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Flow-driven control of calcium carbonate precipitation patterns in a confined geometry[†]

Gábor Schuszter, Fabian Brau and A. De Wit*

Upon injection of an aqueous solution of carbonate into a solution of calcium ions in the confined geometry of a Hele-Shaw cell, various calcium carbonate precipitation patterns are observed. We discuss here the properties of these precipitation structures as a function of the injection flow rate and concentrations of the reactants. We show that such flow-controlled conditions can be used to influence the total amount and the spatial distribution of the solid phase produced as well as the reaction efficiency defined here as the amount of product formed for a given initial concentration of the injected solution.

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1 Introduction

Depending on the operating conditions, a precipitation reaction can generate a spatially distributed solid product in variable amounts. A simple way to experimentally perform precipitation consists in pouring all reactants in a well-stirred reactor where the stirring ensures a fast mixing yielding ultimately a relatively homogeneous suspension of the equilibrium precipitate product. Precipitation can also occur in a gel or a solid matrix through the diffusion of reactants as seen in biomineralization,^{1,2} Liesegang rings in sedimentary rocks³ or in counterdiffusion crystallisation methods used to produce macromolecular protein crystals for instance.⁴ However, this precipitation procedure is slow and produces precipitates embedded in a gel or a solid matrix making their separation problematic if the product needs to be collected.

Flow-driven precipitation, where one reactant solution is injected into the other one is another promising technique producing precipitates under non-equilibrium conditions.^{5–7} Such a technique is nowadays attracting increased attention because gradients induced by the flow or hydrodynamic instabilities may lead to new synthesis modes. For example, it has recently been shown that flow-driven precipitation can affect crystallization kinetics,⁸ lead to the enrichment, compared to well-stirred conditions, of thermodynamically unstable polymorphs,^{9,10} the spatial segregation of different crystalline structures along the spreading direction,^{6,11} directionally asymmetric self-assembly,^{12,13} or can be used to control the microstructure of the precipitate.¹⁴

At the macroscopic level, the presence of flows can influence the precipitation patterns obtained and produce a wide variety of complex forms.^{7,12,15-18} As an example, chemical gardens growing in 3D when placing solid metal salt seeds into alkaline solutions such as silicate are shaped by buoyancy-driven flows among other processes.¹⁹ Control of the growth dynamics of these 3D structures has been attempted succesfully using bubble driving,²⁰ microgravity conditions,²¹ microfluidics,²² or the injection of one reactant into the other.⁵ In confined quasi 2D geometries, such a flow-control has allowed us to obtain in a reproductive way a wealth of different patterns when the concentration of the various chemicals is varied.^{7,12,16,17} Hydrodynamic instabilities can shape some of the structures at lower concentrations: as an example, needles of precipitates may align along convective rolls induced by a buoyancy instability,^{11,23} a viscous fingering instability can shape the precipitate into flowers¹⁷ or local changes in permeability can trigger fingered patterns.^{15,18,24} At larger concentrations, mechanical effects due to the cohesion of the solid phase can select other forms like spirals⁷ or filaments^{7,12,16} that are robust with changes in the reactants.¹⁶ These examples highlight the importance of concentration gradients and convective mixing induced by flow conditions for the production of new materials as well as controlling the micro structure of the solid and/or its macroscopic self-organization.

In this context, our objective is to discuss the influence of flow conditions on optimizing various quantities characterizing the amount and spatial distribution of a solid phase produced when an aqueous solution of one reactant of a precipitation reaction is injected into a solution of the other reactant. To do so, we analyze experimentally macroscopic calcium carbonate patterns produced by injecting radially in a confined geometry an aqueous solution of carbonates (CO_3^{2-}) into a solution of calcium ions (Ca^{2+}). White $CaCO_3$ precipitates appear along the moving miscible interface between the two reactants according to a

Université libre de Bruxelles (ULB), Nonlinear Physical Chemistry Unit, CP231, 1050 Brussels, Belgium. E-mail: adewit@ulb.ac.be; Fax: +32 2 650 5767; Tel: +32 2 650 5774

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precipitation reaction $\operatorname{Ca}^{2^+} + \operatorname{CO}_3^{2^-} \to \operatorname{Ca}\operatorname{CO}_3(s)$ typically important for the mineralisation of CO_2 in soil sequestration processes.^{18,25–29} We have recently shown that coupling between this precipitation reaction and injection can lead to a drastic drop of the amount of precipitate even if the reactant concentrations are large in the vicinity of the reaction zone.¹⁸ In order to better understand how the quantity of calcium carbonate and its spatial distribution depend on reactant concentrations and flow rates, the temporal and spatial evolution of the precipitate patterns are analyzed. Various quantities such as the total gray scale intensity of the pattern, its filling, density or brightness are monitored as a function of time. We also compute the precipitation efficiency defined here as the amount of the solid phase produced per concentration of the injected reactant.

