

Supporting Information for: Impact of Mixing-Driven Calcite Precipitation on Solute Transport Dynamics: Insights from Laboratory Visualization and Tracer tests Analysis

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1. Extended Materials and Methods

1.1. Figure S1: View of the Experimental Setup in the Laboratory

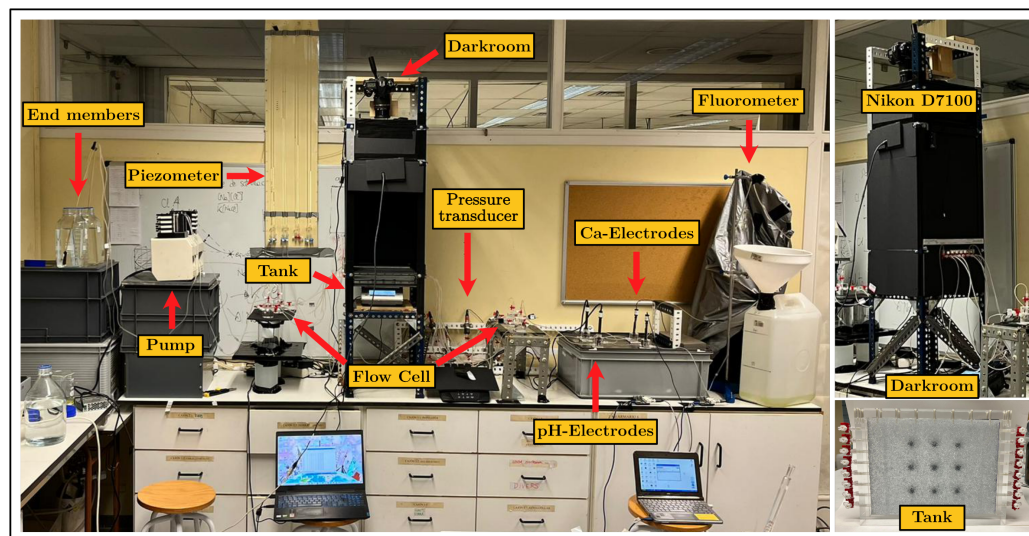


Figure S1. View of the experimental setup in the laboratory. On the left: end-members container solutions, peristaltic pumps, piezometers, synthetic aquifer, flow cells, pressure transducers, darkroom, Ca^{2+} -electrodes, pH-electrodes and fluorometer. On the right: frontal view of the darkroom used for photograph acquisition and the methacrylate tank (synthetic aquifer) filled with glass beads and saturated with deionized water.

1.2. Table S1: Initial Experimental Conditions

Symbol	Property	Value	Unit
Pe	Péclet number	523	–
Q	Total flow rate	1.78×10^{-7}	m^3/s
D	Molecular diffusion (*)	1×10^{-9}	m^2/s
d	Glass beads diameter	2×10^{-3}	m
v	Velocity	2.62×10^{-4}	m/s
ϕ_0	Porosity	0.34	–
A	Cross section	2×10^{-3}	m^2
Δh	Head difference	0.014	m
L	Tank length	0.265	m
i	Hydraulic gradient	5.283×10^{-2}	–
K_0	Initial hydraulic cond.	145.4	m/d

Table S1. Initial Experimental Conditions

Note^a: Information obtained from Perkins and Johnston [1] (*).

1.3. Table S2: Time Span Covered for Each Stage of the Experiment

Stage	Duration (min)	From P_v	To P_v
Deionized water	20	0	1
Tracer test 1 (T_1)	100	1	5.7
MDP	120	5.7	11.4
Equilibrium solution	60	11.4	14.24
Tracer test 2 (T_2)	120	14.24	19
Dissolution (HCL)	210	19	30

Table S2. Time span covered for each stage of the experiment. P_v stands for time expressed as pore volume.

