to more or less hollow patterns where the reactants are separated by the evolving precipitate walls, as seen in Fig.2(a). Since this separation decreases the amount of precipitate, the third intensive quantity is the filling of the pattern, $F = A/A_p \in [0, 1]$. It divides the area A covered by the pattern by the area A_p enclosed by its perimeter (Fig.2(b) and (c)). F is equal to 1 when the precipitate fills the whole surface inside its perimeter and is smaller than 1 if this region contains some (black) areas without precipitate. A case for which $F \ll 1$ indicates a hollow precipitate structure.
4. In the case, when precipitation-driven hydrodynamic fingering is strong enough, elongated shapes can evolve which strongly differ from a simple radial spreading. On this basis, the fourth intensive quantity is the pattern density, $d = A_p/(\pi R_{\text{max}}^2) \in [0, 1]$, com-

paring the area A_p of the pattern to the area of the circle of radius R_{max} , as depicted in Fig.2(a) and (c)^{4,5}. It measures deviations from a symmetric radial growth (for which $d = 1$). Low values of d indicate that precipitation occurs in some preferred directions.

5. The last, intensive quantity is the production efficiency, $P = I_{\text{tot}}/c_{0,\text{CO}_3^{2-}}$, dividing the total intensity I_{tot} by the initial molar concentration of the injected solution $c_{0,\text{CO}_3^{2-}}$. P measures how much precipitate is produced on the basis of a given amount of injected reactant. Its evolution is a good marker to see, whether the faster the injection the shorter the time to produce the same amount of precipitate for given reactant concentrations.

References

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