We show that finding optimal precipitation conditions such that all these quantities are maximized is a challenge, even in a simple Hele-Shaw setup like the one used here.

2 Materials and methods

Experiments are carried out in a horizontal confined geometry maintained between a large lower pool (35 cm \times 35 cm) and a smaller upper plate (21 cm \times 21 cm) made of transparent Plexiglas (Fig. 1) vertically separated by a small interstice (0.5 mm) thanks to 4 spacers. The setup is illuminated from above by two light pads placed symmetrically with respect to a digital camera recording the dynamics (PixeLINK B742U giving images of $N = 1280 \times 1024$ pixels).

The gap of the cell is initially filled by an aqueous solution of calcium chloride CaCl₂. The same solution is then poured around the upper plate, into the pool, to form a 4 mm thick liquid layer. This outer layer is in contact with the 0.5 mm thin layer within the gap and ensures a spatially homogeneous outflow along the sides of the upper plate during the experiment. An aqueous solution of sodium carbonate Na₂CO₃ is next injected radially from the center of the lower pool through an inlet of 1 mm inner diameter using a syringe pump (kdScientific 210P-CE). A fixed total volume of 2.5 mL of solution is injected in all experiments at a given constant flow rate Q = 0.1, 1.0, and 6.5 mL min^{-1} . The experiments are performed for variable initial concentrations of reactants at $T = (21 \pm 1)$ °C. The properties of



Fig. 1 The thin reaction area is confined by two Plexiglas plates (the upper plate and the pool) and filled with Ca^{2+} solution while a CO_3^{2-} solution is injected by a syringe pump through a tiny inlet from below.

the reactant solutions are given in S1 (ESI[†]). The initial pH of the carbonate solution is maintained to 10 by addition of HCl to avoid the formation of Ca(OH)₂ precipitates. During the experiments, the white CaCO₃ precipitate is produced by the reaction $Ca_{(aq)}^{2+} + CO_{3(aq)}^{2-} \rightleftharpoons CaCO_{3}(s)$. For each set of experimental values tested, the experiment is reproduced three times. Examples of the three patterns obtained for the same values of parameters and same initial conditions are presented in S2 (ESI[†]). The reproducibility of the pattern is very good and hence the type of structures obtained for a given value of parameters is robust.

3 Precipitation patterns

Upon injection of one reactant solution into the other one, a white CaCO₃ precipitate layer is formed and various shapes can be observed as shown in Fig. 2 displaying the precipitation patterns as a function of initial reactant concentrations and injection flow rates.¹⁸

At given initial concentrations of reactants, the tendency of the system to form a precipitate may be characterized by the saturation index $SI_0 = log_{10}(IAP_0/K_{SP})$ where IAP_0 and K_{SP} are the initial ion activity product of the reactant solutions and the solubility product of $CaCO_3$ respectively (see S3 for detailed description, ESI†). SI_0 varies thus with the reactant concentrations and the larger the SI_0 , the larger the thermodynamic force to form a precipitate. In our experiments, the system is largely supersaturated for all concentrations scanned ($SI_0 > 1$ in all panels of Fig. 2) and precipitation is expected in all cases. Counterintuitively, we see that the smallest amount of precipitate is obtained at the largest concentrations (highest SI_0) and flow rate (see Fig. 2b5 and c5).

The influence of the flow rate is shown in Fig. 2 by analyzing the patterns along a column for which the initial reactant concentrations, and thus SI₀, are constant while Q increases downwards. We see that at a low flow rate and below some threshold for both concentrations, the patterns remain mainly circular during their growth with a rather homogeneous distribution of precipitates (Fig. 2a1-4). This homogeneity and symmetry is broken when the flow increases because the precipitate is then advected away from the inlet region and accumulates at the periphery, near the miscible reactive interface (Fig. 2b1-3 compared to Fig. 2a1-3). The permeability in this region is then significantly reduced which leads to the emergence of a fingering instability deforming the pattern periphery at larger concentrations and flow rates (Fig. 2b4 and c1-4).¹⁵ Note that, for Fig. 2c2 and c3, $M = \mu_{0,Ca^{2+}}/\mu_{0,CO_2^{2-}} > 1$, where *M* is the ratio between the initial viscosity of the displaced solution $\mu_{0,Ca^{2+}}$ and that of the injected solution $\mu_{0,CO_3^{2-}}$. M > 1 refers to a viscously unstable situation leading to the emergence of a fingering instability. However, as shown previously,¹⁷ for the flow rates used here and on the timescale of the experiments, M is not large enough to lead to viscous fingering in the non-reactive case. The mechanism of fingering results thus rather from the local decrease of permeability.15,24



Fig. 2 Precipitate patterns observed at different flow rates and concentrations after injecting 2.5 mL of carbonate solution. Field of view: 123 mm × 98 mm. The number in the top left corner of the images is the number of the pattern. In the header, initial reactant concentrations, the stoichiometric ratio of the reactants $\gamma = [Ca^{2+}]/[CO_3^{2-}]$, the saturation index SI₀ = log₁₀(IAP₀/K_{SP}) where IAP₀ and K_{SP} are the initial ion activity product of the reactant solutions and the solubility product of CaCO₃, and the viscosity contrast of the reactant solutions $M = \mu_{0,Ca^{2+}}/\mu_{0,CO_2^{2-}}$ are presented.