1.4. Text S1: Mixing Ratio (α) with Wexler's Analytical Solution

The mixing ratio (α) was determined from the analytical solution for the transport of a conservative solute through a two-dimensional homogeneous domain of length L and width W , which is given in Wexler [2]. The analytical model accounts for advection aligned with the x -direction, and two-dimensional dispersion, solving the transport equation

$$\frac{\partial \alpha}{\partial t} + v \frac{\partial \alpha}{\partial x} = D_L \frac{\partial^2 \alpha}{\partial x^2} + D_T \frac{\partial^2 \alpha}{\partial y^2}, \quad (1)$$

where v is the flow velocity, and D_L , D_T the longitudinal and transverse dispersion coefficients, respectively. The boundary condition for the transport equation is given as a continuous solute injection at $x = 0$, expressed as

$$\alpha = \begin{cases} 1, & \text{for } Y_1 < y < Y_2 \\ 0, & \text{for } y < Y_1 \text{ or } y > Y_2, \end{cases} \quad (2)$$

where Y_1, Y_2 are the lower and upper limit of the solute source at $x = 0$, respectively (see Figure S2). Furthermore, no-flux boundary conditions are considered for the upper, lower and downstream walls of the domain. The initial condition for the model considers that the system is free of the conservative tracer. These assumptions lead to the series-based analytical model

$$\begin{aligned} \alpha(x, y, t) = & \sum_{n=0}^{\infty} L_n P_n \cos(ny) \\ & \times \left\{ \exp\left(\frac{x(v - \beta)}{2D_L}\right) \operatorname{erfc}\left(\frac{x - \beta t}{2\sqrt{D_L t}}\right) \right. \\ & \left. + \exp\left(\frac{x(v + \beta)}{2D_L}\right) \operatorname{erfc}\left(\frac{x + \beta t}{2\sqrt{D_L t}}\right) \right\} \end{aligned} \quad (3)$$

where,

$$L_n = \begin{cases} \frac{1}{2}, & n = 0 \\ 1, & n > 0 \end{cases} \quad (4)$$

$$P_n = \begin{cases} \frac{Y_2 - Y_1}{W}, & n = 0 \\ \frac{\sin(\eta Y_2) - \sin(\eta Y_1)}{n\pi}, & n > 0 \end{cases} \quad (5)$$

$$\eta = \frac{n\pi}{W}, \quad n = 0, 1, 2, 3, \dots \quad (6)$$

$$\beta = \sqrt{v^2 + 4D_L \eta^2 D_T}. \quad (7)$$

For each time step, the infinite series expansion is terminated once a convergence criteria is achieved such that the solution is not changing significantly while including further series-terms. The semi-analytical model was applied using the parameters of the synthetic aquifer presented in Table S3. The values for longitudinal dispersivity α_L and transverse dispersivity α_T were implemented based on visual calibration, aiming to achieve a reasonable fit with the shape and extent of the plume at steady-state conditions.

1.5. Figure S2: Model Representation

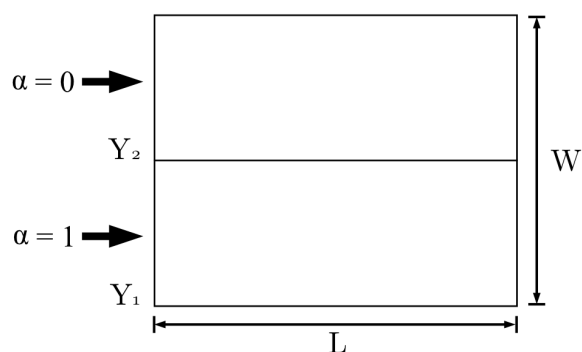


Figure S2. Representation of the model dimensions where W is the width of the tank, L is the length of the tank, Y_1 and Y_2 the limit coordinates for the injection of $\alpha = 1$.

1.6. Table S3: Parameters Used in the Semi-Analytical Model

Symbols	Parameters	Value	Units
α_L	Longitudinal dispersivity	1e-3	m
α_T	Transverse dispersivity	5e-3	m
v	Velocity	2.6152e-4	m/s
D_L	Longitudinal dispersion coefficient	2.6152×10^{-7}	m ² /s
D_T	Transverse dispersion coefficient	1.3076×10^{-6}	m ² /s
W	Aquifer width	0.2	m
L	Aquifer length	0.265	m
H	Aquifer height	0.01	m
Y_1	Lower limit of solute source	0	m
Y_2	Upper limit of solute source	0.1	m
ϕ_0	Porosity	0.34	-