Surprisingly, the patterns obtained at medium and large Q with the largest SI₀ are those characterized by the smallest amount of precipitate (Fig. 2b5 and c5). These examples highlight the strong effects of the coupling between chemical reactions and hydrodynamics on precipitation in a confined geometry. Let us analyze how this coupling can control the precipitate properties produced in confined geometry under flow conditions.

4 Pattern characterization

A large variety of precipitation patterns is thus observed when reactant concentrations and flow rates are varied (Fig. 2). To study those patterns, we first define the ratio of the initial reactant concentrations as $\gamma = [Ca^{2+}]/[CO_3^{2-}]$, where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the initial concentrations of the calcium and carbonate solutions, respectively. $\gamma > 1$ means that the displaced solution is in stoichiometric excess compared to the injected one.

A quantitative image analysis is performed on the basis of seven quantities: (i) the area *A* covered by the precipitate (Fig. 3b); (ii) the area *A*_p enclosed by the pattern perimeter (Fig. 3c); (iii) the total gray scale intensity $I_{tot} \in [0,A]$ of the white precipitate in a given image; (iv) the brightness $B = I_{tot}/A \in [0,1]$ measuring the compactness of the precipitate; (v) the filling $F = A/A_p \in [0,1]$ measuring how much the pattern is filled by the precipitate; (vi) the pattern density $d = A_p/(\pi R_{max}^2) \in [0,1]$ measuring the deviation from a circular growth (Fig. 3a); and (vii) the production efficiency $P = I_{tot}/[CO_3^{2-}]$ measuring how much precipitate is produced for a given initial concentration



Fig. 3 Quantities used to characterize the patterns. (a) Gray scale intensity l(x,y) used to compute l_{tot} and d. The 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 $B = l_{tot}/A$. (c) The area A_p inside the pattern perimeter is used to compute $F = A/A_p$.

of the injected reactant. More details about these quantities can be found in ref. 18 and in S4 (ESI⁺).

All those quantities are measured on the images of three independent experiments performed with the same parameter values in order to compute their averages and standard deviations. The errors bars are generally quite small showing that the measured quantities do not fluctuate significantly for given values of parameters.

5 Precipitation efficiency

The quantities listed in Section 4 characterize our confined precipitation patterns from different view points. They may be used to analyze the efficiency of the precipitate production depending on which characteristic is considered. The different identified optimal regimes are listed in Table 1.

Table 1 Optimal range of experimental conditions to obtain large values of I_{tot} , *F*, *d*, *B*, and *P*

	Experimental conditions		
	[Ca ²⁺]	$[{\rm CO_3}^{2-}]$	$Q (\mathrm{mL} \mathrm{min}^{-1})$
I _{tot}	Low	Large	Low
	Large	Large	Low
F	Low	Low	Low
	Low	Large	Low
	Large	Low	Low
d	Low	Low	Low
В	Low	Large	Medium and large
	Large	Low	Low
	Large	Large	Low
Р	Low	Low	Large
	Large	Low	Any Q

5.1 Amount of precipitate

We first consider the efficiency of precipitation assuming that the production of the largest amount of precipitate is required. The evolution of I_{tot} , which is a semi-quantitative indicator of the amount of precipitate in the cell, is depicted in Fig. 4 as a function of the injected volume V for different experimental conditions. The same scale is used on all graphs to facilitate the comparison.

We see that, when the concentration of one of the reactants is low, I_{tot} increases with the concentration of the other reactant (Fig. 4a and b). Injecting a CO_3^{2-} solution with a large concentration



Fig. 4 Evolution of the total grayscale intensity I_{tot} as a function of the injected volume *V* of carbonate solution. $Q = 0.1 \text{ mL min}^{-1}$ for (a and b) and variable *Q* for (c-f).

into a Ca^{2+} solution with low concentration (Fig. 4a) produces more precipitate than the opposite case (Fig. 4b) even if the values of their SI₀ predicts the reverse (SI₀ = 7.3 and SI₀ = 8.6, respectively, see Fig. 2). This shows that I_{tot} depends not only on SI₀ but also on the ratio γ of initial concentrations.

The effect of increasing the injection rate Q on I_{tot} is shown in Fig. 4c-f for different initial couples of concentrations. For low concentrations of both reactants, the amount of precipitate increases with Q which induces a better mixing between the solutions (Fig. 4c and the first column of Fig. 2). One could therefore expect that the largest amount of precipitate is produced when both solutions are concentrated and Q is large. As shown in Fig. 4f, this is not the case: when the concentrations of both reactants are large, the largest I_{tot} is reached at a low flow rate, while the amount of precipitate sharply drops if Q is increased (Fig. 2b5, c5 and 4f). The large value of SI_0 together with the moderate stoichiometric excess of the displaced solution ($\gamma = 3$) lead in that case to the production of a large amount of precipitate in small localized regions forming solid walls hindering further mixing. The subsequent production of precipitates sharply drops. Therefore, a reaction producing a large amount of cohesive precipitates on a small length scale has a negative feedback at a much larger scale.

In conclusion, the largest amount of precipitate (largest I_{tot}) is produced at a low flow rate when the concentration of the injected CO₃²⁻ solution is large (see Table 1).

5.2 Spatial distribution of patterns

In some applications like CO_2 mineralization in soils, a target may be to obtain a homogeneous distribution of precipitates on the widest possible area. However, the patterns are not always fully homogeneous. To study the spatial distribution of the precipitate and its deviation from an ideal homogeneous radial structure, we consider the evolution of two quantities, the filling *F* and the pattern density *d* as a function of the volume of the injected CO_3^{2-} solution. To do so, we discuss first the area *A* covered by the precipitate and the area A_p enclosed by its perimeter.

5.2.1 Area *A* covered by the precipitate. The evolution as a function of the injected volume *V* of the area *A* covered by the precipitate is shown in Fig. 5. When both reactants have low concentrations (Fig. 5a), the lowest flow rate gives the largest *A* because the precipitate is spread more or less homogeneously within the pattern perimeter (Fig. 2a1). Increasing *Q* lowers the area *A* because the precipitate is then flushed away from the inlet region and accumulates at the pattern periphery (Fig. 2c1). However, this decrease of *A* with increasing *Q* is not monotonic, because a larger amount of precipitate is also produced at larger *Q* for these reactant concentrations (Fig. 4c and 5a).

A similar trend is observed when a concentrated solution of CO_3^{2-} is injected into a less concentrated solution of Ca^{2+} (Fig. 5b). Again, the largest value of *A* is obtained at low flow rates and increasing *Q* lowers *A*. Indeed, for a low injection rate, the precipitate is distributed almost homogeneously (Fig. 2a4), whereas, for larger *Q*, fingering appears inducing an accumulation of precipitates at the rim of the fingers (Fig. 2b4 and c4).



Fig. 5 Evolution of the area A covered by the precipitate as a function of injected volume V of carbonate solution at different flow rates and initial reactant concentrations.

Even if γ and SI₀ remain constant, injection at a faster rate leads to the production of more precipitates per given area which increases the unfavorable mobility gradient between the precipitate layer and the injected fluid. In contrast, the absolute amount of precipitate does not significantly vary with Q (Fig. 4d) leading to a decrease of A.

In the opposite case, *i.e.* when the displaced solution of Ca^{2+} is in large stoichiometric excess (Fig. 5c), the injected reactant is readily consumed on a small area (Fig. 2a3). In that case, a medium injection rate *Q* increases *A* because it helps the spreading of the CO_3^{2-} solution. However, *A* is smaller for the largest *Q* because the flow is then strong enough to displace most particles towards the periphery (see Fig. 2b3 and c3).

For large concentrations of both reactants (Fig. 5d), a similar trend to the one for I_{tot} is observed (Fig. 4f): beyond a critical Q, the area covered by the precipitate sharply drops and its spatial distribution is strongly localized producing hollow patterns (Fig. 2b5 and c5).

We conclude from Fig. 5 that the largest area covered by the precipitate is reached at a low injection rate *Q* if the reactants have similar concentrations (γ is not too large) (Fig. 5a and b). In contrast, when $\gamma = 18$ (Fig. 5c), the injected reactant is consumed by the displaced one over a smaller area leading to a lower *A* at a low flow rate.

5.2.2 Area A_p enclosed by the pattern. In a non-reactive case, the area covered by the injected liquid increases linearly with the injected volume *V* if the thickness of the fluid layer is constant. In our system, with a gap width of 0.5 mm and an injection of a total of 2.5 mL of solution, one could expect a flooded area $A_{flood} = 50$ cm² if the parabolic profile of the injected liquid is neglected or $A_{flood} = 75$ cm² if it is taken into account. Fig. 6 shows that, in most cases, the area A_p enclosed by the pattern indeed grows linearly with the injected volume and reaches a final value compatible with the one expected for non-reactive fluids.

There is however one noticeable exception at a low injection rate Q when a diluted CO_3^{2-} solution is injected into a



Fig. 6 Evolution of the area A_p of the zone inside the perimeter of the pattern as a function of the injected volume *V* of carbonate solution. $Q = 0.1 \text{ mL min}^{-1}$ for (a and b) and variable *Q* for (c-f).

concentrated Ca²⁺ solution. As shown in Fig. 6b, A_p decreases indeed at low Q when the stoichiometric excess of the displaced solution increases. In addition, beyond some threshold of the initial concentration ratio γ , the growth of A_p is no longer linear and saturates once a given amount of reactant has been injected. At $\gamma = 18$, the large stoichiometric excess of the displaced solution leads to a rapid consumption of the CO₃²⁻ ions over a small area. At low Q, the precipitate is therefore not significantly advected and accumulates near the inlet. The precipitate is then progressively surrounded by the supernatant liquid (not visible on the image) leading to a significant decrease of A_p (Fig. 2a3 and 6b). At larger Q, the precipitate is advected by the flow and A_p increases again linearly with V (Fig. 6e).