Table S3. Parameters used in the semi-analytical model

1.7. Figure S3: PHREEQC Calculations

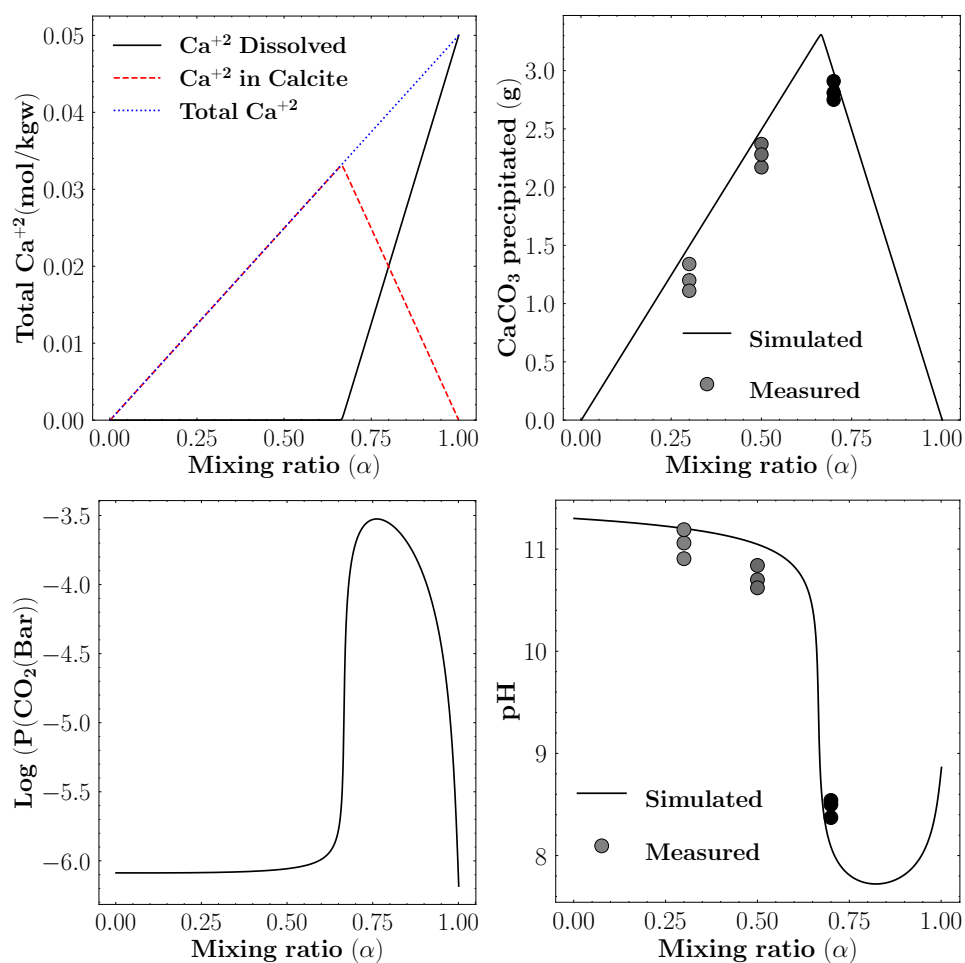


Figure S3. PHREEQC simulations conducted using the values provided in Table 1, where end-members W_1 and W_2 are mixed at various mixing ratio (α). The variables studied include: a) concentrations of dissolved, precipitated and total Ca^{2+} , b) CaCO_3 formation compared to batch experiment measurements, c) $\text{Log}(P(\text{CO}_2(\text{Bar})))$, and d) pH variation compared to batch experiment measurements.

Figure (S3) shows the results of the geochemical calculations carried out with PHREEQC, where end-members W_1 and W_2 (Table 1) are mixed at various mixing ratio (α). For comparison purposes, precipitated calcite and pH of three mixtures were measured in the laboratory through batch experiments, considering the mixing of W_1 and W_2 at three mixing ratio ($\alpha = 0.3$, $\alpha = 0.5$ and $\alpha = 0.7$), with the process repeated three times. The laboratory results show good agreement with the calculated values, which support the validation of our geochemical simulation. Figure (S3a) shows that the concentration of Ca^{2+} dissolved remains practically zero until the mixing ratio approaches $\alpha = 0.67$. Beyond this point, the concentration of dissolved calcium increases linearly up to the 0.05mol/kgw of end-member W_1 . In Figure (S3b), the amount of simulated precipitated calcite correlates with the calcium concentration, indicating the complete consumption for the formation of calcite up to a mixing ratio of $\alpha = 0.67$, where it peaks at 2.7 g. Subsequently, as the mixing ratio continues to the extreme where no CaCl_2 is present, the amount of calcite decreases linearly. For $\alpha < 0.67$ calcite precipitation is limited by Ca^{2+} , while for $\alpha > 0.67$ it is limited by CO_3^{2-} . The partial pressure of CO_2 (Figure S3c) follows a trend similar to that observed for Ca^{2+} maintaining minimal levels until a mixing ratio of $\alpha = 0.67$ is reached. At this ratio, due to a relatively low pH of about 8, the presence of carbon in the form of CO_2 becomes significant. As CO_2 pressure is still much lower than 1 bar, we do not expect gas formation. Lastly, Figure (S3d) shows that pH levels are directly affected by the mixing ratio, showing a sharp decline from $\alpha = 0.5$ to 0.67 .

1.8. Figure S4: Calcium Second Derivative

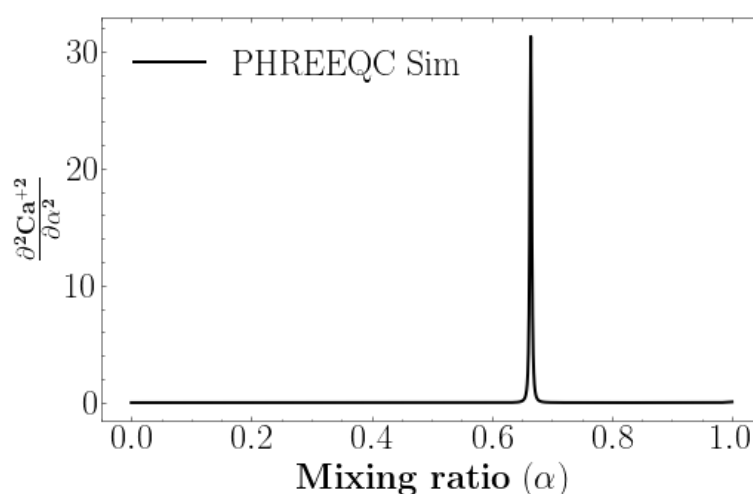


Figure S4. Calcium second derivative. The information presented in the figure was derived from the values in Table 1 using PHREEQC [3]

2. Extended Results

2.1. Figure S5: Linear Calcite Precipitation Patterns

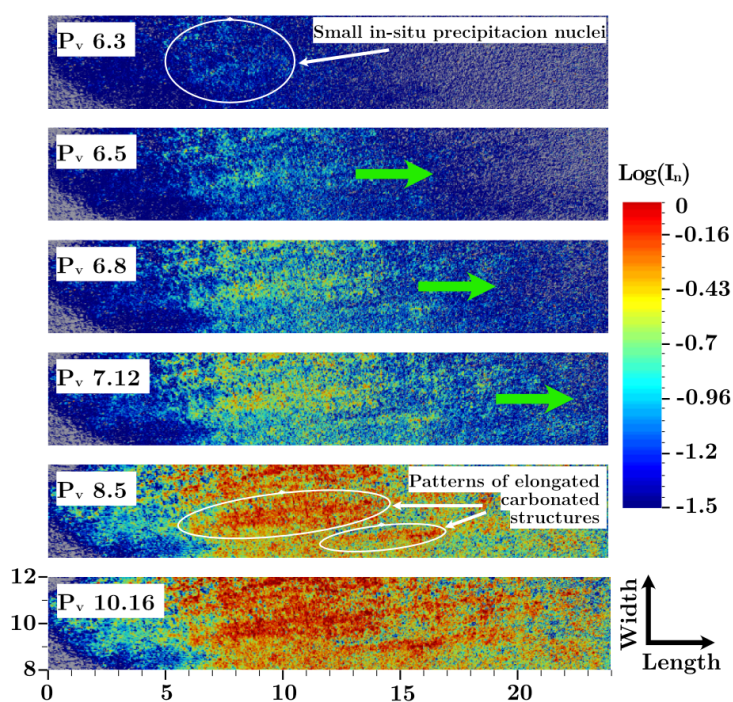


Figure S5. Linear carbonate structures patterns and preferential flow channels expressed in terms of $\log(I_n)$ between 0 and -1.5.