5.2.3 Filling. The spatial homogeneity of the spatial distribution of the precipitate is characterized by the filling $F = A/A_p \in [0,1]$, the evolution of which is shown in Fig. 7 as a function of the injected volume. We see that, if the concentration of at least one of the reactants is low, *F* reaches a constant value close to 1 at low *Q*. The pattern is thus homogeneously filled by some precipitates (Fig. 2a1–4). For larger flow rates, *F* decreases because either the particles are advected away from the inlet (*e.g.* Fig. 2b1 and c1) or fingering emerges (Fig. 2b4 and c4).

If both reactants are concentrated, hollow structures appear once Q is large enough (Fig. 2b5 and c5) and, consequently, F sharply drops (Fig. 7d). A slow increase of F is recovered at $Q = 1.0 \text{ mL min}^{-1}$ due to the emergence of secondary diffusive structures growing on a much larger time scale since the reactants need then to diffuse through the precipitate walls to meet and react (Fig. 2a5). At the largest Q, the wall may be even more compact, hindering the growth of additional diffusive



Fig. 7 Evolution of the filling of the pattern F as a function of injected volume V of carbonate solution at different flow rates and initial reactant concentrations.

patterns in the hollow area during the timescale of the experiments, and hence *F* stays essentially at a constant low value.

In conclusion, Fig. 7 indicates that the most homogeneous spatial distributions of precipitates are obtained if at least one of the solutions is diluted and *Q* is low (see Table 1).

5.2.4 Pattern density. The deviation from a perfectly circular pattern is measured by the pattern density $d = A_p/(\pi R_{\text{max}}^2) \in [0,1]$, where R_{max} is the largest distance between the injection point and the pattern perimeter (Fig. 3a).^{17,30} *d* measures indeed the homogeneity of the spatial distribution of the precipitate along the azimuthal direction (along circles of given radii). Patterns characterized by a low value of *d* tend to grow in some arbitrary preferred directions while, when *d* is close to one, any angular sector of the reactor, with a given angle, contains a similar amount of precipitate.

When the concentration of both reactants is low, the pattern is essentially circular with d close to 1 (see Fig. 8a and the first column of Fig. 2). As seen in Fig. 4c, the precipitate production is enhanced in this regime of concentrations when Q increases.

(a) (b) 0.8 0.8 0.6 0.6 [CO₂²⁻]=0.25 M σ [Ca²⁺]=0.5 M 0.4 0.4 $\Omega = 0.1 \text{ ml} / \text{min}$ 0.01 ²⁻]=1.5 M 0 2 02 Q=1.0 mL/min 1=0.5 M [Ca Q=6.5 mL/min °ò 0.5 1.5 2 2.5 0.5 1.5 2 2.5 (d) (c) [Ca² [CO₂²⁻]=1.5 M 1=4.5 M 0.8 0.8 0.6 0.6 σ 0.4 0.4 [CO32-]=0.25 M 0.2 0.2 [Ca² ⁺]=4.5 M 0 0 0.5 1.5 2.5 1.5 2.5 v/ V / ml mL

Fig. 8 Evolution of pattern density *d* as a function of injected volume *V* of carbonate solution at different flow rates and initial reactant concentrations.

This affects the mobility ratio and produces moderate fingering¹⁵ seen on the border of the patterns (Fig. 2a1, b1 and c1).

Increasing the concentration of one reactant produces more precipitate (Fig. 4d and e) which leads to a larger deformation of the interface, *i.e.* to a decrease of *d* (Fig. 8b and c). When both solutions are concentrated (large SI₀ value), the precipitate forms solid walls which affect significantly the flow and strongly destabilize the interface leading to a low value of *d* (see the last column of Fig. 2 and Fig. 8d). In this case, the coupling between the formation of cohesive solid barriers and hydrodynamics makes the prediction of the precise location of the precipitate impossible.

These results show thus that the most homogeneous spatial spreading is reached if both the reactant concentrations and the injection flow rate Q are low (see Table 1). In this case, the thin precipitate layer does not impact significantly the hydrodynamics.