2.2. Text S2: Image Processing for Visualizing Tracer Test Evolution

During the development of the tracer test, the camera recorded 24-bit RGB color images, focusing on visualizing the evolution of the tracer test before and after MDP. The images were processed using the OpenCV library in Python [4] following the method used by Trabucchi et al. [5] to visualize fluorescein tracer test on wormholes. This process includes: (a) Converting images from raw format (NEF) to 16-bit images (TIFF); (b) Cropping the images resulting in a region of interest (ROI) with a resolution of 3975 × 3000 pixels, each measuring 0.0066 mm²; (c) selecting the green channel signal for analysis, as it was found to be the most sensitive; (d) removing background noise by subtracting from all images the RGB color image obtained immediately before the fluorescein tracer entered the aquifer; (d) rescaling intensities between 0 and 255 to enhance brightness and contrast.

2.3. Figure S6: Tracer Test Evolution: Initial Stages

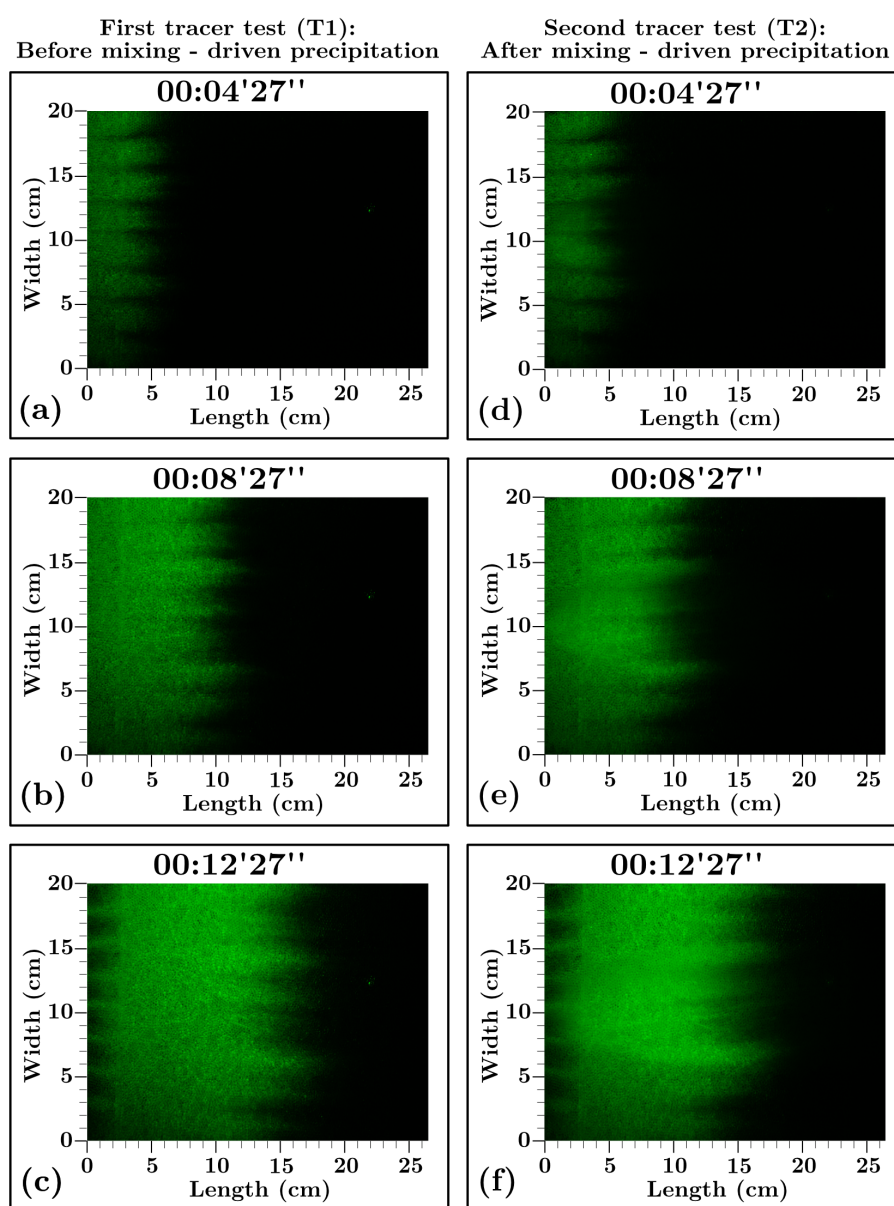


Figure S6. Flow patterns recorded by two tracer tests developed before (T₁) and after (T₂) the Mixing-Driven Precipitation Experiment (MDP) during the initial stages.

2.4. Figure S7: Tracer Test Evolution: Final Stages

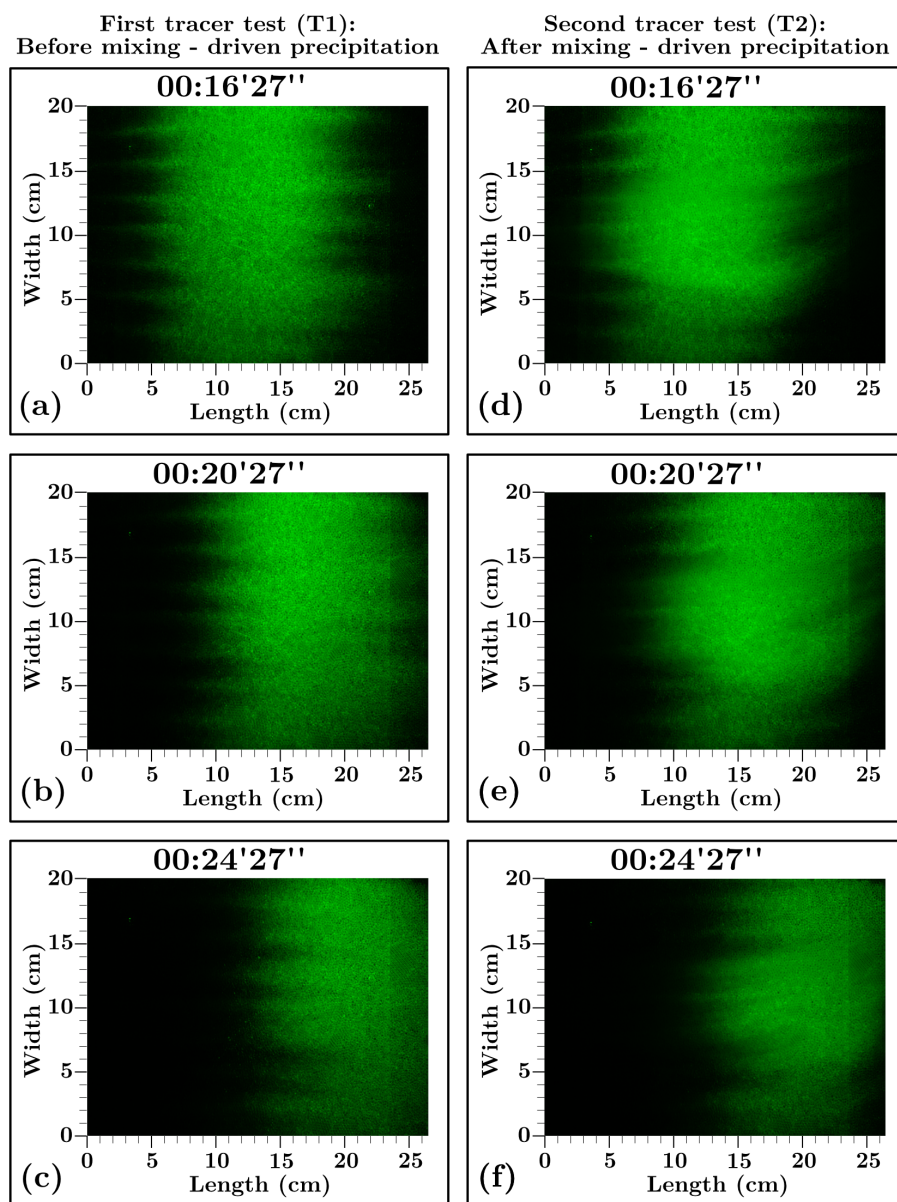


Figure S7. Flow patterns recorded by two tracer tests developed before (T_1) and after (T_2) the Mixing-Driven Precipitation Experiment (MDP) during the final stages.