5.3 Brightness

The amount of precipitate per unit area it covers is proportional to the brightness $B = I_{tot}/A$, the evolution of which during injection is shown in Fig. 9. It is expected that a compact precipitate layer is produced if the concentrations and the flow rate are large. Indeed, Fig. 9a and b show that raising Q leads to a larger value of B. When both concentrations are low (Fig. 9a), this increase of B with Q is due to the production of a larger amount of precipitate (Fig. 4c) over a smaller area (Fig. 5a). For larger concentrations of CO_3^{2-} (Fig. 9b), a larger flow rate induces the emergence of fingers where the precipitate accumulates (Fig. 2b4 and c4). The increase of the brightness B is then mainly due to the decrease of the area A covered by the precipitate, since I_{tot} is similar for all Q (Fig. 4d). However, when the concentration of the displaced solution is large, increasing Q decreases the brightness (Fig. 9c and d). The brightness can however still be large in these cases provided Q is low.

We conclude that the larger values of the brightness B are obtained at low flow rates if the displaced reactant is concentrated (Fig. 2a3 and a5) and at larger flow rates when a



Fig. 9 Evolution of brightness B as a function of injected volume V of carbonate solution at different flow rates and initial reactant concentrations.

concentrated solution is injected into a diluted one (see Fig. 2b4, c4 and Table 1).

5.4 Production efficiency

One way to quantify precipitation efficiency is to check how much precipitate can be produced per amount of reactant injected. This can be quantified by the production efficiency $P = I_{tot}/[CO_3^{2-}]$. Increasing *P* might be relevant for geological carbon dioxide sequestration for instance where the largest amount of mineralization is expected per amount of CO₂ injected. In this context, comparing Fig. 10a and b to Fig. 4a and b shows that, like for I_{tot} , *P* evolves such that the larger the concentration of one reactant, the larger *P* and increasing the stoichiometric excess of the displaced solution (*i.e.* increasing Ca²⁺) increases efficiency.

Increasing the flow rate to Q = 6.5 mL min⁻¹ while one reactant remains diluted and the concentration of the other one is increased, leads to different trends as depicted in Fig. 10c and d. At the lowest CO_3^{2-} concentration, *P* reaches a large value because a larger *Q* ensures a better mixing. *P* decreases with increasing CO_3^{2-} concentration because the injected solution is in stoichiometric excess and cannot be consumed efficiently (Fig. 10c). For the opposite case, when the concentration of Ca^{2+} is increased



Fig. 10 Evolution of production efficiency *P* as a function of the injected volume *V* of carbonate solution. $Q = 0.1 \text{ mL min}^{-1}$ for (a and b), $Q = 6.5 \text{ mL min}^{-1}$ for (c and d) and variable *Q* for (e–h).

while $[CO_3^{2-}]$ is kept at a constant low value (Fig. 10d), *P* increases only slightly with the Ca²⁺ concentration. This shows that a large flow rate *Q* ensures the consumption of the injected reactant, such that increasing the excess of Ca²⁺ is then not necessary to increase *P*. In addition, precipitation is much more enhanced by increasing *Q* if the reactant concentrations are low and close to the stoichiometric ratio (compare Fig. 10a,c and b,d).

The evolution of *P* is shown in Fig. 10(e–h) for a given couple of reactant concentrations when *Q* varies. We see that a large *P* is reached if the CO_3^{2-} concentration is low and either *Q* or the concentration of the displaced reactant is large (Fig. 10e and g). When the concentration of CO_3^{2-} is large, *P* is always significantly smaller for all *Q* (Fig. 10f and h). In addition, when both concentrations are large, *P* even decreases when *Q* is increased (Fig. 10h).

Thus we conclude that a large precipitation efficiency *P* can be achieved either when both concentrations are low and *Q* is large or when the initial concentration ratio γ is large for all investigated *Q* (see Table 1).

6 Discussion

The efficiency of a precipitation reaction carried out in a confined geometry can be evaluated from various different points of views. In Section 5, five different quantitative measures describing the evolution of the precipitate patterns have been computed. They allow us to discuss the efficiency of precipitation depending on whether the precipitation pattern

1. contains a large amount of precipitate (large I_{tot});

2. is homogeneously filled by particles, with few holes within the pattern periphery (a large *F* value);

3. grows radially and spreads uniformly around the injection point (a large *d* value);

4. accumulates on the smallest possible area, forming thick layers (a large *B* value);

5. is such that the largest amount of injected reactant is effectively transformed into the solid precipitate (large *P*).

It can be supposed that, in most cases, the efficiency of transforming the reactants into a homogeneously distributed large amount of solid product corresponds to achieving large values of all the five quantities. It has however been shown in Section 5 that these different quantities reach their maximum in different optimal experimental condition ranges. A summary is presented in Table 1.

We see that using low concentrations and injecting at a low flow rate Q are the optimum conditions if a spatially homogeneous distribution of the precipitate is targeted since both the filling F and the pattern density d are then large. The reactant concentrations may however be increased if one needs to enhance the amount of precipitate produced (large I_{tot}) provided Q remains small. These experimental conditions also yield a compact precipitate layer (large B). In contrast, injecting at a larger flow rate Q is preferable if one wants to efficiently mineralize the injected reactant (large P), especially when the stoichiometric ratio of the reactants cannot be easily varied (*e.g.* the chemical composition of a geological formation). Our results show thus that finding optimal experimental flow conditions such that both the spatial spreading and the amount of solid phase produced per injected reactant consumed are maximized is not obvious even in a simple confined geometry and for a simple reaction like studied here.