Figures S6 and S7 illustrate the progression of two tracer tests (T_1 and T_2) conducted within the experimental tank before and after Mixing-Driven Precipitation experiment (MDP). Figure S6 contains a sequence of images representing the initial stages of the tracer test, covering the first three time steps (4.45, 8.45, and 12.45 minutes), while Figure S7 includes images depicting the final stages, corresponding to the last three time steps (16.45, 20.45, and 24.45 minutes). Before MDP, the tracer test (T_1) exhibits a slightly irregular flow pattern, likely due to minor variations in the flow rate at the inlet ports and small heterogeneities that developed within the tank during the packing process. In contrast, after MDP, the tracer test (T_2) reveals the formation of strong preferential flow channels influenced by self-organized pore-scale heterogeneities resulting from precipitation during the mixing process.

2.5. Text S3: Image Processing for Visualizing Calcite Precipitation Front Evolution

The images obtained during MDP were also processed to visualize the evolution of the precipitation front. The procedure followed was the same as described in the main text for Image Processing for Visualizing the Spatiotemporal Evolution of Calcite, encompassing steps (a) to (d). After that, two additional steps were taken: (e) subtracting images based on their predecessors, and (f) creating a chromatic progression.

2.6. Figure S8: Evolution of the Precipitation Front

The calcite precipitation front can be also observed from Figures S8a to S8f. In images S8a and S8b, there is a clear tendency of the precipitation front to expand towards the CaCl_2 solution inlet. This trend continues until image S8c, at which point the layer begins to bifurcate and shifts towards the Na_2CO_3 side. From image 8d onward, the calcite layer notably expands in both directions, eventually adopting a symmetric bell-shaped morphology fully manifested in image S8f.

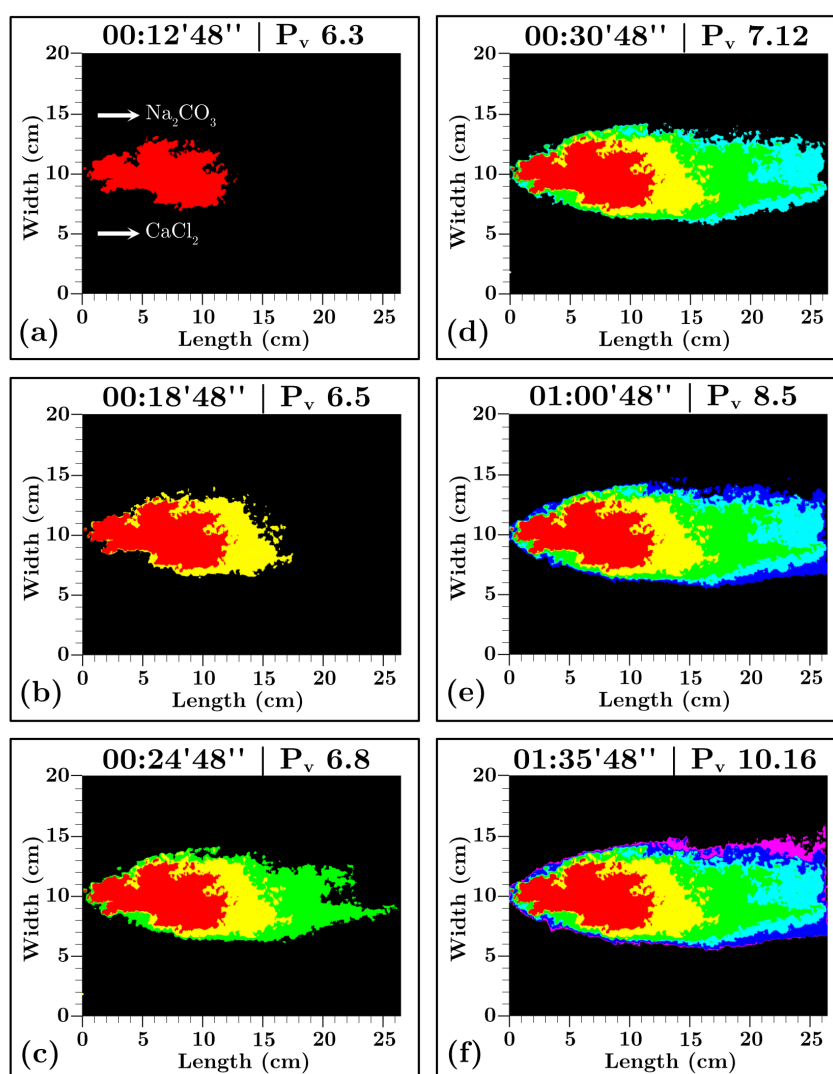


Figure S8. Precipitation front evolution of calcite precipitation during MDP

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