7 Conclusion

We have analyzed experimentally the properties of calcium carbonate precipitates obtained when injecting an aqueous solution of carbonate into a solution of calcium ions in a confined geometry at a constant flow rate. Our objective was to quantify the experimental conditions optimizing the amount of solid phase produced as well as its spatial distribution. To do so, we have computed the total intensity I_{tot} of the white product precipitate, the filling F, the brightness B and the pattern density d of the solid structure produced as a function of the injected volume for various initial reactant concentrations and injection flow rate Q. We have moreover quantified the efficiency P giving an estimation of the quantity of the solid phase produced per injected reactant consumed. We find that maximizing all these various quantities is not possible for one single set of experimental conditions. Indeed, very few precipitate strongly localized in space is obtained at high flow rates and large concentrations for instance while an optimized homogeneous spreading is rather reached for lower values of these quantities.

These conclusions show that out-of-equilibrium flow conditions can be efficiently used to optimize at will specific targets compared to precipitation under simple stirring for instance. For CO₂ mineralisation in sequestration techniques, our analysis also suggests that different operating conditions of the injection of CO₂ into saline aquifers rich in minerals could be used depending on whether a larger spatial distribution or a larger conversion of CO₂ into mineral carbonates is targeted. Of course, the simplicity of a Hele-Shaw cell and of the chemical solutions used here calls for more elaborate studies on real 3D porous media²⁶ before reaching conclusions for sequestration techniques. Nevertheless, in view of the difficulties of *in-situ* analysis in real soils,²⁵ we hope that the current approach will already shed some light on this complex problem.

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References

- 1 Biomineralization: From Nature to Application. Metal Ions in Life Sciences 4, ed. A. Sigel, H. Sigel and R. K. O. Sigel, Wiley-Blackwell, Hoboken, New Jersey, 2008.
- 2 M. Sancho-Tomás, S. Fermani, J. Gómez-Morales, G. Falini and J. M. García-Ruiz, Calcium Carbonate Bio-precipitation in Counter-diffusion Systems Using the Soluble Organic Matrix From Nacre and Sea-urchin Spine, *Eur. J. Mineral.*, 2014, 26, 523–535.

- 3 *Precipitation Patterns in Reaction-Diffusion Systems*, ed. I. Lagzi, Research Signpost, Kerala, India, 2010.
- 4 J.-M. García-Ruiz, Counter-diffusion Methods for Macromolecular Crystallization, *Methods Enzymol.*, 2003, 368, 130–154.
- 5 S. Thouvenel-Romans and O. Steinbock, Oscillatory Growth of Silica Tubes in Chemical Gardens, *J. Am. Chem. Soc.*, 2003, **125**(14), 4338–4341.
- 6 A. Baker, Á. Tóth, D. Horváth, J. Walkush, A. S. Ali, W. Morgan, Á. Kukovecz, J. J. Pantaleone and J. Maselko, Precipitation Pattern Formation in the Copper(II) Oxalate System with Gravity Flow and Axial Symmetry, *J. Phys. Chem.*, 2009, **113**(29), 8243–8248.
- 7 F. Haudin, J. H. E. Cartwright, F. Brau and A. De Wit, Spiral Precipitation Patterns in Confined Chemical Gardens, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 17363–17367.
- 8 D. Richard and T. Speck, The Role of Shear in Crystallization Kinetics: From Suppression to Enhancement, *Sci. Rep.*, 2015, **5**, 14610.
- 9 B. Bohner, G. Schuszter, O. Berkesi, D. Horváth and Á. Tóth, Self-organization of Calcium Oxalate by Flow-driven Precipitation, *Chem. Commun.*, 2014, **50**, 4289.
- 10 B. Bohner, B. Endrödi, D. Horváth and Á. Tóth, Flow-driven Pattern Formation in the Calcium-Oxalate System, *J. Chem. Phys.*, 2016, **144**, 164504.
- 11 B. Bohner, G. Schuszter, D. Horváth and Á. Tóth, Morphology Control by Flow-driven Self-organizing Precipitation, *Chem. Phys. Lett.*, 2015, 631–632, 114–117.
- 12 F. Haudin, J. H. E. Cartwright and A. De Wit, Direct and Reverse Chemical Garden Patterns Grown Upon Injection in Confined Geometries, *J. Phys. Chem. C*, 2015, **119**, 15067–15076.
- 13 A. Varghese and S. Datta, Directionally Asymmetric Selfassembly of Cadmium Sulfide Nanotubes Using Porous Alumina Nanoreactors: Need for Chemohydrodynamic Instability at the Nanoscale, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2012, **85**, 056104.
- 14 E. Tóth-Szeles, G. Schuszter, A. Tóth, Z. Kónya and D. Horváth, Flow-driven Morphology Control in the Cobalt-Oxalate System, *CrystEngComm*, 2016, 18, 2057–2064.
- 15 Y. Nagatsu, Y. Ishii, Y. Tada and A. De Wit, Hydrodynamic Fingering Instability Induced by a Precipitation Reaction, *Phys. Rev. Lett.*, 2014, **113**, 024502.
- 16 F. Haudin, V. Brasiliense, J. H. E. Cartwright, F. Brau and A. De Wit, Genericity of Confined Chemical Garden Patterns With Regard to Changes in the Reactants, *Phys. Chem. Chem. Phys.*, 2015, 17, 12804–12811.
- 17 F. Haudin and A. De Wit, Patterns Due to an Interplay Between Viscous and Precipitation-driven Fingering, *Phys. Fluids*, 2015, 27, 113101.
- 18 G. Schuszter, F. Brau and A. De Wit, Calcium Carbonate Mineralization in a Confined Geometry, *Environ. Sci. Technol. Lett.*, 2016, 3(4), 156–159.
- 19 L. M. Barge, S. S. S. Cardoso, J. H. E. Cartwright, G. J. T. Cooper, L. Cronin, A. De Wit, I. J. Doloboff, B. Escribano,

R. E. Goldstein, F. Haudin, D. E. H. Jones, A. L. Mackay, J. Maselko, J. J. Pagano, J. Pantaleone, M. J. Russell, C. I. Sainz-Díaz, O. Steinbock, D. A. Stone, Y. Tanimoto and N. L. Thomas, From Chemical Gardens to Chemobrionics, *Chem. Rev.*, 2015, **115**(16), 8652–8703.

- 20 J. J. Pagano, T. Bánsági Jr. and O. Steinbock, Bubbletemplated and Flow-controlled Synthesis of Macroscopic Silica Tubes Supporting Zinc Oxide Nanostructures, *Angew. Chem., Int. Ed.*, 2008, **51**, 12754–12758.
- 21 J. H. E. Cartwright, B. Escribano, C. I. Sainz-Díaz and L. S. Stodieck, Chemical-garden Formation, Morphology, and Composition. II. Chemical Garden in Microgavity, *Langmuir*, 2011, **27**(7), 3294–3300.
- 22 B. C. Batista and O. Steinbock, Growing Inorganic Membranes in Microfluidic Devices: Chemical Gardens Reduced to Linear Walls, *J. Phys. Chem. C*, 2015, **119**(48), 27045–27052.
- 23 F. Haudin, L. A. Riolfo, B. Knaepen, G. M. Homsy and A. De Wit, Experimental Study of a Buoyancy-driven Instability of a Miscible Horizontal Displacement in a Hele-Shaw Cell, *Phys. Fluids*, 2014, **26**, 044102.
- 24 P. Shukla and A. De Wit, Fingering Dynamics Driven by a Precipitation Reaction: Nonlinear Simulations, *Phys. Rev. E*, 2016, **93**, 023103.

- 25 J. M. Matter, M. Stute, S. Ó. Snæbjörnsdottir, E. H. Oelkers, S. R. Gislason, E. S. Aradottir, B. Sigfusson, I. Gunnarsson, H. Sigurdardottir, E. Gunnlaugsson, G. Axelsson, H. A. Alfredsson, D. Wolff-Boenisch, K. Mesfin, D. F. de la Reguera Taya, J. Hall, K. Dideriksen and W. S. Broecker, Rapid Carbon Mineralization for Permanent Disposal of Anthropogenic Carbon Dioxide Emissions, *Science*, 2016, **352**(6291), 1312–1314.
- 26 L. Luquot and P. Gouze, Experimental Determination of Porosity and Permeability Changes Induced by Injection of CO₂ into Carbonate Rocks, *Chem. Geol.*, 2009, **265**, 148–159.
- 27 A. R. White and T. Ward, CO₂ Sequestration in a Radial Hele-Shaw Cell via an Interfacial Chemical Reaction, *Chaos*, 2012, 22, 037114.
- 28 A. M. Tartakovsky, G. Redden, P. C. Lichtner, T. D. Scheibe and P. Meakin, Mixing-induced Precipitation: Experimental Study and Multiscale Numerical Analysis, *Water Resour. Res.*, 2008, 44, W06S04.
- 29 C. Zhang, K. Dehoff, N. Hess, M. Oostrom, T. W. Wietsma, A. J. Valocchi, B. W. Fouke and J. C. Werth, Pore-Scale Study of Transverse Mixing Induced CaCO₃ Precipitation and Permeability Reduction in a Model Subsurface Sedimentary System, *Environ. Sci. Technol.*, 2010, 44, 7833–7838.
- 30 J.-D. Chen, Growth of Radial Viscous Fingers in a Hele-Shaw Cell, *J. Fluid Mech.*, 1989, **201**, 223–242.